Materials Letters 128 (2014) 275–278

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Enhanced fire retardancy of polyethylene/alumina trihydrate composites by graphene nanoplatelets

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ARTICLE INFO

Article history:
Received 25 September 2013
Accepted 22 April 2014
Available online 28 April 2014

Keywords:
Polymeric composites
Nanocomposites
Polyethylene
Graphene nanoplatelets
Alumina trihydrate

ABSTRACT

In this work, well exfoliated graphene nanoplatelets (GNPs) were prepared and applied to enhance the fire retardancy of polyethylene/alumina trihydrate (PE/ATH) composites. GNPs with thickness about 5 nm were obtained from expanded graphite by ball milling and ultrasonic treatment. A homogeneous mixture of GNPs and ATH was prepared and used to prepare PE/ATH/GNP composites by melt-blending. The fire retardancy of PE/ATH was improved with addition of GNPs. The peak heat release rate of the PE/ATH/GNP composite with only 0.2 wt% GNPs decreased by 18% of that of the PE/ATH composite. The fire retardancy of PE/ATH/GNP composites was influenced by the GNP contents. A char layer of GNPs was revealed on the surface of the residues after combustion testing, which contributed to the enhanced fire retardancy by acting as a heat shield and a barrier against mass transport. The well exfoliated structure of GNPs and its good dispersion with ATH played an important role in the char formation at very low loading of GNPs.

1. Introduction

Graphene and its derivatives received world-wide attention thanks to their excellent properties such as charge transport and mechanical properties [1]. Due to the limited output of powdered graphene, graphene nanoplatelets (GNPs) were extensively applied in polymer based nanocomposites [2,3]. Recently, GNPs have been found to be effective in flame retardant polymers [4–6]. The flame retardancy of GNPs was reported to surpass that of Na montmorillonite (MMT) and multiwall nanotubes (MWNTs) in poly(vinyl alcohol) [7]. Well exfoliated GNPs were revealed to be preferable to less exfoliated ones in polypropylene [8]. GNPs were also used together with melamine polyphosphate [9], MMT [10], and intumescent flame retardant [11]. Nevertheless, the investigations on the flame retardancy of GNPs are far behind the conductive properties [3]. For polyethylene (PE) based composites, the flame retardant effects of GNPs were seldom demonstrated [12–14]. Alumina trihydrate (ATH) is a common flame retardant for PE [15], however, many challenges need to be addressed due to its poor flame retardant efficiency [16–18]. Hereinafter, GNPs were prepared and attempts were made to enhance the fire retardancy of PE/ATH composites at a low loading of GNPs.

2. Experimental

Expanded graphite (EG) was obtained from expandable graphite (9950250, Qingdao Tianheda Graphite Co. Ltd.) by treating for 1 min in a muffle oven preheated to 800 °C. 0.2 g EG was ground with 100 ml distilled water by ball milling for 2 h and then ultrasonically treated for 4 h to obtain a dispersion of GNPs. The dispersion was mixed with ATH (HF-1, Aluminum Corporation of China) and ground by ball milling for 2 h. The mixed fillers were dried at 100 °C for 8 h and ground for 1 h. The composites were prepared by melt blending PE (Q210, China Petroleum & Chemical Corporation) and the mixed fillers with a mixer rheometer (RM-200C, Hapro Harbin Electric Technology Co. Ltd) at 160 °C with a speed of 60 rpm for 5 min. The loading of mixed fillers was 40 wt% and the GNP contents were 0.2 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt%, respectively. Composites were labeled as PE/ATH/GNP*x*, where *x* represents the content of GNPs. Samples for testing were prepared by compression molding.

Atomic Force Microscopy (AFM) images of GNPs were taken with Bruker Dimension Icon in tapping mode. AFM samples were prepared by casting dispersion onto silicon wafer. Transmission electron microscopy (TEM, JEM-2100, JEOL) was used at an accelerator voltage of 200 kV on the samples prepared by depositing dispersion on 200 mesh Cu grid. Scanning electron microscopy (SEM, Sirion200, Philips) was performed after metal sprayed. The composites samples were fractured in liquid nitrogen. The fire testing was performed according to ISO 5660 by using

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http://dx.doi.org/10.1016/j.matlet.2014.04.148
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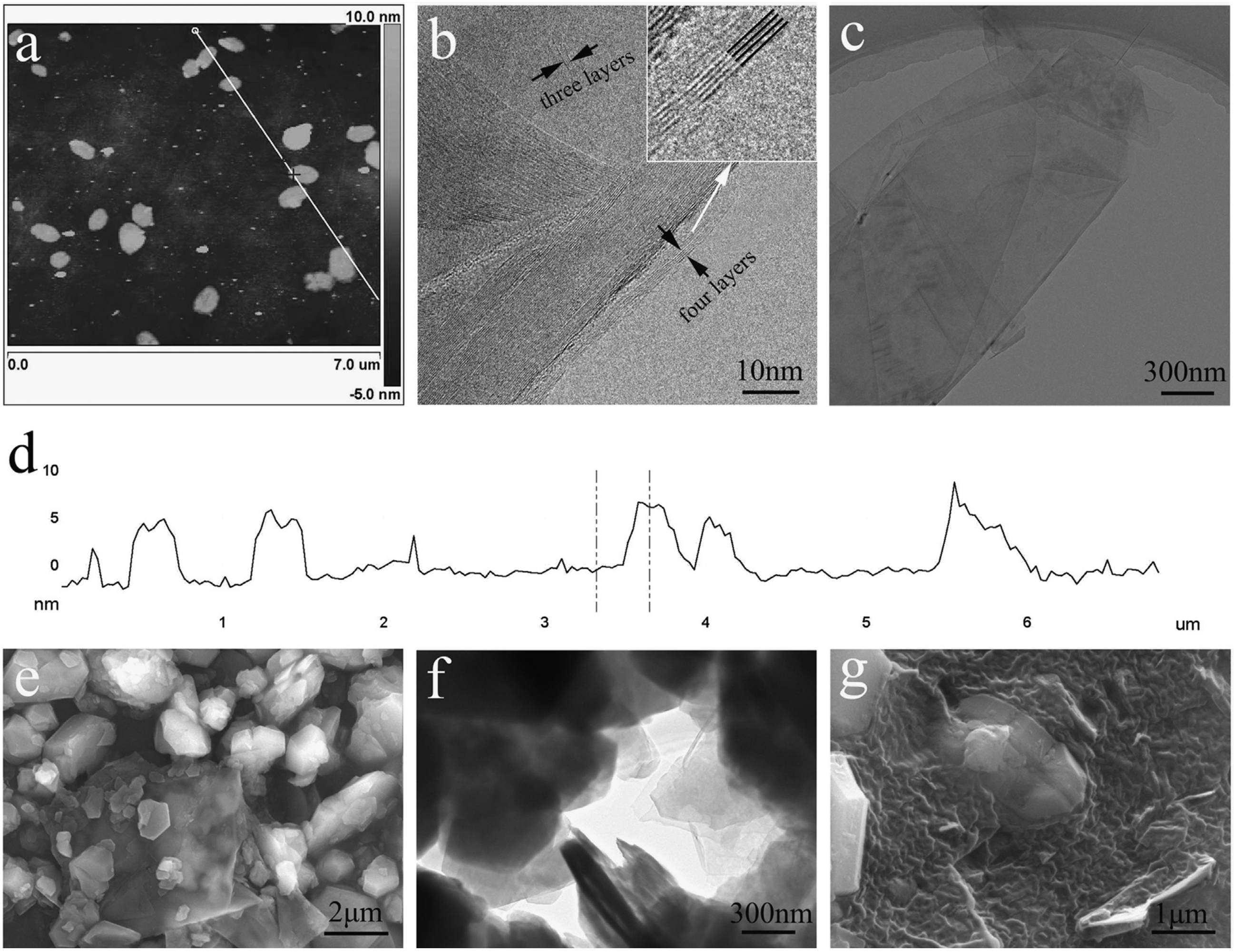

Fig. 1. Typical tapping mode AFM image of GNPs (a) and the section analysis (d); TEM images of GNPs (b and c); SEM (e) and TEM (f) images of ATH/GNPs; SEM image of PE/ATH/GNP1.5 composites (g).

a FTT cone calorimeter (CONE) on the 100 mm × 100 mm × 3 mm samples at a heat flux of 35 kW/m^2 in the horizontal configuration. The morphological structure of the residual materials after testing was characterized by SEM (LEO 1450 VP).

3. Results and discussion

The well exfoliated structure of GNPs is observed by the AFM and TEM images in Fig. 1. According to the AFM section analysis results (Fig. 1d), the thickness of GNPs ranges around 5 nm. Some nanoplatelets composed of about three and four graphene layers are also illustrated in Fig. 1b. When GNPs were deposited on Cu grid, the superimposed image in Fig. 1c formed due to the aggregation of nanoplatelets. The nanoplatelets are homogeneously mixed with ATH, as shown in Fig. 1e and f. Some nanoplatelets are nearly transparent on the surface of ATH. The mixed fillers show well dispersion in PE (Fig. 1g).

The heat release rate (HRR) curves of PE/ATH/GNP composites are shown in Fig. 2. When compared with PE/ATH, PE/ATH/GNP composites present decreased peak-HRRs and mass loss rates (MLR). The peak-HRR and the average MLR of PE/ATH/GNP0.2 are reduced by about 18% and 14% of that of PE/ATH, respectively. The results suggest that GNPs are helpful to form a heat shield and a barrier against mass transport during combustion [5,7,8]. The suppressed second peaks and the prolonged flameout time provide further evidences for the effective barrier.

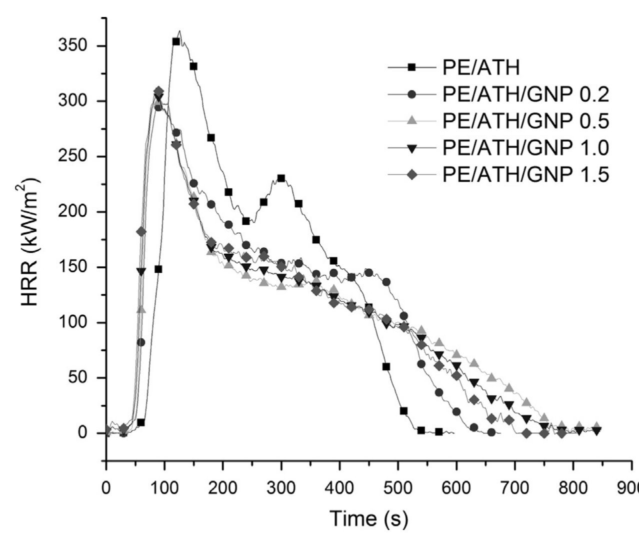

Fig. 2. Heat release rate curves of PE/ATH/GNP composites.

According to the CONE data in Table 1, the fire retardancy of PE/ATH/GNP is influenced by the content of GNPs. PE/ATH/GNP0.5 marked a turning-point of combustion behaviors. A slight increase of peak-HRR and a shortened flameout time of PE/ATH/GNP1.5 are observed in comparison to PE/ATH/GNP0.5. The possible explanations may be from the behaviors of GNPs and ATH during combustion. GNPs