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Influence of exfoliated graphite nanoplatelets on the flammability and thermal properties of polyethylene terephthalate/polypropylene nanocomposites

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ABSTRACT

Nanocomposites based polyethylene terephthalate (PET)/polypropylene (PP) (70/30 wt%) blends and exfoliated graphite nanoplatelets (GNP) as reinforcing fillers were developed using melt extrusion process. The filler concentration was varied between 0 -5.98 wt percent (%) (0–7 phr). The resulting nanocomposites were characterized in terms of flame retardancy, thermal conductivity, thermal behavior, morphology and structure. Cone calorimeter analysis, limiting oxygen index (LOI) and UL94 flame rating tests revealed that addition of GNPs to PET/PP improved the flame retardancy of PET/PP/GNP nanocomposites significantly. Cone calorimeter data show a significant reduction of peak heat release rate (PHRR), mass loss rate and delayed time to ignition (TTI) due to addition of GNPs to PET/PP blend. As much as 37% reduction in PHRR and 32% increase in TTI were observed for the maximum GNP loading. Enhancements of flammability properties were attributed to the development of compact, dense, uniform char layers on the surface of nanocomposites. The effective thermal conductivity was found to vary linearly with GNP loading which was attributed to the formation of effective interconnected heat conduction bridges formed by the GNPs. It was found that the effective thermal conductivity of the nanocomposites was increased by about 80%, i.e. from 1.2 W/m.K for the unreinforced PET/PP blend to 1.9 W/m K for the 5.98 wt% (7 phr) reinforced PET/PP/GNP nanocomposites. Differential scanning calorimetry results indicated that the addition of GNPs increased crystallization temperatures but decreased degree of crystallinity of PET/PP/GNP nanocomposites. However; the melting points remained essentially unaffected. Transmission electron microscopy and field emission scanning electron microscopy showed uniform dispersion of GNPs in the matrix with the formation of interconnected GNP sheets at 3 phr. Isolated instances of exfoliation of GNPs was also observed.

1. Introduction

Engineering thermoplastics such as polyamides, and polycarbonates, possess superior mechanical and thermal properties, and hence are finding widespread use as structural materials in areas such as the automobile, aircraft or electrical/electronic industries. Consequently, growing demand has led to a hike in prizes of these thermoplastics. It is expected that the global revenue for engineering thermoplastics will hit 77 billion dollars by the year 2017 [1]. However, the increasing cost of engineering thermoplastics has motivated researchers both in academia and industry into focusing attention towards finding cheaper alternatives. Commodity thermoplastics such as polyethylene terephthalate (PET) or polypropylene (PP) are relatively inexpensive but have lower performance mechanical and thermal properties when compared to engineering thermoplastics. PET is a semi-crystalline commodity

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thermoplastic with good mechanical properties, low melt viscosity and spinnability. PET has been used in several fields such as food packaging, film technology, automotive, electrical, beverages containers and textile fibers. Despite its diversity of applications, flammability of PET polymers which likely results in fire disaster inevitably limits its functional applications in some special fields such as oil fields or chemical explosive factories. Therefore, many researchers have focused on improving the flame retardancy of PET [2–5]. PP is a linear oleifinic commodity thermoplastic with good processability, light weight, low cost and relatively better impact properties than PET. Its principal applications are in fiber and packaging industries. However, PP is characterized by poor flammability properties, low stiffness, low flexural modulus, and poor thermal properties which make it a poor candidate where these properties are required [5–7]. Blending PET and PP would offer an opportunity to combine the excellent properties of the two polymers due to synergistic effect and to overcome their individual shortcomings. Since PET and PP are thermodynamically incompatible due to differences in chemical structure and polarity, the use of suitable compatibilizers is then necessary in order to produce a material with desired properties. The use of elastomeric compatibilizers such as styrene-ethylene-butylene-styrene-g-maleic anhydride (SEBS-g-MAH) has led to remarkable enhancement of impact properties of PET/PP blends at the expense of other properties such as stiffness and strength [8].

Flame retarded polymers may be obtained by the use of flame retardants which are blended with polymers by physical means [4,9–11]. Carbon-based nanofillers such as carbon nanotubes [12] and graphene [13–15] have been used to reduce the flammability of polymeric materials by inhibiting the vigorous bubbling process in the course of degradation during combustion. Thermally conductive polymer nanocomposites on the other hand, offer new possibilities for replacing metal parts in several applications including power electronics, electric motors, generators and heat exchangers due to their light weight, low cost and ease of production.

Recently there has been increasing interest in the use of exfoliated graphite nanoplatelets (GNP) as a multifunctional reinforcement phase in polymer nanocomposites. These graphitic nanoplatelets, derived from graphite, combine the low-cost and layered structures similar to nanoclays with a unique plethora of properties similar to carbon nanotubes including electrical conductivity, superior mechanical, physical, thermal and flame retardants properties. Presently, research activities into the properties and structure of graphene has moved from curiosity-oriented to application-oriented [16,17]. Graphene is a monolayer carbon nano particle that consists of sp^2 hybridized carbon atoms arranged in hexagonal planar structures. Properties that have endeared this unique material to diverse applications are its exceptional mechanical strength (Young's modulus of 1 TPa, tensile strength of 20 GPa) [18,19], excellent electrical (5000 S/m) [20] thermal conductivities and stability (~3000 W/m K) [21]. Therefore, it is logical to expect that incorporating graphene into polymeric matrices will improve the flammability and thermal conductivity of the host polymers significantly. Consequently, several studies have been reported on the development of multifunctional polymer nanocomposites (PNC) [22–26] using GNP as the reinforcement phase.

Several studies have been conducted to assess the thermal conductivity of graphene reinforced polymer nanocomposites [27–30]. Min et al. [30] observed 157% increases in thermal conductivity of graphite nanoplatelets/epoxy composites over that of pure epoxy. Teng et al. [28] studied the effect of functionalized graphene on epoxy composites and observed that the thermal conductivity was much higher than epoxy reinforced with multi wall carbon nanotubes. Steady state thermal analysis is a method of measurement of thermal conductivity of polymer composites and nanocomposites. This method is useful for specimens having thermal resistance in the range of $10–400 \times 10^{-4}$ m^2 K/W. which can be obtained from materials of thermal conductivity in the approximate range from 0.1 to 30 W/(m K) [31].

Although GNPs have been used to impart flame retardancy in polymer nanocomposites with promising results, its use to reduce flammability of commodity thermoplastics such as PET and PP is still lacking. In this study, flammability, thermal conductivity, thermal behavior, morphological features and structure of GNP reinforced PET/PP blends was investigated as a function of concentration of GNPs. SEBS-g-MAH is expected to serve a dual function; to compatibilize PET/PP blends and to aid the dispersion of GNPs in the polymer matrix. Conventional melt extrusion process is used to prepare PET/PP/GNP nanocomposites because it is more economic, compatible with industrial processes (extrusion and injection molding) and free of environmentally harmful or dangerous solvents. To the best of our knowledge no similar report for same polymer system is published in the open literature.

2. Materials and methods

2.1. Materials

Exfoliated graphite nanoplatelets, GNP-M-5 grade (99.5% carbon) consisting of graphene nanoplatelets of average diameter 5 μm and average thickness of 6 nm was purchased as dry powder from XG Sciences, Inc. (East Lansing, MI, USA) and used as received. The BET surface area of the samples used in this experiment is 158 m^2/g measured in the laboratory. Polyethylene terephthalate (grade M100) was obtained from Espet Extrusion Sdn Bhd (Malaysia) with intrinsic viscosity of 0.82 g/dl. PP, a copolymer grade (SM240) with density of 0.96 g/cm^3 and melt flow index of 35 g/10 min (230 °C and 2.16 kg load) was supplied by Titan chemicals (Malaysia). Styrene-ethylene-butylene-styrene triblock copolymer grafted with 1.84 wt% of maleic anhydride (SEBS-g-MAH) was supplied by Shell Chemical Company under the trade name of Kraton FG 1901X with weight ratio of styrene to ethylene/butylene in the triblock copolymer to be 30/70. Melt flow index (MFI) of 20 g/10 min (270 °C, 5 kg), molecular weight of styrene block is 7000 g/mol and ethylene/butylene block is 37500 g/mol.

2.1.1. BET specific surface area determination

The Brunauer, Emmett and Teller (BET) specific surface area of GNP powder was measured by isotherm nitrogen adsorption at 77 K using Micromeritics Gemini V Surface Area Analyzer. The sample was degassed at 623 K under atmospheric pressure for 4 h prior to the BET test. The BET specific area of the sample was calculated using equation (1).

$$S = \frac{V_m Na}{22400m} \tag{1}$$

V_m	=	Value calculated as 1/(slope + intercept) in the graph of $1/[V_a(P_o/P)-1]$ against P/P_o,
N	=	Avogadro constant (6.022×10^{23} mol^{-1}),
a	=	Effective cross-sectional area of one adsorbate molecule, in square metres (0.162 nm^2 for nitrogen and 0.195 nm^2 for krypton),
m	=	Mass of test powder, in grams,
22,400	=	Volume occupied by 1 mol of the adsorbate gas at STP allowing for minor departures from the ideal, in milliliters.