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Characterization and preparation of conductive exfoliated graphene nanoplatelets kenaf fibre hybrid polypropylene composites

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ABSTRACT

Exfoliated graphene nanoplatelets (GNP) kenaf fiber (KF) hybrid polypropylene (PP) composites materials were prepared by melt extrusion followed by injection molding. PP/KF/MAPP/GNP composites 0–5 phr were prepared and characterized using X-ray diffraction (XRD), differential scanning calorimetre (DSC), thermogravimetry analysis (TGA), heat deflection temperature (HDT), thermal mechanical analysis (TMA), Fourier transform infrared (FTIR) spectroscopy analysis, field emission scanning electron microscopy. The morphological studies revealed a homogenous dispersion of GNPs in PP/KF/MAPP/GNP up to 3 phr loading after which agglomeration occurred. Flexural strength and modulus were enhanced by 70% and 98% respectively at 3 phr GNPs loading which were the highest values obtained. Interestingly, the highest value for the impact strength was also recorded at 3 phr loading. Thermal conductivity increased by 88%, CTE decreased by 80%, water absorption and thickness swelling decreased while HDT improved. The thermal stability of the composites were generally improved at all GNP loading with the highest at 3 phr. From the overall results, it is obvious that the optimum concentration of GNPs in the PP/KF/MAPP/GNP system in terms of both mechanical and thermal properties was 3 phr loading. Although, the mechanical and thermal properties of the composites were improved, the FTIR analysis did not reveal any chemical interaction between GNP and the PP/KF/MAPP system.

1. Introduction

Since the isolation of graphene in 2004, there has been escalating interest in studies with graphene inclusion. Many research investigations have been conducted and numerous studies are emerging in various aspects of its unique properties. Nowadays, research investigations into the structure and properties of graphene have advanced from inquisitive based to applicability [1]. Graphene is a single-layer carbon nanoparticle composed of sp^2 hybrid carbon atoms aligned hexagonally in planar structures. Several unique properties have enhanced the suitabilty of this material for diverse applications such as its exceptionally high mechanical strength with Young's modulus of 1 TPa, and tensile strength of 20 GPa [2,3], excellent electrical (5,000 S/m) and thermal conductivities at 3000 W/m.K. Research investigations using this material has escalated in numerous areas such as conductive polymer composites (CPCs) and intrinsically conducting polymers (ICPs) for wide range of engineering applications such as thermal interface materials, bio-actuators, fuel cells, drug delivery, tissue engineering, antennas, neural-probes, biosensors, chemical sensors and so on [1,4–8].

Nowadays, exfoliated graphene nanoplatelets (GNP) have emerged as a new reinforcing filler for the enhancement of mechanical properties [9–11], thermal properties [12,13], and barrier properties [14] of GNP reinforced polymeric nanomaterials. A major factor for escalating application of GNP in production of polymer nanocomposites is the lower cost of graphene, which is the precursor for GNP [15]. Results from various researches have also demonstrated that GNPs exhibited excellent conductivity and reduced the percolation threshold of nanocomposites. In addition, advantages shown by GNPs when compared with other types of nanofillers such as carbon nanotubes (CNTs), include lowered cost, layered structure similar to nanoclays for ease of dispersion and processability during composite preparation [9]. Several techniques used in composite preparation include melt mixing, in situ exfoliation, and solution polymerization. From an industrial perspective, melt polymerization has proven the most convenient type of processing technique because of easy adaptation to commonly available plastic processing machines such as extruders, in addition to being more economical as zero solvents

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Table 1
BET parameters.

V_m	=	Calculated value from 1/(slope + intercept) in graph of $1/(V_a (P_o/P) - 1)$ versus P/P_o
N	=	Avogadro constant given as 6.0×10^{23} mol^{-1}
a	=	Cross sectional area of single adsorbate molecule in meters square (0.195 nm^2 for krypton and 0.162 nm^2 for nitrogen)
m	=	Mass of GNP test flour in grams
22, 400		Volume of 1 mol of adsorbate gas at STP allowing for slight shift from the ideal, in milliliters

are involved which may also impact negatively on the environment. Numerous studies have been conducted using direct melt mixing technique for even distribution of graphene in polymer matrix [13–17,25]. Polypropylene (PP) is a light weight, low cost, linear-oleifinic commodity thermoplastic with good processability applied in packaging and fibre production. However, PP is characterized by low stiffness and flexural modulus, and poor thermal properties which positions it as a poor material where these properties are essential [25,26]. Numerous investigations have been conducted to enhance the mechanical, thermal, and water absorption properties of biocomposites through inclusion of nanoparticles [14–16]. In a previous study [16], the effects of nanographene on the physico-mechanical properties of bagasse/polypropylene composites was investigated. Results revealed that inclusion of GNP enhanced overall physico-mechanical properties of the material. In another study, multilayered graphene efficiently formed by mechanical exfoliation for nonlinear saturable absorbers in fiber mode-locked lasers [20]. Results revealed improvement of material properties as a result of the inclusion of multilayered graphene. Another study reported effect of GNP on physical properties of polactic acid kenaf fibre filled GNP [13]. Other studies using nanoparticles for enhancement of biocomposite material properties have been reported [29,30]. Results also indicated enhancement of properties through GNP inclusion. To the best of our knowledge, thermal conductivity, coefficient of thermal expansion, morphological characteristics and properties of PP/KF/MAPP filled with GNPs have not received any attention in the open literature. Therefore, in the present study, GNP filled PP/KF/MAPP/GNP composites were developed and their thermal conductivity, coefficient of thermal expansion, thermal stability, morphology, heat deflection temperature, impact strength, flexural strength and modulus, water absorption and thickness swelling were investigated.

2. Experimental

2.1. Materials

SM 240 grade heterophasic polypropylene (PP) copolymer of melt flow index 35 g/10 min (230 °C and 2.16 kg load) and density of 0.901 g/cm^3 was purchased from Lotte Titan Chemicals Malaysia. Maleic anhydride grafted polypropylene (MA-g-PP) compatibilizer of melt flow index 150 g/10 min (230 °C and 2.16 kg load) and melt temperature 167 °C was purchased from Dupont, Dow Elastomers, and Wilmington DE, USA. Kenaf fiber was obtained from Malaysian Agricultural and Development Institute (MARDI), Kuala Lumpur. Exfoliated graphene nanoplatelets, GNP-M5 grade containing 99.5% carbon and graphene nanoplatelets of average diameter 5 μm, and average thickness of 6 nm was purchased as dry flour from XG Sciences, Inc., East Lansing, MI, USA, and applied as received. Calculated Brunauer, Emmett and Teller (BET) surface area of specimens applied in this study is 158 m^2/g obtained from laboratory measurement.

Table 2
Formulation of uncompatibilized PP/GNP nanocomposites.

Sample designation	PP (phr)	GNP (phr)
PP/GNP 3	100	3

2.2. BET surface area measurement

The Brunauer, Emmett and Teller (BET) surface area was ascertained using Gemini V Surface Area Analyzer of isotherm nitrogen adsorption set at 77 K. Prior to BET evaluation, the specimen was degassed at 623 K for 4 h under atmospheric pressure. Eq. (1) was used in the calculation of specific BET surface area of GNP. Table 1 explains parameters used in Eq. (1).

$$S = \frac{V_m N_a}{22400m} \quad (1)$$

2.3. Sample preparation

PP was dried in a vacuum oven for 24 h at 80 °C, while MA-g-PP was dried for 8 h at 60 °C. Kenaf core fibre was ground and sieved using mesh of <500 μm using sieve shaker equipment to obtain kenaf fiber flour of size <500 μm. In order to reduce moisture content, kenaf flour was oven dried at 60 °C for 24 h. The composites were melt intercalated in a single step process using Brabender PL 2000 Plastic Coder counter rotating double screw extruder at optimized temperature of 185–20060 °C from feed zone to die head zone according to sample formulations shown in Tables 2 and 3 for uncompatibilized PP/GNP-3 phr and PP/KF/MAPP/GNP 0–5 phr nanocomposites respectively. Extruder screw speed was maintained at 60 rpm. After melt intercalation, the extrudates were subsequently pelletized. In order to eliminate moisture, pellets were oven dried at 8060 °C for 24 h, prior to injection molding to standard mechanical tests specimens using JSW model NIOOB 11 Muraron-Japan injection molding machine at temperature range of 185–200 °C. As shown in formulation, fibers were varied from 20 wt.%. This is because preliminary experiments revealed fiber control difficult at loadings ≥30 wt.% due to filler–fibre agglomeration. This also agreed with previous works were fiber content were kept constant at 20 wt.% for equal reason [20]. The concentrations of GNP were calculated based on parts per hundred of total composites (phr).

Table 3
Sample formulation for PP/KF/MAPP/GNP hybrid nanocomposites.

Sample designation	PP (wt.%)	MAPP (wt.%)	KENAF (wt.%)	GNP (phr)
PP	100	0	0	0
PP/KF/MAPP	75	5	20	0
PP/KF/MAPP/GNP 1	75	5	20	1
PP/KF/MAPP/GNP 2	75	5	20	2
PP/KF/MAPP/GNP 3	75	5	20	3
PP/KF/MAPP/GNP 4	75	5	20	4
PP/KF/MAPP/GNP 5	75	5	20	5