



Preparation of low-density polyethylene/low-temperature expandable graphite composites with high thermal conductivity by an in situ expansion melt blending process



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ABSTRACT

A facile strategy with the advantages of low cost and ease of mass production was presented to prepare low-density polyethylene (LDPE)/low-temperature expandable graphite (LTEG) composites with relatively high thermal conductivity by an in situ expansion melt blending process. LTEGs were expanded and delaminated into graphite multi-layers and graphite nanoplatelets during processing which synergistically created more thermo-conducting paths in the composites and hence led to great improvements in thermal conductivity. Thermal conductivity of the composite with 60 wt% of LTEG loading was increased by 23 times as compared to the pure LDPE, increasing from 0.47 to 11.28 W/mK. The incorporation of LTEG decreased the melting temperature and the degree of crystallinity of LDPE. Percolation threshold of both the electrical conductivity and rheological measurements was observed at about 8 vol% of LTEG loading. Moreover, the LDPE/LTEG composites showed better thermal stability compared to the pure LDPE.

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1. Introduction

Polymeric thermally conductive materials hold the potential to replace metallic materials in various industrial applications, including circuit boards in power electronics, heat exchangers, electronics appliances and machinery, due to their light weight, low cost, corrosion resistance and easy processing [1]. Various kinds of fillers, such as metallic particles [2], ceramic fillers [3], graphite [4,5], carbon fibers [6], and carbon nanotubes [7] have been used to improve the thermal conductivity of the polymeric matrix. Among these fillers, graphite is usually recognized as the best conductive filler because of its good thermal conductivity, low cost and fair dispersibility in polymer matrix [5]. Recently, increasing attention has been paid to the use of exfoliated graphite [8–10] and exfoliated graphite nanoplatelets (GNPs) [11–16] in polymers to produce thermally conductive nanocomposites, since the thermal conductivity of single graphene sheets constituting graphite was theoretically estimated to be as high as 5300 W/mK [17].

Exfoliated graphite is usually obtained by rapid heating graphite intercalation compounds (GICs) past a critical temperature [18] or exposing them to microwave radiation [19]. It is composed of stacks of delaminated graphite nanosheets whose thickness may

vary from 100 to 400 nm [20], which can be further exfoliated into GNPs with the ultrasonic technique in solvents [21,22]. These GNPs offer the potential to produce multiple conductive pathways in the composites to achieve enhanced thermal conductivity. As a few examples, Debelak and Lafdi [9] dispersed exfoliated graphite flakes in an epoxy resin and found there was a 24-fold increase in thermal conductivity (from 0.2 to 5 W/mK) after adding 20 wt% exfoliated graphite in the pure resin. Drzal and coworkers [12–14] have prepared a series of GNP-filled nanocomposites by melt blending method, including nylon [12], polypropylene [13] and polyethylene [14]. It was found that the thermal conductivity of the composites increased significantly with the graphite loading, reaching more than 4 W/mK for nylon-6 with 20 vol% GNP loading, 1.2 W/mK for HDPE with 20 vol% GNP loading, and 1.2 W/mK for PP with 25 vol% GNP loading, respectively. Haddon et al. [15] prepared GNP with controlled aspect ratio to fabricate epoxy composites via solution mixing. The GNP-epoxy composites (where the number of graphene layers, $n \sim 4$ and thickness ~ 2 nm) were found to have thermal conductivity up to 6.44 W/mK at 25 vol% GNP loading. They attributed the outstanding thermal properties of this material to a favorable combination of the high aspect ratio, two-dimensional geometry, stiffness, and low thermal interface resistance of the GNPs.

However, it is unlikely to completely delaminate the carbon layer in polymer/exfoliated graphite composites, because the exfoliated graphite is so fragile that it will break down during processing of the composites [20]. This is probably one of the reasons why

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the properties of the resulting composites are not as good as expected, or even far below theoretical predictions. On the other hand, exfoliation and dispersion of unmodified GNPs in polymers are also extremely difficult to achieve using conventional processing techniques, due to the coupling effect among graphene sheets and the extremely high aspect ratio of monolayer graphene sheets [23]. Moreover, high treatment temperature (1000 °C) is usually required to obtain exfoliated graphite, and subsequent high intensity ultrasonication with a sufficiently long time in various solvents is needed to obtain GNPs. These processes require adequate equipment and techniques, which will lead to enormous energy consumption and low efficiency for mass production. In addition, some hazardous organic solvents used as processing medium may have negative health impacts. For these reasons, it still represents a significant challenge at present to develop a facile processing method to achieve low cost manufacturing of graphite-filled composites having high thermal conductivity (higher than 4 W/mK) using industrially scalable processing techniques, especially considering high filler loadings (>30 vol%) are typically necessary to achieve the appropriate level of thermal conductivity in thermally conductive polymer composites [1].

Expandable graphite (EG) is a kind of GICs that has been mainly used as an intumescent flame retardant [24–26]. Its derivatives such as exfoliated graphite and GNPs can also be applied to prepare thermally conductive polymer composites as stated above, but EG as a conducting filler has seldom been studied [27]. Recently our research work has found that EG can be directly used to fabricate thermally conductive composites without pretreatment of expansion or ultrasonication. If in situ expansion of the graphite layers of EG could occur when it is compounded with polymers at elevated temperature during processing, either intercalated or delaminated composites would be formed simultaneously, leading to great enhancement of desired properties in comparison to conventional composites. Based on this application, the exfoliation temperature of EG should be lower than the decomposition temperature and preferably close to the processing temperature of polymer. Moreover, sulfur-free EG is preferred due to erosion and environmental pollution caused by sulfur-containing compounds [28]. These allow the use of conventional processing techniques, such as melt blending with a batch mixer or an extruder, which may be a facile, efficient and low cost manufacturing method to obtain a high thermally conductive graphite-filled polymer composite.

The object of this work was to develop a facile and high effective strategy for the large-scale fabrication of graphite/polymer composites with high thermal conductivity by melt blending of low-temperature expandable graphite (LTEG) with low-density polyethylene (LDPE). In this way the commercially available LTEG was supposed to expand at elevated temperature when it was melt-blended with LDPE, and then could be intercalated and exfoliated simultaneously under mechanical shearing force during processing. This paper is mainly focused on the morphology and properties, such as thermal, electrical, rheological, crystallographic and mechanical properties of the obtained composites.

2. Materials and methods

2.1. Materials

Low density polyethylene (LDPE 1254NT) was obtained from the Dow Chemical Company, with a melt index of 8 g/10 min and a density of 0.918 g/cm³. Sulfur-free low-temperature expandable graphite (LTEG KP251) was provided by Shijiazhuang ADT Carbonic Material Factory (Shijiazhuang, Hebei) with particle size of 50 mesh, density of 2.05 g/cm³ and onset exfoliation temperature

at 150 °C. No solvents, modifiers, compatibilizers or processing aids were used.

2.2. Preparation of the LDPE/LTEG composites

LDPE and LTEG were melt-blended in a Brabender Plasti-corder PL2000 mixing machine with a mixing speed 50 rpm for 15 min at 180 °C. The resulting mixture was then put in a molding die and compressed in a hot press at 180 °C under 10 MPa pressure to obtain the composite specimens for testing. Composites with graphite concentrations ranging from 0 to 60 wt% were prepared.

2.3. Characterization

2.3.1. Scanning electron microscopy (SEM)

The morphology of the graphite and the fractured interface of the composite specimens were observed using a JEOL JSM-5600 scanning electron microscope. The fractured surfaces were prepared in liquid N₂ and were sputtered with gold in vacuum prior to observation.

2.3.2. X-ray diffraction (XRD)

XRD patterns of pure LDPE, LTEG and LDPE/LTEG composites were recorded on Philips X-Pert Pro Diffractometer. Ni-filtered Cu K α radiation ($\lambda = 0.1540$ nm) generated at 40 kV and 40 mA. The instrument was run at a scanning rate 0.06°/s within (2θ) angle ranged from 5° to 60°.

2.3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) analyses were performed using a Netzsch instrument DSC 204 F1 in a nitrogen atmosphere. For the LTEG, a standard 10 °C/min heating ramp from 30 °C to 250 °C was employed to determine its actual exfoliation temperature. For pure LDPE and the composites, 5–10 mg samples were used and the nonisothermal crystallization was studied using the following experimental conditions: the sample was heated to 180 °C at a rate of 40 °C/min. The prior thermal history of the sample was erased by maintaining isothermal conditions at 180 °C for 5 min. Then, the sample was cooled down to 30 °C at a rate of 10 °C/min, and reheated at 10 °C/min to 180 °C.

2.3.4. Rheological measurements

Rheological properties were investigated by using a Bohlin Gemini 2000 (Malvern Instruments Ltd. UK) with 25-mm parallel-plate fixtures. A dynamic frequency sweep from 0.01 to 100 rad/s was employed and the material was maintained in a nitrogen atmosphere at 180 °C.

2.3.5. Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were carried out using a Q600 system from TA instrument under flowing nitrogen. Samples of 5–10 mg were heated from 40 to 550 °C at a heating rate of 10 °C/min.

2.3.6. Thermal conductivity

The thermal conductivity of the samples were measured by a Hot Disk thermal analyzer (Hot Disk 2500-OT, Uppsala, Sweden), using the transient plane source (TPS) method based on a transient technique. According to this method, a disk-shaped TPS sensor with a diameter of 3.189 mm is placed between two circular sample pieces with diameters of 20 mm and thicknesses of about 10 mm. The sensor supplied a heat pulse of 0.02–0.2 W for 20–5 s to the sample depending on the thermal conductivity of composites. The thermal conductivity of composites measured in this work is a comprehensive value of all directions, not just the in-plane or through-plane direction.

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