Available online at www.sciencedirect.com
ScienceDirect
Polymer Degradation and Stability 92 (2007) 1204–1212
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Synergistic flame retardant effects of nano-kaolin and nano-HAO on LDPE/EPDM composites

Zhi-Hong Chang [a,b], Fen Guo [a,b,*], Jian-Feng Chen [a,b], Jiang-Hua Yu [c], Guo-Quan Wang [c]

[a] Key Lab for Nanomaterials, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] Research Center of the Ministry of Education for High Gravity Engineering & Technology, Beijing University of Chemical Technology, Beijing 100029, PR China
[c] Institute of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

Received 7 January 2007; received in revised form 30 March 2007; accepted 5 April 2007
Available online 14 April 2007

Abstract

A novel flame retardant system composed of nano-kaolin and nano-HAO (nano-sized hydroxyl aluminum oxalate) was used for flame retarding the low density polyethylene (LDPE)/ethylene propylene diene rubber (EPDM) blends. Results of fire testing showed that nano-kaolin and nano-HAO exhibited excellent synergistic effects on the flame retardancy of the LDPE/EPDM composites. When 12 wt% nano-kaolin took the place of 12 wt% nano-HAO in the composites, the LOI of the composites increased from 31.0% to 35.5% and the composites could meet the UL94V-0 standard. Through thermogravimetric and differential thermal analysis (TG–DTA) it was found that nano-HAO mainly affected the degradation of the experimental composites chemically. Meanwhile, results of scanning electronic microscope (SEM) and Fourier transformation infrared spectra (FTIR) of the composites on the char layer revealed that nano-kaolin mainly affected the transfer process physically by aggregating with nano-HAO and thus the synergistic effect on flame retardancy appeared.

Keywords: Hydroxyl aluminum oxalate (HAO); Kaolin; Flame retardancy; LDPE; EPDM

1. Introduction

Polymeric materials have played important roles in electrical engineering for a long time owing to their excellent insulation and mechanical properties. The application of polymeric materials in this field, however, requires special precautions because fire can be generated easily. Thus the researches on flame retarding polymeric materials become indispensable and the function of flame retardants accordingly is studied.

The most effective flame retardants in markets are brominated flame retardants, which are adopted by most engineering plastics to stop the thermal degradation process by reacting with the plastics [1–3]. However, owing to the bad environmental impact of processing and combustion of certain brominated flame retardants, brominated flame retardants begin to be replaced by some halogen-free flame retardants, particularly metallic hydroxide flame retardants (such as magnesium hydroxide [4,5], aluminum trihydrate [6–8], hydrotalcite [9], magnesium hydroxide sulfate hydrate whisker [10]).

Among the metallic hydroxide flame retardants, aluminum trihydrate (ATH) is a kind of popular flame retardant and smoke suppressant with numerous benefits, such as cheap, safe, elimination of heavy metal promoters (e.g. antimony oxide), halogen-free and nontoxic fume generation [11,12]. However, the efficiency of flame retardancy of ATH is low [13,14] and the decomposition temperature of ATH is as low as 220 °C, which limited the application of ATH in the polymers processed at high temperature. Then a new series of aluminum flame retardants with higher thermal stability are

* Corresponding author. Key Lab for Nanomaterials, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, PR China. Tel.: +86 01064451035; fax: +86 01064434784.
E-mail address: guof@mail.buct.edu.cn (F. Guo).

0141-3910/$ - see front matter
doi:10.1016/j.polymdegradstab.2007.04.001

studied in order to replace ATH in some application areas, which included basic aluminum oxalate (BAO) [15] and nano-sized hydroxyl aluminum oxalate (nano-HAO) [16,17]. According to Ref. [16], nano-HAO has benefits similar to what ATH has and its decomposition temperature is as high as 320 °C. Furthermore, during the decomposition of HAO, only water and noncorrosive gas CO_2 are released. Therefore, such benign properties of nano-HAO as relatively high decomposition temperature and high amount of vapor and gas generation should help it to be a good and environment friendly flame retardant. However, the authors' previous work showed that the efficiency of nano-HAO on flame retardancy is still not sufficient enough to make the polymeric composites self-extinguished. So we are trying to improve the flame retardance ability of the nano-HAO in the polymeric system through adding some synergistic flame retardants.

In recent years, polymer-layered silicate nanocomposites (PLSNs) gained much focus from market owing to their excellent effects on flame retardancy. As reported in Refs. [18–20], when the polymer–clay (layered silica) nanocomposites are introduced into intercalated or exfoliated (delaminate) states within the matrix, upon burning, they may accumulate on the surface of the polymer and form a barrier layer for both outgoing degradation products and incoming gases. Some other works also suggested that even very low levels (1–4%) of nano-clay, mainly montmorillonite, can decrease the peak heat release rate in a cone calorimeter by about 30% [21,22]. An another type of clay, kaolin is a dioctahedral 1:1 layered clay mineral and its structural formula is $Al_2Si_2O_5(OH)_4$. Each layer consists of two sheets: a tetrahedral sheet in which silicon atoms are tetrahedrally coordinated by oxygen atoms; and an octahedral sheet where aluminum atoms are octahedrally coordinated to hydroxyl groups and shared apical oxygens from the silica tetrahedral sheet. Such typical structure of clay in kaolin crystal foreshows that kaolin could have the potential use flame retardancy as what montmorillonite has. Meanwhile in China, kaolin is abundant and cheap. However, researches of its use as synergistic flame retardant are seldom, so it is worthy to do such work.

In this paper, kaolin and nano-HAO are used to flame retarding LDPE/EPDM blends and by means of the fire testing, thermal analysis, FTIR and SEM, the cooperation between them is studied systematically.

2. Experimental section

2.1. Materials

LDPE (Daqing 18D; MFR = 1.5 g/10 min; density = 0.918 g/cm^3) was purchased from Daqing Petrochemical Company (China). EPDM was purchased from DuPont-Dow Elastomers LLC. (USA). LDPE-*g*-MAH (a type of LDPE grafted with 2% maleic anhydride) was manufactured by Nanjing Huadu Technology Co Ltd (China).

Nano-HAO was produced in the Research Center of the Ministry of Education for High Gravity Engineering and Technology (China), whose molecular formula is shown in Fig. 1,

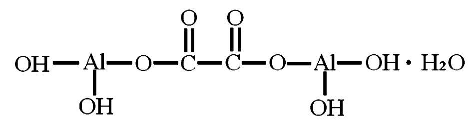

Fig. 1. Molecular formula of nano-HAO.

and its preparation reported by Guo Fen's group [17]. According to the recent research in Guo Fen's group, the thermal degradation mechanism of nano-HAO was concluded as:

$$2[Al_2(OH)_4(CO_2)_2]\cdot H_2O \rightarrow 2Al_2O_3(s) + 5H_2O(g) + 2CO(g) + 2CO_2(g) \quad (1)$$

Nano-kaolin (SK80) was purchased from Shangdong Zaozhuang Sanxing High Tech Co. Ltd. (China). The basic information of nano-kaolin [23,24] and nano-HAO is listed in Table 1.

2.2. Preparation of samples

The raw materials were mixed and formed into pellets via a prism 16 mm twin-screw extruder (TE-20, Coperion Keya (Nanjing) Machinery Co Ltd, China). The operating temperature of the extruder was maintained at 120, 155, 180 and 175 °C from hopper to die, respectively, and the screw speed was adjusted at 60 rpm. For test specimen preparation, a single screw extruder (SJ-25, Beijing association of plastic industry, China) was used subsequently. The extruder was operated at the temperature of 120, 155, 180 and 175 °C from hopper to die, respectively, with screw speed of 50 rpm.

2.3. Characterization of samples

2.3.1. Characterization of char residue

The morphologies of char residue were observed using the scanning electron microscope (SEM, S-4700, Hitachi, Japan) after char layer was coated with a thin layer of gold.

The components in char residue were characterized with a Thermo Bruker VECTOR 22 spectrometer using KBr as dispersing material. Each sample was scanned for 32 times with a resolution of 4 cm^{-1}. All the spectra were scanned within the range 400–4000 cm^{-1}.

2.3.2. Thermal analysis

The thermogravimetric and differential thermal analysis (TG–DTA) data were obtained using a thermogravimetric

Table 1
Material information

	Nano-kaolin	Nano-HAO
Shape	Lamellar	Spindle
Particle size/average diameter (nm)	300–500	200–300
Particle size/average thickness (nm)	20–50	80–90
Specific surface area (m^2/g)	32.0	34.7
Temperature of the extrapolated onset (°C)	209 ± 0.5	320 ± 0.5
Weight loss (%)	23.9 ± 1	52.1 ± 1