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Full scale nanocomposites: Clay in fire retardant and polymer

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ABSTRACT

Full scale nanocomposites of polypropylene and ethylene-co-vinyl acetate with ammonium polyphosphate/MMT nanocompound composites were prepared by melt blending. Their morphologies are assessed by X-ray diffraction and thermal stability and flammability were characterized by thermogravimetric analysis and cone calorimetry. PP full scale nanocomposites show enhanced flame retardancy compared to other PP composites because the clay can control the viscosity during char formation, maintain the layered structure of the clay and function as a barrier. The EVA full scale nanocomposites also show good fire retardancy with a nanoplatelet char.

1. Introduction

Polymer/clay nanocomposites have been extensively investigated over the past two decades due to enhanced mechanical, flame retardant and gas barrier properties [1–3]. Even though polymer/clay nanocomposites can increase thermal stability, char and significantly decrease the peak heat release rate [4], the addition of other kinds of flame retardants are necessary in order to pass fire tests. Polymer/clay/intumescent flame retardants have been extensively investigated in particular in EVA and PP, mainly by the groups of Bourbigot [5,6], and Hu [7,8]. Synergistic effects between clays and flame retardants have been observed, however, most flame retardants cannot be nano-dispersed so the composites contain two phases, the polymer phase and micro-dispersed flame retardants (micro-FR). When the nano-dispersed clay is considered as one part of the FR polymer systems, there will be a total of four kinds of topological structures, as depicted in Scheme 1. (1) FR and polymer without clay; (2) Clay nano-dispersed in polymer; (3) Clay nano-dispersed in FR, which is called herein nanocompound; and (4) Clay nano-dispersed in both the polymer and FR. The term full scale nanocomposites refers to the situation depicted in 4. There has been little work on the topological structures (3) and (4) and one important aspect of this work is to evaluate these topological structures. The results will enable a better understanding of the relationships between polymer, flame retardants and clays.

In previous work, ammonium polyphosphate/montmorillonite nanocompounds (AM) have been prepared and the MMT layers are exfoliated in ammonium polyphosphate, an important inorganic flame retardant. Thus the third topological structure has been studied by using AM with a char source (usually pentaerythritol) and a spumific (usually melamine) to make an intumescent flame retardant (IFR) system in polypropylene (PP). 20 wt% AM IFR in PP enables the PP/AM IFR composite to obtain a UL 94 V-0 rating at 3 mm thickness. The clay also shows synergistic effects and improved flame retardancy when it is nano-dispersed in the flame retardant phase [9].

For this purpose, a non-polar polymer, polypropylene (PP), and a polar polymer, poly(ethylene-co-vinyl acetate) (EVA) are combined with clay to make nanocomposites and then these are melt-blended with AM IFR to produce full scale nanocomposites. These full scale nanocomposites show enhanced flame retardancy compared with other composites.

2. Experimental

2.1. Materials

Polybond 3200, Polypropylene-graft maleic anhydride (PPg), containing 1 wt% maleic anhydride, with a melting point of 157 °C and a melt flow index of 115 g/10 min (190 °C/2.16 kg) was obtained from Chemtura Inc. EVA, containing 18% vinyl acetate, was obtained

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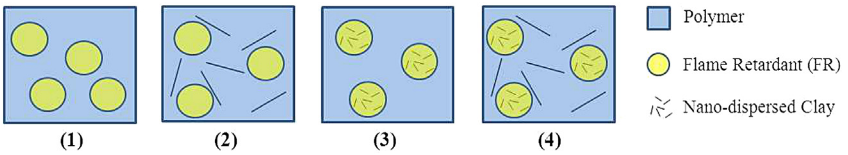

Scheme 1. Topological structures of flame retarded polymer and nano-dispersed clay. (Micro-dispersed FR and polymer without clay (1), FR micro-dispersed in polymer with clay nano-dispersed in polymer (2), clay nano-dispersed in FR (3) and clay in both polymer and FR (4)).

from ExxonMobil. Two organically-modified MMTs (o-MMT), Cloisite 20A and Cloisite 30B, were obtained from Southern Clay Products. Cloisite 20A: the organic modifier is dimethyl, dihydrogenated tallow ammonium (tallow contains ~65% C18, ~30% C16, ~5% C14) and the d_{001} spacing is 2.42 nm. Cloisite 30B: the organic modifier is methyl, tallow, bis-2-hydroxyethyl ammonium (tallow contains ~65% C18, ~30% C16, ~5% C14) and the d_{001} spacing is 1.85 nm. PHOS-CHEK P/42, type II ammonium polyphosphate (APP), was received from BK Giulini Co. Pentaerythritol (PER) was purchased from Aldrich Chemical Co. Melamine (MA) was purchased from Alfa Aesar. Ammonium polyphosphate/MMT nanocompound (AM) was prepared using the same method as in previous work and contained 10 wt% MMT [9].

2.2. Preparation

PPg was melt blended in a Brabender mixer at 165 °C for 20 min with 1 wt%, 3 wt% and 5 wt% organically-modified MMT (Cloisite 20A) (PPg-n1, PPg-n3 and PPg-n5), Then intumescent flame retardants (IFR: APP/PER/MA or AM/PER/MA = 3:1:1 by weight) were added and blended for another 10 min. PPg, PPg/20%APP IFR and PPg/20%AM IFR samples were all melt blended according to the same protocol; all formulations are shown in Table 1.

EVA was melt blended in a Brabender mixer at 130 °C for 30 min with 1 wt%, 3 wt% and 5 wt% organically-modified MMT (Cloisite 30B) (EVA-n1, EVA-n3 and EVA-n5). Then APP or AM, 10 wt%, was added and blended for another 10 min. EVA-control, EVA/10%APP and EVA/10%AM samples were prepared by the same procedure; all compositions are collected in Table 2.

2.3. Characterization

The powder X-ray diffraction (PXRD) was performed using a Rigaku Miniflex II desktop X-ray diffractometer with a Cu (K_α) source, $\lambda = 1.54078$ Å. The samples were scanned in the 2θ range of 2–10° with step size of 0.05° and scanning rate of 2°/min. FTIR spectra were carried out on a TENSOR 27 infrared spectrometer operated at 1 cm^{-1} resolution in the 400–4000 cm^{-1} region using the ATR method with ZnSe crystal. Thermogravimetric analysis (TGA) was performed on an SDT Q600 (TA instruments) under a 50 mL/min nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 800 °C. All samples were run in duplicate and average values are reported; the reproducibility of the instrument is ±0.2% mass and ±2 °C. The cone calorimeter experiments were carried out using an Atlas Cone 2 instrument according to ASTM E 1354, on 3 mm thick 100 × 100 mm^2 plaques at 35 kW/m^2. All samples were tested in triplicate. The cone results are reproducible to within about ±10%. Transmission electron microscope (TEM) image was obtained using JEM-2100, after microtoming at cryogenically using a Leica EM FC7.

Table 1
Formulations and TGA data PPg-control, PPg-n, PPg/APP IFR, PPg-n/APP IFR, PPg/AM IFR and PPg-n/AM IFR.

Sample	Compositions (wt%)						TGA		
	PPg (g)	Cloisite 20A (g)	APP (g)	AM (g)	PER (g)	MA (g)	$T_{10\%}$ (°C)	T_{max} (°C)	Char and (Cal-Char) (%, 800 °C)
PPg	100						422	459	0
PPg-n1	99	1					423	439	1.5
PPg-n3	97	3					421	436	2.2
PPg-n5	95	5					419	434	2.7
PPg/20%APP IFR	80		12		4	4	395	473	5.1
PPg-n1/20%APP IFR	79.2	0.8	12		4	4	392	468	6.6
PPg-n3/20%APP IFR	77.6	2.4	12		4	4	398	470	7.7
PPg-n5/20%APP IFR	76	4	12		4	4	385	468	10.6
PPg/20%AM IFR	80			12	4	4	385	470	9.4
PPg-n1/20%AM IFR	79.2	0.8		12	4	4	400	469	9.6 (10.0)
PPg-n3/20%AM IFR	77.6	2.4		12	4	4	398	471	11.1 (11.2)
PPg-n5/20%AM IFR	76	4		12	4	4	388	468	12.4 (12.4)
PPg-n5/10%AM IFR	85.5	4.5		6	2	2	420	466	8.0 (7.4)
PPg-n5/15%AM IFR	80.75	4.25		9	3	3	412	467	9.5 (9.8)

Table 2
Formulations and TGA data EVA-control, EVA-n, EVA/APP, EVA-n/APP, EVA/AM and EVA-n/AM.

Sample	Compositions (wt%)				TGA		
	EVA (g)	Cloisite 30B (g)	APP (g)	AM (g)	T_{1max} (°C)	T_{2max} (°C)	Char and (Cal-Char) (%, 800 °C)
EVA	100				354	471	2.8
EVA-n1	99	1			315	476	2.8
EVA-n3	97	3			314	471	5.2
EVA-n5	95	5			320	465	7.1
EVA/10%APP	100		11		352	474	5.8
EVA-n1/10%APP	99	1	11		341	471	7.1
EVA-n3/10%APP	97	3	11		333	474	8.4
EVA-n5/10%APP	95	5	11		330	474	11.2
EVA/10%AM	100			11	358	474	7.8
EVA-n1/10%AM	99	1		11	346	472	7.3 (9.1)
EVA-n3/10%AM	97	3		11	327	474	9.9 (10.4)
EVA-n5/10%AM	95	5		11	325	474	13.1 (13.2)

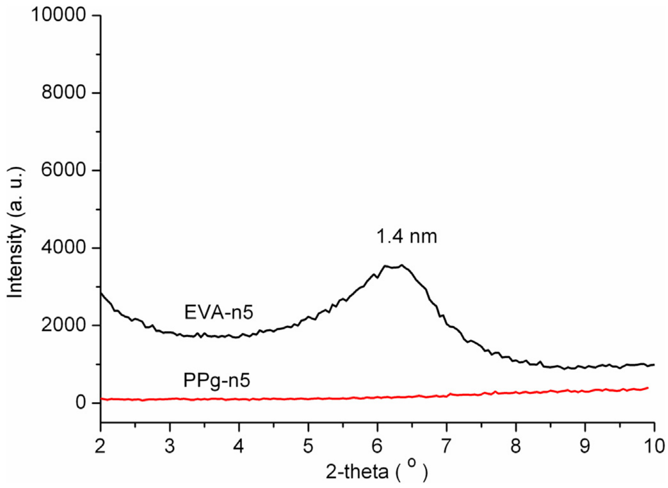

Fig. 1. XRD traces of PPg-n5 (5 min), PPg-n5 (10 min) and PPg-n5 (20 min).