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The effect of graphite nanoplates on the thermal degradation and combustion of polyethylene

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ABSTRACT

Studies of thermal and fire-resistant properties of the polyethylene/graphite nanoplates (PE-GNP) nanocomposites prepared by means of in situ polymerization are discussed.

The key factor of influence of graphite nanoplates on the thermal degradation and combustion of PE-GNP nanocomposites is analyzed using the sets of the data acquired with the aid of thermogravimetry (TG) and gas chromatography – mass spectrometry (GC–MS) experiments. It has been found that the addition of graphite nanoplates changes the composition of polyethylene pyrolysis products resulting in dramatically increase the fraction of heavy hydrocarbons.

The results of cone calorimetric tests lead to traditional conclusion that formation of GNP protective shield plays a key role in the mechanism of flame retardation for PE-GNP nanocomposites. On the other hand, the decrease in PE-GNP nanocomposites combustibility can also be a result of the reduction in the diffusion rate of the degradation products in the liquid pyrolysis phase and gaseous phase of combustion.

1. Introduction

Reduction of polymer flammability is an important issue. The difficulty of reducing the flammability of polymer filled composites is connected with finding effective fillers, addition of which to polymers would not reduce their physical, chemical and mechanical properties. Nanofillers are considered to be the promising additives to enhance mechanical properties as well as flame retardancy of polymeric materials [1].

Graphene is a new type of nanofiller, with two-dimensional structure and with excellent mechanical, thermal and electrical properties [2]. Graphene based materials possess unique physico-chemical properties including large surface area, good conductivity and mechanical strength and high thermal stability. Moreover, thermal stability and the flammability of graphene based polymeric composites is of concern in susceptible applications [3–5]. Recently, Wang et al. reported an improvement in the thermal stability of epoxy nanocomposites containing

0.1% graphene oxide nanoparticles [6]. The presence of graphene oxide slightly changed the thermal stability of the polyurethane/graphene oxide/epoxy nanocomposites. In the case of these nanocomposites, a content of small amount of graphene oxide (0.033%) leads to a slight increase of the degradation temperatures [5]. Bora et al. [7] prepared nanocomposites based on graphene oxide (GO) and unsaturated polyester resin. They verified that the incorporation of 3 wt.% of GO improved the onset of polyester degradation temperature from 230 to 285 °C. This improvement in thermal stability was attributed to the strong interaction between GO and unsaturated polyester resin which restricts the mobility of the polymer matrix segments at the interface. This interaction may be attributed to the formation of hydrogen bonding between oxygen functionality on reinforcement and polymer or dipolar interactions between the two components.

Enhanced thermal stability of polystyrene (PS), polyvinylacetate (PVA), polymethylmethacrylate (PMMA) graphene composites filled with the negligible concentrations of graphene, characterized by the

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shifts (10 °C–100 °C) of the maximum weight loss rates according to thermogravimetric analysis (TGA) data. The enhancement in thermal stability is attributed to restricted chain mobility of polymers near the graphene surface [8]. The rise of the nanocomposites' thermal stability has also been attributed to the movement restriction of the polymer chains inside the graphene nanogalleries. [9].

On the other hand, the presence of graphene nanoplates may also hinder the diffusion of volatile decomposition products within the polymer nanocomposites by promoting char formation. Consequently, the char-formed layer acts as a mass transport barrier that retards the escape of the volatile degradation products [9]. Moreover, during combustion, inflammable anisotropic nanoparticles form a jammed network of char layers that retards transport of the decomposition products [10]. This suggests application of graphene/polymer nanocomposites for flame retardation.

Uhl and Wilkie studied the thermal stability and flammability properties of PS-GO nanocomposites using cone calorimeter [11,12]. They have found the reduction in peak heat release rate from 27 to 54% with the increase amount of GO in composition with PS (from 5 to 16.5%). The proposed flame retardant mechanism of the addition of GO is that the formation of a char layer consisting of GO acts as a thermal insulator and a mass transport barrier, slowing the escape of the volatile products generated from the thermal degradation of polymeric matrix. An improvement in flame retardant effectiveness could be achieved by enhancing the formation of char significantly by making numerous cross-links from specifically functionalized nanoparticles (more carbons in the polymer matrix remain in the condensed phase) [13].

The mechanism of pyrolysis of various polymers considering the quantitative characteristics of degradation products has been widely studied in past decades [14–16]. In particular, the radical chain mechanism of the PE thermal degradation is studied in detail using TGA and GC–MS data [17–23]. Unfortunately, there is deficiency of similar studies relating to influence of various nanofillers on the mechanism of pyrolysis of polymer composites.

In the present study, we have focused on the effect of graphite nanoplates (GNP) on the mechanism of thermal degradation and flammability of PE-GNP nanocomposites.

2. Material and methods

2.1. Materials

GNP with specific surface area of 25.6 m²/g, 20 nm of thickness and the lateral dimensions of 1–10 μm were prepared by thermal exfoliation of expandable graphite followed by sonication in ethanol-water solution. The detailed procedure of preparation and the structure characterization of graphite nanoplates are presented in [24]. PE-GNP nanocomposites with 1.6, 3.7, 7.5, 14 and 50% wt. of GNP filler were synthesized by *in situ* polymerization procedure, detailed in [24]. The catalyst components (VCl₄ and Al(*i*-Bu)₃) were applied on the GNP sequentially. The suspension polymerization of ethylene was performed in *n*-heptane at 40 °C and a monomer pressure of 1 atm under stirring. The resulting polymeric product was washed with ethanol and dried under vacuum at 60 °C. The filler content in the composites was calculated as the mass ratio of the filler to the mass of the synthesized composite. Unfilled PE was prepared under the same conditions as those used for the preparation of the composites with the use of the catalyst VCl₄ + Al(*i*-Bu)₃ supported on the PE powder.

The average molecular weight of unfilled PE and PE matrix in the synthesized nanocomposites was about 2.0–2.5·10⁶ g/mol [24].

2.2. TG measurements

TG analysis of PE-GNP nanocomposites was made by Netzsch TG 209 F1 thermal balance at the heating rate of 20 °C/min in inert atmosphere of Ar and the samples weight of about 5 ± 0.5 mg.

2.3. Pyrolysis experiments

Pyrolysis experiments of PE-GNP samples (6 ÷ 10 mg) were carried out in horizontal quartz tube reactor (3 mm in diameter and 50 mm in length) heated by an electric furnace during 15 min: Ar flow rate – 15 ml/min, temperature of pyrolysis – 500 ± 2 °C. The temperature was controlled by resistance thermometer Pt100. Volatile degradation products were condensed in 1 ml of cold hexane at 4 °C and analyzed without additional pretreatment.

2.4. GC–MS analysis

GC–MS measurements were performed on a gas chromatograph Trace-1310 and ISQ™ Single Quadrupole Mass Spectrometer (Thermo Fisher Scientific Inc.). The pyrolysis products were injected into the GC capillary quartz column (Thermo Fisher Scientific Inc.) 15 m × 320 μm i.d. and 0.25 μm film of GC stationary phase (TR-5MS 5% Phenyl Polysilphenylene – siloxane) under the temperature-programmed conditions in the range of 40–290 °C with gradient 15°/min., injector temperature, –250 °C. The GC–MS detector conditions used were split injection (40:1), temperature-programmed from 40 to 290 °C with gradient of 15°/min, helium carrier gas, and ionization energy of 70 eV in the electron impact mode. Mass spectra collected within the 30–500 *m/z* interval at 3 scans per second. MS-spectra of degradation components were identified and interpreted by matching the results with NIST 2011 Mass Spectral library and reference literature data [16,17,22,23].

All detected degradation products were standardized by relative peak area of particular product (*RPA_i*) according to equation

$$RPA_i = \frac{PA_i}{\sum PA_i} \times 100\%$$

where *PA_i* – peak area of particular product, $\sum PA_i$ – sum of peak areas of all detected products. Relative peak area for hydrocarbon fraction (*RPA_f*) presents a sum of *RPA_i* for corresponded fraction.

2.5. Cone calorimeter tests

The Standard Cone Calorimeter by Fire Testing Technology Ltd. was used to characterize the flammability of PE and PE-GNP nanocomposites [25]. The hot pressed samples (78 × 78 × 2.5 mm) of polyethylene compositions positioned horizontally were exposed to a heat flux of 35 kW/m².

2.6. Scanning electron microscopy

The morphology of residue of PE nanocomposite with GNP (3.7% wt.) after TG experiment was observed on a Philips 515 SEM microscope at an acceleration voltage of 30 kV.

2.7. DSC analysis

DSC analysis of PE-GNP nanocomposites was made by Netzsch DSC 204 F1 instrument. The samples were heated up to 190 °C and cooled to 20 °C at the rate of 10°C/min in Ar.

3. Results and discussion

3.1. Thermal analysis

TGA results of PE and PE-GNP nanocomposites thermal degradation show the significant increase in thermal stability of PE-GNP nanocomposites as compared with pristine PE which is clearly seen by the rise of onset temperatures (Fig. 1a) and the temperatures of the maximum mass loss rates (Fig. 1b). Fig. 1b presents the normalized to PE DTG curves of composites that allows to illustrate the adequate

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