



Swansea University
Prifysgol Abertawe

Next Generation Sandwich Composite Structures with Enhanced Impact Properties

Russo Swart

Swansea University

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ABSTRACT

The primary aim of this project was to successfully produce a ground-breaking PA6/Graphene nanoplatelet reinforced 3D printing filament material, with the intention to fabricate a novel next generation sandwich composite structure with enhanced impact properties. The novel next generation sandwich composite structure contained an auxetic re-entrant core and Amine-functionalised graphene nanoplatelets. This was to enhance the impact resistance, compressive modulus, compressive strength and energy absorption capabilities, and the residual compressive properties of PA6. Additionally, the auxetic re-entrant core and hybrid (a combination of the re-entrant and honeycomb cells) core topology were compared to the conventional honeycomb core. This was to determine if the auxetic core topology was superior in impact resistance and compressive properties, as well as in residual compressive properties, and to explore the possibility of replacing it. The first set of experimental methods involved analysing the in-plane compressive properties and deformation mechanisms of sandwich structures with a honeycomb, hybrid, or auxetic re-entrant core alongside continuous fibre-reinforcement in the face sheets. The properties were evaluated by performing in-plane uniaxial compression and a drop-weight low-velocity impact test to analyse the residual compressive properties. Kevlar fibres and carbon fibres were used as fibre-reinforcements in various fibre orientations, and a continuous fibre reinforcement 3D printer was utilised for the fabrication of the fibre-reinforced sandwich structures. An additional objective was to investigate if fibre-reinforcement enhanced the compressive properties of the core, and if it enhanced the residual compressive properties after low-velocity impact. A comparison in compressive properties and impact resistance between neat PA6 structures and fibre-reinforced sandwich structures showed that fibre-reinforced structures were inferior to neat PA6 sandwich structures. Secondly, the same set of experiments and analysis was replicated for the novel PA6/Amine-functionalised graphene nanoplatelet reinforced sandwich structures. These sandwich structures were printed using fused filament fabrication. Amine-functionalised graphene nanoplatelets were dispersed into a PA6 matrix at 1%, 2%, 3% and 4% concentrations using a co-rotating twin-screw extruder. A filament extruder was used for the manufacturing of the novel 3D printing filament material. A scanning electron microscope was used to investigate graphene nanoplatelet dispersion and their bonding behaviour within the matrix. A high depth of field analysis and microscopy approach was taken to investigate fibre lay-ups, 3D printing defects, core failure, face sheet failure, and indentation failure for both types of sandwich structures. The reinforcement of Amine-functionalised graphene nanoplatelets, in particular 2% filler concentration exhibited improved resistance against impact and enhanced compressive properties when compared to neat PA6. The substitution of the auxetic core reported superior compressive properties and residual compressive properties.

Declarations

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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This thesis is the result of my own investigations, except where otherwise stated. Other sources are acknowledged by footnotes giving explicit references. A bibliography is appended.

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CHAPTER 1

INTRODUCTION

Sandwich structures are utilised in an array of industries and applications. The exceptional strength-to-weight ratio, high bending resistance, stiffness, light weight, and shock absorption capabilities make them a popular choice in the aerospace, automotive, and naval industries. The structural functionality of a sandwich structure is to efficiently resist in-plane and lateral bending loads, shear loads, and buckling loads. It does so by its unique structural configuration of two stiff composite face sheets separated by a lightweight core and an adhesive attachment for the transmission of shear and axial loads. The face sheets are commonly comprised of fibre-reinforced polymer, such as carbon fibre reinforced epoxy composites, and the core is traditionally either cellular foams, honeycomb (Nomex or aluminium), corrugated, or truss, connected to the face sheets with an epoxy adhesive. Their applications subdue them to compressive, shear, and impact scenarios, and consequently the face sheets containing fibre reinforcement can suffer from microscopic fibre failure modes. These failures are invisible to the naked eye and can lead to unique sandwich structure failure modes. The unique configuration of a sandwich structure means face sheets are of a different material to that of the core, resulting in a mismatch of properties. In addition, the necessity for an adhesive means flexural stresses, its application scenarios, and mismatch of properties can cause face sheet debonding and interlaminar cracking, which are significantly common. These failures are detrimental to the structural integrity of sandwich structures, and it can weaken their ability to withstand impact and compressive forces.

Other methods of reinforcement have been sought after to reduce the effects of the common fibre failure modes seen in sandwich structures, such as nanoplatelet reinforcement. Nanoplatelet reinforcement is becoming increasingly popular in the world of next-generation composite materials. This is because it offers a promising way to achieve desirable stiffness and strength at low filler concentrations without compromising on density, toughness, or the manufacturing process. The high specific surface area, surface energy, and low density of nanoplatelets make them ideal for this purpose. Some common types of nanoplatelet reinforcements include carbon nanotubes (CNTs), carbon nanofibres, nano clay, graphene nanoplatelets (GnPs), layered silicates, and nano-Al₂O₃ particles.

Out of these, significant exploration of GnPs and its incorporation into polymer matrices has been undertaken. These composite materials are known now as ‘next generation composite materials’. Their increased usage in structural applications is due to their unique characteristics, i.e. large surface area, a high current density, ballistic transport, chemical inertness, high thermal conductivity, optical transmittance, and significant hydrophobicity at a nanometre scale. Its closely packed covalently bonded two-dimensional hexagonal lattice is the reason for its significant stiffness and strength, and its popularity of consumption. It is a single sheet of Sp^2 bonded carbon atoms varying thicknesses of 0.7 to 100 nm. It is becoming the more favourable candidate out of other nanoplatelets, namely CNTs. This is because CNTs possess limitations, such as difficulty in processing without defects, dispersion issues from their chemically inert nature, their excessively high cost, and toxicity. Additionally, the larger surface area of graphene nanoplatelets and its 2D nature means it achieves more contact with its host matrix and in turn improved bonding.

By incorporating the appropriate amount of GnPs (graphene nanoplatelets) in a sandwich composite, it can effectively address the failure modes that typically arise from low-velocity impact. This is achieved by its toughening mechanisms such as crack pinning during an impact event, thereby impeding the formation of cracks and preventing the emergence of crack initiation sites within sandwich structures. However, one of the challenges in using GnPs is achieving uniform and homogeneous dispersion within a polymer matrix. Issues such as agglomeration and de-adhesion between the GnPs and host matrix can significantly reduce a polymer composite's stiffness, strength, and energy absorption. To prevent these concerns, functionalisation of GnPs, specifically Amine-functionalised GnPs, has proved a promising method to enhance surface energy, encourage wettability, and promote homogeneity between host matrices and GnPs.

Despite the traditional use of honeycomb cores in sandwich structures, there is still concern about their ability to withstand impact damage and provide enough energy absorption and dissipation when the core topology is oriented in the in-plane direction. This is when the struts of the honeycomb cells are aligned axially or perpendicularly to a compressive stress. Recent investigations of the re-entrant core topology have shown that it possesses a negative Poisson's ratio enabling the core to shrink and become denser when constricted laterally under uniaxial compression and expand when stretched longitudinally. These features are commonly classified as ‘auxetic’. It promotes

enhancements in many material properties, in particularly where the honeycomb lacks, such as impact resistance, energy absorption, compressive strength, and indentation resistance. As a result, it can potentially substitute the honeycomb core topology. However, their intricate and complex core geometry limits them from being fabricated with conventional manufacturing methods. Conventional manufacturing techniques rely on a combination of moulding, resin, and reinforcement. Unfortunately, these methods are expensive due to the necessary machinery and tools. They are also time-consuming, requiring a significant number of steps and precise curing conditions. The use of moulds further limits the potential for intricate designs and small prototypes.

Three-dimensional printing (3DP), more commonly known as additive manufacturing (AM), is an emerging method of fabrication for engineering applications in the world today. Fused filament fabrication (FFF) is now the leading and most widely consumed 3DP technology around the world, alongside the recent development of continuous filament fabrication (CFR). The rapid growth of 3DP technology can be attributed to the increasing need for high-performance materials in various industries such as aerospace, military, and automotive. These industries require fast production processes, superior quality parts, cost-effectiveness, precise dimensional accuracy, and low part density, all while ensuring strong and stiff components. Fused filament fabrication and CFR enable the rapid production of customized prototype designs with intricate shapes and complex geometry. This method eliminates the need for moulds, reduces processing steps, labour intensity, and costs, which are otherwise required for traditional manufacturing methods. By using the 3D printing process, sandwich structures can be printed without any adhesive between the core and face sheets as they can be printed as a single structure.

This research has successfully produced a novel 3D printed sandwich composite structure with enhanced impact and compressive properties. The strategy involved harnessing the optimal class of filler reinforcement (Amine-functionalised GnPs), employing the most efficient manufacturing techniques for intricate designs of core topology (CFR and FFF 3DP), and leveraging the promising traits of the auxetic re-entrant core. This resulted in a sandwich structure with a core superior to the honeycomb, the elimination of an adhesive between the core and face sheets, and a delay of crack propagations throughout the structure. Sandwich structures were successfully 3D printed

because a ground-breaking PA6/GnP reinforced 3D printing filament material was produced.

2.1 Fibre-Reinforced Composites Used in Industry

Large sectors use fibre-reinforced composite materials to combat concerns associated within the industries. For example, advanced spacecraft, aircraft components, and the automotive industry frequently use fibre-reinforced composite materials, in particular Kevlar fibres, carbon fibres (CFs), and glass fibres. The fibre-reinforcements are commonly utilised in military and commercial planes, i.e., in the wings, fuselage, bulkheads, flight deck panels, turbine engines etc. (Mrazova, 2013). They are also used in heavy-duty vehicles, such as trucks, sport cars (wheels, bumpers, and dashboards) and F1 cars (Petras, 1998). Moreover, the Airbus A350XWB consists of 53% composite materials and the Airbus A380 at 61%, containing the lowest percentage of aluminium by weight of all flying Airbus models, and thus saving 15 tonnes in overall weight. It indicates that fibre-reinforced composites are positively aiding large industries. Furthermore, large factories where corrosion resistance and strength-to-weight ratio are of main concern see fibre-reinforcement of upmost importance to increase safety and strength in the industrial sector (Nagavally, 2016).

Aluminium alloys are commonly used in these industries; however, they are prone to corrosion and can result in failures, such as fatigue cracking. As a result, this can be detrimental to commercial fuselage structures (Mrazova, 2013). However, the adoption of fibre-reinforced composites combats this limitation. Composite structures provide an enhancement in strength, stiffness, yield capacity, bendability, and resistance against the environment (corrosion, impact, lightning), as well as fatigue under cyclic loading in comparison to aluminium (Rahul et al., 2019). Unfortunately, fibre-reinforced structures can still suffer detrimental damage from hailstones, ballistic damage, tool drops, lightning strikes, runway debris, turbine blade damage, and fatigue from loading and unloading cycles, which metals were designed to conflict (Cantwell & Morton, 1991). Therefore, external forces also need to remain a consideration (Mrazova, 2013).

2.2 Polyamides

Polyamides are classified as thermoplastics containing repeating amide units in their backbone with a semi-crystalline chain structure, and thus consist of crystalline and amorphous regions when solidified from a melt. They can be categorized into aliphatic and aromatic polyamides dependent on the composition of the main chain (Palmer, 2001).

A polymer is considered a polyamide if it contains an amide linkage (-NH-C+O), as seen in Figure 2.1 (Gul et al., 2016). An important engineering plastic is that of an aliphatic polyamide, more commonly known as nylon.

Nylon (PA6) came into existence in 1930, and by 1938 it was publicized by DuPont (McAllister, 1995). Since then, different nylon structures were most commonly utilised, i.e. PA6, PA66, PA11, PA12, etc., as seen illustrated in Figure 2.1 (Gul et al., 2016). The various numbers in the suffixes refer to the number of carbon atoms present in the molecular structure. The aliphatic polyamides cover 90% of the world's total polyamide usage (Diamond et al., 2014). Subsequently, the global consumption seen in the year 2021 was around 8 million tons a year, where PA6 and PA66 were the most consumed aliphatic polyamides (Pouzada, 2021). In 2021 the PA6 market size was valued at USD 2.67 billion, and it is projected to grow from 2.72 billion in 2022 to USD 3.33 billion by 2029, (Fortune business insights, 2022).

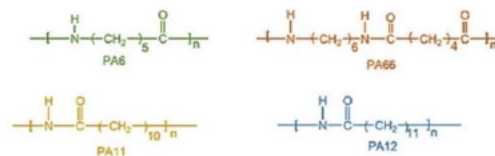


Figure 2.1 Common aliphatic structures (Gul et al., 2016)

Table 2.1 Monomers used to produce a specific polyamide/nylon (McKeen, 2017)

Polyamides/Nylons	Monomers used to fabricate
Nylon 6 (PA6)	Caprolactam
Nylon 66 (PA66)	1,6-Hexamethylenediamine and adipic acid
Nylon 11 (PA11)	Amnioundecanoic acid
Nylon 12 (PA12)	Amniolauric acid

2.2.1 Nylon 6 (PA6)

PA6 has exceptional mechanical, abrasion, wear, impact, and tensile properties. It can be utilised in the forms of film, fibres, and moulded plastic, namely through, melting, forming, or cooling processes, and more recently in 3D printing (Kausar, 2019). PA6 has excellent resistance to chemicals and ultraviolet radiation (UV) (Winnacker & Rieger, 2016) and is accommodated with high toughness, high chemical resistance, and significant impact resistance. Therefore, it is utilised across a wide range of applications, i.e. the automotive industry, cooling fans, engine covers, gears, and bearings (Kausar, 2019). Its superior physical, thermal and mechanical properties originate from its polar -

CONH- groups that occur in regular intervals, so that during polymer crystallisation they produce high intermolecular attractions. In addition, the aliphatic chain segments provide a degree of flexibility in the amorphous region of nylon. Therefore, with the combination of high intermolecular attractions in the crystalline zones and flexibility in the amorphous regions comes the significant toughness and durability of PA6 (Brydson, 1999).

PA6 is very susceptible to moisture absorption and therefore highly hygroscopic by nature. Thus, it can undergo hydrolysis, which is detrimental to the molecular structure, which results in the breaking of amide groups, and thus develops shorter chains and defects within the structure. Hydrolysis is greatly dependent on nylon molecular structure, i.e. the more carbon molecules present the less water absorption. This was reported by (McKeen, 2017), where comparisons of water absorption were made between PA6, PA66, PA11, and PA12, and where PA12 exemplified the lowest absorption of water.

PA6 has recently been utilised in 3D printing technology as it can be printed for repeated handling, it deforms easily when heated above its melting temperature, and it has a controlled combination of properties. Its molecular structure enables it to be combined with fillers of different natures, making it one of the most widely used thermoplastic materials in 3D printing and outside of 3D printing, as similarly demonstrated by Albadrani (2022), Araya-Calvo et al. (2018), Myer (2017), and Mouti et al. (2010).

2.3 Fibre Reinforcement

Since one of the primary methods of reinforcement in this project involves the utilisation of continuous fibre reinforcement, an emphasis will be made on this matter. Fibres add to the stiffness and strength of the matrix material, and therefore they are the predominant entity which will be taking most of the load when placed under force (Callister & Rethwisch, 2019).

The type of fibre, its orientation, the lay-up configuration, using continuous or discontinuous fibres, the volume fraction (the ratio of the volume of fibres present to the total volume of the polymer layers (Qiao & Davalos, 2013)), and fibre technology (number of strands and orientation of the specific strands), are all key elements that can determine what application the composite will be best suited for (Hull et al., 1996).

Additionally, FRPCs are also categorized by their processing methods, and the fibre type, as shown in Figure 2.2 (Campbell, 2010).

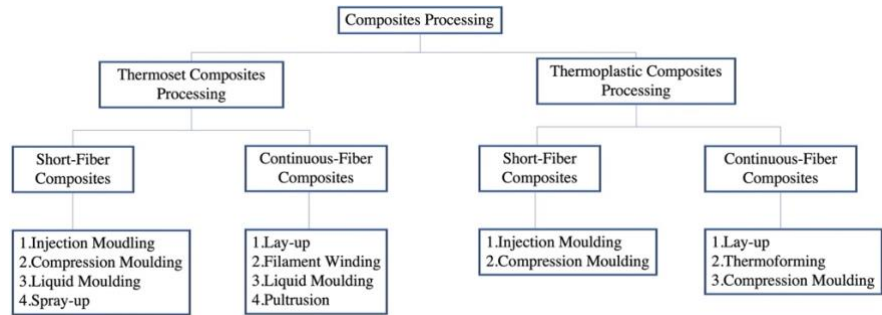


Figure 2.2 Polymer composite fabrication processes (Campbell, 2010)

2.3.1 Carbon Fibre Reinforcement

Carbon fibres are considered to be advanced fibres and are most frequently used within aerospace structures due to their high specific stiffness and light weight. Carbon atoms are arranged in a manner where they are stacked in a hexagonal array in a regular ABABAB sequence. Consequently, the atoms are held together by strong covalent bonds and weak Van der Waal forces. Conventionally they are 8mm in diameter and have small crystallites of turbostratic graphite, which is an allotropic of carbon (Khayyam et al., 2020). They are highly desirable because of their enhancement of stiffness and strength of polymer matrix composites, and their high chemical stability. Therefore, they exhibit superior tensile strength (2-7 GPa) compressive strength, an exceedingly high Young's modulus (200-900 GPa), and exceptional fatigue properties. The popular demand for CF stems from its high strength-to-weight ratio, and tensile strength more than six times that of steel depending on the precursor used (Gibson, 2016). The property values of the various CF precursors, and other fibre reinforcements are tabulated in Table 2.2.

Table 2.2 Property values of fibrous materials (Gibson, 2016) and specific tensile and densities of Kevlar and Carbon yarns (DuPont, 2019)

Material	Tensile Strength (MPa)	Tensile Modulus (GPa)	Ultimate Strain	Specific Tensile strength, *10 ⁶ in	Specific Density, lb/in. ³
PAN-Based CFs					
T-300, 12K	3650	231	0.014		
T-650/35, 12K	4550	248	0.0175		
T-400H, 6K	4410	250	0.018		
High Tenacity Carbon	-	-	-	6.93	0.065
Glass fibres					
E-glass	3448	72	0.048		
S-2 glass	4890	87	0.057		
Polymeric fibres					
Kevlar 29 aramid	3620	70	0.036		
Kevlar 49 aramid	3620	112	0.024		
DuPont Kevlar 29 aramid	-	-	-	8.15	0.052
DuPont Kevlar 49 aramid	-	-	-	8.37	0.052

2.3.1.1 Carbon Fibre Reinforced Polyamides

This section will seek to analyse previous work that has been done on PA6 and other polyamides, reinforced with CFs to compare to neat PA6, and to establish if improvements can be seen in their tensile strengths or flexural strengths, and Young's modulus or flexural modulus.

The light weight, high specific strength, specific modulus, fatigue resistance and corrosion resistance of CF was reported by An et al. (2014). The authors added continuous CF to PA6, whereby they successfully increased the tensile strength, tensile modulus, and flexural strength of PA6, and this was especially so as the fibre volume increased. Consequently, PA6 containing the highest CF volume fraction (8.18%) obtained a tensile strength of 110 MPa, indicating a 184.2% increase when compared to neat PA6, and a tensile modulus of 6.49 GPa, demonstrating a 1148% increase when compared to neat PA6. It was noted that continuous CFs improved the mechanical properties more effectively than short CFs. Long CFs were embedded into a PA6 matrix by Luo et al. (2014), to evaluate if the tensile strength and Young's modulus of PA6 are affected by manipulating the wettability of the CFs, the fibre lengths and increasing fibre volume. It

was reported that the strength and modulus of the CF-reinforced PA6 samples were proportional to the interfacial adhesion rather than sizing concentrations. However, composite samples with 20 and 24%wt. CF fibre content on average indicated a 112% increase in tensile strength, a 780% increase in tensile modulus and a 128% increase in flexural modulus when compared to neat PA6 samples. A similar approach was taken by Wu et al. (2001), where the authors prepared a CF-reinforced PA6 composite. The tensile strength and Young's modulus of the 10 wt% CF samples promoted considerably higher tensile strength and Young's modulus than neat PA6. Owing to the CF reinforcement, the PA6/CF composite obtained a tensile strength and modulus of 70.9 MPa and 3261 MPa, respectively. Conversely, the neat PA6 sample had a tensile strength of 51.8 MPa and a modulus of 1073 MPa. Likewise, Ma et al. (2017) studied the tensile strength, Young's modulus and failure behaviour of PA6/CF unidirectional composites. The tensile strength and the Young's modulus of the PA6/CF composites improved when compared to neat PA6. It was seen that the PA6/CF composite had an improved Young's modulus and tensile strength of 8.2 GPa and 1308 MPa, respectively, and the neat PA6 samples showed a Young's modulus and tensile strength of 2.4 GPa and 82 MPa, respectively.

2.3.2 Aramid Fibre Reinforcement

Aramid fibres, also known as aromatic polyamides, are one of the first organic fibres with a high enough tensile modulus and strength to be utilised as reinforcement in advanced composites. It is a manufactured fibre containing a long chain synthetic PA6, with 85% amide linkages bonded directly to two aromatic rings. The family of aramid structures are, Kevlar, Nomex, Technora, Tejinconex, Twaron, etc. (Jassal & Ghosh 2002) and the most prevalent aramid structures are Kevlar and Nomex (Xie et al., 2021). In relation to other synthetic fibres, their toughness, tensile strength, and modulus are 5-10% greater, displacing metal wires and inorganic fibres normally used in structural composites for applications in aerospace, marine, and the automotive sectors, involving ropes for offshore oil rigs and bullet proof vests. As a result of their molecular structure, they are utilised in ballistic protection for the military, prosthetic devices, sporting goods, and cables for the securing of large vehicles (Jassal & Ghosh, 2002). Their chemical structure are of a 'zigzag' pattern, aligned straight, with a carbon backbone, fully aligned and very closely packed. Figure 2.3 shows Kevlar's molecular structure, indicating the many inter chain hydrogen bonds between the molecules resulting in the high strength of the fibre, alongside the carbonyl and NH bonds. When spun into fibres, it causes the

polymers to arrange in a crystalline manner, where the polymer chains are aligned and orientated parallel to the fibre axis, enhancing it with strength (Abe & Yabuki, 2012). This is illustrated in Figure 2.3 where its chain structure is compared to the conventional polymer chain structure. For the structure to fail, all the thousands of hydrogen bonds must be broken simultaneously, hence their significant rigidity and toughness. However, the fibres are vulnerable to low velocity damage, which leads to buckling or kinking of the fibres (Jassal & Ghosh, 2002).

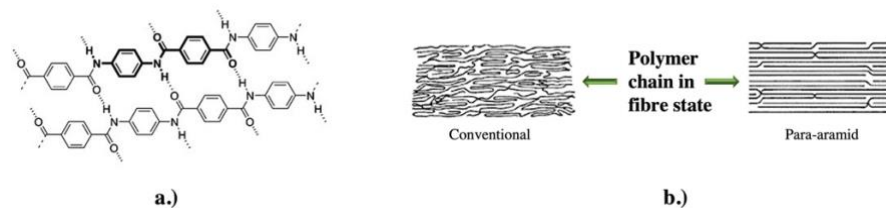


Figure 2.3 Molecular structure of Kevlar where the bold section shows the single monomer unit of Kevlar fibre. The dotted lines show the hydrogen bonds (Darapu & Darapu, 2014) in image (a) and a comparison between conventional polymers and aramid polymers (Elmogahzy, 2020) in image (b)

2.3.2.1 Kevlar Reinforced Polyamides

Studies have been done investigating the reinforcement of Kevlar fibres in thermoplastic matrices, such as Styrene-acrylonitrile, Acrylonitrile Butadiene, and polyethylene (Yeung & Rao, 2012). It was seen that thermoplastics can promote increased toughness, and damage tolerance in combination with fibre reinforcement, and can often match the properties of Kevlar/epoxy-based composites (Yeung & Rao, 2012).

Kevlar's characteristics, namely, its high tensile strengths, as seen in Table 2.2, which are over twice that of nylon and polyester, enable them to be utilised in high strength-based applications, and make them exceptional in impact-resistant structures (Deepak et al., 2020; Jassal & Ghosh, 2002). Subsequently, in comparison to high tenacity CFs, Kevlar has a higher specific tensile strength with a lower specific density, as seen in Table 2.2. A limited number of studies have been reported on PA6/Kevlar structures because of its popular usage with epoxy resins, the difficulty in moulding with nylon, especially for intricate designs, and the poor adhesion of Kevlar with most thermoplastics (Brisson & Canada, 1991). On the contrary, nylon is commonly paired with Kevlar fibre as its reinforcement because polyamides, such as PA12 and PA6 are hydrogen bonding

polyamides, similar to Kevlar fibres. This increases the interfacial adhesion, resulting in improved reinforcement (Eagles et al., 1976).

Some of the few studies that utilise polyamides as host matrices demonstrate that the volume fraction of Kevlar fibres and their fibre orientations within the matrix is an effective contributor to the tailoring of the composite's properties. The tensile strength of nylon/aramid plain knitted composites was investigated by Khondker et al. (2004). Nylon/aramid and epoxy/aramid composites were compared, and it was reported that the non-normalized tensile strength of nylon/aramid composites surpassed the epoxy/aramid composite structure by 25.38%. This was in relation to the nylon/aramid composite containing a greater volume fraction (23.9%) in comparison to the epoxy/aramid composite (13.6%). The authors discussed the importance of knitting direction and mechanical testing direction, where the nylon/aramid composite obtained superior tensile stress (79 MPa) in the wale direction of the fibres when compared to the course direction tensile stress (43 MPa). Brisson & Canada (1991) investigated the incorporation of Kevlar fibres in PA6, PA11, and PA66. The authors noticed improvements in the mechanical properties (tensile modulus, tensile strength, and elongation at break) for the polyamide/Kevlar composites when compared to the neat PA6 samples as the fibre volume fraction increased. Subsequently, the PA6/Kevlar composite exhibited a 31.25% increase in tensile modulus with 10%wt. Kevlar, a 6.38% increase in tensile strength with 10%wt. Kevlar, and a 75% reduction in elongation at break with 10%wt. Kevlar. More recently, Wang et al. (2021) focused on the design and characterization of continuous Kevlar fibre reinforced polyamide 3D printed composites. It was concluded that the polyamide composite with the incorporation of Kevlar fibres alongside CFs obtained the highest indentation resistance and energy absorption (4409 N*mm), and thus exhibiting a 242% increase in energy absorbed when compared to the neat polyamide matrix. Consequently, it was evident that fibre location influenced the toughness of the composites, as it was discovered that the Kevlar fibres with high toughness situated at the bottom side of the composites offered elevated resistance to bear the tensile stresses over CFs in this case. Albadrani (2022) examined and compared glass fibres to Kevlar fibres embedded into a nylon matrix. The author revealed that fibre orientation and loading direction significantly affected the outcome of the maximum stress values. As a result, Kevlar fibres orientated in the direction of tension (90°) obtained a stress of 8.4 MPa which was 76.1% greater than the 0° composite orientated perpendicular to the tensile

test direction. The volume fraction of experimented composites remained equal, and thus indicated that the main contribution to the differences in stress-strain was related to the fibre orientations. Kevlar fibres were incorporated into a nylon matrix and reported by Li et al. (2022). One of the objectives was to investigate the performance of Kevlar reinforced nylon composites when placed under tension and orientating fibres in different directions. A number of fibre orientations were selected, namely, 0° , 90° and $\pm 45^\circ$. It was discovered that the continuous Kevlar 0° fibre orientation (orientated parallel to the tensile test direction) obtained a stress of 200 MPa. On the contrary, when fibres were orientated perpendicular to the test direction (90°) subjects showed a 90% reduction in stress.

2.4 Laminates

2.4.1 Fibre Direction in Laminates

Fibres can be altered in different directions for an individual lamina to achieve more balanced properties throughout a composite laminate or to achieve improved strength and stiffness in a given direction. A lamina can be positioned in various orientations, such as $[0/+45/90/-45]_s$, resulting in a ‘quasi-isotropic’ (QI) laminate. This permits the fibres to have equal strength and stiffness in all directions of the laminate (Letchumanan et al., 2021). On the contrary, uni-directional (UD) laminates are exceptionally strong and stiff along the fibre direction owing to all lamina directed at 0° . However, their limitations arise when force is applied transversely since the bulk of the load is being carried by the matrix (Chung, 2010). A comparison of both laminate structures is shown in Figure 2.4. Fibre direction is critical since laminates are particularly strong in the fibre direction but very weak in the through-thickness direction resulting in a failure mode known as “delamination”. This occurs when the interlaminar stress levels exceed the interlaminar strength. The interlaminar strength is the restraint because it relies on the matrix properties and the bonding strength of the fibre/matrix interface (Chung et al., 1989; Dransfield et al., 1994). Nonetheless, the prediction of laminates’ strength is never entirely accurate, because each lamina has an individual strength, separate to the laminate as a whole, and therefore different reliability (Frangopol & Recek, 2003).

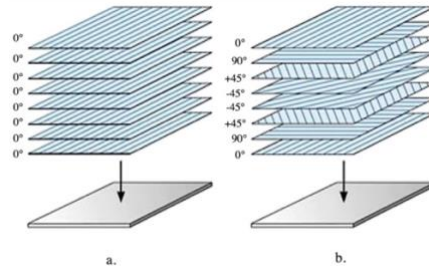


Figure 2.4 A unidirectional lay-up (a.) Quasi-isotropic lay-up (b.) (Letchumanan et al., 2021)

2.4.2 Previous Work Comparing UD and QI Composite Laminates

Cordin et al. (2018) reported that fibre orientations can govern the properties of an FRPC. It was apparent that both UD composites and QI composites offer different moduli and strengths in comparison. It was discussed that the type, quantity of reinforcement, and layer orientations dictate the final composite properties. The authors indicated a 46% reduction in ultimate tensile strength with a fibre direction of 22.5° , indicating the importance of considering an appropriate fibre direction. Moreover, the 0° fibre orientation when compared to the 90° fibre orientation, experienced an 86% higher tensile strength. Consequently, Goh et al. (2019) reported that the 90° orientation obtained the weakest tensile strength. Hence, alignment relative to the applied stress is an important factor and influence in FRPCs. Comparisons of woven glass, CF and aramid fibres were investigated by Ekşi & Genel (2017) and it was concluded that in terms of shear stress, elastic modulus, and compression strengths, UD 0° portrayed the highest performance in comparison to 90° laminates. It experienced a 77% greater compressive strength for CF samples, and tensile strengths were 95% greater. Further insight into the reliability, the orientation of fibres, and fibre types was conducted by Frangopol & Recek (2003) and it was evident that fibres with random orientations (e.g., short fibres or continuous), produce an isotropic behaviour, and so are more commonly used in low performance parts. Nevertheless, UD composites demonstrate higher strength and stiffness with force applied in the direction of the fibres, and thus will be weaker in any other direction. Letchumanan et al. (2021) compared UD and QI laminates reinforced with glass fibres and CF to be wrapped around piping systems. The optimum chosen laminate was the QI orientation as it provided orthotropic properties where it possessed the same strength and stiffness in all directions which was a requirement for the piping systems.

2.5 Limitations of Fibre-Reinforced Polymer Composites

Despite the significant usage of FRPCs and their noteworthy strength-to-weight ratios, stiffness, and damping properties, many studies have shown that FRPC materials are greatly susceptible to damage from low-velocity impact scenarios. Low-velocity impact can occur during manufacturing, servicing, and during maintenance (Bonavolontà et al., 2007; Ranjit et al., 2016). It can occur from, tool drops (accidental damage incurred during routine maintenance) in service, taxiing manoeuvres, hard landing, heavy loading or taking-off, hail strikes, etc, when utilised in aerospace. Consequently, it can induce a substantial amount of damage to the fibres and polymer resulting in fibre failure modes (Akatay et al., 2015; Tan et al., 2015). Fibre failure modes are detrimental to the structural integrity of FRPCs and significantly reduces their service life (Cantwell & Morton, 1991).

2.5.1 Failure Modes in Fibre-Reinforced Polymer Composites

Under low-velocity impact, failure modes can result in: (1) fibre breakage/fracture; (2) matrix deformation and cracking; (3) fibre debonding; (4) fibre pull-out; and (5) delamination. Fibre breakage or fibre fracture develops when fibres have reached their highest fracture strain resulting in complete catastrophic failure of an individual fibre, and eventually a bundle of fibres. This increases the degree of concentrated stress on the fibres relative to more distant fibres, and thus increasing the probability of failure at that position, and neighbouring fibres. As a result, it can translate to broken fibre clusters, as similarly reported by Yamamoto et al. (2019). Moreover, matrix deformation/cracking includes the occurrence of micro-crack and macrocrack development in the matrix, resulting in a debonding between fibres and the matrix. It is significantly influenced by material property mismatching. Therefore, when two adjacent lamina have different fibre angles, both the extensional stiffness and the bending stiffness will be different, resulting in non-homogeneity, and thus matrix cracking (Liu & Malvern, 1987). Furthermore, one of the first authors to report on the development of matrix cracking was Takeda et al. (1982).

Fibre debonding commonly initiates when there is a weak interaction between the fibres and the matrix, resulting in a reduction of interlaminar shear strength, and ultimately delamination or debonding of the fibres. Cracks can propagate, which can be influenced by an applied load, consequentially developing parallel to the fibres, and thus separating the matrix from the fibres since the interfacial strength has been compromised

(Edie & Stoner, 1992; Shirvanimoghaddam et al., 2017). Correspondingly, this can further start constituent debonding (Agarwal et al., 2006). On the contrary, fibre pull-out is related to brittle or discontinuous fibres. This failure causes fracture at the weak cross sections that are normally out of plane in the composite structure, and thus exposing the fibres from the matrix (Agarwal et al., 2006). Therefore, successful homogeneity between the two constituents is necessary to promote a strong interfacial strength and to permit an appropriate load-transfer mechanism from the matrix to the fibres.

2.5.2 Previous Work on Low-Velocity Induced Damage in Fibre-Reinforced Polymer Composites

It was revealed by Sinmazçelik et al. (2006), that low-velocity impact testing on unidirectional carbon fibre reinforced polyetherimide composites resulted in debonding of fibres, fibre pull-out, and shear fracturing of fibre bundles. These failure modes and the incrementation of impact energy demonstrated a reduction in max force after final impacting of the samples took place. Consequently, samples started at 0.19 N of force at 0.35 J of impact energy and reduced to 0.11 N at 0.75 J of impact energy. Compared with the above finding, Dear et al. (2005) reported that low-velocity impact caused failure modes, namely, cracking of the fibres, delamination, matrix cracking, fibre fracture, and other sub-surface damages. This in addition to fibre weight fractions led to a reduction in the composite's stiffness, peak load, and total energy absorbed. As a result, the glass mat thermoplastic (GMT) with the lowest fibre volume showed a peak load of 2.3 kN and the sheet moulding compound (SMC) with the highest fibre volume obtained a peak load of 6kN. Additionally, the total energy absorbed for the GMT and SMC was 12J and 25J, respectively. Lastly, the peak stiffness obtained by the GMT was 0.51 MN/m and 0.77 MN/m for the SMC, indicating the differences in properties obtained after impact. Zhao & Cho (2007) also reported that the damage modes witnessed from low-velocity impact were matrix cracking, fibre breakage, and delamination. The authors demonstrated that FRPCs are significantly reliant on the stacking sequence of the plies, exhibiting that under low-velocity impact that the maximum damage size, maximum contact force, and bending stiffness varies. Maximum damage sizes ranged between 1.5 cm-4 cm, bending stiffness ranged between 10.8 N/m² -26 N/m², and maximum contact force ranged between 1.77 kN-2.1 kN. Additionally, Bigg (1994) indicated that brittle local fracturing of the fibres, the concentration of fibres, and the length of the fibres were the main contributors affecting the energy absorption of the composites. Subsequently, a

comparison between PA6 with 43.3% wt. glass fibres and PA6 with 31.9% wt. glass fibres demonstrated that the sample with the greater fibre concentration absorbed 97.5 J/cm of energy and the PA6 sample with 31.9% wt. absorbed 38.8 J/cm of energy. Furthermore, Korkees et al. (2016) investigated the low-energy impact of $\pm 45^\circ$ carbon/epoxy laminates by performing a drop-weight impact test at impact energies 1.3J, 2.3J, 2.6J, and 3.4J. Subsequently, samples underwent a three-point bend test following impact. It was revealed that the propagation of damage was catastrophic after low-energy impact resulting in fibre failures, namely, fibre fracture, matrix cracking and delamination. This diminished their flexural strength resulting in a 3.5%, 5.95%, 26.19%, and 33.33% decrease in flexural strength at impact energies, 1.3J, 2.3J, 2.6J, and 3.4J, respectively.

2.6 Particulate Reinforcement

Particulate reinforcement can be utilised as a method to enhance the stiffness of FRPC structures. Potluri et al. (2019) discovered that the addition of boron carbide particles to an FRPC resulted in an increase in transverse Young's modulus and longitudinal Young's modulus when compared to a FRPC with no particle inclusion. At an increasing volume fraction of Kevlar49 fibre with the inclusion of boron carbide particles, there was an average increase of 1.4% in longitudinal Young's modulus and an average increase of 12.26% transverse Young's modulus. Conventionally, particle-toughening systems contain thermoplastic particles that can be introduced into a thermoset epoxy resin with varying sizes. These particles are normally much larger in size when compared to nanoparticles, ranging in size from 0.1-100 μm . Furthermore, particle toughening-systems can restrict polymer chain mobility and delay plastic deformation. The cost of particle reinforcement depends on the application, size, and type of particle used. Subsequently, these particles enhance the yield strength, tensile strength, and hardness of a polymer (Tanzi et al., 2019).

2.6.1 Particulate Reinforcement Limitations

In comparison to FRPCs, particle-reinforced composites (PRC) can be manufactured by utilising uncomplicated inexpensive processing techniques (Llorca, 2004).

Particulates can reinforce a polymer composite structure by enhancing its toughness, strength, and resistance to low-velocity impact. This is typically by the

promotion of toughening mechanisms, including crack front pinning, particle bridging, crack-path deflection, and matrix cracking (Qin, 2015). However, the commonly applied traditional toughening agents, such as, rubbers or elastomers, clay or nano clay, and glass beads, for example, require either a large concentration of dispersed particles, which can result in an increase in polymer weight, or they can reduce local yield stress but to the expense of a composite's moduli (Wetzel et al., 2006). Furthermore, the mechanical properties of particulate-polymer composites depend greatly on particle size, particle-matrix interface adhesion and particle loading. As such a study by Bull et al. 2015 revealed that adding 4-30 μm into an epoxy thermoset resin resulted in an earlier onset of delamination which forms by particle-resin debonding after impact testing. This created a discontinuous crack separated by ligaments within the interlaminar region. Smaller particle sizes, i.e. nanoscale in place of microscale, has shown to provide higher strength for polymers at a given particle loading. Consequently, Sumita et al. (1983) highlighted the interest of replacing microscale silica by its nanoscale counterpart, as the nanoscale silica particles possessed superior modulus, strength, and rigidity.

2.7 Nanoplatelet Reinforcement

Nanoplatelet reinforcement is prevailing in the world of next generation composite materials, as they can be a promising tool to achieve desirable mechanical properties, such as high elastic modulus, ultimate strength, modulus, and fracture toughness at exceptionally low filler concentrations (Quaresimin et al., 2015). A composite containing nanoplatelets as reinforcement is known as a “nanocomposite”. Exceptional changes in strength, stiffness, and toughness can be expected as low as <2vol%, with common nanofillers, such as CNTs, carbon nanofibres, nano clay, GnPs, layered silicates, and nano- Al_2O_3 particles, when compared to conventional composites that contain 60vol% of filler bound in a polymer matrix for enhancement to be achieved (Ramanathan et al., 2008).

A nanocomposite material can be defined as a solid material of two or more distinct phases, in which at least one phase has one or more dimensions of 100 nm or smaller in length. The implementation of nanoplatelets in advanced composites, result in the enhancement of specific performance with respect to stiffness, strength, ultimate properties/impact properties, and enhancements of permeation, fire retardancy, electrical properties, and fracture toughness (Sadasivuni et al., 2020). This is accredited to their 2D

nature and large surface area to volume ratio when compared to micro and macro additives. As a result, this improves the interfacial area and improves interfacial strength (Visakh et al., 2017). Nanoscale reinforcements, namely, CNTs, graphene, and layered silicates have recently provided improved methods of reinforcement for polymer nanocomposites (Xin et al., 2020). Many cases of FRPC structures and polymer materials with the incorporation of nanoplatelets have been reported and their effects on the properties, mainly ballistic performance, and stiffness, have been studied, showing great enhancement for these properties (Hajmohammad et al., 2019; Johnsen et al., 2007; Stewart et al., 2010).

Research has indicated that it is an established method for improving the damage tolerance of composites, and increasing delamination resistance, since nanoplatelets can enhance the matrix's load carrying ability (Davis et al., 2010). It was concluded by Davis and co-workers that there was an improvement in the tensile strength (18%), stiffness (24%), and durability under tension-tension and tension-compression cyclic loadings of epoxy with the reinforcement of CNTs in a CF epoxy composite structure. This was in comparison to neat epoxy. Therefore, nanoplatelets have significant potential in improving the weak out-of-plane interlaminar properties of laminate structures.

2.7.1 Advantages of Nanoplatelet Reinforcement in PA6

PA6's molecular structure enables it to be utilised with a variety of fillers, e.g., continuous/short fibres or nanoplatelets and additives, such as plasticisers, light stabilisers, or flame retardants, with the intention to enhance its elongation at break (%), notch sensitivity, and durability (Myer, 2017). The prevalent usage of PA6 for under-the-hood applications, such as an engine oil pan in light utility vehicles, means it needs to match the mechanical duties of metals that were previously utilised for these applications (Mouti et al., 2010). Consequently, the PA6 substitutes need to be service life capable, and this involves making them more impact resistant because of their weak response and limitation to localized impact (Mouti et al., 2010). PA6 is susceptible to the formation of notches after low-velocity impact, resulting in detrimental stress concentration points. Due to its sensitivity to notches and brittleness, they can possess poor impact properties, which brings light to the utilisation of fillers or nanofillers into the nylon matrix. This was similarly conveyed by Avanzini et al. (2022), indicating that its static strength life was jeopardized with failure onset from the notch tip.

The addition of nanoplatelets can restrict polymer chain mobility and prevent the effects of plastic deformation from impact that can result in brittle fracturing, whilst also improving its energy absorption capabilities. Studies have been done in areas regarding the usage of rubber toughening particles (Oshinski et al., 1992), CNTs (Roth et al., 2022) and GnPs (Kazemi-Khasragh et al., 2018), as they can protect polymers from localized impact scenarios. Their unique properties make them favourable candidates for their use as advanced reinforcing fillers for lightweight, high-strength, and functional polymer nanocomposites. Therefore, this indicates the promising features that next generation composite materials are capable of possessing. Moreover, authors De et al. (2010) and Karevan & Kalaitzidou (2013) explored chain immobilization and interfacial interactions in polyamides. The aforementioned authors revealed that chain immobilization and interfacial interactions were very high at very low and high GnP concentrations. In addition. It was revealed that the GnPs interfered with the large segmental motion of the polymer chains, resulting in an increase of modulus and strength.

2.8 Graphene

Graphene is a common choice of nano reinforcement because of the many advantages it provides for next generation composite materials. It contains a one-atom thick planar sheet of sp^2 -bonded carbon atoms that are closely packed into a two dimensional (2D) hexagonal lattice (Papageorgiou et al., 2020). Each layer consists of aromatic carbon atoms that are covalently bonded to one another, providing it with significant stiffness and strength. The in-plane breaking strength of graphene (40N/m) surpasses that of traditional materials used, with a Young's modulus of 1TPa, and tensile a strength of 125 GPa (Bragg et al., 2004; Geim, 2009). It is a single atomic plane of graphite, and the stacking sequence can consist of AA, AB or ABC sequence in which Van der Waal forces form the bulk of the counterpart, graphite, as seen in Figure 2.5 (b). It consists of 3 in-plane σ bonds/atoms and π orbitals perpendicular to the plane. Therefore, the strong σ bonds work to provide a rigid backbone of the hexagonal structure, and the out-of-plane π bonds control the interaction between different graphene layers, as shown in Figure 2.5 (c) (Choi et al., 2010). Its exceptional properties include, high current density, ballistic transport, chemical inertness, high thermal conductivity, optical transmittance, large surface area, and significant hydrophobicity at a nanometre scale (Chen et al., 2008; Choi et al., 2010). They are commonly utilised for applications, such as nanoelectronics, sensors, or energy storage materials (Seretis et al., 2017). A low

filler concentration of graphene is enough to significantly enhance the properties of a composite (Korkees et al., 2021).

2.8.1 Graphene Nanoplatelets

Graphite is composed of a high number of carbon sheets that are bonded via covalent bonds. Carbon atoms contain 3 covalent bonds and a free electron. Its limitation stems from its shear planes, its high brittleness and carbon sheets that are not available to interact with the host matrix (Kelly, 1983). However, by breaking the bonds connecting the sheets, stacked graphene layers with varying thicknesses of 0.7 to 100nm, in the form of platelets can be produced (Cataldi et al., 2018; Madhad et al., 2021). Subsequently, this can be achieved through the implementation of high-speed shearing methods or sonication, therefore promoting improved interaction with the host matrix (Ramanathan et al., 2008).

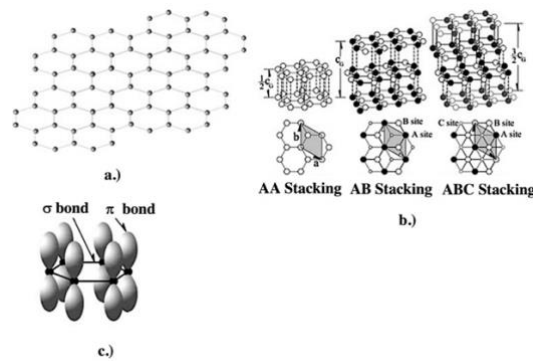


Figure 2.5 Graphene's two-dimensional hexagonal sheet of carbon atoms (a.) The three most common graphene structures and their stacking sequences (b.) Illustration of the in-plane σ bonds and the π orbitals (c.) (Hass et al., 2008)

Graphene nanoplatelets are widely utilised as nanofillers within a large range of matrices, i.e. polymers, concretes, and metals. This is due to their enhancement of mechanical, electrical, and tribological properties, and improved thermal conductivity at low concentrations whilst maintaining a high strength-to-weight ratio when utilised in nanocomposites (Young et al., 2012). Their morphology in addition to the correct concentration of GnPs can result in a composite that can combat the failure modes that initiate from low-velocity impact, such as crack initiation sites (Sadasivuni et al., 2020). In recent years improvements of the fibre-matrix interface were seen for FRPC structures (Kazemi-Khasragh et al., 2018), and improvement in their impact resistance with the

incorporation of fibres alongside GnPs as reinforcement have also been demonstrated by Khakzad et al. (2019).

2.8.1.1 Toughening Mechanisms of GnPs in Polymers

The rigidity of GnPs is considerably greater than its host matrix. Therefore, when crack propagation develops, toughening mechanisms, namely, plastic yielding of the matrix in the vicinity of the platelets transpire. This can result in subsequent void formations, alongside yielding at the interface of the rigid particles when crack propagation occurs (Park et al., 2015). In addition, toughening mechanisms also causes crack deflection and crack pinning, which develops at the interface of the GnPs. Therefore, when a crack encounters a platelet, tilting or twisting of the crack develops, resulting in deflection, and thus hinders any further growth, as shown in Figure 2.6. The GnPs contain high stress concentration zones, which causes a localized stress zone around the platelets, eventually resulting in debonding between the GnPs and the host matrix (Park et al., 2015). Crack pinning and the debonding effects are two of the main mechanisms that contribute to the overall toughening effect of the polymer structure, also revealed by Tang et al. (2013) and Wetzal et al. (2006). Subsequently, Park et al. (2015) discusses ‘micro-void formation’, which can develop in front of a crack tip opening of a GnP due to the micro-crack formation and debonding between the GnP and matrix. This results in secondary crack propagation, contributing to the toughness of the structure. Therefore, the addition of GnPs to a polymer matrix can enhance the structure against mechanical loads, impact scenarios that result in fracturing or cracks, and it can provide it with higher energy absorbing capabilities.

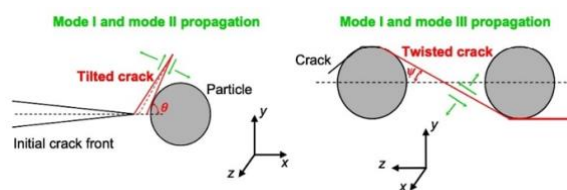


Figure 2.6 Schematic of a crack experiencing tilt and twisting (Quaresimin et al., 2015)

2.9 Additive Manufacturing

Additive manufacturing, in particular, material extrusion (3D printing), will remain the scope of focus for this section. Figure 2.7 expresses the many classifications

of additive manufacturing methods. Subsequently, a focus will be centred on fused filament fabrication (FFF) and continuous fibre reinforcement (CFR).

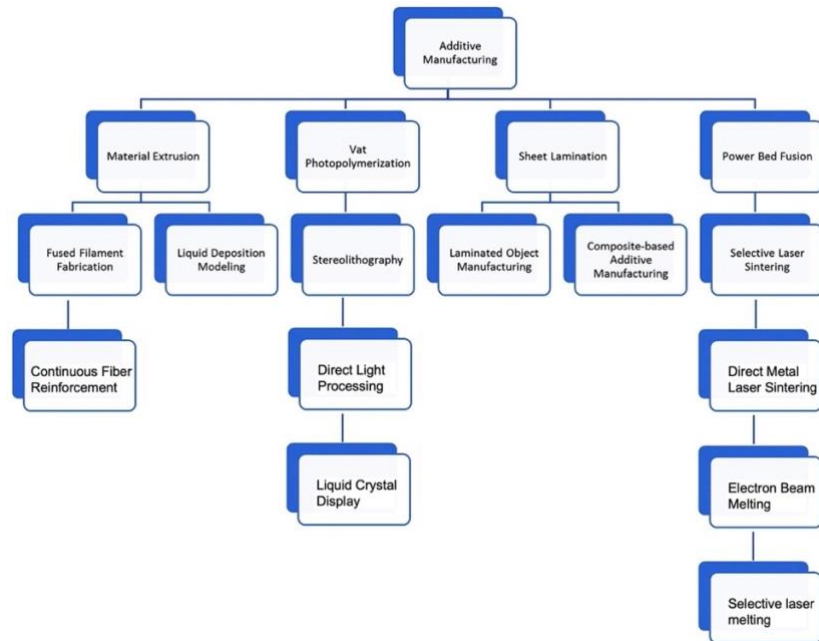


Figure 2.7 Classifications of the various additive manufacturing methods (Goh et al., 2019)

2.9.1 The Fused Filament Fabrication Procedure

Consumer-based 3D printers commonly involve FFF as a method of printing since they are undemanding and straightforward to operate. The technique and process involved are as follows; they utilise thermoplastics, i.e. PLA, ABS, PET, PET-G, and HIPS, where the most common 3D printed thermoplastics are PLA and ABS, supplied in the form of a filament, bundled, and lapped around a spool. Figure 2.8 illustrates a FFF printer. The filament is fed through a Bowden tube connected to the plastic nozzle located on the printer head. It is guided through the tube by a feeder, with an appropriate amount of force and appropriate feed rate to extrude material through the nozzle, reaching a maximum nozzle temperature of 260°C. Nozzle diameters are commonly 1.75mm or 2.85mm. Furthermore, accurate viscosity of the thermoplastic is dispersed in appropriate quantities at a constant rate onto the build plate/heated bed, as seen in Figure 2.8. The build plate and or printer, functions through the commands of the desired slicer software (i.e. Eiger, Cura, etc.), and operates in the z-axis, y-axis, and x-axis, with respect to the build plate axis. Therefore, for the fabrication of a component, the build plate moves in the z-direction from the commands given by the slicer software to manufacture parts of desired

geometry, shape, and detail. Subsequently, upon extrusion of the initial layer, the build plate moves in the z-direction (downwards), enabling the creation of the next layer. The printer head moves in the y-axis and x-axis which is determined by the dimensions of the part. At times build plates have built-in temperature sensors and heating elements, permitting the option of heating it to a desired temperature (Ćwikła et al., 2017).

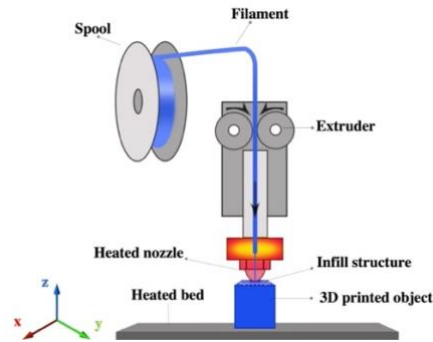


Figure 2.8 Fused filament fabrication illustration (Ma et al., 2021)

2.9.1.1 Advantages of Fused Filament Fabrication

The FFF method, constructs parts of geometrical complexity with ease, eliminating the requirement of moulds used in conventional methods of manufacturing. Therefore, this simplifies production runs, and saves on cost and time during the manufacturing processes. Moreover, through the assistance of CAD, designs are fully customizable, permitting the fabrication of large components and intricately complex components with very fine precision and resolution, whilst remaining at higher speeds and lower costs. Additionally, FFF has revealed its potential to reduce waste material commonly seen by conventional manufacturing, since it utilises material efficiently, resulting in an increase in productivity levels (Dehghanghadikolaei et al., 2018; Gero, 1995).

2.9.1.2 3D Printing Key Words and Key Build Parameters

This section will seek to outline the key build parameter considerations. These are changes made to the CAD file through the slicer software that can affect the geometrical features of the deposited material. It will also outline the keywords related to 3D printing. Build parameters and keywords involve (1) raster thickness/bead width, which is related to the thickness of an individual plastic layer after deposition, (2) air gap/voids are another common occurrence in 3D printing, involving the space between rasters of deposited FFF material. If the airgap is zero, then this results in successful material adhesion between

neighbouring rasters. Moreover, (3) infill and infill pattern are terms used to describe the volume percentage of material to fabricate a 3D printed part and the specific pattern, respectively, e.g. square, triangles, etc. Lastly, (4) dimensional accuracy is commonly used to explain the geometrical accuracy of the 3D printed part in comparison to the CAD dimensions (Ahn et al., 2002; Fidan et al., 2019).

2.9.1.3 Previous Work on the Disadvantages of FFF Printed Thermoplastics

Unfortunately, thermoplastic parts printed by FFF do not reflect great application performance. This is because, 3D printed parts are utilised commonly for prototyping, and thus do not require high strength and stiffness. Parts usually fail under low mechanical loads because of the absence of reinforcement in the thermoplastic material (Matsuzaki et al., 2016). Consequently, in comparison to conventional manufactured polymers, they are significantly weaker. Studies have explored methods in which to improve the strength and stiffness of 3D printed parts.

It was reported by Blok et al. (2018) that one of the major process variables is that of the raster angle. It can influence the properties across the principal material directions, the contact area between the polymer and the build plate, and if there is efficient raster width then there is good chemical bonding between the polymer chains of adjacent rasters for effective load transfer. It was further concluded that neck formation, diffusion, and neck growth or randomization, as seen in Figure 2.9, can develop. As a result, it can negatively affect the void content in the structure, resulting in a reduction of part strength. Moreover, parameters, such as infill pattern, infill direction and density, shell thickness, and printing temperature, were changed by Ćwikła et al. (2017). This was done to investigate if the tensile strength could be improved. However, it was revealed that the changes still would not enable it to replace conventional manufacturing techniques for mass applications due to their limitations in mechanical strength, problems with the quality stemming from environmental conditions (exposure to the air), and high accuracy of calibration (build plate levelling) to obtain significant build plate adhesion. In conclusion, parameter changing does not enhance or change the mechanical behaviour of 3D printed parts enough for them to be utilised for structural components in aerospace or automotive products.

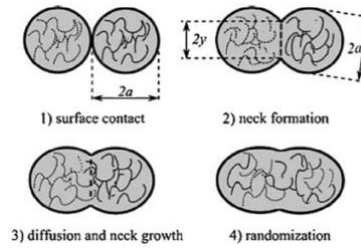


Figure 2.9 Overview of various bead contacts (Blok et al., 2018)

2.10 Continuous Fibre Reinforcement 3D Printing

Continuous fibre reinforcement has gained significant attention to act as a new and improved method of fabricating 3D printed parts with a similar method of layer-by-layer printing as FFF. It is capable of reinforcing parts with layers of various continuous fibres into a thermoplastic matrix, improving its compressive modulus and flexural modulus (Araya-Calvo et al., 2018). An illustration of the CFR process can be seen in Figure 2.10. It acts as an effective way of designing and creating composites, with the flexibility of altering the same parameters as FFF, but with the addition of changing fibre orientation, changing the fibre type, and amount of fibre layers within a part (Taormina et al., 2018).

2.10.1 Advantages of Continuous Fibre Reinforcement 3D Printing

It was revealed by Howard et al. (2020), that the 3D printed FRPCs were sufficient for use in real world scenarios rather than prototype parts. Another study by Luo et al. (2019), demonstrated that CFR printed parts increased in interlaminar shear strength and flexural strength, making it suitable for utilisation in the preparation of complex structural parts in aviation and aerospace as a metal replacement. A study by Dickson et al. (2017) evaluated the performance of altering fibre volume fraction ($V_f\%$) and indicated that significant increases in flexural strength and tensile strength can be achieved with 3D printed CFR technology, with strengths increasing by 516% at 13.5% volume fraction when compared to a neat structure. A comparison between Panda et al. (2009) and Dickson et al. (2017) reveals that samples printed with fibres as reinforcement, increased in their flexural properties and tensile properties when compared to the FFF printed samples. The highest tensile strength for FFF samples averaged near 17 MPa, however, CFR samples experienced tensile strengths of up to 216 MPa, which is an approximate thirteenfold increase.

2.10.2 Previous Work on 3D Printed CF and Kevlar Reinforced PA6 Laminates

This section exploits the potential of CFR printing and its ability to print with PA6 thermoplastic to be utilised as a substitute for structural applications. Highlighting this interest, Araya-Calvo et al. (2018) reinforced PA6 with continuous fibres using a Markforged 3D printer, exposing the possibility of fabricating face sheets identical to conventional laminate composites. The authors described that the CFR technique enabled the possibility of altering fibre patterns. Fibre patterns, reinforcement distribution, and print orientation were altered to enhance the compressive and flexural properties of PA6 reinforced with continuous CF (CCF). Fibre orientations of 0°, -45°, 90°, +45° and a concentric pattern, where 24 layers of CCF were embedded into the PA6 matrix were used. Furthermore, under compression testing, it was evaluated that reinforcement distribution and reinforcement type, as well as the interaction between the PA6 matrix, significantly contributed to the compressive modulus of the structures. The authors concluded a 24.4% improvement in compressive modulus with CF reinforcement, and thus demonstrating a 26.6% increase in compressive modulus when compared to 8.18% for neat PA6. Similar increases were noted by Dong et al. (2018) with fibre reinforcement.

2.10.3 Disadvantages of Continuous Fibre Reinforcement

Despite the added advantages of CFR technology, challenges such as post-processing and voids still remain a problem. Void involvement results in a reduction of mechanical strength and initiation of larger stress concentrations in printed materials. Post-processing, however, is necessary at times as the removal of any material used as supports is required, and support inclusion is necessary to aid in the dimensional accuracy of the part (Fidan et al., 2019). Unfortunately, 3D printed FRPC structures still suffer from the common failure modes experienced by traditional FRPC structures imposed by various mechanical loads, specifically, tension, compression, 3-point bending, and low-velocity impact scenarios, as similarly reported by Naranjo-Lozada et al. (2019), Li et al. (2016), Araya-Calvo et al. (2018) and Andrzejewski et al. (2022), respectively.

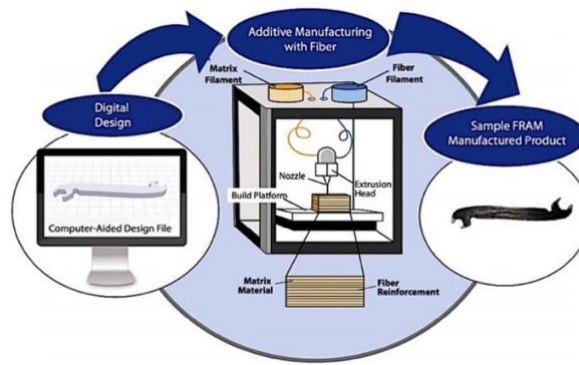


Figure 2.10 Illustration of a continuous fibre reinforcement 3D printer (Fidan et al., 2019)

2.11 Sandwich Composite Structures

Sandwich structures are one of the most significantly favoured composite structures now established in an array of industries and applications, combined with advanced composite structures. The use of sandwich composites can be seen utilised largely in the aerospace, automotive, and naval industries, due to their exceptional strength-to-weight ratio alongside their high bending resistance, high stiffness, light weight, and impressive shock absorption capabilities (Pethrick, 2010). Consequently, they are superior to solid/monolithic structures, or FRPC structures, such as laminates.

The structural functionality of a sandwich structure is to efficiently resist in-plane and lateral bending loads, shear loads, and buckling loads. A conventional sandwich structure comprises of (1) two stiff composite/metal face sheets positioned at the bottom and top surfaces of a (2) moderately thick but lightweight core, as seen in Figure 2.11. They are joined to the core by a (3) adhesive attachment enabling the transmission of shear and axial loads, to and from the core (Allen, 1969; Karlsson and Åström, 1997; Victor Birman and Kardomateas, 2018). This unique configuration produces a structure with enhanced energy absorption abilities, excellent ballistic resistance, and exceptional thermal and noise isolation properties (Sahu et al., 2022). However, these properties are determined by the design of the core structure, materials used for the face sheets and core, the joining technique, and performance characteristics. Applications that require high performance and low weight, such as aeronautical structures, high speed marine craft, and high-speed cars, utilise sandwich structures (Petrus, 1998).

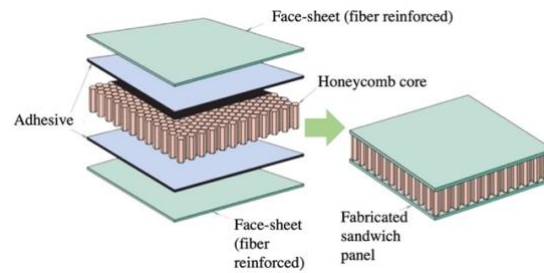


Figure 2.11 Conventional method of bonding face sheets for sandwich structures
(Al-fatlawi et al., 2021)

2.11.1 The Face Sheets

The exceptional stiffness of a sandwich structure is generated from the combination of the properties of the face sheets and core. For example, by splitting a solid laminate down the middle and separating the two halves with a core topology (core geometry and type), the result is a sandwich structure. However, although the new structure is slightly heavier, its flexural stiffness and strength is much greater (Petras, 1998). A large amount of the combined stiffness stems from the face sheets. Commonly sandwich structures comprise of FRPC face sheets because of their high flexural stiffness-to-weight ratio, hence their popularity in the aerospace industry. The face sheet's objective is to provide resistance to in-plane shearing and out-of-plane compressive and bending loads, preventing a sandwich structure from failing by bending or fracturing. It is necessary for the face sheets to have good toughness, hardness, and significant impact resistance (Sahu et al., 2022). Advanced composite materials including CF-reinforced polymers (CFRP) and Kevlar-49/epoxy (Pekbey et al., 2017; Rhodes, 1975) have been utilised as structural components in airframes, and for face sheets of sandwich structures, owing to their significant reduction in weight, in contrast to aluminium. This results in an approximate 20-25% reduction of fuel consumption, and CO₂ emissions (Timmis et al., 2014). Moreover, FRPC face sheets have sought to improve sandwich structures in areas related to strength and stiffness, whilst enabling improved shearing properties and doing so at significantly lower densities than bulk materials or monolithic structures (Strong, 2008).

2.11.2 The Core

The core is the centrally positioned layer of the sandwich structure. It separates the face sheets and carries loads from one face sheet to the other. Its prime attribute is

that it improves and adds compressive and shear strength to the sandwich structure. Subsequently, it aids the face sheets by providing the structure with a high bending stiffness, shear stiffness, improved resistance against buckling loads, and improved energy absorption capabilities (Yang, et al., 2012; Yazdani, et al., 2018). Furthermore, it augments the thickness of the sandwich structure without adding an increased amount of weight to it (Petras, 1998; Sahu et al., 2022). These properties are necessary for sandwich structures since some of the main failures, i.e., facing-core delamination and wrinkling of the face sheet arise from the local instability of the face sheets (Gibson, 2007; Gibson, et al., 2008).

The core of a sandwich structure can be classified into two categories, “structural” or “cellular”. The prime difference is the area within the material. Cellular implies that the material contains “cells” which is open space contained by walls in a manner which is repetitive so that the rest of the space can be filled, e.g., cellular foams, a honeycomb core, and balsa wood. Structural implies that no “cells” exist in the material itself, rather, it is a solid material manipulated into a specific shape, e.g., a web core, which is a continuous web made from solid materials separating the face sheets, or a corrugated structure (Carlsson & Kardomateas, 2011). Cores can be categorised to be either traditional (honeycomb, foam, corrugated, or truss etc.), or innovative (auxetic, hybrid, graded corrugated etc.).

The most desirable core property is one that has a Young’s modulus high enough in the direction of force applied to provide stiff support for the face sheets. The cores should also be strong enough in the direction of applied force such that they do not buckle under compressive loads or fail under shear loads. Consequently, the shear strength of the core must be sufficient to carry the shear load caused by the bending in sandwich structures (Christensen & Kim, 1999).

Several studies such as Cheng et al. (2019), Fila et al. (2017), and Luo et al. (2022) utilise a foam core type and indicated that the core can be fabricated from materials which best suit the engineering application. If the foam core undergoes impact scenarios and compression, an open cell is better suited. This typical structure is commonly seen and is very desirable in aerospace applications where sound, insulation and impact are of considerable importance. However, it has been revealed that the traditional core materials and topology still suffer from common failure modes (Pethrick, 2010).

2.11.3 Adhesive

The adhesion between the core and the face sheets is significantly important because its role is to transmit shear and axial loads to and from the core. It is a potential energy transforming unit for the face sheet to the core, thus it requires successful amalgamation. Common adhesive techniques include a heated press, vacuum bagging, Z-pinning, J-hooking, stitching, bolting, and adhesives such as epoxy resins (Sahu et al., 2022).

2.11.4 Conventional Manufacturing of Sandwich Composite Structures

Typically, conventional manufacturing of FRPCs involves some form of moulding, resin, and reinforcement, as shown in Figure 2.12. A mould and various mould tools are utilised to permit resin and reinforcement to be formed to a desired shape (Nagavally, 2016).



Figure 2.12 Conventional manufacturing method for fibre reinforced polymer composites (Nagavally, 2016)

The production methods of composites depend on the polymer type (thermoset or thermoplastic) and the fibre types used. Conventional methods for thermoset-based composites include hand lay-up, vacuum bagging, resin infusion, filament winding, pultrusion, and resin transfer moulding (Chung, 2010; Gay, 2014). Pre-preg plies can be used to create the face sheets for sandwich structures by the hand lay-up method, specifically known as 'wet lay-up'. The layers are then cured in an autoclave, which involves leaving it at room temperature, then applying heat, whilst simultaneously applying pressure, by means of a vacuum bag (Karlsson & Åström, 1997). Finally, the laminates are bonded to an aluminium or Nomex honeycomb core or expanded polymer foams with epoxy adhesive following the same procedure.

Conventional sandwich manufacturing involves flexible production rates but is labour-intensive, time-consuming, and expensive due to the required machinery and tools. Quality can suffer from human or machine errors. It is best suited for short production runs and large structures, lacking potential for small prototypes or intricate designs (Karlsson & Åström, 1997; Raji et al., 2018).

2.11.4.1 Limitations of Conventionally Manufactured Sandwich Structures

Since sandwich composite structures are more frequently utilised for structural applications, they are at risk of continuous loading cycles and low-velocity impacts (Rahul et al., 2019). The impacted regions can act as damage initiation sites, resulting in crack propagations and delamination in the face sheets, thus severely reducing the residual compressive properties, and their high specific strength and stiffness (Hull et al., 1996). Moreover, the unique configuration of a FRPC sandwich structure results in a structure that contains face sheets of a different material to that of the core, causing a mismatch in properties. Consequently, a strong adhesive is always required to bond the core and face sheets; however, a significant drawback is that the adhesive utilised often fails under compressive or flexural loads and from a mismatch of properties, resulting in face sheet debonding and interlaminar cracking/failure. This is detrimental to the structural integrity (Daniel et al., 2002). Lastly, the conventional manufacturing methods, limit any potential of fabricating geometrical complex core topologies, making it difficult to fabricate innovative cores beyond that of the honeycomb (Yazdani Sarvestani et al., 2018).

Furthermore, a sandwich composite's compressive strength is most susceptible due to the delamination's and interlaminar failures that can form from low-velocity impact. This can cause local instability and premature failure. Since sandwich structures are the primary load bearing components in the applications they are used for, it is important to consider their residual stiffness and strength (Nettles et al., 2008). Under localized damage from low-velocity impact, the damage is confined to the top facing face sheet at low impact energies, thus translating to the core-top facing interface, and the core material. Due to the nature of the process, a significant amount of stress is transferred to the core, resulting in crushing, shearing, and buckling, which was similarly witnessed by Meo et al. (2005). Elamin et al. (2021) studied the CAI behaviour of carbon-fibre foam-

core sandwich composites under low-velocity impact (5J and 10J) testing and indicated that matrix cracking of the face sheets, localized back face sheet delamination-induced buckling, and front face sheet debonding all took place. Moreover, the indentation response and energy absorption properties of aluminium honeycomb sandwich panels were subjected to a drop weight spherical impact head by Zhang et al. (2017), at impact energies 1.47, 2.94, 3.81, and 4.41J. Results revealed bending of the top face sheet, core crushing, and cell wall buckling with greater impact energies (4.41J). It was concluded that 80% of the impact energy was absorbed mostly by the top face sheet and honeycomb core. Moreover, Bulut (2020) reported debonding of the face sheet in the localized region of impact, resulting in buckling of the core for a basalt fibre/polypropylene honeycomb core. The authors reported delamination, fibre ruptures, fibre bending, and matrix cracking, as well as shear failure after low-velocity impact at 10, 20, and 30J.

2.11.5 Sandwich Structure Failure Modes and Core Orientations

One of this project's primary emphases is on the in-plane compressive behaviour of sandwich composite core topologies, due to the complexity of its deformation mechanisms. Relevant details regarding out-of-plane orientations, which have been extensively researched, are discussed briefly.

2.11.5.1 Out-of-Plane Core Orientation

The deformation of the core material is significantly influenced by its topology and its orientation in relation to an applied load. Figure 2.13 depicts the difference between a honeycomb core orientated in-plane and out-of-plane. Typically, sandwich structures are utilised with a honeycomb core topology orientated in the out-of-plane orientation (X_3), relative to the applied force. In this orientation, when placed under compression, the core is vulnerable to elastic buckling and bulging of cell walls, specifically if it is of a low density. If the honeycomb cells are of greater density, then fracturing can transpire. The occurrence of buckling, possible fracturing, and shearing of the sandwich structure can result in the initiation of debonding of the epoxy adhesive commonly utilised for bonding the core to the face sheets. Overall, the out-of-plane orientation means the structure relies significantly on the cell walls to provide it with stiffness and appropriate load carrying abilities. Therefore, the out-of-plane orientation typically showcases significantly improved compressive modulus and compressive strength in comparison to one orientated in-plane (X_1 and X_2) (Zhang & Ashby, 1992).

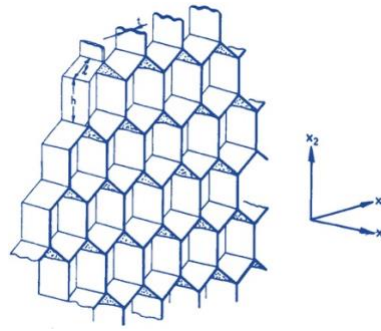


Figure 2.13 The honeycomb core showing the in-plane properties are those relating to loads applied to the surfaces normal to X_1 and X_2 ; the out-of-plane properties are those relating to loads applied to the surfaces normal to X_3 (Zhang & Ashby, 1992)

Sandwich structures are typically tested and utilised in compression, three-point bending, tensile testing, or low-velocity impact. Under these loads cores orientated in the out-of-plane direction experience face-sheet buckling, debonding between the face-sheet and core, face-sheet delamination, micro-cracking of fibres (in the face sheets), and cracking of the face sheets and core, as shown in Figure 2.14. Other forms of failure, namely, indentation of the face sheets, are common after low-velocity impact. As a result, the compressive face, or impacted face, can undergo buckling locally, or wrinkling, translating to microscopic fracturing of the bond between the faces, and ultimately leading to delamination. These failure modes are present in many studies (Yoon et al., 2001; McCormack et al., 2001; Petras & Sutcliffe, 1999). Furthermore, Akil Hazizan & Cantwell (2003) and Edgren et al. (2004) describes that these are all common failure modes experienced by sandwich structures, especially for advanced composite face sheets. The aforementioned failure modes are of concern in face sheets fabricated with fibres as reinforcements. This leaves room for further research into the development of enhancing their resistance to these failures and finding methods to improve their impact properties (Triantafillou & Gibson, 1987).

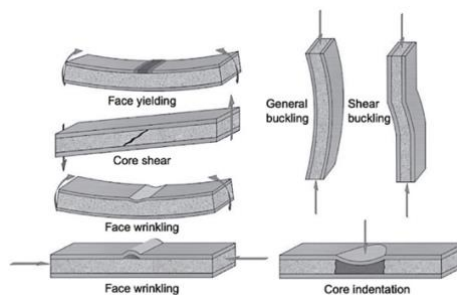


Figure 2.14 Sandwich structure failure modes (Oterkus et al., 2016)

2.11.5.2 In-Plane Compressive Failure of Honeycomb Cores

In-plane compression of honeycomb cores result in significant complexity in their deformation mechanisms. Authors Gibson & Ashby (2014) report that when honeycomb cores are compressed in-plane, their stiffness and strength, are presumed to be much lower than out-of-plane compression because the cell walls experience bending to employ conflict against compressive forces. The in-plane orientation means struts of a selected core topology, in this case, the honeycomb struts, are orientated parallel/in-plane to the X_2 compressive load or perpendicular to the X_1 compressive load, as shown in Figure 2.13. With core topology orientated in the in-plane direction stiffness and load carrying abilities are determined by the cells buckling and bending strength, and collapse stresses. Typically, under compression, the sandwich structure will follow a linear elastic behaviour before the occurrence of plastic deformation. This is followed by a plastic collapse stress at which a plateau region develops, and the structure under-goes a cyclic response. The cyclic response is where cells are under-going buckling, hinge rotation, and collapsing until their final densification is seen. At the point of final densification, a spike in stress is usually noted since the structure behaves monolithically at this point (Zhou et al., 2023).

Authors Xie et al. (2020) illustrate the significant difference in load carrying abilities between a Nomex honeycomb structure being compressed in the in-plane orientation and in the out-of-plane orientation, as seen in Figure 2.15. Stress-strain plots indicated that both orientations revealed a 3-phase phenomenon, i.e. an elastic deformation phase, a compression/plateau phase, and a densification phase. However, the in-plane structure developed significant complexity and large volatility in its compression phase. This was due to its deformation mechanisms that are distinctive to the out-of-plane orientation, i.e. its structural response resulting in cell wall buckling, bending, and membrane deformation. The compression phase was caused by three different failure modes, including elastic buckling, plastic damage, and or brittle fracturing of cell walls. Therefore, the high volatility transpired from brittle fracturing of cells that developed inconsistently and layer-by-layer throughout compression, where eventually the curve rises in stress because of the densification of cells.

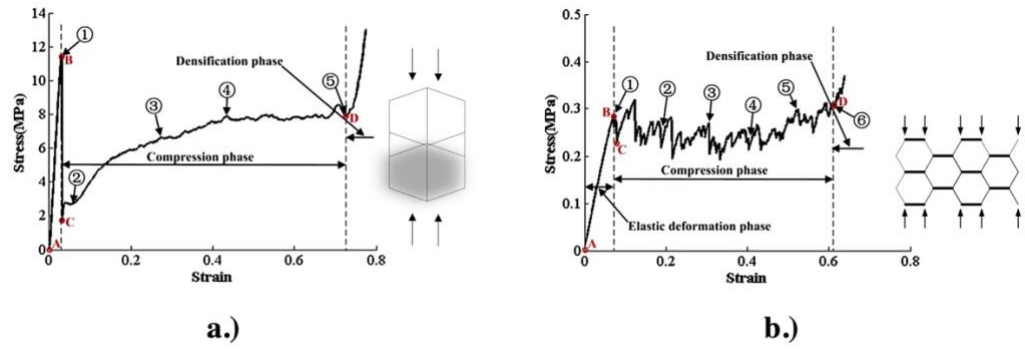


Figure 2.15 Stress-strain plot of a honeycomb core undergoing out-of-plane compression (a.) and a honeycomb core undergoing in-plane compression with struts orientated perpendicular to the compression direction (b.) (Xie et al., 2020)

Similarly, Zhou et al. (2023) performed quasi-static compression testing on 3D printed honeycomb structures orientated in the in-plane direction. The authors evaluated the difference in performance between struts orientated parallel and perpendicular. It was illustrated that both directions showed an elastic phase, plateau/compression phase and densification phase. However, more volatility was exhibited by the struts orientated parallel to compression, in the plateau/compression phase since it promoted the structure with greater deformation complexities.

Moreover, Hönig & Stronge (2002) investigated the compression of honeycomb structures in-plane. It was concluded that successive rows of the struts undergo misalignment and rotate in opposite directions, causing hinge rotation and finally a collapsing of individual cells, as seen in Figure 2.16. This was because cell walls carry large axial stresses alongside flexural stresses before reaching a complete plastic moment. Initially, the cells experience elastic buckling, finally resulting in plastic collapse. A similar approach was taken by Ruan et al. (2003), and it was reported that the honeycomb structures deformed in oblique “X” shaped bands when undergoing low-velocity impact and compression. It was then seen that at a high impact velocity, cells formed localized “I” bands perpendicular to the loading direction, and at medium velocity the cells form a “V” mode. The various deformation modes are presented in Figure 2.17. During the formation of the shapes, cells undergo plateau stress, eventually resulting in collapsing of the cells, followed by cell densification. Zheng et al. (2005) simulated the dynamic crushing of 2D honeycomb structures and noted that the honeycombs structures deformed in the same manner as that reported by Ruan et al. (2003). These same deformation shapes

were also discovered by Feng et al. (2006) and Li et al. (2007), when performing low-velocity impact testing also. It was revealed that “X” and “V” shaped deformations occurred at low ($v = 8.5$ m/s) to moderate ($v = 17$ and 34 m/s) impact velocities, and the “I” shape at high velocities ($v = 68$ and 136 m/s). Correspondingly, Zhu & Mills (2000) also reported buckling of the honeycomb walls resulting in a S-shaped pattern. It was established that the honeycomb structure overall develops 2 modes of deformation failure. Mode 1 considered no rotation of the vertical walls, and mode 2 indicated that the struts rotate about the nodes producing a conflicting behaviour with neighbouring cell struts that rotate in opposite directions. Hence, the development of the S-shape pattern and the collapse of the cells.

Moreover, Ingrole et al. (2017) performed in-plane compression on the honeycomb structures, and reported that cell walls undergo bending, consequentially resulting in linear elastic deformation. Eventually, upon reaching the critical strain limit, cells start to collapse by elastic buckling, plastic yielding, creep, or brittle fracturing. The authors noticed that the deformation of the honeycomb structure was greatly influenced by the bending of the inclined struts as seen for an individual honeycomb cell. The similar hinge rotation behaviour seen by Hömig and Stronge (2002), and Ruan et al. (2003) corresponded well in their analysis, indicating that the honeycomb structure collapses sideways and rotates about the node (where three cell walls meet).

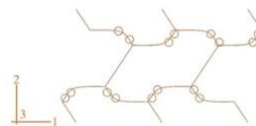


Figure 2.16 Illustration of the conventional honeycomb cell collapsing, where circles indicate possible locations of plastic hinges as seen by (Hömig & Stronge, 2002)

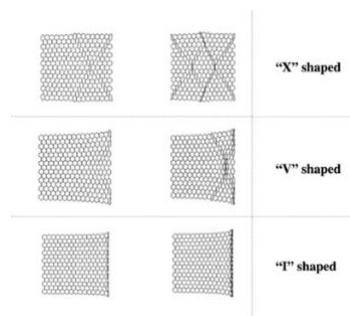


Figure 2.17 Deformation shapes commonly seen for in-plane compression of honeycomb cores reported by (Ruan et al., 2003)

2.11.6 Development of Sandwich Structures Using Auxetic Cores

It is common for sandwich structures to utilise honeycomb cores due to their inherent stiffness and strength. However, in comparison to more novel core designs, honeycomb cores may exhibit lower energy absorption and compressive properties. Authors Wadley et al. (2013) and Wu & Jiang (1997) indicated that the design and geometrical alteration of cellular topology could improve the impact energy absorption performance of sandwich structures, their compressive stiffness, and strength, and thus counteract the failure modes associated with sandwich composite structures.

2.11.7 Auxetic Core Structures

In recent years, uniquely modified cores for sandwich composites have been studied resulting in the fabrication of “auxetic” cores. Consequently, findings by Cheng et al. (2019), Wiernicki et al. (1991), and Yazdani et al. (2018) compare conventional core materials, i.e. aluminium and polymer foams, made with auxetic core topology. As a result, the auxetic core topology demonstrated the highest energy absorption.

For a material to be perceived as auxetic, it needs to contain a negative Poisson's ratio (NPR). A negative Poisson's ratio delivers features that enable a structure to expand perpendicular to the direction of tension stretched. Therefore, auxetic materials shrink and become denser when constricted laterally under uniaxial compression, and they expand when stretched longitudinally, as shown in Figure 2.18 (Prawoto, 2012). As per the positive strain energy theory of isotropic elasticity explained by Fung (1965), it is conceivable for materials to exhibit negative Poisson's ratios within the range of -1 to 1/2. The first record and description of a material possessing auxetic qualities was reported by Love (1944), but it was expected that materials possessing negative Poisson's ratio existed more than 100 years ago. After the discovery led by Love, the mechanics of two dimensional cellular (honeycomb) materials and the properties of three-dimensional cells (foams) were reported in 1982 by Gibson et al. (1982).

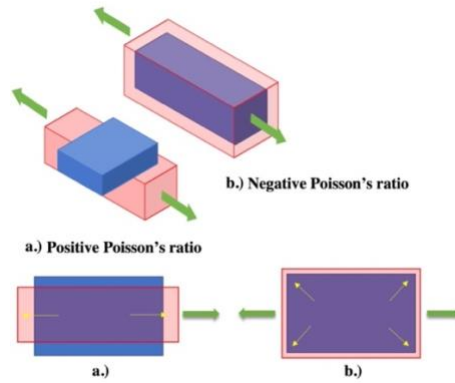


Figure 2.18 Illustration of positive Poisson's ratio (a.) and negative Poisson's ratio (b.) (Mirante, 2015)

2.11.7.1 Auxetic Cellular Solids

It was very early on discovered by Lakes (1987), that foam can be manipulated to possess auxetic features. The authors used open-cell polymer foams causing the ribs of each cell to permanently protrude inward, resulting in a re-entrant cell structure (Figure 2.19). This newfound design, originating from the honeycomb core structure, promoted enhancements in many material properties, i.e. impact absorption, damage resistance, damage tolerance, plane strain fracture toughness, resilience, shearing modulus, and indentation resistance, when it was compared to conventional foam materials containing a positive Poisson's ratio (Lakes, 1987; Lee et al., 1996).

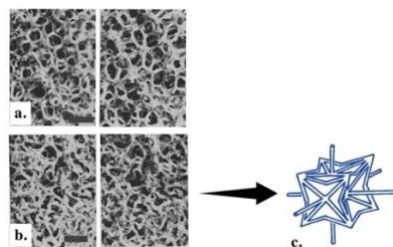


Figure 2.19 Stereo photograph of conventional open-cell polymer foam (a.) Stereo photograph of re-entrant foam (b.) Perfected model of the intended re-entrant unit cell of a 24-sided polyhedron (c.) reported by (Lakes, 1987)

2.11.8 The Re-entrant Cell Structure

Figure 2.20 shows the positive angle for the honeycomb in (image a) and the negative angle for the re-entrant in (image b). The process of inverting the honeycomb cells to form a negative angle, transforms a honeycomb cell to a re-entrant cell. Therefore,

it contains a negative Poisson's ratio, thus, enabling the cells to behave 'auxetically', as described and revealed by Almgren (1985) and Kolpakov (1992).

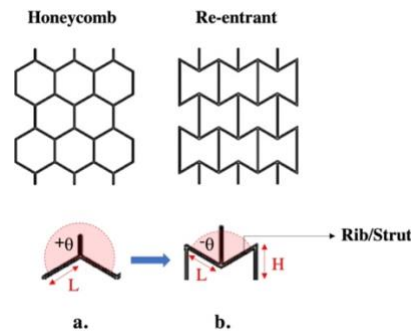


Figure 2.20 Illustration of the honeycomb and re-entrant cells and the conversion of the honeycomb cell (a.) to the re-entrant cell (b.) (Chen & Wang, 2022)

The behaviour of re-entrant cell structures depends greatly on the angle of the cell rib, as shown in Figure 2.20 (image b). The bending and deformation behaviour of the cell ribs is determined by their hinging and angle. As a result, when the structure is subjected to tensile forces, it exhibits auxetic behaviour (Alderson, 1999). When an applied uniaxial load is present, the horizontal alignment of the ribs exerts a force that separates the vertically aligned ribs (Ingrole et al., 2017), as shown in Figure 2.21. Based on this effect, it was proposed by Alderson & Alderson (2007) that utilizing the auxetic re-entrant for core materials can increase properties such as strength and stiffness. It was also reported that auxetic composite laminates containing auxetic constituents show significant enhancements in fracture toughness, and static and low-velocity impact performance. This is because material flows towards the localized region of impact, as opposed to the outward flow of material demonstrated by the honeycomb, as seen in Figure 2.22 (images a and b), respectively. Similarly, Qi et al. (2017) reported that as the re-entrant cells deform towards the impact zone, it results in material concentration, improving ballistic and impact resistance. In a previous study by Qi et al. (2013), the authors stated that the densification of material towards the localized impact region can be due to the auxetic deformation mechanisms of the re-entrant structure cell. This correlated well with Yang et al. (2013), revealing that auxetic sandwich structures possessing a negative Poisson's ratio concentrate material below the vicinity of impact.

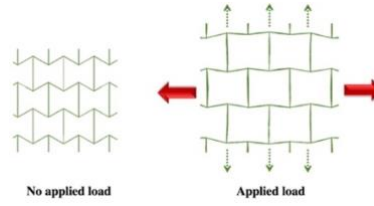


Figure 2.21 The re-entrant structure deforming under a uniaxial load (Ingrole et al., 2017)

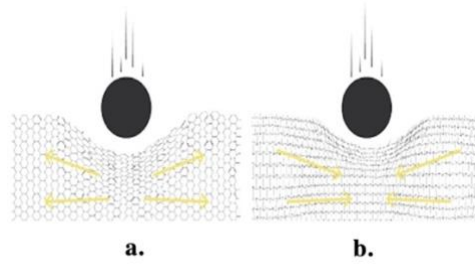


Figure 2.22 Indentation resistance and deformation behaviour of the honeycomb core (a.) and the re-entrant core (b.) under low-velocity impact (Mirante, 2015)

2.11.8.1 Cell and Strut Behaviour Under Impact and Compression

Modifying the geometric configuration of the re-entrant cell, i.e. cell shape, size, density, strut length, and cell angle, can have a significant impact on the mechanical behaviour of the structures', especially when subjected to compressive forces (Koudelka et al., 2016). A study by Beharic et al. (2018) revealed that the re-entrant core structures undergo bending-dominated deformation modes, and structures that do not exhibit a negative Poisson's ratio (the honeycomb), exhibit stretch-dominated deformation modes. Illustrative of the above statement, similar findings were reported by Li et al. (2018). Consequently, stretch-dominated structures exhibit higher elastic modulus and higher ultimate strength, whereas bending-dominated structures exhibit higher compliance, making them more favourable in energy absorption because of greater elastic-plastic deformation. Studies by Beharic et al. (2018) and Yang et al. (2013) indicated that the vertical strut (H), the angle (θ), and struts (L) of the unit cell, as seen in Figure 2.20 contribute significantly to the mechanical strength of the structure. It was noted that if the re-entrant angle was critically reduced then it would result in less bending-dominated features since the strut would contribute more to the modulus and the strength of the structure. When uniaxial compression was applied, each vertical strut at the corner of each unit cell was shared by the other three neighbouring unit cells, indicating a uniform

distribution of force across four adjacent cells. It was concluded that the primary reason for the collapse of the cells was because of elastic bending of both struts in the cells.

Moreover, Ingrole et al. (2017) showed that the re-entrant structure can be combined with honeycomb cells, resulting in a hybrid structure. The struts themselves can be modified to enhance the compressive strength, Young's modulus, energy absorbed, and specific energy absorbed when placed under compression. Therefore, the authors modified the re-entrant struts, adding split ends at both sides of an individual cell, as seen in Figure 2.23, image a, and made similar adjustments to the other designs as seen in Figure 2.23 (image a). The authors proposed the idea of potentially utilising the hybrid's structure in structural applications. Furthermore, they performed in-plane uniaxial compression testing on the auxetic structures (hybrid and re-entrant) and the conventional honeycomb. It was found that the addition of the strut in the re-entrant cells produced improved auxetic features and enhanced its compressive modulus in comparison to the honeycomb structure, where the honeycomb obtained 36 MPa and the re-entrant obtained 54 MPa. The authors state the importance of rotational stiffness of the nodes in the re-entrant and honeycombs structures, where these structures greatly rely on the degree of constraint to rotation at the nodes which are caused by the inclined walls. As a result, buckling and bending of the walls tend to occur within these core structures, showing a large dependence on the moments (M), as seen in Figure 2.23 (image b). Hence, why the structures fail in a sideward manner. It was established that all five structures exhibited an elastic-plastic collapse behaviour, but the re-entrant revealed a snap-through instability mechanism and a cyclic phenomenon because the re-entrant cores underwent cell row collapse (trough on stress-strain curve) and cell densification from collapsed cells (peaks on stress-strain curves).

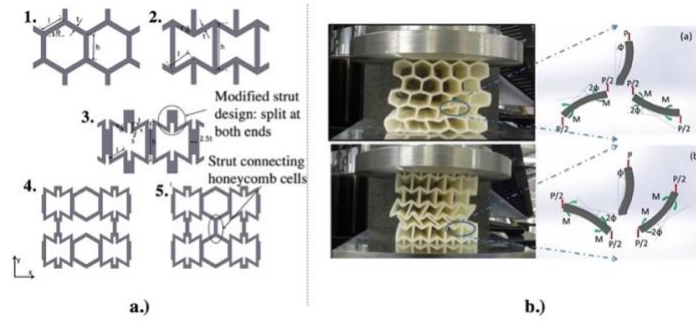


Figure 2.23 Conventional honeycomb (1a.) Re-entrant (2a.) Re-entrant with modified strut design (3a.) Hybrid 1 with no strut connecting the honeycomb cells (4a.) Hybrid 2 with a strut connecting the honeycomb cells, and the deformation behaviour of the honeycomb and re-entrant cores under uniaxial compression (5b.) (Ingrole et al., 2017)

2.11.8.2 Previous Work Comparing Re-entrant and Honeycomb Sandwich Structures

Recent findings reveal that the re-entrant structure exhibits energy absorption, average peak loads, and resistance against blast scenarios that are comparable, and in certain cases, superior to those found in conventional honeycomb structures. Therefore, studies explored the idea of substituting the honeycomb core with a re-entrant core to develop a novel sandwich structure concept.

Correspondingly, Li (2015) impacted two distinctive 3D re-entrant designs (A1 and A2) by altering their core topology to study these effects in comparison to 3D hexagonal cores, 3D Octahedral, and 3D Rhombic topologies. It was highlighted that the A1 design with a larger angle (75°) for the inclined strut was 50% greater in compressive strength when compared to the hexagonal formation. The A2 design with a smaller angle (45°) for the inclined strut demonstrated an 88% greater modulus in comparison to the hexagonal formation. Additionally, the auxetic re-entrant cores demonstrated a 61% greater energy absorption capacity than the hexagonal cores. Consequently, it obtained the highest peak load because of its successful force transmission and altering of core topology, thus obtaining a 64.14% greater average peak load compared to the hexagonal topology. Similarly, Jin et al. (2016) evaluated the dynamic response of sandwich structures with re-entrant auxetic cores subjected to a blast scenario. Results revealed that the re-entrant structure provides improved resistance against blast loading and can be utilised in applications that use explosion-proof equipment, tires, and floorboards of a military automobile, broadside defensive structures of naval vessel, or morphing wings

of aircrafts. Moreover, Faraci et al. (2020) proposed the utilisation of the re-entrant lattice structure and the conventional honeycomb structure to design lightweight stratified structures with efficient impact absorbing properties. It was underlined by numerical impact analysis that the auxetic configuration, through its densification mechanisms was more effective at protecting from impact than the honeycomb core. Consequently, the re-entrant showed a larger displacement on its stress-strain curve and showed a more efficient time evolution of kinetic energy. As a result, the ball rebound initiates at 1.0 ms for the honeycomb and 1.35 ms for the re-entrant. Therefore, the re-entrant showed that it had a higher total elastic strain energy because significant deformations occurred for a longer timeframe. Also, the maximum force transmitted is lower when adopting the re-entrant core, indicating that it obtained a force of 17N instead of 27N with the honeycomb core because of its more tortuous force transmission path. This was contrary to Li (2015), showing that the re-entrant obtained higher average peak forces. This was since 3D printing build orientations, and core topology was different to that seen by Faraci et al. (2020). Faraci and co-workers also utilised a numerical impact analysis rather than experimental. This demonstrated that changing the parameters and core features can significantly tailor the outcome of results. In addition, the impact and close-in blast response of auxetic honeycomb-cored sandwich panels were investigated numerically and experimentally by Qi et al. (2017). The authors performed field blast tests and drop-weight tests on the proposed sandwich structures. The re-entrant core provided substantial auxetic characteristics and saw significant force mitigation and blast-resistance performance in comparison to the honeycomb core. The re-entrant absorbed 8.72 kJ which was 19.1% greater than the 7.32 kJ energy absorbed by the honeycomb core. Consequently, they performed better than the honeycomb structures with the same size, areal density, and material. The authors reported great potential for re-entrant cores to be used as lightweight blast protection and impact resistant materials, enhancing sandwich structures used in civil, mining, military, nuclear infrastructure, and vehicle sectors. Moreover, Jin et al. (2017) numerically impacted the re-entrant and honeycomb sandwich structures with various nose shaped projectiles. Analysis indicated that the auxetic re-entrant structure showed superior ballistic performance in comparison to the conventional honeycomb structure because of enhanced resistance to deformation, promoting it with a higher capacity for energy absorption. Therefore, it absorbed 5.3% more energy in comparison to the conventional honeycomb. Hou et al. (2018) performed low velocity impact testing on re-entrant and conventional honeycomb sandwich structures to explore

cell deformation patterns and the influence of the core structure. The proposed sandwich structures went through cyclic loading conditions (3-point bend test) and low velocity impact. The authors concluded that the re-entrant topology presented superior robustness and durability and performed the best in both force mitigation and energy dissipation under low-velocity impact. This was attributed to the re-entrant's global instability pattern under deformation promoting less stress concentration in the core, and so stabilising face sheet penetration. The re-entrant presented a much larger ultimate impactor displacement (15.90 mm), whereas the honeycomb revealed a 9.97 mm displacement. Lastly, the re-entrant panel took 5.15 s longer to absorb the impact energy when compared to the honeycomb.

2.11.9 Previous Work on Additive Manufacturing of Auxetic Structures

Auxetic cores possess significant potential to be utilised in sandwich structures, however, their complex designs and intricate geometrical configurations limit their availability commercially. Nevertheless, Table 2.3 demonstrates the abundance of studies that have utilised 3D printing to expand the fabrication of auxetic designs and overcome conventional manufacturing drawbacks.

Table 2.3 Summary of authors who have 3D printed non-auxetic and auxetic topologies.

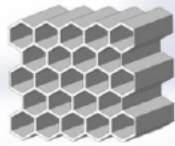
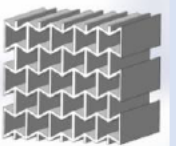
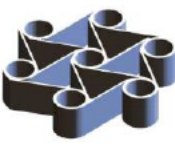
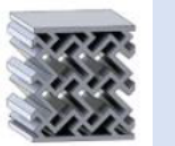
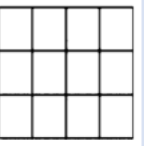
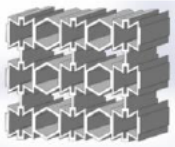
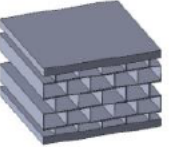
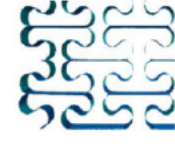
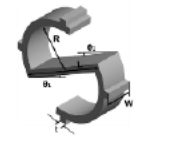
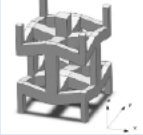
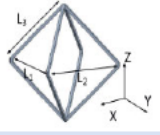
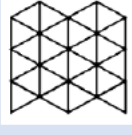
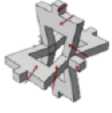
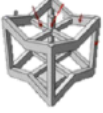
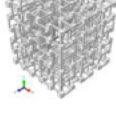
Honeycomb structure	Re-entrant structure	Chiral-Hexachiral structure	2D missing rib structure	Tessellated square structure
				
Authors: (Ingrole et al., 2017)	Authors: (Ingrole et al., 2017)	Authors: (Klepka et al., 2012)	Authors: (Fila et al., 2017)	Authors: (Grima et al., 2011)
Hybrid structure	Truss structure	S-hinged structure	S-hinged structure	Re-entrant with altered geometry
				
Authors: (Ingrole et al., 2017)	Authors: (Sarvestani et al., 2018)	Authors: (Khare et al., 2018)	Authors: (Meena & Singamneni, 2019)	Authors: (Shokri et al., 2019)

Table 2.3 (continued)

Octet-truss structure	3D re-entrant structure	BCC octet-truss structure	Equilateral triangle	Conventional 3D re-entrant structure
				
Authors: (Deshpande et al., 2001)	Authors: (Li et al., 2012)	Authors: (Beharic et al., 2018)	Authors: (Grima et al., 2005)	Authors: (Shokri et al., 2019)
Auxetic 3D re-entrant structure	Auxetic 3D re-entrant structure	Cubic chiral structure	3D isotropic anti-tetra chiral structure	
				
Authors: (Shokri et al., 2019)	Authors: (Shokri et al., 2019)	Authors: (Warmuth et al., 2017)	Authors: (Xia et al., 2018)	

As illustrated in Table 2.3 some core topologies, i.e., chiral models, 2D missing rib, S-hinged, and truss core, in particular have commonly been studied since they provide interesting bending stiffness, strength, and high energy absorbing properties. The honeycomb and re-entrant structures will be disregarded as they are discussed in detail in the previous and following sections.

The chiral models namely, the tetra chiral and hexachiral formations are commonly seen in Table 2.3 because they have been utilised in various fields of technology. In particular they have been utilised in the aerospace sector for wing constriction to expand the flight envelope, eliminate flap-type mechanisms, reduce aerodynamic drag, and help control vibrations. Its chirality is its most important characteristic, resulting in a rotative feature in its core whilst exhibiting a negative Poisson's ratio (Klepka et al., 2012). Conversely, this rotative phenomenon is illustrative of that seen for the 2D missing rib structure and the s-hinged structures. Subsequently, the 2D missing rib models are effective at predicting the Poisson's ratio function and marginally better at predicting stress-strain behaviour. However, they are geometrically

difficult to classify appropriately (Ren et al., 2018). On the contrary, the popularity of truss structures as seen in Table 2.3 stems from their favourable weight-efficiency, strength, and stiffness. In light of research executed by Sarvestani et al. (2018), it was highlighted that truss-like lattice cores can significantly increase the buckling resistance and energy absorption capabilities when utilised for sandwich structures. Truss panels can carry high bending and compression loads, as compared to alternatives such as the honeycomb core or stringer stiffened plates (Deshpande et al., 2001). The limitations with truss structures are that they have exceptionally high response forces and smaller densification deflections when compared to auxetic materials. Consequently, truss structures are not global dominant in their deformation mechanisms, and thus their deformations are irreversible because of local fractures in the core. Therefore, truss structures are ideal candidates for applications requiring high specific stiffness and strength and are inferior for energy absorbing applications when compared to auxetic structures, such as the re-entrant (Li & Wang, 2017).

To conclude, a large number of the models exhibited in Table 2.3, including the truss, chiral models, s-hinged, and missing rib structures discussed in this section are not cost effective making them expensive to fabricate. Although 3D printing can be used to fabricate the various models, it is still difficult to impose mass production with a lower cost, and this significantly constrains the wide applications for these models. Moreover, while they show desirable properties, they are not imperative, and this could be another reason as to why majority of the models have been fabricated for experimental purposes but not been utilised in the practical stages of real-world applications (Ren et al., 2018).

2.12 Previous Work Done on 3D Printed Sandwich Structures with Auxetic and Non-Auxetic Cores

2.12.1 Similar Work Done on Existing Sandwich Structures

This section reviews studies that have fabricated similar sandwich structures to that produced in this research. As such, Basurto-Vázquez et al. (2021) utilised polyethylene terephthalate glycol (PET-G) and the FDM method to fabricate unreinforced 3D honeycomb structures. The authors performed an in-plane compression test on the samples with various infill densities, i.e., 30%, 70%, and 100% and obtained energy absorption values ranging from 21.80 J to 66.71 J with incrementation of filler percentage to 100%. A comparison was made between print orientations (upright, flat and

edge), revealing that an upright print orientation (with cells facing flat on the bed) obtained superior energy absorption capabilities. It was demonstrated that the 100% filler concentration with a honeycomb core obtained superior energy absorption capabilities (66.71 J), which was 206% greater than the honeycomb structure printed on its edge with supports required between cells. This was accredited to the correct parameter configuration, and successful layer-by-layer welding, protecting the structure from delamination and fragmentation or abrupt catastrophic failure.

Sugiyama et al. (2018) successfully attempted to 3D print composite sandwich structures entirely from continuous CF. The authors described how conventional sandwich structures involve complicated and costly bonding processes between the face sheets and core. Therefore, CFR 3D printing was utilised to fabricate honeycomb, rhombus, rectangular, and circular sandwich structure core topologies as a single piece. The structures were fabricated by a Markforged 3D printer, and a tensile test and three-point bend tests was performed. It was revealed in the tensile specimen test, that the tensile strength and elastic modulus corresponded to 62% and 89%, respectively, of the theoretical values derived from the compound rule numerical analysis. This was believed to have been caused by bonding defects and printing errors caused by gaps between individual printed rasters after printing. The authors emphasised that a 3D printed structure can obtain a positive or negative air gap, depending on the selected infill percentage. A positive air gap is defined as individual rasters that do not make contact with neighbouring rasters, at times, as seen in Figure 2.24, with a 70% infill density. A negative air gap is one where individual rasters overlap one another, this being the optimum outcome for 3D printed structures. The negative air gap can only be achieved at high infill percentages, in this case, 100% and with an upright print orientation as seen in Figure 2.24. Consequently, there was a 41.67% increase in maximum peak force for the 100% infill structure when compared to the 70% infill structure due to its negative air gap.

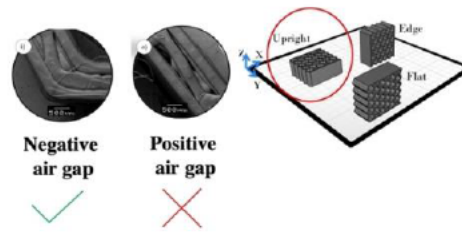


Figure 2.24 Microscopic characterization of welding lines/raster bonding by (Sugiyama et al., 2018)

A novel auxetic and hybrid honeycomb structure was 3D printed via FDM by Ingrole et al. (2017). The conventional honeycomb, re-entrant, auxetic-strut, auxetic-honeycomb1 (AH-V1), and auxetic honeycomb2 (AH-V2) were fabricated all as a single entity, owing to the flexibility of parameter changing and advantages of 3D printing. The build material was ABS and the method of testing involved in-plane uniaxial compression testing of the sandwich structure cores, experimentally and by simulations. The average in-plane uniaxial compression testing results from their work are revealed in Table 2.4. It was discovered experimentally that the re-entrant had a 56.49%, 34.86%, and 22.54% greater compressive strength (MPa), Young's Modulus (MPa) and energy absorbed ($\times 10^4 \text{J/m}^3$), respectively, when compared to the conventional honeycomb structure. The authors reported the significant capabilities that 3D printing permits, allowing the user to create bespoke, and complex designs to fabricate a core in which auxetic features can be controlled to one's desire.

Table 2.4 Compressive properties of samples by Ingrole et al. (2017)

Design	Compressive Strength (Mpa)	Young's Modulus (Gpa)	Energy absorbed ($\times 10^4 \text{J/m}^3$)
Honeycomb	1.61	35.5	0.55
Re-entrant	3.70	54.5	0.71
Hybrid AH-V2	2.38	25.71	0.56

Another study performed by Li & Wang (2017), proposed 3 distinct sandwich cores fabricated using an Objet Connex260 Stratsys 3D printer from an acrylic-based photopolymer VeroWhite. A conventional honeycomb structure, a re-entrant structure, and a truss structure were fabricated. The face sheets of the sandwich structures were woven CFs reinforced polymers (W-CFRP), and unidirectional CFs reinforced polymer (U-CFRP), that were adhesively bonded to the cores, and a sandwich structure printed entirely from VeroWhite. The authors utilised a combination of conventional methods

and 3D printing to fabricate the structures, where the conventional method involved a cold-bonded process of the CFRP in vacuum and an epoxy adhesive to adhere the printed cores to the face sheets. All sandwich structures under-went three-point bend testing to obtain the bending performance of the structures to compare. It was concluded that the re-entrant structures with no fibre reinforcement in the face sheets (VeroWhite face sheets) obtained a peak force of 25 MPa and the uni-directional re-entrant sandwich structure exhibited a peak force of 500 MPa. Consequently, a 1900% increase in force was experienced by incorporating fibre-reinforcement when compared to a neat polymer. Importantly, all sandwich structures with the bonded fibre-reinforced face sheets revealed significant failure of the adhesive bond in addition with a dominant failure mode of core shearing. Therefore, energy absorption relied more on the adhesive bond and the strength of the face sheets as opposed to the core topology.

2.12.2 No Fibre Reinforcement: Compression and Impact Testing Comparison of Non-Auxetic and Auxetic Sandwich Structures

The current section provides an overview of preceding research that has explored the potential of 3D printing auxetic designs for revealing the utilisation of 3D printing and leveraging the auxetic distinctive characteristics in low-velocity impact and compression. Moreover, it will proceed to compare non-auxetic structures to auxetic structures under low-velocity impact and compression testing. The designs have been predominantly centred on thermoplastic materials utilising FFF printing, with CFR printing being excluded from consideration (which will be explored in the subsequent section).

A study by Yang et al. (2018) performed a theoretical, computational, and experimental study on 3D printed auxetic structures. The structures were conventional honeycomb, re-entrant honeycomb, and an arrowhead core structure, implemented as cores between two thermoplastic face sheets. All the designs were done on SolidWorks to create 3D CAD models to be 3D printed from PLA, thermoplastic polyurethane (NinjaFlex), and thermoplastic polyurethane (SemiFlex). The three structures were analysed in relation to their structural characteristics through FEA models, and then the samples went through a simulated impact scenario. 3D printing permitted the successful creation of the prototypes. Moreover, the stiffness and shock absorption properties were investigated by impacting the structures at 1000N. The re-entrant indicated a Von Mises

stress of 2×10^7 and the honeycomb revealed a value of 7.5×10^7 , revealing a significant improvement in shock absorption and improved stress distribution. The results implied that auxetic structures can provide greater protection against impact scenarios in contrast to non-auxetic cores.

Faraci et al. (2020) compared numerical simulations of the auxetic re-entrant and conventional honeycomb structures with experimental results under various impact scenarios, using a drop-weight hemispherical head. Results indicated that the densification mechanisms of the auxetic structures resulted in enhanced protection from impact and indicated that the maximum transmitted force is lower when implemented in comparison to the honeycomb lattice (17 N instead of 27 N obtained for the honeycomb). However, the total elastic strain energy was 4.08% greater for the re-entrant lattice due to its ability to deform under a longer strain, thus resulting in superior strain-to-failure.

Finite element analysis and experimental impact testing were performed on 3D printed (FFF) PLA sandwich panels by Yazdani et al. (2018). The energy absorption and low-velocity impact resistance of the re-entrant core structure was compared to the conventional honeycomb structure and truss structure, to evaluate its elastic-plastic behaviour. The main scope of the study was to analyse the auxetic core topology, and its effect as a core in the sandwich structure relative to its density, and how this affected energy absorption using 3D printing when impacted in-plane and out-of-plane. Samples were impacted with a semi-spherical tip weighing 12kg. As a result, the out-of-plane samples indicated that the auxetic structure deflected a greater load in comparison to the rectangular and honeycomb samples. It was concluded that the sandwich panels with auxetic cores can have a higher level of energy absorption capability of up to 33% when compared to the honeycomb or truss sandwich structures if the impact energy and relative density is selected appropriately. This can be seen by the large force-displacement curve for the re-entrant sandwich structure in Figure 2.25.

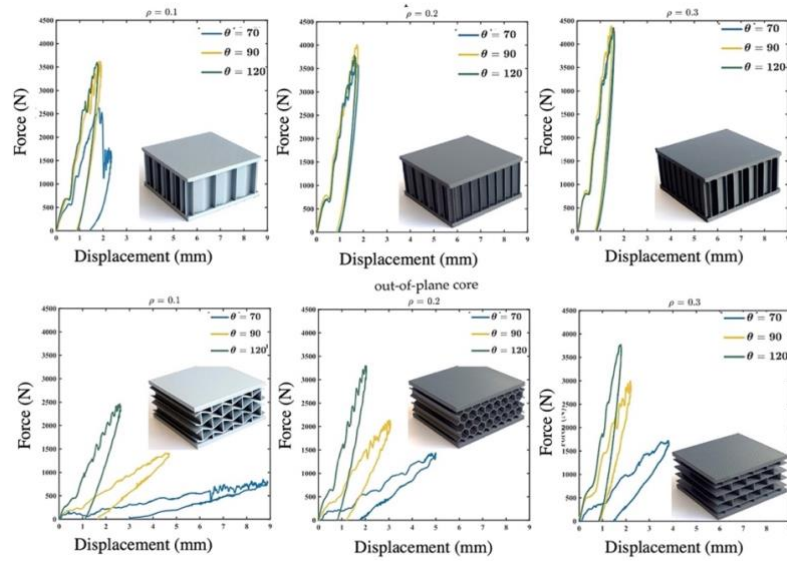


Figure 2.25 Force-displacement curves of 3D printed sandwich structures produced by Yazdani et al. (2018)

Moreover, Beharic et al. (2018) studied the effect of 3D printed cellular structures under a drop weight impact scenario. Core designs, re-entrant, octet-truss, and BCC lattice were all tested under low-velocity impact. The lattices were printed as sandwich structures for accurate comparison to be made if they were substituted as cores, where the face sheets were the same as the core material used (PA12). A laser sintered 3D printer was utilised for the fabrication of PA12 and a hemispherical impactor head weighing 3.969kg was used to impact the samples. The weight was increased incrementally until the damage was prominent on the face sheets. It was revealed that a higher improvement in impact energy absorption was witnessed in the auxetic lattices in contrast to the octet-truss and BCC lattices. The auxetic re-entrant structures experienced the highest average peak force under multiple impacts at 20612 N, which was 94.3% greater than the BCC lattice. The auxetic re-entrant structure, displayed consistent and enhanced damage tolerance when continuous and accumulating impact was made. For the bulk of the examined re-entrant structures perforation was not prominent, however, the octet-truss and BCC models suffered from perforation damage. Therefore, the auxetic structures saw enhanced stress distribution, and thus improving impact resistance, which resulted in the highest per-strike energy absorption capabilities, and the highest structural performance efficiency. Due to the absence of adhesives, results indicated no interlaminar failure.

Authors Li et al. (2018) used an Objet Connex260 (Stratsys, Ltd) printer alongside materials VeroWhite (opaque white Polyjet resin) and TangoPlus (Silicone) to 3D print a

re-entrant, chiral truss, honeycomb, and truss core structure of cubic geometry. The structures underwent uniaxial compression testing with a 10 kN load cell under a quasi-static regime and a constant strain of 0.001 s^{-1} . Out of the other three lattice designs, the re-entrant core structure exhibited superior compressive modulus and energy absorption capabilities. The Young's modulus of the re-entrant honeycomb reinforced composites was 4x larger than that of the chiral truss design and the conventional honeycomb core, and 5x larger than that of the truss design.

Yang et al. (2015) performed low-energy drop-weight tests and uniaxial compression tests on sandwich panels with re-entrant, rhombic, hexagonal, and octahedral cores to investigate the energy absorption capabilities and compressive properties of the various core topologies. The lattice structures were fabricated by selective laser sintering (SinterStation Pro) from PA12 (ALM PA650 powder), and this method was utilised due to its ability to alter and control the performance of the structures. Subsequently, impact testing involved a drop-weight tower with a hemispherical head weighing 5.5kg and a diameter of 19mm, to impact structures at energies varying from 1-1.3J at a velocity of 0.6-0.7 m/s. The sandwich structures were impacted multiple times and the total average energy absorbed was calculated. As a result, the honeycomb exhibited the highest compliance but with the poorest energy absorption capabilities. Conversely, the re-entrant structure presented the highest average energy absorption per impact, revealing an 88.35% greater energy absorption in comparison to the honeycomb structure. It also exhibited response forces of over 3700 N, which is over 100% higher than the rhombic, honeycomb, octahedral, and auxetic 2 structures.

A successful attempt was made to investigate several re-entrant structures with different geometrical parameters and compared to conventional ones by Shokri et al. (2019). The authors utilised the FFF technique to show the possibility of creating unique 3D auxetic geometry out of Acrylonitrile Butadiene Styrene (ABS) filament. Deformation analysis was conducted by impact testing the structures and performing quasi-static compression testing at a rate of 1.5mm/min. Subsequently, an investigation into the energy absorption capabilities, impact properties, and elasticity modulus was made. Shokri and co-workers reported that changing a unit cell from a positive Poisson's ratio to one possessing auxetic nature, resulted in a 40% increase of energy absorption when compared to a conventional structure containing a positive Poisson's ratio. Consequently, this simultaneously improved the indentation resistance and toughness of

a unit cell design. It was noted that the enhancement in energy absorption was because the auxetic structures exhibited more repeating units and a negative Poisson's ratio. As a result, the gap spacing between unit cells was smaller in dimension than the other lattices used, hence a denser structure to enhance the energy absorption capacity. Thus, cell geometry indicated a significant contribution to the energy absorption of the structures.

More recently, Türkoglu et al. (2023) performed in-plane quasi-static compression tests and 3-point bend tests on non-auxetic and auxetic PLA+ sandwich structures to obtain static energy-absorbing capabilities of the structures. A sinusoidal corrugated structure, conventional honeycomb, re-entrant, double arrowhead, and a tetra chiral core structure were fabricated by FDM. Compression testing was done at a test speed of 10mm/min and the test was repeated for each core topology. The authors also performed a dynamic compression test by employing a gas gun and incident bar of a Split-Hopkinson compression bar system. Overall, the damage behaviour of the structures was analysed, and the compressive strength, modulus and energy damping capabilities of the sandwich structures were evaluated. It was reported that the auxetic cores exhibited superior crush force efficiency when compared to the honeycomb, obtaining values of 0.464 and 0.374, respectively. Additionally, the mean crush force of the re-entrant was 36.08% greater when compared to the honeycomb structure. It outlined that the re-entrant structure had a crush energy absorption capacity significantly higher than conventional cores.

2.12.3 Fibre Reinforcement: Compression and Impact Testing Comparison of Non-Auxetic and Auxetic Sandwich Structures

Numerous efforts have been undertaken to develop sandwich structures using 3D printing technology, with an emphasis on auxetic cores and fibre-reinforcement in the face sheets. Despite these advancements, conventional techniques such as hand lay-ups and epoxy adhesives are utilised to manufacture the face sheets and bond the face sheets to the 3D printed core, respectively. Conversely, other authors have fabricated sandwich structures containing continuous fibre-reinforced cores; however, the face sheets are still conventionally fabricated and adhesively bonded to the core. Therefore, only a limited number of studies have successfully produced sandwich structures entirely from polymer, featuring reinforced continuous fibres in the face sheets, and without the use of epoxy glue to join the cores to the face sheets. Similar to the aforementioned section, this section

will also outline compression tests and low-velocity tests that have been performed on auxetic and non-auxetic cores.

Auxetic anti-tetra chiral honeycomb samples were manufactured utilising a Stratsys 3D printer by Chen et al. (2013). A flatwise compressive test was performed to evaluate the compressive strength and compressive modulus of the core structure, with a 600kN load cell and a constant displacement rate of 0.5mm/min. The 3D printed core was then adhesively bonded with a 2-part paste epoxy (REDUX 810) to unidirectional CF pre-pregs (IM7/8552) with ply angles of (+45/-45), and face sheet thickness of 0.4mm. The chosen anti-tetrachiral core produced excellent properties and showed to be a promising candidate for the use in sandwich structures. The authors also revealed the method of rapid prototyping to exhibit its potential in the creation of intricate parts that can be utilised in structural applications.

Correspondingly, Hou et al. (2018) used an Objet Connex260 Stratsys 3D printer with digital material FLX9795-DM to fabricate polymer a re-entrant, diamond lattice, and conventional honeycomb core structures. The printed core structures were adhesively bonded to unidirectional CFRP face sheets, and low-velocity cyclic impact tests were performed by a Split-Hopkinson pressure bar system to characterize the deformation patterns between the auxetic and non-auxetic cores. The hemispherical striker had a nose radius of 3.2mm, weighing 0.333 kg, impacting the structures at a speed of 4.7 m/s. Results showed that the sandwich panel performed better under impact with the 3D printed re-entrant core, attaining improved energy dissipation, robustness, and durability in comparison to the conventional 3D printed honeycomb core. It was noted that the re-entrant core yielded larger ultimate impactor displacement (15.90 mm in Figure 2.26a.), it took longer to absorb the impact energy (5.15 s), and indicated enhanced post velocity (2.83 m/s in Figure 2.26b.). Consequently, the authors reported that the re-entrant core resulted in attenuated oscillations on the stress-strain graphs and velocity-time graphs, as seen in Figure 2.26 (image c), thus, indicating that the re-entrant core structure performed better at mitigating the transmitted impact load due to its oscillating path and plateau region.

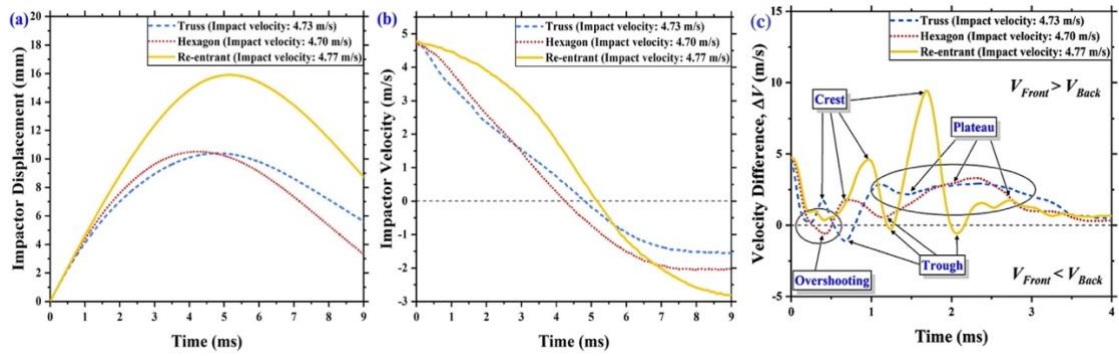


Figure 2.26 Stress-strain curves of the impacted three-lattice sandwich composite structures (a and b) (Hou et al., 2018) and a velocity-time graph of the tested lattices (c) (Hou et al., 2018)

Recently, a Kevlar reinforced PLA re-entrant and honeycomb structure was fabricated utilising 3D printing by Quan et al. (2020). Subsequently, in-plane uniaxial compression tests were performed at a rate of 2mm/min in both the vertical and horizontal directions. As a result, the authors compared the deformation behaviour of the cells with Kevlar as reinforcement, to determine how this affected the Poisson's ratio. Interestingly, stress-strain plots seen in Figure 2.27, revealed that the addition of Kevlar fibres to the matrix improved the compressive strength and modulus, permitting the structures to overcome a larger magnitude of compressive stress. Similar to Hou et al. (2018), the negative Poisson's ratio of the re-entrant core alongside Kevlar reinforcement resulted in 6 stages on the stress-strain plot, as seen in Figure 2.27. It was noted that under compression, the re-entrant structures produced a peak stress initially, translating gradually to a decline in stress, owing to the instability of the re-entrant cells and printing defects that had arisen in the struts. Stages 2-3 demonstrated localized deformation which was caused by the rotation of the inclined struts, and thus led to a short stress plateau. Stages 3-5 showed localized densification of the structures occurring layer by layer, finally reaching stage 6 where complete densification unfolded. On the contrary, it was noted that the Kevlar fibre bundles delayed any crack propagation in the struts. Under compression, cracks were seen to initiate at the edges of the matrix where there was a lack of fibre reinforcement, propagating along the cross-section of the cells until meeting the fibres. The authors noted that there was interfacial debonding from high shear stresses in the interface region and the occurrence of fibre pull-out. With the addition of the Kevlar fibres the structure was able to remain at equilibrium when full densification of the structure was reached because Kevlar possessed a high strength, preventing the failure of

the struts and any fracturing of the structure to occur. Therefore, the structures saw improvement in energy absorption and compressive stiffness by 87% and 98.7%, respectively, indicating similar in-plane compression stiffness to the model described by Gibson & Ashby (1988) for a classic centre-symmetric hexagonal configuration.

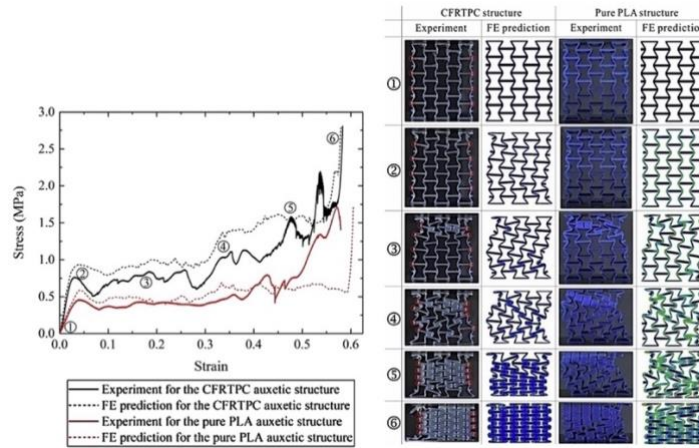


Figure 2.27 The in-plane compressive stress-strain response of the Kevlar reinforced PLA re-entrant structure versus pure PLA (Quan et al., 2020)

Similarly, Andrzejewski et al. (2022) presented a novel study on 3D printed sandwich structures, performing tensile, flexural, and impact testing on cores printed via FDM from a copolymer of polyethylene terephthalate-based filament (GPET). In addition, the authors compared these cores to a CF-reinforced GPET core with 15% CF content of rectilinear topology. The sandwich structures face sheets were liquid-crystal polymer-fibre fabric (LCP) with a GPET matrix in a prepreg form, and they were prepared by compression moulding. The 3D printed cores were then bonded to the LCP face sheets to perform mechanical testing. Furthermore, impact testing of the samples was performed by a Charpy impactor, equipped with a 5J pendulum, and a drop-weight impact test method with a spherical penetrator consisting of a diameter of 20mm and a weight of 1kg. The drop-weight impact tests involved 2 different impact energies, 5 N and 10 N. It was concluded that the stiffness of the sandwich structures was greater in the CF-reinforced samples, which was due to the presence CF-reinforced filament. For example, the GPET/CF structure with 20% infill was 81.96% greater in flexural modulus than the neat GPET with a 20% infill. It was revealed through impact testing that enhanced impact strength was achieved for the fibre-reinforced face sheets. The impact strength increased from 1.7 kJ/m² for the pure GPET samples to 50.4 kJ/m² for the fibre-reinforced sandwich composite samples.

The analysis and failure mechanism of 3D printed bio-based sandwich structures with auxetic cores was investigated by Essassi et al. (2021). The authors used a bio-based material containing polylactic acid reinforced with flax fibre to construct the sandwich structures for both a re-entrant core and the face sheets. The experimental tests involved the use of a hydraulic machine to perform three-point bend tests and fatigue tests consisting of a 10kN and a 1kN load cell, respectively. Three-point bend tests were performed at a rate of 5mm/min. It was concluded that the material possessed promising qualities, however, its flexural modulus, energy absorption, and fatigue resistance reduced, because of crack propagation, core buckling, and local progressive decohesion between the bottom skin and the core interface. A 49.46% reduction in stiffness was noted with a relative core density of 8.3% when compared to a core density of 33.5%. The occurrence of crack propagation hindered its energy absorption and stiffness, leading to the delamination of 3D printed layers within the re-entrant core and face sheets.

Moreover, Li & Wang (2017) proposed 3 distinct sandwich cores fabricated using an Objet Connex260 Stratsys 3D printer from an acrylic-based photopolymer VeroWhite. A conventional honeycomb structure, a re-entrant structure, and a truss structure were fabricated. The face sheets of the sandwich structures were woven CFs reinforced polymers (W-CFRP) and a unidirectional CFs reinforced polymer (U-CFRP). The authors utilised a combination of conventional methods and 3D printing to fabricate the structures, where the conventional method involved a cold-bonded process of the CFRP in vacuum and an epoxy adhesive to adhere the printed cores to the face sheets. All sandwich structures under-went quasi-static compression testing and three-point bend testing, with a 10 kN load cell, under a strain of 0.005 s^{-1} and a loading rate of 0.008 mm/s, respectively. Under compression, the re-entrant core indicated shrinking of the lateral boundaries exhibiting a negative Poisson's ratio and the honeycomb and truss exhibited lateral expansion exhibiting a positive Poisson's ratio. The re-entrant structure exhibited a cyclic response under compression, similar to Quan et al. (2020) and Hou et al. (2018). It failed in a row-by-row failure pattern exemplifying a decrease of stress on stress-strain plots. Inclined ligaments and vertical ligaments made contact, and thus led to an increase in stress. The authors discovered that the re-entrant experienced local catastrophic failure at times and buckling of the ligaments. Consequently, these behaviours produced a larger deflection curve for the re-entrant core, when compared to the truss and honeycomb structures.

More recently Zhou et al. (2023) compared in-plane uniaxial compression tests, in addition to simulated compression tests in the axial and in-plane orientations of 3D printed re-entrant, honeycomb, and double arrowhead core structures. The build material was nylon and onyx (chopped CF-reinforced composite). It was revealed that the double arrowhead auxetic structure exhibited superior energy absorbing capabilities in contrast to the non-auxetic cores. Reinforcing the nylon double arrowhead sample with CF, increased the specific energy absorbed by 125% and 244% compared to the conventional honeycomb and auxetic re-entrant structures, respectively. This was because the double arrowhead structure was of greater mass than the honeycomb and re-entrant structures, and therefore was able to provide more strength under identical loading conditions. The authors proposed the potentiality to revolutionize sandwich structure cores using auxetic cellular structures fabricated by fibre-reinforced 3D printing and revealed how relative cell density could also influence the outcome of results.

Contrary to the study conducted by Zhou et al. (2023), a study by Yang et al. (2018) highlighted that the double arrowhead core is significantly weaker under an increasing tensile force when compared to the re-entrant structure as its negative Poisson's ratio can change to a positive Poisson's ratio. This is due to the geometric deformation of each cell, changing the arrowhead formation to a rhombus formation, and thus lateral dimensions starts shrinking.

The literature discussed above indicated that the re-entrant core is widely regarded as the preeminent choice for auxetic core topology, owing to its superior compressive properties and unparalleled capacity for energy absorption. It was revealed that this was largely attributable to its distinctive auxetic nature and bending-dominant deformation modes, which combine to confer superior performance characteristics.

2.13 Processing GnPs with Polymers

Limited efforts have been made to fabricate sandwich structures entirely from polymer/GnPs with auxetic or non-auxetic cores utilising FFF. This is because of the challenges that arise with the various mixing techniques and processing routes that include the mixing of GnPs in polymers, i.e. challenges with the polymer matrix interface from the lack of appropriate adhesion with the polymer surface, agglomeration of GnPs from π - π interactions and secondary forces, and clogging of the plastic nozzle from high filler concentrations when 3D printing (Aumnate et al., 2018). Despite these challenges,

many studies have successfully reported enhancement of compressive modulus, strength, and energy absorption when compared to neat polymer structures with polymer/GnP nanocomposites. This is once successful dispersion is achieved, and effective exfoliation has taken place. Therefore, this section will underline the importance of GnP processing routes, the risk that agglomeration can have on sandwich structures, and the enhancement that GnPs can promote to a structure if processed correctly.

2.13.1 Processing Methods

There are a few methods in which to disperse GnPs within a polymer matrix; however, only a few promote successful dispersion of the GnPs alongside successful exfoliation of the sheets. The methods involve:

1. Solution blending
2. In-situ polymerisation
3. Melt blending

Solution blending has proven to be environmentally polluting, very expensive, and cannot be achieved at large productions (Wang et al., 2019). In-situ polymerisation requires a low elastomer viscosity, hindering the ability of exfoliation and loading fraction, as seen also reported by Papageorgiou et al. (2015) and Galpaya et al. (2012). It is also solvent consuming and environmentally-contaminating (Wang et al., 2019).

2.13.1.1 Melt Blending

An emphasis will be made on melt blending as it is the chosen method for the compounding of the nylon/GnPs nanocomposites for this research. Melt blending involves a combination of high temperature and high-shear forces to intercalate GnPs within a polymer, where the melt is (1) mixed mechanically with a polymer, and then (2) extruded, injection moulded, or melt spun to formulate polymer/GnP nanocomposites (Fu et al., 2015). The polymer is taken to its melting temperature at which the high-shear rates introduce internal mixing by, sigma, banbury, cam or roller blades, or by the rotation of screws, i.e. single, twin, triple or quad screws to amalgamate the GnPs into the polymer matrix (Papageorgiou et al., 2020). Subsequently, the mixing can be improved greatly by the rotors or screw configurations, i.e. co-rotating or counter rotating screws. It is inexpensive and environmentally friendly, owing to the lack of solvents in its process. It is functional, workable, and very efficient for fabricating nanocomposites, especially when

utilising polyamides at a large scale (Fu et al., 2015). Tabulated in Table 2.5 are the advantages and disadvantages of melt blending.

To achieve successful dispersion and exfoliation of the GnPs with melt blending techniques, a good affinity between the polymer and the GnPs are necessary, in addition with the correct altering of parameters of the melt blending method used. This has a significant effect on the properties of the polymer/GnP and its morphology (Chavarria et al., 2007). Consequently, the low bulk density of graphene can result in a difficulty of feeding it within melt mixers; however, appropriate parameter control can result in improved dispersion and feeding (Kim et al., 2010). Difficulty in feeding also means the shear forces generated within the barrel can lead to the formation of folds/wrinkles, or breaking of the nanoplatelets, reducing the possibility of enhancing the nanocomposite structure.

The utilisation of high temperatures and high-shear forces present in melt processing with co-rotating screws, can produce an intercalated nanofiller within the PA6 matrix (Mayoral et al., 2015). The temperature of the extruder barrel, screw speed, pellet feeder rate, GnP feeder rate, and the pelletizer speed, are parameters that can determine the rate at which production is completed and the outcome of the diameter of the extruded material and the final diameter of the filament when exiting the bath into the pelletizer (Chavarria et al., 2007).

Table 2.5 Advantages and disadvantages of melt blending (Fu et al., 2015)

Advantages	Disadvantages
1. More economical.	1. Need large machines that are specialized for the use of polymers, nanofillers, and high temperatures.
2. Can be used for large scale production.	2. Can result in poorer dispersion of GnPs in a polymer matrix when compared to in-situ and solvent blending.
3. It is compatible with numerous polymers and nanofillers and industrial practices.	3. Buckling and rolling or shortening of the GnPs can occur from strong shear forces.
4. Environmentally friendly.	4. There is a risk of aggregation at high concentrations of GnPs.

2.13.2 Twin-Screw Extrusion

Twin-screw extrusion is a popular melt blending method. The operation involves extruding polymers in their molten state by force of co-rotating or counter rotating screws,

as seen illustrated in Figure 2.28. The polymers utilised are in pelletised form, mixed, and sheared into the heating zone where the polymer reaches its molten state (melting zone, zone C in Figure 2.28). Following the melt zone, the molten polymer is fed to the melt conveying zone (zone D, Figure 2.28) ready for extrusion (Zone E), into a cooling bath, permitting a strand of polymer to be reeled through into a pelletizer (cutting the filament into pellets of desired size) (Wilczyński et al., 2019).

Many studies, such as that reported by Gaikwad et al. (2012), Mindivan (2017), Liu et al. (2010), Karevan and Kalaitzidou (2013), Ong et al. (2015), Mayoral et al. (2015), You et al. (2018), Blanco-Villalba et al. (2019), Jiang et al. (2019), and Karatas et al. (2019) investigated the utilisation of twin-screw extrusion and reported its benefits for the purpose of mixing nanofillers/fillers with polymers. It was discovered that appropriate dispersion and successful mixing of GnPs within polymers matrices was seen. Furthermore, successful exfoliation of GnPs was recorded; however, agglomeration was still of some concern, as similarly reported by Karevan & Kalaitzidou (2013). Conversely, other properties, specifically, mechanical, thermal, and electric properties were improved because of improved dispersion between the GnPs and polymers. A twin-screw extruder was utilised by Wang et al. (2016) to prepare polylactic acid/CNT indicating the potential of using other fillers and polymers. It was revealed that successful distribution and dispersion of the CNTs was achieved; however, agglomeration was present. It was concluded that the twin-screw extruder was environmentally friendly and an easy solution to process polylactic acid /CNT.

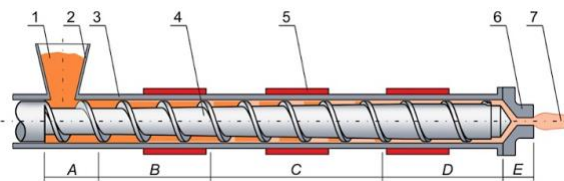


Figure 2.28 Nylon/GnP pellets (1) Hopper (2) Barrel (3) Screw (4) Heaters (5) Die (6) Solid conveying zone (A) Pre-melting zone (delay zone) (B) Melting zone (C) Melt conveying zone (D) Melt flow zone in the die (E) (Wilczyński et al., 2019)

2.13.2.1 Screw Configuration

Twin-screw extrusion can operate either by utilising counter rotating screws or co-rotating screws. It was reported by Shah & Gupta (2004) that the use of co-rotating extrusion is more effective in rotational speed, axial velocity, and degree of mixing when

compared to counter-rotating extrusion processes. However, some authors report better dispersion with counter rotating twin-screw extruders (Liu et al., 2010). Nonetheless, the benefits of co-rotating screws are related to the flight tips that possess opposite velocity directions. The opposite velocity directions form a figure-eight pattern, with closely matched profiles/dimensions upon turning, forming a sealing line along the flanks, resulting in a continuous wiping movement of the screws, and thus form a self-wiping property at high axial velocities. This aids in avoiding pressure peaks and allows screws to be placed in significantly close vicinity to one another whilst operating at high rotational speeds (Harold Giles et al., 2005). Co-rotating screws produce a higher axial velocity and higher throughput in comparison to counter-rotating screws because of the intermeshing region where axial velocity is at its highest during extrusion (Shah & Gupta, 2004).

2.13.2.2 Twin-Screw Extrusion Parameters

Many authors have also analysed the effects of altering twin-screw extrusion parameters to evaluate if improved dispersion, exfoliation, and bonding of GnPs can be achieved in polyamides. One such study was by Dennis et al. (2001), investigating the effects of melt processing conditions using a twin-screw extruder. The investigation revealed that the most appropriate shear rate suitable for the dispersion of nanofillers, and the enablement of platelet delamination, is that of a low-to-medium shear environment. Without considering the shear environment, platelet delamination could be hindered, and the modulus of the nanocomposite can reduce significantly. Moreover, Cho & Paul (2001) revealed that PA6 indicated suitable modulus, yield strength, elongation at break, and Izod impact strength over an extensive range of processing conditions with the twin-screw extruder. The processing of the melt improved when increasing the screw speed, however, it needed a long enough residence time within the barrel and appropriate shear rate for platelet delamination to occur. Similarly, Chavarria et al. (2007) reported that the shear rate and mixing conditions of a twin-screw extruder have considerable influence over the morphology and material properties of PA6. It was noticed that appropriate melting of PA6 before reaching a nanofiller, in conjunction with a low-to-medium level of shear and longer residence time leads to significantly higher platelet delamination and PA6 matrix reinforcement. Another study by Fasulo et al. (2004) revealed that agglomeration can be limited if the processing conditions are considered and optimized. Consequently, not considering processing conditions can result in a greater chance of aggregates which can

lead to an increase in pressure. The authors indicated that a lower screw rotation speed produced less energy distribution into the filler sheets, resulting in a slower breakdown of the stacks which also slows down exfoliation.

2.13.3 Challenges of GnP Dispersion in Polymer Matrices

Graphene nanoplatelets face challenges in achieving uniform and homogeneous dispersion within a polymer matrix accredited to its zero-band gap in addition to inertness to reaction. Therefore, hydrophobic-hydrophobic interactions between the nanofiller and polymer can result in poor interfacial compatibility, significant amounts of agglomeration, and wrinkling. This occurs because during twin-screw extrusion, graphene sheets break down due to poor interactions and weak Van der Waals forces. As a result, the sheets tend to strongly re-aggregate, leading to stacking over neighbouring sheets from the strong " π - π " interactions between the sheets. This can result in significant agglomeration within the polymer matrix, as also reported by Ahmadi-Moghadam et al. (2015) and Chen et al. (2017). The molecular interactions are what contribute to and determine how well GnPs can be dispersed and how critical the effect of agglomeration is within the PA6 matrix (Uhl et al., 2005; Zhu et al., 2013). Subsequently, appropriate dispersion of GnPs, therefore, determines how effectively the GnPs operate to reinforce a nanocomposite material. If the GnPs have been dispersed effectively then the stress experienced by a load can be successfully transferred from the matrix to the GnPs during a fracturing process, thus, enhancing the material properties (Wang et al., 2019). Wan et al. (2013) revealed that the elongation at break, tensile fracture toughness, and overall strength were greater in the samples with improved dispersion. In addition, Tang et al. (2013) described that the nanocomposites with appropriately dispersed RGO indicated greater glass transition temperatures and strength than the poorly dispersed samples. Comparably, Ahmadi-Moghadam et al. (2015) discovered that the fracture toughness increased by 82% for epoxy/graphene composites with improved GnP dispersion.

2.13.3.1 Re-processing Effects of Extrusion

If a thermoplastic, namely PA6, requires to be re-processed it can negatively impact its mechanical properties. A study conducted by González et al. (2000) analysed the physical properties (molecular weight, melt flow index etc.), mechanical properties (tensile strength, flexural modulus, and elongation at break) of recycled PA66. The authors stated a 11% increase in tensile strength, a 10% increase in flexural modulus, and

a 70% reduction in elongation at break from neat PA6 at the ninth cycle. Moreover, Russo et al. (2007) studied the rheological and mechanical properties, i.e. the tensile modulus, relative modulus, stress at break, and elongation at break of PA66 nanocomposites submitted to reprocessing with twin screw extruders. Approaching the third extrusion cycle the neat PA6 exhibited a 9.7% reduction in tensile modulus and a 8.1% reduction in stress at break. Similarly, Thompson & Yeung (2006) demonstrated that tensile modulus reduced by 8.2%, the Young's modulus reduced by 18%, and elongation at break reduced by 60% by the ninth cycle. Therefore, the studies revealed that repeated processing causes minor changes in the physical and mechanical properties of nanocomposites of thermoplastic nature.

2.14 Functionalised GnPs

The surface modification of graphene resulting in synthetization and the incorporation of functional groups can reduce agglomeration, improve dispersion, and improve interfacial strength/homogeneity within a polymer matrix. The bonding of functional groups to the surface of GnPs, results in a structure that is chemically compatible with the host matrix, promoting enhanced interfacial strength between each GnP and the PA6 matrix (Ahmadi-Moghadam et al., 2015). Consequently, the functional groups added to the surface of the nanoplatelets exploits Van der Waals forces and ionic interactions between graphene and the functionalised molecule (Georgakilas et al., 2012). Functional groups with a well-defined reactivity enhances the surface energy, accredited to a change in surface composition. This produces radical sites resulting in an improved homogeneity and wettability with a host matrix (Georgakilas et al., 2012; Booth et al., 2022).

Functional groups tend to be located around the edge of a nanoplatelet as shown in Figure 2.29 (white region), alongside minor amounts on the basal plane (red and black regions). Functional groups found on the basal plane breaks the strong hexagonal structure of graphene and results in defects, such as voids (Legge et al., 2020). Moreover, Figure 2.30 illustrates the sp^2 -bonded carbon network of graphite oxide. It reveals that the surface chemistry can alter significantly with the inclusion of hydroxyl (OH) groups, resulting in a large percentage of the network bonding to the hydroxyl groups. The OH groups within polymers find polarity and better compatibility, and thus improve in dispersion (Lerf et al., 1998; Park & Ruoff, 2009).

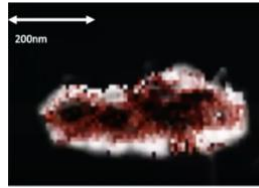


Figure 2.29 Image of hydroxyl molecules (in white) around edges of GO platelet (Legge et al., 2020)

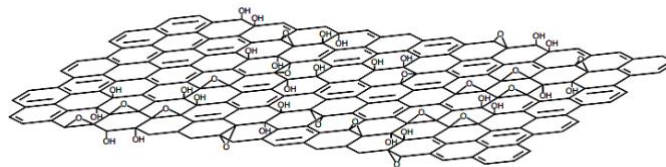


Figure 2.30 The chemical structure of graphite oxide (Park & Ruoff, 2009)

2.14.1 Surface Modification of Graphene

Functionalisation of graphene can take place by covalent or non-covalent modifications. These processes provide a chemical treatment to withdraw the strong forces and weaker attractive forces between the platelets (Gouda et al., 2021). The differences between both can be seen in .

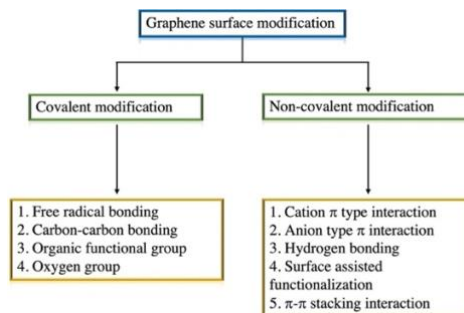


Figure 2.31 Covalent and non-covalent modification processes (Gouda et al., 2021)

2.14.1.1 Covalent and Non-Covalent Modification of Graphene

Covalent surface modifications involve the direct binding of heteroatoms or functional moieties to the carbon lattices via the removal of carbon atoms (Alam et al., 2017). One technique in doing so is by employing methods, such as plasma functionalisation or chemical modifications (Ackermann et al., 2022). As a result,

covalent bonds will tend to occur at the edges and the surfaces of graphene flakes and can be found between the graphene sheets and functional groups (Gouda et al., 2021; Papageorgiou et al., 2020). The non-covalent process does not change the chemical or electronic structure of a platelet, and it involves a more complicated chemical synthesis route and a time-consuming cleaning process of the platelets (Chen et al., 2017).

2.14.1.1.1 Plasma Functionalisation

The type of plasma used in a process depends on the gases involved. If oxygen gases or noble gases are used then the plasma treatments are referred to as ‘plasma oxidation’ or ‘plasma activation’, respectively. However, if gases other than oxygen are used, it is generally referred to as ‘plasma functionalisation’. Plasma functionalisation works by exposing graphite to a cold hydrogen plasma ray, e.g. Argon gas, to undergo plasma functionalisation. Similar studies have attempted this, as reported by Elias et al. (2009), and Ryu et al. (2008). This results in exfoliation of the graphite, negating Van der Waal forces, following exposure to oxygen, silane, or nitrogen plasma to introduce new functional groups to the surface of graphene. The functional groups aim to improve the hydrophilicity, intra-layer distances between the sheets, enhance thermal stabilities, improve dispersion stability and enhancements in their separation factors (Jafari et al., 2022). Subduing graphene to plasma functionalisation prepares functional groups to be positioned at the outermost surface, and thus developing free radical sites (Booth et al., 2022). Plasma hydrogenation was performed by Felten et al. (2014), demonstrating its success in modifying the properties of graphene. The successful chemical modification of graphene was reported by Haberer et al. (2011) and the tuning of graphene’s electronic properties through plasma hydrogenation was seen by Jayasingha et al. (2013). More recently, Moschetta et al. (2021) indicated that plasma functionalisation improved the wettability for functionalised graphene, and enhanced cell-cell communication when compared to pristine graphene.

2.15 Amine-Functionalised GnPs

Amine-functionalised GnPs (NH_2 -GnPs) are considered in this section since the project involves this derivative as the main form of reinforcement in a PA6 matrix. Figure 2.32 illustrates the theory of functionalisation Amine-GnPs. It reveals new functional groups being added, namely, the basic nitrogen atoms, resulting in bonding between the hydroxyl groups and hydrogen atoms. As a result, the alteration of surface chemistry

enforces chemical compatibility with the host matrix PA6 (Hossain et al., 2016). Subsequently, Figure 2.33 exemplifies nylon's molecular structure, illustrating that within the single monomer (caprolactam) of PA6, an amide link is found, hence chemical compatibility is achieved with amide groups found in NH₂-GnP (Figure 2.32) (Seong & Kim, 2015). As a result, an improvement in interfacial interactions between the inorganic GnPs and nylon occur, owing to an alteration of surface chemistry. Comparably, Korkees et al. (2021), described that there is a reduction in agglomeration because the functionalisation of graphene promoted improved dispersion and improved interfacial adhesion.

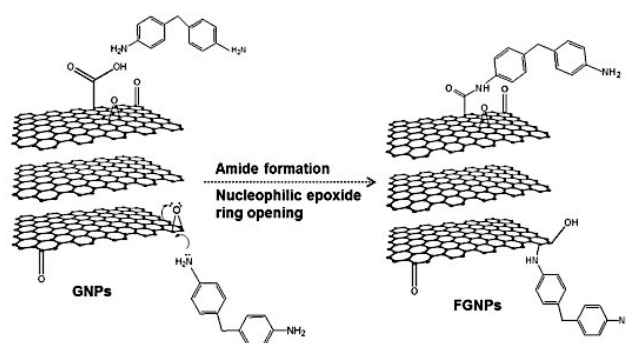


Figure 2.32 Schematic diagram showing the preparation of functionalised Amine-GnPs (Seong & Kim, 2015)

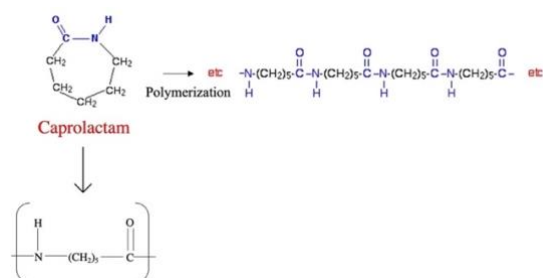


Figure 2.33 Molecular structure of PA6 (González et al., 2000)

2.15.1 Previous Work on Amine-Functionalised GnPs in Polymers

Many disquisitions investigate reinforcing epoxy with functionalised NH₂-GnPs, and few mention the utilisation of polyamides as host matrices. However, the mentioned studies below state their reinforcement in polymers, so assumptions can be made as to how they interact with the molecular structure of polyamides, if improvements in

dispersion can be achieved, and if these improvements result in enhanced strength and modulus.

A study by Seong & Kim (2015), reported improved interfacial bonding between NH_2 -GnPs and that of an epoxy matrix, in addition to an increase in curing rate, storage modulus, thermal dimensional stability, and impact strength of the nanocomposite structure. Moreover, a systematic study was conducted by Hossain et al. (2016) to enhance the mechanical, viscoelastic, and thermal properties of epoxy-EPON 828 by the integration of NH_2 -GnPs. Filler concentrations from 0.1-0.5 wt% were incorporated, and 0.4 wt% exhibited the most prominent properties. Consequently, SEM micrographs of the nanocomposites showed smoother fracture surfaces and indicated an improvement in the dispersion of the NH_2 -GnPs. The improvement in dispersion resulted in 20% and 40% improvement in flexural strength and modulus, respectively. Similarly, GnPs were chemically functionalised with the incorporation of amine groups within a poly (methyl methacrylate) poly (ethylene oxide) blend by Aram et al. (2016). It was compared to a nanocomposite containing non-functionalised GnPs. Transmission electron microscopy images revealed that the NH_2 -GnPs promoted improved dispersion, exhibiting enhanced homogeneity with the host matrix in comparison to non-functionalised GnPs. The NH_2 -GnPs also provided improved storage modulus, glass transition temperature, and thermal stability. More recently, recycled PA6/PA66 blends were mixed with functionalised GnPs, i.e. NH_2 -GnPs and O_2 -GnPs by Korkees et al. (2021). It was discovered that the NH_2 -GnPs indicated successful dispersion in the PA6 matrix. In addition, it demonstrated strong interfacial strength because of the strong nylon-to-graphene hydrogen bonding. Consequently, the nanocomposites demonstrated an impressive tensile modulus (3.6 GPa), tensile strength (78 MPa), and flexural strength (82 MPa) at 2% GnP concentrations, resulting in a 38.5%, 16.4%, and 13.8% increase, respectively, compared to O_2 -GnPs. Subsequently, experimentation showed a large reliance on the functionality type. Moreover, exfoliated graphite oxide sheets with hydroxyl groups and amine groups were prepared and incorporated with the blend, poly (2-(dimethylamino) ethyl methacrylate) by Yang et al. (2009). It was revealed that improvements in the dispersion of the GO sheets were noted, which was because of the bonding of hydrogen molecules, polymer molecules, and amine groups. Correspondingly, Park et al. (2015) reinforced epoxy with NH_2 -GnPs and witnessed improved dispersion and improved interfacial adhesion. There was an improvement in fracture toughness and 2.4-fold improvement in

fracture energy, observed at 0.04wt% concentration. It indicated that a low concentration of NH₂-GnPs still enhanced the mechanical properties and interfacial adhesion of nanocomposite structures. Additionally, Wang et al. (2012) dispersed NH₂-GnPs in epoxy resin and it was reported that improved dispersion was seen through micro-Raman spectroscopy due to a favourable interaction between the functionalised-amine groups and the polymer interface. Furthermore, there was a 15% increase in flexural modulus at 2 wt.% GnP concentration compared to neat epoxy. The hardness of 1.5 wt.% was 7.94% greater than neat epoxy. Lastly, at only 0.1 wt.% there was a 66% increase in fracture toughness compared to neat epoxy.

More recent studies have been reported using amine groups to improve interfacial properties. One such study is by Tiwari & Shaikh (2022), where NH₂-GnPs and carboxyl functionalised GnPs were dispersed in epoxy. It was revealed that the amine groups resulted in covalent and non-covalent bonding with the matrix. There was a 3.5% and 6.8% improvement in elastic modulus compared to unmodified epoxy due to improved interfacial bonding promoting efficient stress transfer between the polymer and the GnPs. Therefore, there was a uniform distribution of the platelets using amine-groups, and thus better dispersion within the matrix when compared to pristine graphene. Better dispersion and enhanced mechanical properties were similarly seen by Hossain et al. (2015), where the authors incorporated NH₂-GnPs to epoxy resin-EPON 828. The NH₂-GnP loaded samples revealed improved flexural strength and modulus by 20% and 40%, respectively. The authors Hossain et al. (2015) also conducted another experiment on CF-epoxy composites, embedding NH₂-GnPs into its matrix. Various filler concentrations were considered, i.e. 0.1, 0.2, 0.3, 0.4, and 0.5 wt%, and it was noted that samples with 0.4 wt% saw the greatest improvement in mechanical properties. The amine functionalised GnPs added 19% improvement in flexural strength and 15% in flexural modulus. Furthermore, their tensile modulus increased by 18% and tensile strength by 19%. It was concluded that these enhancements were related to the increased interfacial adhesion/interaction to the matrix. As a result, morphological analysis indicated improved dispersion and more effective load transfer ability between the NH₂-GnPs and the epoxy resin. More recently, Ackermann et al. (2022), dispersed amine-functionalised reduced graphene oxide within a bisphenol A-(epichlorhydrin) epoxy matrix, and the results indicated that a more homogeneous dispersion was seen with the amine-groups involved. However, that was dependent on the filler concentration and functionalisation type of the

GnPs. In addition, at higher weight fractions (1-1.5 wt%) improved homogeneity and dispersion was noted, but lower weight fractions resulted in more facile formations of agglomeration. A hybrid nanofiller approach was taken by Prolongo et al. (2018), where the authors combined NH₂-GnPs with CNTs. To avoid the weak interface of laminar nanofillers, the GnPs were functionalised with amine groups. It was revealed that there was a well-established nanofiller dispersion because of the present functionalisation of the amine-groups on the surface of the GnPs. Yu & Drzal (2020) considered using functionalised graphene oxide as a coupling agent for GnPs/epoxy composites. It was established that the chemical bonds formed between the amine functional groups on the graphene oxide surface and epoxy resin were seen to provide increased sheet/matrix interfacial adhesion, promoting improved dispersion of the GnPs and improved interfacial strength. All the functionalised GnP samples dispersed in epoxy showed an increase of up to 110% in toughness when compared to pristine graphene.

2.15.2 Previous Work on Graphene Oxide and GnP Reinforced Polyamides

Findings in this section reveal the improvements that GnPs promote when utilised in polyamides and their potential for improving polymer materials. Consequently, grafted graphene oxide (GO) was incorporated into PA6 by Nguy et al. (2014) revealing an enhancement in modulus by 139% with a filler concentration as low as 0.015 wt%. The authors indicated good dispersion and good adhesion with the GO nanoplatelets and the nylon matrix, hence, the improvement in its modulus. The incorporation of Amine-GnPs and O₂-GnPs was added to recycled PA6 and PA66 blends by Korkees et al. (2021). It was reported that there was a 20%-40% reduction in ductility from the rigid 2-D phase GnPs, however, the modulus of the virgin recycled nylon increased between 5%-50% with increasing GnP concentration. The strong interfacial hydrogen bonding between nylon and graphene was believed to have been the reason for the enhancement in the stated mechanical properties. Moreover, Men et al. (2019) noticed an improvement in tensile strength and yield strength by 50.3% and 134.8%, respectively, using ethylenediamine-modified graphene oxide/co-polyamide as the nanofiller and PA6 and PA66 as the host matrix, when compared to neat PA6. Graphene oxide was added to PA6 as a nanofiller by Dixon et al. (2015) and it was reported that tensile strengths increased in comparison to neat PA6. Subsequently, the tensile strength rose by 7.09% when compared to neat PA6, with a filler concentration of 0.65 wt%. Moreover, Zang et al. (2015) used poly (diallyldimethylammonium chloride)-modified graphene and negatively

surface-charge CF in order to improve the mechanical properties of PA6. It was concluded that the impact strength and bending properties were enhanced with the addition of these nanofillers. Subsequently, there was a 113.17% increase in impact strength when compared to raw-CF and neat PA6. More recently, Roth et al. (2022) examined the dispersion of CNTs, and graphene (CNT-G) in PA6 using molecular dynamics simulation to enhance the properties of PA6. They reported an increase of 0.05 GPa in bulk modulus after the addition of 2% CNT or 2% graphene. It was also noted that the Young's modulus increased as the wt.% increased with carbon nanofiller in the PA6 matrix. A similar trend was discovered by Navarro-Pardo et al. (2013). The authors investigated the effects of PA66 reinforced with one-dimensional and two-dimensional carbon nanomaterials. The nanomaterials were pristine CNTs, oxidised CNTs (OCNTs), reduced graphene oxide (RGO) and graphene oxide. It was highlighted by the authors that superior dispersion of the nanomaterials was achieved because of functionalisation. The, OCNTs and RGO resulted in a more homogeneous confinement of the crystals in PA66, and by functionalising the carbon nanomaterials it was discovered that crystal sizes in PA66 reduced. Lastly, the storage modulus of OCNT was nearly double that of pristine CNT. It was exhibited that those containing 1 wt% OCNTs resulted in a 97% increase in mechanical response. Conversely, the most significant improvement was discovered by the GO nanocomposites revealing a 139% improvement compared to neat PA66. The highlighted improvements were attributed to the 2D nature of graphene, generating improved interaction with PA66 and enhancing the stress transfer from the nanofiller to the matrix.

2.16 Previous Work on 3D Printed Thermoplastic Graphene and GnP Reinforced Polymer Structures

Most of the reported works that are mentioned below utilise common printing materials, such as PLA and ABS, because of their ease of manufacturing and usability; thus, resulting in a lack of work done on 3D printed PA6/GnP structures. Many studies focus on the enhancement of electrical properties and tensile properties of GnPs in polymers instead of compressive modulus, strength, and energy absorption. Moreover, an emphasis was placed largely on the morphology of the printed samples to investigate the bonding strength and dispersion of GnPs in 3D printed samples. The fabricated parts were commonly printed as dog-bone shaped structures or solid rectangular shaped structures revealing an absence of cellular structures, or sandwich structures. Consequently, this

section has compiled a collection of work centred around 3D printing of polymer/GnPs to show that which has already been achieved, and to note if enhancements were discovered in comparison to neat polymer structures. Finally, a focus will be made on how conventional manufacturing methods, namely, compression moulding, compares to 3D printing, in relation to the impact performance, modulus, strength and ease of manufacturing, and to investigate the potential of reinforcing PA6 structures with GnPs.

Recently, Ceretti et al. (2022) successfully 3D printed several ABS-based mono- and hybrid nanocomposites to analyse tensile, flexural and impact properties (Charpy impact testing). A comparison was made between neat ABS, ABS/GnP, ABS/GnP/TiO₂, ABS/GnP/CNT, and ABS/GnP/CNT/TiO₂. A micro-extruder with a co-rotating conical twin-screw configuration was the utilised melt blending technique. The impacted fractured surfaces were evaluated by a VHX500, Keyence microscope, to analyse void content formed, since the inclusion of GnPs promoted void nucleation sites. It was discovered that the combination of GnPs and optimal printing parameters yielded significantly improved tensile properties in relation to neat ABS. Structures with 0.5 wt.% GnPs revealed an 18% increase in tensile strength. Furthermore, the GnP reinforced samples revealed the most preeminent coalescence between deposited filaments and indicated that no obvious changes were necessary to the processing parameters of the 3D printers. However, it was reported that the build orientation of the samples had a significant impact on the performance of the printed samples such that it can lead to a poorer bond strength between individual printed layers with GnP reinforcement, and high anisotropic characteristics accredited to the fabricated nature of FDM printing.

A study showing great relation to the scope of this project was by Zhu et al. (2017), where the authors utilised the FDM printing technique to fabricate PA12/GnP dog-bone and rectangular shaped specimens to evaluate tensile modulus, thermal conductivity, and dynamic mechanical analysis (DMA). The optimum filler concentration was revealed as 6 wt% of GnPs out of 2, 4, 6, 8 and 10wt.%. The mixing of PA12 and GnPs was done using a co-rotating twin screw extruder (screw diameter=20mm L/D ratio=40) for the production of pellets to be used for compression moulded parts and for a comparison to 3D printed parts. Subsequently, a single screw extruder was utilised for the fabrication of filament material. Moreover, SEM characterization was implemented to investigate the dispersion of GnPs and the interfacial strength between the GnPs and PA12 matrix by freeze fracturing the printed samples. Results indicated an increase of

51.4% and 7% in thermal conductivity and elastic modulus, respectively, for the GnP reinforced 3D printed samples. Furthermore, SEM analysis indicated signs of agglomeration in the polymer matrix because of the Van der Waals forces and π - π interactions, and this was increasingly so with the higher content of GnP inclusion. Additionally, agglomeration promoted the development of voids, resulting in high stress concentration zones, and thus lowering the ability for the GnPs to transmit force between the matrix and platelets. Therefore, lower filler concentrations of 2, 4, and 6 wt% exhibited improved dispersion and less agglomeration, thus, successfully printing structures with higher resolution.

Similarly, Caminero et al. (2019) fabricated PLA-based composites reinforced with GnPs to investigate the tensile and flexural stresses, dimensional accuracy, and texture of dog-bone shaped samples after FFF. Mechanical testing involved tensile, flexural (three-point bending), Charpy impact testing performed at 10J, and interlaminar shear strength tests. It was concluded that the most significant performance was that of the PLA/GnP samples, indicating a 1.2x higher interlaminar shear strength compared to the neat PLA samples. In addition, PLA/GnP samples demonstrated improved performance in relation to flexural stiffness, indicating a 5.30%, 5.35%, and 8.10% increase printed in flat, on-edge, and upright orientations, respectively, compared to neat PLA. The fractured surfaces of the samples were analysed by SEM, and it was determined that the GnPs obtained relatively good dispersion of GnPs, however, voids were prominent in the polymer matrix. Furthermore, the PLA/GnP samples revealed a reduction in impact strength, therefore the neat PLA samples were 1.2-1.3x greater in strength. This was due to the increased brittleness of the PLA matrix from the presence of GnPs, especially when printed on-edge or in flat orientations. On the contrary, there was no effect on the dimensional accuracy of the samples with GnP reinforcement, and overall, they presented the greatest surface finish. Similarly, Marconi et al. (2018), revealed that PLA/GnP samples demonstrated superiority in elastic modulus in contrast to neat PLA samples. However, only with correct GnP concentrations, as samples with 2% GnPs reduced the ultimate stress from 52 MPa to 45 MPa for samples printed at 0° and it also reduced the samples printed at 90° from 24 MPa to 14 MPa.

Three-dimensional printing of multiscale CF-reinforced polymer composites containing GnPs and CNTs was reported by Residori et al. (2022). The authors added 3, 6, and 9 wt% of GnPs to an ABS matrix, or 1-3 wt% of CNTs, or 20/30 wt% of milled

CFs, and this was achieved by melt compounding, utilising an intermeshing co-rotating twin-screw extruder. After the mixing process, the selected compounded materials, already mixed, were converted to filament material to enable 3D printing. Dog-bone and rectangular shaped samples were 3D printed using a Sharebot next generation desktop 3D printer. Subsequently, the fabricated samples were mechanically tested under quasi-static tensile testing (load cell of 50kN and crosshead speed of 10mm/min), a nanoindentation test to evaluate hardness and elastic modulus, electrical resistivity test, thermogravimetric analysis, victat softening temperature test, and a heat deflection temperature test. Moreover, SEM analysis was also performed on fractured surfaces to evaluate the effect of the dispersion of the GnPs in the ABS matrix. It was concluded that good dispersion was achieved since twin-screw extrusion inhibited the development of aggregates. On the contrary, the neat ABS presented a higher strain at break in comparison to samples with GnP inclusion since there was an increase in brittleness of the samples. However, the GnPs (3wt.%) improved the tensile modulus of the structures by 27.45% when compared to neat ABS. It was reported that a clogging phenomenon occurred in the nozzle with the presence of GnPs, especially at higher filler concentrations of 6 and 9 wt%. This demonstrated a great reliance on the melt flow of the material, the quality of the filler (macro- and nano-type), and their total aspect ratio in the matrix.

Correspondingly, Butt et al. (2021) used an Anet ET4 Pro desktop 3D printer to manufacture dog-bone samples from PLA and PLA/graphene. The authors performed tensile testing of the samples at a crosshead speed of 1.5 mm/s and investigated the effects of extrusion temperatures and material extrusion rates. The objective was to examine, dimensional accuracy, surface finish, skewness and kurtosis, height characterization, ultrasonic testing, microstructural analysis, and material quality analysis through SEM. These objectives are commonly the main concern when utilising FFF. Moreover, an investigation was also done on how flow rate, alongside temperature changes, influence the printability of PLA and PLA/graphene. This was to determine how the tensile stress behaved and how the average load was affected. Consequently, experimentation revealed that increasing the flow rate above 120% resulted in over extrusion, dimensional inaccuracy, layer drooping, stringing, oozing, and blobs. Conversely, reducing the flow rate below 100%, resulted in under-extrusion and larger void development between printed layers. This was also discovered when printing temperatures were too low, from high print speeds, or from clogging of the nozzle. Therefore, under-extrusion led to poor

bridging performance, layer delamination, and poor bed adhesion. As a result, the greatest surface finish was achieved by a flow rate of 90% and the largest improvements in average load were seen with a flow rate of 150%. The improvement in mechanical properties was caused by the tightly packed rows of rasters, resulting in less void formation between layers. This optimized adhesion between the rasters and improved overall strength. It was concluded that over extrusion should be the selected parameter for 3D printing if dimensional accuracy is not of concern and mechanical strength is. If surface finish and dimensional accuracy need to be achieved, it is necessary to select flow rates leading to under-extrusion (90% for PLA and 80% for PLA/graphene) to achieve the smoothest surface possible. Therefore, the pre-selected 100% flow rate on most desktop 3D printers is not always the optimum flow rate selection. In conclusion, the PLA/graphene structures indicated the most consistent trends throughout tests performed and increased in their fracture load values compared to neat samples. Lastly, a common failure mode during tensile testing was delamination which developed before the bulk strength of the structures was reached, thus reducing tensile strength and stiffness.

An ABS/Graphene oxide (GO) composite structure was fabricated using FFF (WANHOA Duplicator 6) by Aumnate et al. (2018). The ABS/GO filament material was manufactured and mixed by dry mixing, solvent mixing and melt extrusion. A filler concentration of 2 wt% of GO was added to ABS and sonicated for 2 hours before these steps were implemented. Moreover, a co-rotating twin-screw extruder was utilised to extrude the melt, and mechanical testing involved subjecting the ABS/GO samples to tensile testing. It was noted that the twin-screw extruder enabled the ability to successfully manufacture filament ready for 3D printing of ABS/GO. Subsequently, the presence of GO enhanced the tensile strength and Young's modulus of the samples by 20% and 37.14%, respectively, in comparison to neat ABS. On the contrary, the filament produced by the dry mixing method did not successfully 3D print, since it developed high amounts of agglomeration resulting in die clogging, thus inhibiting the printing process. Therefore, melt compounding is the preferred option if the intention is to 3D print. Similarly, Yamamoto et al. (2019) incorporated functionalised GO into an ABS matrix with the objective to create filament for 3D printing. Carboxyl and hydroxyl groups were added to the surface of GO to analyse if improved yield strength, ultimate tensile strength, fracture strength, stiffness and successful dispersion can be achieved throughout the ABS matrix. Furthermore, 0.02, 0.04 and 0.06 wt% of GO were incorporated into the ABS

matrix, and dog-bone shaped samples were fabricated for tensile testing to compare to neat ABS. Furthermore, the solvent mixing process was also utilised by the authors in addition to the sonication method to produce a homogeneous mixing of water-dispersed GO and acetone. Subsequently, a Rigibot Big 3D printer was used to fabricate the samples, and thus tensile testing could proceed. An investigation of tension, extension, strain, and load were done. As a result, samples with 0.02 wt% of GO, revealed that the yield strength, ultimate tensile strength, fracture strength and stiffness all improved by, 13.3%, 21.9%, 4.30% and 29.3%, respectively. Consequently, properties were reduced when the 0.04 wt% was compared to 0.02 wt%. However, when the filler concentration increased to 0.06 wt%, there was a 5.88%, 3.03%, and 3.38% improvement in yield strength, ultimate tensile strength, and fracture strength, respectively, but there was a reduction in stiffness by 6.05%. The authors demonstrated that increasing the concentration of functionalised GO resulted in a rise of ductility and enabled them to maintain their fracture strength. It was described that the solvent mixing method can lead to a decrease in strain-to-failure and toughness.

Exfoliated GnPs (xGnPs) were embedded in an ABS matrix by Dul et al. (2016) to investigate the feasibility of 3D printing ABS/xGnPs and if the ultimate strength and strain at break of ABS could be improved with the incorporation of xGnPs reinforcement. A counter-rotating internal mixer was utilised to mix and disperse 2, 4 and 8 wt% of xGnPs within the ABS matrix. Subsequently, the compounded material was mixed in an intermeshing co-rotating twin-screw extruder where screw speeds were regulated to fabricate filament for 3D printing on a Sharebot next generation desktop 3D printer. Dog-bone shaped samples in 3 different print orientations (vertical, horizontal, and perpendicular) were fabricated to perform quasi-static tensile testing with a 50kN load cell. The ultimate strength, and strain at break were determined with a crosshead speed of 10mm/min. Moreover, a comparison was made between 3D printed samples and samples manufactured by a compression moulder. Analysis of the xGnPs was achieved by SEM, differential scanning calorimetry, melt flow index, and dynamic mechanical thermal analysis. It was revealed that the optimised filler concentration of 4 wt% xGnPs reported a 30% enhancement in elastic modulus compared to neat ABS. Dul and co-workers also reported the significance of print orientation and indicated that there was an improvement of 32%, 28% and 8% in elastic modulus for horizontal, vertical, and

perpendicular print directions, respectively. The authors concluded that the addition of xGnPs meant that there was an improvement in their stability under long lasting loads.

An investigation by Zhang et al. (2016) led to successful reinforcement of PLA, by incorporating reduced GO (r-GO). This proposed the possibility of 3D printing PLA/r-GO and utilising it for flexible circuits. Processing methods involved, a modified two-step in-situ reduced method to synthesize r-GO, and the mixing of PLA and r-GO was completed by melt blending with a twin-screw extruder to homogeneously disperse the r-GO and to create filament for 3D printing. Subsequently, 2D and 3D flexible circuits were fabricated by a MakerBot, and mechanical tests were performed involving stretching the circuits at a speed of 50mm/min to determine the Young's modulus. Furthermore, the morphology and surface chemistry of GO and r-GO was evaluated using SEM and high-resolution transmission electron microscopy. The authors reported that there was a homogenous dispersion of GO in the PLA matrix using the twin-screw extrusion method. The SEM images indicated good inter-layer adhesion between the first printed layer and the rest of the layers because of lower surface tension. As a result, the r-GO and GO reinforcement enabled the printed layers to maintain their shape whilst cooling because of the significant strength of the interface bonding force between the substrate and fillers. In conclusion, PLA and r-GO revealed good compatibility, indicated by suitable dispersion and strong interfacial adhesion. It was noted that the ultimate tensile strength of 6wt.% was 55.67% greater than neat PLA.

2.17 Summary of the Literature Review

Throughout the literature, it was determined that traditional advanced composite materials exhibit impressive flexural properties tensile properties, and compressive properties, and that fibre-reinforcement is the most common form of reinforcement for structural applications. However, FRPC materials suffer significantly from common failure modes, i.e. micro-cracks, delamination, fibre fracturing, fibre pull-out, and matrix cracking as a consequence of low-velocity impact. This is unavoidable throughout factories, and their applications, such as aerospace and the automotive industry. These failure modes are commonly found across all types of FRPCs, including 3D printed FRPCs, and they are detrimental to the above-mentioned mechanical properties of a structure, because it significantly reduces the overall lifetime of a FRPC.

Sandwich composites commonly involve the use of FRPC laminates as their face sheets, promoting high bending stiffness, and compressive and bending strength to a cellular core. Sandwich composites used in aerospace, marine sectors, or automotive undergo low-velocity impact scenarios, and can obtain the defects and damage modes which arise in FRPCs. Alongside the failure modes of FRPCs, sandwich structures suffer from failure modes, specifically, face yielding, core shearing, face wrinkling, general buckling, or indentation, and interlaminar failure from the de-bonding of the face sheets and core. The combination of failure modes results in a diminishment in the sandwich structure's ability to resist an applied compressive load, and thus can reduce compressive strength, compressive stiffness, energy absorbing capabilities, and their ability to maintain their structural integrity against low-velocity impact scenarios.

The incorporation of GnPs in a sandwich structure has the potential to enhance and protect it from the common failure modes in FRPCs and enables it to combat low-velocity impact scenarios. It does so by the development of toughening mechanisms resulting in crack deflection and crack pinning, thus hindering crack propagation and crack initiation sites. Therefore, this prevents the possibility of delamination and micro-crack formations in laminates. Subsequently, it requires a low filler concentration to produce a nanocomposite with significant stiffness and strength without adding exceptional overall weight to it.

Auxetic core structures, i.e. the re-entrant cell topology, have sought to enhance energy absorbing capabilities and promote greater protection against low-velocity impact in comparison to conventional honeycomb cell topology. This is due to its bending dominant features possessing a negative Poisson's ratio, and thus results in the densification of material forming inwards and towards a localized impact region. However, there is difficulty in fabricating auxetic core structures through conventional manufacturing techniques because of their intricate and complex geometrical designs. As a result, 3D printing has provided a new route to fabricate auxetic topology.

Moreover, melt compounding, i.e. twin-screw extrusion, enables the ability to mix GnPs and thermoplastic material to successfully disperse the GnPs throughout a thermoplastic matrix and to initiate appropriate exfoliation to the platelets. Subsequently, filament material can be created and used for FFF.

Throughout the literature review, findings reported that thermoplastic polymers reinforced with GnPs increased in their compressive, flexural, tensile, and energy absorbing properties after 3D printing. However, it was discovered that agglomeration and wrinkling occurred consistently in polymer matrices, even after appropriate melt blending procedures and processing history. This resulted in a reduction of interfacial strength between GnPs and led to a reduction in compressive properties. Consequently, functionalised GnPs were utilised instead to improve the dispersion and reduce agglomeration, and it was reported through numerous studies that this was successful in comparison to unfunctionalized GnPs.

Overall, there was a lack of work and findings on sandwich structures fabricated entirely from PA6/GnP without any fibre reinforcement, as well as the inclusion of an auxetic core. There was also an absence of findings expressing 3D printed FRPC sandwich structures with auxetic cores bonded to the face sheets solely utilising 3D printing. As a result, many authors recorded:

1. GnP reinforcement alongside fibre inclusion but with conventional cores and conventional methods to produce the cores.
2. 3D printed auxetic sandwich structures with no reinforcement whatsoever.
3. 3D printed auxetic and cellular cores with fibre reinforcement but no GnP reinforcement.
4. 3D printed auxetic and cellular cores with no GnP reinforcement and using conventional methods to fabricate the face sheets in addition with an adhesive method to bond the face sheets to the cores.

This chapter will cover the methods undertaken to investigate the compressive properties of 3D printed fibre and GnP reinforced sandwich composites with core topologies honeycomb, re-entrant and hybrid (a combination of the honeycomb and re-entrant cells). Additionally, the chapter provides a comprehensive overview of general equipment, the machinery utilised to perform all testing, the materials used, and the techniques involved in the fabrication of 3D printed fibre-reinforced sandwich composite structures.

3.1 Design and Manufacturing of Fibre-Reinforced Sandwich Structures

For the 3D printing fabrication of the sandwich structures, the honeycomb, re-entrant, and hybrid cores were selected based on their widespread use in sandwich composites and their exceptional compressive stiffness and strength when placed under uniaxial compression (Ingrole et al., 2017), three-point bending (Hou et al., 2013), and tensile testing (Zaharia et al., 2020). The sandwich structures were printed such that the face sheets were fixed to the cores without requiring adhesive, as seen in Figure 3.1. The structure's face sheets composed of Kevlar and CF fibres orientated in various directions to explore how this would determine the deformation behaviour of the cores orientated in-plane under uniaxial compression and how it affected their compressive modulus, compressive strength, and energy absorption during compression.

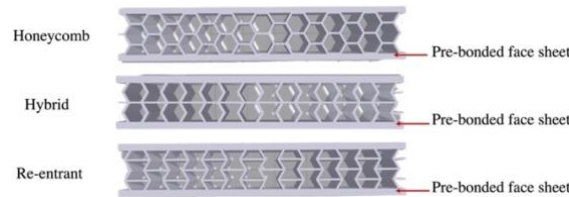


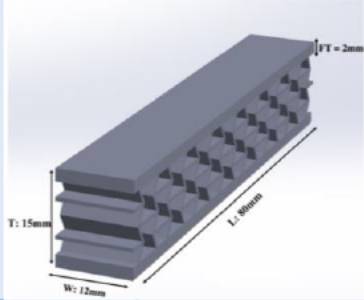
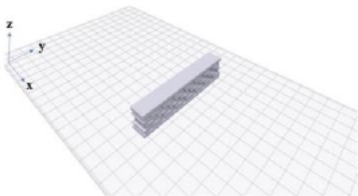
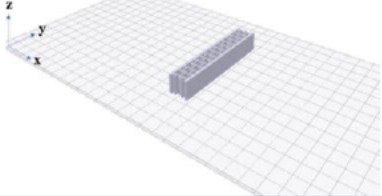
Figure 3.1 Illustration of the sandwich structures where face sheets were bonded during printing

The sandwich structures were designed via SolidWorks 2019 student version to produce CAD models, as illustrated in Figures 3.2-3.4. The individual cell geometries were fabricated first so that they can be connected and grouped together to create a core lattice structure. Similarly, the face sheets were designed via SolidWorks and bonded together with the core to produce a complete part to be 3D printed as a single entity. This can be seen illustrated in Table 3.1 (dimension illustration), where l is the length of the

sandwich structure, t is the thickness of the sandwich structure, w is the width of the face sheet and f is the face sheet thickness. Figure 3.1 exhibits the completed CAD models of all the sandwich structures.

Table 3.1 Dimensions of printed samples and an illustration of the sandwich structure build orientation

3D printed sample dimensions	
Dimensions	(mm)
Length	80
Thickness	15
Width	12

Dimension illustration	
	
Sample orientation for FRPC structures on build plate (X:0° Y: 0° Z:90°) 	Sample orientation for unreinforced structures on build plate (X:270° Y: 270° Z:0°) 

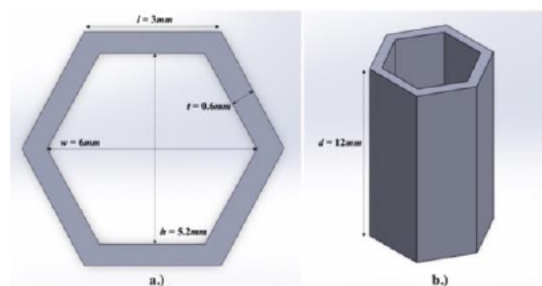


Figure 3.2 In-plane geometry and dimensions of the honeycomb cell (a.) isometric view of honeycomb cell (b.)

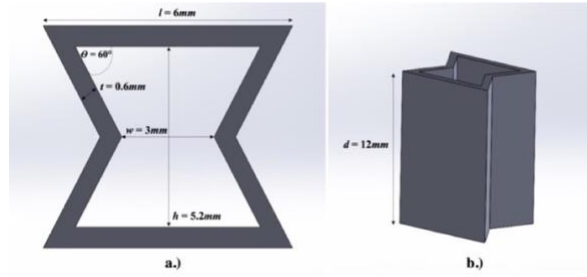


Figure 3.3 In-plane geometry and dimensions of the re-entrant cell (a.) isometric view of honeycomb cell (b.)

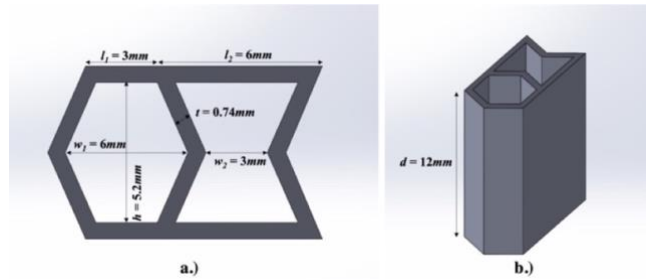


Figure 3.4 In-plane geometry and dimensions of the hybrid cell (a.) isometric view of honeycomb cell (b.)

The chosen fibre types, CF and Kevlar were utilised in different fibre orientations. Figure 3.5 exhibits an X-ray view of the fibre orientations, indicating precisely how the fibres were orientated within the face sheets of the 3D printed sandwich structures. Fibres are represented as the colour ‘yellow’; nylon support material was represented as the colour ‘purple’, and ‘white’ represents the nylon matrix. Hence, fibre directions consisted of:

1. 2 concentric unidirectional (2CUD)
2. 5 concentric unidirectional (5CUD)
3. Isotropic-unidirectional (isotropic-UD)
4. Quasi-isotropic (QI) where the lay-up is $[+0^\circ/+45^\circ/+90^\circ/-45^\circ]_s$
5. A $[+90^\circ]_s$ fibre orientation

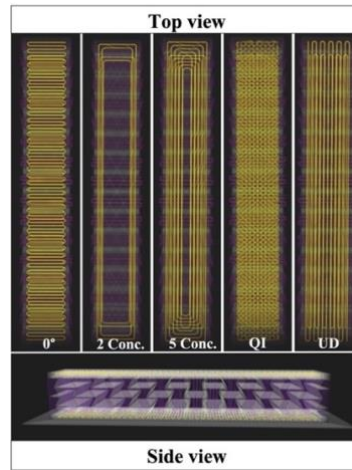


Figure 3.5 X-ray image from slicer software ‘Eiger’ distinguishing the difference in fibre orientations in the sandwich structures face sheets

All sandwich structures exhibited in Figure 3.5 contained 8 total fibre layers. The top and bottom face sheets each contained 4 fibre layers, resulting in the maximum fibre volume that can be attained for each face sheet at 2 mm thickness, as seen in Figure 3.5 (side view). Notably, the 90° fibre orientation is termed 0° throughout all the results discussed in this chapter and later in Chapter 4, as due to its alignment with the build orientation as outlined in Table 3.1 (sample orientation). Therefore, in comparison to the isotropic-UD fibre orientation, fibres were orientated along the face sheet, whereas the 0° fibre orientation was directed across it, illustrated in Figure 3.6. The 5CUD fibre orientation was specified with 5 revolutions because the objective was to have a batch of CUD sandwich structures with maximum fibre capacity. Five concentric rings fit the width (12mm) of the face sheets amounting to maximum fibre volume. This is because a greater number of concentric fibre rings placed in the printed components can result in an increase in mechanical performance (Imeri et al., 2018). Subsequently, the 2CUD fibre orientation was selected so that it could be compared to the 5CUD structure. Lastly, the QI lay-up, as seen in Figure 3.5, had 4 fibre layers in orientations of 0°/+45°/+90 °/-45° situated in the top face sheet and -45°/+90 °/+45/0° in the bottom face sheet, as shown in Figure 3.5 (side view image). The selected fibre orientations utilised in this project were centred around common conventional fibre reinforced sandwich structures containing the specified fibre orientations, i.e. QI, +90° and 0°. In addition, the CUD fibre orientations were centred around the commonly studied fibre orientations in CFR 3D printing, recognised within the many studies reported in the literature in sections 2.10, 2.10.1 and 2.10.2, and some of the studies mentioned in this chapter, as seen in sections 3.1.3.

Moreover, a comparison of the compressive properties and energy absorption attained by the reinforced structures was then compared to the unreinforced sandwich structures, as well as between the two types of fibres to distinguish their differences. The objective was to determine which fibre direction achieved the highest level of optimal compressive qualities and whether fibre-reinforced structures improved compressive properties and energy absorption capabilities in comparison to unreinforced structures.

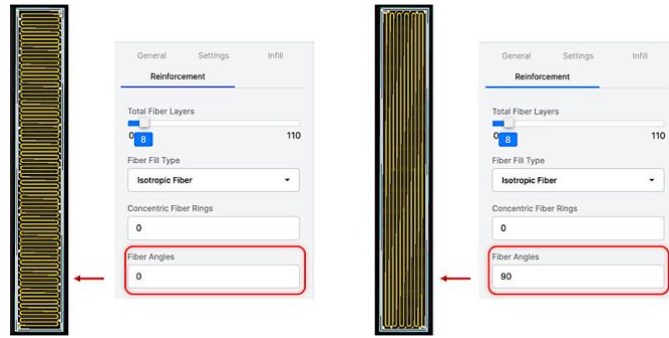


Figure 3.6 An illustration between the 0° and 90° fibre angles

Following the successful compression testing of the sandwich composites, an additional batch of samples with identical fibre kinds, orientations, and core topologies were printed to subject them to low-velocity impact (Figure 3.26) and to measure residual compressive properties through a compression after impact (CAI) test (Figure 3.25). The purpose of this investigation was to determine which sandwich structure, between reinforced and unreinforced, exhibited the most desirable residual attributes.

3.1.1 Materials

The material utilised for the manufacturing of the 3DP fibre-reinforced sandwich structures was Nylon White produced by Markforged®. Each spool included approximately 800 cm³ of Nylon White and is compatible with fibre embedment (Markforged, 2023). The material data tested by Markforged can be found tabulated in Table 3.2. Furthermore, continuous Kevlar fibres were utilised as fibre reinforcement and Carbon fibres were subsequently selected as another type of fibre reinforcement based on their popular demand throughout literature by Albadrani (2022), Dickson et al. (2017), Dong et al. (2018), Imeri et al. (2018), Korkees et al. (2020), and Swart et al. (2022). The material data for partially impregnated tows of continuous Kevlar and CF can be seen tabulated in Table 3.3.

Table 3.2 Markforged NylonWhite material data (Markforged, 2023)

Mechanical tests	Test (ASTM)	Nylon white
Tensile modulus (GPa)	D638	1.7
Tensile stress at yield (MPa)	D638	51
Tensile stress at Break (MPa)	D638	36
Tensile strain at Break (%)	D638	150
Flexural Strength (MPa)	D790 ¹	50
Flexural Modulus (GPa)	D790 ¹	1.4
Heat Deflection Temperature (°C)	D648 B	41
Izod Impact – notched (J/m)	D256-10 A	110
Surface Resistance (Ω)	ANSI/ESD STM11.11 ³	-
Density (g/m ³)	-	1.1

Table 3.3 Material data for partially impregnated tows of continuous Kevlar fibre and carbon fibre (Markforged, 2023)

Mechanical tests	Test (ASTM)	Carbon Fibre	Kevlar®
Tensile Strength (MPa)	D3039	800	610
Tensile Modulus (GPa)	D3039	60	21
Tensile Strain at Break (%)	D3039	1.5	3.9
Flexural Strength (MPa)	D790 ¹	540	420
Flexural Modulus (GPa)	D790 ¹	51	21
Flexural Strain at Break (%)	D790 ¹	1.2	2.2
Compressive Strength (MPa)	D6641	420	216
Compressive Modulus (MPa)	D6641	62	21
Compressive Strain at Break (%)	D6641	0.7	0.8
Heat Deflection Temp (°C)	D648 B	105	150
Izod Impact – notched (J/m)	S256-10 A	960	3100
Density (g/m³)	-	1.2	1.5

3.1.2 The Inspiration Behind the Selected Sandwich Structures

The fabricated sandwich structures discussed in this section are centred on comparable findings explored in the literature review in sections 2.11.9, 2.12.1 and 2.12.2. To investigate all the stated characteristics and objectives for this project, it was essential to select build parameters as well as sandwich structure geometries that enabled faster printing times, sufficient build quality, and appropriate strength to produce all required fibre-reinforced and unreinforced structures. Hence, sandwich structures were inspired by the three-point bend specimens produced in a study by Zaharia et al. (2020). The three-point bend samples were chosen since the scope of this project involves the incorporation of fibre reinforcement, and the objective is that it would result in

appropriate flexural characteristics of the fibres, enabling them to play a role in the deformation of the chosen cores (Hou et al., 2013; Li & Wang, 2017).

3.1.3 3D Printing Parameter Selection

Many studies such as Albadrani (2022), Caminero et al. (2018), Dong et al. (2018), Imeri et al. (2018), Kabir et al. (2020), and Sugiyama et al. (2018) report various parameter choices for the Markforged printers and parameter selections that produce high strength and high-quality structures. These findings are indicative of commendable consistency in the parameter selection process, as seen in Table 3.4.

Table 3.4, shows a layer height of 0.1mm was selected since it was reported that layer height was commonly adjusted to 0.1mm. This is particularly when 3D printing with fibre reinforcement because Eiger assigns this parameter to 0.100 mm for Kevlar and HSHT fibreglass, and 0.125 mm for CF reinforcement. Additionally, Table 3.4 indicates that supports were selected. Subsequently, brim adhesion was selected as it showed to be useful in negating the effects of warping. Moreover, a common fill pattern was that of a triangular fill pattern delivering sufficient strength and lower overall part density. Commonly seen in the studies aforementioned, the chosen plastic infill densities were 100% for greater strength in printed parts. However, the choice of 37% infill density, as seen in Table 3.4, was the default parameter for Eiger, resulting in a part with a reduction in mass and therefore remained as the selected infill density. Furthermore, roof and floor layers were set to default (5 layers) as advised by the Eiger software. There were 5 roof layers in the top face sheet and 5 floor layers situated in the bottom face sheet, as shown in Figure 3.7. Additionally, wall layers deviated between 1 and 2; however, for the purpose of this project it remained as 2 wall layers to provide additional protection to the fibres. Lastly, the total fibre layers in Table 3.4 was the sum of the 4 layers in the top face sheet and the 4 layers in the bottom face sheet, as seen in Figure 3.7. The total concentric fibre rings were the total revolutions of continuous fibre within one face sheet for the sandwich structures containing concentric unidirectional reinforcement.

An attempt was made to keep as many pre-selected parameters on Eiger as possible, as the scope of the project did not involve an investigation into print parameters. Nonetheless, Eiger employs its own algorithm to calculate the most optimal parameters for printing selected parts. Therefore, the most efficient print could be employed whilst

reducing the volume of plastic consumption and the time between prints in order to have the most optimum print quality for strength in testing.

Table 3.4 Printing parameters for in-plane fibre-reinforced nylon samples printed on the Markforged Mark two printers

Printing parameters	
Material (Plastic)	Nylon White
Reinforcement material	Kevlar/CF
Layer Height	0.1 (mm)
Use of supports	Yes
Support Angle (re-entrant)	0°
Support angle (Hybrid and Honeycomb)	90°
Bed adhesion	Brim
Fill pattern	Triangular fill
Fill density	37%
Roof & floor layers	4
Wall layers	2
Total fibre layers (Isotropic)	8
Total concentric fibre rings	2/5

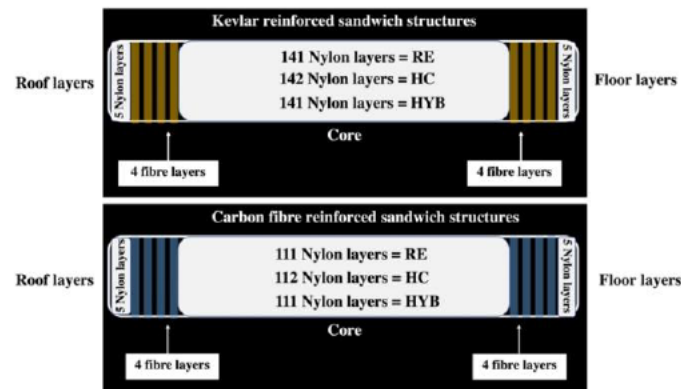


Figure 3.7 Diagram of the internal layer composition for all samples containing Kevlar fibre and carbon fibre where RE is the re-entrant, HC is the honeycomb and HYB is the hybrid sandwich structure

3.1.3.1 Build Orientation

In light of FDM build orientations studied by Ahn et al. (2002), selection of the optimum build orientation for the 3D printed sandwich structures were made so that the compressive load exerted on the sandwich structures might be transferred and carried successfully throughout the core topology. Build orientations are outlined in Table 3.1 under sample orientation on build plate. Models were orientated in X: 0°, Y: 90° and Z: 90° for FRPC structures to permit the successful laying up of the fibres. The orientations

of X: 270°, Y: 270°, and Z: 0° did not enable fibre lay-up as it is not uniform to the build plate, and thus, unreinforced samples could be printed in this orientation. It was necessary for the FRPC sandwich structures to include supports because of their build orientations. As a result, Figure 3.8 illustrates that supports must be removed for testing to proceed, resulting in plastic waste. A flat head screwdriver was utilised carefully to break away the bonded supports, followed by pliers to appropriately remove them after the debonding procedure. One of the features of supports is that it permits larger components to be 3D printed, however it comes at the cost of a higher volume of printed nylon supports, an increase in plastic waste generated from post processing, more time consumed removing supports, and increased possibility of premature failure to the cells from attempted support removal. Unreinforced structures required no supports and thus no removal or consequence of potential premature failure to the cells. Finally, the chosen dimensions of the sandwich beam structures resulted in a reduction of print time, enabling all fibre orientations to be printed for comparisons to be made. To note, raster direction cannot be changed within the system parameters of the Eiger software and so rasters are always printed in the +45/-45 direction with Markforged printers, as also reported by Kabir et al. (2020).



Figure 3.8 Support removal from the fibre reinforced honeycomb sandwich structure resulting in plastic waste

As distinguished in Figure 3.9, toolpaths, such as infill are affected by the orientation of the sandwich structures on the build plate and the type of fibre utilised. Due to Eiger being a closed system, in relation to minimal parameter control, this factor cannot be changed. Consequently, Table 3.5 exhibits infill is positioned in different locations depending on fibre orientations, and thus also affects the number of nylon layers within the core. On the contrary, the selected triangular infill pattern does not take place within the core topology since a larger width of an individual cell is required. Consequently, cell geometries presented previously in Figures 3.2-3.4 are fabricated entirely from the wall layers, and infill and wall layers are used to fabricate the face sheets of the sandwich

structures. As a result of support requirement for cells, post processing significantly altered the thickness (t) and width (w) of each cell topology and of individual cells, however, a more accurate cell topology was noted with the absence of supports and post processing. Consequently, deviations resulted in ± 0.3 in thickness (t) and width (w) for FRPC sandwich structures, and ± 0.1 in thickness (t) and width (w) for unreinforced sandwich structures. Conversely, infill was not affected by the deviations in wall thicknesses since it was not present.

Table 3.5 Layer composition of sandwich structures where ‘N’ is nylon layers, ‘F’ is fibre layers, and ‘ Δ ’ is triangular infill

Sample (FRPCs)	Layer composition
HC-CF reinforced	5N/4F/1N/1 Δ /3N/Core(92N)/5N/4F/5N
HC-Kevlar reinforced	5N/4F/1N/5 Δ /2N/Core (116N)/2N/2 Δ /4N/4F/5N
HC-unreinforced	120 wall and infill (Δ) layers
RE-CF reinforced	5N/4F/1N/1 Δ /5N/Core (88N)/7N/4F/5N
RE-Kevlar reinforced	5N/4F/1N/5 Δ /5N/Core (110N)/5N/2 Δ /4N/4F/5N
RE-unreinforced	120 wall and infill (Δ) layers
HYB-CF reinforced	5N/4F/1N/1 Δ /5N/Core (88N)/7N/4F/5N
HYB-Kevlar reinforced	5N/4F/1N/5 Δ /5N/Core (110N)/5N/2 Δ /4N/4F/5N
HYB-unreinforced	120 wall and infill (Δ) layers

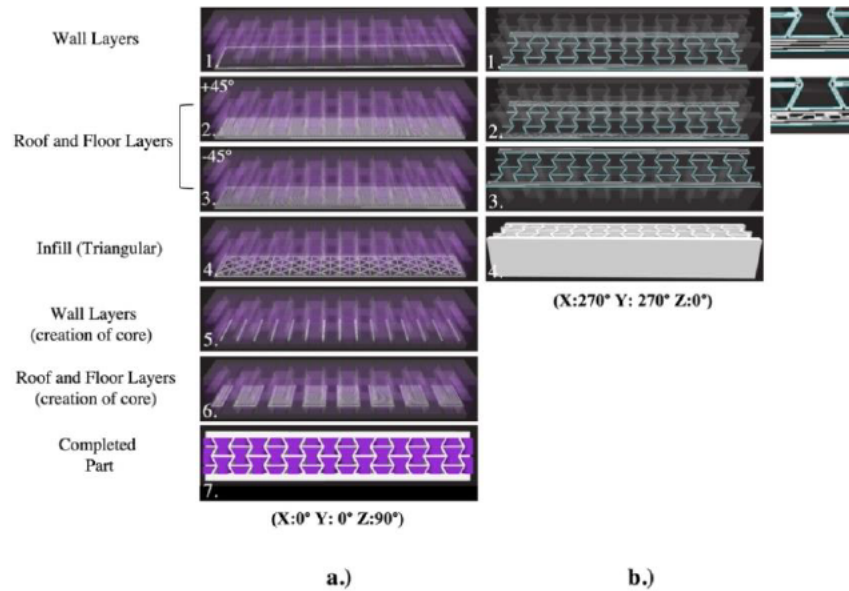


Figure 3.9 X-ray image of toolpaths and volumes of the re-entrant sandwich structure for FRPC sandwich structures (a.) and unreinforced sandwich structures (b.) showing the build-up of the sandwich structures

3.1.3.2 Markforged Mark Two Desktop 3D Printer

The Markforged Mark two desktop 3D printer, as seen in Figure 3.10 was utilised in this research to fabricate fibre-reinforced sandwich structures. The Markforged 3D printers apply the foundational principles of the FFF technique and that of CFR printing as mentioned in the literature in sections 2.9.1 and 2.10, respectively. The quality of the 3D printed sandwich structures were significantly reliant on the levelling of the Markforged printer bed . A greater levelling of the bed can result in superior print quality and an improved surface finishing of the final part (Kabir et al., 2020). Subsequently, Markforged TrueBed permits the removal of the print bed, enabling left-over contamination or traces of adhesives to be cleaned. It is easily replaced and realigns with 10- μ m accuracy (Markforged, 2023). Therefore, the bed was levelled periodically after each print assuring certainty in a high-quality part for all sandwich structures. Furthermore, to assure appropriate bonding to the build plate PVA glue was applied in the print region. This procedure is essential to limit the possibility of warping or delamination from the print bed (Kabir et al., 2020).

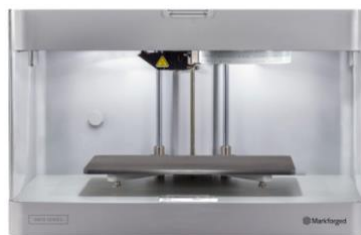


Figure 3.10 Image of the Markforged Mark Two Desktop 3D printer used to manufacture the samples tested (CREAT3D, 2023)

Markforged produces flagship fibre types for the purpose of composite base reinforcement (matrix reinforcement) which range from, carbon fibre, carbon fibre FR (flame retardant), Aramid fibre (Kevlar), HSHT (high strength high temperature) fibreglass and fibreglass (Markforged, 2023). The continuous fibres can be embedded into the common composite bases also produced by Markforged, i.e. Onyx (chopped carbon fibres), Onyx FR (flame retardant), Onyx ESD (static-dissipative), ULTEM 9085 filament (high temperature printing polymer), Smooth TPU, Precise PLA and nylon. The combination of the composite bases alongside fibre reinforcement result in fabricated parts equivalent to the strength of machined aluminium (Markforged, 2023). Its high strength is related to the addition of fibre reinforcement that can overcome the common

drawbacks associated with FFF printing. Therefore, larger 3D printed structures can be fabricated with improved mechanical properties (Dong et al., 2018).

3.1.3.3 Markforged Mark Two Print Parameters and Setup

The CAD models were exported into (.stl) file format so that they can be imported into Eiger.io (version 3.16.56). Once imported, the desired print parameters were adjusted to those tabulated in Table 3.4 and the models were sliced (slicer version 3.107.0), estimating part details based on parameter selections. The sliced CAD designs were exported onto the Markforged desktop 3D printer as a (.mfp) file format. The Eiger slicer software is a closed system, implying minimal control at each step, i.e. from the selection of plastic material, to the parameter settings, until the final print. Therefore, the software can calculate estimated print time, part dimensions, fibre volume, plastic volume, and lastly the overall weight of the printed sandwich structures.

3.1.3.4 Sandwich Structure Printing Details

The fabricated FRPC sandwich structures and printing details are tabulated in Table 3.6 and Table 3.7. An example of the fabrication, lay-up of the fibres in the Nylon White matrix, and printer apparatus are shown in Figure 3.11. The core type refers to the cell topology utilised, i.e. re-entrant, honeycomb, or hybrid. Furthermore, the fibre orientation was the direction of the fibres within the face sheets of the sandwich structures. Fibre type was the type of fibre used in the face sheets, i.e. Kevlar or CF, and the number of structures was the number of sandwich structures printed for each core type. Moreover, the print time indicated an average of how long it took to print 3 sandwich structures of a particular core type. Three sandwich structures of each core type were required to establish an average of compressive properties. Lastly, the number of batches correlates directly with the total number of identical sandwich structures printed. Overall, each core type, fibre orientation, and fibre type were printed twice, as shown in both tables (Table 3.6 and Table 3.7), referred to in the ‘number of batches’ section. The first batch of samples was strictly subjected to uniaxial compression, while the second batch of structures was subjected to low-velocity impact testing followed by a CAI test. Overall, 45 sandwich structures were printed with Kevlar fibre reinforcement, as seen in Table 3.6. Subsequently, 45 sandwich structures were printed with CF reinforcement, as seen in Table 3.7. Therefore, a total of 180 fibre-reinforced sandwich structures were manufactured. Moreover, an additional 9 samples were printed with no fibre

reinforcement for all core types, as shown in Table 3.7, and another 9 structures were printed for low-velocity impact testing producing a total of 18 sandwich structures with no fibre reinforcement. Overall, a total of 198 sandwich structures were manufactured by the Markforged Mark Two 3D printer.

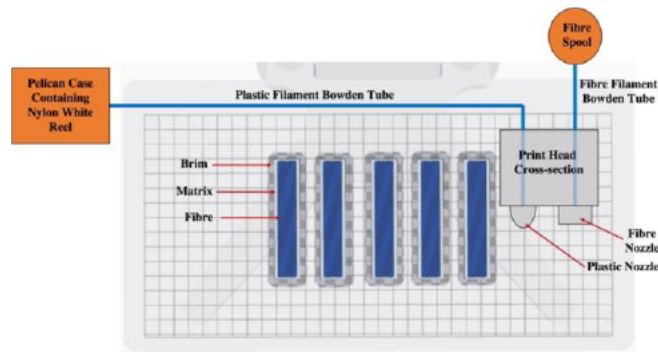


Figure 3.11 Illustration of the fabrication of the sandwich structures with a Kevlar fibre lay-up

Table 3.6 Printing details of Kevlar fibre-reinforced sandwich structures

	Core type	Fibre orientation	Number of structures	Print time	Number of batches
Kevlar fibre sandwich structures	Re-entrant	Isotropic UD	3	9h 42m	X2
	Honeycomb		3	10h 14m	
	Hybrid		3	11h 16m	
	Re-entrant	2 concentric UD	3	9h 34m	
	Honeycomb		3	10h 6m	
	Hybrid		3	11h 8m	
	Re-entrant	5 concentric UD	3	9h 43m	
	Honeycomb		3	10h 15m	
	Hybrid		3	11h 17m	
	Re-entrant	0°	3	10h 2m	
	Honeycomb		3	10h 34m	
	Hybrid		3	11h 36m	
	Re-entrant	QI [0/45/90/-45] _s	3	9h 55m	
	Honeycomb		3	10h 27m	
	Hybrid		3	11h 30m	

Table 3.7 Printing details of carbon fibre-reinforced sandwich structures

	Core type	Fibre orientation	Number of structures	Print time	Number of batches
Carbon fibre sandwich structures	Re-entrant	Isotropic UD	3	7h54m	X2
	Honeycomb		3	8h 13m	
	Hybrid		3	9h 9m	
	Re-entrant	2 concentric UD	3	7h 47m	
	Honeycomb		3	8h 6m	
	Hybrid		3	9h 1m	
	Re-entrant	5 concentric UD	3	7h 56m	
	Honeycomb		3	8h 15m	
	Hybrid		3	9h 10m	
	Re-entrant	0°	3	8h 14m	
	Honeycomb		3	8h 33m	
	Hybrid		3	9h 29m	
	Re-entrant	QI[0/45/90/-45] _s	3	8h 7m	
	Honeycomb		3	8h 26m	
	Hybrid		3	9h 22m	
	Re-entrant	No fibre	3	8h 45m	
	Honeycomb		3	9h 20m	
	Hybrid		3	10h 21m	

3.1.4 Determining the Volume Fraction of Fibres in the 3D Printed Sandwich Structures

The volume of fibre (F_v) and volume of plastic (P_v) for each sample was estimated by Eiger software in (cm^3) and was used to determine the fibre volume fraction (V_f) of each sample. Eiger calculates these parameters by its own algorithm to determine the values for F_v and P_v . This is based on the number of fibre layers used and the number of plastic layers printed to fabricate the structures. However, the calculation of V_f % is not an exact representation of the fibre volume content. Fibre filaments produced by Markforged are composite in nature since the created filaments come as a bundle of fibres (1000 filament strands) and are sized with nylon to bond single strands of fibres together to facilitate extrusion from the printer nozzle (Kabir et al., 2020; Markforged, 2023). However, it provides some relative accuracy, enough to accurately distinguish between the various fibre types and plastics utilised to fabricate 3D printed structures. Moreover, the P_v and F_v values estimated by Eiger were extrapolated and inputted into Equation to calculate the V_f % of the printed samples. Therefore, plastic and fibre specification of all samples are tabulated in Table 3.8 for each sandwich structure produced.

$$[\text{fibre volume} / ((\text{fibre volume} + \text{plastic volume})) \times 100] \quad (1)$$

The objective was to have the same number of fibre layers within the faces of each sample for each different core types. However, the total $V_f\%$ would differ between the sandwich structures depending on two constraints: (1) cell geometry/relative cell density and (2) the diameter of the fibre used. As a consequence of the dissimilar diameter of Kevlar and CF fibre reinforcements, the volume of fibre per cm^3 differentiated. In addition, the fibre orientation also affected the fibre volume content. These features are shown in Table 3.8 where the $V_f\%$ was calculated using Equation for an individual face sheet and P_v , F_v , and final part mass were estimated by Eiger's own algorithm.

Table 3.8 Volume fraction and final part mass of the fibre reinforced 3D printed face sheets

Part Details				
Material	$P_v (\text{cm}^3)$	$F_v (\text{cm}^3)$	$V_f (\%)$	Final part mass (g)
Carbon fibre (CF) structures				
Isotropic (UD)	1.76	0.86	32.82	2.82
2 concentric (UD)	1.86	0.32	14.68	2.17
5 concentric (UD)	1.71	0.74	30.21	2.59
0°	1.64	0.87	34.66	2.71
QI (0/45/90/135) $^\circ$	1.67	0.88	34.51	2.75
Kevlar structures				
Isotropic (UD)	1.60	1.07	40.07	2.77
2 concentric (UD)	1.71	0.38	18.18	2.03
5 concentric (UD)	1.53	0.88	36.51	2.46
0°	1.45	1.09	42.91	2.64
QI (0/45/90/135) $^\circ$	1.49	1.09	42.25	2.68
No fibres	1.59	-	-	1.75

3.2 Manufacturing of GnP Reinforced Sandwich Structures

This section will seek to provide details on the methods involved in fabricating the unique and novel PA6/GnP filament material and the fabrication of the PA6/GnP sandwich structures.

3.2.1 Materials

3.2.1.1 Nylon (PA6)

The thermoplastic material utilised for the production of PA6/GnP sandwich structures was Radilon® S 40E 100 NAT produced by RadiciGroup, where (S 40E) is the material code and (NAT) is the colour code. It is a high viscosity, extrusion grade PA6;

therefore, it is suitable for the extrusion and the fabrication of tubes, profiles, bars, rods, sheets, etc. (RadiciGroup, 2023). Consequently, it is of semi-crystalline nature, possessing excellent strength, toughness, and impact resistance. In addition, it has a low density, along with excellent wear and chemical resistance (Pelin et al., 2017). Some of the essential technical data of the PA6 relevant to the experimentation in this chapter is tabulated in Table 3.9.

Table 3.9 Technical data of PA6 Radilon® S 40E 100 NAT (RadiciGroup, 2023)

Property	Standard	Unit	Value
Physical properties			
Density	ISO 1183	Kg/m ³	1140
Moisture absorption 23°C-50%RH	ISO 62	%	3.1
Viscosity Index	ISO 307	ml/g	245
Mechanical properties			
Tensile Modulus	ISO 527-2/1A	MPa	3000 (DAM*) 1150(Cond**)
Stress at Yield	ISO 527-2/1A	MPa	75 (DAM*) 40 (Cond**)
Flexural Modulus	ISO 178	MPa	2450 (DAM*) 750 (Cond**)
Flexural Strength	ISO 178	MPa	95 (DAM*) 30 (Cond**)
Thermal properties			
Melting Temperature	ISO 11357-1-3	°C	220

***DAM = Dry as moulded state **Cond= Conditioned state**

3.2.1.2 Graphene Nanoplatelets

The nanoplatelets utilised in the project were amine functionalised graphene nanoplatelets (NH₂-GnPs), manufactured and supplied by Perpetuus Carbon Technologies Ltd. The NH₂-GnPs were utilised as the main form of reinforcement for the PA6 matrix. They have a surface area of 500m²·g⁻¹ and are attached with amine functional groups. These groups feature the basic nitrogen atoms that facilitate appropriate hydrogen bonding with other hydroxyl groups, hydrogen atoms, and molecules. The fabrication process of NH₂-GnPs involved the utilisation of plasma-processing in a multi-electrode dielectric barrier discharge plasma reactor, as similarly reported in the literature in section 2.14.1.1.1. Consequently, the graphite powders were exposed to an argon plasma for 60 minutes at 3 and 6 kW, resulting in the exfoliation of graphite and negation of the Van der Waals forces between the layers. Finally, an amine

plasma was utilised to introduce NH_2 functional groups to the graphene surfaces with the aim to reduce the effect of agglomeration (Jarrett & Korkees, 2022).

3.2.2 Production Equipment and Sample Preparation

The necessary equipment and machinery used within the experimentation of Chapter 5 is chronologically outlined below:

- A standard 18L laboratory oven heated by Incology sheathed elements was used to dry the PA6 material.
 - 200g of PA6 was weighed in a drying tray and placed within a glass container with desiccants in the oven.
 - The oven was heated at a temperature of 50°C and the PA6 was left for 7 days to remove any excess moisture absorbed, as there could be a hindrance in its ability to mix and compound, thus affecting the results (McKeen, 2017).
- A Rondol microlab (micro compounding and pelletising line) twin-screw extruder was used to melt compound the PA6/GnP, as seen in Figure 3.12 and discussed in section 3.2.2.1.
- A Felfil Evo single screw filament extruder was utilised for the creation of 3D printing filament after melt compounding.
- An Ultimaker Original + 3D printer was used to print all GnP reinforced sandwich structures after filament extrusion with the Felfil Evo.

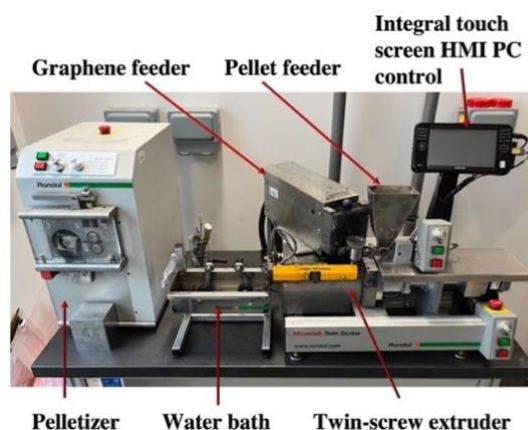


Figure 3.12 Microlab twin-screw extruder showing all components used in the process

3.2.2.1 PA6/GnP Compounding using the Twin-Screw Extruder

As shown in Figure 3.12, a Rondol microlab 10mm diameter twin-screw extruder was used for the mixing of PA6/GnPs. The twin screws are co-rotating, intermeshing, and self-wiping (Rondol, 2013), and the configuration and profile of the twin-screw extruder can be seen illustrated in Figure 3.13.

Following the drying of the PA6 material, the pellets were mixed with varying concentrations of GnPs (1% 2%, 3% and 4%), as tabulated in Table 3.10 alongside the measured quantity of PA6. The quantity of PA6 pellets in grams and the concentration of GnP powder in grams equates to 200g, thus, as the percentage of GnPs increased, the amount of PA6 decreased. On the contrary, for accurate compounding to be achieved, and to attain the selected filler concentration, calibration between the pellet and powder feeder was implemented to discover the average rate at which the PA6 pellets and GnP powder were being fed. This involved timing each feeder for 1 minute on 3 successive runs to calculate the overall average, resulting in the appropriate feeding rate for each. Therefore, both feeders are tuned to feed at the same rates allowing for the accurate and consistent mixing of the GnPs and PA6.

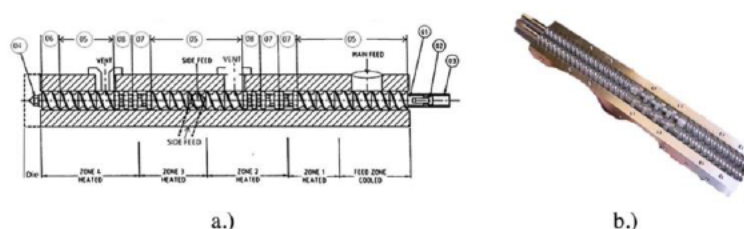


Figure 3.13 Configuration and profile of the twin-screw extruder: 01(Hex Shaft), 02 (Coupling retaining screw), 03 (Coupling), 04 (Screw tip), 05 (Feed screw), 06 (Extrusion screw), 07 (4x60° Mixing/Kneading blocks), and 08 (4x90° Mixing/Kneading blocks) (a) (Korkees et al., 2021) Top view of the screw configuration (b) (Rondol, 2013)

Table 3.10 The ratio of GnPs to PA6 for the mixing process with the Twin-Screw Extruder

Amine – GnPs (%)	PA6 (g)	GnPs (g)
1	198	2
2	196	4
3	194	6
4	192	8

Throughout the processing of the varying filler concentrations, the feeding rate of the GnP feeder was increased in rpm with an increasing percentage of GnPs. The greater concentrations of GnPs within the mixer required more time for the powder to manoeuvre in between the GnP feeding screws. Therefore, high concentrations of GnPs, i.e. 3% and 4%, made it challenging for the screws to feed appropriate concentrations at the required rate. To address this concern, GnPs were added periodically at various intervals throughout the compounding process to promote greater area within the GnP feeder for ease of mixing, and thus achieving accurate filler concentrations. Failure to do so may result in the premature reduction of the PA6 pellets before the GnPs have successfully been mixed. All the settings utilised to process the PA6 and GnP mixture are tabulated in Tables 3.11-3.14. The varying zones (1-4 and the die) for all tables is the temperature related to the extruder barrel, as seen in Figure 3.13 (image a), and the screw speed was the speed of the co-rotating twin-screw.

Table 3.11 Neat PA6 and PA6 Amine -GnPs settings mixing 1%GnPs into 198g PA6

Processing parameters for PA6 Amine – GnPs settings (neat and 1%)	
Zone 1	180°C
Zone 2	250°C
Zone 3	280°C
Zone 4	260°C
Die	230°C
Screw speed	3.8 (rpm)
Pellet feeder	3.2 (rpm)
GnP feeder	3.2 (rpm)
Pelletizer	2.2/2.0 (rpm)
Pellet length (pelletizer)	2.0mm

Table 3.12 PA6 Amine -GnPs settings mixing 2%GnPs into 196g PA6

Processing parameters for PA6 Amine – GnPs settings (2%)	
Zone 1	180°C
Zone 2	250°C
Zone 3	280°C
Zone 4	260°C
Die	230°C
Screw speed	3.8 (rpm)
Pellet feeder	3.2 (rpm)
GnP feeder	3.6 (rpm)
Pelletizer	2.2/2.0 (rpm)
Pellet length (pelletizer)	2.0mm

Table 3.13 PA6 Amine -GnPs settings mixing 3%GnPs into 194g PA6

Processing parameters for PA6 Amine – GnPs settings (3%)	
Zone 1	180°C
Zone 2	250°C
Zone 3	280°C
Zone 4	260°C
Die	230°C
Screw speed	3.8 (rpm)
Pellet feeder	3.2 (rpm)
GnP feeder	4.3 (rpm)
Pelletizer	2.2/2.0 (rpm)
Pellet length (pelletizer)	2.0mm

Table 3.14 PA6 Amine -GnPs settings mixing 4%GnPs into 192g PA6

Processing parameters for PA6 Amine – GnPs settings (4%)	
Zone 1	180°C
Zone 2	250°C
Zone 3	280°C
Zone 4	260°C
Die	230°C
Screw speed	3.8 (rpm)
Pellet feeder	3.2 (rpm)
GnP feeder	4.9 (rpm)
Pelletizer	2.2/2.0 (rpm)
Pellet length (pelletizer)	2.0mm

3.2.2.2 Felfil Evo Filament Extruder

Following the melt compounding with the twin-screw extruder, the Felfil Evo extruder was utilised to fabricate 3D printing filament material, as shown in Figure 3.14. Compared with the twin screw extruder, the Felfil Evo uses a 12.7 l/d ratio single conic profile screw resulting in an improvement of material compression for pelletised thermoplastics within the chamber (Felfil, 2023), as shown in Figure 3.15.

Prior to using the filament extruder, the mixed PA6/GnP pellets were dried in the laboratory oven at 55°C for 3 days after the mixing process in the twin-screw extruder, to remove any additional moisture absorption during or after the melt compounding. Figure 3.17 illustrates a comparison between PA6/GnP pellets containing moisture and PA6/GnP pellets that have been dried. A lack of moisture removal results in air pockets within the extruded material, producing a serrated, poor surface finish. This results in a filament material with an inconsistent diameter which is detrimental to the print quality, as there is a greater possibility of filament blockage within the Bowden tube of the Ultimaker 3D

printer. Therefore, if the diameter of the filament surpasses 2.85 mm (filament diameter size for the Ultimaker) then it can be prevented from extruding, as illustrated in Figure 3.16. Consequently, a filament diameter below 2.20mm remained unusable because an insufficient amount of material could be extruded by the Ultimaker. Therefore, Tables 3.15-3.19 show the selected parameters based on the most consistent diameter and with the closest diameter to that of 2.85mm. The values ranged between 2.36-2.61 mm, where 2.36 mm was the lowest obtained filament diameter, and 2.61 mm was the greatest. However, the diameter sensors indicated that the filament diameter remained approximately at 2.40 mm, consistently.

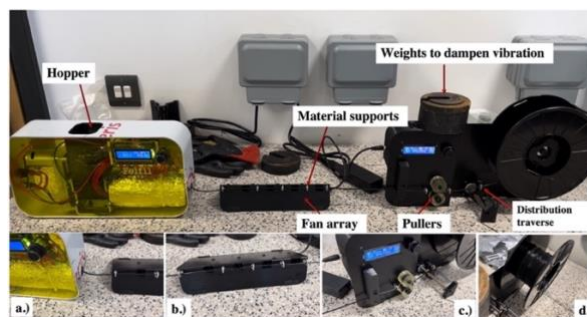


Figure 3.14 Extrusion of PA6/GnP (a) Cooling fan array (b) Pullers (c) Spooler (d)



Figure 3.15 Illustration of the Felfil Evo filament extruder screw (a) (Felfil, 2023)
Illustration of the Rondol microlab 10mm diameter Twin-screw extruder screws (b)
(Rondol, 2013)



Figure 3.16 Illustration of extruded filament using the Felfil Evo, indicating the change of diameter through the length of the filament ranging from 2.36 to 2.61mm

After the drying process, the PA6/GnP pellets were placed inside the filament extruder hopper, as shown in Figure 3.14 where the parameters were selected on the digital monitor, based on the parameters as seen in Tables 3.15-3.19, and the extrusion

process could proceed. During the extrusion process, a fan array, as shown in Figure 3.14 (image b), cooled the extruding material, therefore resulting in moderate solidification to maintain its diameter and shape. The metallic rings surrounding the filament on the cooling fan array in Figure 3.14 (image b) supports the filament, and thus reduces buckling so that the filament can maintain its shape whilst being pulled in a straight path by the pullers (Figure 3.14, image c). Furthermore, for the filament material to maintain a consistent diameter, it was necessary to consider the speed of the pullers integrated on the spooler machine. Therefore, Tables 3.15-3.19 exhibit the parameters utilised to maintain filament diameter and quality whilst increasing filler concentration. Tables 3.17-3.19 provide evidence that the incrementation of GnPs resulted in minor changes to the parameters of the filament extruder. Specifically, it influenced the temperature of the screw/nozzle in the filament extruder, the speed at which the screw turned and mixed the pellets (RPM of the screw), and the spool speed which dictated how fast the filament was pulled by the pullers. Additionally, it affected the pull speed, which determined the speed at which the pullers were drawing the filament from the nozzle, through the cooling fan array, and into the diameter sensor. It was essential that the pull speed and spool speed match, since a mismatch of speeds could result in material jamming between the pullers and the distribution traverse mechanism, as seen in Figure 3.14. At higher speeds of both pull and spool components, the filament diameter would decrease resulting in a thinner filament, and vice versa. The RPM of the screw inside the extruder also directly influenced the filament diameter. Consequently, a high RPM resulted in a larger diameter filament since more material was being extruded from the nozzle. Overall, each component within the filament extrusion process had some relation with another and directly influenced the next.

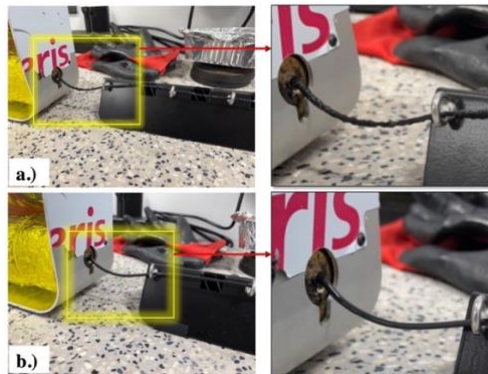


Figure 3.17 Serrated surface finish using pellets containing a high moisture content (a)
clean and smooth surface finish using dried pellets (b)

Table 3.15 Settings used to filament extrude PA6 with no inclusion of GnPs

Neat PA6 – Radilon	
Temperature	250°C
RPM of screw	7
Spool speed	50
Pull speed	0.4
Mode	Manual

Table 3.16 Settings used to filament extrude PA6/1%GnPs

PA6 – 1%GnPs	
Temperature	290°C
RPM of screw	6
Spool speed	50
Pull speed	0.27
Mode	Manual

Table 3.17 Settings used to filament extrude PA6/2%GnPs

PA6 – 2%GnPs	
Temperature	290°C
RPM of screw	5
Spool speed	33
Pull speed	0.17
Mode	Manual

Table 3.18 Settings used to filament extrude PA6/3%GnPs

PA6 – 3%GnPs	
Temperature	290°C
RPM of screw	8
Spool speed	50
Pull speed	0.15
Mode	Manual

Table 3.19 Settings used to filament extrude PA6/4%GnPs

PA6 – 4%GnPs	
Temperature	290°C
RPM of screw	8
Spool speed	25
Pull speed	0.15
Mode	Manual

3.2.2.3 PA6/GnP Reinforced 3D Printed Sandwich Structure Fabrication

Identical honeycomb, re-entrant, and hybrid sandwich structures as shown in section 3.1 were 3D printed on the Ultimaker original + (UMO+), as seen in Figure 3.18. The CAD designs can be seen in Figure 3.19, and their build plate orientations are displayed in Figure 3.20. All sandwich structures were placed in orientations X: 0°, Y: 0°, and Z: 0° in relation to the build plate to eliminate the need for support generation.

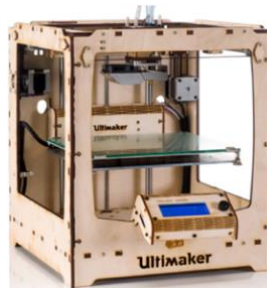


Figure 3.18 Image of the Ultimaker Original + which was used to fabricate the PA6/GnP samples (Ultimaker, 2014)

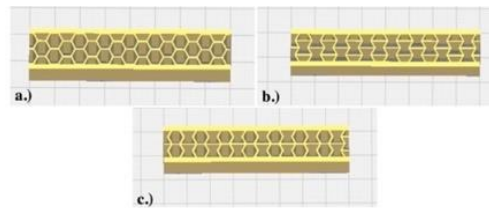


Figure 3.19 CAD designs of the honeycomb (a) re-entrant (b) and hybrid (c) in the slicer software Cura

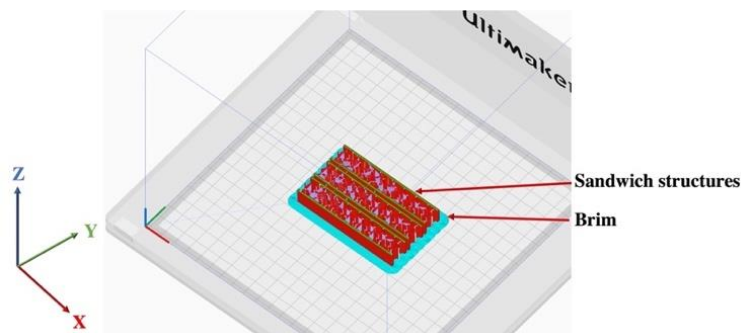


Figure 3.20 Orientation of all the neat PA6 and PA6/GnP sandwich structures on the Ultimaker build plate in slicer software Cura

3.2.2.4 Utilising the Ultimaker Original + 3D Printer to Print PA6/GnP Samples

The fabrication of the PA6/GnP sandwich structures was accomplished by utilising FFF printing. Tabulated in Tables 3.20-, are the precise specifications and dimensions of the UMO+ printer. The build volume of the printer is denoted by the X, Y, and Z measurements, found in Tables 3.20-3.22. Moreover, the neat PA6 and PA6/GnP filament material produced by the Felfil Evo was utilised as the filament material for the UMO+ to fabricate all of the sandwich structures. Prior to 3D printing, and similar to that of the fibre reinforced sandwich structures seen in section 3.1.3.2, the CAD designs in (.stl) format were imported into the UMO+ slicer software known as Ultimaker Cura (version 5.0.0). The slicer software was used to convert the (.stl) files into G-code, enabling the UMO+ to read the files and propose commands to the machine controller. Moreover, the UMO+ was selected as the primary printer since its user interface permits an extensive range of parameter modifications. Therefore, it permitted more prospects for experimentation whilst attempting to print a novel PA6/GnP filament material. Table 3.23 shows all the parameters selected to 3D print the sandwich structures and it is a summary of the most crucial parameters that required modifying to facilitate improved printing quality. The parameters that were thought to directly influence the behaviour of the PA6/GnP filament (Table 3.23) were tampered with first, to investigate if any differences in print quality could be noticed and if improvements could be conducted thereafter. The modification of print parameters was done because the fabricated filament from the Felfil Evo suffered from inconsistent diameter throughout its length, thus adversely influencing the print quality and the quantity of material that can be extruded from the nozzle. Therefore, it was necessary to find parameters permitting sufficient material extrusion to fabricate sandwich structures without sacrificing part strength.

Table 3.20 Ultimaker Printer settings

Printer Settings	
X (Width)	205.0 (mm)
Y (Depth)	205.0 (mm)
Z (Height)	200 (mm)
Build plate shape	Rectangular
Origin at centre	Unticked
Heated bed	Ticked
Heated build volume	Unticked
G-code flavor	Marlin

Table 3.21 Print head settings

Print head Settings	
X min	-75 (mm)
Y min	-18 (mm)
X max	18 (mm)
Y max	35 (mm)
Gantry height	55.0 (mm)
Number of extruders	1
Apply Extruder offsets to Gcode	Ticked

Table 3.22 Extruder settings

Extruder Settings	
Nozzle size	0.4 (mm)
Compatible material diameter	2.85 (mm)
Nozzle offset X	18 (mm)
Nozzle offset Y	35 (mm)
Cooling fan number	0

Table 3.23 All parameter settings selected on the Ultimaker Cura slicer software

Parameter Settings	
Profile	
Normal	0.15 (mm)
Quality	
Layer height	0.15 (mm)
Walls	
Wall thickness	0.8 (mm)
Infill	
Infill density	37.0 (%)
Infill pattern	Triangles
Material	
Printing temperature	260 (°C)
Printing temperature initial layer	260 (°C)
Build plate temperature	80 (°C)
Build plate temperature initial layer	80 (°C)
Flow	120.0 %
Speed	
Print speed	30.0 (mm/s)
Travel speed	30.0 (mm/s)
Brim speed	15.0 (mm/s)
Travel	
Enable retraction	Ticked
Retract at layer change	Unticked
Cooling	
Enable print cooling	Unticked
Supports	
Generate support	No generated supports
Build plate adhesion	
Build plate adhesion type	Brim
Brim width	8.0 (mm)
Special Modes	
Print sequence	One at a Time

3.2.2.5 Ultimaker Parameter Selection Details

The overall print speed was adjusted from 100mm/s to 30.0 mm/s within the Cura slicer software. In addition, wall speed, outer wall speed, top/bottom speed, initial layer speed, and skirt/brim speed were modified to 15 mm/s. With the increase of GnP% the morphology of the PA6 resulted in an increase in viscosity, inconsistent filament diameter, and an increase in brittleness once successfully printed (Caminero et al., 2019). This made it challenging for it to appropriately extrude. Consequently, the default print speeds set by Cura prevented the correct quantity of PA6/GnP to be extruded from the print nozzle, resulting in inadequate extruded material on the print bed to fabricate the

sandwich structures. As a result, the high viscosity and presence of GnPs, at times, caused a blockage of the plastic nozzle, resulting in a lack of extruded material, as shown in Figure 3.21. Subsequently, the sandwich structures were incomplete or incapable of being compression tested or impacted. Thus, it was necessary that the rate of retraction of the filament match the print head travel rate. Moreover, it was a challenge to extrude GnP concentrations of 3% and 4% since it resulted in a high viscosity and inconsistent diameter. This was mostly when the filament material was retracted at high speeds, at the initial print layer, at end points (when a new layer was fabricated), or at layer changes of the print. Therefore, the reduction of speeds permitted an accurately filled and well bonded layer-by-layer part, and sandwich structures that obtained improved part strength and print quality.

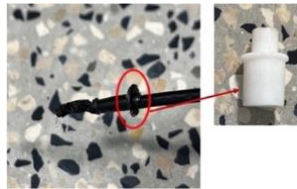


Figure 3.21 The collection of material within the plastic filament housing resulting in filament blockage

The printing temperature of 260°C is the maximum temperature of the printer and it was selected for neat PA6 and PA6/GnP filaments. As seen in Table 3.23, the initial and final print temperature were successfully maintained at 260°C. Fabricated PA6 and PA6/GnP filaments did not extrude below a temperature of 250°C since they did not achieve their appropriate melt temperature, thus resulting in blockage within the plastic nozzle. Therefore, it was necessary to maintain temperatures at 260°C throughout the entirety of the print to ensure a consistent material flow rate through the nozzle, and to maximise the bond strength when printing onto the bed. Notably, a print head temperature above 260°C would have been more beneficial for the extrusion of PA6/GnP filaments. However, due to equipment limitation it was not feasible to surpass.

Concurring with the above alterations, a temperature of 80°C was selected for the build plate and the build plate initial layer. At the selected build plate temperatures, it enabled the filament material to remain at a high temperature for appropriate and gradual cooling of it. As a result, bonding between the PA6/GnP and the print bed improved,

consequently resulting in less warpage of the overall part, better dimensional stability, and greater structural integrity.

The flow rate indicated significant relevance and importance in improving the print quality, layer adhesion, and bonding strength of printed layers. The default material flow rate on Ultimaker Cura is set as 100.0%; however, a value of 120% was pre-selected. The selected flow rate was centred around that seen in the literature review by Butt et al. (2021). Consequently, increasing the flow rate % resulted in a greater quantity of material extrusion onto the build plate, and permitted a larger thickness and width to individually printed rasters. Figure 3.22 shows the Ultimaker printer printing a single raster at 100% and another printed at 120% flow rate illustrating, as an example, a difference in raster thickness.

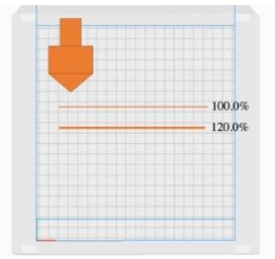


Figure 3.22 Illustration of 100.0% and 120.0% flow rate on the Ultimaker Original +

A common phenomenon when printing PA6/GnP was that upon material deposition onto the build plate, cooling of the PA6/GnP material occurred at a rapid rate, interfering with the bonding of the material to the build plate as it was unable to cool appropriately. It therefore resulted in warpage and shrinkage of the sandwich structures. To stop this, the enable cooling parameter was deactivated, resulting in progressive cooling of the PA6/GnP at ambient temperature. Additionally, the special mode feature 'one at a time' was enabled to print one sandwich structure at a time before progressing to print another sandwich structure. The print feature permitted effective amalgamation of the initial and final print layers and thus improved interfacial strength.

To negate the shrinkage and warpage of the PA6/GnP sandwich structures, a brim was selected for the build plate adhesion of a printed part. Shrinkage and warpage were caused from the high brittleness of the sandwich structures and the change in PA6 morphology. Therefore, this resulted in the corners of the sandwich structures de-adhering from the build plate, which led to deformation of the parts and imprecise dimensions.

3.3 Printing Nylon (PA6) Radillon with no GnP Inclusion

A similar selection of parameters to that of PA6/GnP was implemented for neat PA6. Specified changes to print parameters are tabulated in Table 3.24, and all other parameters left unmentioned remained identical to that of Table 3.23. Table 3.24 reveals that with the absence of the GnP fillers, there was no interference to the processability of the PA6 material, and thus the majority of print parameters remained as the default selections. The printing temperature was adjusted to 250°C since a printing temperature of 260°C was not required. The print speed was changed to the default print speed of the UMO+ (100 mm/s). The flow rate was reduced to 100% because PA6 without GnP inclusion proposed improved layer-to-layer adhesion. Cooling was enabled; however, only after the initial print layer to ensure appropriate adhesion with the bed. Finally, the build plate temperature did not require a temperature as high as 80°C, resulting in a chosen temperature of 60°C.

Table 3.24 Print parameters for nylon (PA6) Radillon®

Print parameters for nylon (PA6) Radillon	
Printing temperature	250°C
Print speed	100 mm/s
Flow rate	100%
Cooling	Fan at 100%
Build plate temperature	60°C

3.4 Test Equipment

Below are the necessary equipment and machinery used within the experimentation of this project to manufacture and test the 3D printed sandwich composite structures:

- A Hounsfield electro-mechanical test machine was utilised for the uniaxial compression testing of the sandwich structures after the sandwich structures were successfully 3D printed.
 - The Hounsfield electro-mechanical test machine contained a 25 kN load cell.
 - Two circular compression plates were used of diameters 99.59 mm to compress the sandwich composite structures.
- For the batch of sandwich structures undergoing low-velocity impact the same procedure was followed as that seen above; however, the structures

were impacted by a drop-weight impact tester first before proceeding to a compression after impact test (CAI).

- A 5N weight was placed onto the impact head.
- A CAI test was performed to obtain the residual compressive and energy absorbing properties of all the sandwich structures.

A detailed summary and the necessary implications taken to execute the tests of all the steps mentioned above will be provided in the sections below.

3.4.1 Compression Testing of the 3D Printed Sandwich Composites

Following all slicer software parameter adjustments, all 3D printed sandwich structures were compression tested in-plane with the core facing the X₂ direction, as seen in Figure 3.23. To note, the face sheet will be out-of-plane in relation to the compression test and the orientation of the core. Nevertheless, for the purpose of this project, all tests will be referred to as in-plane compression, as depicted in Figure 3.23 for ‘sandwich structure’ related to the core orientation, and the face sheet orientation will not be considered unless specified. The loading nature of the core and reasoning for why it is known as ‘in-plane’ was similarly explained in sections 2.11.5, 2.11.5.1, and 2.11.5.2 in the literature.

The uniaxial testing was performed using a Hounsfield electro-mechanical test machine, supplied with a 25 kN load cell and circular compression plates to compress the sandwich composites, as seen in Figure 3.24 (image a, and images 1, 2 and 3). Consequently, a compression test speed of 2 mm/min was applied and recorded every 0.2 seconds. This was determined by the BS EN ISO 844:2014 standards, used to determine the compression properties of rigid cellular plastics (bsi, 2009). The sandwich structures were compressed until contact was made with neighbouring cells (Figure 3.25, image b) and a rise of force (N) was exemplified on the Hounsfield digital monitor, indicating densification of the core. As a result, the test was stopped.

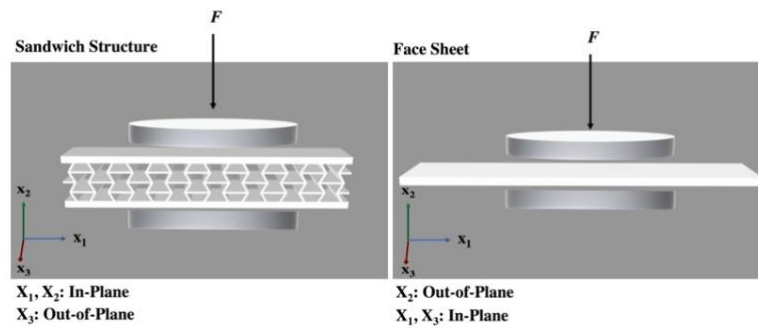


Figure 3.23 Illustration of how all sandwich structures where compression tested, where the in-plane properties are those related to the loads applied to the surfaces normal to X_1 and X_2 ; the out-of-plane properties are those related to loads applied to the surfaces normal to X_3 (for ‘sandwich structure’ image); the face sheet shows X_1 and X_3 as in-plane and X_2 as out-of-plane

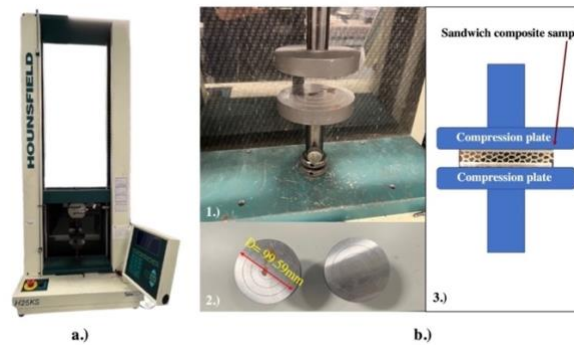


Figure 3.24 A Hounsfield electro-mechanical test machine (a) and images of the circular compression plates (b.1), dimensions of the plates (b.2) and an illustration of the compression (b.3)

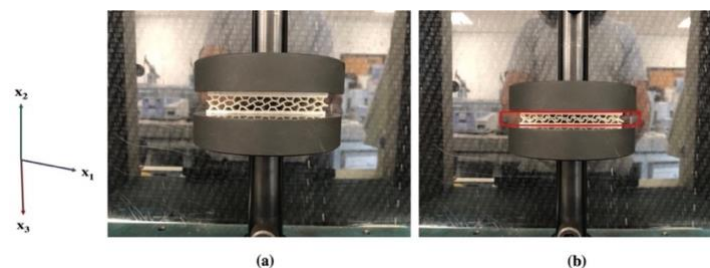


Figure 3.25 Initial stage of in-plane fibre-reinforced 3DP honeycomb sample being compressed (a) Final stage of in-plane fibre reinforced 3DP honeycomb sample being compressed at which the test was stopped (b)

3.4.1.1 Finite Element Analysis

The uniaxial compression test discussed in section 3.4.1 was replicated through finite element analysis (FEA). The objective was to compare the experimental analysis to a FEA model to distinguish any similarities in the deformation mechanisms of the core topologies. Geometry of the sandwich structure models that were created in SolidWorks, as seen in Figure 3.1 was firstly imported into ANSYS SpaceClaim 2024 R1 where compression plates were constructed and assembled onto the selected sandwich structure geometries to replicate the compression test seen in Figure 3.24. Subsequently, ANSYS Workbench and Mechanical 2024 R1 was utilised to perform the simulation testing. The simulation comprised of three geometries, i.e., two circular compression plates and the sandwich structure geometry. The selected materials for the geometries were structural steel for the compression plates and PA6 for the sandwich structure geometry, where the properties of PA6 was selected based off Table 3.2, as to replicate the material properties utilised for the Nylon White structures in Chapter 4. The selected testing method was a displacement controlled ‘static structural’ method as to imitate the compression testing in the experimental in section 3.4.1. The details of the boundary conditions and the selected testing parameters are further discussed in Chapter 4 section 4.5.

3.4.2 Calculations for Stress and Strain

The standard BS EN ISO 844:2014 was used to determine the compressive stress and strain of the sandwich structures, and thus was used to produce stress-strain plots after the compression testing of all the 3D printed sandwich structures (bsi, 2009). Consequently, stress and strain was calculated using Equation (2) and Equation (3), respectively. Equation (2) shows σ is the stress parameter in question, in megapascals; F is the force measured in newtons; and A is the initial cross-sectional area of the specimen in square millimetres. Equation (3) shows, ε is the strain parameter in question, expressed as a dimensionless ratio or as a percentage; L_0 is the gauge length of the test specimen in millimetres; and DL_0 is the decrease in the specimen length between the gauge marks in millimetres (bsi, 2009).

$$\sigma = \frac{F}{A} \quad (2)$$

$$\varepsilon = \frac{\Delta L_0}{L_0} \quad (3)$$

3.4.3 Calculations of Compressive Properties and Energy Absorption During Compression

The BS EN ISO 844:2014 standard was used to determine the compressive modulus, strength, and energy absorption of the sandwich structures (bsi, 2009). As a result, the compressive modulus of the sandwich structures was calculated using Equation (4). Equation (4) exhibits notations, E_c , denoting the compressive modulus in megapascals; σ_1 is the stress in megapascals, measured at a strain (ε_1) value of 0,0005; σ_2 is the stress in megapascals, measured at a strain (ε_2) value of 0,0025. However, Equation (4) most effectively applies for conventional plastic manufacturing methods, where stress and strain are usually much greater than in-plane 3D printed cellular structures. Hence, $\sigma_2, \sigma_1, \varepsilon_2, \varepsilon_1$ resulted in values that were extremely small, preventing the stress values from being at the required strain values stated by the BS EN ISO 844:2014 standards. As a solution, the compressive modulus was calculated using the linear portion of the stress-strain graphs alongside a linear trendline generating an equation on the chart ($y = mx + c$). As a result, the gradient was generated to determine the compressive modulus, allowing for a more accurate result.

$$E_c = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} \quad (4)$$

The compressive strength was calculated using Equation (5), as also stated in the BS EN ISO 844:2014 standards. The notation F_m is the maximum force reached in newtons; and A_0 is the initial cross-sectional area in square millimetres of the test specimen. Subsequently, the absorbed energy (AE) was calculated using Equation (6) originating from the area under the stress-strain curves, where b is the base, and h is the height of the curve.

$$\sigma_m = \frac{F_m}{A_0} \quad (5)$$

$$AE = \frac{1}{2} \times b \times h \quad (6)$$

3.4.4 Drop-Weight Impact Testing of the 3D Printed Sandwich Composites

The second batch of 3D printed sandwich composites was impact tested with a drop-weight impact tester following the regulations of ASTM D7136/D7136M-12 (ASTM International, 2012). Figure 3.26 exhibits the impacting rig utilised to impose low-velocity impact on the second batch of 3D printed sandwich composite structures, where (image a) shows the rig and its components. The impact tester utilises a Tenma 72-8690 power supply. The power supply generates a magnetic field, operating as an electromagnet, whereby the hemispherical impact head (component 3 in Figure 3.26 image a) can clamp into position in preparation for the placement of a weight plate upon it. Subsequently, the sandwich structures were impacted at 5N, at a height of 0.25m (Figure 3.26, image b), where the energy was calculated by using Equation (7), equating to 2J. The impact mass of 5N along with the produced energy was selected in relation with the work produced by (Swart et al., 2022). The authors reported that above 2J, face sheets of identical dimensions and fibre orientations resulted in catastrophic failure. Furthermore, the height was measured from the tip of the hemispherical impact head down to the support frame of the impact tester where the samples were placed, as seen in Figure 3.26 (image b). The dimensions of the impact tester can be found in Figure 3.27. In conclusion, the objective was to impact the samples as close to the centre of the top face sheet as possible for appropriate distribution of impact force, and thus aiming to damage fibres embedded into the face sheets or any individual cells in the core. Therefore, a comparison could be made between the samples that were compression tested and samples that were CAI tested, to distinguish if a diminishment in compressive properties could be witnessed in the latter and how the residual properties are affected.

$$E = \text{mass (Kg)} \times \text{gravity (9.81 m/s}^2\text{)} \times \text{height (m)} \quad (7)$$

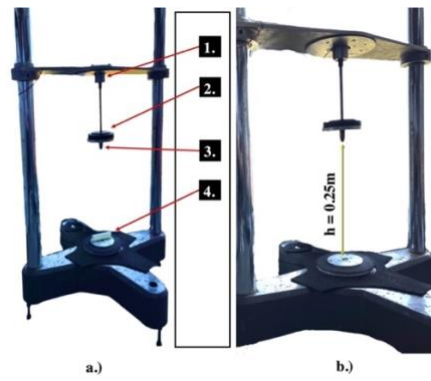


Figure 3.26 Image of impact tester (image a.) containing the electromagnet (1.) 5N weight plate (2). Hemispherical impact head (3.) In-plane honeycomb fibre reinforced sandwich composite sample (4.) and a magnified image of the impact tester indicating how the height was measured (image b.)

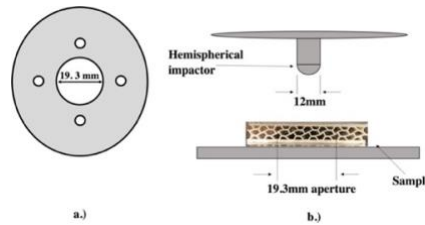


Figure 3.27 Impact specimen support frame (a) Hemispherical impactor with support frame (b)

3.4.5 Light Microscopy

3.4.5.1 Mounting Process and Optical Image Analysis

Microscopy image analysis was employed mainly to analyse fibre orientations and locations. Prior to image analysis, all 3D printed fibre reinforced sandwich structures that underwent compression were cautiously cut at the end sections with a hacksaw to obtain part of the structure ready for image analysis. The sectioned part was mounted utilising a cold-setting resin method, i.e. 1-part polyester and 2-part epoxy resin, and left for 24 hours to enable appropriate curing. Subsequently, surface layers of the cured resin were removed to reveal the sandwich structure fibres by grinding it down to an appropriate depth with a mechanical rotating disc of abrasive silicon carbide paper. The utilised abrasive paper progressed in stages from 600, 800 and 1200. Samples were thoroughly washed following the grinding process, removing any contaminants or residue, and then dried. Once a desired amount of grinding was achieved polishing commenced. The ground samples were subjected to a mechanically rotating disc of

impregnated abrasive diamond particles and oil lubricant. The coarser polish contained 6 microns in diameter of diamond particles to remove the scratches produced by the 1200 grit paper. This was followed by a finer polish of diamond particles with 1 micron in diameter. The polished samples were left for 24 hours before imaging commenced so that left-over liquid from the abrasive grinding and polishing processes has been sufficiently evaporated. Lastly, the prepared and mounted sandwich structures were analysed by optical light microscopy using a ZEISS Primotech microscope, and images of x5, x10 and x50 magnifications were recorded for CF and Kevlar sandwich structures of all fibre orientations.

3.4.5.2 High Depth of Field Image Analysis

A high depth of field (HDoF) digital microscope (Keyence VHX-1000) was used to capture fibre orientations, face sheet failures, and core failures. Analysis of the sandwich structures by HDoF ensured that accurate analysis of the deformation mechanisms of the cores was attained and macroscopic failure modes could be examined. The VHX-1000 utilises progressive imaging alongside high dynamic range to capture images of high quality. It enables 3D depth of field analysis, which utilises images that are stitched together producing clarity in the images where depth was a concern. This is achieved by the combination of the lens used and a free-angle observation system base unit (VH-S30B). Hence, accurate analysis of individual fibre bundles and matrix failure of the cores could be distinguished. Furthermore, a standard VH-Z00R macro/zoom lens with magnifications 0.1-50x, and a VH-Z20R standard zoom lens with magnifications of 20-200x was used to capture all images.

All the 3D printed sandwich structures that underwent, compression, low-velocity impact testing and CAI testing, in addition to the unreinforced sandwich structures were analysed by HDoF analysis. Therefore, failure modes were distinguishable and could be compared to one another. Moreover, the same procedure in obtaining a section of the sandwich structures discussed in section 3.4.5.1 was implemented to do HDoF analysis. However, for fibre-reinforced structures, a larger section was cut to visually enable all locations of the fibre lay-ups within the matrix. Additionally, sandpaper of 600 grit was used to remove any residual nylon in the way of the fibres after hacksawing, permitting fibres to be free from any interruption of nylon debris that may hinder the quality of images. No sections were cut from the PA6/GnP structures.

3.4.6 Sputter Coating and SEM Fractography Analysis of PA6/GnP Structures

Prior to sputter coating and SEM analysis of the sandwich structures, one sandwich structure from each filler concentration was fractured and imaged by utilising the freeze fracturing technique. The procedure involves immersing the PA6/GnP sandwich structures into liquid nitrogen for 2 hours until complete confinement of the polymer chains was reached. Afterwards, the immersed structures were removed, clamped by a vice, and fractured through the centre of the structure for a complete surface fracture to be revealed. The fractured samples were mounted to stumps and coated in conductive silver paint as shown in Figure 3.28 (image b and image c), which permitted conductivity of the structures and the mounting of them. The mounted, fractured structures were sputter coated in platinum with a coating thickness of 8 nm within Argon gas using an Agar high resolution metal sputter coater, as seen in Figure 3.29. A Hitachi SU3500 SEM, as shown in Figure 3.28 (image a) was utilised to image the sputter coated structures at 10.0 kV at x3000 and 7000 SE. Therefore, successful distinguishment between the various filler concentrations and the morphological characteristics of the PA6/GnP material could be made.

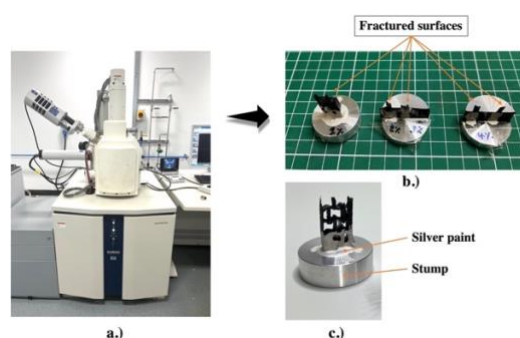


Figure 3.28 Hitachi SU3500 SEM (a.) Fractured surfaces of mounted structures (b.) Section of the re-entrant sandwich structure coated with conductive silver paint (c.)

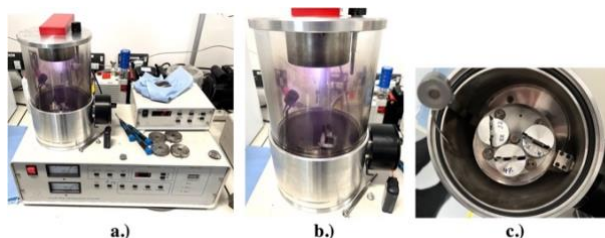


Figure 3.29 Agar high resolution coater (a.) Sputter coating of platinum taking place (b.) Positioning of mounted fractured surface within the coater chamber (c.)

In this chapter, the results of the compressive properties and energy absorbing capabilities of 3D printed fibre-reinforced and unreinforced sandwich structures will be discussed. An evaluation of the deformation mechanisms will be made between core topologies, honeycomb, re-entrant and hybrid under uniaxial compression in the in-plane orientation, as seen in Figure 3.23, Chapter 3. The objective was to imitate traditional fibre-reinforced sandwich composites. Moreover, the auxetic re-entrant core topology will also be investigated specifically to evaluate if it promoted superior compressive properties and energy absorption capabilities out of the other cores and if fibre reinforcement aided all the cores under uniaxial compression. The second half of the chapter will investigate the residual performance of the same 3D printed sandwich structures by performing low-velocity impact tests and the implementation of compression after impact tests. This was to evaluate if fibre reinforcements, Kevlar or CF, in various fibre lay-ups and orientations, enhanced the residual compressive properties of the structures.

4.1 Compression Properties of 3D Printed Sandwich Composites Before Impact

The sandwich structures, fabricated by 3DP, contain an auxetic core (re-entrant), a regular honeycomb core, or a hybrid core, as seen in Figures 3.5-3.7 in Chapter 3, indicating the individual cell dimensions and core topologies. Figure 4.1 expresses a chart of all three core topologies experiencing uniaxial compression. The re-entrant core experienced the highest compressive modulus and compressive strength, obtaining a value of 26.89 MPa and 2.58 MPa, respectively. As a result, the re-entrant experienced a 33.02% and 38.89% greater compressive modulus than the honeycomb and hybrid cores, respectively. Additionally, its compressive strength was 2.78% and 75.51% greater than the honeycomb and hybrid cores, respectively. Conversely, the honeycomb core absorbed the largest amount of energy (0.31 J/m³), owing to the isotropic characteristics of the honeycomb cell, as opposed to the anisotropic features of the auxetic re-entrant cell. As a result, the honeycomb absorbed 34.78% and 93.75% more energy than the re-entrant and hybrid cores, respectively. Subsequently, the hybrid lattice indicated no improvements in its compressive properties with the combination of the two cells (honeycomb and re-entrant). This was due to the honeycomb and re-entrant cells deforming coherently, as similarly seen in the literature by Scarpa et al. (2000), and

explained further in section 4.4. The compressive properties obtained by the sandwich structures was illustrative of that seen for the sandwich structures by Ingrole et al. (2017), as seen in Table 2.4, however some differences were noted due to the greater relative density of the structures. Thus, the re-entrant, honeycomb, and hybrid sandwich structures revealed a 94.6%, 97.22%, and 60.69% reduction in compressive modulus, respectively. Moreover, the re-entrant, honeycomb, and hybrid sandwich structures revealed a 42.31%, 55.28%, and 13.04% reduction in compressive strength. Lastly, the re-entrant, honeycomb, and hybrid sandwich structures revealed a 545.46%, 243.75%, and 56.25% reduction in energy absorbed.

Figure 4.2 shows a stress-strain graph, displaying that all three core structures experienced a similar stress-strain response under compression. The elastic response of the curves indicated that the re-entrant core demonstrated greater overall stiffness in contrast to the other cores. On the contrary, the honeycomb core handled more strain before plastically deforming exhibiting less initial stiffness, which places the hybrid core at a moderately high stiffness. Additionally, the hybrid core revealed minor elastic response and plastic deformation before reaching its ultimate compressive strength (UCS) at 1.48 MPa, at which failure commenced. Therefore, the hybrid structure's compressive properties reduced significantly earlier than the other core structures, as also seen in Figure 4.1.

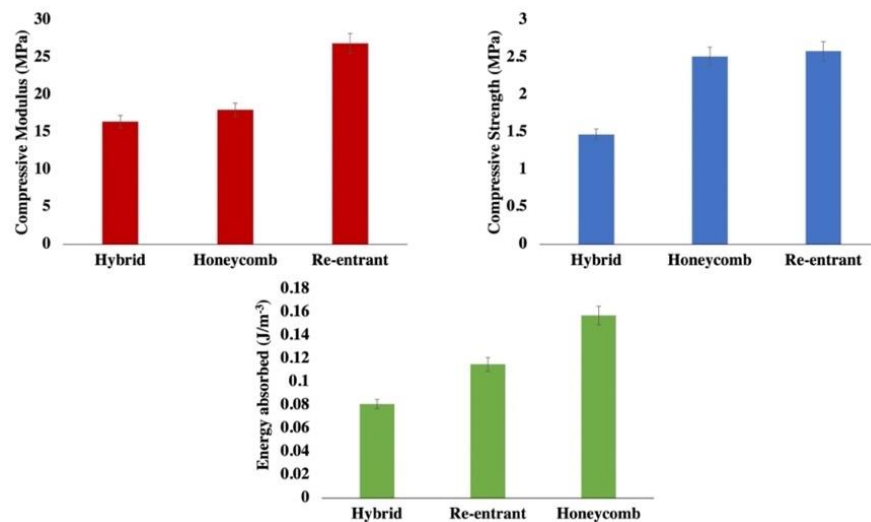


Figure 4.1 Charts showing the average compressive modulus, average compressive strength, and average energy absorbed under uniaxial compression of the honeycomb, re-entrant, and hybrid cells

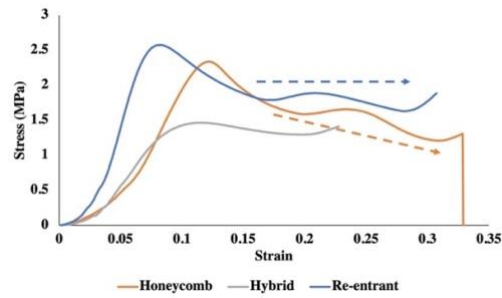


Figure 4.2 Stress-strain plot of the honeycomb, re-entrant, and hybrid sandwich structures under compression

4.2 In-Plane Compression Behaviour of the Honeycomb Core

The following sections will proceed to discuss in detail the deformation mechanisms of the different core topologies, compressed in the in-plane direction to evaluate why and how they individuate from one another. The sandwich structure face sheets contained no fibre-reinforcement in this section. This section will begin by evaluating the deformation mechanisms of the honeycomb core.

Figure 4.3 shows a stress-strain plot of the honeycomb sandwich structure. Alongside the graph are images showing the deformation mechanisms of the cells as they undergo testing, where the points indicated on the graph in each region relate to the images to show the specific point at which the 3D printed structures reacted to the mechanical loading. A common feature that develops for the sandwich structures under compression is a plateau zone following initial failure, as shown in Figure 4.3. This stage is where cells undergo plastic deformation and eventually a cyclic region, i.e., where there is instability in the displacement of the structure, and peaks and troughs of the curve fluctuate even without an increase of an applied load. With reference to point 2 in Figure 4.3 it is expected for most sandwich structures to reveal a gradual decrease in stress until uniaxial compression has promoted cell contact areas, as seen in Figure 4.3 (image 3 and point 3), and the structure is forced into the cyclic region. As a result of cell contact, stress rises until further plastic deformation or local catastrophic failure arises, leading to more reduction in stress and eventually core densification (annotated by the blue arrow in Figure 4.3), similarly witnessed by Beharic et al. (2018). Consequently, the larger and longer the plateau stage the greater the expectation for higher energy absorption capabilities. This was shown in Figure 4.1. and Figure 4.2, where the honeycomb core presented the highest energy absorption due to its high strain-to-failure of 0.328. At this

point, tests were stopped. This was due to a rise of stress occurring (see Figure 4.3 annotated by the arrow) as a result of core densification, also illustrated in Figure 4.7. These features are the reasons for a sandwich structure to promote enhancements in compressive properties compared to traditional foam core sandwich structures. A cyclic region is not seen in regular foam sandwich structures, as seen illustrated by Park et al. (2019) in Figure 4.4. A regular foam structure under compressive loading will typically produce a stress-strain graph with three stages on it, i.e. the initial elastic stage, a plateau stage, and a densification stage. Conversely, the pattern exhibited in Figure 4.3 is that commonly witnessed for traditional cellular honeycomb cores of aluminium and of polymer nature. This is because the cells undergo a layer wise failure pattern, further illustrated in Figure 4.8. Additionally, the cyclic behaviour developed because the yield strength of the struts and cell walls were compromised (Yang, et al., 2012), which is further discussed in the next section.

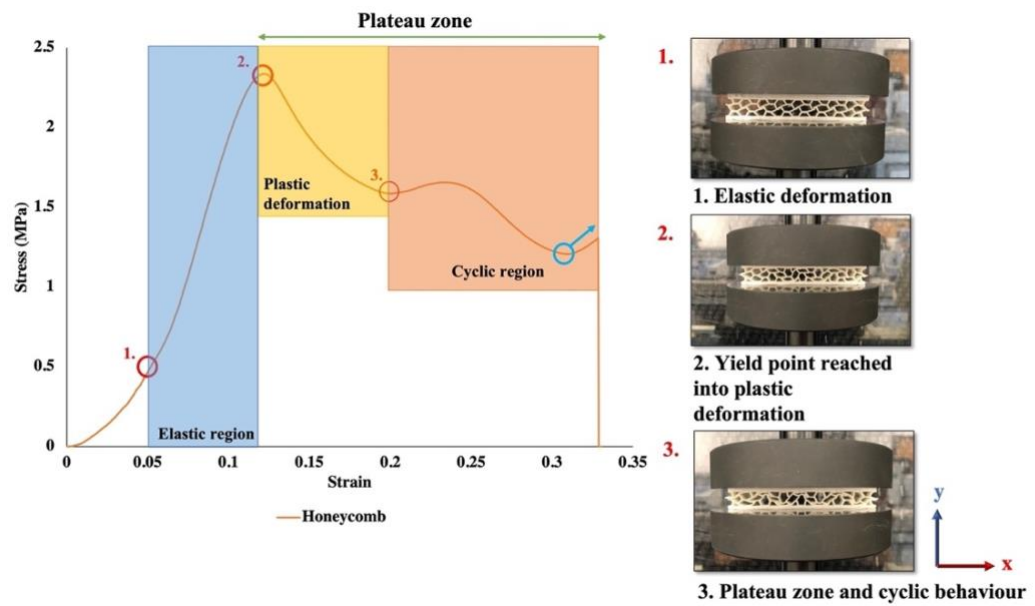


Figure 4.3 Stress-strain graph of the honeycomb sandwich structure under compression showing regions of elasticity, plastic deformation, and the cyclic region

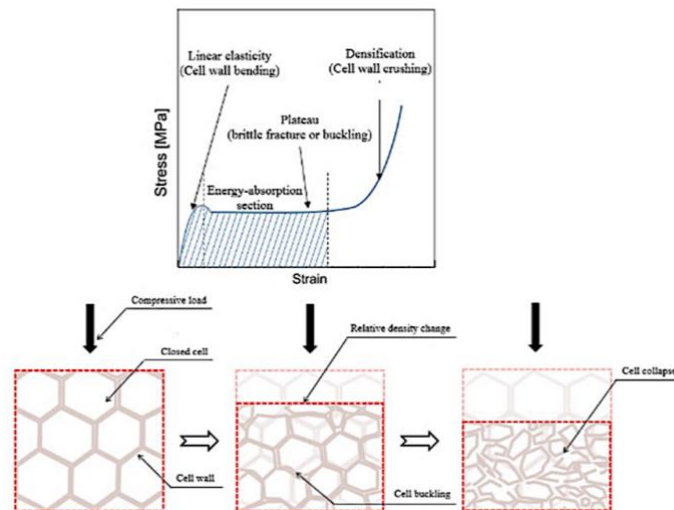


Figure 4.4 The mechanical behaviour characteristics of rigid polyurethane foam under a compressed load (Park et al.,2019)

4.2.1 Node Rotation of the Honeycomb Core

The deformation of the honeycomb cell is influenced by many factors. Figure 4.5, illustrates the in-plane bending moment of a honeycomb core. Under uniaxial compression, the horizontal struts (h) and inclined struts (l) are significantly affected. The design parameters are as follows; l being the length of the inclined strut, θ being the angle of the inclined strut, and h being the length of the horizontal strut. Each connection of a strut is connected by n a 'node', and under compression, a phenomenon known as 'node rotation' occurs, where moment M denotes node rotation (see Figure 4.5 b and c). Node rotation causes the inclined strut angle to reduce due to the straightening of the horizontal and inclined struts from the stress applied. This occurs when the load of the cell walls exceeds that of the Euler buckling load, causing buckling of the struts (Gibson & Ashby, 1988, 2014). This occurs not by the influence of the node, but by the influence of the inclined strut and the horizontal strut applying localised stress at the node. Stress is being applied from all three directions (F_1 , F_2 , and F_3), as seen in Figure 4.5 (image c), due to stress distribution, where stresses are unequal and moment M initiates rotation. As a result of unequal force, the direction of the stress being applied to the node from the struts will be different for each one, triggering further rotation and plastic deformation of the struts until densification of the core has been reached. Therefore, rotational stiffness at the node depends on the degree of constraint to the rotation at the node, which is caused in this case, by the inclined walls/struts and horizontal wall (Gibson & Ashby, 1988). Figure 4.6 (image b) shows an undeformed and deformed section of a honeycomb core from the

literature (Hönig & Stronge, 2002) illustrating its behaviour under compression, which is in good agreement with the results (Figure 4.6 image a). Additionally, Figure 4.8 (image b) shows results were compared with Gibson et al. (1982), as seen in Figure 4.8 (image a), which indicated good correlation. This deformation behaviour is one of the reasons for its unique curve in Figure 4.3 and the development of the cyclic region.

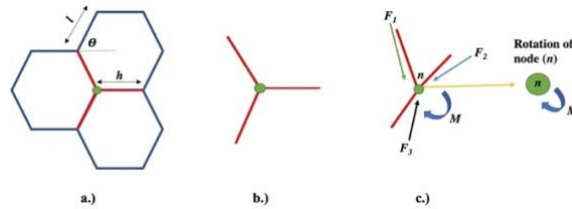


Figure 4.5 In-plane bending moment of nodes in the honeycomb cell under compression

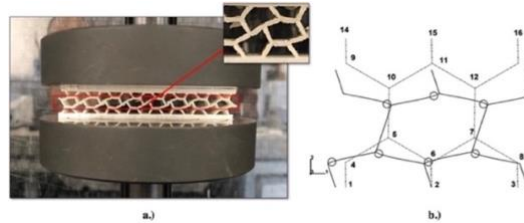


Figure 4.6 Diagonal bending of honeycomb cells under uniaxial compression (a.)
typical deformation behaviour of honeycomb cells under uniaxial compression (b.)
(Hönig & Stronge, 2002)

4.2.2 Strut Deformation and Stress-Strain Analysis

Another influential factor determining the deformation mechanisms of the honeycomb core is its strut behaviour. By nature, when the honeycomb core is subjected to compressive forces whilst in the in-plane orientation, cell walls start to bend and exhibit linear elastic deformation. Under the continuation of an increasing strain, the structure reaches a critical strain limit. Cells will start to collapse due to common failure modes, firstly by elastic buckling, then either by plastic yielding, creep, or brittle fracturing. It is important to mention that these failure modes differ depending on the properties of the cell wall material (Bitzer, 1997). Moreover, before the plateau zone can be reached the honeycomb core needs to undergo a set of stages. Figure 4.3 (image 1) shows the initial reaction of the cells to the compressive mechanical loading. Due to the stiffness of the cells, elastic deformation is seen linearly in the blue region of the graph. Subsequently,

Figure 4.3 (image 2) shows plastic deformation, exemplified by the bending of the struts seen in the structure and the formation of smaller angles within the honeycomb cells. This is the true failure of the honeycomb structure before reaching the cyclic region. Beyond the first stress peak (point 2), localized deformation starts to occur, and this is where cells collapse in an asymmetric pattern until point 3 is reached. The rise in stress in the cyclic region after point 3 is because of the distribution of stress across the core, eventually resulting in contact of neighbouring cells, as seen in Figure 4.7 indicating points of contact. Consequently, a reduction of the honeycomb angle and a reduction of the area within the cells occur, resembling a monolithic structure by the time complete core densification is reached. Points of contact and eventually densification allows the structure to cope with more force, thus imitating an increase in stiffness, nevertheless, stress is just being shared between the collapsed cells (Ingrole et al., 2017). At this point, it is the end of ‘cell collapse’, as similarly reported in the literature by Hönig & Stronge (2002), Ingrole et al. (2017), Xie et al. (2020), and Gibson & Ashby (2014).

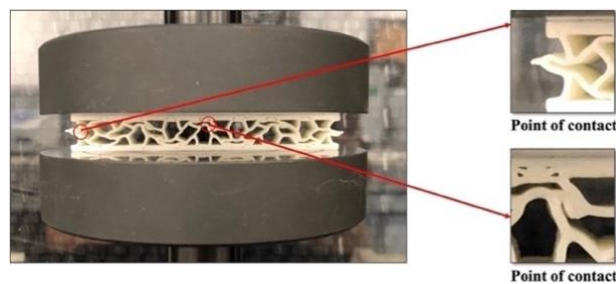


Figure 4.7 Honeycomb sandwich structure under compression displaying contact of neighbouring cells in the magnified images

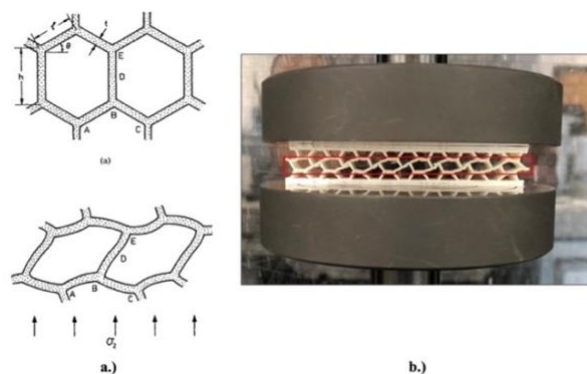


Figure 4.8 In-plane deformation of honeycomb cells under compression (a.) (Gibson et al., 1982) Honeycomb sandwich structure in the in-plane orientation tested under uniaxial compression (b.)

4.2.3 Mechanics of the Honeycomb Core

Figure 4.1 reveals that the honeycomb core had a lower compressive modulus and compressive strength than that of the re-entrant sandwich structure. This was due to honeycomb struts experiencing elastic buckling from compression in the in-plane direction. The critical stress was reached resulting in an earlier onset of plastic deformation. Thus, cells have reached a maximum moment in the bent members (strut walls), as seen in Figure 4.5, because their plastic yield point has been reached (Gibson & Ashby, 2014). Subsequently, in contrast to the re-entrant core, core densification is reached at a later stage for the honeycomb core because there is a larger area within each cell. Therefore, this results in a longer period before opposing cell walls make contact, hence its higher strain-to-failure.

On the contrary, the honeycomb core obtained higher energy absorption than both hybrid and re-entrant structures in Figure 4.1. The deformation behaviour of the cores differs from one another, exhibiting distinctive stress and failure distributions. Subsequently, due to the lower stiffness (Figure 4.1) and greater strain-to-failure (Figure 4.2) of the honeycomb core in comparison to the re-entrant, its cyclic region was larger; thus, a greater opportunity for superior energy absorption. Additionally, cells in the honeycomb only exhibited linear elastic deformation starting from a strain of 0.031, providing the core with more time to distribute the stress and bear the load. Conventionally (with nomex honeycomb cores), compressed in the in-plane direction, a similar behaviour is noted where initial linear-elastic deformation occurs. This can be due to cells experiencing buckling, and then failure by tearing or crushing, resembling a stress-strain curve that has a greater number of peaks and a larger cyclic region, as seen similarly by Xie et al. (2020) in Figure 4.9. Correspondingly, the high volatility promoting a cyclic region is because of the stretch-dominated deformation modes of honeycomb cells - also discussed in the literature review in section 2.15.10.1, and similarly reported by Li et al. (2018).

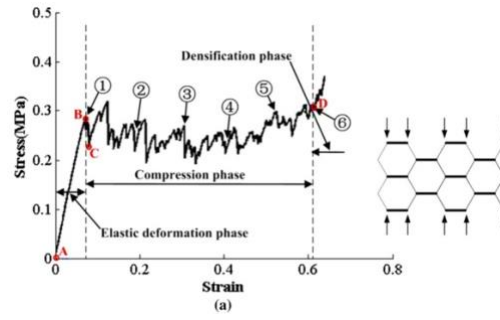


Figure 4.9 In-plane compression of Nomex honeycomb sandwich structure showing a larger compression phase (Xie et al., 2020).

4.3 In-Plane Compression Behaviour of the Re-entrant Core

4.3.1 Node Rotation of the Re-entrant Core

Typically, one of the most effective methods of influence over the re-entrant cell is the adjustment of the inclined strut l and the cell rib angle θ , illustrated in Figure 4.10. The angle θ has significant influence over the re-entrant's deformation/densification behaviour in comparison to the H/L ratio. Correlating with previous literature, i.e. Beharic et al. (2018) and Yang et al. (2012) showed that by increasing the re-entrant angle, an increase in negative Poisson's ratio can be achieved, assisting the re-entrant cell to behave more 'auxetically'. As a result of this effect, the re-entrant cells exhibit a bending-dominated deformation mode.

Figure 4.2 illustrated that the re-entrant core sustained its cyclic behaviour within the plateau zone and did not have an apparent downward trend, as seen for the honeycomb in Figure 4.2. The re-entrant core did not display a decrease in stress because the negative Poisson's ratio results in the structure collapsing within itself, leading to localized material concentration allowing it to maintain the applied load. Comparatively, Figure 4.11 demonstrates this phenomenon where cells tend to bend inwards and towards the centre of the structure; also reported by Ingrole et al. (2017).

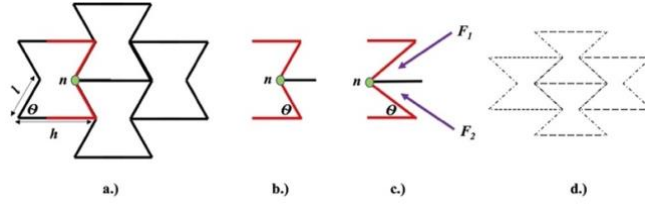


Figure 4.10 Undeformed section of the re-entrant structure (a.) section of the undeformed structure in a. (b.) compression influencing direction of force applied showing bending of inclined l struts and smaller angle θ (c.) final deformation of the re-entrant structure showing partial densification of cells (d.)

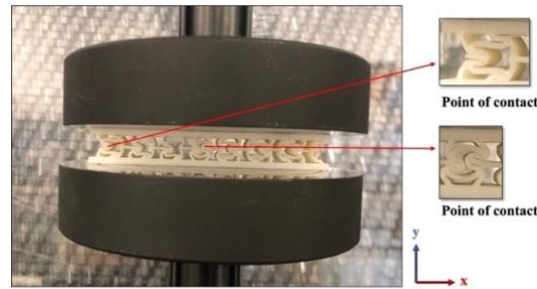


Figure 4.11 Re-entrant sandwich structure under in-plane compression showing contact of neighbouring cells in the magnified images

Figure 4.10 illustrates the localised material densification phenomenon occurring in Figure 4.11. Figure 4.10 (image a) shows the undeformed structure of the re-entrant cells, and image b shows a section of the cell in red. Subsequently, in Figure 4.10 (image c), the horizontal strut from the above layer and bottom layer cells distributes its stress to the adjacent cell forcing the inclined strut/cell rib angle θ to become smaller, resulting in compaction of the cells. Theoretically, a re-entrant cell would typically deform in the mentioned manner. However, if the re-entrant structure is considered as one entire structure, such as the 3D printed structures in these results, the deformation mechanisms can alter, influencing the rotation of the nodes and the behaviour of how the structure deforms globally. Consequently, the deformation mechanism of individual cells can result in a global instability of the re-entrant structure, yielding a more bending dominant deformation, as opposed to the layer wise stretch-dominant failure of the honeycomb core. This behaviour was seen in the literature by Hou et al. (2018) and witnessed in the results in Figure 4.11.

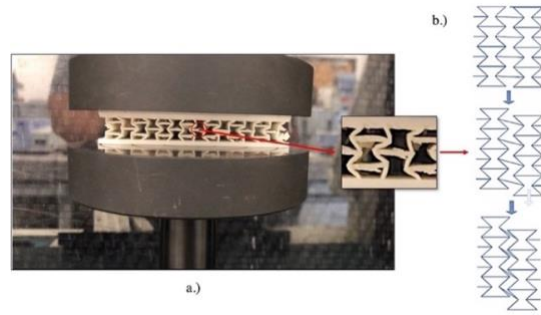


Figure 4.12 In-plane densification of the re-entrant cells under uniaxial compression and bending of horizontal struts (a.) typical deformation behaviour of re-entrant cells under uniaxial compression showing similar behaviour from previous work (b.) (Yang et al., 2012)

4.3.2 Deformation Stages of the Re-entrant Core

Figure 4.13 shows a stress-strain graph of the re-entrant cell structure under compression. The auxetic re-entrant structure exhibited an ‘elastic-plastic collapse’ deformation behaviour, similar to the honeycomb core in Figure 4.3. Under initial compression of the re-entrant structure, deformation occurs elastically, hence the curve expressing linearity. Once the yield strength of the struts was encountered, it yielded further, as seen in Figure 4.13 (image 2 and point 2), resulting in plastic deformation, translating into the plateau region. Eventually, after any individual struts have encountered failure, stress will be distributed to a neighbouring cell within the same layer or to any remaining struts in the cells deforming. Consequentially, failure of struts is shown in Figure 4.13 (image 3) and plastic deformation of the cells can be seen in Figure 4.11, indicating contact made with neighbouring cells. The failure of the cells is the cyclic behaviour conveyed on the graph in Figure 4.13. Therefore, once a cell strut has reached failure, seen as the reduction of stress in the plastic deformation zone in Figure 4.13, a new layer within the structure is affected, seen as the increase in stress in the cyclic zone in Figure 4.13. This happens until once again a new layer experiences the same failure of the previous layer, producing the cyclic phenomenon on the curve (Yang et al., 2012).

The deformation behaviour of the re-entrant cells displayed a symmetrical behaviour (Figure 4.12) in its localized band, which was compared and in good agreement with Yang et al. (2012). As depicted in Figure 4.12, the layer in parallel started to create another localized band with the increase in strain. Consequently, this showed similarity to the honeycomb, in that once the strength of cells was overcome, then the rows of cells

eventually make contact with their neighbours. As a result of its deformation behaviour, plastic deformation occurred at a higher stress (2.5 MPa) in comparison to the honeycomb (2.3 MPa), as seen in Figure 4.2. Due to its nature to densify under compression, the re-entrant core reached the cyclic region before the honeycomb core. Moreover, the re-entrant's ability to maintain its stress in the cyclic region can be due to the auxetic nature of the re-entrant core, ensuring more prominent densification of cells, and thus a greater increase of stress on the curve at the core densification point (blue arrow in Figure 4.13). Therefore, the continuation of the test would result in the re-entrant curve obtaining higher values of stress without reducing, since maximum densification would be achieved.

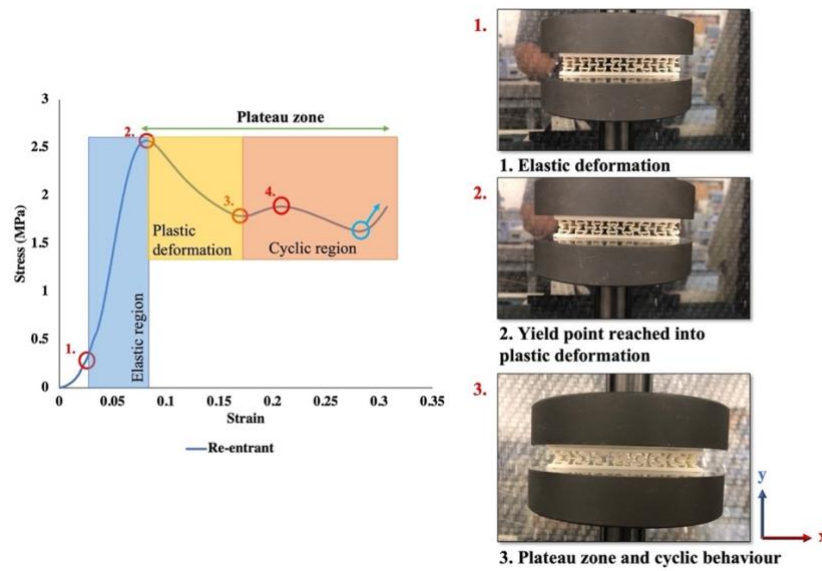


Figure 4.13 Stress-strain graph of the re-entrant structure under uniaxial compression showing the region of elasticity, plastic deformation, and the cyclic region

4.3.3 Mechanics of the Re-entrant Core

Figure 4.1 showed that the re-entrant core obtained the greatest compressive modulus and compressive strength. The mechanics of the re-entrant cell determined this behaviour, due to the failure of the inclined struts (l) and inclined strut angle (θ), (Liu et al., 2016; Yang et al., 2013; Yang et al., 2015), as presented in Figure 4.10. Additionally, Figure 4.11 shows strut angles decrease at a fast rate under load in the y -direction. Compressive modulus is greater than all other cellular designs because strut walls (h and l) perpendicular to one another make contact initially in the elastic region just prior to plastic deformation, as seen in Figure 4.13. Therefore, cell contact between the strut

angles increases the stiffness of the structure aiding it in coping with more load. Thus, the re-entrant core experienced cell contacts earlier at a strain of 0.17 (Figure 4.13) in comparison to a strain of 0.2 for the honeycomb core (Figure 4.3). This was because the maximum moment was reached in the bent members, influenced by the smaller angle between h and l , as seen in Figure 4.14 (image b). This phenomenon develops because, under load, the inclined re-entrant struts (l) directing inwards, alongside the negative Poisson's ratio, results in contraction of the cell walls occurring much sooner after the plastic yield point of the struts has been met. Thus, there is less relative space within individual cells; hence, contact of h and l walls occurs at a lower strain than the honeycomb, producing an increase of stiffness thereafter. On the contrary, Nylon White has significant plasticity, providing it with high amounts of ductility and strength. As a result, strut angle (θ) can undergo large amounts of deformation rather than fracturing, allowing the cell to cope with more load. Contrarily, a lack of plasticity would result in an absence of the plateau stage (Liu et al., 2016). Therefore, given this behaviour, the re-entrant core can remain in its elastic state for a long period before yielding in comparison to the honeycomb core.

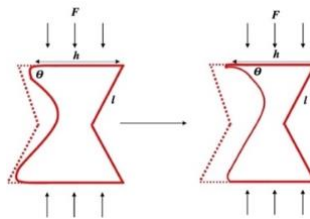


Figure 4.14 Initial in-plane deformation of re-entrant cell at angle θ (a.) further deformation of re-entrant cell where angle (θ) has reduced and bending occurred with strut (l) (b.)

4.4 In-plane Compressive Properties of the Hybrid Core

The objective of the hybrid cell design (Figure 3.7 in the methodology) was to produce a lattice structure with the combined characteristics of the re-entrant core and honeycomb core, with the intention that it will provide an enhancement to the re-entrant and honeycomb structures. The 3D printed hybrid core was similarly fabricated and uniaxially compressed by Ingrole et al. (2017). Figure 4.15 exhibits the stress-strain graph where the properties of the hybrid structure presented a different behaviour under compression, due to different deformation mechanisms taking place in comparison to the re-entrant and honeycomb cores. Moreover, Figure 4.1 shows the hybrid produced

compressive properties lower than the re-entrant and the honeycomb cores. It experienced a 9.6% and 63.6% lower compressive modulus, and a 70.9% and 75.7% lower compressive strength, when compared to the honeycomb and re-entrant cores, respectively. Therefore, it was 42.2% and 94.0% lower in energy absorption when compared to the re-entrant and honeycomb cores, respectively.

The hybrid structure resulted in a distributed deformation pattern, i.e. demonstrating both a stretch-dominated and bending-dominated behaviour. Moreover, Figure 4.15 (image 1) shows how the honeycomb cells in the hybrid core deformed in a similar manner to Figure 4.6, tilting sideways. This mechanism of deformation resulted in the initial increase of stress within the elastic region (Figure 4.15) since cells in the top and bottom layers are reacting with opposing forces of direction to one another. Figure 4.15 (images 1-3) reveals that under compression, in the y-direction, the honeycomb cells within the structure deformed as if tension was applied in the x-direction (elongating). This corresponded with the remarks made in section 4.2, in relation to its stretch-dominant deformation mode.

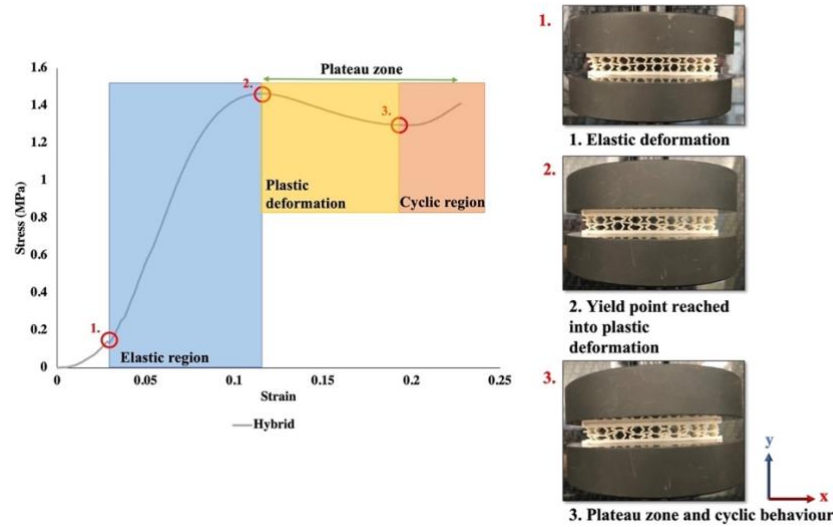


Figure 4.15 Stress-strain graph of the hybrid sandwich structure under in-plane uniaxial compression showing the region of elasticity, plastic deformation, and the cyclic region

The influence of the re-entrant cells on the hybrid structure is shown in Figure 4.17, indicating the inward deformation and auxetic nature of the core. Subsequently, the honeycomb cells seemed to stimulate and facilitate the re-entrant cells to react more ‘auxetically’ with its lateral expansion. Nonetheless, the auxetic nature declined and the structure deformed with stretch-dominated features instead, as seen in Figure 4.15 (image

2), exhibiting a positive Poisson's ratio, and shown in Figure 4.15 (image 3). This can be due to the inclined struts l of the honeycomb cells and their connection to the re-entrant cells, which cause the re-entrant cells to convolute increasingly more. Thus, the combination of the positive and negative Poisson's ratio of the honeycomb and re-entrant cells, respectively, work with a congruent nature which does not enhance the performance of the structure. Eventually, if compression testing proceeded further into the cyclic region (Figure 4.15), it would behave with a positive Poisson's ratio and end up densifying completely until stiffness will once again rise from the compaction of cells. On the contrary, Figure 4.15 indicated that the hybrid core developed a cyclic region corresponding well with the re-entrant and honeycomb structures, due to cell contact, as seen in Figure 4.16. It was revealed that at the end of the cyclic region, as seen in Figure 4.15 (image 3), the honeycomb cells were the last to deform. This was related to its stretch-dominated features providing the honeycomb cells with high elastic modulus and higher ultimate strength when combined with the re-entrant cells (Li et al., 2018).

4.4.1 Mechanics of the Hybrid Core

The hybrid cell configuration meant the inclined struts (l) in the re-entrant structure stimulated it to collapse progressively faster because of the absence of neighbouring re-entrant cells working to enhance the auxetic behaviour. Consequently, the hybrid structure yielded at 1.34 MPa which was 44.62% and 41.48% lower than the re-entrant and honeycomb cores. Therefore, it resulted in earlier cell contact, seen as point 3 in Figure 4.15. Conversely, it does not have a localized material concentration area but rather a uniform distribution of material. Hence, Figure 4.16 shows that the hybrid structure deforms greatly in the (h) struts for both the re-entrant and honeycomb cells, causing a volatile resemblance inside the core structure, as seen in Figure 4.18. The lines in Figure 4.18, are a visual annotation of the cores reacting under uniaxial compression. Moreover, the re-entrant structure appeared uniform and consistent in its deformation and the honeycomb revealed a variable and inconsistent deformation pattern in Figure 4.18. The properties experienced by the hybrid structure were distinctive to the honeycomb and re-entrant base structures. Consequently, the hybrid structure had no particular method for resisting deformation under uniaxial compression, instead it was able to tailor and control its deformation. Therefore, the hybrid cell structure did not resist the stress applied to it (Figure 4.1) to the same extent as the honeycomb and re-entrant. As a result, the combination of the two base structures did not improve the compressive properties or

energy absorption capabilities of the structure. Therefore, there is a lower volatility displayed on its curve in Figure 4.15 and a reduction in cyclic behaviour because of its distinctive bending deformation that does not correspond to the deformation patterns of the honeycomb or re-entrant cells in isolation.

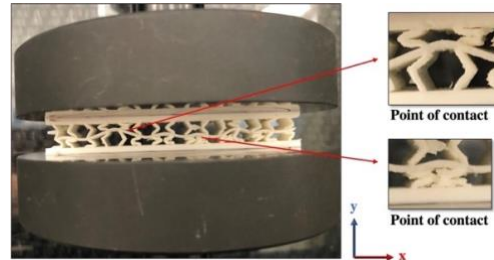


Figure 4.16 Hybrid sandwich structure under in-plane uniaxial compression showing contact of neighbouring cells



Figure 4.17 Auxetic behaviour indication from re-entrant cells

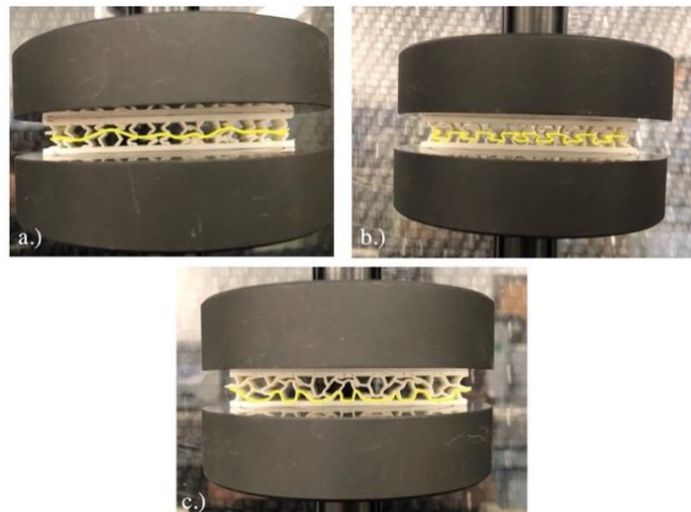


Figure 4.18 In-plane deformation patterns of the hybrid sandwich structure (a.) the re-entrant sandwich structure (b.) and the honeycomb sandwich structure (c.)

4.5 Finite Element Analysis

This section will seek to investigate the deformation mechanisms of the sandwich structures by FEA. To note, the mesh involved two element sizes, an element size of 1.00 mm for the sandwich structure geometry and an element size of 5.00 mm for the compression plate geometries, as seen in Figure 4.19, Figure 4.21, and Figure 4.23. The sandwich structure element size was refined as to expose greater detail of the core deformation mechanisms during the compression simulation. Furthermore, due to software and hardware limitations refinement of the sandwich structures was limited to 1.00 mm. The boundary conditions involved a fixed support that was applied to the bottom compression plate as to fix all degrees of freedom, alongside a bonded contact and target point between the bottom compression plate and bottom face sheet, as seen in Figure 4.19, Figure 4.21, and Figure 4.23. The top compression plate involved a displacement of 4.55 mm in the z-direction since this displacement was recorded for the experimental tests, alongside a frictional contact with a friction coefficient of 0.2 between the top compression plate and the top face sheet. Additionally, the step end time was set to 75 seconds, since the experimental approximated around this value until completion of the test. This took place with a minimum time step of 0.1 seconds and a maximum time step of 2 seconds. Lastly, numerous frictionless contact and target points were added within the cells of the core topologies as to imitate the behaviour of the core deformations as seen in the experimental.

4.5.1 Honeycomb Structure

As seen in Figure 4.20 a successful correlation between the core deformation mechanism is found when compared to the experimental compression seen in Figure 4.7. It is revealed in Figure 4.20 in stage 2 that the lateral expansion of the cells in the x-direction transpires in a similar manner to that shown in Figure 4.7. The simulation indicates cell contact is made firstly within the core rather than the outer edges, like that highlighted in stage 4 of Figure 4.20. This is similar to the point of contacts witnessed in Figure 4.7. Furthermore, Figure 4.20, stage 3, demonstrated the same symmetrical failure of the honeycomb cells as seen in Figure 4.7, and approximately identical contact regions. To note, Figure 4.20 aided in exposing stress concentration regions, indicating that they occur at the node of the honeycomb cells throughout the entirety of the honeycomb sandwich structure, further exposing where failure first initiates. Overall, comparisons

between simulations and results exposed the positive Poisson's ratio of the honeycomb cells and mutually agreed on the stretch-dominated behaviour of the honeycomb sandwich structure. In conclusion, a comparison between Figure 4.20 and Figure 4.22, for stages 3, reveal that even when the honeycomb core reaches an equal time to that of the re-entrant core cell contact would still not be made for the honeycomb until a time of 75 seconds has been reached. This ascertained why there were longer periods before cell contact was made on the stress-strain graph seen in Figure 4.3 for the honeycomb structure in relation to cell space, such as that discussed in section 4.2.3.

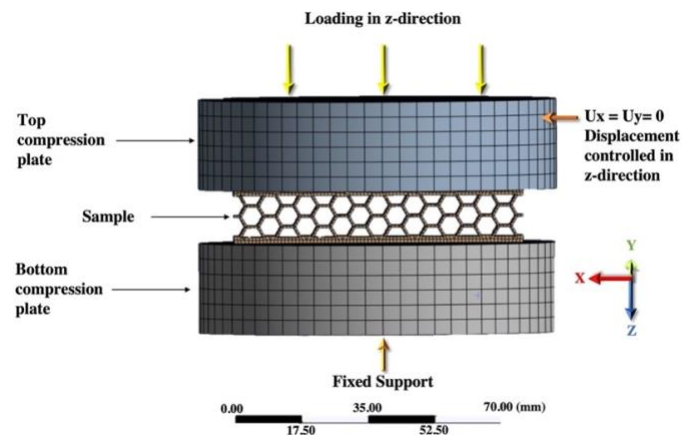


Figure 4.19 Mesh of the honeycomb sandwich structure and its boundary conditions

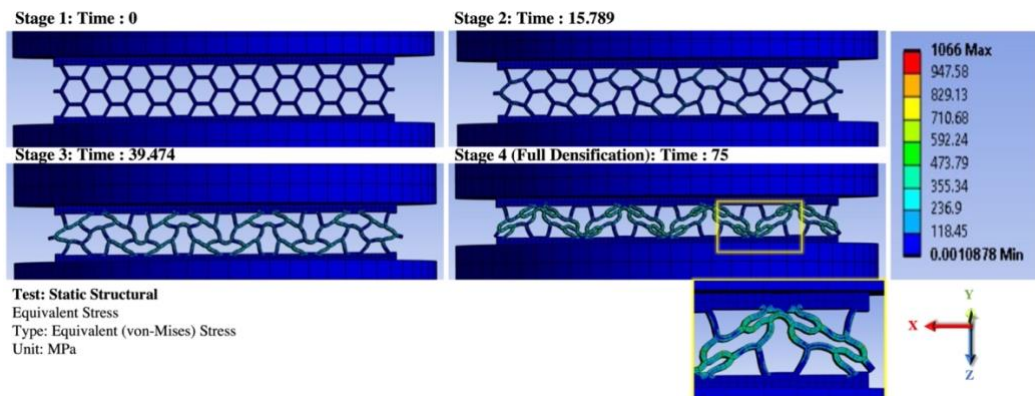


Figure 4.20 Static structural analysis showing the deformation pattern of the honeycomb sandwich structure

4.5.2 Re-entrant Structure

The FEA revealed in Figure 4.22 for the re-entrant sandwich structure demonstrates the characteristics of negative Poisson's ratio, whereby cells deform inwards under compression. This is illustrated more evidently in stage 3 of Figure 4.22,

showing that cells under-go deformation in the x-direction. The full densification image revealed in stage 4 of Figure 4.22 shows good agreement with the full densification of the experimental image as seen in Figure 4.11. It indicated a similar phenomenon in relation to contact regions and overall distribution of cell deformation. Moreover, Figure 4.22 (stage 2), indicated that lateral contraction of the cells initiated at the ends of the structure, also found in the results in Figure 4.11, thus revealing the beginning of material densification. This was caused by the bending dominant deformation mode and angle θ , as discussed in section 4.3.1. Subsequently, highlighted in stage 4 in Figure 4.22, cell contact was evident, therefore correlating with the cell contact regions shown in Figure 4.11. Due to the auxetic nature of the structure a high degree of cell contact was seen to occur at the outer edges of the sandwich structure (image a.) and significant cell wall contact was recorded for the highlighted image, image b, as seen in stage 4 of Figure 4.22. An identical occurrence of this was noted in Figure 4.11 as seen in the bottom point of contact image. Therefore, the auxetic features of the re-entrant sandwich structure demonstrated higher cell contact regions when compared to the honeycomb core as seen in Figure 4.20 (stage 4). The observation of both Figure 4.11 and Figure 4.22 suggests that cell deformation initiated at the outer edges of the re-entrant sandwich structures and gradually propagated inwards towards the centre of the structure. Lastly, high stress concentration points accredited to the nature of the auxetic cells was seen to occur, similar to the honeycomb, at the nodes of the re-entrant cells as seen in the highlighted images in Figure 4.22, stage 4.

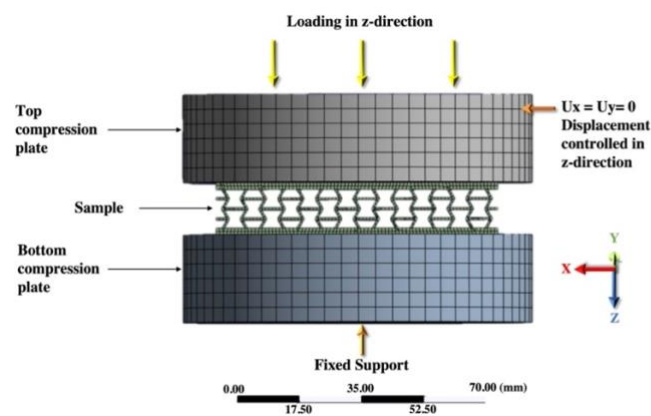


Figure 4.21 Mesh of the re-entrant sandwich structure and its boundary conditions

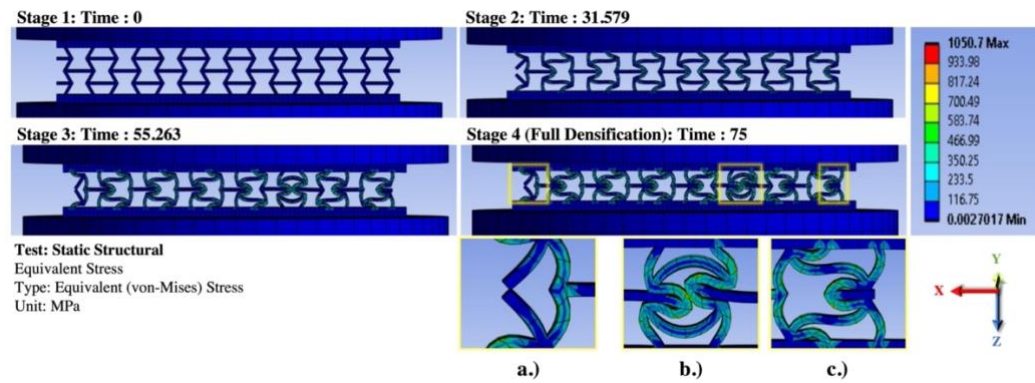


Figure 4.22 Static structural analysis showing the deformation pattern of the re-entrant sandwich structure

4.5.3 Hybrid Structure

Figure 4.24 highlights good agreement with the results in Figure 4.17. Stage 2 in Figure 4.24 reveals that deformation and collapsing of cells initiates from the re-entrant cells on the left side of the sandwich structure, as similarly demonstrated in the results in Figure 4.17. It is further indicated in image (a.) of Figure 4.24. This indicated that the deformation behaviour of the core is dominated by the re-entrant cells, thus resulting in a highly localized stress region. Consequently, the influence of the re-entrant cells directed the honeycomb cells to deform along the x-axis in the direction of the re-entrant's deformation, as seen in stage 3 of Figure 4.24. As a result, the re-entrant cells support the deformation mechanisms of the honeycomb cells. Furthermore, accredited to the re-entrant deformation mechanisms it can be seen highlighted in stage 4, in Figure 4.24 (image b.), at full densification, stress concentration points are distinguishable at the bottom edges of the honeycomb/re-entrant cells, and at the inclined struts (l). Overall, the hybrid configuration effected the singular deformation mechanisms of the honeycomb and re-entrant cells, stopping them from behaving in their conventional manner of deformation and rather portrays more of a congruent nature. In addition, the added stretch-dominant features, and the interference of the bending moment in the honeycomb cells in Figure 4.24 means there will be overall less resistance to the mechanical loading for the hybrid sandwich structure.

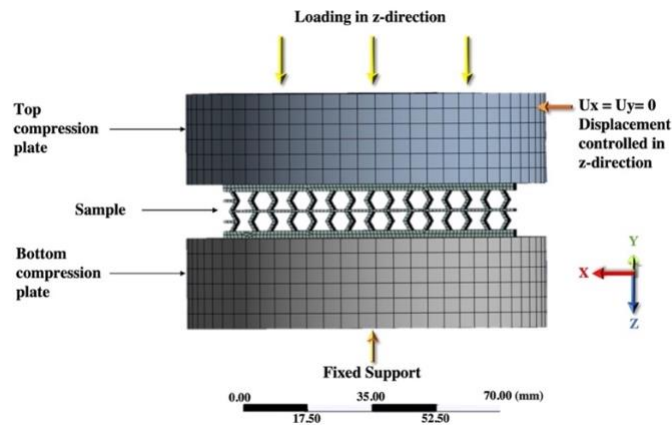


Figure 4.23 Mesh of the hybrid sandwich structure and its boundary conditions

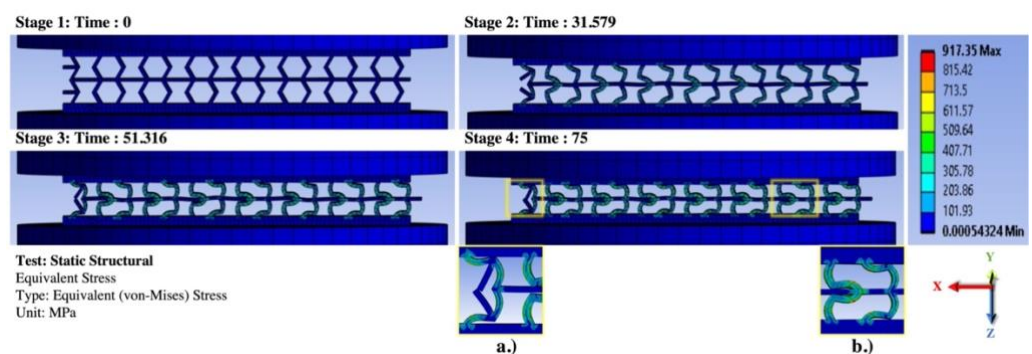


Figure 4.24 Static structural analysis showing the deformation pattern of the hybrid sandwich structure

4.6 High Depth of Field Cross-Sections and Microscopy Images of Fibre-Reinforced Sandwich Structures

This section will seek to analyse the behaviour of the same 3D printed sandwich structures, as seen in the previous section, however, the face sheets will contain fibre reinforcements. This was to investigate whether improvements in the compressive properties and energy absorption capabilities were noticed compared to their neat polymer sandwich structure relatives (same core type). For this section and those that follow, re-entrant, hybrid, and honeycomb will be abbreviated to “RE”, “HYB”, and “HC”, respectively. Kevlar is abbreviated to “Kev.”, carbon fibre is abbreviated to “CF” and impact is abbreviated to “IMP.”

To compare between the fibre orientations, fibre packing location, and the nature of the Kevlar and CF fibres within the 3D printed sandwich structures, HDof and microscopy image analysis was performed, as seen in Figures 4.25-4.28. Figures 4.25-

4.28, images 1,3 and 5, show the fibre positions in the matrix and images 2,4 and 6 show the fibre lay-ups at a higher magnification (x100). Figure 4.25 and Figure 4.26, show the coarse appearance of the CFs and reveals their brittle nature, demonstrated by the clean fractured surfaces of the fibres. Conversely, Figure 4.27 and Figure 4.28 show the Kevlar fibres in the same orientation, but the fibres are sparse and fibrous, displaying some with greater lengths than others which is due to their elongation when damaged, as a result of their ductile nature. The HDoF images showing Kevlar fibres, as seen in Figure 4.27 and Figure 4.28 indicated cleaner surfaces and more de-bonding between neighbouring fibres. This suggested possibly a weaker fibre interface and a reduction in its wettability with the nylon matrix. The reason for this may be that the thermoplastic nylon has not thoroughly permeated the internal fibre bundles. Therefore, there was a limited number of external fibres that could adhere to the matrix (Caminero et al., 2018).

Microscopy images, as seen in Figures 4.25-4.28, show the cross-sections of the CF fibres and Kevlar fibres, resembled by colours black and yellow, respectively, and the polymer matrix is the reflected white zones between the fibres. Microscopy images as seen in Figures 4.25-4.28, at times, show indication of print deformities, namely voids. On the contrary, any fibre failures will be considered lightly as a factor that may influence the compressive properties of the sandwich structures. This is because samples were cut with a hacksaw, in turn significantly damaging the fibres and the matrix. As such, damage modes and print defects will not be investigated based off microscopy images but will still be considered as a minor issue.

Both Kevlar fibres and CFs indicated reasonable wettability with the matrix, resulting in successful fibre-matrix adhesion. Carbon fibre structures, as seen in Figure 4.25 and Figure 4.26 exhibited aggregates of polymer rich regions (seen as the reflected white zones in between fibre bundles), indicating better fibre-matrix adhesion in comparison to Kevlar structures, as seen in Figure 4.27 and Figure 4.28. Since all fibres are coated in a nylon sizer, the 3DP structures revealed in Figures 4.26-4.28, are expected to contain polymer rich regions separating the bundles of fibres. However, this can result in areas of high stress concentration and probable premature failure (Kahla, 2019), thus possibly affecting compressive properties. On the contrary, the microscopy images exhibit distinctions between the various fibre orientations. Figures 4.25-4.28 show that the CUD and UD fibre orientations have fibre cross-sections directed normal to the microscope lens. Opposingly, 0° fibre orientations have fibre cross-sections directed

perpendicular to the microscope lens. This was similarly seen for the QI fibre orientation; however, some fibres were also normal to the microscope. Moreover, the Kevlar UD structure, as seen in Figure 4.28, illustrates clearly the 4 layers of fibres that each of the face sheets for all sandwich structures contained. This is distinguished by the layer separation as identified by the annotations. As a result, the laying up of fibres, amount of fibre layers, and the fibre direction can be deemed successful for the 3D printed fibre-reinforced sandwich structures.

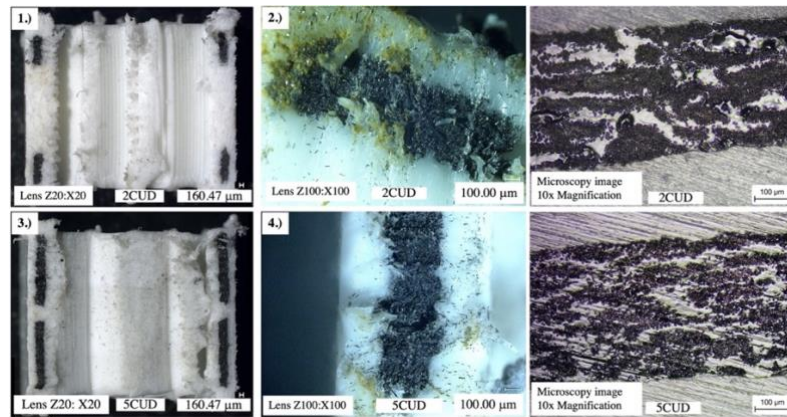


Figure 4.25 High depth of field cross-section of CF-reinforced sandwich composites with a 2CUD or 5CUD fibre orientation alongside microscopy images

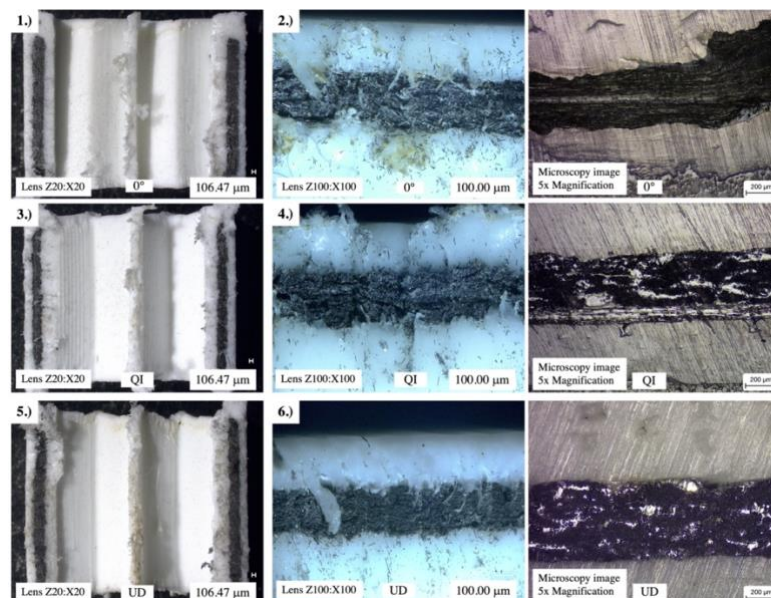


Figure 4.26 High depth of field cross-section of CF-reinforced sandwich composites with a 0°, QI, or isotropic UD fibre orientation alongside microscopy images

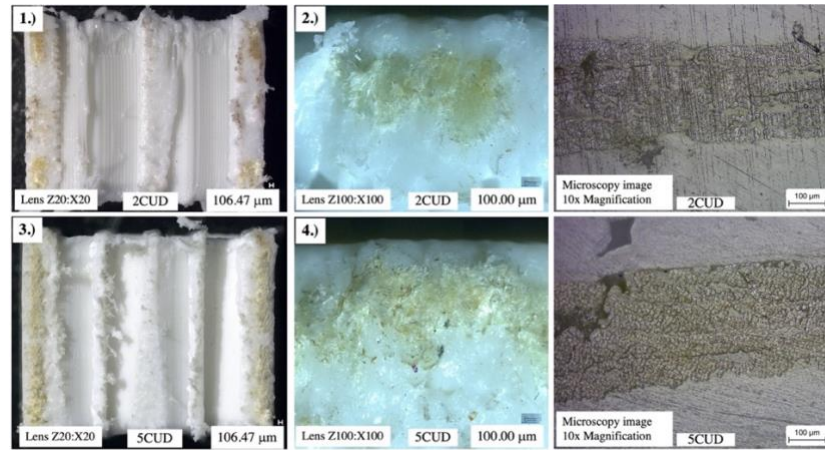


Figure 4.27 High depth of field cross-section of Kevlar-reinforced sandwich composites with a 2CUD or 5CUD fibre orientation alongside microscopy images

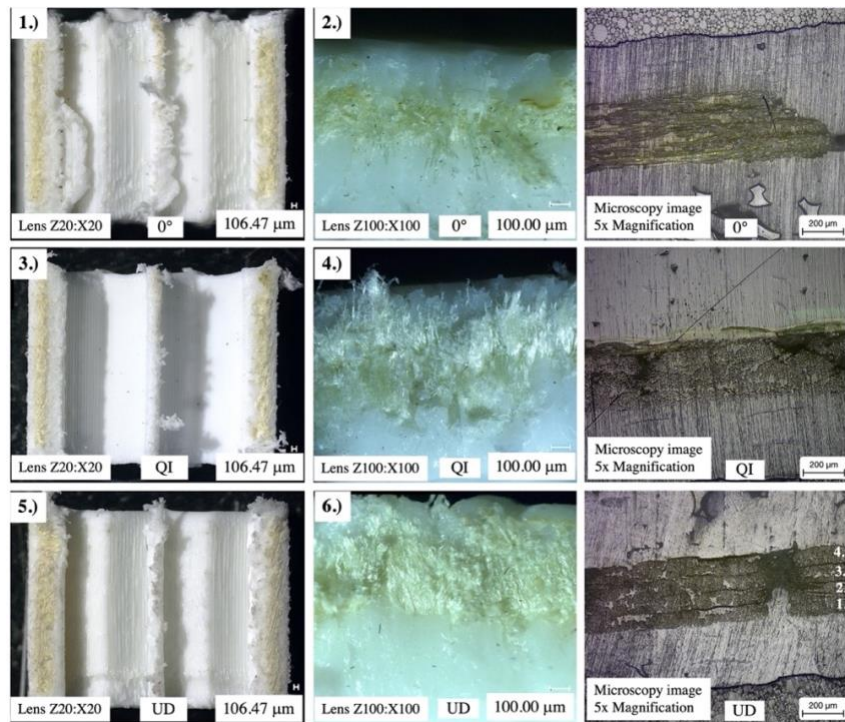


Figure 4.28 High depth of field cross-section of Kevlar-reinforced sandwich composites with a 0°, QI or isotropic UD fibre orientation alongside microscopy images

4.7 Fibre Lay-Up and Orientation Evaluation

4.7.1.1 Isotropic Concentric Uni-Directional Lay-Up

The CUD fibre pattern is one where fibres are in a continuous circular pattern that follows the perimeter of a selected component until the circular pattern is completed, as shown in Figure 3.5, Chapter 3. It is noticeable which CUD structure contains the higher fibre volume fraction when Figure 4.25 and Figure 4.27 are compared. The 2CUD lay-up indicates a smaller packing of fibres at each of the four corners of the structure as seen in Figure 4.25 and Figure 4.27 for image 1. A larger packing area of fibres can be seen for the 5CUD lay-up in Figure 4.25 and Figure 4.27 for image 3.

4.7.1.2 Isotropic Uni-Directional Lay-Up

The isotropic uni-directional UD (isotropic-UD) lay-up determines that all fibres in all planes are aligned in the same direction, as seen in Figure 4.26 and Figure 4.28 for the microscopy images. Due to the alignment of continuous fibres, they are highly dependent on the direction of the mechanically applied load (Pethrick, 2010). Fibres acting in the direction of an applied load contain higher strengths (Kabir et al., 2021). Furthermore, due to the predominant longitudinal alignment of the CUD fibre orientations, it can be considered that their mechanical properties are similar to an isotropic-UD fibre orientation. However, under flexural or bending it is reported that the concentric pattern is expected to perform better (Dickson et al., 2017).

4.7.1.3 Quasi-Isotropic Lay-Up

Figure 4.26 (images 3 and 4) exhibit the HDoF images, where image 4 shows the irregular directions of the CF fibres. Additionally, Figure 4.28 (image 3 and 4) also shows the QI lay-up. However, it is difficult to tell the lay-up from the fibre fractured surface in image 4 due to the weaker bond of the fibres and the fibrous appearance. The fibre orientations of $(0/45/90/135)^\circ$ can also be seen in the micrographs in Figure 4.26 and Figure 4.28. The lower portion of Figure 4.28 (image 4) shows fibres are flat and not directed normal to the microscope. Consequently, the fractured surfaces are a common occurrence for QI lay-ups. Since fibres are distributed in different directions, upon fracture, the surface represents greater coarseness with irregular fibre directions and different heights of the individual layers of fibres. This is illustrated in Figure 4.29, where

the damage of a QI lay-up is exaggerated to show this behaviour and that which is seen for conventional laminates (Morioka & Tomita, 2000).

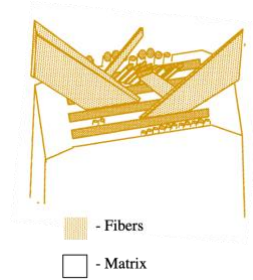


Figure 4.29 A QI laminate showing the direction of fibres after experiencing fracture (Morioka & Tomita, 2000)

4.7.1.4 Zero-Degree Fibre Orientation

The 0° fibre orientation have fibres orientated at 90° , directed across the face sheet of the sandwich structures. This can be distinguished between other lay-ups because fibres are no longer normal to the microscope, but the cross-sections of the transverse fibres are seen instead, as shown in Figure 4.26 and Figure 4.28.

4.8 Volume Fraction of 3DP Structures

Volume fraction (V_f) is considered in this section and the following sections due to its relevance in determining mechanically the material properties of a fibre-reinforced composite (Hull et al., 1996). An increase in fibre volume (F_v) can result in improved impact properties (Caminero et al., 2018), as well as strength and stiffness (Chacón et al., 2019). Increasing the F_v can result in a technique in which to tailor the mechanical properties of a composite (Kabir et al., 2021). Therefore, the values F_v and P_v (plastic volume) calculated by Eiger are inputted into Equation (1) in section 3.1.1, producing a value for V_f . Plastic and fibre specifications of all structures can be found in Table 3.8 in Chapter 3. It can be seen in Figure 4.30 that there is a direct correlation between the fibre content and the $V_f\%$ in a given sandwich structure, i.e. as the amount of fibre content increases so does the $V_f\%$ (Niranjan, 2012).

Improvement with increasing V_f remains true in an individual lamina of continuous fibres in conventionally manufactured composite materials (Hull et al., 1996). However, sandwich structures in the results contain various core topologies between the composite face sheets, manipulating the outcome of the compressive properties of the

structures and thus need to be considered as a factor that can affect this statement. The chart in Figure 4.30 shows the largest discrepancy was revealed by the Kev.-2CUD and CF-2CUD structures, when compared to all other fibre orientations. The Kev.-2CUD structures revealed values around 2.5% V_f and the CF-2CUD structures revealed values around 3% V_f . The highest V_f was exhibited by the CF-5CUD and CF-isotropic UD fibre orientations, exhibiting values around 7.5% and 8%, respectively. Subsequently, the CF-2CUD structures revealed a 90.0% difference in V_f when compared to the CF-isotropic UD structure. The Kev.-2CUD structures revealed a 104.7% difference in V_f when compared to the CF-isotropic UD structure. Overall, Figure 4.30 demonstrates that CF structures contained marginally higher V_f when compared to Kevlar reinforced structures. The CF reinforced structures obtained on average a 22.2% higher V_f , as a result of the higher fibre diameter (Kevlar= 0.33mm and CF=0.39mm).

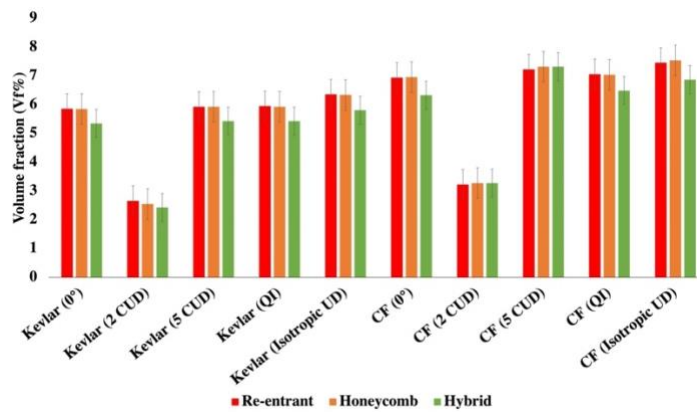


Figure 4.30 Volume fraction chart showing the re-entrant, honeycomb, and hybrid cores with CF or Kevlar reinforcement

4.9 Stress-Strain Relationships of 3D Printed Fibre-Reinforced and Unreinforced Sandwich Structures

4.9.1 Fibre-Reinforced and Unreinforced Honeycomb Structures

Figures 4.31-4.33, show the stress-strain plots of the HC, the RE, and the HYB fibre-reinforced sandwich structures. Out of the HC structures, the highest UCS was experienced by the unreinforced structure. It revealed a UCS of 2.32 MPa with a strain at a maximum load of 0.124, as seen in Figure 4.31. Its UCS was 8.18% lower than the RE and 37.06% greater than the HYB-no fibre structures. The HC-no fibres produced a strain-to-failure of 0.200, indicating an earlier failure of the structure in contrast to the fibre-reinforced structures. However, it exhibited a larger plastic deformation in contrast to

structures with fibres, exposing its greater ductility. The fibre-reinforced structures all reacted in a similar manner to one another, yielding within a strain region of 0.03-0.06, but at a variance of stress readings (see Figure 4.31). Consequently, it demonstrated that fibre-reinforced structures had nearly no obvious distinctions when comparing fibre lay-ups and fibre types.

Sandwich structures with Kevlar reinforcement produced curves with marginal differences in strain-to-failure and UCS when compared to CF structures. Catastrophic failure points were exemplified by the Kevlar-reinforced structures, annotated in Figure 4.31. The catastrophic failure points, annotated by the circles (also seen for Figure 4.32 and Figure 4.33), are believed to be related to the core under-going its complex failure mechanisms, such as crack propagations developing at the nodes of individual cells, resulting in catastrophic failure (Ingrole et al., 2016; Xie et al., 2020). This is encouraged by damage that initiated during post processing and the build orientation of the FRPC structures. A comparison between CF and Kevlar fibres show, superior UCS was seen by the CF-QI structure in Figure 4.31. It revealed a 63.6% increase in UCS in contrast to the Kev.-QI structure. However, the CF-QI and the Kev.-QI structures saw a 27.15% and 135.3% lower UCS, respectively, when compared to the HC-no fibre structure, as shown in Figure 4.31. Moreover, the Kev.-2CUD revealed a 34.8% lower strain-to-failure when compared to the CF-2CUD structure, and a 43.5% lower strain-to-failure compared to the HC-no fibre structure. Overall, major variance of results was noted when FRPCs were compared to unreinforced structures, as seen in Figure 4.31.

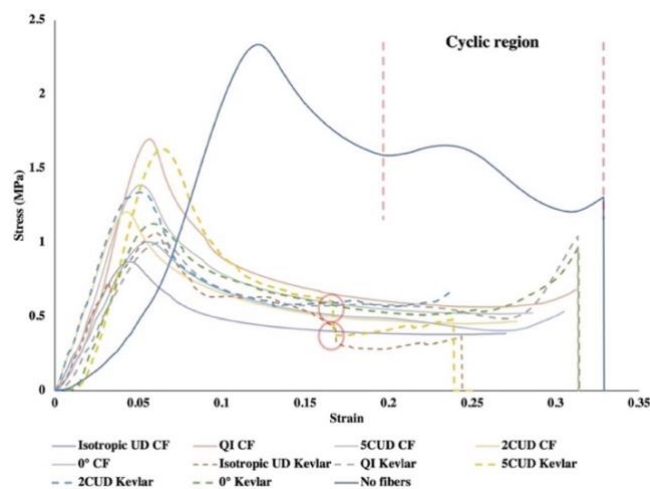


Figure 4.31 Stress-strain graph of the honeycomb sandwich structures reinforced with CF compared to those reinforced with Kevlar

4.9.2 Fibre-Reinforced and Unreinforced Re-entrant Structures

Figure 4.32 shows that the unreinforced re-entrant sandwich structure produced superior results in comparison to its fibre-reinforced relatives. This is in relation to its UCS and strain at maximum load, where it exhibited values of 2.51 MPa and 0.08, respectively. It revealed a 41.83% higher UCS than the HYB no fibres structure. However, it presented a strain-to-failure of 0.173, which was significantly lower than the fibre-reinforced structures. Nevertheless, Figure 4.32 shows that the fibre reinforced re-entrant structures reached plastic deformation earlier than the RE-no fibre structure, owing to a weaker stress response and weaker load carrying ability of the fibre-reinforced structures. Once again, the Kevlar fibre-reinforced structures indicated catastrophic failure points on the curves, as seen annotated in Figure 4.32. The bulk of the FRPC structures showed that they yielded around similar strain values of 0.03-0.058. For example, the Kevlar reinforced structures showed that the isotropic UD, 2CUD, and 5CUD structures failed before a strain of 0.05. A comparison between Kevlar and CF fibres reveals that the isotropic UD-CF structure was 20.7% higher in UCS in comparison to the isotropic UD-Kev, and it had a 23.6% higher strain-to-failure. On the contrary, when the isotropic UD-Kev. structure was compared to the RE-no fibre structure it showed, a 112.4% and 56.9% decrease in UCS and strain-to-failure, respectively. Overall, the fibre-reinforced structures showed lower UCS values, a reduction in cyclic response, and lower strain-to-failure values in comparison to the RE-no fibre structure.

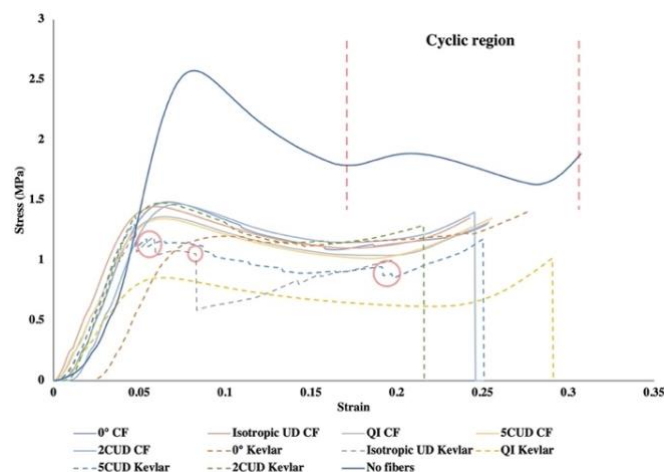


Figure 4.32 Stress-strain graph of the re-entrant sandwich structures reinforced with CF compared to those reinforced with Kevlar

4.9.3 Fibre-Reinforced and Unreinforced Hybrid Structures

The HYB-no fibres structure produced a higher UCS than that experienced by the fibre-reinforced structures, with a value of 1.46 MPa and a strain at maximum load of 0.11. Consequently, it revealed the lowest UCS out of the HC and RE structures. However, it experienced a strain-to-failure of 0.204 which was 1.96% and 15.20% greater than the HC and RE structures, respectively. This could be related to its bending deformation mechanisms, resulting in an absence of a large cyclic region and more of a conventional elastic-plastic collapse, allowing it to sustain the applied compressive load for longer. Moreover, the HYB-no fibres had a 50.2% greater UCS, and a 17.6% greater strain-to-failure when compared to the QI-CF structure as seen in . On the contrary, when Kevlar and CF fibres were compared, the QI-CF-reinforced structure exhibited a 4.2% and 28% greater UCS and strain-to-failure, respectively, in comparison to the QI-Kevlar reinforced structure. Moreover, the HYB structures, with Kevlar reinforcement, displayed catastrophic failure points annotated in Figure 4.33. These failure points resulted in a minor reduction of experienced stress and strain when compared to CF-reinforced structures. In conclusion, the above values indicate that the fibre-reinforced structures had no cyclic behaviour but behaved in a conventional manner regarding its stress-strain curve, and thus indicating an elastic region, plastic deformation region, and eventually cell densification/failure.

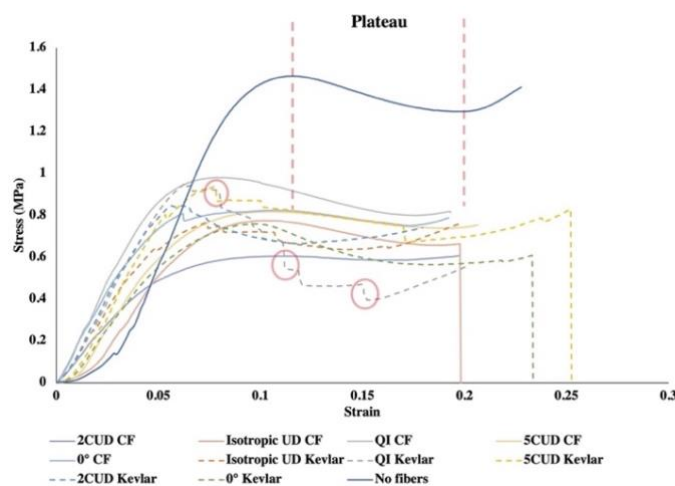


Figure 4.33 Stress-strain graph of the hybrid sandwich structures reinforced with CF compared to those reinforced with Kevlar

4.10 Residual Stress-Strain Comparisons of 3D Printed Fibre-Reinforced and Unreinforced Sandwich Structures

It is known that laminates utilised for the face sheets of sandwich structures suffer significantly from low-velocity impact scenarios, resulting in fibre failure modes (Bonavolontà et al., 2007; Ranjit et al., 2016). Therefore, this section reveals stress-strain graphs of the sandwich structures after low-velocity impact. The objective was to evaluate if the fibre-reinforcements aided the 3D printed sandwich structure cores in resisting impact damage from a drop-weight test. An additional objective was to investigate if the auxetic re-entrant core influenced the stress-strain response of the impacted sandwich structures. The stress-strain graphs of all the sandwich structures impacted at 2J are shown in Figures 4.34-4.36.

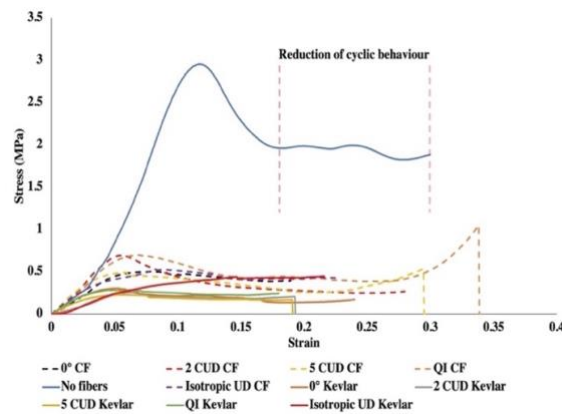


Figure 4.34 Stress-strain graph of the honeycomb sandwich structure with CF, Kevlar, or no fibre reinforcement after 2J of impact

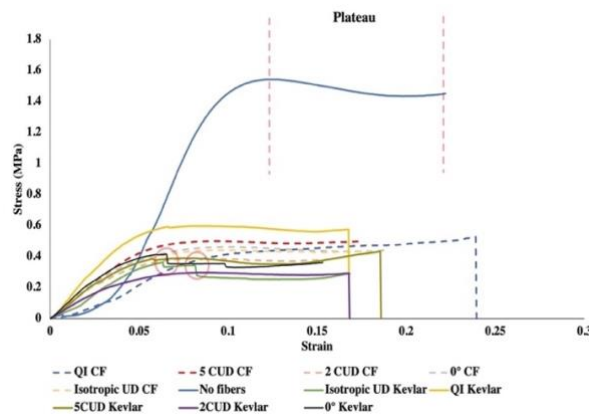


Figure 4.35 Stress-strain graph of the hybrid sandwich structure with CF, Kevlar, or no fibre reinforcement after 2J of impact

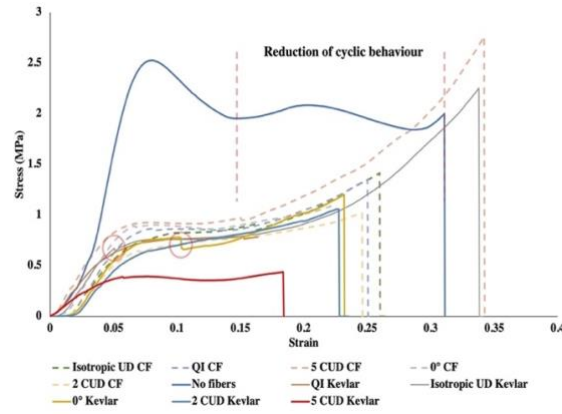


Figure 4.36 Stress-strain graph of the re-entrant sandwich structure with CF, Kevlar, or no fibre reinforcement after 2J of impact

4.10.1 Residual Stress-Strain Properties of Unreinforced Sandwich Structures

All unreinforced structures that experienced an impact in Figures 4.34-4.36, indicated a reduction in their cyclic behaviours, annotated by the dotted lines in contrast to their unimpacted relatives in Figures 4.31-4.33. Figure 4.34 reveals that the impacted HC-no fibres exhibited the greatest UCS, strain at maximum load, and strain-to-failure, obtaining a value of 2.95 MPa, 0.118, and 0.176, respectively. Thus, it was 82.2% greater in UCS than the bulk of the sandwich structures with fibre-reinforcement. Additionally, it exhibited a 26.6% higher UCS than the unimpacted neat honeycomb structure in Figure 4.31. However, the impacted HC structure experienced a 12% reduction in strain-to-failure after being impacted. This revealed that low-velocity impact could cause damage to occur in the core and fibres. Moreover, Figure 4.34 exhibits that the HC-no fibres structure remained consistent in load displacement upon reaching its cyclic region, remaining approximately at 2 MPa and reducing to 1.82 MPa in the reduced cyclic zone. This revealed the successful structural integrity of the honeycomb sandwich structure even after low-velocity impact. On the contrary, the HYB-no fibre-IMP structure in Figure 4.35 produced a UCS of 1.54 MPa, a strain at maximum load of 0.119, and a strain-to-failure of 0.201, indicating that it reduced in strain-to-failure by 1.47% after being impacted but it experienced a 5.19% increase in UCS. Furthermore, it produced a similar stress-strain curve to its unimpacted relative in Figure 4.33, expressing only a plateau stage and no cyclic region. However, it did indicate a reduction in its cyclic behaviour after being impacted. The RE-no fibres-IMP showed a 1.98% reduction in UCS after impact, indicating a drop in performance and a reduction in UCS from damage imposed

by impact as seen in Figure 4.36. Additionally, the RE-no fibre-IMP structure had a UCS of 2.57 MPa, strain at maximum load of 0.082, and strain-to-failure of 0.149, indicating a 13.87% decrease in strain-to-failure after being impacted. Consequently, it revealed a similar behaviour in load displacement to that of its unimpacted relative in Figure 4.32, expressing only minor reductions in its compressive behaviour. Similar to the hybrid core, it showed a reduction in cyclic behaviour.

The increase in UCS demonstrated by both the HC and HYB structures can be because of the absence of fibres, resulting in a less complex failure of the structures since only the matrix can fail from impact. Therefore, low-velocity impact initiates initial matrix failure of the face sheets and cells, which once the structure is compression tested, results in a curve with less abrupt failure points in its cyclic region or plastic deformation region as failure has already transpired. As a result of the initial failure of the matrix and core, strain-to-failure occurs earlier since the sandwich structures have reduced in their load carrying abilities. Conversely, the re-entrant sandwich structure appeared to reduce marginally in its UCS capability after impact, evident in Figure 4.36. As a result, the matrix damage was more prominent, and thus had a larger influence on the re-entrant sandwich structure and hindered its ability to perform with optimum auxetic capabilities; hence, the reduction in the cyclic region, as revealed in Figure 4.36.

4.10.2 Residual Stress-Strain Properties of Reinforced Sandwich Structures

Figure 4.34 shows that the HC reinforced structures UCS values diminish as far as 0.24 MPa, expressing an 85% reduction after low-velocity impact. The fibre-reinforced HYB structures diminished to a UCS value of 0.25 MPa, exhibiting a 72.22% reduction after low-velocity impact, as seen in Figure 4.35. Furthermore, the fibre-reinforced RE structures UCS value diminished to 0.38 MPa, indicating a 72.86% reduction in UCS after low-velocity impact, as seen in Figure 4.36. Consequently, the fibre-reinforced structures revealed susceptibility to fibre failure modes; hence, the reduction in UCS after impact and under uniaxial compression.

Figure 4.34 revealed that for the bulk of the fibre-reinforced sandwich structures, a notable lack of catastrophic failure points was witnessed. The reduction of catastrophic failure points was governed by the failure of the core structures and crack propagations that occurred during impact (Zhang et al., 2017). Therefore, it results in less strut and global core failure whilst undergoing compression, and thus representing a smoother

stress-strain curve. However, the structures that did indicate catastrophic failure points, namely, the HYB-5CUD-Kev, HYB-0°-Kev (Figure 4.35), the RE-0°-Kev and RE-isotropic-UD (Figure 4.36), could have been due to undamaged cells after low-velocity impact, and thus the structures experience localised catastrophic failure during CAI. There is a significant amount of complexity that takes place during impact, where subtle amounts of pre-buckling of cell walls, fibre breakage, matrix cracking, fibre pull-out, and face sheet wrinkling, can all transpire within the period of impact, and thus can affect the stress-strain response (Zhang et al., 2017).

4.11 Compressive Properties and Energy Absorption

4.11.1 Compressive Modulus Comparison of Fibre-Reinforced and Unreinforced Structures

Figures 4.37-4.39 exhibit the compressive properties and energy absorbed of CF and Kevlar fibre reinforced structures, and unreinforced structures during compression. The reinforced structures experienced superior compressive modulus, as shown in Figure 4.37, in comparison to unreinforced structures, but no large variance in compressive modulus between fibre type and fibre lay-ups was noted. The unreinforced structures in Figure 4.37 indicated that the re-entrant structure experienced a similar compressive modulus (26.89 MPa) to that of QI (26.71 MPa), and 0° (26.91 MPa) CF structures. This indicated the possibility of achieving similar or greater compressive modulus than reinforced structures without the need for fibre reinforcement.

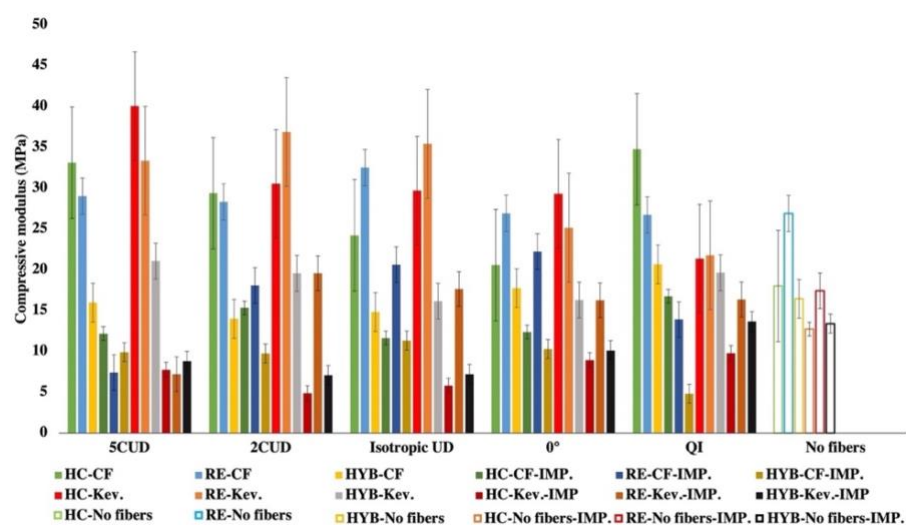


Figure 4.37 Compressive modulus chart comparing all impacted and unimpacted fibre-reinforced sandwich structures to unreinforced sandwich structures

The HYB-Kev-5CUD fibre orientation produced the highest modulus (21.06 MPa) out of its fibre-reinforced relatives. As a result, it was 28.1% greater in compressive modulus compared to the HYB-no fibres (16.44 MPa). Furthermore, the HC-no fibres structure exhibited a compressive modulus of 18.01 MPa, indicating no superiority in contrast to its fibre-reinforced relatives. The greatest compressive modulus out of the fibre-reinforced HC structures was the HC-Kev-5CUD (40.04 MPa), exhibiting superiority in comparison to every sandwich structure in Figure 4.37. Consequently, it experienced a 55.02% greater compressive modulus than that of the HC-no fibres. Lastly, the HC-no fibres produced a 33.02% lower compressive modulus than the RE-no fibres structure and an 8.77% greater compressive modulus than the HYB-no fibres.

4.11.2 Residual Compressive Modulus Comparison of Unreinforced and Fibre-Reinforced Structures

The residual properties of all the sandwich structures with fibre reinforcement and without were compared in Tables 4.1-4.3. The values in the tables are the values for the structures seen in the charts in Figures 4.37-4.39. Furthermore, an overall average was calculated to evaluate which structures showed improved residual properties, as tabulated in Table 4.4.

The unreinforced structures matched and at times surpassed the compressive modulus of the fibre-reinforced structures, as seen in Figure 4.37. The bulk of the fibre-reinforced structures that were impacted did not surpass unreinforced structures because damage was inflicted to the fibres, matrix, and core from low-velocity impact (Ashby, 1993). Consequently, some sandwich structures that significantly diminished in compressive modulus was the RE-0°-CF structure in Figure 4.37, reducing by 17.4% after impact. This was similarly revealed by the HC-5CUD-Kev structure in Figure 4.37, showing a significant reduction of 80.7% in compressive modulus after being impacted. Moreover, the compressive stiffness of the HYB-5CUD-Kev structure was reduced by 58.21% after impact.

As a result of the absence of fibre failure modes present in the unreinforced sandwich structures and their print build direction, a superiority in compressive modulus was seen. Consequently, the RE-no fibres-IMP structure in Figure 4.37 surpassed all RE-QI-IMP fibre orientations for both CF and Kevlar fibre types, by 20.12% and 6.2%, respectively. It also surpassed the RE-0°-Kev-IMP structure by 6.67%. Furthermore, it

provided better residual compressive modulus than the RE-5CUD-Kev-IMP and RE-5CUD-CF-IMP structures, surpassing the reinforced structures by 58.59% and 57.39%, respectively. On the contrary, the HC-no fibres-IMP structure in Figure 4.37 surpassed the HC-QI-Kev-IMP fibre orientation by 30.1%. It also surpassed both the HC-0°-Kev-IMP and HC-0°-CF-IMP structures by 42.6% and 2.91%, respectively. Furthermore, it showed a 29.87% and 9.3% increase in contrast to the HC-isotropic UD-Kev-IMP and HC-isotropic UD-CF-IMP structures, respectively. In addition, it demonstrated a 64.3% and 4.51% greater compressive modulus in contrast to the HC-5CUD-Kev-IMP and HC-5CUD-CF-IMP structures, respectively. The HYB-no fibres-IMP structure in Figure 4.37 surpassed the HYB-QI-CF-IMP fibre orientation by 63.96%. It also surpassed both the HYB-0°-Kev-IMP and HYB-0°-CF-IMP structures by 32.7% and 30.2%, respectively. Furthermore, it had an 86.1% and 18.4% increase in comparison to the HYB-isotropic UD-Kev-IMP and HYB-isotropic UD-CF-IMP structures, respectively. In addition, it was 88.9% and 37.4% greater in compressive modulus in comparison to the HYB-2CUD-Kev-IMP and HYB-2CUD-CF-IMP structures, respectively. A 52.2% and 35.2% increase was seen when compared to the HYB-5CUD-Kev-IMP and HYB-5CUD-CF-IMP structures.

Table 4.1 Compressive modulus values of all core types, fibre types, and fibre orientations

	Compressive modulus (MPa)						Core types
	5CUD	2CUD	UD	0°	QI	No fibres	
Unimpacted CF structures	29.01	28.31	32.50	26.91	26.71	26.89	Re-entrant
	15.97	13.98	14.81	17.752	20.66	16.43	Hybrid
	33.13	29.37	24.22	20.56	34.77	18.01	Honeycomb
Impacted CF structures	7.43	18.08	20.62	22.24	13.91	17.41	Re-entrant
	9.92	9.75	11.32	10.29	13.40	4.83	Hybrid
	12.18	15.32	11.64	12.37	12.72	16.75	Honeycomb
Unimpacted Kevlar structures	33.35	36.86	35.42	25.15	21.77		Re-entrant
	21.07	19.55	16.15	16.28	19.64		Hybrid
	40.05	30.53	29.69	29.30	21.36		Honeycomb
Impacted Kevlar structures	7.21	19.56	17.63	16.25	16.35		Re-entrant
	8.80	7.10	7.21	10.11	13.67		Hybrid
	7.75	4.87	5.79	8.92	9.79		Honeycomb

Considering only the unreinforced structures in Figure 4.37, the greatest residual properties was exhibited by the re-entrant sandwich structure, showing a compressive modulus of 17 MPa. The honeycomb and hybrid exhibited a compressive modulus of 12.72 MPa and 13.40 MPa, respectively, thus the re-entrant obtained a 36.9% and 29.9% greater compressive modulus than the honeycomb and hybrid sandwich structures, respectively.

Table 4.2 Compressive strength values of all core types, fibre types, and fibre orientations

Compressive strength (MPa)							Core types
	5CUD	2CUD	UD	0°	QI	No fibres	
Unimpacted CF structures	1.42	1.38	1.48	1.41	1.32	2.59	Re-entrant
	0.78	0.66	0.76	0.80	0.96	1.47	Hybrid
	1.38	1.20	0.89	1.02	1.64	2.51	Honeycomb
Impacted CF structures	0.94	1.02	0.95	1.09	0.85	2.21	Re-entrant
	0.59	0.46	0.30	0.15	0.40	1.32	Hybrid
	0.38	0.69	0.50	0.54	0.76	2.45	Honeycomb
Unimpacted Kevlar structures	1.28	1.50	1.33	1.28	0.90		Re-entrant
	0.94	0.98	0.74	0.80	0.92		Hybrid
	1.62	1.31	1.47	1.13	1.02		Honeycomb
Impacted Kevlar structures	0.38	1.07	0.81	1.37	0.74		Re-entrant
	0.43	0.33	0.36	0.39	0.58		Hybrid
	0.25	0.24	0.41	0.28	0.31		Honeycomb

Table 4.3 Energy absorbed values of all core types, fibre types, and fibre orientations

Energy absorbed (J/m ³)							Core types
	5CUD	2CUD	UD	0°	QI	No fibres	
Unimpacted structures	0.042	0.053	0.045	0.044	0.044	0.041	Re-entrant
	0.039	0.033	0.037	0.040	0.036	0.081	Hybrid
	0.034	0.026	0.020	0.030	0.042	0.157	Honeycomb
Impacted structures	0.039	0.039	0.040	0.036	0.034	0.104	Re-entrant
	0.022	0.017	0.019	0.024	0.023	0.069	Hybrid
	0.011	0.017	0.020	0.018	0.025	0.138	Honeycomb
Unimpacted Kevlar structures	0.031	0.050	0.030	0.048	0.022		Re-entrant
	0.031	0.025	0.027	0.034	0.027		Hybrid
	0.055	0.033	0.039	0.034	0.030		Honeycomb
Impacted Kevlar structures	0.015	0.047	0.028	0.046	0.034		Re-entrant
	0.012	0.016	0.011	0.016	0.021		Hybrid
	0.006	0.006	0.022	0.007	0.006		Honeycomb

Table 4.4 Overall average difference in compressive properties and energy absorbed under compression of FRPC structures

Compressive modulus (MPa)			Compressive Strength (MPa)		Energy absorbed (J/m ³)	
Carbon fibre	Re-entrant	12.24	Re-entrant	0.43	Re-entrant	0.008
	Hybrid	5.70	Hybrid	0.41	Hybrid	0.016
	Honeycomb	15.57	Honeycomb	0.65	Honeycomb	0.01
Kevlar	Re-entrant	15.11	Re-entrant	0.41	Re-entrant	0.002
	Hybrid	9.16	Hybrid	0.46	Hybrid	0.014
	Honeycomb	22.76	Honeycomb	1.00	Honeycomb	0.029
No fibres	Re-entrant	9.48	Re-entrant	0.21	Re-entrant	0.011
	Hybrid	11.61	Hybrid	0.09	Hybrid	0.012
	Honeycomb	1.26	Honeycomb	0.25	Honeycomb	0.019

4.11.3 Compressive Strength Comparison of Fibre-Reinforced and Unreinforced Structures

Figure 4.38 shows that the bulk of the unreinforced structures had higher compressive strengths than the fibre-reinforced structures. The compressive strength values for the RE, HYB, and HC-no fibres structures were 2.58 MPa, 1.47 MPa, and 2.51 MPa, respectively. It was distinguished that the HC-no fibres were 55.9% greater in compressive strength compared to the highest fibre-reinforced structure, HC-Kev-5CUD. Subsequently, the RE-no fibres structure was 72% greater than the RE-Kev-2CUD, and the HYB-no fibres was 50% greater than its HYB-Kev-2CUD relative. Interestingly, Figure 4.38 exhibited that the bulk of Kevlar reinforced structures experienced greater enhancements in compressive strength in contrast to CF-reinforced structures.

4.11.4 Residual Compressive Strength Comparison of Unreinforced and Fibre-Reinforced Structures

Figure 4.38 shows that the unreinforced sandwich structures demonstrated superior residual compressive strength after low-velocity impact in comparison to their relatives with fibre-reinforcement. A significant loss of strength was recorded for the fibre-reinforced structures, indicating the presence of microscopic failure modes and the presence of flaws within the fibres because of damage from impact. It could also be related to defects as discussed in section 4.12. Consequently, this can negatively affect their performance under compression (Beharic et al., 2018). Figure 4.38 shows the RE-no fibres-IMP produced a value of 2.21 MPa, the HYB-no fibres-IMP a value of 1.32

MPa, and HC-no fibres-IMP resulted in 2.45 MPa. As such, the HC-no fibre-IMP structure experienced a 68.98% greater compressive strength in comparison to the fibre-reinforced HC-QI-CF-IMP structure that indicated superiority, with a result of 0.76 MPa. The highest fibre-reinforced impacted structure for the RE core type was RE-0°-Kev-IMP with a compressive strength of 1.37 MPa; however, the RE-no fibres-IMP structure produced a value that was 38.00% greater. Finally, the HYB-5CUD-CF-IMP obtained the greatest compressive strength out of the fibre-reinforced hybrid structures, with a value of 0.59 MPa, but the HYB-no fibres was 55.30% greater in compressive strength.

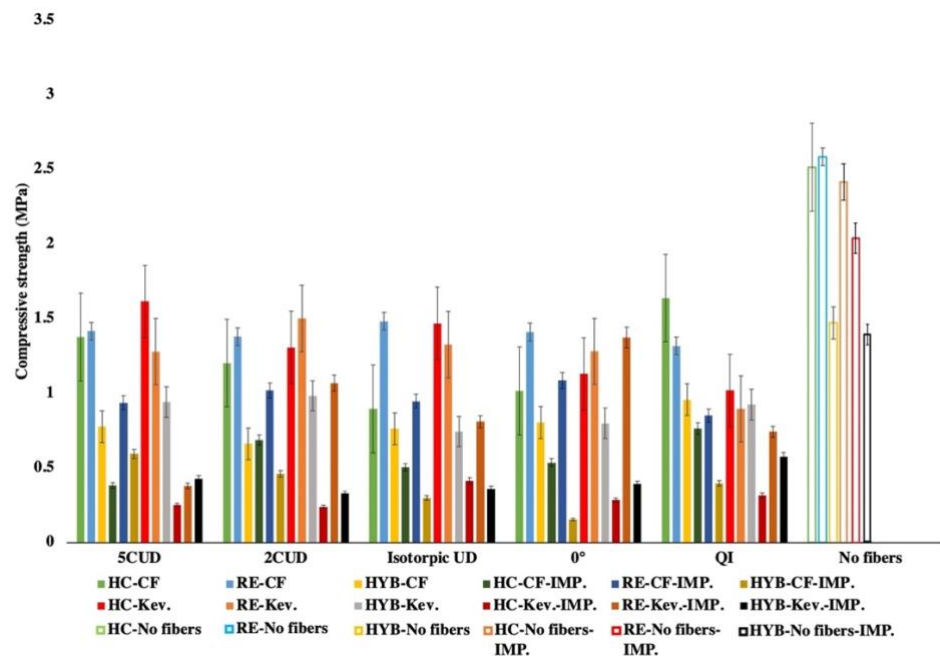


Figure 4.38 Compressive strength chart comparing all impacted and unimpacted fibre-reinforced sandwich structures to unreinforced sandwich structures

After impact, the HC-no fibres experienced a 2.39% reduction in compressive strength, the RE-no fibres experienced a 14.34% reduction in compressive strength, and the HYB-no fibres experienced a 10.20% reduction in compressive strength. It can be assumed that part strength and structural integrity were compromised because of matrix cracking, face sheet indentation, and cell buckling or failure (Ruan et al., 2003; Xie et al., 2020).

Overall, the reinforced re-entrant core structures revealed superior residual compressive strength compared to the other core topologies, as seen in Figure 4.38. For example, the highest overall compressive strength was demonstrated by the RE-0°-Kev-IMP, obtaining a value of 1.37 MPa. It surpassed the HYB and HC cores with the same

fibre orientation by 56.9% and 44.5%, respectively. At times, reinforced structures might demonstrate greater compressive strengths after experiencing low-velocity, i.e., the RE-0°-Kev (7.0% increase). This is believed to be related to print quality. Since this was not a common occurrence for impacted structures to surpass unimpacted structures, it can be assumed that after post processing, the unimpacted subjects might have suffered from greater damage during support removal. In addition, there could have been more defects present, such as voids, reducing their compressive strength further (Kabir et al., 2020). This is discussed further in section 4.12.

4.11.5 Energy Absorption Comparison of Fibre-Reinforced and Unreinforced Structures

Figure 4.39 shows the energy absorbed chart for the sandwich structures. The unreinforced structures demonstrated greater energy absorption capabilities during compression in comparison to the reinforced structures. The RE-no fibres obtained a value of 0.23 J/m⁻³, the HYB-no fibres structure obtained a value of 0.16 J/m⁻³ and the HC-no fibres a value of 0.31 J/m⁻³. Therefore, the HC-no fibres absorbed 28.81% more energy than the RE-no fibres and 48.39% more energy than the HYB-no fibres structure, demonstrating its superiority. Conversely, the cores that obtained the highest energy absorption with fibre-reinforcement were, HC-Kev-5CUD with a value of 0.109 J/m⁻³, RE-CF-2CUD with a value of 0.106 J/m⁻³, and HYB-CF-0° with a value of 0.08 J/m⁻³. As a result, the HC-no fibres absorbed 64.84% more energy in comparison to HC-Kev-5CUD, the RE-no fibres structure absorbed 65.81% more energy in comparison to RE-CF-2CUD, and the HYB-no fibres structure absorbed 74.19% more energy in comparison to HYB-CF-0°.

4.11.6 Residual Energy Absorption Comparison of Unreinforced and Fibre-Reinforced Structures

As seen in Figure 4.39, all unreinforced sandwich structures presented the highest absorption of energy after low-velocity impact when compared to reinforced structures. Figure 4.39 shows the highest residual energy absorbed after impact was demonstrated by the HC-no fibres, exhibiting a value of 0.157 J/m⁻³. It was followed by the RE-no fibres structure with a value of 0.115 J/m⁻³, and lastly the HYB-no fibre structure with a value of 0.081 J/m⁻³. Therefore, the HC-no fibres-IMP was 36.52% and 93.82% greater than RE-no fibres-IMP and the HYB-no fibres-IMP, respectively, revealing the honeycombs'

superiority. Nevertheless, the unreinforced structures reduced in their energy absorbing capabilities after low-velocity impact, as signified in Figure 4.39. It was revealed that the HC-no fibres absorbed 12.12% less energy after low-velocity impact, the RE-no fibres absorbed 10.43% less energy after low-velocity impact, and the HYB-no fibres absorbed 14.81% less energy after low-velocity impact. As a result, the re-entrant core lost less energy after low-velocity impact indicating a more efficient energy dissipation and stress distribution system because of its negative Poisson's ratio and localised material densification during impact (Yang et al., 2018). Furthermore, when comparing the unreinforced structures to the reinforced structures, the RE-no fibres-IMP absorbed 54.76% more energy in comparison to the RE-2CUD-Kev-IMP structure which was the highest impacted reinforced structure, as seen in Figure 4.39.

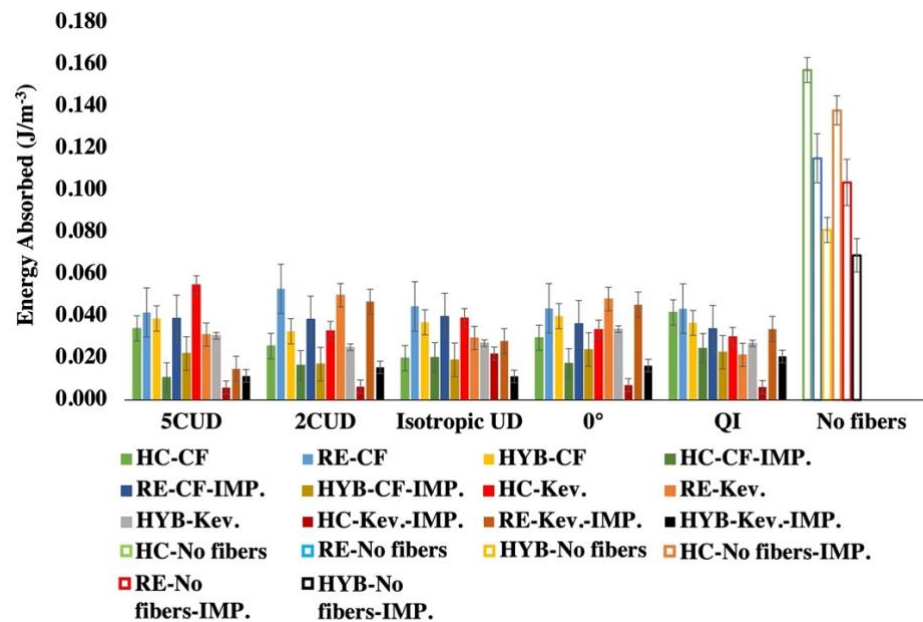


Figure 4.39 Energy absorbed chart comparing all impacted and unimpacted fibre-reinforced sandwich structures to unreinforced sandwich structures

Additionally, the HC-no fibres-IMP absorbed 11% more energy in comparison to the HC-QI-CF-IMP, which was the highest impacted fibre-reinforced structure with a honeycomb core. Subsequently, the HYB-no fibres-IMP absorbed 65.11% more energy in comparison to the HYB-0°-CF-IMP structure, resulting in the highest impacted fibre-reinforced structure with a hybrid core. This revealed a significant difference in energy absorption capabilities and showcases the superiority of the unreinforced structures' energy absorption capabilities.

Overall, the reinforced re-entrant structures revealed superior residual properties out of the other core topologies, in Figure 4.39. For example, the RE-2CUD-Kev-IMP structure, absorbed 0.046 J/m^{-3} of energy under compression. As a result, it absorbed 47.33% and 48.66% more energy than the HC-QI-CF-IMP (0.025 J/m^{-3}) and HYB-0°-CF-IMP structures (0.024 J/m^{-3}), respectively, which were the greatest in residual properties for their core types. This indicated that in both instances, for compressive strength (Figure 4.38) and energy absorption (Figure 4.39), that fibre type and fibre lay-up was irrelevant in relation to providing the structure with greater energy absorption capabilities, as it was superior irrespective of fibre placement and fibre type. Therefore, the re-entrant core topology successfully facilitated the absorption and dissipation of residual energy absorption (Zhou et al., 2017).

4.11.7 Plateau Regions and Softening Stages of Stress-Strain Curves

The greater strength and energy absorption capabilities exhibited for the unreinforced sandwich structures as seen in Figures 4.38-4.39 can arise from the size of the plateau zone during compression (Beharic et al., 2018), as illustrated in Figure 4.40. Before encountering the plateau stage, the ‘softening stage’ initiates, as shown in Figure 4.40. The softening stage is the point at which a considerable reduction of stress can be observed on the curve after initial failure/plastic deformation. The unreinforced impacted structures indicated more consistent plateau stages, maintaining their stress levels, which was illustrated by the HC and the RE structures in Figure 4.40. It was also revealed that the unreinforced HC and RE structures showed a greater plateau stage in comparison to the fibre-reinforced structures and the HYB-no fibres structures. The HYB-no fibres-IMP in Figure 4.40, showed a smaller softening stage and less of a plateau stage, resulting in a lower compressive strength (Figure 4.38) and energy absorbed (Figure 4.39). This can be because of the deformation mechanisms of the HYB core lattice. Conversely, the larger plateau stages seen for the RE and HC could be because of their deformation mechanisms containing bending and stretch dominant deformation characteristics, respectively (Hou et al., 2018). It can also be from the significant ductility of nylon and its considerable elastic recovery. Its extensive elastic recovery upon impact is a characteristic that prepares the nylon sandwich structures for impact, aiding it from catastrophic damage, and thus undergoes a large amount of deformation before failure is reached (Beharic et al., 2018). Nonetheless, if the impact energy of 2J was equal to the penetration threshold of the sandwich composites, then a larger reduction in the plateau region occurs alongside a

decrease in compressive strength and energy absorbed (Amir et al., 2020). Since 2J did not surpass the penetration threshold of the unreinforced structures and reinforced structures, it resulted in an “enhanced” damaged tolerance (Beharic et al., 2018). On the other hand, because of the complex failure modes present in the fibres and the core after low-velocity impact, the plateau stages were affected, resulting in infrequent stress occurrences in the plateau region, and thus dissimilar behaviours on the curve in comparison to the unreinforced structures (Ahmad et al., 2015).

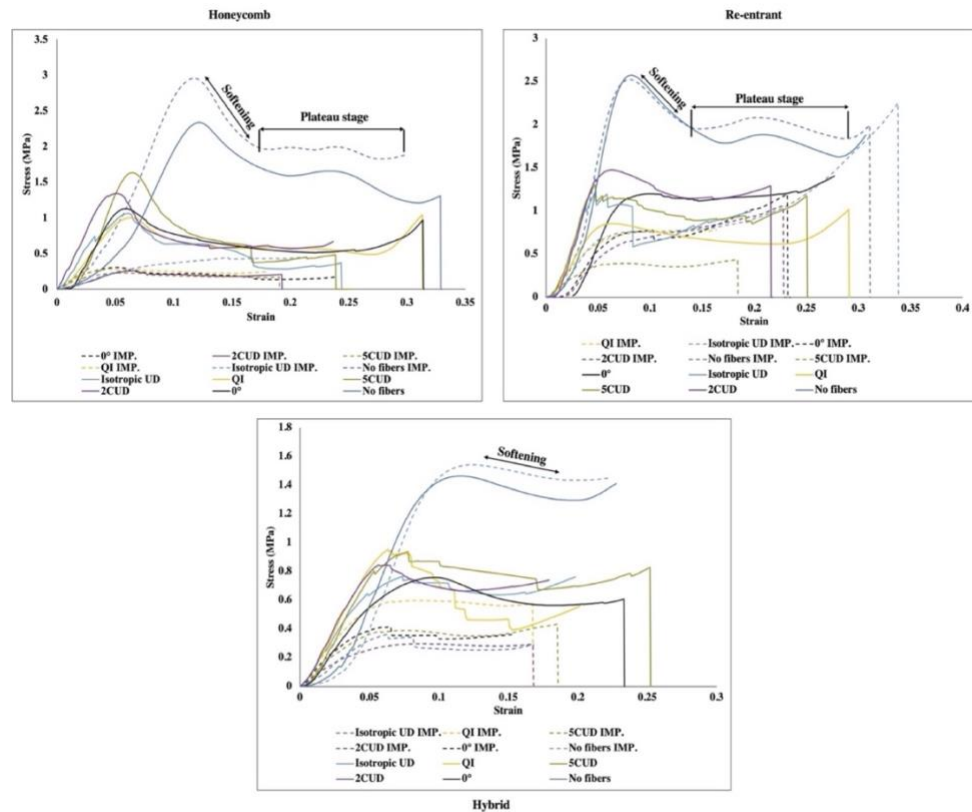


Figure 4.40 Stress-strain plots of all Kevlar reinforced sandwich structures with all core types showing their softening stages and plateau regions

4.11.8 Concluding Remarks for Compressive Properties and Stress-Strain Graphs

The charts as seen in Figures 4.37-4.39, revealed that there was successful correlation to the compressive properties demonstrated by Ingrole et al. (2017) in the literature review as seen in section 2.12.1, and in Table 2.4 in Chapter 2 when compared to the compressive properties seen for the results in Tables 4.1-4.4. However, the fibre-reinforced sandwich structure energy absorption capabilities were far more inferior to their work, and thus, more correlation was noted with unreinforced sandwich structures.

Figures 4.37-4.39, exhibited that the unimpacted fibre-reinforced structures showed no superiority in compressive strength or energy absorbed, but rather vastly superior properties were witnessed for the no fibre structures. For fibre-reinforced structures that were not impacted, there was a lack of discrepancy between fibre orientations, made evident in the charts as seen in Figures 4.37-4.39. More of a difference between fibre types was demonstrated, however, not enough to enhance or alter the compressive properties. Therefore, for unimpacted sandwich structures, the fibres included in the face sheets revealed that they had no influence over the outcome of the compressive properties or the behaviour of the stress-strain curves, as seen in Figures 4.31-4.33. Instead, the core topology showed the greatest contribution to the outcome of the compressive properties and the outcome of stress-strain curves.

Figure 3.23 in Chapter 3 exhibited the orientation of the face sheets under uniaxial compression, revealing that the face sheets play no discernible role in the test performance. The face sheet is being compressed out-of-plane, with fibres orientated perpendicular to the force direction. Therefore, due to the loading nature of the face sheets, they have no ability to under-go any flexural stress, inhibiting it from bending, and thus inhibiting the fibres from bending. As a result, the fibres and face sheet experience no ability to distribute the experienced force to aid the core, and thus, are irrelevant in the compression test. Contrarily, the in-plane direction of the core means it will bear all of the applied force, and thus the compressive properties are reliant on the core topology, its deformation mechanisms, and the matrix material properties. Since fibres are embedded into the face sheets only and not within the cell structures, there is overall a higher percentage of plastic volume. Consequently, the 3D printed sandwich structures will be mostly governed by the properties of the matrix (Kuchipudi, 2017). It was made evident in Figures 4.31-4.33, that all sandwich structures reduced significantly in compressive properties after low-velocity impact. However, when fibre orientations were compared, there was not enough discrepancy to verify that fibre orientation was able to enhance the compressive properties after low-velocity impact. Instead, fibre failure modes influenced the compressive properties significantly more, and instead it is clearer to note that fibre-reinforced structures significantly diminished in their compressive properties for this reason.

4.12 Unreinforced and Fibre-Reinforced 3D Printing Defects and Their Effects

4.12.1 Build Orientation

Figures 4.37-4.39 revealed that the compressive properties of the unreinforced sandwich structures were far superior to the reinforced structures. This is believed to be because unreinforced sandwich structures were printed with superior build quality in contrast to fibre-reinforced structures. This was related to the build orientation, absence of fibres, and the orientation of rasters. Rasters have a defined width and thickness which is an individual printed layer that makes up a 3D printed part, as seen Figure 4.41. The raster angle is the angle of the raster tool path deposited with respect to the x-axis of the build plate (Masood, 2014).

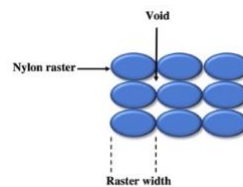


Figure 4.41 Illustration of a raster deposition pattern, showing the raster width, the individual nylon rasters, and void location

Since the fibres do not enhance the compressive properties of the sandwich structures with core topology in the in-plane direction and the face sheets in the out-of-plane orientation (Figure 3.23, Chapter 3), it is therefore necessary to consider the effects of the raster orientations, because it is evident that build direction has a clear correlation with compressive properties (Ahn et al., 2002; Dou et al., 2022). Table 3.4, as mentioned in Chapter 3, revealed the difference in build orientation between reinforced and unreinforced structures. As a result of these orientations there is a difference in raster orientations. This was similar to the findings in the literature review by Basurto-Vázquez et al. (2021) in section 2.12.1. Figure 4.42 reveals these distinctions, and it indicates that the cells for the FRPC structures were composed of horizontal parallel fused rasters (red lines), orientated perpendicular to the compression force. The FRPC raster orientation suggests that there is significant reliance on the inter-layer bonding strength. This is because large amounts of stress are placed on the interface between raster layers when the cells undergo their natural deformation mechanisms. In this orientation layers are susceptible to delamination under compression (Basurto-Vázquez et al., 2021), and particularly when removing supports. This was illustrative of the charts seen in Figures

4.37-4.39, revealing that all FRPC structures obtained inferior compressive properties in comparison to the unreinforced structures from the reliance of interlayer bonding, and other factors that will be discussed in the following section. On the contrary, since unreinforced structures were printed flat as seen in Figure 4.42, no overhanging of cell elements was involved, meaning there was no support requirement, and thus enhanced structural integrity and bonding between rasters. Subsequently, the unreinforced structures showed rasters (red) were fused in a vertical and parallel orientation in relation to the compression force. As a result of the axial orientation, cells are able to rely on the matrix properties, and thus cells are able to successfully deform in their natural manner, and not left to rely on the inter-layer bonding strength alone (Ashtankar et al., 2013). This raster orientation permits the cells to behave with more ductility and a higher flexural strength, accredited to its direction under compression (Basurto-Vázquez et al., 2021). Thus, structures with this build direction will collapse in a progressive manner, hence the significantly greater cyclic behaviour, as seen in the stress-strain graphs in Figures 4.31-4.36.

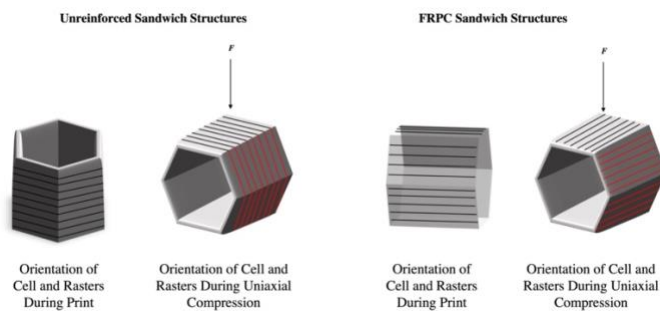


Figure 4.42 Raster orientation comparisons under uniaxial compression between unreinforced sandwich structures and FRPC sandwich structures, where rasters are identified as the black and red contours

4.12.2 Welding of Rasters

Figure 4.43 and Figure 4.44 reveals the welding between rasters and the direction of rasters for the unreinforced sandwich structures and the FRPC sandwich structures, respectively. A successful weld of the rasters is one that indicates a negative air gap, explained in section 2.12.1 in the literature review, and as seen in Figure 4.43 (images a, b and c). This illustrates strong adhesion between neighbouring rasters. An unsuccessful weld of a raster is one that shows deformities or a positive air gap. This is illustrated in Figure 4.43 (image c). The negative air gap was attributed to the build orientation of the

unreinforced sandwich structures. Whereas, the positive air gap can be expected to transpire alongside a negative air gap since the sandwich structures had a 37% infill density, corresponding well with the upright orientation as seen by Sugiyama et al. (2018) in the literature (section 2.12.1). Unreinforced structures as seen in Figure 4.43 showed successful welding of rasters, and this results in a more ductile structure that can bear large amounts of deformations during compression. On the contrary, the horizontal parallel welded rasters for the FRPC structures in Figure 4.44 (HC images a and b, and RE images a and b) would therefore demonstrate a significant reduction in plastic deformation and the occurrence of brittle fracturing (Basurto-Vázquez et al., 2021). Both phenomena are revealed in Figures 4.31-4.36, evidently demonstrating the smaller inelastic deformations and catastrophic failure points of the FRPC curves, and large plastic deformations of the unreinforced structures.

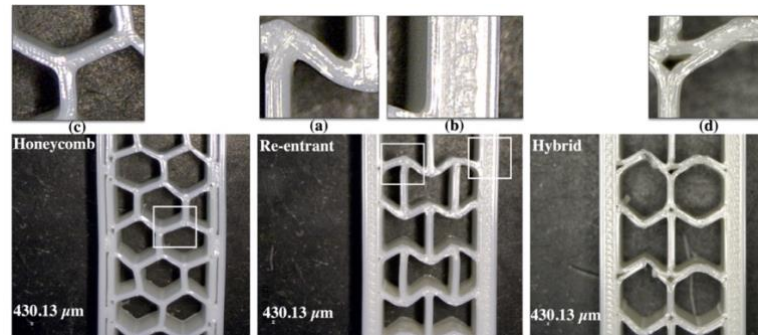


Figure 4.43 Print quality of the honeycomb, re-entrant, and hybrid core sandwich structures with no fibre reinforcement in the X:270°, Y:270°, Z:0° orientation

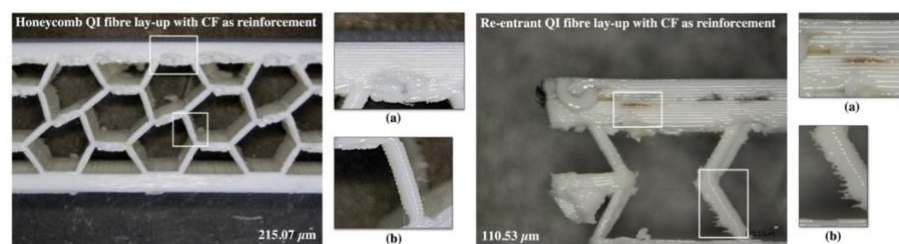


Figure 4.44 The honeycomb and re-entrant QI fibre lay-up which underwent post processing, where images (a.) and (b.) reveal raster direction, printed in the X:0°, Y:0°, Z:90° orientation

4.12.3 Post Processing

Another important factor to consider is post processing. The absence of post-processing for unreinforced structures meant that they showed improved part quality and

structural integrity, since there were no indications of macroscopic deformations after compression, i.e. delamination of the face sheets, macroscopic cracking, or matrix cracking, as seen in Figure 4.43. Conversely, the fibre-reinforced structures as seen in Figure 4.44 showed otherwise. The effects that can arise from post processing can be seen in images (a.) and (b.). It is noticeable that there is irregularity in the raster layers, generally smaller widths of the cell walls, and sharp features from the removal of the supports (as seen in Figure 4.44 for the RE image). These can be considered crucial contributors to the inferior compressive properties as seen for the FRPC structures in Figures 4.37-4.39. Therefore, emphasising print quality and the fusion between rasters is important to produce a structurally sound part and one with improved compressive modulus and strength (Zhang & Peng, 2012; Turner & Gold, 2015).

4.12.4 Residual Stress and Interfacial Adhesion

Residual stresses are considered because it can become more prominent in 3D printed FRPC structures. Thermal residual stresses arise due to a mismatch coefficient of thermal expansion between fibres and matrix, weak interfacial bonding, and an inconsistent toolpath (Goh et al., 2019). The temperature of the semi-molten nylon is higher than the print bed temperature and that of the fibres used, thus inducing a micro-heating process which promotes residual stress (Peng et al., 2019; Zhang et al., 2017). Residual stresses can result in ineffective adhesion between the fibres and the matrix, and thus an interface that is compromised and damaged. This can interfere with an appropriate transfer of load from the matrix to the fibres, and it can affect the wettability between the reinforcement and matrix. Hence, the reduction in properties for the FRPC structures in Figures 4.37-4.39. The absence of fibres for unreinforced structures can reduce the effects of mismatch coefficient of thermal expansion, and results in a part with strong interfacial adhesion and fewer defects (Li et al., 2022), producing superior properties, as seen in Figures 4.37-4.39, mainly for compressive strength and energy absorbed.

4.12.5 Fibre Exposure

Fibre exposure is another defect that occurs in FRPC structures and CFR printing. Figure 4.45 shows the CF fibres become exposed between the nylon layers after a completed print. When consecutive fibre layers are printed, fibres escape the PA6 wall layers and become exposed on the exterior surface, which may decrease the adherence of layers in the manufacturing process. As a result, there is a consequence of delamination

and premature failure of the FRPC sandwich structures (Araya-Calvo et al., 2018). Commonly, a consecutive fibre pattern as opposed to a more equidistant fibre pattern results in this occurrence. Although nylon sizer has been used to improve the fibre-matrix interfacial properties (Markforged, 2023), fibre exposure can still take place because of the print pattern. The location of exposed fibres is dependent on the fibre orientation, e.g. 0° shows fibres exposed across the structure (Figure 4.45).

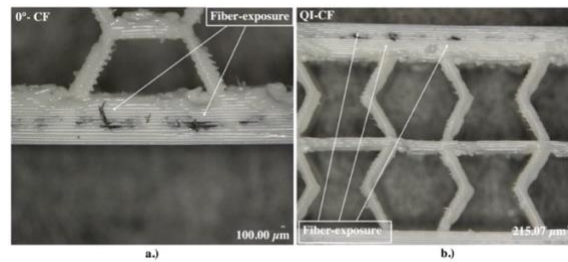


Figure 4.45 Exposure of CF fibres for the 0° orientation structure with a honeycomb core and CF as reinforcement (a.) alongside the QI fibre lay-up with CF as reinforcement and a hybrid core (b.)

4.12.6 Microstructural Characterisation and Voids

Void formation is a prominent deformity that can transpire for FRPC structures and in CFR printing. The internal structure of the composites influences the performance characteristic of the final sandwich composite part, and a structure with high void content can result in premature failure (Kabir et al., 2021). Figure 4.46 exhibits a few of the FRPC sandwich structures that exhibited voids. A few reasons as to why voids develop are found below (Kabir et al., 2021):

- (1) Imperfect joining and adhesion between the adjacent rasters of the nylon plastic and adhesion between fibres leaving air gaps (Figure 4.46, 5CUD-CF, isotropic UD-CF, and Kevlar micrographs).
- (2) Inconsistent travel and accurate movement of the print head that can occur during the print.
- (3) Gap between the wall and infill rasters due to the nature of the print pattern for a given fibre/polymer orientation (Figure 4.46, isotropic-UD-CF).
- (4) All fibre orientations and lay-ups have a point at which bending of the fibres takes place to fill a chosen area leading to unavoidable void content.

Figure 4.46 shows that the CF structures contained a high structural void concentration within and around the fibre placements. Similarly, Kevlar reinforced structures, indicated more prominent void concentration outside of the fibre placement zone, resulting in voids populating in the matrix. It is believed that these distinctions might contribute to the minor discrepancies between Kevlar and CF compressive properties (Dickson et al., 2017), as seen in Figures 4.37-4.39. The nature of the raster and fibre angles present in the structures means voids are inevitable for 3D printed structures (Turner & Gold, 2015; Zhang et al., 2017). Conventional methods of manufacturing utilise high temperatures alongside high pressures to remove the formation of voids. However, FFF and CFR printing techniques do not include these methods and so it is difficult to remove voids (Dickson et al., 2017). In conclusion, the presence of voids can reduce the interfacial strength between fibres and matrix, which significantly reduces the stiffness and strength (Figure 4.37 and Figure 4.38) of the sandwich composites. Contrarily, unreinforced structures are expected to show less void formation and better print quality, because (1) they indicated superior compressive and energy absorbing properties (Figures 4.37-4.39), and most importantly (2) they were not influenced by the lay-ups of fibres which could result in void formation around the fibres.

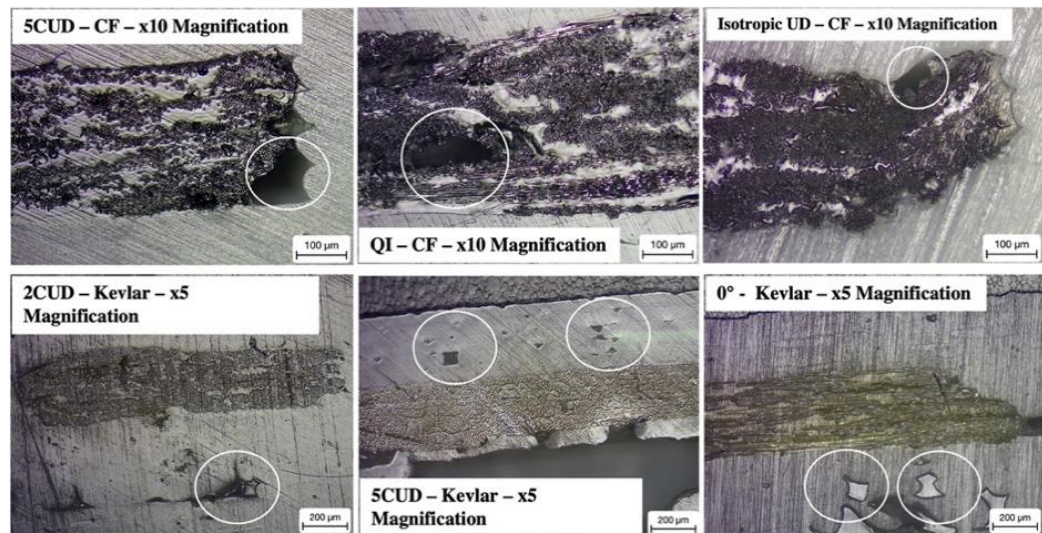


Figure 4.46 Micrographs of Kevlar and CF reinforced sandwich structures with void locations

4.13 Analysis of the Fibre Failure Modes Present in the Face Sheets

This section seeks to analyse the face sheets for failure modes, the deformation mechanisms of the cores, and how the cell failure modes were affected after low-velocity

impact and CAI testing. The findings are then linked to the charts as seen in Figures 4.37-4.39. Figure 4.47-4.52, and Figures 4.54-4.58, show HDoF images of all the sandwich structures impacted at 2J.

4.13.1 Failure Modes

4.13.1.1 Matrix Cracking

The most significant contribution to the reduction of compressive properties are the failure modes/mechanisms induced by low-velocity impact (Sekine et al., 1998; Li et al., 2002; Swart et al., 2022). Failure of the sandwich composites was led by matrix cracking, as seen to occur for all the sandwich structures present in Figure 4.47-4.52 and Figures 4.54-4.58. Since the matrix is significantly weaker in comparison to the fibres, structures resulted in crack propagation through the thickness of the matrix and failure of the fibre-matrix interface (Bhandary et al., 2012; Kabir et al., 2021). The 0° fibre orientation experienced the largest catastrophic damage to the face sheets in comparison to the other fibre orientations. It indicated a through-thickness crack of the matrix in the transverse direction, as well as splitting of the fibres, as seen in Figure 4.47, Figure 4.48, and Figure 4.50, showing good agreement with Li et al. (2022). Figure 4.47 (CF-0°-2) indicates that the failure of the matrix occurred in all three of the tested structures (annotated by the circles). Hence, the 0° fibre orientation provided no resistance to cracking. Consequently, Figure 4.47 (Kev-0°-2), and Figure 4.50 (Kev-0°) indicate the direction in which cells deformed during impact and they show the localized impact region (annotated by the arrows). The localized impact region for both structures in Figure 4.47 and Figure 4.50 show a large area of damage from impact, resulting in signs of fibre pull-out, indicated in Figure 4.47 (Kev-0°-1) and Figure 4.48 (CF-0°), and fibre fracture as seen in Figure 4.47 (CF-0°-1).

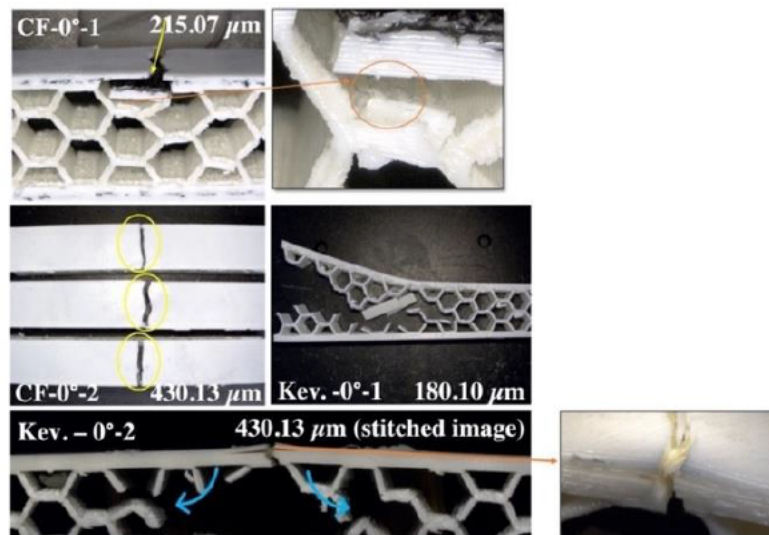


Figure 4.47 Honeycomb sandwich structures reinforced with CF or Kevlar with a fibre direction of 0°

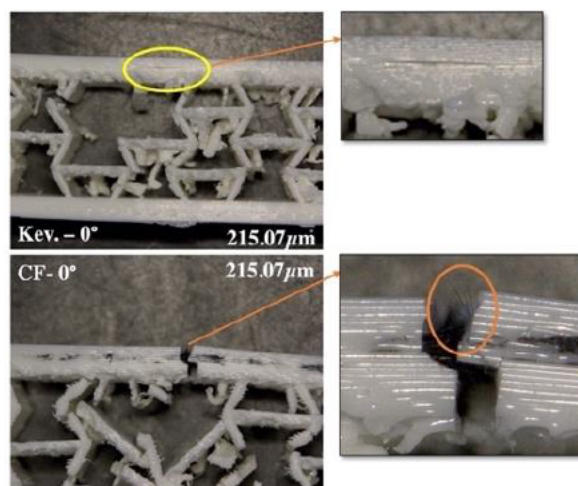


Figure 4.48 Re-entrant sandwich structures reinforced with CF or Kevlar with a fibre direction of 0°

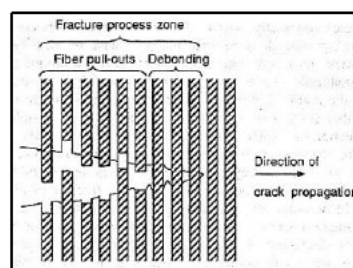


Figure 4.49 A model of the fracture-process zone showing local failure events near the crack tip (Agarwal et al., 2006)

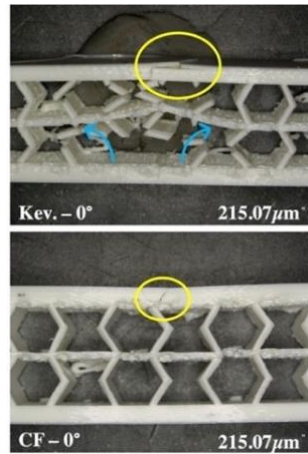


Figure 4.50 Hybrid sandwich structures reinforced with CF or Kevlar with a fibre direction of 0°

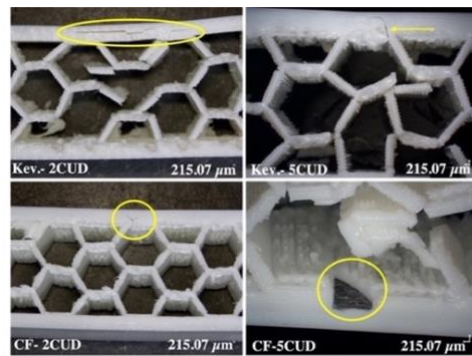


Figure 4.51 Honeycomb sandwich structures reinforced with CF or Kevlar, with fibre directions 2CUD and 5CUD

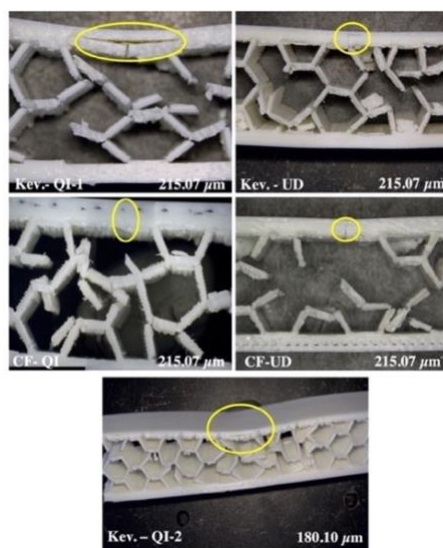


Figure 4.52 Honeycomb sandwich structures reinforced with CF or Kevlar, with a fibre direction of QI and isotropic UD

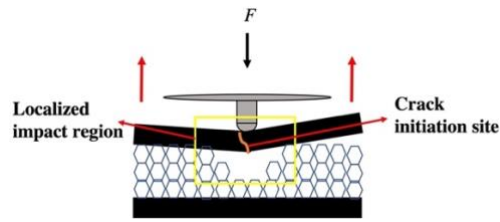


Figure 4.53 Illustration of the hemispherical head impacting the top face sheet where ‘F’ is the downward force, the ‘red arrows’ are the direction at which the face sheets wish to bend from imposed impact, the ‘orange line’ shows where crack initiation is and the ‘yellow rectangle’ is the localized impact region where cells have cracked and failed showing no support to the top face sheet

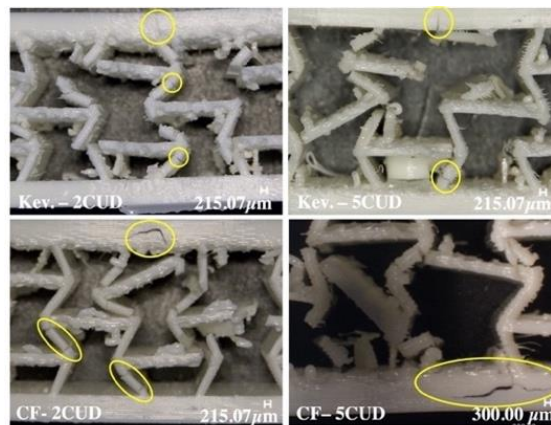


Figure 4.54 Re-entrant sandwich structures reinforced with CF or Kevlar with a fibre direction of 2CUD and 5CUD

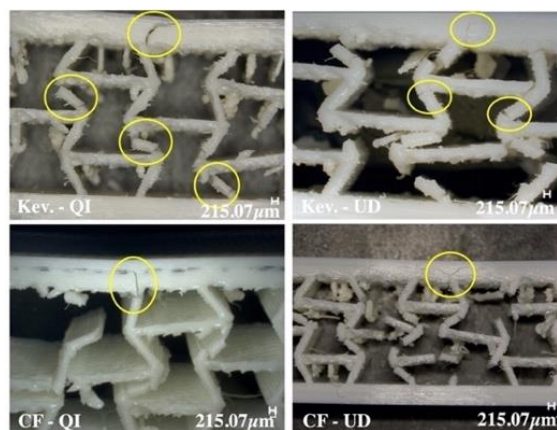


Figure 4.55 Re-entrant sandwich structures reinforced with CF or Kevlar, with a fibre direction of QI and isotropic UD

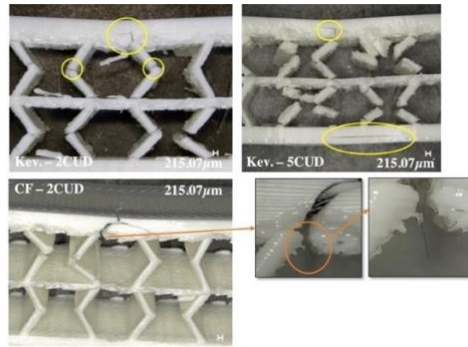


Figure 4.56 Hybrid sandwich structures reinforced with CF or Kevlar, with a fibre direction of 2CUD and 5CUD

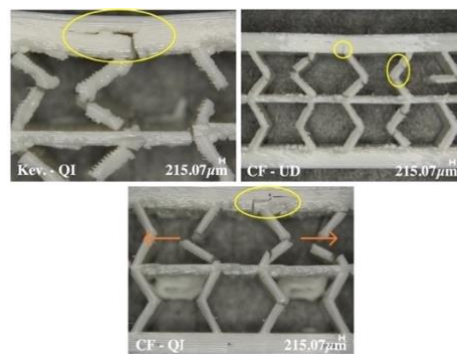


Figure 4.57 Hybrid sandwich structures reinforced with CF or Kevlar, with a fibre direction of QI and isotropic UD

4.13.1.2 Delamination

A common failure mode seen to occur after low-velocity impact was delamination, distinctively taking place for the bulk of the sandwich structures with fibre reinforcement. Structures that exhibited delamination was Figure 4.47 (CF-0°-1 and Kev-0°-2), Figure 4.48 (Kev-0°), (Kev-0°), Figure 4.51 (Kev-2CUD), Figure 4.52 (Kev-QI-1 and Kev-UD), Figure 4.56 (Kev-5CUD, annotated by the larger circle), and Figure 4.57 (Kev-QI and CF-QI). Majority of the sandwich structures demonstrating delamination were those containing Kevlar fibre. Delamination occurred because the interlaminar stress levels exceeded the interlaminar strength. Since the interlaminar strength is the restraint, it relies significantly on the matrix properties and the bonding strength of the fibre-matrix interface. However, the bonding strength between the Kevlar fibre-matrix interface was jeopardised; thus, resulting in failure of the sandwich composites by delamination in the face sheet (Chung et al., 1989; Dransfield et al., 1994). Furthermore, microscopy images shown in Figure 4.27 and Figure 4.28 reveal that the fibre-matrix

interface contained voids and interface spacing, exhibiting the poor wettability of the fibres with the nylon matrix. This suggests that a limited number of fibres could adhere successfully to the matrix and suggests a weaker bond when compared to CF (Caminero et al., 2018). This conclusion is supported by the extensive delamination of the Kevlar fibre reinforced sandwich structures.

4.13.1.3 Fibre Pull-Out

Fibre pull-out is expected to be seen for fibre-reinforced structures regardless of their fibre orientation, because it is a common local failure event during the fracturing of a fibre composite. Before fibre pull-out takes place, it is expected that micro-cracking also occurs since fibre pull-out cannot occur without crack initiation (Agarwal et al., 2006). Earlier, Figure 4.49 illustrates the initiation of fibre pull-out. It shows, at some distance ahead of the crack tip fibres are still intact, but within the high stress region of the crack, fibres fracture due to fibres pulling apart behind the crack tip and thus debonding from the matrix.

4.13.1.4 Transverse Intralaminar Micro-cracks and Translaminar Micro-cracks

Cracking can occur within the layers that are in the off-axis orientations with respect to the load direction and impact (Nairn, 2000). Thus, the magnitude of micro-cracking is dependent on the orientation of the fibres and the stiffness and strength of a continuous fibre. The development of cracks, fibre pull-out, and delamination can result in transverse intralaminar micro-cracks, and translaminar micro-cracks during impact (Opelt et al., 2018). It can be assumed, after impact, that sandwich structures with fibre reinforcement will contain some form of micro-cracking sites within the face sheets. Micro-cracking indicates great relevance to composite structures, and it suggests that it can be an intrinsic characteristic of interlaminar failures for the 3D printed sandwich structures after low-velocity impact in the results.

Transverse intralaminar cracks are associated with fibre layers perpendicular to the loading direction, as seen in Figure 4.47 (for all structures), Figure 4.48 (CF-0°), Figure 4.50 (CF-0°), Figure 4.52 (for all QI structures), and Figure 4.55 (for all QI structures). When there is excessive intralaminar stresses taking place, it promotes interlaminar stresses to develop at the interface between the adjacent fibre layers. The interlaminar stresses can result in more crack development and can translate to the

separation of the fibre layers, hence the onset and growth of delamination (Kahla, 2019). It is common to see both crack propagation and forms of delamination in composites because cracks tend to develop and choose a path along the interface of laminates, especially those containing various fibre orientations. Consequently, QI fibre lay-ups such as Figure 4.52, Figure 4.55, and Figure 4.57, exhibits this behaviour. Moreover, equally orientated fibre composites around the mid-plane, such as the QI structures, can alter the direction of a crack because of the various orientations of the fibres (Agarwal et al., 2006). However, this does not seem to hinder delamination in the results. Finally, at the latest stage of the fibre failure modes fibre breaking takes place, proceeding to catastrophic failure of the sandwich structures (Kahla, 2019).

One such sandwich structure indicating catastrophic failure was that seen in Figure 4.47 (Kev-0°-1). The core displayed a high degree of separation from adjacent neighbouring cells, where the top face sheet bowed away from the adjacent face sheet. This is believed to have been because the honeycomb cells absorbed the energy from the impact head, dissipating it through the core by its deformation and bending behaviour characteristics, and damaging the core-face sheet interface. Therefore, the cells have reached their highest ability of deformation resulting in cracking and failing at the nodes, consequentially leading to separation of the inclined struts, and thus, no support structure for the face sheet after impact. Additionally, the high impact force instigated the top face sheet to bend from the localized impact, constraining it downwards into the cells. This phenomenon is commonly seen when sandwich structures undergo three-point bend tests (Sayahlatifi et al., 2021). As a result, crack initiations start in this manner and this can cause the face sheets to bend in the test direction from the significant tension placed on the opposite surface of the face sheet (Sayahlatifi et al., 2021), and from face wrinkling (Zaharia et al., 2020). Furthermore, the HC-Kev-0° and the HC-CF-isotropic UD structures in Figure 4.47 and Figure 4.52, respectively, show that the majority of the cells away from the vicinity of impact are still intact. Therefore, they are capable of supporting the outer edges of the face sheet to cope with a compressive load, as seen for the structures in Figure 4.53.

4.13.1.5 Sandwich Structures Core Failure

Figures 4.47-4.52 show macroscopically that the HC core revealed significantly more prominent failure modes in comparison to the re-entrant (Figure 4.48, Figure 4.54,

and Figure 4.55) and the hybrid structures (Figure 4.50 and Figure 4.56). This can be related to the cells hinge rotation and lateral expansion, as later explained in section 4.14. Consequently, this results in crack development and crack propagation, leading to fracturing, as seen in Figure 4.51, Figure 4.52, Figure 4.56, and Figure 4.57, for all the honeycomb cells. On the contrary, for the re-entrant structures revealed in Figure 4.54, Figure 4.55, and Figure 4.57 (Kev-QI), face sheet cracking initiated from the inclined strut of the re-entrant cell joined to the face sheet. It resulted in consistent cracking along the length of the face sheet which led to delamination and failure of the node at the joint of the face sheets. During impact, a large degree of localized stress acted at the joint because of its bending nature. This places large amounts of force at the nodes and walls of the cells, and thus surpasses their load bearing capabilities under compression, which results in greater crack propagation (Wang et al., 2021). This can be accredited to the anticlockwise hinge rotation phenomenon alongside horizontal tension, as seen in Figure 4.62. Moreover, the hybrid core structure as seen in Figure 4.57 demonstrated the collective deformation mechanisms of the honeycomb and re-entrant cells, for the CF-QI structure, where the arrows annotate this behaviour. Hence, it can result in catastrophic failure of the core, as seen in Figure 4.56 (Kev-5CUD), and a reduction in compressive and energy absorbing capabilities. Therefore, it displayed the poorest compressive properties and energy absorption during compression in contrast to the RE and HC sandwich structures, as seen in Figure 4.37-4.39, respectively.

On the contrary, Figure 4.56 (Kev-2CUD and Kev-5CUD) and Figure 4.57 (Kev-QI and CF-UD) indicate large amounts of crack development occurring at the nodes for the re-entrant cells in the hybrid core. As a result, there is more prominent damage inflicted to the individual cells within the core, alongside signs of fibre pull-out (Figure 4.56 CF-2CUD), delamination (Figure 4.57 CF-QI and Kev-QI), matrix cracking (Figure 4.50, Figure 4.56, and Figure 4.57), and fibre-matrix interface failure (Figure 4.56 Kev-5CUD), observed for the face sheets. In conclusion, the hybrid sandwich structure was more reliant on the fibre type utilised to determine how large the vicinity of damage was after low-velocity impact. Hence, the HYB structures with CF reinforcement structures displayed smaller areas of damage, compared to Kevlar reinforced structures with larger zones of cell failure, as seen in Figure 4.65.

4.13.1.6 Kevlar Fibre Failure Modes

Kevlar fibres can be more susceptible to ‘fibre pull-out’ because of interlaminar failure (Dickson et al., 2017), but owing to its flexibility and toughness, this was not as apparent as expected. Kevlar fibres contain large amounts of ductility. The combination of the para-aramid structure alongside the lack of brittleness which also results from the addition of a PA sizing agent, results in a restriction of crack development in the fibres (Agarwal et al., 2006; Clements, 1998; Composite materials handbook, 2002). Consequently, Kevlar-reinforced structures are expected to suffer more from interlaminar cracking aggregating at the interface. Therefore, reducing the interfacial strength, subsequently leading to delamination between adjacent plies and matrix cracking (Li et al., 2022). Figure 4.47 (Kev-0°-2) illustrates this. Furthermore, during the formation of micro-cracks, the fibres can stabilise crack propagation by creating new fracture surfaces resulting in higher energy absorbing capabilities, improved modulus, and strength (Opelt et al., 2018). Figures 4.37-4.39 demonstrate that the bulk of Kevlar-reinforced sandwich structures were superior in compressive properties when compared to the CF sandwich structures indicated.

4.13.1.7 Carbon Fibre Failure Modes

The CF-reinforced sandwich structures appeared to be more vulnerable to fracturing. They revealed higher cases of fibre fracture and fibre pull-out, as seen in Figure 4.47 (CF-0°-1), Figure 4.48 (CF-0°), Figure 4.56 (CF-2CUD). It can be expected that even without macroscopic evaluation, with the presence of a matrix crack, it is still possible for the fibres to possess micro-crack formations. This can result from perforation caused by the impact head, and localized inter-layer fractures accredited to the fragile nature of CF (Wang et al., 2021). Based on the evidence of the charts in Figures 4.37-4.39 it can be assumed that this is a significant cause for the reduction in compressive properties after low-velocity impact in comparison to their unimpacted relatives with CF reinforcements (Swart et al., 2022). Moreover, this can also be because of the brittle nature and poor transverse stress between CF layers (Peng et al., 2019), and the defects that occur for fibre-reinforced structures as discussed in section 4.12.

4.13.2 Perforation Damage

Several sandwich structures exhibited perforation damage of the face sheets imposed from impact damage of the hemispherical impactor, as seen in Figure 4.47 (CF-

0°-1 and CF-0°-2), Figure 4.48 (CF-0°), Figure 4.50 (Kev-0° and CF-0°), and Figure 4.56 (CF-2CUD). Notably, 5 out of the 6 structures were 0° fibre orientations. Figure 4.50 (Kev-0°) exhibited perforation of both face sheets, however, the bottom face sheet (circled) did not experience the impact from the hemispherical head. Instead, damage to the bottom face sheet was because of significant core failure, i.e. fracturing of cell ligaments and nodes, and crack propagations, consequentially fracturing the bottom face sheet, leading to matrix failure (Akatay et al., 2015; Meo et al., 2005). The bulk of the FRPC RE and HC sandwich structures indicated no signs of perforation, owing to the enhanced perforation resistance and enhanced core deformation mechanisms of the cores. Figures 4.37-4.39 demonstrated this, exhibiting overall that superior compressive properties and energy absorbing capabilities, were gained for sandwich structures with less perforation damage, and reduced core failure.

4.13.3 Fibre Lay-Up Damage Comparisons

Figures 4.51-4.56 indicates significant transverse crack propagation, cell failure (cell wall separation, strut separation and cracking), and delamination. The fibre lay-up of 2CUD and 5CUD as shown in Figure 4.51, Figure 4.54, and Figure 4.56 exhibit evident crack propagations and delamination for both fibre lay-ups. The HC-5CUD structures in Figure 4.51 exhibited a crack initiation site and matrix cracking. However, the RE-5CUD and HYB-5CUD in Figure 4.54 and Figure 4.56, respectively, indicated significantly more node failures, delamination, and crack initiation sites. The QI and isotropic UD lay-ups displayed catastrophic failure of cells and large amounts of crack propagation in the face sheet and cores, for both fibre types in Figure 4.52, Figure 4.55 and Figure 4.57. Moreover, the HC-Kev-QI structure as shown in Figure 4.52, experienced the largest diminishment in compressive properties out of the other core topologies with the same lay-up. Catastrophic failure of the cells and face sheet was prominent; hence, its significant reductions in properties, as seen in Figures 4.37-4.39, respectively. This was due to the high indentation zone witnessed, resulting in delamination, as seen in Figure 4.52 (image Kev.-QI-1). Because of the failure modes, the QI lay-up indicates a reduced plateau stage, as shown in Figure 4.40. Therefore, its residual energy absorption capabilities diminished, as similarly witnessed by Akatay et al. (2015). This logic can be applied to the reasonings behind the reductions seen for other fibre lay-ups and orientations.

Moreover, the charts in Figures 4.37-4.39 revealed that the bulk of the 2CUD structures obtained lower compressive properties and energy absorbing capabilities in contrast to the 5CUD fibre orientations. This is believed to not be from fibre orientation but rather caused by the lower $V_f\%$ of the 2CUD fibre orientations (Khondker et al., 2004), in addition to significant fibre failure modes and sandwich failure modes (mostly when the same fibre type was compared). For example, Kevlar-reinforced structures experienced improved residual properties compared to CF-reinforced structures, even though they demonstrated lower $V_f\%$ overall, as exhibited in Figure 4.30. Therefore, enhancement of residual properties was more related on the core topology and the mechanical properties of the fibre type utilised, rather than the $V_f\%$ when comparison is made between Kevlar and CF reinforcements.

4.13.4 Unreinforced Sandwich Structure Damage Comparisons

Figure 4.58 shows the unreinforced sandwich structures. Fracturing at the nodes (Figure 4.58, re-entrant 1), and cracking of the face sheet (Figure 4.58, honeycomb and re-entrant 2) were the two predominant forms of failure mechanisms. There was no fracturing of the HYB-No fibres-IMP structure, as seen in Figure 4.58, however, it still indicated the lowest overall compressive properties and energy absorption capabilities, as seen in Figures 4.37-4.39. Due to a higher quality print and potentially less void concentration between the rasters, it has an absence of failure modes. However, its inferior core deformation in comparison to the HC and RE cores was its downfall, discussed further in section 4.14.3. On the contrary, node failure occurred below the impact region for the re-entrant cell structure in Figure 4.58 (re-entrant 1), however, no node failure was seen for the HC or HYB structures in Figure 4.58. Transverse and through-thickness cracking of the matrix took place instead for the HC and HYB structures, revealing the natural weakness of the matrix. The re-entrant structure revealed impressive residual compressive properties and residual energy absorption, considering node failure, and it was still vastly superior in compressive properties when compared to the hybrid structure that did not suffer any failure modes, as seen in Figures 4.37-4.39. This was accredited to the re-entrant's successful load distribution, maintaining a high stiffness and strength even after low-velocity impact. Unreinforced structures, as seen in Figure 4.58, revealed less failure in the cells and face sheets compared to structures with fibre reinforcement, as seen in Figures 4.47-4.50 and Figures 4.51-4.57. This is largely

related to the absence of fibre failure modes; 3D printing defects and build orientation as discussed in detail in section 4.12.

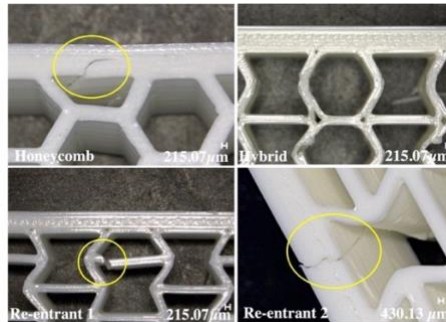


Figure 4.58 Honeycomb, hybrid, and re-entrant sandwich structures, with no fibre reinforcement

4.14 Analysis of the Bending Behaviour of the Sandwich Structures After Impact

4.14.1 Honeycomb Deformation

Figure 4.59 illustrates the honeycomb cell under compression. By nature, the honeycomb cell desires to expand laterally away from the impact zone, eventually reaching full densification. Consequently, localized stress regions develop at the nodes, resulting in the propagation of cracks at the points where tension occurs, as seen in Figure 4.59. This eventually develops enough for fracturing of the ligament to occur at the node location (Schmidt and Fleck, 1999). Moreover, the honeycomb structure experienced global deformation and layer wise failure resulting in catastrophic failure of the cells, as seen in Figure 4.47 (Kev-0°). However, at times, under impact, failure and damage developed to the cells positioned below the localized impact region, as seen in Figure 4.61, indicating that global deformation does not always transpire. On the contrary, hinge rotation can develop because of the bending moment in the honeycomb cells, as illustrated in Figure 4.60. It exemplifies the deformation mechanism at the nodes whilst the cells undergo compression. The bending moment/rotational moment can produce torsion in the cells, as similarly seen in Figure 4.5. As opposed to the cell in Figure 4.60, the cell in Figure 4.59 is joined to the face sheet, anchoring the horizontal strut h from moving, thus flattening of the cell occurs and no occurrence of the bending moment. Therefore, the deformation mechanisms of the honeycomb cells aid the structure globally which results in its superior stiffness, strength, and energy absorbed, as seen in Figures 4.37-4.39.

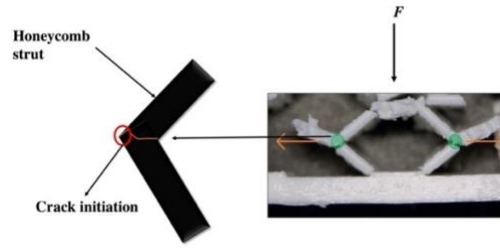


Figure 4.59 Lateral expansion of the honeycomb cell under impact and compression where the (arrows) express the direction of expansion outwards, the (black arrow) shows the force acting as the compressive force plates, and the (green circles) are the nodes

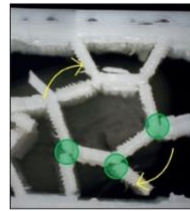


Figure 4.60 Bending moment inducing hinge rotation at the nodes where the green circles are the nodes, and the arrows indicate the rotational moment

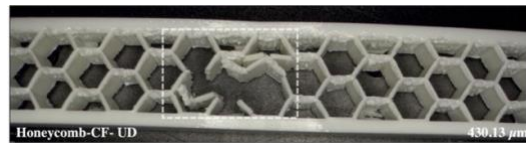


Figure 4.61 Honeycomb sandwich structure reinforced with CF containing a UD lay-up, showing the vicinity of damage after a CAI test

4.14.2 Re-entrant Deformation

Overall, the RE sandwich structure did not suffer any global deformation compared to the HC and HYB core structures, due to its distinctive crushing behaviour. The re-entrant sandwich structures experienced greater local bending corresponding well with Ingrole et al. (2016) and Wang et al. (2021). The failure of the cells took place within the localized impact region, as shown in Figure 4.62. This was because of material densification beneath the impact zone, correlating well with the literature in section 2.11.8. Consequently, the lateral contraction of the cells from the negative Poisson's ratio means material flows into the vicinity of impact. This movement creates an area of denser material occurring directly below the point of impact, aiding the structure in resisting further deformation. Higher energy absorption is expected to occur because more material

gets involved in this process, which is another cause for the significantly higher residual energy absorption capabilities of the FRPC re-entrant sandwich structures as seen in Figure 4.39 (Yang et al., 2013).

The deformation mechanism of the re-entrant cells expresses an anti-clockwise hinge rotation phenomenon alongside horizontal tension whilst performing a CAI test, illustrated in Figure 4.63. The bending behaviour of the ligaments was instigated by the impact head, resulting in stress arising at the top two nodes of the cell (Figure 4.63). Hence, anti-clockwise hinge rotation develops, encouraging crack initiation. This phenomenon, and negative Poisson's ratio, cause the natural bending behaviour of the ligaments, and results in large amounts of stress at the nodes (Wang et al., 2021). This is indicated by the marked points in Figure 4.63 revealing failure similar to that witnessed in the results for Figure 4.54 and Figure 4.55.



Figure 4.62 Re-entrant sandwich structure reinforced with CF containing a UD lay-up, showing the vicinity of damage after a CAI test

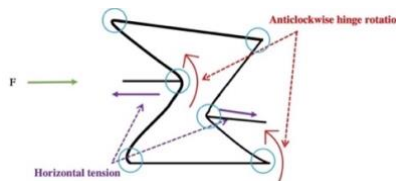


Figure 4.63 Illustration of Anticlockwise hinge rotation and horizontal tension (Wang et al., 2021)

Furthermore, the re-entrant cells under impact showed improved resistance to deformation along its longitudinal direction in contrast to the transverse direction. As a result of the negative Poisson's ratio and low-velocity impact, the transverse deformation of the cells is expected to be more vulnerable which leads to densification and plastic deformation of individual cells, especially those in the vicinity of impact, as seen in Figure 4.62 (Jin et al., 2016; Qi et al., 2017).

4.14.3 Hybrid Deformation

The properties of the hybrid structures need to be seen as inferior to the base structures (honeycomb or re-entrant cores), because of the collective deformation mechanisms of the honeycomb and re-entrant cells. As a result of the lateral expansion of the honeycomb cells Figure 4.59 and the lateral contraction of the re-entrant cells seen in Figure 4.63, the honeycomb cells deform collectively with the re-entrant cells. Consequentially, this results in global deformation, as seen in Figure 4.64, preventing the core from appropriately combatting the compressive load. Furthermore, the negative angle of the inclined strut l in the re-entrant cell (Figure 4.10) coincides with the positive inclined strut angle l of the honeycomb (Figure 4.5). Therefore, this aids the re-entrant cell in its auxetic traits. As a result of its deformation mechanisms, during impact, it revealed no material densification, as seen to occur for the re-entrant structure, indicating that negative Poisson's ratio was not taking place to the same extent as the re-entrant core structure.

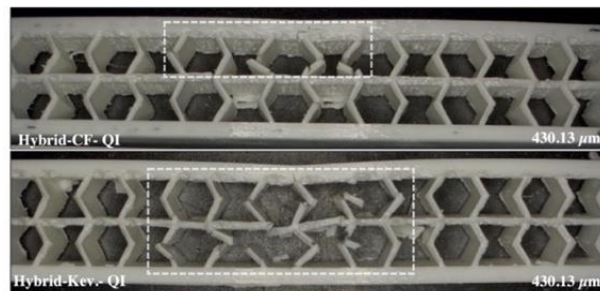


Figure 4.64 Hybrid sandwich structure reinforced with CF containing a QI lay-up (Hybrid-CF-QI), showing the vicinity of damage after a CAI test compared to the hybrid sandwich structure reinforced with Kevlar containing a QI lay-up (Hybrid-Kev. - QI) but showing a greater damage vicinity

CHAPTER 5 3D PRINTED GRAPHENE NANOPATELET REINFORCED PA6 NANOCOMPOSITES

5.1 Development of Nanocomposites for 3D Printing of Sandwich Structures

The objective of this chapter was to successfully fabricate a ground-breaking PA6/Graphene nanoplatelet reinforced 3D printing filament material, with the intention to fabricate a novel next generation sandwich composite structure with enhanced impact properties. Compression testing of 3D printed PA6 and PA6/ GnP honeycomb, re-entrant, and hybrid sandwich structures enabled an evaluation to be made on their compressive modulus, compressive strength, and energy absorption during compression. Subsequently, the deformation mechanisms of the individual cells with GnP reinforcement and their morphology were studied to determine whether enhancements in properties were observed with varying GnP concentrations. Lastly, PA6 and PA6/GnP sandwich structures underwent low-velocity impact testing and CAI testing to further investigate their residual properties with GnP reinforcement.

5.2 Results

A stress-strain comparison of all 3D printed sandwich structures with and without NH₂-GnP reinforcement can be seen in Figure 5.1. Their compressive modulus, compressive strength, and energy absorbed during compression are shown in Figures 5.3-5.5, respectively. Table 5.1 presents the obtained compressive properties and energy absorption values from the charts in Figures 5.3-5.5.

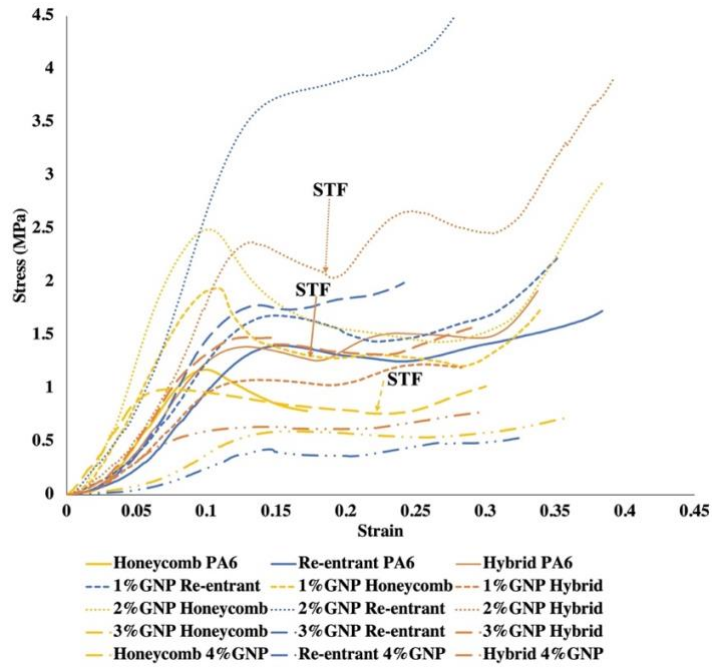


Figure 5.1 Stress-Strain graph of all unimpacted structure types and all structures with GnP inclusion in them

5.2.1 Neat PA6 Sandwich Structures Stress-Strain Analysis

The honeycomb PA6 structure revealed in Figure 5.1 resembled an earlier onset of deformation (1.19 MPa), where the cells lost their ability to return to their original shape, indicating permanent deformation translating to a reduction in stress. Additionally, the hybrid and re-entrant PA6 structures deformed at similar stresses (approximately 1.38 MPa), expressing a 15.97% greater stress value compared to the honeycomb. To note, the strain-to-failure (STF) of the structures was indicated as the point on the curves after initial plastic deformation occurred before an abrupt increase in stress. This was illustrated on the graph in Figure 5.1 referred to as STF, where examples were annotated. The STF values were indicated at the stated positions in Figure 5.1 because this is where the structure fails first. After this point all structures display cyclic regions accredited to cell wall contact. Therefore, failure of the structures occurred when full densification of the cells was reached. Most non-cellular materials do not possess cyclic qualities and therefore indicate a clear representation of strain-to-failure (Swart et al., 2022). Subsequently, the re-entrant PA6 structure resembled a strain-to-failure of 0.235 and the hybrid and honeycomb PA6 structures exhibited a strain-to-failure of approximately 0.17. Consequently, the re-entrant sandwich structure obtained a 38.23% greater strain-to-failure than the hybrid and honeycomb structures. By contrast, Figure 5.2 exhibits a

strain-to-failure chart where ‘HC’ represents the honeycomb, ‘RE’ represents the re-entrant, and ‘HYB’ represents the hybrid. It suggests that a higher strain-to-failure was achieved with the re-entrant PA6 and hybrid PA6 sandwich structures in contrast to the honeycomb PA6 structures, thus indicating that the core topology contributes significantly to the compressive properties of the sandwich structures.

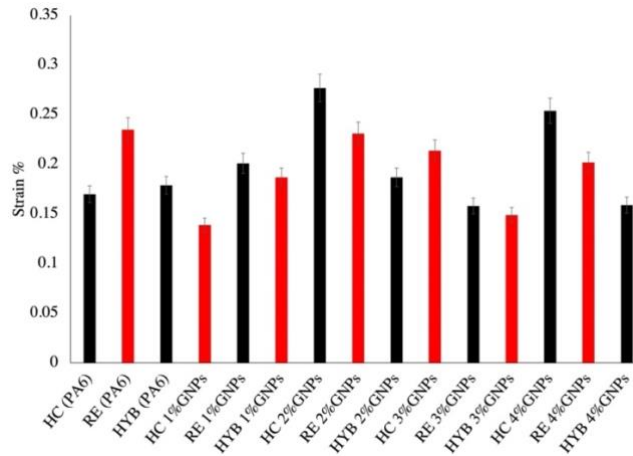


Figure 5.2 Strain-to-failure chart of all structure types and all GnP% concentrations of unimpacted structures

5.2.2 PA6/GnP Reinforced Sandwich Structures Stress-Strain Analysis

The stress at which yielding occurred was greater with the presence of GnPs. However, cell deformation behaviours largely contributed to the outcome of this. This was noted for the re-entrant 1%GnPs structure which revealed an enhanced behaviour in relation to the hybrid 1%GnP structure, in all areas of the investigated compressive properties and energy absorption which were shown in Figures 5.3-5.5. The re-entrant structure produced a stress value of 1.68 MPa and the hybrid produced a stress value of 1.07 MPa, which was 36.31% greater in its stress carrying capability. On the contrary, the honeycomb 1%GnPs revealed the greatest stress value of 1.91 MPa in contrast to the other 1%GnPs sandwich structures. Therefore, it was 13.69% and 78.50% greater than the re-entrant and hybrid sandwich structures, respectively. Nonetheless, a comparison between 1%GnPs structures and neat PA6 structures demonstrated that the honeycomb 1%GnPs structure experienced an increase of 60.50%, the re-entrant experienced an increase of 20%, and the hybrid experienced a decrease of 22.46%.

The most significant increase in compressive properties was exhibited by the 2%GnPs structures. Figure 5.2 shows improvements were also noted in strain-to-failure

with 2%GnPs. Figure 5.1 indicated that the honeycomb 2%GnPs increased by 101.68%, the re-entrant by 139.72%, and the hybrid by 73.48% in relation to their stress carrying capabilities when compared to their neat relatives. In addition, the most optimum enhancement in strain-to-failure was seen for the HC 2%GnPs structure, obtaining a strain value of 0.277, as seen in Figure 5.2. In comparison to its neat HC PA6 relative, it saw an increase in strain-to-failure of 38.63%. On the contrary, the re-entrant core topology demonstrated greater strain-to-failure with the absence of GnP reinforcement compared to its 2%GnPs relative, obtaining a strain-to-failure of 0.235. It demonstrated a 1.70% greater strain-to-failure in comparison, as seen in Figure 5.2. Conversely, filler concentrations above 2%GnPs, i.e. 3%GnPs and 4%GnPs, experienced a reduction in stress for sandwich structures with honeycomb core topology, as indicated in Figure 5.1. The re-entrant and hybrid sandwich structures with 3%GnPs produced stress readings greater than their neat PA6 relatives but lower than 2%GnPs filler concentrations. Consequently, sandwich structures containing 4%GnPs exhibited the lowest attained stress values for all sandwich structures. Finally, a reduction in strain-to-failure, as seen in Figure 5.2, was recorded for the 3%GnPs structures; however, for the bulk of the 4%GnPs structures, enhancements were noticed when compared to lower filler concentrations.

5.2.3 Compression Properties Comparison

This section will seek to evaluate the compressive properties and energy absorbing capabilities of the sandwich structures based on results obtained from the charts provided in Figures 5.3-5.5. Alongside the charts are tables representing the average values obtained for each core topology, where the integers highlighted in bold are those that obtained the greatest values. The relationship between neat PA6 and reinforced structures will be assessed to determine if improvements in compressive properties are seen with GnP reinforcement.

5.2.3.1 Compressive Modulus of the Sandwich Structures

Figure 5.3 shows the compressive modulus of all 3D printed sandwich structures. All sandwich structures with GnP reinforcement demonstrated an increase in compressive modulus, as seen in Figure 5.3. The neat PA6 sandwich structures revealed similar results in compressive modulus when core topologies were compared to one another. This could be because the structures were more reliant on the physical and chemical structure of the

PA6, instead of the behaviour of the cores. Another reason could be related to the time dependant deformation of the material, i.e., the structure was not given enough time for an appropriate reading of the modulus to take place. Therefore, a slower rate (1.00 mm/min) of compression could reveal a more accurate reading (Ye et al., 2021). Lastly, print defects might influence the structures to the point where it lacks stiffness significantly. Therefore, the chosen core topologies were unable to under-go their natural deformation mechanisms, and as such, the compressive modulus of the neat PA6 cores were similar.

With the addition of 1%GnPs, Figure 5.3 shows the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures experienced a 4.65% and 2.00% increase, and a 31.09% decrease in compressive modulus, respectively. With the addition of 2%GnPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures showed an increase of 77.67%, 3.24% and 62.99% in compressive modulus, respectively. Moreover, with the addition of 3%GnPs the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures all saw an increase of 29.01%, a reduction of 4.71% and a reduction of 20.14% in compressive modulus, respectively. Finally, with the addition of 4%GnPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure and the neat hybrid PA6 sandwich structures saw a reduction of 66.11%, 71.97% and 66.83% in compressive modulus, respectively. Therefore, the reduction in compressive modulus with increasing filler concentration correlates well with the stress-strain plots and their reduction in stress capabilities, as shown in Figure 5.1. Notably, Figure 5.3 indicated that the honeycomb sandwich structure demonstrated an increase in compressive modulus up until 3%GnPs, where a reduction was seen with a greater filler concentration of 4%GnPs. Conversely, the re-entrant and hybrid sandwich structures exhibited enhancement in their properties up until 2%GnPs, however, a reduction in their properties was noted at 3% and 4%GnP concentrations.

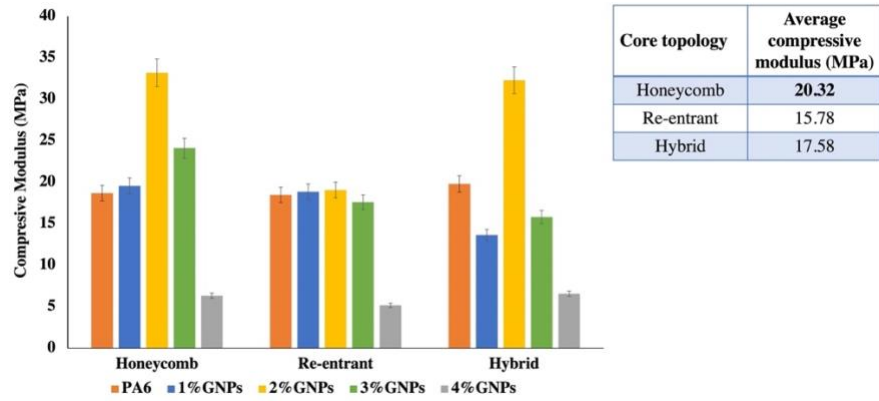


Figure 5.3 Average compressive modulus chart of all unimpacted structure types with various GnP concentrations

5.2.3.2 Compressive Strength of the Sandwich Structures

Figure 5.4 exhibits the compressive strength values obtained after compression for all 3D printed sandwich structures. With the addition of 1%GNPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures showed an increase of 42.62%, 11.47% and a reduction of 13.97% in compressive strength, respectively. Subsequently, with the addition of 2%GNPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures showed an increase of 90.16%, 128.0% and 72.06% in compressive strength, respectively. With the addition of 3%GNPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures showed a reduction of 13.11%, an increase of 10.82% and a reduction of 5.88% in compressive strength, respectively. Moreover, with the addition of 4%GNPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures saw a reduction of 53.27%, 72.61% and 54.41% in compressive strength, respectively. In conclusion, Figure 5.4 indicated that the re-entrant sandwich structure showed an increase in compressive strength up until a filler concentration of 4%GNPs, expressing good compatibility with higher concentrations of GNPs. Conversely, the honeycomb and hybrid sandwich structures indicated an earlier reduction in their compressive strength, as a reduction was noted with a filler concentration of 3%GNPs and a further reduction was shown with 4%GNPs.

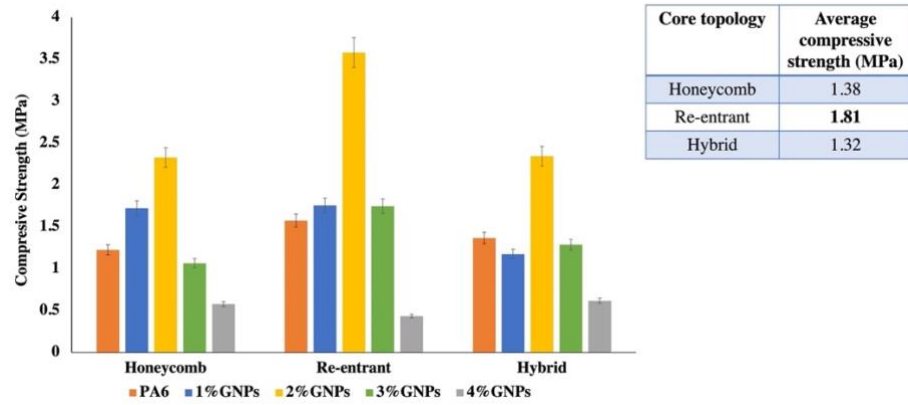


Figure 5.4 Average compressive strength chart of all unimpacted structure types with various GnP concentrations

5.2.3.3 Energy Absorption of the Sandwich Structures

Figure 5.5 expresses the energy absorption capabilities during compression of all the 3D printed sandwich structures. Similar to Figure 5.3 and Figure 5.4, energy absorption capabilities showed improvement with GnP reinforcement and improvement with higher concentrations of GnPs. As a result, Figure 5.5 exhibited that with the addition of 1%GnPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures showed an increase of 48.15%, 17.25% and a reduction of 11.86% in energy absorption, respectively. Additionally, with incrementation to 2%GnPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure and the neat hybrid PA6 sandwich structures showed an increase of 95.98%, 144.87% and 69.12% in energy absorbed, respectively. With the addition of 3%GnPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures showed a reduction of 32.39%, an increase of 13.87% and an increase of 2.80% in energy absorbed, respectively. Finally, with the addition of 4%GnPs, the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures saw a reduction of 30.25%, 72.14% and 52.16% in energy absorbed, respectively. In conclusion, Figure 5.5 indicated that the re-entrant and hybrid sandwich structures surpassed neat PA6 in energy absorption capabilities up until a filler concentration of 3%GnPs and reduced significantly at 4%GnPs. Nonetheless, the honeycomb sandwich structures indicated an earlier onset in the reduction of its energy absorbing capabilities, revealing a reduction upon reaching a filler concentration of 3% and 4%GnPs.

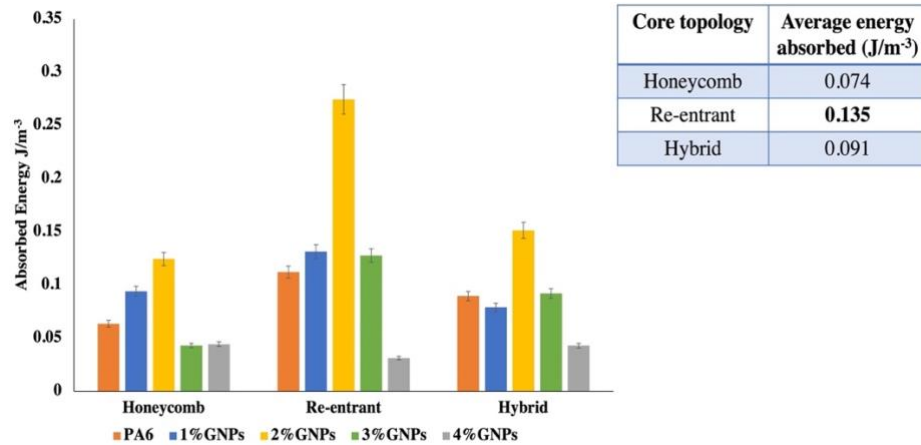


Figure 5.5 Average absorbed energy chart of all unimpacted structure types with various GnP concentrations

5.2.3.4 The NH_2 -GnP Concentration and Core Type with Superior Properties

For all sandwich structures containing filler concentrations of 2%GNPs the most optimum compressive properties and energy absorption were obtained. Superior compressive modulus was attained by the honeycomb core topology, with 2%GNPs reinforcement, producing a value of 33.19 MPa, as seen in Figure 5.3. Thus, it was 42.51% and 2.71% greater in compressive modulus in relation to the re-entrant and hybrid structures with 2%GNPs, respectively. The honeycomb core topology also produced the greatest average compressive modulus (20.32 MPa), as seen in the table in Figure 5.3. Subsequently, Figure 5.4 demonstrated, that the re-entrant with a filler concentration of 2%GNPs, exhibited superior compressive strength of 3.58 MPa. Therefore, it was 35.20% and 34.64% greater in compressive strength in relation to the honeycomb and hybrid structures with 2%GNPs, respectively. As a result, the re-entrant structure with a filler concentration of 2%GNPs obtained superior average compressive strength properties (1.81 MPa), as seen in the table in Figure 5.4. Figure 5.5 indicated that the re-entrant structure with 2%GNPs absorbed the greatest energy during compression, obtaining a value of 0.27 J/m³. As a result, it absorbed 54.66% and 44.86% more energy in comparison to the honeycomb and hybrid structures during compression, respectively. Overall, the re-entrant core topology also indicated the greatest average energy absorption (0.135 J/m³), as seen in the table in Figure 5.5.

Table 5.1 Average mechanical properties of unimpacted PA6 structures after compression testing

Material	Compressive Modulus (MPa)	Compressive Strength (Mpa)	Energy Absorbed (J/m-3)
PA6			
Cell type			
Honeycomb	18.68	1.22	0.063
Re-entrant	18.48	1.57	0.112
Hybrid	19.81	1.36	0.089
PA6/1%GnPs			
Cell type			
Honeycomb	19.57	1.742	0.094
Re-entrant	18.85	1.75	0.131
Hybrid	13.65	1.17	0.079
PA6/2%GnPs			
Cell type			
Honeycomb	33.19	2.32	0.124
Re-entrant	19.08	3.58	0.274
Hybrid	32.29	2.34	0.151
PA6/3%GnPs			
Cell type			
Honeycomb	24.10	1.06	0.043
Re-entrant	17.61	1.74	0.128
Hybrid	15.82	1.28	0.092
PA6/4%GnPs			
Cell type			
Honeycomb	6.33	0.57	0.044
Re-entrant	5.18	0.43	0.031
Hybrid	6.57	0.62	0.043

Improvements were seen for sandwich structures with 3%GnPs when compared to their relatives with a lower filler concentration of 1%GnPs. The honeycomb and hybrid sandwich structures with 3%GnPs indicated 18.79% and 13.72% enhancement in its compressive modulus, respectively, when compared to its 1%GnPs relatives in Figure 5.3. An improvement of 8.59% in compressive strength was seen for the hybrid 3%GnPs compared to its relative with 1%GnPs in Figure 5.4. Additionally, the hybrid 3%GnPs structure in Figure 5.5 also showed superior energy absorbing properties in comparison to its 1%GnPs relative, indicating an enhancement of 14.26%. Nonetheless, enhancements were mostly noted for the hybrid sandwich structures at higher filler concentrations of 3%GnPs. Conversely, 4%GnPs had no overall improvement to the properties of the structures, thus resulting in significantly lower compressive properties

and energy absorption. In conclusion, a combination of filler concentration and the correct core topology needs to be considered, rather than considering them each in isolation.

5.3 Discussion

5.3.1 The Effect of Varying Concentrations of NH₂-GnPs in PA6

At higher concentrations of GnPs, i.e. 3% and 4%GnPs, it proved difficult to produce structures with high compressive properties and energy absorption. This was because the dispersion of GnPs within the PA6 structure becomes a concern resulting in agglomeration (Karevan et al., 2013; Wang et al., 2016; Seong & Kim, 2015). A rise in agglomeration results in a reduction of the sandwich structure's density. Since the GnPs occupy a large volume of the PA6 matrix, the occupation can result in void formation (Imran & Shivakumar, 2019). In addition, the combination of poor adhesion between the Amine-GnPs and the PA6 matrix, and agglomeration significantly affects the overall quality of the 3D printed sandwich structures at increased filler concentrations (Dul, Fambri and Pegoretti, 2016). Hence, the reduction in compressive properties (Figure 5.3 and Figure 5.4) and energy absorption capabilities (Figure 5.5) with filler concentrations of 4% and periodically at 3%GnPs, and the reduction in stress and strain capabilities, as seen in Figure 5.1.

5.3.1.1 The Polyamide Chain Structure with GnPs

The incrementation of GnP filler concentration resulted in a profound linear elastic response from an increase in stiffness, as revealed in Figure 5.1. As a result, there was an increase in their strain resistance, as shown in Figure 5.2, and a significant increase in compressive strength, as seen in Figure 5.4. This was on account of the GnPs interfering with the polymer chains and thus restricting chain mobility when undergoing compression and low-velocity impact (Kazemi-Khasragh et al., 2018). During the melt processing of GnPs and PA6, the extruded PA6/GnP filament approaches its glass transition temperature and undergoes crystallisation. The process of polymer chain confinement occurs at this stage from the large surface area of the GnPs incorporated (Seong & Kim, 2015). It is assumed that the added GnPs at higher filler concentrations might disrupt the crystallisation process, and possibly the crystal sizes, since the GnPs can produce a new and dominant crystal form within the polymer chains (Mindivan, 2016). Therefore, there is possibility of change in the molecular structure of PA6 with a rise in GnP concentration. This phenomenon arises from the incrementation of

functionalised GnPs which is denser and harder than the PA6 used, corresponding with the work of Li et al. (2019), Mindivan (2016), and Korkees et al. (2021). Therefore, the superiority in compressive modulus (Figure 5.3), compressive strength (Figure 5.4) and energy absorption (Figure 5.5) of the 2%GnPs sandwich structures are on account of the positive contribution and modification of its chain structure.

5.3.1.2 Micro-cracks and Coalescence

The enhancement of energy absorption demonstrated in Figure 5.5 with the reinforcement of GnPs is largely due to the unique characteristics of the functionalised nanoplatelets and their ability to absorb and dissipate energy within the structure. A ‘Micro-cracks and Coalescence Mechanism’ (MCM) occurs, as shown in Figure 5.15, whereby the GnPs develop micro-cracks around the rigid graphene nanoplatelet boundary as a result of local plastic deformation when undergoing compression or low-velocity impact (Yamamoto et al., 2019). The MCM defends the sandwich structure from progressive damage and further crack propagation under compressive force, and thus enhances its energy absorption capabilities (Yamamoto et al., 2019). This is shown in Figure 5.6, by the formation of micro-cracks which contribute to the absorption and dissipation of energy. Hence, it is assumed at higher quantities of GnPs, i.e. 4%GnPs, a lower fracture toughness would be observed, and therefore lower absorbed energy, as seen in Figure 5.5. This can be due to the increasing development of micro-crack coalescence from greater GnP concentration and the closer packing of neighbouring nanoplatelets (Figure 5.6). Consequently, with reference to Figure 5.5, Figure 5.6, and Figure 5.15, it is revealed that filler concentrations 1%GnPs and 2%GnPs indicate the onset of micro-crack initiation due to the lower concentration of platelets and an absence of coalescence with neighbouring GnPs. Therefore, 2%GnPs provided the appropriate concentration of GnPs which enhanced compressive modulus, strength, and energy absorption, promoting successful energy dissipation, as shown in Figure 5.5. In conclusion, the enhancement of properties for the sandwich structures depends on the degree of nanoplatelet dispersion in the PA6 matrix and the interfacial interaction between the GnPs and PA6 (Celasco et al., 2019).

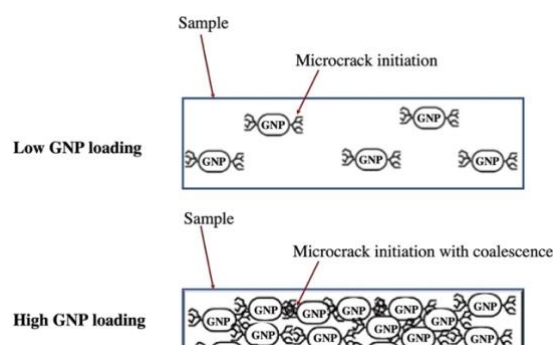


Figure 5.6 Illustration of the behaviour of micro-crack formation and coalescence at different filler concentrations (Yamamoto et al., 2019)

5.3.1.3 Interfacial Interaction of the NH_2 -GNPs and PA6 Matrix

As a result of the large specific area of the GNPs, a development of interfacial strength between the GNPs and PA6 occurs by Van der Waal's forces (Ma et al., 2013). An enhanced interfacial strength between the PA6 matrix and GNP reinforcement results in a structure that is capable of efficiently transferring stress from the polymer to the GNPs interface. Consequently, because of the excellent mechanical properties of graphene, such as its high specific stiffness and strength, alongside its 2D nature, this enables an effective coherence of properties between PA6 and GNPs to produce an enhanced structure (Chatterjee, Nafezarefi, et al., 2012). However, agglomeration disrupts the ability to promote adequate interfacial strength. The difficulty in appropriate dispersion and likelihood of agglomeration arises from the intermolecular forces within the stacked GNPs, and thus require appropriate exfoliation.

The twin-screw extruder provides the means to disperse the GNPs within the PA6 matrix in a well distributed manner when compared to other methods, such as in-situ polymerisation and solvent blending, or solution mixing to prepare PA6 reinforced with GNPs. Therefore, successful exfoliation can take place. It promotes disruption between the molecular interactions, i.e. the Van der Waals forces, $\pi - \pi$ stacking (Figure 5.7), and hydrophobic-hydrophobic interactions between the GNPs and the polymer interface. These interactions take place during melt processing and significantly affect the dispersion of GNPs (Zhang et al., 2015). The Van der Waal forces contribute greatly to the interfacial strength between the GNPs and the polymer used because of intimate contact and extensive specific surface area of the platelets (Aram et al., 2016). In addition, the $\pi - \pi$ stacking interactions between the layered GNPs result in restacking of the

platelets (Aram et al., 2016). Nonetheless, the hydrophobic-hydrophobic interactions are necessary for the binding of the GnPs in hydrophobic polymer matrices (Hu et al., 2014). Hence, the higher filler concentrations (4%GnPs) indicate a reduction in overall properties, as shown in Figures 5.3-5.5.

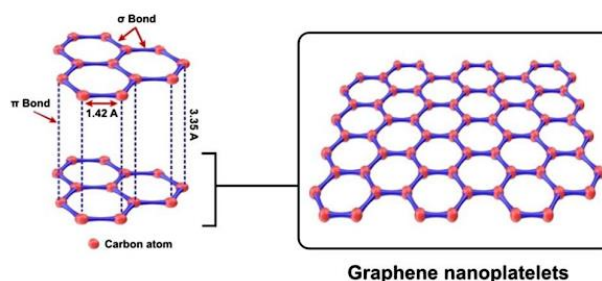


Figure 5.7 Atomic structure of GnPs (Madhad et al., 2021)

5.3.2 Melt Flow Rate and Chain Mobility

Common difficulties experienced with Polymer/GnP melts, is a reduction in the melt flow index (MFI) and an increase of viscosity with the addition of GnPs at a high filler concentration (Gomez et al., 2020). This was highlighted in the literature review in section 2.16. The quality of the resulting 3D printed structures depends significantly on the consistency of material in the nozzle of the 3D printer and the viscosity of the melt flow whilst undergoing extrusion; hence, highlighting the importance of it. Achieving suitable extrusion can determine the strength of the 3D printed sandwich structures, and thus extend its service life. Therefore, the material must be able to flow after fusion, and then solidify.

Commonly thermoplastic polymers are suited for this (González-Henríquez et al., 2019), however, the molecules in a semi-crystalline polymer, i.e., PA6, typically contain long chains that can become entangled with one another. Since the semi-crystalline chain mobility can be influenced with NH₂-GnP inclusion, it can affect the chosen print temperature and the quality of the extruded material (McKeen, 2012). Evidence shown in Tables 3.15-3.19 in Chapter 3, illustrates that there was a significant increase in melt temperature compared to the neat PA6 structures with the addition of GnPs in the polymer matrix. This is because the presence of GnPs creates hard regions within the polymer chains, consequentially limiting the mobilization of the polymer chains, resulting in mechanical interlocking (Karevan & Kalaitzidou, 2013; De et al., 2010). Figure 5.1 and Figures 5.3-5.5, demonstrate that the large restriction of chain movement significantly

increased the brittleness and stiffness of the GnP reinforced structures, in contrast to their neat PA6 relatives. Nevertheless, the pressure conditions required to extrude the semi-crystalline polymers can be controlled by tuning the temperature of the nozzle related to their gradual variation of viscosity as a function of temperature. The pressure conditions are controlled because as the temperature rises during 3D printing the force necessary to produce flow reduces (Karevan & Kalaitzidou, 2013). Although this was not necessary to perform for twin-screw extrusion (Tables 3.11-3.14), it was necessary for filament extrusion, as seen for Tables 3.15-3.19, and for 3D printing, as seen when comparing Table 3.23 to Table 3.24.

5.3.2.1 The Effect of Re-processing (Stages 1-3)

The PA6/GnP mixture was compounded more than once. First, it was mixed in the twin-screw extruder, then processed through the filament extruder, and lastly extruded by the 3D printer. Figure 5.8 shows stage 1, the melt compounding process, using the twin-screw extruder where the mixture of PA6/GnPs is converted into pellets. Stage 2 shows the pellets converted to a filament and wound onto a spool ready for stage 3, where it was 3D printed and compression tested in stage 4. It can be assumed, in relation to the processing routes and the studies mentioned in section 2.13.3.1, that a change in the material properties, i.e. stiffness, toughness, and strength, could transpire from processing at high temperatures more than once, and thus could have some effect to the results. However, the compressive properties in Figures 5.3-5.5, demonstrated greater influence from the filler concentrations rather than the effects of re-processing, evident by the differences in properties with incrementation of GnP concentrations.

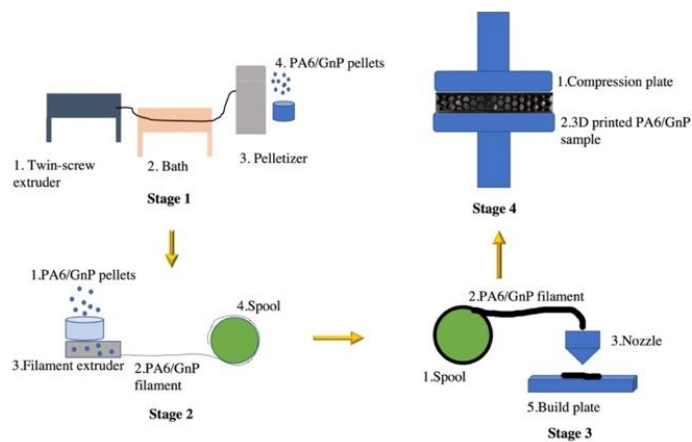


Figure 5.8 Diagram of the stages required to process PA6/GnP

5.3.2.2 Flowability of the Melt

Processing temperatures increased with the incrementation of GnPs between filament extrusion (Stage 2) and 3D printing extrusion (stage 3), as shown in Figure 5.8. and in Tables 3.15-3.19 and Table 3.23. Processing temperature and other parameters such as nozzle temperature, build plate temperature, layer thickness, and lower printing speeds are also important to consider because it is relevant in contributing to the printability of the sandwich structures (Goh et al., 2019). Furthermore, it is expected for there to be an increase in the flowability of the melt at low concentrations and increased viscosity at high concentrations (Altay et al., 2019). As a result, the low concentrations of GnPs (1% and 2%GnPs), showed improved flowability at a print head temperature of 260°C. However, higher GnP concentrations needed increased filament extrusion temperatures and print head temperatures exceeding 260°C to promote improved flowability. Consequentially, insufficient temperature adjustments made to the print head and filament maker with GnP reinforcement resulted in a restriction of extrusion (Chavarria et al., 2007; Mayoral et al., 2015). Therefore, it can be concluded that an increase in flowability revealed an improvement in printing ability, and hence improved compressive properties for structures such as the 2%GnPs sandwich structures in Figures 5.3-5.5 from successful printing quality.

Improved print quality for structures with lower filler concentrations could have resulted from a reduction in viscosity and the development of the lubricant effect (Gomez et al., 2020). Therefore, successful mechanical interlocking took place producing a plasticizing effect which was far superior in the 2%GnPs sandwich structures. The lubricant effect possibly promoted a reduction in the friction coefficient owing to the development of a nano-bearing layer (Eswaraiah et al., 2011). However, for filler concentrations of 3%-4%GnPs, the lubricant effect of the GnPs decreased from a rise in viscosity. As a result, a reduction in part quality can transpire. Therefore, higher compressive properties, as seen in Figure 5.3 and Figure 5.4, and an increase of absorbed energy, was seen in Figure 5.5 for structures containing 2%GnPs. Furthermore, it is believed that with the incrementation of filler concentration there was an increase of brittleness because of an altering of the crystalline phases α and γ of PA6 (Gomez et al., 2020; Korkees et al., 2021). On the contrary, the sandwich structures with lower filler concentrations, such as the 2%GnPs structure, improved the dispersion of GnPs (Figure

5.12 x3000SE image), improved the interfacial strength, and reduced aggregation of the GnPs within the matrix (Figure 5.12 x7000SE).

5.3.3 SEM Fractography Analysis

The objective of this section is to discuss the morphological state of the printed PA6/GnP structures to determine the state of dispersion of the GnPs, any likely defects, and their structure-property relationship. Uneven distribution of the GnPs and agglomeration can decrease the load-carrying ability of the sandwich structure, the GnPs within the polymer matrix, and its reinforcing phase, if not considered, hence the concern (Karevan & Kalaitzidou, 2013; Wan et al., 2013).

5.3.3.1 Dispersion and Agglomeration Analysis

Figure 5.9-Figure 5.13 show the fractured PA6/GnP sandwich nanocomposites for all filler concentrations. The GnPs are the reflective white structures, distinguishable by their sharp flake or plate-like features with respect to their orientation of embedment (for all x3000 and x7000 images). The surrounding matrix phase is resembled as the dark grey and black areas. Subsequently, images at x3000 SE, reveal that the increase of filler concentrations, i.e. 1-4%, was proportional to the rate of dispersion. The quantity of dispersed GnPs in the matrix, as seen in Figures 5.9-5.12, showed to increase from a rise in filler concentration. The different size variations and features of the platelets seen for filler concentrations 1%GnPs (Figure 5.9), 2%GnPs (Figure 5.10), and 4%GnPs (Figure 5.12), indicated acceptable exfoliation of the GnPs. This was due to the absence of agglomeration and the non-existent stacking between neighbouring platelets. Filler concentrations 1% and 2%GnPs, in Figure 5.9 and Figure 5.10, respectively, show that the bulk of GnPs exemplified suitable adhesion to the matrix. This was demonstrated by their successful embedment in the matrix, which revealed effective homogeneity, as shown in Figure 5.9 (images 1, 2, 3, 4 and 5) and in Figure 5.10 (images 1 and 3). The suitable bonding behaviour of the platelets can be due to the compatibility of the Amine functional groups and PA6 matrix, promoting improved interfacial bonding (Li et al., 2019). This prevents the number of aggregates seen with unfunctionalized GnPs, and so promotes improved dispersion in the PA6 matrix (Seong & Kim, 2015).

In contrast, Figure 5.11 showed significant aggregation of the GnPs in certain proximities of the PA6 matrix. Figure 5.11 (image x7000 SE) exhibited the region of agglomeration, seen as sharp translucent clusters of closely packed platelets. The

difficulty in dispersion was due to the presence of Van der Waal's forces amongst the layers of GnPs, which has caused reaggregation and stacking of the platelets (Aram et al., 2016; Park & Kim, 2014). Furthermore, the platelets in Figure 5.11 show deadhesion to the matrix, signifying a reduction in interfacial strength between the platelets and the polymer matrix, resulting in unsuccessful embedment. Consequently, Figures 5.3-5.5 exhibits the diminishment in compressive properties and energy absorption capabilities, respectively, when 3%GnPs are compared to lower filler concentrations. Nonetheless, due to the high concentrations of GnP inclusion, there are proximities of GnPs that have successfully adhered to the matrix, as shown in Figure 5.11 (image 1). Successful bonding can be identified when a GnP is flush with the matrix or when a large percentage of the platelets surface area is resting within the polymer, as illustrated in Figure 5.9 (images 5 and 6).

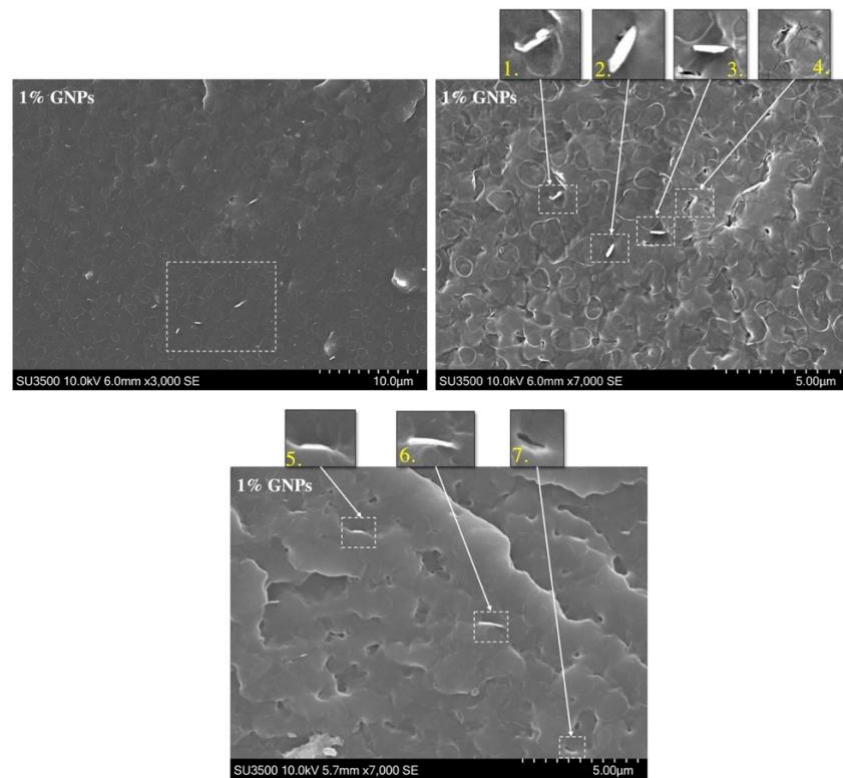


Figure 5.9 SEM images of PA6/1%GnP showing the fractured surface of the sandwich composite revealing the GnPs

5.3.3.2 Defects Analysis

Although the functionalised GnPs revealed consistent bonding, defects were noticeable at lower filler concentrations where Figure 5.9 (image 7) exhibits a pre-existing platelet zone indicating poor adhesion. A non-existent GnP could imply that there was a

lack of appropriate interfacial strength preventing the GnP from adhering to the matrix. The filler concentrations 2%, 3% and 4% in Figure 5.10 (image 4), Figure 5.11 (image x7000 SE and image 5) and Figure 5.12 (images 2, 3 and 6), respectively, revealed signs of wrinkling. This is a common defect witnessed for GnP- reinforced nanocomposites and indicates poor bonding to the matrix, and thus could result in the pre-existing platelet zones. Wrinkling results from non-uniform dispersion of the platelets and occasional overlapping of the GnPs (Naveen et al., 2019). Wrinkling of GnPs can also occur as the filler concentration increases (Li et al., 2019), evident in Figure 5.11 (image taken at x7000 SE) and Figure 5.12 (image 6), revealing the higher number of wrinkled GnPs. A larger number of wrinkled GnPs inhibits the sandwich structures from effectively transferring experienced compressive stress to the GnP interface (Chatterjee et al., 2012). As a result, the 4%GnP sandwich structures diminished significantly in compressive properties (Figure 5.3 and Figure 5.4) and energy absorption during compression (Figure 5.5).

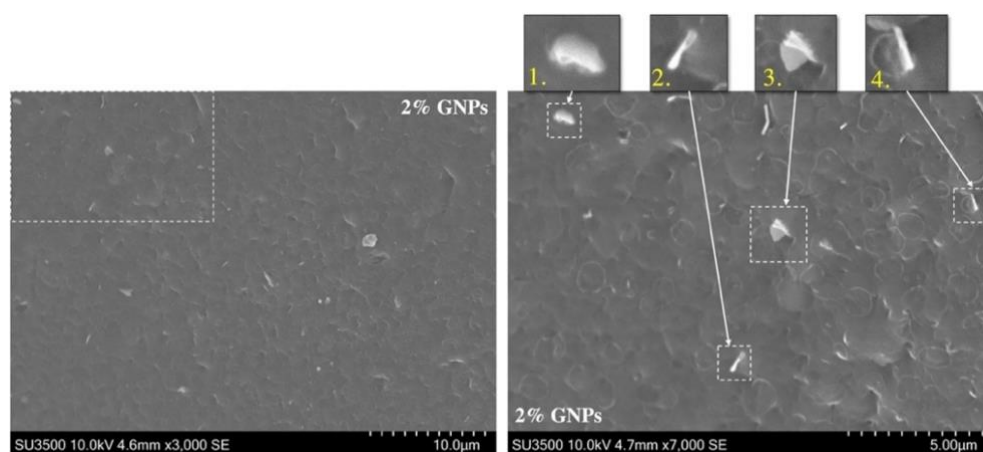


Figure 5.10 SEM images of PA6/2%GnP showing the fractured surface of the sandwich composite revealing the GnPs

It was revealed that there was increased signs of agglomeration, de-adhesion, and wrinkling occurring for sandwich structures with higher filler concentrations, as seen in Figure 5.11 and Figure 5.12. Therefore, stronger π - π interactions developed and a diminishment in appropriate exfoliation occurred (Li et al., 2019). Conversely, as seen in Figure 5.9 and Figure 5.10, it is possible that the mechanical shear forces produced by the twin-screw extruder successfully permitted exfoliation and dispersion of the platelets for the structures that contained lower filler concentrations. This is by reason of the high

shear forces overcoming the π - π interactions and Van der Waals forces, therefore resulting in less evident defects, such as wrinkling.

5.3.3.3 Toughening Mechanisms

The MCM, is the primary toughening mechanism taking place, as shown in Figure 5.9 (image 4), and Figure 5.13, where micro-crack development is revealed in close vicinity to individual GnPs (Figure 5.13, zone 1). Micro-crack propagation does not progress past the platelets but surrounds them due to their large surface area and significant rigidity. Hence, the MCM phenomenon promotes a toughening mechanism that results from plastic yielding of the matrix around the platelets and develops a crack deflection and crack pinning phenomenon, as illustrated in Figure 5.13 (image 1). Therefore, the crack plane is deflected by tilting or twisting of the GnPs, and thus crack propagation is pinned (Park et al., 2015). As a result of the platelets' high rigidity, areas of micro-cracks develop, as shown in Figure 5.13, and debonding of the GnPs from the matrix transpires (Figure 5.9, image 3). The process of crack pinning and the debonding of the platelets contributed significantly to toughening the sandwich structures (Ma et al., 2008; Opelt et al., 2015). Therefore, sandwich structures with GnP reinforcement exhibited superiority in energy absorption in contrast to their neat PA6 relatives, as shown in Figure 5.5.

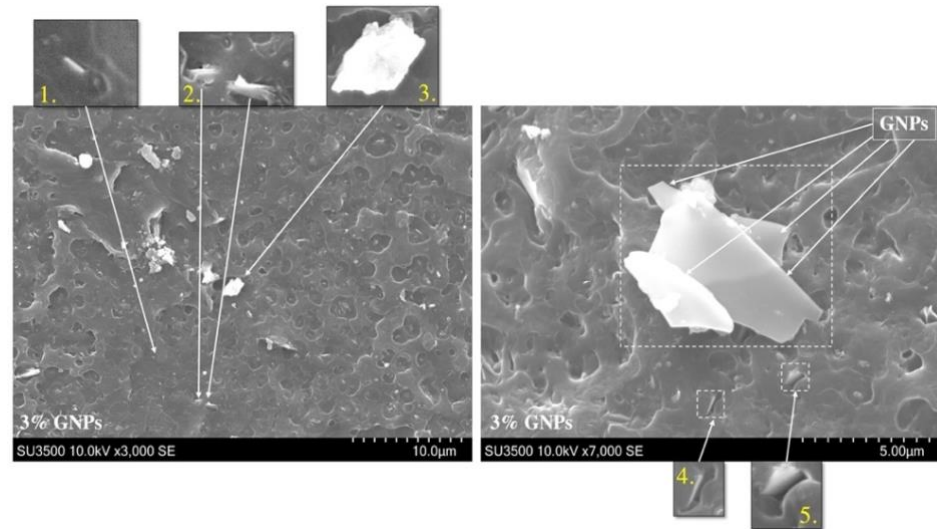


Figure 5.11 SEM images of PA6/3%GnP showing the fractured surface of the sandwich composite revealing the GnPs

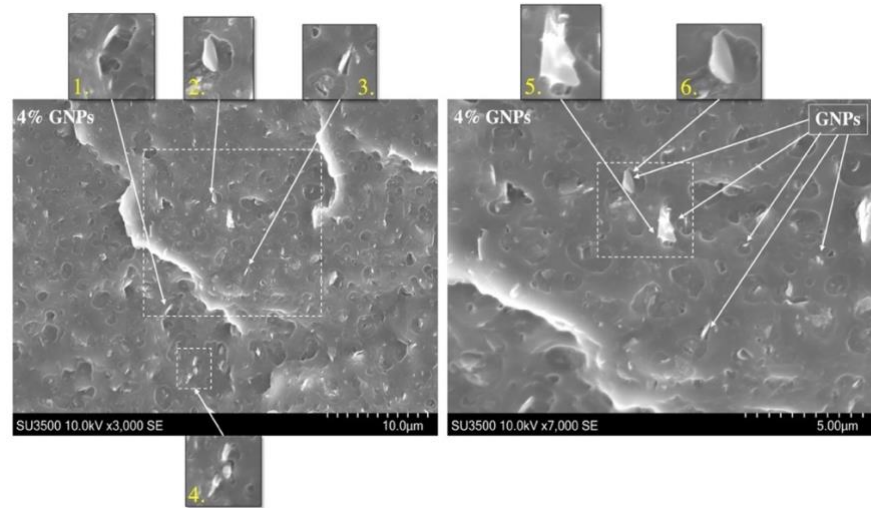


Figure 5.12 SEM images of PA6/4%GnP showing the fractured surface of the sandwich composite revealing the GnPs

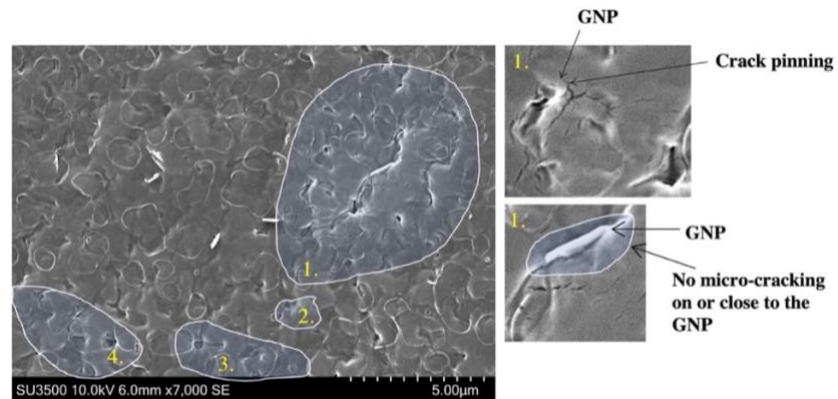


Figure 5.13 Micro-crack formation indicated in 4 different zones of the PA6/1%GnPs structure, where coalescing and crack pinning took place in zone 1

5.3.4 Failure Modes and Defect Analysis

This section evaluates the effects of the inclusion of GnPs on the inter-layer bonding of the sandwich structures at varying filler concentrations. The objective was to determine if damage was noticeable to the structures, i.e. if there was debonding of printed layers and fracturing of cells, after compression.

5.3.4.1 Inter-Layer Bonding

Figures 5.14-5.18 show HDoF images of the uniaxial compression tested sandwich structures. The red arrows represent node failure, the yellow arrows indicate layer separation, from either the face sheets, or separation between cell walls. The yellow circles represent inter-layer separation of the face sheets. All 3D printed sandwich

structures in Figures 5.14-5.18 indicated cell layer separation and cell separation from the face sheets. Inter-layer failure of the face sheets was identified for the 2%, 3% and 4%GnPs structures, as seen in Figure 5.16 (images d, e, and f), Figure 5.17 (images d and e) and Figure 5.18 (image d), respectively. Conversely, neat PA6 (Figure 5.14) and 1%GnPs (Figure 5.15) exhibited layer separation between cells and cell separation from the face sheets.

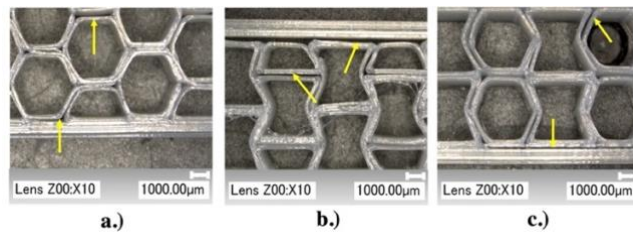


Figure 5.14 Neat PA6 honeycomb (a) re-entrant (b) and hybrid (c)

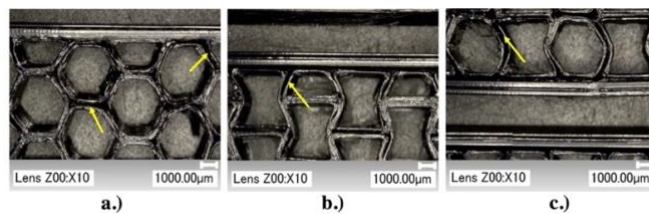


Figure 5.15 PA6/1%GnPs honeycomb (a) re-entrant (b) and hybrid (c)

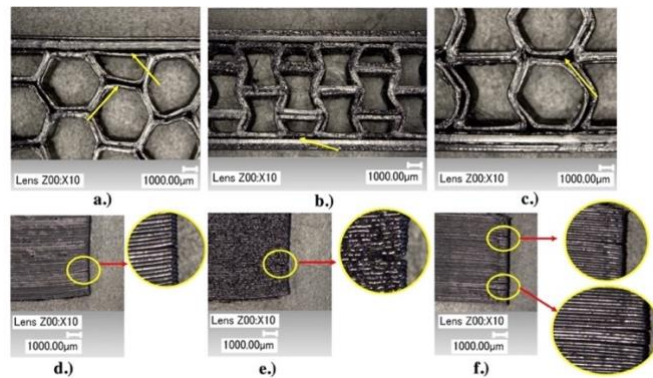


Figure 5.16 PA6/2%GnPs honeycomb (a) re-entrant (b) and hybrid (c) indicating layer failure for the honeycomb (d) layer failure for the re-entrant (e) and layer failure for the hybrid (f)

Inter-layer failure was common for the bulk of the structures and identified to occur at the edges, eventually propagating towards the centre of the structure and acting along the sandwich structure face sheets, as seen in Figure 5.17 (images d and e) and Figure 5.18 (image d). The separation between the printed layers in the face sheets and

for cells occurred because the compressive force was distributed to the individual cells of the structure; however, the cells could no longer sustain any additional force. This resulted in the failure of the layers between neighbouring cells upon full densification of the sandwich structures. This indicated that under compression there was a significant reliance on the interlamellar strength of the sandwich structures. Therefore, it can be assumed that inter-layer failure of the face sheets initiated from failure at the edges of the face sheets (Figure 5.16, images d, e and f) and the development of micro-cracks (Figure 5.13, image 1). This was due to changes in internal thermal stresses during printing, resulting in unsuccessful bonding of the layers and ultimately failure from an applied stress (Wei et al., 2015). In conclusion, all 3D printed sandwich structures exhibit a common layer failure between the cells in the sandwich structures and express less inclination to fail at the nodes during their deformation mechanisms. Due to the absence of an adhesive such as epoxy, there was no failure of the nodes bonded to the face sheets (Schaedler & Carter, 2016).

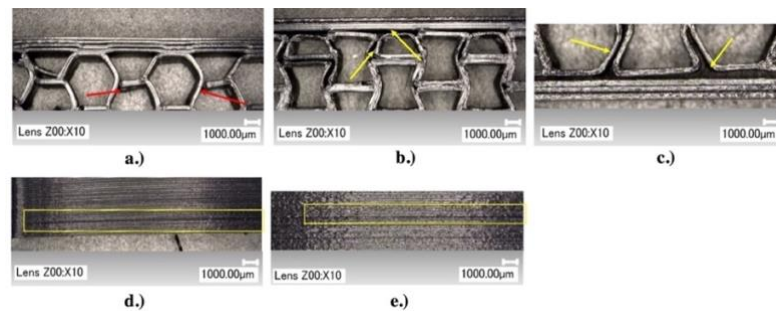


Figure 5.17 PA6/3%GnPs honeycomb (a) re-entrant (b) and hybrid (c) indicating layer failure for the honeycomb (d) and layer failure for the re-entrant (e)

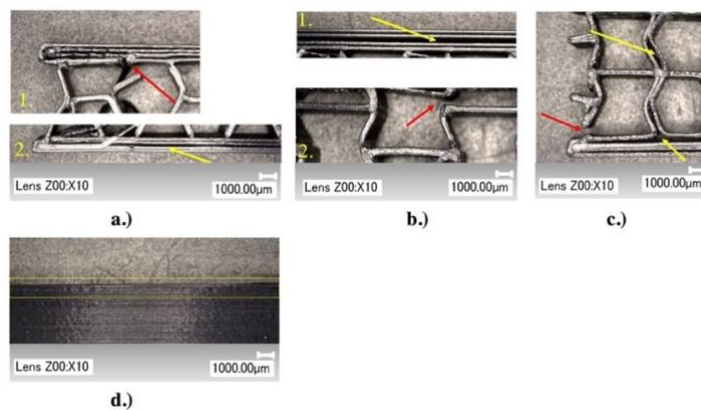


Figure 5.18 PA6/4%GnPs honeycomb (a) re-entrant (b) and the hybrid (c) indicating layer failure for the honeycomb (d)

5.3.4.2 Warping

The 2%GnPs structure showed signs of warping at the edges (see Figure 5.16 images d, e, and f). The inclusion of GnPs may have contributed to this print behaviour since the neat structures did not reveal commonality, suggesting that GnPs play a role in the de-bonding/de-adhesion of the printed layers. However, associations can also be attributed to the FFF printing technique. Issues associated with bed levelling, exposure to the environment for long periods of time, moisture absorption in the filament, and a high fan speed, resulting in excessive cooling are other contributors. This could occur by thermal stresses that arise as the melt solidifies and cools to the build environment temperature (Turner & Gold, 2015). Comparatively, uneven heat distributions produced by thermal gradients can also promote warpage and shrinkage of part structures, resulting in the delamination of layers (Figure 5.17 (image c)) or cracking of final printed parts (Anhua & Xingming, 2012; Wang et al., 2019; Zhang & Peng, 2012).

5.3.4.3 Node Failure

A comparison between Figures 5.14-5.18 exhibit node failure only occurring for the higher filler concentrations 3%GnPs (Figure 5.17) and 4%GnPs (Figure 5.18). This is believed to be related to the reduction in interfacial strength at higher filler concentrations, itself caused by a change in morphology, resulting in a weaker adhesion between printed layers, and for GnP-matrix adhesion (Park et al., 2015). Correspondingly, the natural inclination for the honeycomb cores to undergo a layer wise failure and buckling of the struts can contribute significantly to the failure of the nodes (Sarvestani et al., 2018). In addition, the anti-clockwise hinge rotation demonstrated by the re-entrant cells places large amounts of stress upon the nodes connected to the face-sheets. These high zones of stress directly propagate into the face sheets affecting the bonding strength between the layers in the face-sheet (Ingrole et al., 2016; Wang et al., 2021). Therefore, there is an evident indication that there is a reliance on the GnPs to provide strength to the interface, since lower filler concentrations revealed reduced node failure in the cores of the sandwich structures, as seen in Figure 5.15 and Figure 5.16.

A rise in ductility and reduction in stiffness for higher filler concentrations (3% and 4%GnPs), as shown in Figure 5.1 and Figure 5.3, respectively, indicates that a diminishment in strength occurs, as shown in Figure 5.4, which also effects node failure and similarly demonstrated by Yamamoto et al. (2019). Consequently, the core of the

sandwich structure suffers from failure since it bears a predominant part of the acting load in the in-plane orientation (Ruan et al., 2003). The rise in ductility from an increased filler concentration, therefore, results in a diminishment of the cores elastic deformation ability and overall diminishment in its compressive properties translating to node failure. Hence, the reduction in UCS for 4%GnPs structures in Figure 5.1 is due to the faster rate of cell collapse and greater node failure. In contrast to the structures with 1% and 2%GnPs, they will exhibit improved compressive modulus and strengths, as seen in Figure 5.3 and Figure 5.4, respectively, since their higher strengths and stiffness permit cells to bear a greater quantity of the compressive load to combat node failure.

5.3.4.4 The Effect of Voids

Raster width and voids are considered together in this section, since the gap between rasters determines the number of apparent voids within the matrix of the sandwich structures (Turner & Gold, 2015). The quality of a printed part can be severely affected by the presence of voids, and the inter-layer adhesion can become compromised, thus diminishing the compressive properties of the sandwich structures (Banjanin et al., 2018; Kabir et al., 2020a; Turner & Gold, 2015). This is because voids can inhibit the natural deformation mechanisms of the cells during compression, and they can affect the the GnPs ability to enhance the properties of the sandwich structures (Wang et al., 2019; Kabir, Mathur and Seyam, 2020).

Figure 5.19 exhibits SEM and HDoF images of the fractured surfaces of the 3D printed sandwich structures. The annotations indicate void concentrations and quality of inter-layer bonding. High void concentration was apparent in the SEM images for the 1%GnPs and 4%GnPs structures, as seen in Figure 5.19. The filler concentration of 4%GnPs indicated voids were larger in size when compared to lower filler concentrations, i.e. 2%GnPs and 3%GnPs. It was distinguished that the highest filler concentration showed the most significant void concentrations. As such, void concentration indicates direct proportionality to filler concentration. As a result, the voids had a detrimental effect on the compressive properties of the structures; therefore, producing the weakest compressive properties (Figure 5.3 and Figure 5.4) and the lowest energy absorbing capabilities (Figure 5.5). This suggests that sandwich structures with high void concentrations and large void sizes can result in a reduction of quality and property defection (Aumnate et al., 2018). Hence, 4%GnPs structures exhibit the most defective

and largest reduction in compressive properties and energy absorbing capabilities, as seen in Figures 5.3-5.5, respectively.

On the contrary, the SEM image in Figure 5.19 shows that 2%GnPs exhibited fewer void concentrations and resultingly produced superior compressive modulus and strength, as seen in Figure 5.3 and Figure 5.4, respectively. Additionally, 2%GnPs absorbed the largest amount of energy under compression, as seen in Figure 5.5. Therefore, the correct GnP concentration can prevent voids around their close vicinity, and it can protect the sandwich structure from compressive stress (Hsieh et al., 2010; Ma et al., 2008).

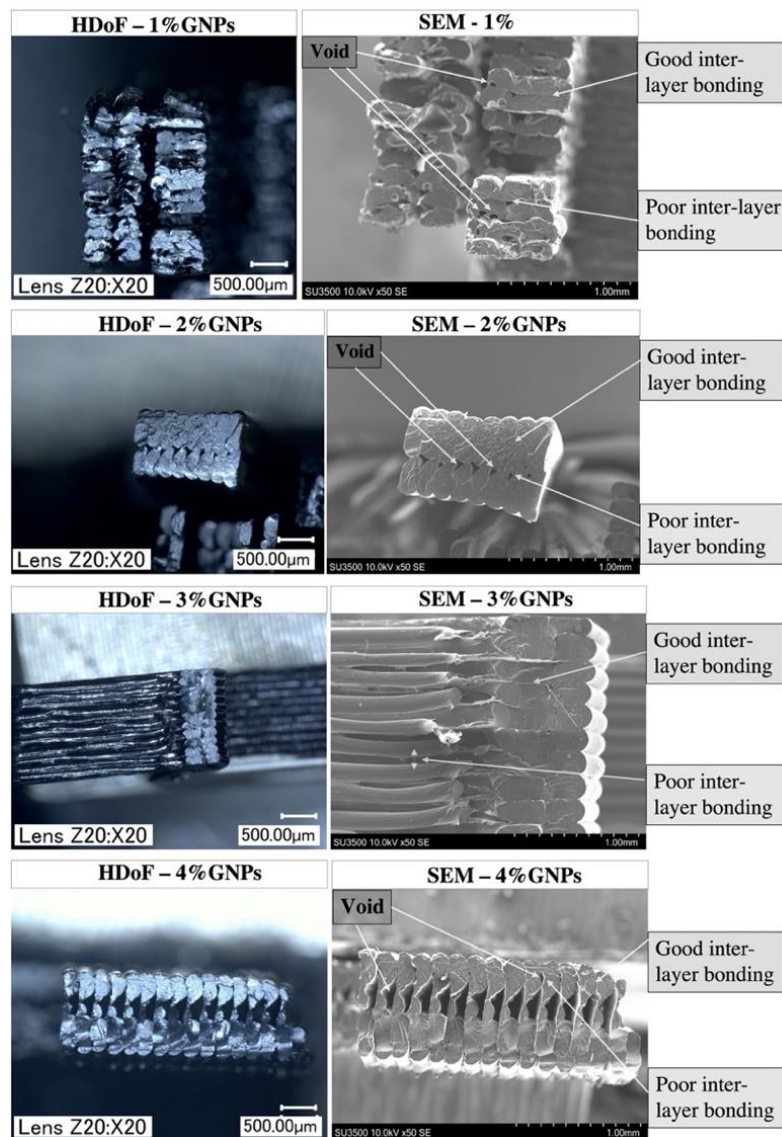


Figure 5.19 High depth of field images and SEM images of the fractured surfaces of the 3D printed sandwich structures where SEM images were taken at 10.0kV at x50 SE

5.3.4.5 Layer Adhesion

Poor inter-layer bonding was exhibited by all GnP reinforced structures, however, PA6/1%GnPs and PA6/4%GnPs saw the poorest inter-layer bonding in the SEM images of Figure 5.19. The PA6/1%GnPs (SEM image) structure in Figure 5.19, indicates that voids initiated between the layers of PA6 and propagate into individual layers of PA6, similarly seen by Wei et al. (2015). Filler concentrations 2% and 3%GnPs, as seen in Figure 5.19 (SEM images), showed improved inter-layer adhesion. Therefore, successful inter-layer adhesion meant the PA6/3%GnPs structures revealed notable improvement in their compressive properties in contrast to its 1%GnPs relative for the bulk of the hybrid sandwich structures in Figures 5.3-5.5.

The 3%GnPs in Figure 5.19 (SEM image) showed the individual layers in the core suffered from successful bonding, exposing large air gaps. Unsuccessful bonding in the cells resulted in poor compressive properties for the honeycomb and re-entrant sandwich structures with 3%GnPs reinforcement compared to their 1%GnPs relatives in Figures 5.3-5.5. Furthermore, void formations was found between the layers in Figure 5.19 for the 3%GnPs (SEM image) and this can be due to the state of the polymer melt changing with the addition of GnPs, thus resulting in an in-consistent flow of material from the print nozzle (Li et al., 2019), and possibly from an increase in aggregation and viscosity which can lead to nozzle clogging (Yamamoto et al., 2019). Moreover, along with these factors, agglomeration of the GnPs after melt blending, directly affects the FFF printing ability since the GnP dispersion homogeneity is also affected (Wei et al., 2015). Therefore, the PA6/GnP sandwich structures reveal significant reliance on the affinity between the GnPs and the PA6 matrix in order to improve print quality and reduce void formations (Chavarria et al., 2007).

5.3.4.6 Water Absorption of PA6

The hygroscopic nature of PA6 can catalyse the development of voids, and the volume of moisture absorption depends on the length of time PA6 is exposed to the ambient environment. The printed PA6/GnP filament was not enclosed during printing and thus can result in minor moisture absorption over time. Moisture absorption can translate to a plasticizing effect on the PA6 matrix, inducing dimensional changes and internal stresses, decreasing its compressive properties (Celestine & Zhu, 2017). This is evident for the micro-crack initiation sites revealed in Figure 5.13 (image 1) and the void

formations seen in Figure 5.19. Therefore, filler concentrations 1%GnPs and 4%GnPs potentially revealed greater moisture absorption, which can also contribute to the development of voids.

5.3.5 Deformation Stages of the Sandwich Structures

This section will discuss the differences in the deformation mechanisms of the various structures and the question of which cores exhibited superior compressive properties. An evaluation will also be made to determine which filler concentration is best suited to a specific core topology. Deformation mechanisms will not be discussed in detail here, as this has already been addressed in Chapter 4. Figure 5.20 illustrates the common in-plane deformation stages that the sandwich structures (honeycomb, re-entrant and hybrid) are expected to undergo, as illustrated with the re-entrant sandwich structure. Additionally, Figures 5.21-5.23 show stress-strain plots of all the neat PA6 sandwich structures where the stages in Figure 5.20 are annotated, thus, indicating the locations on the curve where the stages are expected to develop.

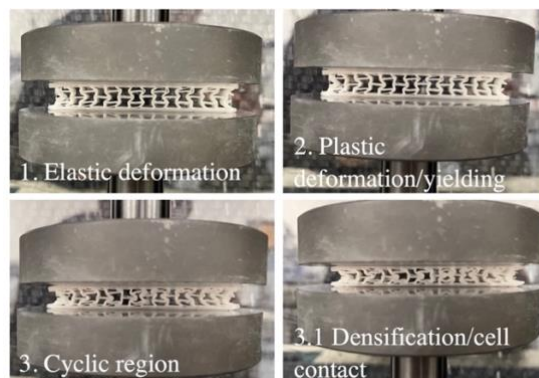


Figure 5.20 Elastic deformation stage of the re-entrant PA6 structure under compression (1.) Plastic deformation of the re-entrant PA6 structure under compression (2.) Cyclic region of the re-entrant PA6 structure under compression (3.) Densification of the re-entrant PA6 structure where cells make complete contact as the cyclic region progresses (3.1)

5.3.5.1 The Hybrid Sandwich Structures

Figure 5.21 shows a cyclic region and upward incremental trend in stress after the occurrence of plastic deformation and at the beginning of cell contact (point 3 in Figure 5.21 image 1). The initiation of the upward trends was similar to that seen in Chapter 4, where an increase in stress response was due to cell wall contact. The PA6 and

PA6/2%GnP structures exhibit a similar plastic response indicating a short period of deformation in the plastic deformation region. Consequently, this suggests that the hybrid structure could not support the acting load, showing a reduction in compressive strength (expressed previously in Figure 5.4) from the increased rate of cell contact. Despite this, the hybrid core topology indicated a tailoring of the sandwich structure properties influencing the effect of the filler concentration. It achieved a cyclic region and upward trend in stress because of the combination of the re-entrant and honeycomb cells. Subsequently, the diverse stress-strain curves, which are presented in Figure 5.21 (image 1 and 2), are due to the tailoring and control of the collapsing of cells within the whole structure. Hence, the graph results in an increasing stress trend since the failure of a set of cells (re-entrant + honeycomb = set) permitted the distribution of the experienced stress to the next set of neighbouring cells sequentially (Ingrole et al., 2017).

A steep upward behaviour of the curve was not replicated by the higher filler concentrations, i.e. 3 and 4%GnPs, as illustrated in Figure 5.21 (image 2). Instead, upward trends were gradual and occurred over continuous amounts of strain, thus exhibiting an increase of ductility at 3% and 4%GnPs concentrations. On the contrary, Figure 5.21 (image 2) exhibits cyclic behaviour for the 2%GnPs curve, hence, demonstrating superior compressive modulus and compressive strength, as shown in Figure 5.3 and Figure 5.4, respectively, when compared to the higher filler concentrations. The significant cyclic region seen by the 2%GnPs structure, resulted in higher energy absorption when compared to the lower filler concentrations with the same core topology, as seen in Figure 5.5. This is related to the greater compressive stress variation that occurs in the cyclic region, which in turn indicates that the sandwich structure is absorbing energy within the region until the final stage of cell contact is made (Yamashita & Gotoh, 2005). This phenomenon is also shared by the other core topologies in the following sections.

Consequently, with the incrementation of filler concentrations, the hybrid structures with 4%GnPs indicated a reduction in its cyclic region (Figure 5.21, image 2), and thus a reduction in energy in comparison to 2%GnPs, as seen in Figure 5.5. An assumption can be made that the increase of void concentration, higher filler concentration, and the increase of agglomeration, reduced inter-layer adhesion and thus reduced the hybrid core's ability to deform because of a reduction in strength and an earlier onset of failure. Moreover, the PA6/3%GnPs structure saw signs of brittleness, as depicted by the abrupt failure point on the curve in Figure 5.21 (image 2). This can be

due to the restriction of segmental motion in the polymer chains (Korkees et al., 2021; Karevan & Kalaitzidou, 2013), consequently resulting in fracturing of the hybrid cells under a compressive load.

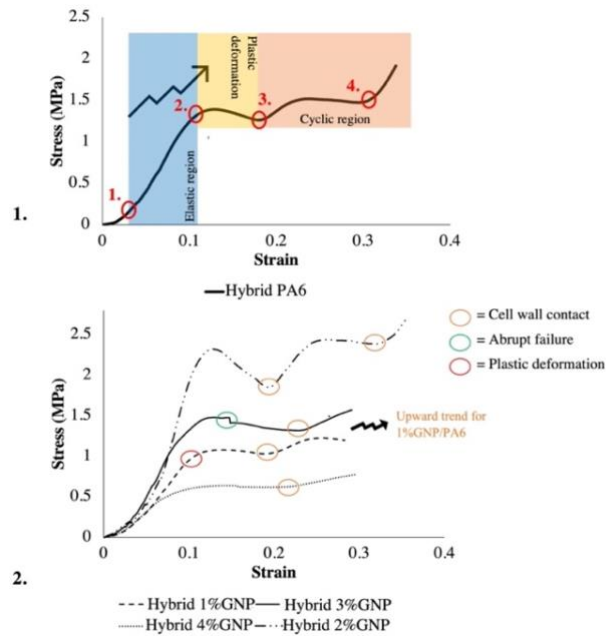


Figure 5.21 Stress-Strain graph of the hybrid cellular structure in image 1 indicating an upward trend (black arrow), showing the elastic region (1.) the plastic deformation region (2.) and the cyclic region, with cell contact (point 3) and cell contact (point 4) and a stress-strain graph of the reinforced hybrid structures in image 2

5.3.5.2 The Re-entrant Sandwich Structures

The re-entrant stress-strain curve is shown in Figure 5.22, indicating 4 points at which noticeable changes to the stress of the material were witnessed on the curve. The re-entrant sandwich structure showed a 23.07% higher elastic strain in comparison to the hybrid structure in Figure 5.21. This was related to the re-entrant's high compressive strength (Figure 5.4) exemplified by the larger cyclic region and higher steepness of the curve. Thus, there was less plastic deformation in between points 3 and 4, as shown in Figure 5.22. The cell wall collapse at point 4 led to a final stage of densification of the structure, therefore behaving similar to a monolithic structure promoting additional assistance to the structure, as similarly reported by Ingrole et al. (2017), and discussed in the previous chapter (Chapter 4, section 4.3.1). The steepness of the curve in the cyclic region can be accredited to the superior strength and deformation mechanisms of the auxetic re-entrant cells.

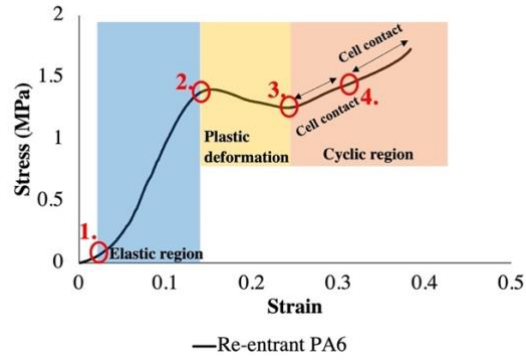


Figure 5.22 Stress-Strain graph of the re-entrant auxetic structure showing the elastic region (1.) the plastic deformation region (2.) the cyclic region and cell contact (3.) and cell contact (4.)

Previously, Figure 5.1 indicated that the reinforced re-entrant sandwich structures saw no catastrophic failure points and thus successful stress distribution of the re-entrant sandwich structure. All reinforced re-entrant sandwich structures revealed cyclic regions, which was similarly seen for the hybrid structure in Figure 5.21, indicating cell wall contact and appropriate deformation of the re-entrant core. On the contrary, the 1%GnPs structure failed at an 8.69% lower strain than its neat PA6 relative (Figure 5.1). The 2%GnPs structure in Figure 5.1 showed an abrupt increase of stress that occurred at 3.9 MPa, thus demonstrating the superior compressive strength (Figure 5.4) of the re-entrant 2%GnPs structure. Overall, the large area under the curve, as depicted in Figure 5.1, revealed that the re-entrant cores absorbed the largest amount of energy when compared to the honeycomb and hybrid cores, as seen in the table in Figure 5.5. However, at 3%GnPs, the re-entrant core showed increased signs of ductility and a reduction in strength, exemplified by the smaller region of the cyclic region in Figure 5.1. This was similarly experienced by the hybrid 3%GnPs structure in Figure 5.21. The reduction in its cyclic region resulted in the reduction of energy absorption, as seen in Figure 5.5, compared to its relatives. Cyclic regions reduced with increased filler concentrations because rates of cell contact increased in comparison to neat PA6, 1%GnPs and 2%GnPs, as shown in Figure 5.22. Therefore, the deformation mechanisms of the cells were significantly relevant to the compressive stress variation resembled on the curves in Figure 5.1.

Moreover, Figure 5.1 indicated that at 4%GnPs points of cell failure was more evident on the stress-strain curve, expressing sharper zones of cell failure, and thus

signifying a more brittle behaviour and greater catastrophic failure. The first failure of cells was witnessed at 0.36 MPa (Figure 5.1), which indicated minor points of potential node failure, evident in Figure 5.18 (image b). After that, the structure continued to carry higher loads before eventually failing at 0.42 MPa. This translated into the cyclic region where more failure of cells occurred at 0.49 MPa, resulting in an upward trend of the curve. In conclusion, with higher GnP concentrations the re-entrant structure indicated greater node failure which resulted in greater cell wall collapse and faster contact with neighbouring cells. Because of the auxetic nature of the re-entrant cells in combination with the filler concentration, a greater cyclic behaviour was witnessed for the re-entrant sandwich structures.

5.3.5.3 The Honeycomb Sandwich Structures

Figure 5.23 exhibits the behaviour of the PA6 honeycomb structure, demonstrating its cyclic pattern, similarly resembling that of the re-entrant and hybrid structures as seen in Figure 5.21 and Figure 5.22, respectively. Contrary to the hybrid and re-entrant structures, the honeycomb PA6 in Figure 5.23 exhibited a significant reduction in stress after significant plastic deformation at point 2, and layer deadhesion, as shown in Figure 5.14 (image a) until point 3 was reached. Additionally, an insignificant increase of stress was noted after point 3 at a strain of 0.2, however, a continuation in the reduction of stress was seen approaching point 4. Cell contacts at point 4 resulted in a significant increase of stress, indicating that complete core densification was reached. The honeycomb core showed reliance on the bending moment of the nodes, as discussed in Chapter 4 in section 4.2.1. As such, the honeycomb PA6 structure indicated a downward trend in stress, rather than incremental increases.

The reduction of stress between points 3 and 4 can be a consequence of the rotational moment of the nodes, inducing hinge rotation, eventually resulting in an elastic-plastic collapse and layer wise failure of the core (Hönig & Stronge, 2002) (see Chapter 4, section 4.14.1). As a result of this, alongside a reduction in strength of individual cells that have plastically failed, it generates a downward trend of stress on the curve. A comparison between the re-entrant and honeycomb deformation is distinguished in Figure 5.24, where n represents the nodes, l is the length of the inclined strut, h is the length of the vertical strut, θ is the angle of the inclined strut, F is the force applied from compression, and the red lines indicate the walls mostly likely to make contact first as

compression proceeds (Qiao & Chen, 2016). Similarly, the reinforced honeycomb sandwich structures in Figure 5.1 indicated this behaviour, correlating well with Liu et al. (2016).

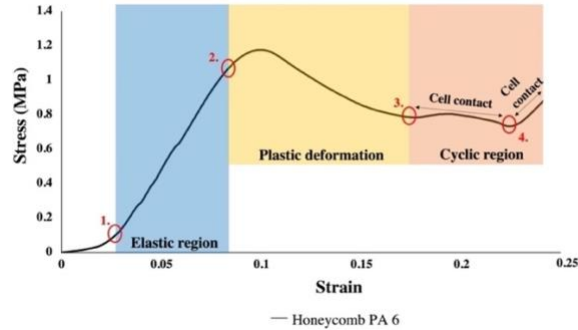


Figure 5.23 Stress-Strain graph of the honeycomb 1%GnPs cellular structure showing the elastic region (1.) the plastic deformation region (2.) the cyclic region and cell contact (3.) and cell contact (4.)

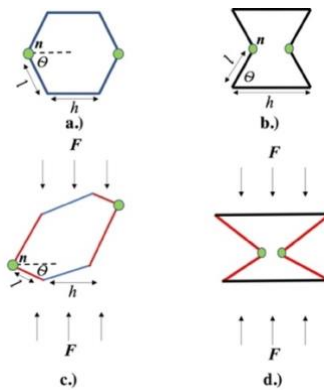


Figure 5.24 Illustration of the honeycomb cell (a.) and how it deforms under compression (b.) and the re-entrant cell (c.) and how it deforms under compression (d.) whilst representing how walls and nodes react under the load

Earlier in Figure 5.1 it revealed that the 2%GnPs filler concentration with honeycomb core topology indicated a more apparent downward trend and no cyclic behaviour, demonstrating why its energy absorption was 35.20% and 34.64% lower than the re-entrant and hybrid structure, respectively. Nevertheless, the increase of filler concentration aided the structure in its compressive strength (Figure 5.4). This promoted enhanced hinge rotation and improved the strength of the nodes whilst undergoing its rotational moment, hence the larger growth in stress, as seen in Figure 5.1. Moreover, at filler concentrations 3%GnPs and 4%GnPs the honeycomb structure indicated no cyclic

behaviour (Figure 5.1). Therefore, the increase of brittleness and greater defects within the matrix reduced the compressive properties and the energy absorption capabilities, as seen in Figures 5.3-5.5.

In conclusion, the GnP concentrations for the bulk of the sandwich structures determined the amount of stress and strain the sandwich structures could manage; however, the core topology determined the trend of the curve, the number of cell contacts made, and the size of the cyclic region.

5.3.6 Relative Cell Densities

The relative cell density can support the reason for structures indicating higher/lower resistance to bending or cells collapsing. It can also indicate the reasons for the difference in compressive modulus, compressive strength, absorbed energy and the deviation of plateau stresses from one another.

Cell wall thickness contributes mainly to the relative densities of the structures, thus, all cell walls of the printed sandwich structures contained identical thicknesses. The relative cell densities were calculated by Equation (8), Equation (9), and Equation (10) and were utilised for the honeycomb structures, the re-entrant structures, and the hybrid structures, respectively. Equation was similarly used by Bitzer (1997), where ρ^* and ρ_s denote the densities of the unit cell and bulk material, which in this case is PA6/GnPs, respectively. Variable h is the length of the vertical strut, θ is the angle of the inclined strut, l represents the length of the inclined strut, and t is the thickness of the struts. Equations (2) and (3) were extracted from Ingrole et al. (2017) expressing similar work done on 3D printed cellular structures where Equation (2) was derived similarly to that of the honeycomb. Equation (3) was calculated considering the unit cell of the honeycomb, and the unit cell of the re-entrant cell. Consequently, suffix a is a denotation for the auxetic re-entrant cell and h for the honeycomb unit cell. Therefore, tabulated in Table 5.2 are the dimensions for all sandwich structures and their relative cell densities.

Relative cell density equation for the honeycomb:

$$\frac{\rho^*}{\rho_s} = \frac{\frac{t}{l}(\frac{h}{l} + 2)}{2\cos\theta(\frac{h}{l} + \sin\theta)} \quad (8)$$

Relative cell density equation for the re-entrant:

$$\frac{\rho^*}{\rho_s} = \frac{2lt + 1.75ht + 2t^2}{3ht + 2hl\cos\theta + 3ltsin\theta + 2l^2sin\theta\cos\theta} \quad (9)$$

Relative cell density equation for the hybrid:

$$\frac{\rho^*}{\rho_s} = \frac{4l_a t + 4h_a t + 4l_h t + 0.5h_h t + 3t^2}{(2h_a - 2lsin\theta)(2l_a\cos\theta + 2l_h\cos\theta + 2t)} \quad (10)$$

Table 5.2 Design parameters for the cellular structures

Design	h (mm)	l (mm)	t (mm)	$\theta(^{\circ})$	ρ^*/ρ_s
Honeycomb	3	3	0.6	120	0.2331
Re-entrant	6	6	0.6	60	0.1628
Hybrid	N/a	N/a	N/a	N/a	0.4759

Table 5.2 shows that the hybrid structure experienced the highest relative cell density, and the re-entrant structure experienced the lowest relative cell density. Commonly, higher relative cell densities can result in greater shear strengths, as also seen by Li & Wang (2017). On the contrary, if the relative cell density for the re-entrant structure is too high it can result in a reduction of cyclic behaviour. An increase in relative cell density can also result in an increase in cell wall thickness, thus making the cell structure more susceptible to brittle failure due to the restriction and buckling of ligaments (Li & Wang, 2017). This phenomenon can be seen in Figure 5.21 (image 1), which shows the neat hybrid PA6 displaying a reduction in cyclic behaviour, due to its greater relative cell density as compared to Figure 5.22 and Figure 5.23.

The honeycomb exhibits greater buckling loads than the hybrid, thus promoting a higher maximum peak force with increasing GnP concentration, as similarly seen by Sarvestani et al. (2018). Conversely, too high of a relative cell density can reduce energy absorption, especially for in-plane structures (Sarvestani et al., 2018). On the contrary, Figure 5.14 reveals that there were no obvious signs of brittle failure, macroscopically, for the neat structures, indicating appropriate relative cell densities. Moreover, the calculated relative cell densities as shown in Table 5.2, promoted successful global deformation patterns for the sandwich structures. Subsequently, core topology revealed to have a large influence over the outcome of the compressive properties and energy absorption and deformation mechanisms of the sandwich structures when paired with an appropriate relative cell density (Li & Wang, 2017). In conclusion, the calculated relative cell densities permitted successful buckling of ligaments hindering the occurrence of

fractured cells for neat and lower filler concentrations, i.e. neat PA6, 1%GnPs and 2%GnPs, as seen in Figures 5.14-5.18. It also permitted appropriate cyclic behaviour, as seen in Figures 5.21-5.23, promoting sufficient energy absorbing capabilities for the sandwich structures.

5.3.7 Effects of Screw Speed

The type of extruder used and the amount of shear it produces from the screw speed have significant implications on the morphology, the modulus, yield strength, and impact resistance of PA6 nanocomposites (Chavarria et al., 2007; Cho & Paul, 2001; Dennis et al., 2001).

The importance of ‘screw speed’ in the twin-screw extruder was evident throughout the results. Tables 3.11-3.14 in Chapter 3 indicated that neat PA6 was processed with a screw speed of 3 rpm. This was sufficient for melt compounding, whereas PA6/GnP mixtures required screw speeds of 3.8 rpm. An increase in screw speed increased the shear forces and improved the mixing energy. As such there was a reduction in agglomerate size translating to an enhancement of distribution and dispersion, ultimately enhancing the bulk properties of the sandwich composites (Mayoral et al., 2015; Khanam et al., 2016). The increase of screw speed indicated appropriate dispersion of the GnPs even at 4%GnPs concentration, as seen in Figure 5.12 (image taken at x3000 SE).

It is possible that at high filler concentrations, the high mixing energy from the increase in screw speed still did not exfoliate the GnPs entirely. This is indicated by Figure 5.11 (image taken at x7000 SE). This is important for property improvements to be noted since enhancements usually rely on the degree of exfoliation. Hence, the reduction exhibited for the compressive properties (Figure 5.3 and Figure 5.4) and energy absorption (Figure 5.5) of 3%GnPs and 4%GnPs compared to 2%GnPs. This is because, with an increase in GnP concentration, there is an increased difficulty of successful exfoliation even at high screw speeds from the increased ratio of π - π interactions and intermolecular forces taking place (Dennis et al., 2001).

5.4 Low-Velocity Impact Results of the Sandwich Structures

The objective of this section and those to follow is to consider if damage imposed by low-velocity impact influenced the deformation mechanisms of all the sandwich

structure cores and if it reduced their compressive modulus, compressive strength, and energy absorption properties. An evaluation will be done to investigate if the addition of GnPs enhanced the residual compressive properties of the structures when compared to neat structures and unimpacted structures, and to what degree properties were lost.

Figure 5.25 shows the stress-strain curves for all the sandwich structures impacted at 5N (2J). Table 5.3 exhibits a matrix of the sandwich structures that passed and those that failed at the energy they were impacted. Passed structures relate to those with damage to the core, damage to the face sheets or both, permitting the structures to still undergo compression testing. Conversely, the failed structures were those that showed a catastrophic failure to the core, damage to the face sheets, or both, with no possibility to undergo compression testing. Furthermore, Figures 5.26-5.28 show the compressive modulus, compressive strength, and energy absorbed charts, respectively, compared to the unimpacted sandwich structures discussed in the previous section. The tables alongside the charts displayed in Figures 5.26-5.28 are the average values for each cell topology that was impacted under low-velocity, where the bold integer represents the highest obtained value.

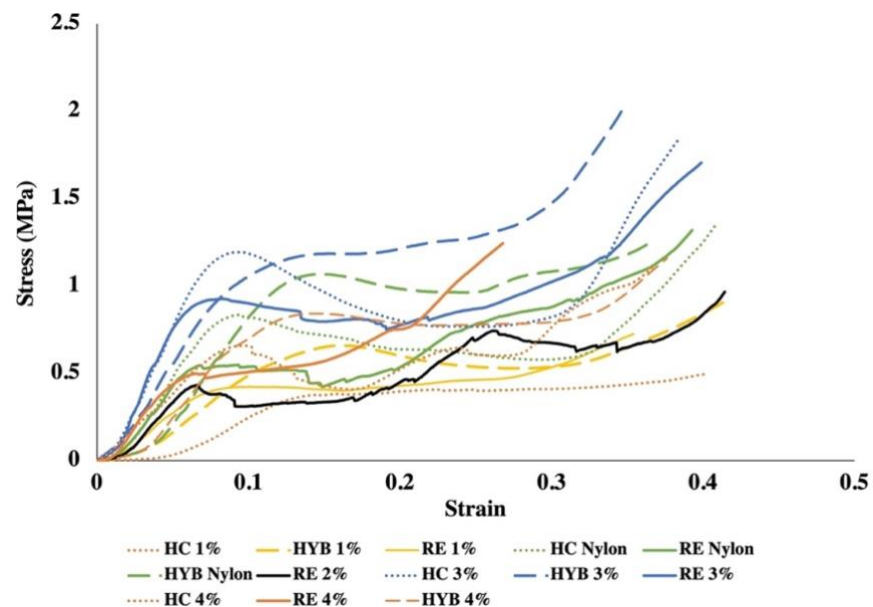


Figure 5.25 Stress-strain graph of all impacted cellular PA6/GnP structures

Table 5.3 Passed and failed structures impacted with 5N at an impact energy of 2J and height of 0.25m

Impacted PA6/GnP structures				
	Impact energy			
	2J			
Cellular structure/GnP (%)	1%	2%	3%	4%
Honeycomb GnP	Pass	Fail	Pass	Pass
Honeycomb neat PA6	Pass			
Re-entrant GnP	Pass	Pass	Pass	Pass
Re-entrant neat PA6	Pass			
Hybrid GnP	Pass	Fail	Pass	Pass
Hybrid neat PA6	Pass			

5.4.1 Compressive Modulus of all Cores

A significant reduction in compressive modulus was experienced for all sandwich structures impacted at 2J, as seen in Figure 5.26. The residual compressive modulus did not exceed that of the unimpacted sandwich structures and indicated that low-velocity impact was detrimental to the sandwich structures properties.

After damage imposed from impact, Figure 5.26 shows that the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures experienced a 43.63%, 42.04% and 63.69% reduction in compressive modulus, respectively. The honeycomb 1%GnPs, re-entrant 1%GnPs and hybrid 1%GnPs saw a reduction of 75.60%, 71.08% and 69.50%, respectively after damage imposed from impact. Subsequently, the honeycomb 2%GnPs and hybrid 2%GnPs failed catastrophically, whereas the re-entrant 2%GnPs that underwent a CAI test did not fail and saw a reduction of 42.92% in compressive modulus after damage imposed from impact. The honeycomb 3%GnPs, re-entrant 3%GnPs and hybrid 3%GnPs saw a reduction of 4.73%, an increase of 16.97% and a reduction of 17.63% in compressive modulus, respectively, after damage imposed from impact. Finally, the honeycomb 4%GnPs, re-entrant 4%GnPs and hybrid 4%GnPs saw an increase of 19.77%, an increase of 61.97% and a reduction of 25.16% in compressive modulus, respectively, after damage imposed from impact. Consequently, an increase in filler concentration resulted in higher residual properties, and the highest residual compressive modulus in Figure 5.26 was obtained by the honeycomb structure with a 3% filler concentration. As a result, the concentrations above 1%GnPs indicated effective toughening mechanisms against low-

velocity impact, suggesting they are the correct concentrations to deflect and pin crack propagations (Park et al., 2015).

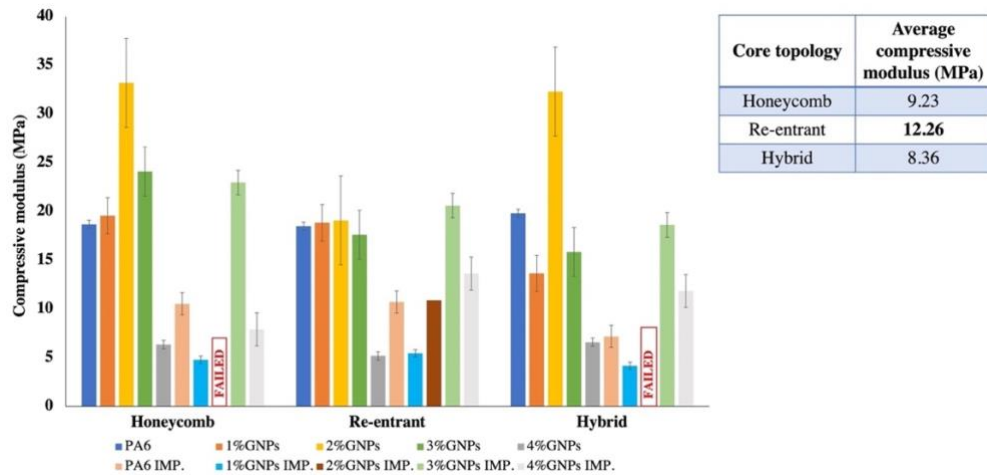


Figure 5.26 Compressive modulus chart of impacted PA6/GnP structures vs unimpacted structures PA6/GnP structures

5.4.2 Compressive Strength of all Cores

The residual compressive strength values did not exceed the unimpacted sandwich structures. After low-velocity impact, Figure 5.27 shows that the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures experienced a 27.87%, 63.69% and 17.65% reduction in compressive strength, respectively. Subsequently, the honeycomb 1%GnPs, re-entrant 1%GnPs and hybrid 1%GnPs saw a reduction of 77.32%, 76% and 42.74% in compressive strength, respectively, after low-velocity impact. The honeycomb 2%GnPs and hybrid 2%GnPs resulted in the failure of the core structure and an inability to CAI test the structures. Furthermore, the re-entrant 2%GnPs passed impact testing (revealed in Table 5.3) and saw an 85.47% reduction in compressive strength. The honeycomb 3%GnPs, re-entrant 3%GnPs and hybrid 3%GnPs saw an increase of 17.18%, a reduction of 43.68% and a reduction of 3.13% in compressive strength, respectively, after low-velocity impact. Finally, the honeycomb 4%GnPs, re-entrant 4%GnPs and hybrid 4%GnPs saw an increase of 13.63%, 12.23% and an increase of 62.30% in compressive strength, respectively, after low-velocity impact. Consequently, the damage imposed on the sandwich structures from low-velocity impact reduced the compressive strength of the structures. In conclusion, the residual compressive strength increased with incrementation of filler concentrations, since compressive strength increased at filler concentrations 3%

and 4%GnPs in comparison to 1% and 2%GnPs, as seen in Figure 5.27. Overall, the honeycomb 3%GnPs structure demonstrated superior residual compressive strength properties.

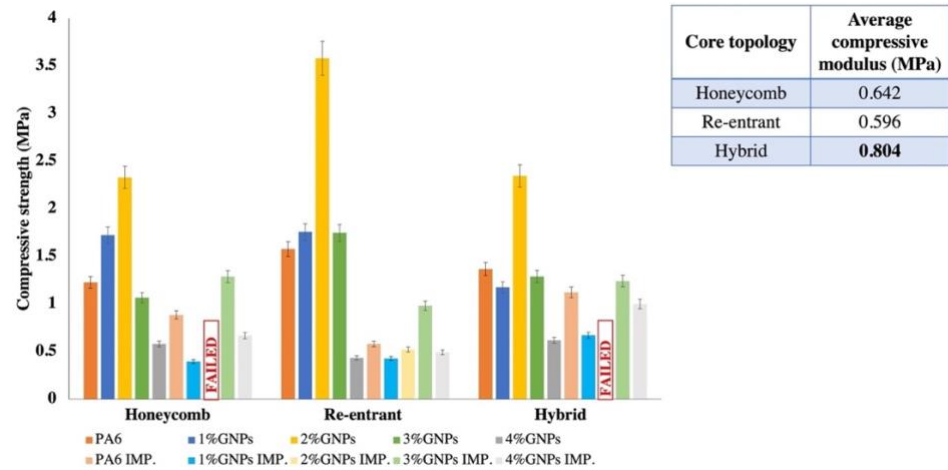


Figure 5.27 Compressive strength chart of impacted PA6/GnP structures vs unimpacted PA6/GnP structures

5.4.3 Energy Absorption of all Cores

After low-velocity impact, Figure 5.28 shows that the energy absorption capabilities for the neat honeycomb PA6, the neat re-entrant PA6 sandwich structure, and the neat hybrid PA6 sandwich structures experienced a 33.33%, 81.82% and 1.59% reduction in energy absorbed, respectively. The honeycomb 1%GnPs, re-entrant 1%GnPs and hybrid 1%GnPs saw a reduction of 62.82%, 81.56% and 27.99% in energy absorbed, respectively, after low-velocity impact. Moreover, the honeycomb 2%GnPs and hybrid 2%GnPs structures resulted in failure of the core and an inability to CAI test the structures. However, the re-entrant 2%GnPs passed impact testing (as seen in Table 5.3) and saw a 92.72% reduction in energy absorbed after low-velocity impact. Subsequently, the honeycomb 3%GnPs, re-entrant 3%GnPs and hybrid 3%GnPs experienced an increase of 51.71%, a reduction of 75.10% and a 4.33% reduction in energy absorbed, respectively, after low-velocity impact. Finally, the honeycomb 4%GnPs, re-entrant 4%GnPs and hybrid 4%GnPs saw a reduction of 22.03%, a reduction of 41.29% and an increase of 85.04% in energy absorbed, respectively, after low-velocity impact. Overall, the re-entrant sandwich structure experienced the largest diminishment in energy absorption after low-velocity impact. Figure 5.28 reveals that the energy absorption capabilities reduced for all the sandwich structures during compression because of

damage from low-velocity impact. The residual energy absorption capabilities did not exceed the unimpacted sandwich structures. In conclusion, the hybrid structure containing 3%GnPs exhibited superiority in its residual properties. It was demonstrated that the optimum filler concentration to enhance residual compressive properties for all core types was 3%GnPs.

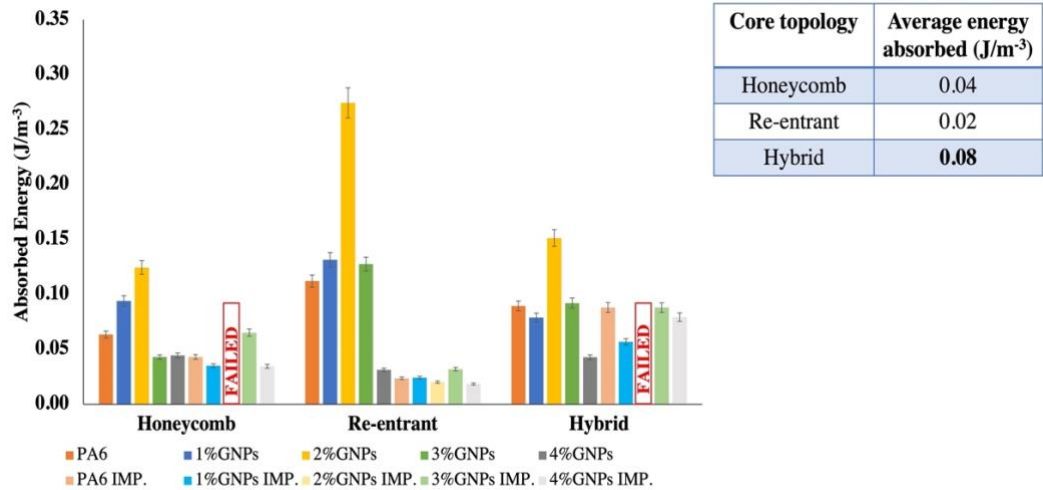


Figure 5.28 Absorbed energy chart of impacted PA6/GnP structures vs unimpacted PA6/GnP structures

5.5 Discussion

5.5.1 Deformation Stages of the Honeycomb Sandwich Structures

The stress-strain curves in Figure 5.25 demonstrated similar ductile features to that seen for the curves in Figure 5.1. For the bulk of the impacted neat structures and those with low filler concentrations, i.e., 1% and 2%GnPs, there were no prominent regions displaying evident brittle deformation behaviour of the cells after impact. Instead, the curves resembled a linear elastic response and eventual plastic deformation until cell contact transpired, leading ultimately to failure.

Honeycomb sandwich structures with high filler concentrations, i.e. 3% and 4%GnPs, displayed prominent occurrences of local catastrophic failure, signs of cell wall contact, and cell densification on the curves as seen in Figure 5.25. This is exemplified by the honeycomb 4%GnPs (IMP.) structure as shown in Figure 5.29, where the transition regions are annotated by the numbers, the cell contact regions are annotated by red circles, and the brittle failure regions of the honeycomb structure are annotated by the purple

circles on the curve. Figure 5.29 (HC 4%GnPs IMP.) revealed that after plastic deformation, at point 2, plastic failure of individual cells initiated.

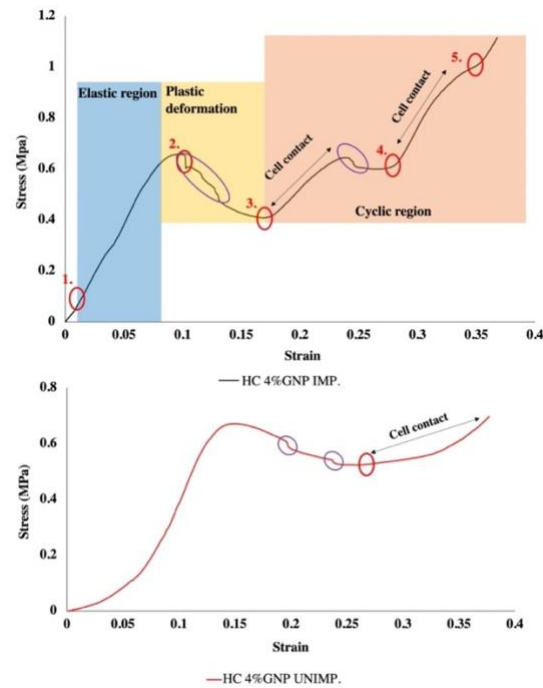


Figure 5.29 Stress-strain curve of the PA6/4%GnPs honeycomb structure after being impacted by 2J and the stress-strain curve of the PA6/4%GnPs honeycomb structure that was unimpacted

This can be due to possible micro-crack propagations that developed from low-velocity impact damage (Wang et al., 2019), in addition to the possibility of high void concentration and inter-layer failure, as seen in Figures 5.9-5.13. Catastrophic cell failure was exhibited by the sharp and volatile area, which is highlighted by the purple circles on the curve in Figure 5.29 (HC 4%GnPs IMP.). However, a comparison between the HC 4%GnPs (UNIMP.) and the HC 4%GnPs (IMP.) in Figure 5.29 shows that both curves reached similar peak force values of 0.66 MPa. This indicates that the ultimate compressive strength was not significantly compromised for the HC 4%GnPs (IMP.) structure after low-velocity impact. Nevertheless, the impacted honeycomb structure in Figure 5.29 revealed a larger cyclic behaviour. This was because after low-velocity impact the honeycomb cells reached their critical strain limit, and thus their plastic moment was reached. This is due to the cells surpassing their axial and flexural stresses. As a result, linear elastic deformation cannot take place at the same rate as the unimpacted honeycomb structure as hinge rotation is compromised by damage from low-velocity impact, and so elastic buckling into plastic yielding occurs at a faster rate (Ruan et al.,

2003). Consequently, the impacted structure experienced a strain value of 0.07 at which plastic deformation occurred, indicating a 100% reduction in strain compared to the unimpacted structure that deformed at a strain of 0.14. As such, it indicated 2 occasions of cell contact and only 1 for the unimpacted sandwich structure. In conclusion, Figure 5.29 shows the larger occurrences of cell contact and earlier onset of plastic deformation indicated a reduction in compressive properties and a reduction in cyclic behaviour. This can result in a reduction in energy absorption, as seen in Figure 5.28, when impacted honeycomb structures are compared to their relatives.

5.5.2 Deformation Stages of the Re-entrant Sandwich Structures

Table 5.3 revealed that the re-entrant sandwich structure with 2% filler concentration surpassed 2J of impact, enabling CAI testing to proceed. It displayed enhanced compressive properties to that of the hybrid and honeycomb structures with the same filler concentration since both catastrophically failed. Moreover, Figure 5.30 exhibits the curve for the 2%GnPs (IMP.) structure indicating a significant number of cell wall contact, failure of cells, and a large cyclic region. Point 1 to 2 exhibits the linear elastic behaviour of the structure. At point 2, an elastic-plastic collapse of the structure initiates, indicating an 85.47% reduction in ultimate compressive strength after low-velocity impact when compared to the RE 2%GnPs (UNIMP.) relative in Figure 5.30. From point 3 to point 8, cell failure is prominent and demonstrated by the volatility of the curve, in addition with local catastrophic stress reductions at all the annotated points, as seen in Figure 5.30 for the RE 2%GnPs (IMP.) structure. This behaviour revealed that the re-entrant structure suffered significantly from impact damage generated from micro-crack initiation sites, therefore compromising its bending dominant features inhibiting the natural hinging of the diagonal ribs. Therefore, the higher level of instability mechanisms of the cells results in the stacking of the ligaments, thus, losing the ability to contest against compressive deformation, as similarly reported by Hou et al. (2018). This translated to a reduction in energy absorption for all the impacted re-entrant structures as exhibited in Figure 5.28.

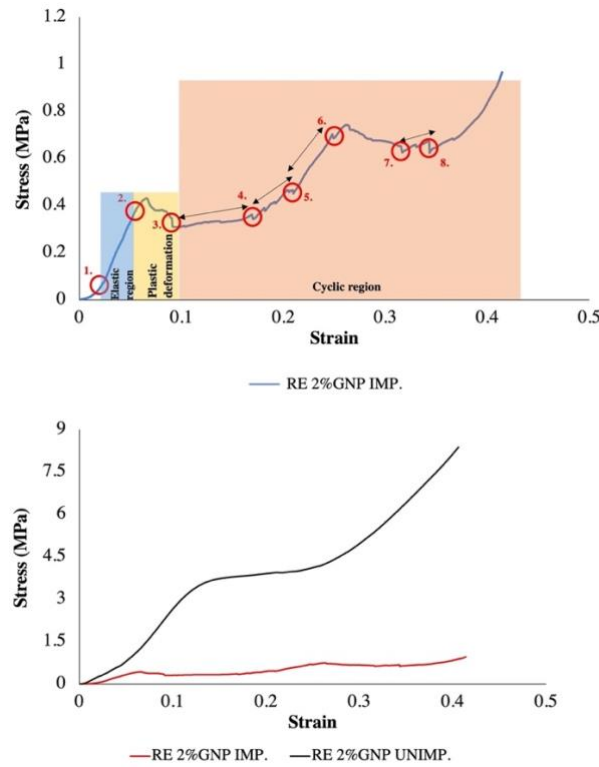


Figure 5.30 Stress-strain graph of the re-entrant structure with 2%GnPs inclusion impact tested at 2J and a stress-strain graph comparison of the re-entrant 2%GnPs (UNIMP.) and the 2%GnPs (IMP.)

An upward trend was experienced by the RE 2%GnPs (IMP.) structure in Figure 5.30. This trend can be related to the re-entrants auxetic nature, resulting in greater cell contact sites, but it is also due to a reduction in compressive modulus and compressive strength (Figure 5.26 and Figure 5.27, respectively) after impact. Subsequently, the auxetic nature of the re-entrant core enabled the sandwich structure to undergo a large amount of strain during the CAI test. This was because the re-entrant core structure provides significant enhancements in fracture toughness, as well as static and low-velocity impact performance (Alderson & Alderson, 2007). This was accredited to the localized densification of material, where cells deform and flow toward the localized impact region enhancing strength and stiffness in the proximity of impact (Qi et al., 2017). As a result, the re-entrant structure demonstrated superiority in its compressive deformation mechanism compared to the hybrid and honeycomb structures with 2%GnPs. The results in Figure 5.28 and Table 5.3 indicate that the bending-dominate deformation modes, influenced by the vertical struts (H) and unit cell angle (θ) of the re-entrant cell topology, provides superior elastic and plastic deformation, and hence, more favourable

energy absorption, enabling it to overcome 2J of low-velocity impact (Beharic et al., 2018). Additionally, a 2%GnPs concentration promoted enhancement to the re-entrant structure because of the occurrence of toughening mechanisms in the matrix. However, the superiority of the 2%GnPs re-entrant structure in contrast to the honeycomb 2%GnPs and hybrid 2%GnPs structure, indicates that cell topology contributes significantly to facilitate enhancement in compressive properties and low-velocity impact, independent of the filler concentration, since the re-entrant passed 2J of impact.

5.5.3 Deformation Stages of the Hybrid Sandwich Structures

Beforehand in Figure 5.25, it was illustrated that the hybrid sandwich structures (neat or reinforced) indicated no sharp reductions in stress on the curves from cell failure. As a result of the superior compressive properties of the hybrid 3%GnP structure, a comparison is illustrated in Figure 5.31 between the unimpacted and impacted relatives. The impacted relative revealed a 3.72% reduction in compressive strength and a 4.33% reduction in energy absorbed after being impacted, as seen in Figure 5.27 and Figure 5.28 in comparison to its unimpacted relative with the same filler concentration. This reduction could be from the increase in cell failure after damage from low-velocity impact. A large number of cells have already undergone plastic deformation and the initiation of their deformation mechanisms translates to some local catastrophic failure during impact. Hence, the absence of sharp stress reductions, reduction of compressive properties, and cell contact points on the curve, as seen in Figure 5.31 for the 3%GnPs HYB IMP. Furthermore, the absence of conflict between the re-entrant and honeycomb cells promoted an increased rate of cell densification after impact and an increased rate of local catastrophic failure during impact. Therefore, the remainder of cells left to undertake the compressive force after impact will not be revealed as prominently on the curve due to a prior reduction in the overall failure of individual cells. Eventually, an upward trend is seen after point 3 in Figure 5.31, since core densification is the last stage to develop. Overall, the hybrid indicated the poorest average compressive modulus compared to the honeycomb and re-entrant structures, as seen in Figure 5.26. However, it attained superior average compressive strength and average energy absorption capabilities, as seen in the table presented in Figure 5.27 and Figure 5.28, respectively, from the large area under its curve and its high strain-to-failure.

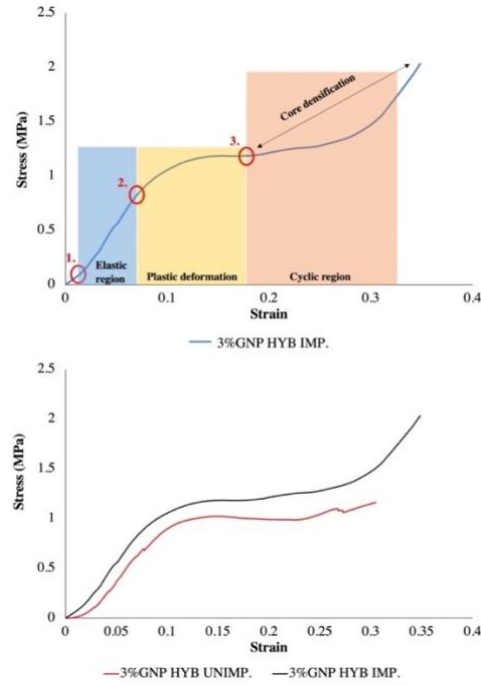


Figure 5.31 Stress-strain curve of the 3%GnPs hybrid impacted at 2J and a stress-strain graph comparison of the hybrid 3%GnPs (UNIMP.) and the hybrid 3%GnPs structure (IMP.)

5.5.4 Failure Mode Analysis

5.5.4.1 Node Failure

The failure modes of all impacted sandwich structures are distinguishable in Figures 5.32-5.36. The failure modes were observed using HDoF image analysis after CAI testing, where the red arrows indicate the failure of the nodes in the cells and the yellow arrows indicate the failure of layers, i.e. inter-layer failure or delamination of layers.

Node failure was most noticeable in the honeycomb and re-entrant sandwich structures, as seen in Figures 5.32-5.36, owing to the stretch dominant features of the honeycomb cell and the bending dominant features of the re-entrant cell. The re-entrant experienced node failure because the natural bending behaviour of the re-entrant structure promotes high stress concentrations on the ligaments. As a result, localized stress develops at the nodes because the nodes are being constrained (Ling, 2017). On the contrary, the folding of the re-entrant cells initiated a stable force transmission path, as shown between points 7 and 8 in Figure 5.30 (RE 2%GnPs IMP.), due to its progressive crushing process (Zhou et al., 2017; Liu et al., 2016). This behaviour and the global

deformation pattern of the re-entrant cells enabled successful impact resistance. Thus, Figure 5.34 revealed that the re-entrant face sheet still had regions of intact layers in comparison to the honeycomb and hybrid which did not progress to a filler concentration of 2%GnPs.

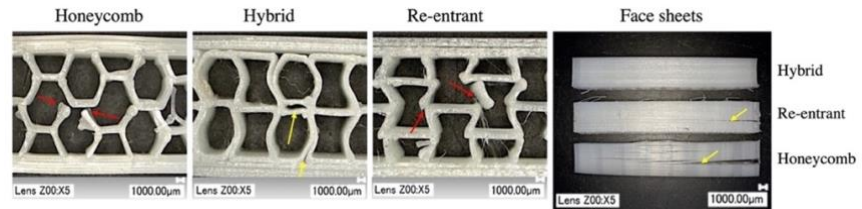


Figure 5.32 Impacted neat PA6 cellular structures

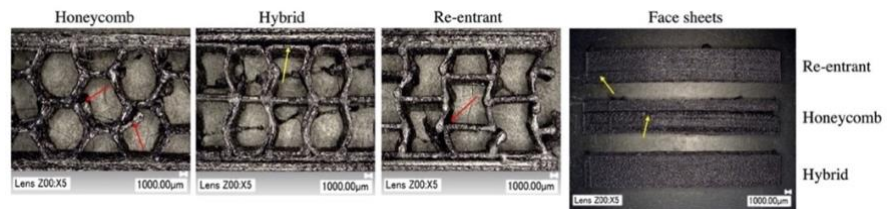


Figure 5.33 Impacted 1%GnPs cellular structures

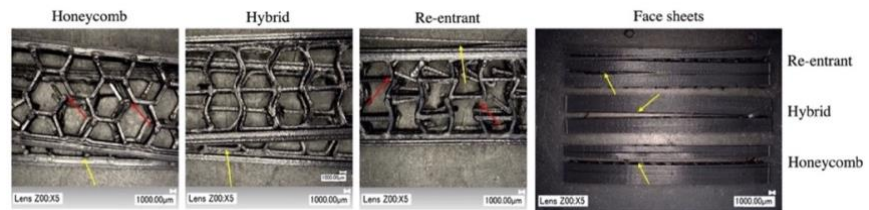


Figure 5.34 Impacted 2%GnPs cellular structures

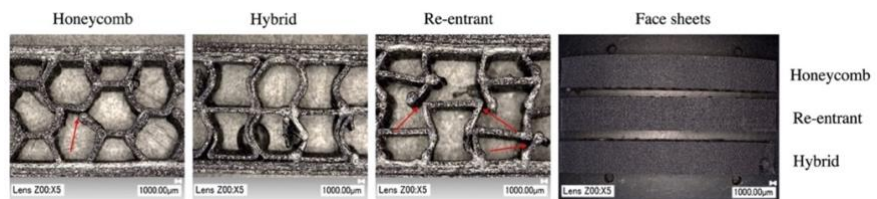


Figure 5.35 Impacted 3%GnPs cellular structures

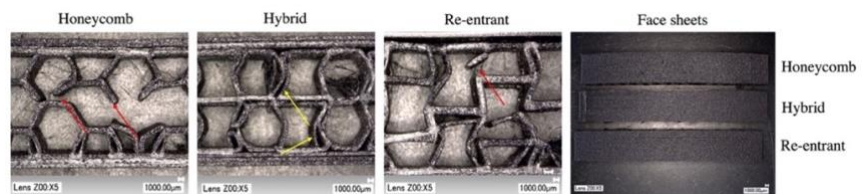


Figure 5.36 Impacted 4%GnPs cellular structures

The honeycomb's structure demonstrated node failure, since the axial and flexural stresses were compromised from lateral expansion inflicted by the impact head. The damage imposed from low-velocity impact translated to the yielding of the face sheet at the impact region resulting in core indentation, a finding comparable to that explored by Oterkus et al. (2016) in the literature. Face sheet failure is evident in Figures 5.32-5.34 for the honeycomb structures, and similarly also seen for the hybrid and re-entrant structures. This is because the honeycombs' dominant in-plane deformation mechanism is failure from the occurrence of buckling and misalignment of the struts/ribs, causing cells to rotate in opposite directions, eventually resulting in the collapsing of individual cells (Hönig & Stronge, 2002). Furthermore, the honeycombs containing 3%GnPs concentration, as seen in Figure 5.27, demonstrated a high compressive strength because the honeycomb cell topology could maintain its robustness under the compressive load. This, in addition to the 3%GnPs added to the matrix, possibly further restricted the deformation mechanisms of the honeycomb cells. However, its catastrophic failure, as depicted in Figure 5.34, indicates that at times, its stretch dominant characteristics, results in the axial and flexural stresses to reduce strength capabilities whilst undergoing low-velocity impact. This resulted in plastic deformation of the cells, ultimately leading to failure of the ligaments and nodes, and thus leaving the face sheets vulnerable to catastrophic failure (Qi et al., 2017; Yang et al., 2018).

The hybrid structure in Figure 5.34 indicated no node failure, which suggests that there was an enhancement in the core structure with 3%GnPs filler concentration. Therefore, the core could elastically and plastically collapse with the applied compressive force and successfully undergo its deformation mechanisms to combat the compressive force. As a result, the absence of node failure translated to the large area under the curve, presented in Figure 5.31 (3%GnPs HYB. IMP.), promoting enhanced energy absorption capabilities, as seen in Figure 5.28. Since the hybrid sandwich structure did not present superior compressive modulus and compressive strength, it can be assumed that filler concentration enhanced the hybrid cell topology.

5.5.4.2 Delamination

The superior node strength of the hybrid structure, as seen in Figure 5.35, indicated successful bonding of cell walls and raster layers, hence the enhancement of compressive properties and energy absorption capabilities at higher filler concentrations,

as seen in Figures 5.26-5.28. Suitable strength of the nodes provides strength to the core structure, and can prevent face sheet delamination, aiding the structure under compression. Figure 5.32 and Figure 5.33 shows the neat hybrid structure indicates no face sheet delamination and no node failure in its core. Conversely, the fracturing of nodes for the re-entrant and honeycomb resulted in significant delamination of face sheet layers, as seen in Figures 5.32-5.34, translating to delamination of cell layers, as depicted in Figure 5.34 (images of the honeycomb, hybrid, and re-entrant). As a result of delamination, the re-entrant and honeycomb sandwich structures diminished in their compressive strength and absorbed less energy during a CAI test, in contrast to the hybrid structures, as seen in Figure 5.27 and Figure 5.28, respectively. On the contrary, for the hybrid and honeycomb structures with a filler concentration of 2%GnPs, significant delamination and through thickness failure was apparent, translating to catastrophic failure of the sandwich structures. This could be because of the significantly superior compressive modulus (Figure 5.26) of the 2%GnPs structures before impact, resulting in a brittle fracturing of cells and face sheets under low-velocity impact. Additionally, the development of macro and micro-crack formations, distinguishable in Figure 5.13 (image 1), are more reasons for failure (Hou et al., 2018). Moreover, Figure 5.9 (image 7) indicated that the lower filler concentration of 1%GnPs showed signs of GnP debonding and non-existent platelet areas. This indicated that the matrix-GnP interaction was not strong enough and thus increased the platelets pull-out action (Wang et al., 2019), therefore reducing the interfacial strength, and compromising the bonding strength between raster layers. These defects can result in inter-layer failure, as distinguishable in Figures 5.32-5.34.

Sandwich structures with 3% and 4%GnPs exhibited an absence of delamination, as seen for the face sheets in Figure 5.35 and Figure 5.36. Consequently, the higher filler concentrations prevented damage from low-velocity impact which could be related to the GnP toughening mechanisms and appropriate and uniform dispersion of GnPs in the PA6 matrix, as shown in Figure 5.11 and Figure 5.12 (x3000 SE images). This enhances their load carrying abilities, toughens the structures, and aids the deformation mechanisms of individual cells for all core topologies. Subsequently, this demonstrated that the functionalisation of the GnPs improved interfacial strength between the GnPs and PA6 matrix, supporting layers from debonding after low-velocity impact. Hence, the improved residual properties in Figures 5.26-5.28 when high filler concentrations (3% and

4%GnPs) are compared to low filler concentrations (1% and 2%GnPs). This shows good agreement with Seong & Kim (2015) and Yang et al. (2018) in the literature. Therefore, higher filler concentrations indicated an appropriate level of GnP concentration was found to enhance the impact properties of the structures.

5.5.4.3 Toughening Mechanisms During Low-Velocity Impact

Figures 5.32-5.36 and Figure 5.13 (image 1) reveals that micro-crack initiation is a common occurrence for all sandwich structures after experiencing a compressive load, irrespective of high/low GnP concentration. Low-velocity impact indicated a contribution to the development of micro-crack formation and eventually macrocrack development (Gómez-del Río et al., 2005), made evident in Figures 5.32-5.36. However, the previous section revealed that sandwich structures with high filler concentrations (2-4%GnPs), resulted in improved face sheet strength and core strength. This is due to the reinforcement of the GnPs in the PA6 matrix, enabling the sandwich structures the ability to dissipate crack development, thus improving the toughening mechanism of the structure at higher concentrations (Tang et al., 2013).

The toughening mechanisms involved during low-velocity impact in particle filled polymer systems include: (a) crack deflection (b) crack branching (c) crack pinning/bowing, (d) particle bridging, (e) particle debonding, (f) micro-cracking or crazing of the matrix, and (g) inelastic deformation of the matrix (Zhang et al., 2008). Among the mentioned mechanisms the listed (a)-(d) are known as the ‘on-fracture plane process’ relating to the mechanisms occurring within the vicinity of the fractured surface. The processes occurring below the fractured surface (e)-(g) and around the crack tip are known as the ‘off-fracture plane process’. Both fracture processes occur simultaneously, significantly contributing to the toughening of the structures. However, the results indicate that the sandwich structures were toughened primarily by crack deflection and crack pinning, as seen in Figure 5.13 (image 1). Upon impact and compression, it is possible that crack deflection and crack pinning occurred more prominently for the higher concentrations (2-4%GnPs), since the higher concentrations were able to consistently instigate an approaching crack to change in direction (Faber and Evans, 1983; Oterkus et al., 2016). A schematic diagram in Figure 5.37, depicts this phenomenon and illustrates the various toughening mechanisms that can contribute to the overall toughness of the sandwich structures with GnP reinforcement. Therefore, it can be assumed that there is a

greater chance for crack trajectories to change because of the greater quantities (i.e. 3% and 4%GnPs) of dispersed GnPs. Furthermore, the strong two-dimensional GnPs can promote the development of crack bridging between the nanoplatelets resulting in a delay in crack propagation, stabilizing it before developing into larger more harmful cracks (Tang et al., 2013). Since filler concentrations remained relatively low it is difficult for this to develop. However, interfacial debonding/delamination between the GnPs and matrix can result in an enhancement of the fracture toughness because the local plastic deformation of the matrix system increases (Wang et al., 2005). This can be seen in Figure 5.10 (images 2 and 4), Figure 5.11 (image 3) and Figure 5.12 (images 1, 2, 3 and 6). As a result, there is less possibility of face sheet yielding and core indentation. Therefore, the 3% and 4%GnPs structures encourage the cracks to take a more tortuous path, and thus increases their toughness and residual energy absorption capabilities (Imran & Shivakumar, 2017), as seen in Figure 5.28.

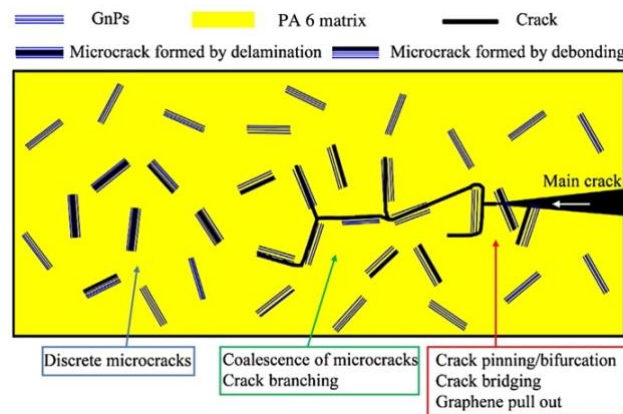


Figure 5.37 Schematic diagram of the failure mechanism indicating the direction and trajectory of crack propagation as seen by Wu et al. (2015)

The reduction in compressive properties for the 4%GnPs structures could be related to poor bonding of the GnPs to the matrix, resulting in brittleness and greater polymer chain confinement (Seong & Kim, 2015; Chandrasekaran et al., 2014; Quaresimin et al., 2016). Here then, rather than enhance the structure in contrast to 3%GnPs, it diminished its properties (Figures 5.26-5.28). In the case where debonding of the GnPs are prominent, the promotion of crack pinning and deflection can pose a challenge. However, if the filler concentration is maintained at an appropriate level, i.e. 3%GnPs, the GnPs and matrix display strong bonding capabilities, leading to effective crack deflection and coalescence (Yamamoto et al., 2019).

6.1 Conclusions

The primary aim of this project was to successfully produce a ground-breaking PA6/Graphene nanoplatelet reinforced 3D printing filament material, with the intention to fabricate a novel next generation sandwich composite structure with enhanced impact properties. The analysis started with investigating CFR 3D printed fibre-reinforced sandwich composites to evaluate the compressive properties, energy absorption capabilities, and impact properties of sandwich structures. Sandwich structures with three different core types: an auxetic core, conventional honeycomb, and hybrid core, alongside two fibre types (CF and Kevlar) and various fibre orientations in the face sheets were fabricated. A comparison was then made between core topologies to evaluate whether auxetic cores can substitute conventional honeycomb cores and whether reinforced structures improved in compressive modulus, compressive strength, and energy absorbed when compared to the unreinforced structures. This demonstrated the possibility of (1) fabricating the novel geometrical auxetic design with the developing technology of 3D printing and (2) the novelty of fabricating FRPC structures with 3D printing.

Subsequently, an innovative NH₂-GnP reinforced PA6 material was developed by melt blending PA6 and varying concentrations of NH₂-GnP in a twin-screw extruder, followed by single screw extrusion to produce filament material for 3D printing PA6/GnP sandwich structures. This validated the possibility of (1) successfully 3D printing with a bespoke and novel filament material and (2) successfully enhancing a common thermoplastic polyamide. The same core topologies and experiments were performed for these sandwich structures. The experimental results were then compared to neat PA6 3D printed sandwich structures to evaluate whether enhancements could be distinguished and if improvements in residual properties were noted. The following remarks can be made:

1. During compression the neat PA6 re-entrant structure demonstrated apparent auxetic characteristics, indicating a bending-dominant deformation mechanism resulting in anti-hinge rotation due to its negative Poisson's ratio. Under low-velocity impact, the re-entrant core underwent material densification, compelling the core to collapse towards the localised impact region. Consequently, its deformation mechanisms enhanced its compressive properties resulting in

superior compressive modulus and compressive strength in relation to the honeycomb core and hybrid cores under compression.

2. The neat PA6 honeycomb exhibited a positive Poisson's ratio and thus no auxetic effect. It possessed a stretch-dominant deformation mechanism resulting in lateral expansion of the sandwich structure under compression, relying significantly on the vertical struts (H) and the unit cell angle (θ). Therefore, the cells underwent hinge rotation and misalignment, causing collapsing of individual cells. The honeycomb sandwich structure indicated poorer compressive properties but superior energy absorbing capabilities under compression.
3. The hybrid core topology contained a combination of the stretch-dominant and bending-dominant deformation mechanisms from the honeycomb and re-entrant cores. However, the core seemed more influenced by the stretch-dominant features of the honeycomb cells. Therefore, the honeycomb cells stimulated and facilitated the re-entrant cells to react in their natural auxetic manner, supporting lateral expansion. With this congruent nature, the combination of both cells did not enhance the compressive properties or energy absorbing capabilities, and so resulted in the poorest compressive modulus, compressive strength, and energy absorption under compression.
4. Reinforcing sandwich structures with Kevlar and CF fibres did not enhance the compressive properties of the sandwich structures under uniaxial compression with the core in the in-plane direction. However, they did reveal some discrepancy in results when compared to one another.
5. The fibre type, fibre orientation, and face sheet experience no ability to distribute the experienced force to aid the core, and thus, are irrelevant in the compression test. Therefore, the in-plane direction of the core means it will bear all of the applied force, and thus the compressive properties are reliant on the core topology. As such, unreinforced structures were superior in compressive properties.
6. All cores exhibited a 3-phase phenomenon on stress-strain plots after compression. The 3 phases were: an elastic-plastic deformation region, a cyclic region, and a densification region. The re-entrant core exhibited the largest cyclic region and greatest curve volatility owing to its negative Poisson's ratio and number of cell wall contacts. As a result, it produced superior compressive properties and energy absorbing capabilities.

7. It was concluded that reinforced sandwich structures were inferior to unreinforced sandwich structures since its build orientation resulted in the need for supports, resulting in pre-mature failure from post processing, and the development of positive and negative air gaps from unsuccessful welding of rasters.
8. Print defects such as voids, residual stress, and unsuccessful interfacial adhesion were more factors that commonly occurred for all structures, particularly for those with fibre-reinforcement. These defects were detrimental to the compressive properties of the sandwich structures.
9. Under compression, the re-entrant sandwich with no fibres revealed the greatest compressive strength and the honeycomb with no fibres revealed the greatest energy absorption during compression. On the contrary, structures with fibre-reinforcement revealed significant diminishment of compressive strength and energy absorption when compared to unreinforced structures.
10. It was discovered that low-velocity impact significantly reduced the compressive properties and energy absorbing capabilities of all sandwich structures. Those with fibre-reinforcement saw the largest diminishment in properties because of damage induced to the fibres, resulting in the promotion of fibre failure modes, namely, delamination, fibre pull-out and fibre fracture. The absence of fibre failure modes and the superior print quality of the unreinforced sandwich structures resulted in superior residual properties. Therefore, fibre reinforcement did not enhance impact resistance with 3D printed sandwich composites.
11. The PA6/GnP sandwich structures were successfully fabricated by utilising a 3D printer. The NH₂-GnP reinforcement has resulted in an overall improvement in compressive modulus, compressive strength, and energy absorption capabilities for neat PA6. A filler concentration of 2%GnPs enhanced the compressive properties considerably more than any other filler concentration and indicated to be the most suitable filler concentration.
12. The re-entrant core topology under compression obtained superior average compressive strength and average energy absorbed, and thus was the optimum choice of core topology for the PA6/GnP sandwich structures, disregarding low-velocity impact. On the contrary, the honeycomb core obtained superiority in compressive modulus in comparison to the other core topologies. This indicated that the chosen sandwich structures need to be based on their required applications that can indicate the required property.

13. After low-velocity impact the hybrid core exhibited the highest average compressive strength and average energy absorbed and the re-entrant exhibited superior average compressive modulus. The hybrid demonstrated this because with GnP reinforcement, the structural integrity of the hybrid structure was enhanced, and so it experienced no local catastrophic failure. In addition, it had improved print quality, a reduction in void content, and a lack of agglomeration.
14. Sandwich structures with 1% and 2% GnPs saw the largest diminishment in properties after CAI testing from low-velocity impact. The honeycomb and hybrid structures with 2% GnPs resulted in catastrophic failure after low-velocity impact of 2J. Conversely, the re-entrant core resisted 2J of impact because of its ability to stabilise the force transmission, resulting in a progressive crushing process, and thus enabling successful impact resistance. The honeycomb and hybrid failed because of a rise in brittleness and a rise in defects. However, above 2% filler concentration there was less reduction in properties owing to the promotion of toughening mechanisms by the GnPs.
15. It was concluded that low-velocity impact was detrimental to all core topologies, regardless of filler concentration, since impacted structures exhibited a reduction in properties compared to unimpacted relatives. For the bulk of the sandwich structures reinforced with 3% and 4% filler concentrations the residual properties were improved, and thus obtained enhanced compressive modulus, compressive strength, and energy absorbed in comparison to neat PA6 structures that also experienced impact. Therefore, the optimum filler concentration for enhanced impact properties is 3%GnPs. These enhancements were due to the GnPs ability to promote crack pinning and crack deflection, obstructing further crack propagation that could result in catastrophic failure. Overall, the HC3%GnPs structure revealed superior residual compressive properties.
16. Twin-screw extrusion promoted successful exfoliation of GnPs indicating that there was an absence of agglomeration and successful bonding with the host matrix. This was due to the amine-functional groups increasing homogeneity with PA6 and thus increasing hydrophilicity.
17. It was exhibited by SEM analysis that sandwich structures with higher filler concentrations, namely, 3% and 4%GnPs, had a higher probability of aggregating because of an increased concentration of GnPs, hindering successful exfoliation

of the sheets. Therefore, defects such as wrinkling can occur, and the interface could become jeopardized.

6.2 Future work

1. The in-plane compressive behaviour of the 3D printed sandwich composite structures was investigated, however, cells orientated in this manner involve complex deformation mechanisms, and they are weakest when placed in this orientation. Research has most commonly investigated out-of-plane compression, so a comparison between both orientations could reveal the difference in compressive properties, impact resistance, and energy absorbing capabilities.
2. The buckling resistance and shear resistance of sandwich composite cores are of significant relevance. Consequently, vertical in-plane compression testing utilising grips to secure the 3D printed sandwich structures, is one method to investigate the shear resistance and buckling resistance of the reinforced structures, and to investigate if the properties of the sandwich structures in this orientation can be improved with fibre reinforcement or GnP reinforcement.
3. Another common functionalised GnP is functionalised O₂-GnPs. These functional groups allow for hydrogen bonding with other hydroxyl groups, hydrogen atoms, and other molecules. By reinforcing PA6 with O₂-GnPs it can be expected that improvement will occur. Therefore, a comparison between NH₂-GnPs and O₂-GnPs could have revealed which functionalised GnPs obtain superior compressive properties for the sandwich structures.
4. The semi-crystalline nature of PA6 indicated favourable impact resistance and compressive properties. However, other thermoplastics, such as polycarbonate (PC), and ABS, are commonly utilised in the automotive industry for exterior parts, such as bumpers, body panels, dashboard components, etc. In addition, low-density polyethylene (LDPE) are polymers commonly utilised for general packaging materials, gas and water pipes, containers, etc. By potentially combining the significant impact resistance of PC with one of the most common 3D printing filaments, ABS, and reinforcing it with NH₂-GnPs, a comparison could be made to PA6/GnPs. In addition, LDPE is one of the most utilised polymers because of its high strength, easy processability, and semi-rigid properties. By fabricating a 3D printed LDPE/GnP sandwich structure this could

also be compared to PA6/GnP sandwich structures to evaluate the difference in compressive properties and impact resistance.

5. Since the Markforged Mark Two desktop 3D printers have a closed system, preventing the possibility of altering print temperatures, fan speeds, print head travel speeds, etc., users are restricted to materials other than their own. However, by melt blending Markforged PA6 with a low filler concentration of NH_2 -GnPs, there is a possibility of fabricating a 3D printed sandwich structure with GnPs, reinforced alongside fibres in the face sheets with an auxetic GnP reinforced core. Therefore, an experiment could be done to investigate if the GnPs enhanced the fibres in the sandwich structure and whether improvement in residual properties could be achieved.

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