

Effect of Montmorillonite Clay on the Burning Rate of High-Impact Polystyrene

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The effect that montmorillonite clay has on the burning rate of high impact polystyrene (HIPS) is examined. Two clays are considered a pristine montmorillonite (MMT-Na⁺) and a montmorillonite clay intercalated with triphenyl phosphite (TPP). In addition to the burning rate tests, mechanical, impact and rheological properties are determined. Results show an increase of 55% in the burning rate of the nanocomposite when the neat MMT-Na⁺ clay is added. Thermal measurements indicate a diminishing HIPS decomposition temperature as the MMT-Na⁺ clay concentration rises. On the other hand, when TPP is incorporated in MMT-Na⁺ (MMT-i-TPP) and the clay is added to HIPS, a substantial reduction (42%) of the burning rate is observed, while the mechanical properties are kept at the level of those of the original HIPS. The system HIPS-MMT-i-TPP presents a steeper reduction in the viscosity as compared to HIPS in the high-temperature range.

Keywords: burning rate, flame retardants, high-impact polystyrene, nanocomposites, triphenyl phosphite

INTRODUCTION

Flame-retardant properties of layered-clay polymer nanocomposites have been given ample attention recently due to their ecological and

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environmental advantages over the more conventional halogenated flame-retardant compounds. Improvements in the reduction of flammability of polymers with low clay contents and better processability have been reported, in addition to reductions in the concentration of toxic vapors produced in the combustion stage [1–5]. In connection to their flame-retardant properties, exfoliated nanocomposites based on polypropylene [6–9], polystyrene [8–10], poly(ethylene-vinyl acetate) [11–12], styrene-butadiene rubber [13], poly(methyl methacrylate) [14], polyesters [15], acrylonitrile butadiene styrene [16] and polymeric foams [17] have been the subject of increasing attention. In general, it is found that polymeric nanocomposites not only have the ability to reduce in various proportions the rate of heat release and mass loss during the combustion process, but they also reduce the burning rate. The flame-retardant mechanism involves the formation of a carbonaceous char layer on the surface of the burning material due to the presence of clay particles that act as an insulating barrier. The extent of this layer depends, among various factors, on the concentration, distribution, dispersion and compatibility of the particles with the polymer. On the other hand, phosphorous compounds are among the most popular non-halogenated flame-retardant agents used with thermoplastic polymers, thermo-sets, textiles and coatings. In these systems, the mechanism of flame-retarding depends mainly on the type of phosphorous compound and on the polymer microstructure [18].

The production of polymer nanocomposites requires, in a first step, a chemically controlled clay modification process to ensure an increasing gap between the clay galleries as the polymer molecules intercalate, leading to platelet exfoliation. However, in some cases, like in the polyethylene terephthalate system, it is possible to exfoliate the clay by extrusion without previous clay treatment [19].

In this work, a comparative study is carried out on the use of pristine layered MMT- Na^+ and MMT- Na^+ intercalated with TPP, as flame retardant agents when mixed with HIPS. Results of the burning rate, mechanical, impact and rheological properties of the HIPS nanocomposite are presented.

EXPERIMENTAL PROCEDURE

Materials

HIPS from Resirene Mexico had a density of 1.05 g/cm^3 (according to ASTM D792 norm), a melting temperature of 220°C , a glass-transition temperature of 100°C (as determined by DSC with a heating rate of

10°C/min under nitrogen atmosphere) and a butadiene content of 15 wt% (determined by thermogravimetry, at a heating rate of 2°C/min under nitrogen). MMT-Na⁺ clay from Nanocor with an ionic interchange capacity of 135 meq/100g and triphenyl phosphite (TPP) from Crompton Corporation were used as received.

Equipment

A twin-screw counter-rotating extruder (Haake Rheocord 90 TW-100 of 31 mm length) was used to prepare the blends. Drying of samples before processing was carried out in a Pagani dehumidifier. A Demag-Ergotech 50–200 (L/D ratio of 20) mold-injection machine was used to produce specimens for mechanical, impact and burning rate tests. Specific mechanical properties were measured in an Instron 1125 machine under a constant strain rate of 50 mm/min according to ASTM D638. Impact tests were performed following ASTM D256 Izod-notched type on rectangular specimens of 12 mm each side and 60 mm long. Burning rates were determined according to ASTM D635 on specimens of 12 mm width, 3 mm thickness and 123 mm long in horizontal position for flame application. Thermal properties were measured in a DuPont 910 differential scanning calorimeter at a heating rate of 10°C/min. The mass loss was measured in a DuPont 951 thermogravimetric analysis device. Viscosity measurements were made in a TA-AR-1000-N controlled-stress rheometer equipped with parallel plates of 25 mm diameter. To measure inter-lamellar clay distances, a X-ray Brucker AXS-X diffractometer was used. Finally, a scanning electron microscope (Leica-Cambridge-440) provided micrographs of samples.

RESULTS AND DISCUSSION

HIPS-MMT-Na⁺ Clay Preparation

HIPS and dried MMT-Na⁺ were blended in the extruder at 195°C applying 70 rpm rotational speed. Pellets produced were dried at 100°C for 8 h, and then they were injection-molded to produce samples for the mechanical and burning-rate combustion tests.

Figure 1 shows results of the burning rate as a function of montmorillonite concentration. Contrary to what is expected, the burning rate increases with increasing clay content, up to a maximum observed at 10 phr (parts per hundred of resin) clay. Even at high clay concentrations (20 phr) the amount of clay is not sufficient to reduce the burning rate. Formation of the carbonaceous char layer is not observed,

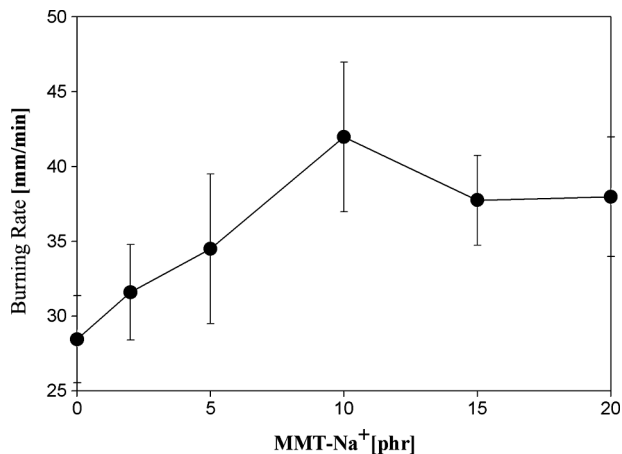


FIGURE 1 Burning rate versus clay content in the HIPS-montmorillonite nanocomposite.

because low-viscosity material flows from the condensed phase into the combustion region. These effects support the idea that the increase in the burning rate is related to the reduction in viscosity by the presence of nanoparticles. In fact, reports have mentioned [20,21] that in some polymer melts the clay nanoparticles may induce more orientation and disentanglement of molecular chains (albeit a possible slip within the fluid layers or next to solid walls) producing an increase in fluidity of the material in the flow region. Figure 2 presents the simple-shear flow curves at 250°C corresponding to blends of HIPS with various clay contents. In the low shear-rate region ($0.01\text{--}0.1\text{ s}^{-1}$), the viscosity at a given shear rate increases with clay content, and this enhancement is more pronounced for concentrations larger than 10 phr. However, in the high shear-rate region ($1\text{--}10\text{ s}^{-1}$) shear-thinning is more drastic in samples with larger clay contents (15–20 phr). Indeed, viscosity reduction due to flow at moderately large shear rates is much more pronounced as the clay concentration increases, confirming that particles promote a large orientation and disentanglement of polymer chains for large shear rates. Reports [22] on the viscosity behavior of HIPS-montmorillonite nanocomposites agree with data presented here.

Not only shear viscosity is affected by the presence of clay nanoparticles, but also the thermal dependence of the microstructure of HIPS-clay nanocomposites. Figure 3 shows the complex viscosity (η^*) as a function of temperature. The viscosity of HIPS and that of the

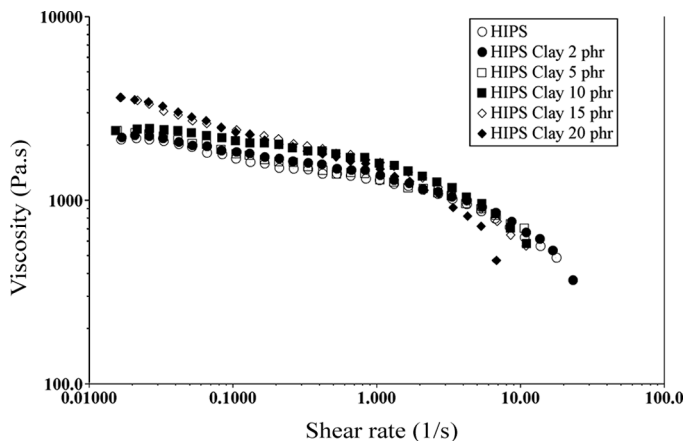


FIGURE 2 Viscosity versus shear rate curves of the HIPS-clay system. Clay contents are 2, 5, 10, 15 and 20 phr (parts per hundred resin). Test temperature is 250°C.

nanocomposites is strongly affected by temperature, decreasing almost two decades from 250°C to around 400°C. This variation in viscosity level may explain the dripping of burning melt during the combustion stage. However, with 20 phr montmorillonite (MMT- Na^+) a steep increase of viscosity is observed at 375°C, signaling the beginning of the primary decomposition stage, where primary char is produced.

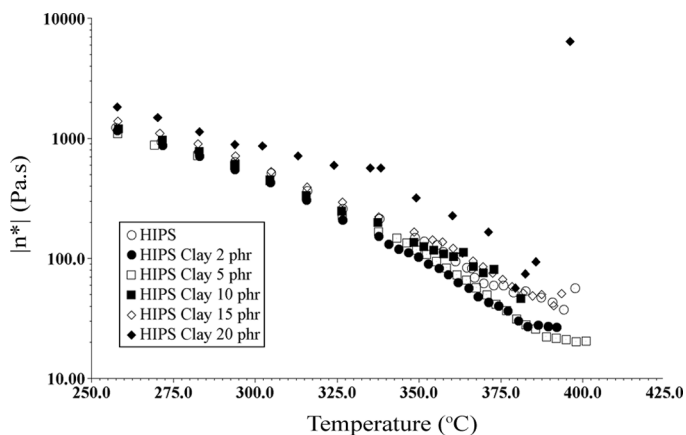


FIGURE 3 Complex viscosity versus temperature of the HIPS-clay system. Frequency is 1 rad/s, and the heating rate is 10°C/min.

The critical temperature at which the steep rise in viscosity is observed is here termed decomposition temperature. The decomposition temperature decreases with increasing clay concentration, indicating that the thin polymer layers adsorbed onto clay nanoparticles provide more combustible material for flame propagation. This implies that the char layer is unstable as the temperature rises because it disappears and leads to flame propagation.

In Figure 4 the X-ray spectrum of the HIPS-clay nanocomposites shows that the sample with 2 phr is the material that does not show the peak associated with crystalline arrangements. The presence of this peak is related to a low exfoliation of the clay tactoids. Results in this figure indicate that as the clay concentration increases from 5 to 20 phr, a large fraction of non-exfoliated clay is present in the system.

In Figure 5, impact and tensile mechanical properties are reported. Melt strength is not affected as the clay is added. On the other hand, impact resistance decreases for clay contents larger than 5 phr, attributed to lack of exfoliation. Here agglomerates act as stress concentrators promoting fracture propagation, as observed in Figure 6, where clay agglomerates with size of around 2 microns are seen in the micrographs. Young's modulus increases with a small slope from 15 phr, indicating that particle clusters act as fillers in the system.

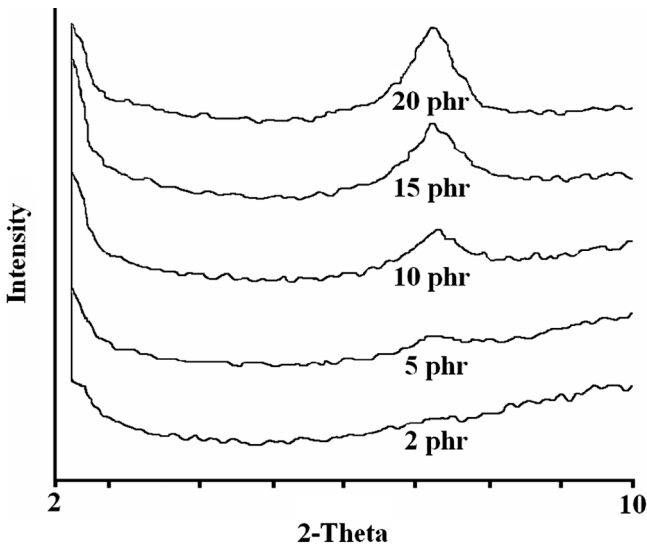


FIGURE 4 X-ray diffraction patterns of the HIPS-clay system. Clay content is 2, 5, 10, 15 and 20 phr.

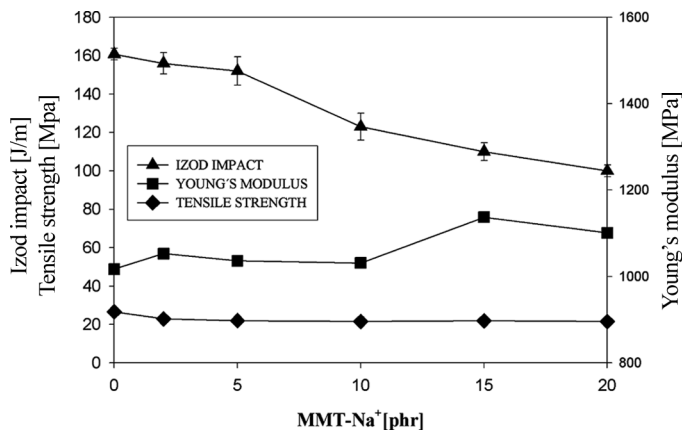


FIGURE 5 Izod-notched impact strength, tensile strength and Young's modulus as functions of montmorillonite content. HIPS-clay system.

HIPS-MMT-i-TPP Clay Preparation

Dried clay and TPP (in various proportions) are mixed with continuous stirring for 10 min at constant temperature to obtain a TPP-intercalated clay (MMT-i-TPP). HIPS and MMT-i-TPP clay are blended in the extruder at the same processing conditions used to

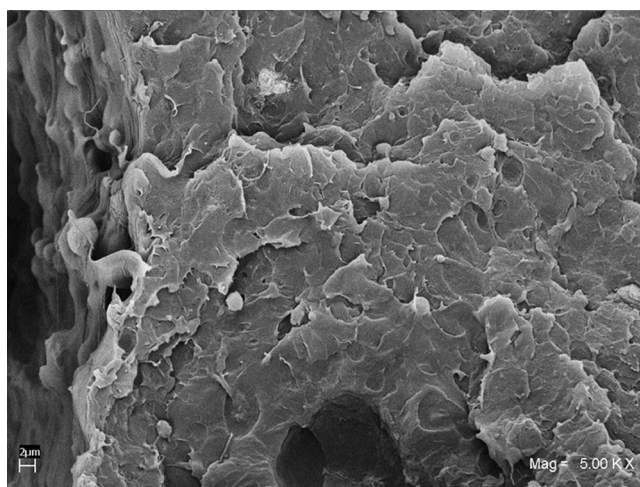


FIGURE 6 SEM micrograph of a fracture surface of the HIPS-clay (5 phr) blend.

produce the HIPS-clay blends. In the same manner, specimens for mechanical and impact tests were produced.

To evaluate the effect of TPP content on the blends, the clay concentration was kept constant (5 phr). In Figure 7 the burning rate diminishes (around 30%) with low TPP concentration, presenting the largest reduction at 5 phr content. When the TPP concentration in the clay reaches 10 phr, the flame stops as soon as the material starts melting, and dripping of the burning material occurs. Reports [23, 24] have pointed out that the mechanism by which phosphorous compounds act in the combustion process is by inhibiting the reaction in the gas phase, since a carbonaceous char is usually formed. Phosphorous molecules at high temperatures dissociate into smaller compounds with relatively low oxidation states, inhibiting the chain reaction during combustion in the gas phase [25]. Similarly as in HIPS, these compounds present a poor char formation after combustion. However, when TPP is intercalated in alternative mineral samples like Kaolin, the flame-retardant mechanism changes from the gas phase to the condensed phase, as identified elsewhere [26] in polyvinyl alcohol and nylon. In the latter case, an increase in the generation of the carbon layer of 4 to 6 times has been observed.

The behavior of the burning rate for TPP concentrations larger than 6 phr indicates that the excess TPP that is not intercalated migrates to the surface of the burning material. Due to its low thermal stability, it

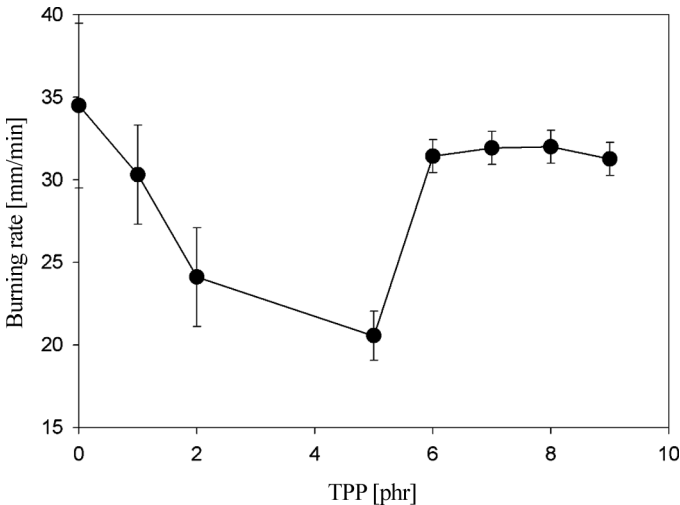


FIGURE 7 Burning rate as a function of TPP content of the HIPS-clay (5 phr)-TPP system.

decomposes before the combustion stage reaches the ignition temperature, generating volatile compounds that help with the combustion reaction. With 10 phr TPP, flame self-extinguishes by dripping of burning melt as the material viscosity falls during combustion. The presence of this liquefied material is not convenient for flame-retardant agent uses.

In Figure 8 the steady-state viscosity is plotted versus shear rate for various HIPS-MMT-i TPP systems. The blends present a trend toward the zero shear-rate Newtonian asymptote at low shear rates with values depending on the TPP content. For high shear rates ($>1 \text{ s}^{-1}$) a very steep shear thinning region is observed in the blends with TPP. Notice that in the system with 5 phr TPP, the drop in the viscosity occurs at lower shear rates, implying a larger flow of material to the combustion region. Being the clay with a high TPP content, this flow of material promotes a better fire retardant action, and hence the lowest rate of combustion (see Figure 7). In comparison, the blend with 6 phr TPP presents the drop in viscosity at higher shear rates and an excess of non-intercalated TPP which decomposes rapidly, inducing a larger rate of combustion.

The blends containing TPP are also structurally affected by temperatures larger than 370°C . In Figure 9, the complex viscosity of the blends with clay is lower than that of HIPS; in addition, the rise associated with the presence of burned material is more evident in the 5 phr TPP blend. A zoom of the last segment of the curves in Figure 9 corresponding to the high temperature region is presented

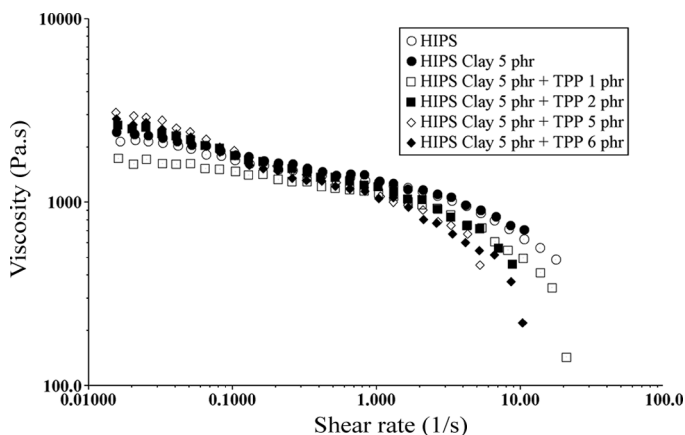


FIGURE 8 Viscosity versus shear rate of the HIPS-clay (5 phr)-TPP system. TPP contents are 1, 2, 5 and 6 phr. Test temperature is 250°C .

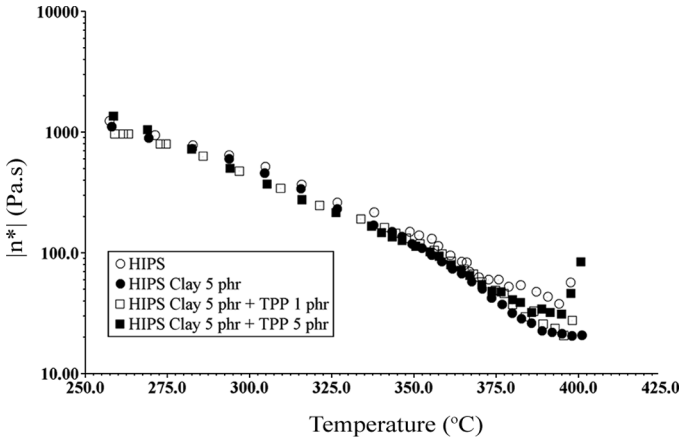


FIGURE 9 Complex viscosity as a function of temperature of the HIPS-clay (5 phr)-TPP system. TPP contents are 1 and 5 phr. Frequency is 1 rad/s with a heating rate of 10°C/min.

in Figure 10. The blend with very low TPP content (1 phr) does not show large differences with the blend with no TPP, and the curves are indistinguishable, whereas for high TPP contents evidence of highly viscous burned material is observed at temperatures larger than 395°C. It is also relevant that the degradation temperature (that

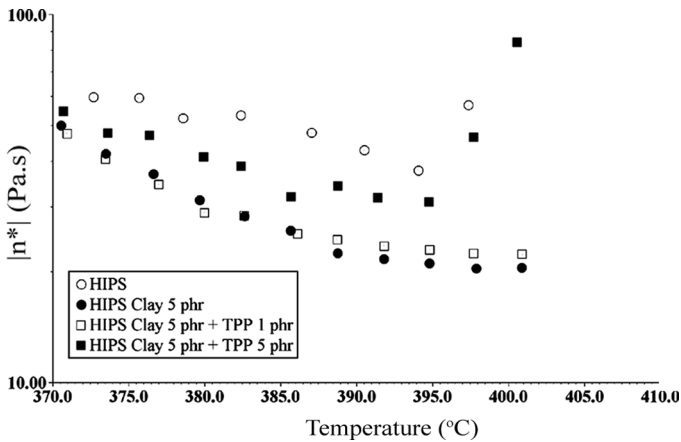


FIGURE 10 A magnification of the complex viscosity versus temperature curves of the HIPS-clay (5 phr)-TPP system in the high temperature range. TPP contents are 1 and 5 phr.

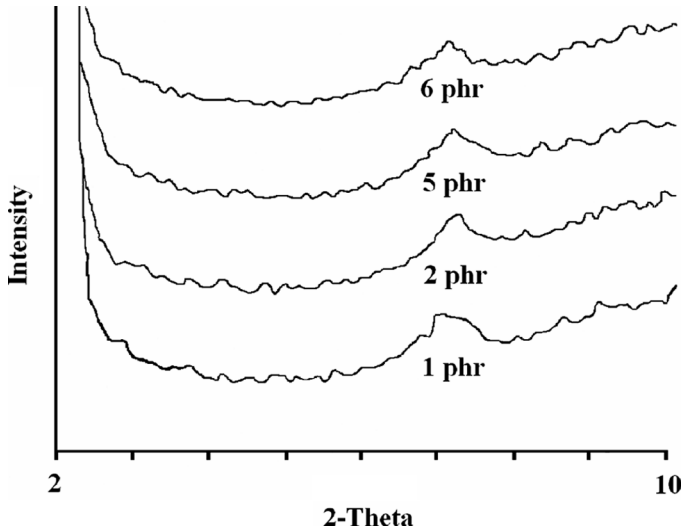


FIGURE 11 X-ray diffraction patterns of the HIPS-clay (5 phr)-TPP system. TPP contents are 1, 2, 5, and 6 phr.

at which the viscosity augments steeply) does not change appreciably with respect to that of HIPS, as compared to the high clay content blend (20 phr) of Figure 3.

The exfoliation degree of the HIPS-clay (5 phr) blends with various TPP contents (from 1 to 6 phr) is quantified in Figure 11. Peaks in the

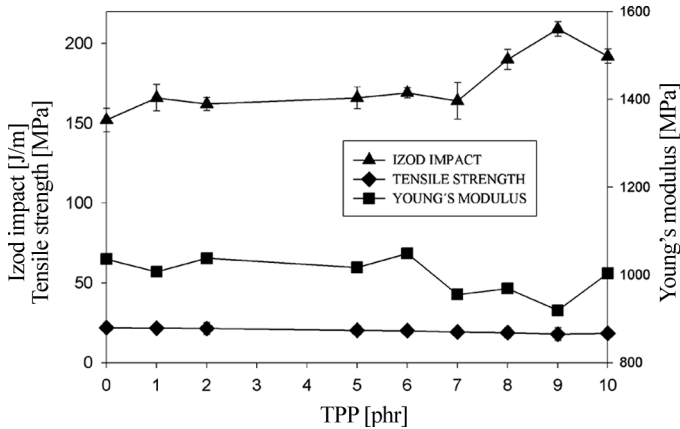


FIGURE 12 Izod-notched impact strength, tensile strength and Young's modulus as functions of TPP concentration in the HIPS-clay (5 phr)-TPP system.

X-ray spectrum at low angle reveal that the clay is not exfoliated by the thermo-mechanical stresses produced in the extruder. This means that TPP is an efficient adhesion agent of clay platelets and hence retards the exfoliation action of the extruder. Alternative tools like ultrasonic oscillations in the extrusion process are necessary to assure a level of exfoliation of the clay tactoids in this case.

As expected, the HIPS-MMT-i-TPP blends tensile strength and Young's modulus do not show substantial changes due to the TPP content, see Figure 12. However, the impact strength increases for concentrations higher than 7 phr, perhaps through slight modification of the fracture mechanism, since TPP does not show a plastification effect on the blends.

CONCLUSIONS

The HIPS-montmorillonite clay (MMT-Na⁺) blends present increasing burning rate with clay content as compared to that of the HIPS alone, even at high clay concentrations. TPP acts as a flame-retardant agent when it is intercalated in the clay galleries. These results have been explained on the basis of the combined effect of decreasing viscosity of the flowing blend and temperature. The difference between both systems is that in the former, the HIPS-clay blends flow to the combustion area without fire-retardant agent in the clay. In the blends with TPP (5 phr) the mechanical properties of HIPS are retained. For TPP concentrations larger than 6 phr, the material self-extinguishes as dripping of the burning material occurs. In the MMT-i-TPP blends, the degradation temperature of the nanocomposite compared with that of HIPS is not affected. MMT-i-TPP blends work as a fire-retardant agent although in the extrusion process the clay with TPP is not exfoliated. Further experimental work on this particular issue is in progress.

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