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Mechanical and Thermal Properties of Cellulose Nanocrystal/Graphene Nanoplatelet Reinforced Polylactide Acid Biocomposites

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ABSTRACT

In this research, cellulose nanocrystal (CNC) and graphene nanoplatelet (GNP) were introduced as hybrid nanofillers at a total loading level of 5wt.% in poly(lactic) acid (PLA) as matrix material. PLA-CNC/GNP biocomposites were successfully fabricated with the utilisation of compression moulding to study the effect of CNC and GNP on the mechanical and thermal properties of the biocomposites. The produced PLA-CNC/GNP biocomposite materials, including pure PLA for comparison purposes, were characterised by mechanical and thermal properties. Overall, the results of the flexural properties showed that the PLA biocomposite had a formulation of 2.5 wt.% CNC and 2.5 wt.% GNP contributed significantly to the enhancement of flexural strength and the modulus, up to 47% and 76%, respectively. The thermal properties also seem to be optimally improved as the thermal stability of the biocomposite samples was analysed accordingly. Overall, the incorporation of CNC and GNP with 5 wt.% of total hybrid filler loading showed a favourable impact on the mechanical and thermal properties of PLA biocomposite for environmentally friendly automotive components.

Keywords: Polylactic acid; cellulose nanocrystal; graphene nanoplatelet; mechanical properties; thermal properties

1. Introduction

Biocomposite is a material composite that consists of a matrix (either synthetic or natural polymer resin) and reinforcement (natural fibres), which provides biocompatibility properties. Biocomposite production aims for property improvement due to its deficiency in strength and stiffness compared to synthetic polymer matrix, which can lead to limitations in applications [1-2]. To overcome this limitation, many strategies have been explored, including bio and nanocomposite, copolymers, the addition of nano reinforcement additives, and blending with tough polymers so that the properties could be enhanced [3]. It has been studied as a nano-sized particle (1-100nm) with a genuinely low content below 10 wt.%, which can essentially increase the mechanical, barrier, and thermal properties [4]. So, due to the environmental problems, cellulose nanocrystals (CNC) are suitable nano-sized particles of material that can be used as reinforcement to PLA biocomposite for properties improvement because of its availability, stiffness, low weight, high strength, renewability, reinforcing capability, and biodegradable [5-6].

In this study, CNC/GNP reinforced PLA biocomposites were prepared by fabricating the GNP and CNC with PLA polymer resin using hot compression moulding. The study aims to investigate the effect of CNC/GNP hybrid filler loading on the mechanical and thermal properties of PLA biocomposites. Furthermore, the compatibility of both nanofillers in the PLA matrix was interesting to investigate in order to comprehend their interfacial bonding in future research.

2. Materials and Methods

2.1 Materials

The matrix material utilised in the study was poly(lactic acid) (PLA) in pellet form. It was obtained from Teraslab Saintifik Sdn. Bhd, Kota Bharu, Kelantan, Malaysia. For reinforcement materials that had been utilised as hybrid nano-fillers were cellulose nanocrystal (CNC) and graphene nanoplatelets (GNP) which the materials used in powder forms with the following properties: particle size of 20 μm for CNC while surface area 120 to 150 m^2 g^{-1} and particle size of 5 μm for GNP. The nano-materials were supplied by Sigma-Aldrich (M) Sdn. Bhd.

2.2 Preparation, Fabrication, and Characterisation of PLA-CNC/GNP Biocomposites.

For the materials preparation, PLA polymer resin and CNC powders were dried in the oven for 24 hours at 70 ℃ and 105 ℃, respectively, to remove the moisture in the materials so that impurities of the final samples could be avoided. This mixing process was manually done in the 50 ml beaker using a spatula, and each sample was weighed at 40 g for 1 mm and 60 g for 3 mm stainless steel mould plate samples by using an electronic weighing balance. At the same time, the total loading level of 5 wt was maintained.%, CNC, and GNP as nanofillers were prepared with different ratios reinforcing PLA with fixed weight percentages of 95%, as shown in Table 1. The neat PLA without reinforcements was also fabricated as a control sample.

In the next stage, the PLA sheets were prepared by using a compression moulding technique at 180 ℃. This process included a preheating process, hot-press heating, and cooling of PLA sheets within 10, 5, and 5 minutes, respectively, using a 1 mm stainless steel mould plate. Finally, CNC/GNP was distributed within two PLA sheets, forming a sandwich structure using a 3 mm stainless steel mould plate. Then, the PLA biocomposite samples underwent a compression moulding process at 180 ℃ for 12 minutes of preheating, 6 minutes of hot-press heating, and 5 minutes of cooling. The samples, hence, were cut using a whipsaw into specimens with the appropriate geometry according to ASTM D790 and then measured by utilising a vernier calliper for further process of characterisations. All the samples had undergone mechanical (flexural) and thermal thermogravimetry analysis (TGA) characterisations.

Table 1: Formulation for fabrication of PLA-CNC/GNP biocomposites

Samples	Compositions		
	PLA (wt%)	CNC (wt%)	GNP (wt%)
PL	100	0	0
PLC5	95	5	0
PLG5	95	0	5
PLC2.5G2.5	95	2.5	2.5
PLC4G1	95	4	1
PLC1G4	95	1	4

3. Results and Discussion

3.1 Tensile Test

Fig. 1 and Fig. 2 show the flexural strength and modulus of PLA and its biocomposites. The result shows that the flexural strength and modulus of the biocomposites decreased with the increase in the replacement of CNC by GNP. This is probably due to the poor dispersion of nanofillers incorporated into the PLA matrix. Other than that, there are also reports by many researchers that high concentrations of nanofillers can cause agglomeration of nanofillers and cause heterogeneous dispersion in the polyester matrix [7]. Nevertheless, there is a synergistic effect in the case of the hybrid filler composite when compared with the single-filler composites (PLC5). Based on the result, PLC2.5G2.5 shows the highest flexural strength, which was 97.18 MPa, when compared to other samples, especially PLC4G1 and PLC1G4, which have similar incorporation with only difference in weight percentages of CNC and GNP. This might be due to good dispersion and strong interaction between the fillers and matrix with the formulation of PLC2.5G2.5 compared to other formulations. The result also shows the decrease in flexural strength with the incorporation of the

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single and hybrid CNC/GNP fillers for other samples, which resulted from PLA neat resin having the second highest flexural strength, 66.03 MPa. The reason for this may be assigned to the dispersion problem, which is a common behaviour that occurs when nano-scale materials are incorporated into the composite [8]. In addition, the decrease in flexural strength can be ascribed to GNP agglomeration that might form steric obstacles, limiting the polymers to stream into the agglomerates and bringing about the formation of voids and holes within GNP and PLA matrix that work as stress concentration centres, leading to interfacial failure [9-11].

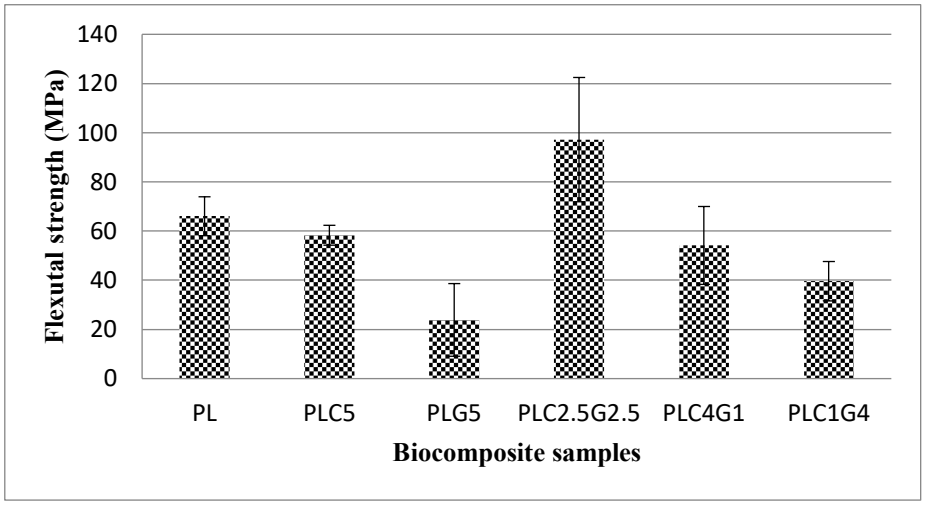

Fig. 1: Flexural strength of PLA biocomposites.

On the result in Fig. 2, the graph shows the increment in flexural modulus by PLC5 and PLC2.5G2.5 for 19% and 76%, respectively, compared to neat PLA. Generally, the increase in the modulus of polymer composites can only be caused by (1) the substitution of polymer matrix by the largely more rigid filler and (2) the filler restricting the mobility and deformability of the matrix by the introduction of a mechanical restraint [12]. Furthermore, the addition of nano-fillers induces the decrease of polymer chains and hence leads to brittleness or rigidity, which enhances the flexural modulus [10, 13]. It was noted that PLC2.5G2.5 shows the highest value of flexural modulus, which is 4.11 GPa among the samples, probably due to good dispersion of both CNC and GNP within the PLA matrix [14-15]. Ramires et al. [16] reported that CNC used as reinforcement of lingo-polyurethane matrix has increased its flexural modulus up to 670%. The reason for this would be assigned to CNC, which has a high elastic modulus that helps to reinforce the whole composite [17].

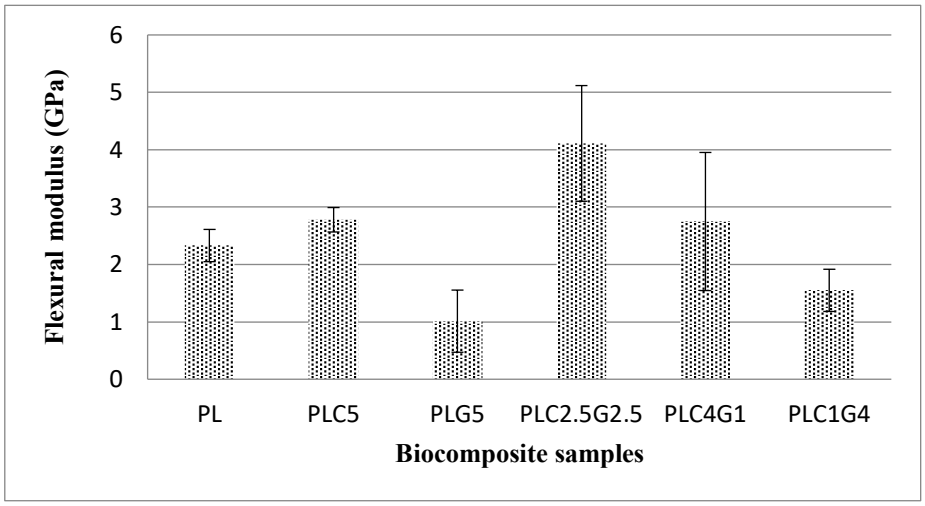

Fig. 2: Flexural modulus of PLA biocomposites.

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3.2 Thermal Properties

Fig. 3 presents the TGA and DTG curves stated for PLA biocomposites, while Table 2 summarises thermal stability data based on the temperature at mass loss of 10% ($T_{10\%}$), maximum degradation temperature (T_{max}), and percentage (%) of char residue at 700 °C. From the result, PLC5, representing the highest amount of graphene (5 wt.%) incorporated into PLA, contributed the highest thermal stability (334.0 °C) according to the $T_{10\%}$. Graphene, known for its exceptional thermal conductivity and mechanical strength, helps improve the thermal properties of polymers by increasing their resistance to thermal degradation and enhancing heat dissipation. When integrated into materials, GNPs form efficient thermal pathways, allowing heat to spread quickly and evenly [18]. For instance, a study by Liesenfeld et al. [19] has shown that the incorporation of graphene into PLA has increased the thermal stability of the composites by altering their crystallinity and thermal decomposition behaviour. Even though the T_{max} of PLG5 has almost the same value as PLA neat resin (PL), the hybrid PLC4G1 showed the maximum T_{max} values, indicating that the influence of CNC cannot be avoided.

It was interesting to observe that the hybrid PLA biocomposite (PLC2.5G2.5) demonstrated an optimum enhancement in $T_{10\%}$ (329.0°C) and T_{max} (375.6 °C) compared to other hybrid CNC/GNP reinforced PLA formulations. In addition, a study conducted by Montes et al. [5] reported that the PLA sample with a combination of 50/50 amounts of CNC and GNP resulted in the highest thermal stability. This might be due to good interfacial interaction between the matrix and nanofillers, which GNP functioned well as a great thermal conductor. Poor interfacial interaction will contribute to an increase in thermal boundary resistance, which will then lead to the prevention of thermal flow from filler to matrix or matrix to filler [20]. Hence, good interfacial interaction between the matrix and reinforcement can be assumed to be one of the significant factors in the improvement of thermal stability. Other than that, the improvement in thermal stability can also be spotted with the increment in the percentage of char residual at 700°C, as shown by all biocomposite samples, compared to the neat PLA, which only has 3.2%.

Table 2: TGA data of PLA-based biocomposites.

Samples	Degradation Temperature (°C)		Char residue at 700 °C (%)
	$T_{10\%}$	T_{max}	
PL	332.0	381.9	3.2
PLC5	318.0	376.0	11.6
PLG5	334.0	381.1	13.2
PLC2.5G2.5	329.0	375.6	8.3
PLC4G1	330.0	383.7	11.4
PLC1G4	320.0	370.1	5.9

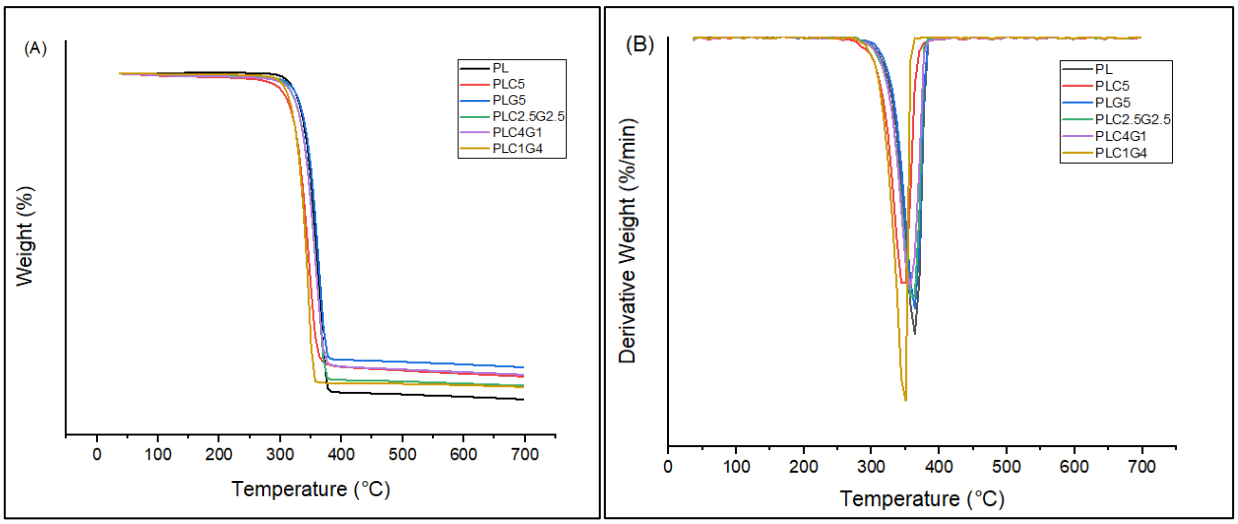

Fig. 3: A) TGA and B) Derivative thermogravimetric (DTG) curves for neat PLA and PLA-based biocomposite.

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4. Conclusion

PLA and its biocomposites were successfully fabricated by the utilisation of compression moulding. The use of CNC or GNP alone as an individual filler is not sufficient in contributing to the optimum result of mechanical and thermal properties of PLA biocomposites. It was interesting to conclude that the PLA biocomposite has a formulation of 2.5 wt.% CNC and 2.5 wt.% GNP (PLC2.5G2.5) contributed to the enhancement in flexural strength and modulus up to 47% and 76%, respectively. Other than that, there were also optimal enhancements in the thermal stability of PLC2.5G2.5 biocomposite samples according to data analysis obtained from the $T_{10\%}$, $T_{max,}$ and percentage of char residual at 700 °C.

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