

HYBRID COMPOSITES WITH A HIERARCHICAL STRUCTURE FOR HIGH-PERFORMANCE STRUCTURAL APPLICATIONS

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ABSTRACT

Given the global energy crisis, high-performance transportation sectors are swiftly adopting lightweight materials to enhance energy efficiency and ensure long-term sustainability. Notably, a mere 10% reduction in weight results in a significant 14% increase in mileage, underscoring the pivotal role of lightweighting in the evolution of electric vehicles. Dedicated to advancing the realm of lightweight structural composite materials by developing hybrid composites with synergy-induced properties, these composites incorporate multiple nano-scale and micro-scale reinforcements within a common matrix material. Utilising widely employed polymer matrices as substitutes for metallic structural components in the automotive sector, specifically polypropylene (PP), our hybrid composites are strategically enhanced. The incorporation of bio-inspired fibrous reinforcements, mirroring hierarchical architectures in biological systems, sets our composites apart. These self-assembled reinforcements are achieved through the covalent bonding of nano-sized Graphene Nanoplatelets (GnPs) to chemically modified micro-sized Glass Fibres (GFs). The interface of these meticulously crafted hybrid composites is tailored by optimising the bonding density of the nano-filler, resulting in exceptional mechanical performance and improved processability induced by synergy. Specifically, our hybrid composites outperform industrial polymer substitutes for metallic structural components, demonstrating improvements in tensile strength and an 86% improvement in impact strength, all while achieving a noteworthy 18% weight reduction.

1 Introduction

With net-zero emissions by 2050 sustainability goals ahead, strategies to producing lightweight components imparting high performances are crucial for energy conservation [1]. To meet such demands, polymer-based composites have hence emerged as a prominent choice in industrial settings due to their exceptional physical and mechanical properties, low density, chemical resistance, processability, and affordability [2]. On top of lightweighting, by incorporating specific functional fillers into a polymeric matrix, for instance, polypropylene (PP), polyamide and epoxy, advanced multifunctional composite structures can be achieved synergistically, tailoring the properties of the composite to suit diverse applications, hence reducing material redundance. Typical fillers such as glass fibres (GFs) and carbon fibres have been used in past decades due to their ability to enhance mechanical properties in polymer composites. Despite the benefit of improving stiffness of the composite, higher GF loadings often result in increased density, heightened brittleness and reduced melt flow hence reduced processability [3]. This highlights the need for a better reinforcement system that simultaneously provides a strong and tough lightweight solution with multifunctionality and improve stress transfer mechanisms.



Since the first reported isolation of graphene, advancements in nano-manufacturing technologies have paved the way for other nanosized fillers like carbon nanotubes, montmorillonite and graphene nanoplatelets (GnPs), which are capable of simultaneously enhancing various properties unlike conventional fillers. GnPs in particular have garnered attention with their high aspect ratio, high electrical and thermal conductivity [4], high mechanical performances and lubricating property, making them an effective reinforcement in polymer composites with high demands for multifunctionality. While the superior stiffness and strength of GnPs suggest significant enhancements in mechanical properties with only small amounts of reinforcing material needed, achieving strength on par with high performance metallic substitutes with GnP-reinforced polymers solely remains a challenge. By combining two or more material phases, hybrid composites imparting novel properties from all phases can be achieved, gaining traction in engineering applications [5]. Polymer-based hybrid composites exhibit tailored properties compared to traditional, single-filler composite materials. These properties stem from factors like structure, particle geometry, crystallisation behaviour, filler-matrix interaction, concentration, and processing methods [6]. Pedrazzoli et al. have elucidated the synergistic effects of combining different fillers in PP composites, resulting in enhanced mechanical properties, crystallinity, and thermal conductivity [4]. In addition, Papageorgiou et al. further investigated the synergistic effect of the addition of GnPs and GFs in PP on the thermal conductivity and fire retardancy in the composites, demonstrating the multifunctionality of GnPs [7].

While these studies provide valuable insights, a comprehensive understanding of the mechanisms driving the synergistic effects in hybrid composites is still lacking, where a self-assembling mechanism via covalent bonding should be observed due to the surface chemistry of the two fillers. This also suggests the possibility of tailoring of self-assembly bonding density via surface modifications. Hence, this work aims to report novel findings in PP/GnP/GF composites, quantifying these effects and understanding how they are influenced by the combination and concentration of reinforcements, shedding light on the underlying mechanisms. Such insights could facilitate the fine-tuning of physical and functional properties in hybrid composites for high-performance applications across automotive, aerospace, military, and beyond.

2 Discussions

2.1 Interfacial Interactions

As reported by Aguiar et al. [8], commercially available as-purchased e-GFs are typically coated with an aminosilane sizing, where the amino functional groups are enabled to covalently bond to the carboxylic groups present on the surface of GnPs, forming a siloxane network. By varying the chain configuration of the aminosilane coupling agent, the amount of GnPs bonded to a GF, i.e. bonding density (B_d), can be tailored, hence improving the grafting of GnPs onto GFs. In this study, five different types of aminosilanes were used, and the resultant bonding densities and synergistic effects were compared to those of the control unsized GF-reinforced composites. To identify and quantify the bonding density between GnPs and GFs, X-ray photoelectron spectroscopy (XPS) analyses were performed in both unsized and sized GFs, as well as their hybrid composite counterparts. The higher density of non-protonated amino groups suggests a higher likelihood of covalent bonding between the GFs and GnPs, which is observed in sizings 2 and 3 in the study, namely n-(6-aminohexyl)-aminomethyltriethoxysilane and n-butylaminopropyltrimethoxysilane, which are both secondary amines with shorter carbonic chains. This creates a steric effect, reducing the possibility of amine protonation. In addition, the presence of amide groups in the XPS spectra for the hybrid composites were used to confirm the successful bonding between GFs and GnPs, where B_d was defined as the ratio of intensity of amide peak to the total intensity of the N1s XPS peak. This higher B_d indicates



a higher amount of GnPs bonded to the GF surface, promoting a higher degree of trans-crystallisation and reducing the creation of stress concentration sites in the bulk matrix.

2.2 Crystalline Structure

With the introduction of GnPs in PP and PP/GF composites during injection moulding, the overall degree of crystallinity of the composite remain similar despite the change in crystallisation mechanism, as demonstrated by Sansone et al. through X-ray diffraction (XRD) analyses as well as differential scanning calorimetry (DSC). However, the total fraction of β -phase (\mathcal{K}_{β}) as well as degree of trans-crystallisation (\mathcal{T}_r ; $\mathcal{T}_r = I_{\alpha(040)}/I_{\alpha(110)}$) increased, where the tabulated results are shown in Table 1, as calculated from XRD analyses [9]. Overall, the degree of crystallinity of the composite increases slightly with the addition of GnPs in both PP/GnP and PP/GnP/GF composites.

Table 1. Analysed results from XRD analyses for PP-composites. The nomenclature PPGnPxGFy is used to denote the composite composition with x and y wt.% of GnPs and GFs in the composite respectively.

Sample Name	<i>ℋ_β</i> (%)	${\mathcal T}_r$	Sample Name	$\mathcal{K}_{oldsymbol{eta}}$ (%)	${\mathcal T}_r$
Neat PP	0.30	1.28	PPGnP0.5GF40	10.00	5.51
PPGnP0.5	6.05	7.92	PPGF60	1.12	1.10
PPGF40	2.00	1.01			

This is attributed to the addition of GnPs, where the nanofillers act as a nucleating agent of a softer, tougher crystal polymorph, namely β -phase, and can be quantified using the Turner-Jones equation from XRD analysis results [10]:

$$\mathcal{K}_{\beta} = \frac{I_{\beta(300)}}{I_{\beta(300)} + I_{\alpha(110)} + I_{\alpha(040)} + I_{\alpha(130)}} \times 100\%$$
(1)

Where $I_{\alpha(110)}$, $I_{\alpha(040)}$, and $I_{\alpha(130)}$ are the intensities of the (110), (040), and (130) diffraction peaks of the α -phase respectively, and $I_{\beta(300)}$ is the intensity of the (300) peak of the β -form. In all composites with GnPs added compared to composites without the GnPs, \mathcal{K}_{β} increases, where, an 8% increase in \mathcal{K}_{β} was observed when comparing PPGnP0.5GF40 and its biphasic counterpart. In addition, as GnPs are bonded to the surfaces of GFs, the hybrid hierarchical reinforcements promote trans-crystallisation in the hybrid composites. The degree of trans-crystallisation can be calculated by considering the extent of epitaxial growth of the α -crystals. For neat PP and PPGF40, the \mathcal{T}_r values obtained were 1.28 and 1.01 respectively, however, these increased to 7.92 and 5.51 for PPGnP0.5 and PPGnP0.5GF40 respectively, suggesting the role of GnPs and GnP/GF as nucleating agents of trans-crystals in PP. As trans-crystals are morphologically distinct from the pre-dominant α -spherulites within the bulk matrix, it can be hypothesised that the introduction of trans-crystals would facilitate the stress transfer between the hybrid filler and the PP matrix. The presence of trans-crystals in PP/GF composites was confirmed by Aguiar et al. utilising a polarised optical microscope (POM) [8], and the trans-crystals are seen growing epitaxially from the surface of the hybrid reinforcements as seen in Figure 1.

2.3 Mechanical Properties and Synergistic Effect

To validate the effectiveness of the introduction of β -phase and trans-crystals on the enhancements in mechanical performance in the hybrid composites, Sansone et al. performed tensile and impact tests on PP/GnP/GF composites with varying filler contents, and the results are shown in Figure 2A and B [11]. At a fixed GF wt.%, it is evident that



with increasing GnP wt.%, the tensile modulus increases proportionally at each GF wt.% by at least 5%. One of the biggest challenges in creating composites suitable for high-performance application is balancing high stiffness and high strength, which is proven to be achievable through the incorporation of hybrid reinforcement fillers, where a 0.5 wt.% addition of GnPs in PPGnP0.5GF40 results in a 4% enhancement in tensile strength compared to the automotive application baseline of PPGF60, while offering a weight reduction of 18%. Similar trends were also observed for impact strength, where the impact strength of PPGnP0.5GF40 exceeds that of the industrial baseline by 86%.



Figure 1. POM images of the hybrid composite melt with (A) GFs sized with sizing 3 and of (B) unsized GFs. (C) POM image showing the process of trans-crystallisation during processing. Reprinted with permission from [8].

To further investigate the interfacial synergistic effect of GnP/GF on PP reinforcement, Aguiar et al. studied the effect of \mathcal{B}_d on the mechanical properties on PPGnP0.5GF20 composites, which is demonstrated in Figure 2C and D [8]. Although the tensile moduli remain similar as predicted by rule of mixtures, the tensile strength and toughness of the composites changes drastically with the change in aminosilane coupling agents used, implying a shift in load transfer mechanism with varying \mathcal{B}_d . The hybrid composite with GFs treated with sizing 3, which showed the highest \mathcal{B}_d of 68.8%, exhibits a tensile strength 40% higher than both the hybrid composite with unsized GFs and the biphasic composite containing 20 wt.% GF. Additionally, its tensile strength is 18% higher than the biphasic composite with 30 wt.% unsized GF. Furthermore, the tensile toughness of this hybrid composite surpasses that of both the hybrid composite with unsized GFs and the biphasic composites with 20 wt.% and 30 wt.% GF by 77%. This enhanced mechanical performance is attributed to the presence of trans-crystallisation, which produces a gradient interphase, and β -phase in the hybrid composites. The high aspect ratio of GnPs facilitates bonding with GF, thereby increasing the surface area between the hierarchical reinforcement structure and matrix. This promotes efficient load transfer from the matrix due to a greater surface area for load transfer. Moreover, the bonding of GnPs to GFs promotes trans-crystallisation, reinforcing the filler-matrix interface, which enhances stress transfer by facilitating the absorption/adsorption of polymer chains along the filler surface. This is showcased in Figure 2E-H, where a shift in failure mechanism from fibre pull-out in PP/GF and PP/GnP/GF composites with lower \mathcal{B}_d to fibre breakage in PP/GnP/GF composites with higher \mathcal{B}_d was observed.





Figure 2. (A) Tensile modulus and (B) tensile strength with varying GnP and GF wt.%, respectively; (C) and (D) demonstrated the effect of \mathcal{B}_d on (C) tensile toughness and (D) tensile strength on PP/GnP/GF composites with surface-modified GFs. Scanning electron micrographs showing the fractographies of the tensile tested (E) GF-reinforced biphasic composite, (F) PPGnPGF with unsized GF, (G) PPGnPGF with GFs sized with sizing 2, and (H) PPGnPGF with GFs sized with sizing 3. Reprinted with permission from [8].

2.4 Electrical Conductivity and EMI Shielding Effectiveness

Apart from introducing mechanical enhancements, GnPs can also be introduced in hybrid composites to impart multifunctionalities due to their superior electrical and thermal conductivities, further reducing the need for discrete functional components. Our group investigated the electrical performance of PP/GnP/GF composites, where the electrical conductivity, EMI shielding effectiveness (*SE*) and thermal conductivity were assessed [12]. Notably, the introduction of 10 vol.% GF facilitates in creating a preferred fibre orientation, hence assisting in the synergistic formation of a percolative conductive network in PPGnP10GF10. This synergistic effect introduced by the addition of 10 wt.% GF resulted in an increase in EMI *SE* from ~ 11 dB to 20.5 dB and a heightened thermal conductivity from 0.67 W·(m·K)⁻¹ to 1.09 W·(m·K)⁻¹ while simultaneously achieving superior tensile strength and tensile modulus of 80 MPa and 9.4 GPa respectively.

3 Conclusions

These studies showcased the novel superior enhancements in mechanical, electrical conductivity and EMI shielding effectiveness imparted by the multiscale hybrid self-assembled GnP/GF architecture, demonstrated via synergistic effects of the covalently bonded fillers. With a better underlying understanding of the synergies between the fillers, better microstructural control can be achieved via composition optimisation and interfacial interaction tailoring, granting drastic improvements in macroscopic bulk multifunctional properties. In particular, our hybrid composites excel beyond industrial polymer composite alternatives, showcasing enhancements in tensile strength and a remarkable 86% in impact strength, alongside achieving a significant 18% reduction in weight; while reducing material redundancy by simultaneously providing high electrical and thermal conductivity and EMI shielding



performance. This highlights on the promising potential of this hierarchical architecture in polymer composites as a prominent strategy as a high-performance structural metallic alternative, paving the path to a sustainable future.

4 References

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