Effect of Organo-Modified Layered Silicates on Flammability Performance of High-Density Polyethylene/ Rice Husk Flour Nanocomposite

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ABSTRACT: This research was carried out to investigate on the effect of organomodified montmorillonite (OMMT) on the flame retarding characteristics and clay dispersion of composites based on high-density polyethylene and rice husk flour. To meet this objective, the blend nanocomposites were prepared through the melt mixing of high-density polyethylene and rice husk flour at 50% weight ratios, with various amounts of OMMT (0, 2, 4, and 6 per hundred compounds) in Hakee internal mixer; then, the samples were made by injection molding. Results indicated that the burning rate, total smoke production, and heat release rate of samples decreased with increasing the OMMT content. Also, the char residue and time to ignition increased with increasing the nanoclay loading. X-ray diffraction patterns revealed that the nanocomposites formed were intercalated. Also, morphological findings showed that samples containing 2 per hundred compounds of OMMT had higher order of intercalation and better dispersion. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 607–610, 2011

Key words: nanocomposite; organomodified montmorillonite; high-density polyethylene; rice husk flour; flammability properties; intercalation

INTRODUCTION

Nanocomposites form a new class of composite materials, which, in at least one dimension of the dispersed particles, is in the nanometer range. Polymer nanocomposites form an emerging class of mineral-filled plastics that contain relatively small amounts (usually 5–10%) of nanometer-sized inorganic particles. Although still an embryonic segment of the industry, nanocomposites comprising either manacles or nanocarbon fillers are expected to be a major growth segment for the plastics industry.[1–3] Nanocomposite technology with layered silicate nanoclays as *in situ* reinforcement has been intensively investigated in recent years.[4–7] Nanoclay is the most commonly used layered silicate because of its natural occurrences and beneficial properties (high cationic exchange capacity, high surface area, and large aspect ratio).[5–8] Essential improvements of physical and mechanical properties, including tensile modulus and strength, flexural modulus and strength, thermal stability, flame resistance, and barrier resistance, have been observed for various thermoplastic and thermoset nanocomposites at low silicate content.[9–13]

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Barrier, resistance, and mechanical properties are of great importance for the successful application of selected wood products. Many efforts have been made in the formation of wood polymer composite, to improve such properties to meet specific end-use requirements. Both thermoplastic and thermosetting systems have been used and have achieved certain improvements in wood properties, but both showed limitations.[14,15] Nanomodified wood polymer composites could be a promising new approach to obtain better products. Few attempts, however, have been made with this regard. The main objective of this study was to evaluate the flame-retarding effects of organomodified layered silicates on polymer composite based on high-density polyethylene (HDPE)–rice husk flour (RF).

EXPERIMENTAL

Materials

HDPE with a melt flow index of 11 gr/10 min and a density of 0.954 g/cm^3 was supplied by Arak Petrochemical Industries, Iran. RF used as the reinforcing fiber material was from Cellulose Aria Co. (Iran); the average particle size of RF was 100 meshes. Maleic anhydride (MA) provided by Merck Co. (Whitehouse Station, NJ) was used as the coupling agent. Montmorillonite modified with a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium with cationic exchange capacity of 90 mequiv/100 g clay, density of 1.98 g/cc, and a *d*-spacing of d_{001} = 18.5 Å was obtained from Southern Clay Products Co. (Gonzales, TX), with the trade name Cloisite 30B.

Method

Composite preparation

Before preparation of samples, RF was dried in an oven at (65 ± 2)°C for 24 hr. Nanocomposite profiles consisting of HDPE and RF at 50% weight ratios, with various amounts of organomodified montmorillonite (OMMT; 0, 2, 4, and 6 per hundred compounds [phc]) were produced. The mixing was carried out by a Hakee internal mixer (HBI System 90, USA). First, the HDPE was fed to the mixing chamber, and, after melting of HDPE, coupling agent and nanoclay were added. At the fifth minute, the RF was fed, and the total mixing time was 13 min. The compounded materials were then ground using a pilot-scale grinder (Wieser, WGLS 200/200 Model). The resulted granules were dried at 105°C for 4 hr. Test specimens were prepared by injection molding (Eman Machine, Iran). Finally, specimens were conditioned at a temperature of 23°C and relative humidity of 50% for at least 40 hr according to ASTM D618-99 before testing.

Measurements

The combustion parameters such as char residue (CR), total smoke production (TSP), time to ignition (TTI), and heat release rate (HRR) tests were measured according to the ASTM E1354, using a cone calorimeter (FTT Company, UK), The tests were performed at an incident heat flux of 50 kW/m^2. In this study, the burning rate (BR) test of nanocomposite was carried out according to ASTM D 635. Wide-angle X-ray diffraction (XRD) analysis was carried out with a Seifert-3003 PTS (Germany) with CuKα radiation (λ = 1.54 nm, 50 kV, and 50 mA) at room temperature, at a scanning rate of 1°/min.

RESULTS AND DISCUSSION

The effect of OMMT layered silicates content on the CR are shown in Figure 1. As can be seen, the CR increases with increase in nanoclay loading. It is well known that the homogeneously dispersed or even intercalated/exfoliated clay structure may form in organic shell-like till the ignition by heating. Other researches showed that the carbonaceous silicate char formed at the surface of the nanocomposite from start before ignition.[16] The inorganic-rich surface had better barrier property in result that the combustion of the nanocomposite was remarkably hindered. The inorganic over coat acts as an excellent insulator of heat and oxygen transport barrier so that the ignition of the composites with low loading of OMMT layered silicates was effectively delayed. Besides, MA couples HDPE and wood flour with nanoclay, and the stronger adhesion prevents the advancement of fire.

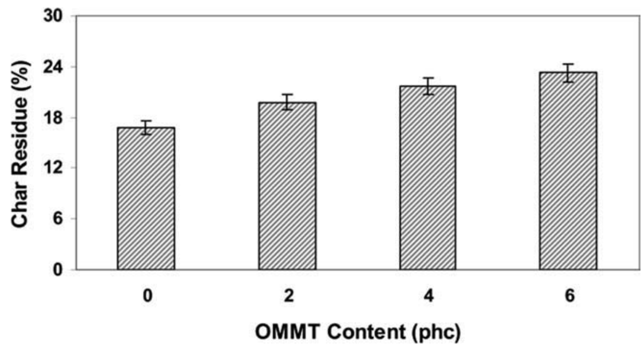

Figure 1 Effect of OMMT content on the char residue of nanocomposites.

The effect of OMMT layered silicates content on the BR is shown in Figure 2. As can be seen, as the nanoclay content increased, the BR decreased. It is attributed to the fact that achieving a higher degree of exfoliation of nanoclay is the key point to enhance the flame-retarding properties when a very small amount of clay is issued. Zhao et al.[17] reported that the OMMT clay must be nanodispersed to enhance the flame-retarding properties of the nanocomposites. In general, the flame-retarding mechanism of the nanocomposites involves a high-performance carbonaceous-silicate char, which builds on the surface during burning. This insulates the underlying material and slows the mass loss rate of decomposition products.[17]

Average specific extinction area (SEA) (m^2/kg) is a measure of smoke obscuration averaged over the whole test period. Smoke production rate can be expressed as the SEA. The relationship of TSP, average SEA (av-SEA), and mass loss (ML) can be expressed as the following equation[17]:

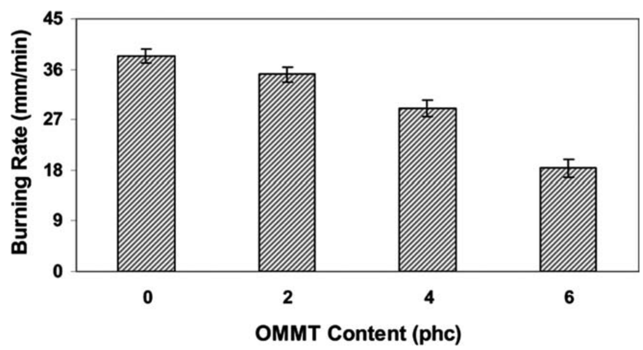

Figure 2 Effect of OMMT content on the burning rate of nanocomposites.

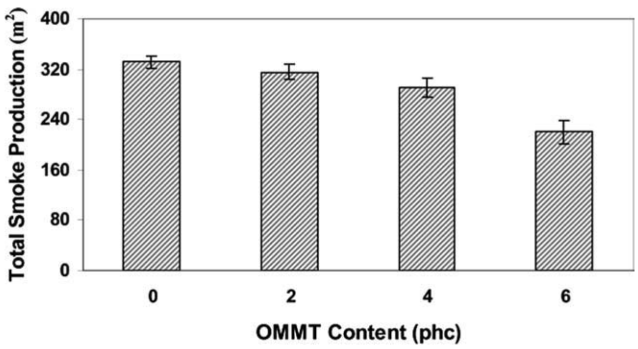

Figure 3 Effect of OMMT content on the total smoke production of nanocomposites.

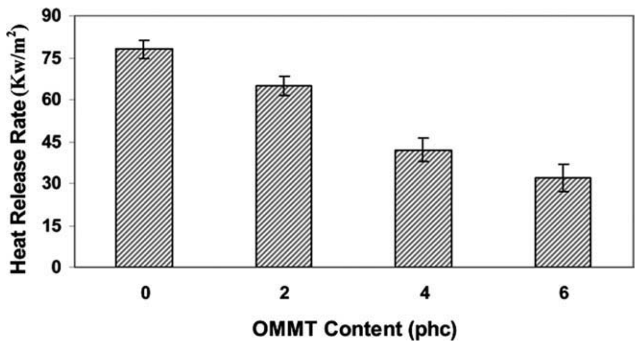

Figure 5 Effect of OMMT content on the heat release rate of nanocomposites.

$$TSP = av - SEA \times ML$$

The effect of OMMT layered silicates content on the TSP is shown in Figure 3. As can be seen, the TSP decreases with increase in nanoclay loading. It is well known that the smoke suppression by the ceramic skin on the surface of the samples was produced by condensed inorganic nanodispersed layered silicate lamellae in the cone calorimeter, which effectively protects nanocomposite from thermodegradation. Thus, a small quantity of OMMT reduces the smoke emission, which is favorable for visibility from around and helpful for persons to escape from fire. It also reduces the toxic smoke quantity, which is especially important for HDPE composites.

The effect of OMMT layered silicates content on the TTI is shown in Figure 4. As can be seen, as the nanoclay content increased, the TTI increased. It is attributed to the fact that the time to destruction of the char shield strongly depends on the formulation and the dispersed or intercalated structure of the compounds. More of OMMT incrassated formation of the char shields delays TTI, and the thickened char shield needs higher temperature to break down. The longer TTI means the higher temperature of samples. Consequently, the higher temperature makes the larger maximum combustion for combustible gases release violently and immediately after the time to collapse of the char shield on the sample surface.[18,19]

The effect of OMMT layered silicates content on the HRR is shown in Figure 5. As can be seen, the HRR decreases with increase in nanoclay loading. Nonflammability of nanoclay does not produce more heat, which implies the lower total flame heat for the composite with higher OMMT content. The decompositions can be alleviated by more well dispersed when adding small quantity of OMMT.[17–19]

Tensile modulus was evaluated to confirm the effect of OMMT layered silicates content on the flammability properties of HDPE/RF composite (Fig. 6). As can be seen, the tensile modulus increases with increase in OMMT up to 2 phc and then decreases. It is well known that the nanoscale filler with very high aspect ratio can improve the tensile modulus of the composite.[10,14] A maximum tensile modulus of composite was observed at 2 phc of OMMT content. The main reason for this behavior may be due to the agglomeration of nanoparticles at 6 phc concentration of the nanoclay.

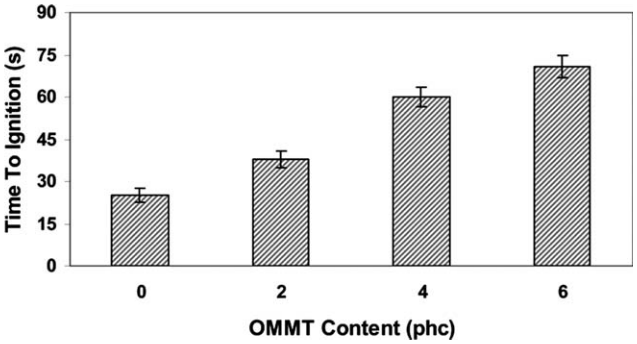

Figure 4 Effect of OMMT content on the time to ignition of nanocomposites.

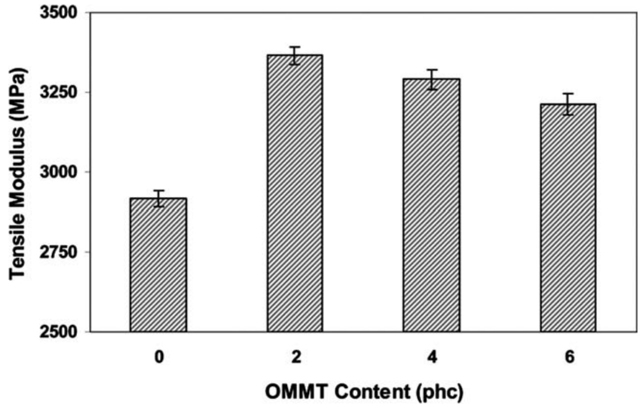

Figure 6 Effect of OMMT content on the tensile modulus of nanocomposites.

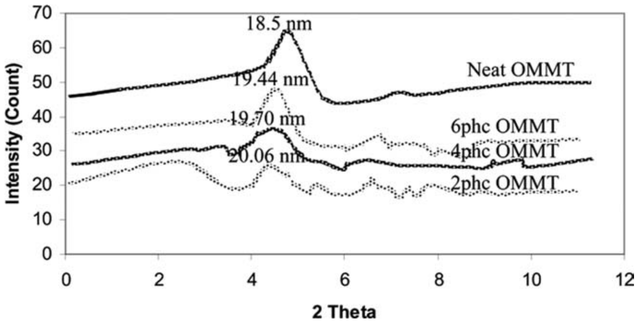

Figure 7 XRD patterns of OMMT content at 0–12° in nanocomposites.

Dispersion behavior of OMMT in composites

Characterization of morphological state of the hybrid composite has been accomplished using XRD. The X-ray scattering intensities for OMMT layered silicates and hybrid composites with different levels of nanoclay at the 2 phc MA concentration are demonstrated in Figure 7. This figure shows that with increasing the nanoclay content the order of intercalation decreases. In other words, formation of the intercalation morphology and better dispersion was shown in 2 phc concentration of OMMT, because the peak of sample with 2 phc concentration of nanoclay was shifted to a lower angle. It seems, this is because of the limited value of MA in the nanocomposites. It is well known that through the improvement of the compatibility between neat HDPE and clay (using MA), the polymer chains could be well diffused into the clay layers and the basal spacing of clay layers might be increased.[15,17] In other words, the MA in lower concentration of clay has higher efficiency to *d*-spacing of the layers.

CONCLUSIONS

The following conclusions could be drawn from the results of this study:

1. The BR, TSP, and HRR of samples decreased with increase in OMMT layered silicates content. Also, the CR and TTI increased with increasing the nanoclay loading.
2. Nanoclay effectively boosts the flame retardancy and smoke suppression. Thus, a small quantity of OMMT reduces the smoke emission, which is favorable for visibility from around and helpful for persons to escape from fire.
3. XRD revealed that the nanocomposites formed were intercalated. Also, morphological findings showed that samples containing 2 phc of OMMT had higher order of intercalation and better dispersion.

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