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Processing and assessment of high-performance poly(butylene terephthalate) nanocomposites reinforced with microwave exfoliated graphite oxide nanosheets

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ABSTRACT

To improve the physical properties of poly(butylenes terephthalate) (PBT), a series of nanocomposites based on PBT and microwave exfoliated graphite oxide nanosheets (MEGONSs) are prepared *via* melt compounding technique, and their structures, thermal stabilities, mechanical, rheological and electrical properties are reported. Scanning electron microscope and X-ray diffraction exhibit that graphene platelets of MEGONS are well dispersed and exfoliated in the PBT matrix even at high MEGONS content of 4.0 wt.%. DSC cooling and following heating thermograms of the nanocomposites demonstrate that graphene platelets of MEGONS play a role as effective nucleating agents for PBT a-phase crystals and thus lead to accelerating the overall crystallization of the nanocomposites. Thermal stability of PBT/MEGONS nanocomposites improved substantially due to the gas barrier effect of graphene platelets of MEGONS dispersed in the PBT matrix. The rheological analysis shows the low frequency plateau of shear modulus and the shear thinning behavior of the nanocomposites. The mechanical modulus of the nanocomposites enhanced significantly with increasing MEGONS content. The electrical conductivity test shows a pronounced increase in electrical conductivity from an insulator to almost a semiconductor with increasing MEGONS content. The electrical percolation threshold of the nanocomposites is found to be formed at the MEGONS concentration between 1.0 and 2.0 wt.%.

1. Introduction

Among the various nanofillers used in the field of nanostructured materials, graphene represents one of the most promising as demonstrated by the number of recent publications [1–4]. As far the preparation of graphene-based nanocomposite is concerned, the challenge is clearly the attainment of a fine dispersion of the above nanofiller in the polymer matrix [2–4]. Indeed, while it is difficult to obtain homogeneous dispersions of graphene in polymer matrices, it is much easier to do it with single sheets of graphite oxide (GO), which contains hydroxyl and epoxy groups on the basal planes and carboxy groups on the hedges. As GO, due to its hydrophilic nature, can be readily exfoliated and reduced *via* solvent exfoliation [1] or thermal exfoliation (TEGO) [5] to create "wormlike" structures with a high specific surface area. These fully exfoliated graphene oxide platelets have been widely investigated as nanofillers for wide range polymer nanocomposites [1–4]. Still, the main obstacle linked to GO incompatibility with most polymer systems remains. Thus, it is necessary

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to proceed to surface property modification of GO by functionalization in order to make easier its dispersion in polymer matrices. Using GO after chemical modification with isocyanate or amine, composites have also been produced in aprotic solvents with hydrophobic polymers such as polystyrene (PS) [1] and polyurethane (PU) [6–8]. Another route generally used to disperse graphene into polymers is subjecting GO to microwave treatment to form microwave exfoliated graphite oxide nanosheets (MEGONSs) before blending with polymers [9,10]. Recent literatures survey shows that MEGONS has a similar structure to TEGO [9,10], which suggests MEGONS may also be dispersed using melt blending and might afford property enhancements comparable to TEGO. Interestingly, the procedure for making MEGONS is less time and energy intensive than the typical TEGO synthesis. Moreover, there are some differences in the reported physical properties of TEGO and MEGONS, such as different O:C ratios (i.e., a generally higher O:C ratio for MEGONS compared to TEGO) and different values of electrical conductivity, which could possibly affect dispersion and the final composite properties.

Poly(butylene terephthalate) (PBT) is a thermoplastic and semicrystalline polymer and, as a member of the poly(alkylene terephthalate) family, is derived from a polycondensate of terephthalic acid with 1,4-butanediol. PBT has relatively rapid crystallization rate and high elasticity compared with poly(ethylene terephthalate) (PET), but it has somewhat lower strength and stiffness than PET. Nonetheless, because of its combining excellent mechanical properties with robust chemical resistance and dimensional stability, PBT has been widely used for an engineering thermoplastic [11,12] or for a component in blends [13–15], copolymers [16–18] and composites [19–21]. However, for high-performance applications, thermal and mechanical properties of PBT need to be enhanced. Besides, PBT exhibits some other disadvantages like low notch impact strength and low heat deflection temperature. In response to demand for high performance materials it is often modified by blending with other polymers and use of reinforcements. Among the various reinforcements for PBT, calcium carbonate [22], carbon black [23], glass fibers [24], carbon fibers [25], montmorrilonite [26] and carbon nanotubes [21,27] are most often used. However, literature survey reveals that very little research works have been published about processing of graphene nanopletes reinforced PBT nanocomposites through the melt blending technique. Recently, Li and Jeong [28] prepared PBT/exfoliated graphite nanocomposites by melt blending, which showed the addition of small amounts of the above filler could result in a marked improvement in thermal and electrical conductivity (percolation threshold was between 3 and 5 wt.%.) of the composites. In-situ polymerization approach has been applied by Fabbri et al. [29] to prepare PBT/graphene oxide nanocomposites, and the results indicate that increasing amounts of graphene oxide did not strongly influence the degree of crystallinity and the crystallization temperature of PBT, while its thermal stability is significantly increased by the presence of graphene oxide. All the PBT/graphene oxide composites demonstrated to be electrically conductive and the electric field assisted thermal annealing of the composites induces an increase in conductivity. However, in general the use of graphene oxide involves a previous oxidation of graphite and subsequent reduction of GO, in order to restore the material electrical conductivity. In this light, the development of methods able to disperse graphene in one step into a polymer matrix is a significant current research issue.

In this work, a series of PBT-based nanocomposites reinforced with microwave exfoliated graphene platelets has been attempted by applying a simple procedure, which consists of a preliminary dispersion/exfoliation of graphite by using microwave exfoliation, and a subsequent melt blending with PBT. The effects of graphene platelets on melting/crystallization behavior, thermal stability, mechanical modulus, rheological property and electrical conductivity of PBT have been investigated by adopting various measurements. This work differs substantially from the previous studies, because MEGONS presumably enhance the interfacial interaction with the PBT matrix and shows a high affinity for PBT, and it could therefore be used effectively in the fabrication of PBT nanocomposites. Herein, we present, to our knowledge, the first report on the morphology and properties of a MEGONS-filled PBT nanocomposites.

2. Experimental

2.1. Materials

A commercially available PBT particle with intrinsic viscosity of 1.25 dL/g was used as polymer matrix. In order to improve the uniformity of mixing, PBT particles were firstly frozen in liquid nitrogen then grounded into fine powder. The natural graphite powder (NGP, SP-2, $C > 99\%$, $D = 5$ μm) was purchased from Qingdao Tianhe Graphite Co., Ltd. (Qing-Dao, China). $KMnO_4$ (C.P.), $NaNO_3$ (C.P.), H_2SO_4 (>96%), H_2O_2 (30%), isopropyl alcohol (IPA) and *N,N*-dimethylformamide (DMF) were purchased from Ke-Long Reagent, Inc. (Cheng-Du, China). All the chemicals were used as received without further purification.

2.2. Synthesis of graphite oxide (GO) and MEGONS

GO used in this research was synthesized from NGP by graphite oxidation with $KMnO_4$ in concentrated H_2SO_4 according to the procedures depicted in our previous work [30]. The GO was loaded into a glass beaker, put into a domestic microwave oven (General Electric), and heated for ~20 s to cause rapid exfoliation and reduction of the material (the yield of MEGONS relative to the starting amount of GO was ~35%). The black, fluffy MEGONS powder was collected and kept free to maintain its original morphology before use.

2.3. Fabrication of PBT/MEGONS nanocomposites

PBT/MEGONS nanocomposites containing various MEGONS contents were prepared by melt-compounding method. Before processing, all the components were dried in vacuum at 120 °C for 24 h. Since MEGONS has low bulk density (0.01–0.02 g/mL), some MEGONS powder was