

Burning Rate, Mechanical and Rheological Properties of HIPS-PET and Clay Nanocomposites

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We analyze the effect of montmorillonite clay nanoparticles on the burning rate (BR), mechanical and rheological properties of high-impact polystyrene (HIPS) and blends of polyethylene terephthalate (PET) and HIPS produced by a twin-screw extrusion process. It is found that the BR of the HIPS-PET system is considerably reduced at relatively high clay concentrations. On the other hand, the increase in clay concentration in the HIPS matrix none leads to an unexpected rise in the BR. The degradation temperature is determined by measurements of complex viscosity as a function of temperature. It is found that degradation temperature decreases with clay concentration, particularly in the HIPS-PET-clay nanocomposite, diminishing by 28°C with respect to that of HIPS at high clay contents. This low degradation temperature means that a char layer is formed at lower temperatures, so the BR decreases as well. Mechanical properties are also affected, such as the fracture strain.

Keywords: burning rate, clay, nanocomposites, polyethylene terephthalate, polystyrene

INTRODUCTION

High-impact polystyrene (HIPS) is widely used in the audio, video, automotive, and aircraft industries, and in electric appliances, among

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others. Small rubber particles embedded in the polystyrene matrix provide high-impact resistance [1,2]. However, this polymer is highly flammable when exposed to fire, due to its chemical structure, where aliphatic groups bound to aromatic moieties contribute to the combustion reaction without forming any char layer that could prevent fire propagation [3,4].

To improve flame retardation in HIPS, agents formulated from halogenated compounds have traditionally been used [5,6]. Nevertheless, these compounds form highly toxic vapors during the combustion process. Recently, alternative flame-retardant compounds have been developed, among them those made by the addition of clay nanoparticles to a polymer matrix, the so-called polymer nanocomposites. With these materials, no toxic vapors are expelled and they present an augmented thermal stability at low clay contents. Furthermore, reports have highlighted that a carbonaceous layer is easily formed during combustion, acting as a barrier to energy transfer and mass loss [7–9]. Attention in the recent literature has been given to the flame retardation properties of polymer nanocomposites [10–12].

In this work, polyethylene terephthalate (PET) is used in blends with HIPS and montmorillonite clay. The use of PET is justified since this polymer self-extinguishes a few seconds after the flame is removed. In addition to studying the flame-retardant properties of the HIPS-clay and HIPS-PET-clay systems, mechanical and rheological properties are measured to provide explanations of the mechanism by which the polymer nanocomposites inhibit flame propagation.

PROCEDURE

Materials

HIPS (Resirene, Mexico) had a density of 1.05 g/cm^3 (according to ASTM D792 norm), a melting temperature of 220°C and a glass-transition temperature of 100°C (as determined by DSC with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere). Butadiene content is 15 wt% (as determined by thermogravimetry, at a heating rate of $2^\circ\text{C}/\text{min}$ under nitrogen). PET from Vordian-Mexico had melting and glass transition temperatures of 238°C and 83°C , respectively, as determined in a DSC with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The montmorillonite clay (MMT- Na^+) was provided by Nanocor with an ionic exchange capacity of 135 meq/100 g. Reactants were used as received.

Equipment

A twin-screw counter-rotating extruder (Haake Rheocord 90 TW-100 of 331 mm length) was used to blend the compounds. Samples were

dried 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, and the burning rate was determined according to ASTM D635. Thermal properties were evaluated in a DuPont 910 differential scanning calorimeter with 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. For measurements of interlamellar clay distances, an X-ray Brucker AXS-X diffractometer was used. Finally, a scanning electron microscope (Leica-Cambridge-Stereoscan 440) with a voltage of 20 Kv, provided micrographs of fractured samples.

HIPS-Clay System Sample Preparation

HIPS and clay (previously dried) are blended in the extruder at 195°C with 70 rpm rotational speed. Pellets produced are dried at 100°C for 8 h, and then they are injection-molded to prepare samples for the mechanical and burning rate tests.

HIPS-PET Blend

HIPS and PET were dried and mixed in a twin-screw extruder at 70 rpm with a temperature profile of 255°C. Preparation of specimens for mechanical and burning rate determinations followed the same procedure described above.

HIPS-PET-Clay Nanocomposites

PET and the clay are blended in the twin-screw extruder at 255°C with a rotational speed of 70 rpm. Residence time in the extruder is 3 min. Pelletized samples are mixed with HIPS and extruded again to obtain the nanocomposites. Specimens for mechanical and burning rate tests were produced as described above.

RESULTS AND DISCUSSION

HIPS-PET Blend

As opposed to HIPS, PET under combustion shows char forming due to its chemical structure [13]. Although thermodynamically incompatible,

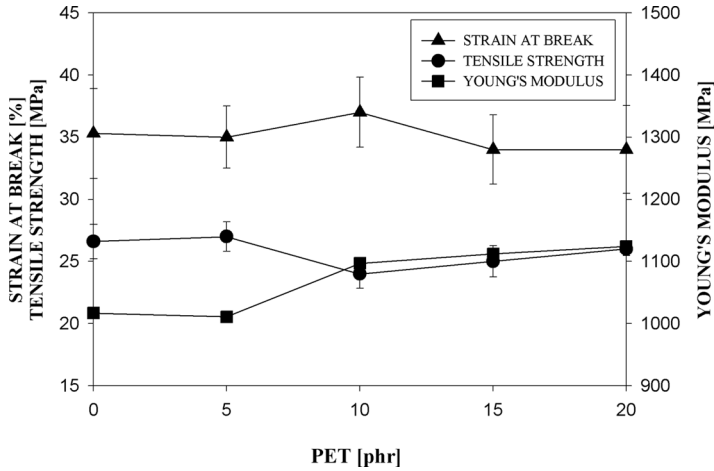


FIGURE 1 HIPS-PET system. Mechanical properties as functions of PET concentration.

the PET-HIPS mixture in theory should represent an alternative system to reduce the burning rate of HIPS. To evaluate the influence of increasing PET concentration on the mechanical and burning rate properties of HIPS, primarily tensile tests were made and the results are disclosed in Figure 1. As observed, up to 20 phr, PET content does not substantially influence the magnitude of the strain at break, tensile strength or the Young's modulus. The influence of PET concentration on the burning rate is shown in Figure 2. Although a decreasing burning rate with PET content is expected, the burning rate is almost constant up to 20 phr PET.

To provide an explanation of these results, the morphology of the blend is analyzed by SEM. A micrograph (Figure 3) of a fracture surface shows PET microspheres embedded in the HIPS matrix, ranging around 5 micron size or less, produced after the extrusion process. The flow of melted HIPS carries the PET spheres to the combustion region. Due to their large surface area, the microspheres burn rapidly, without generating any sizable stable char residue layer, so the burning rate of the HIPS-PET mixture does not decrease.

HIPS-Clay and HIPS-PET-Clay Nanocomposites

Results of the nanocomposites' mechanical properties as functions of the clay content are given for the HIPS-clay system (Figure 4) and the HIPS-PET (10 phr)-clay system (Figure 5). The tensile strength

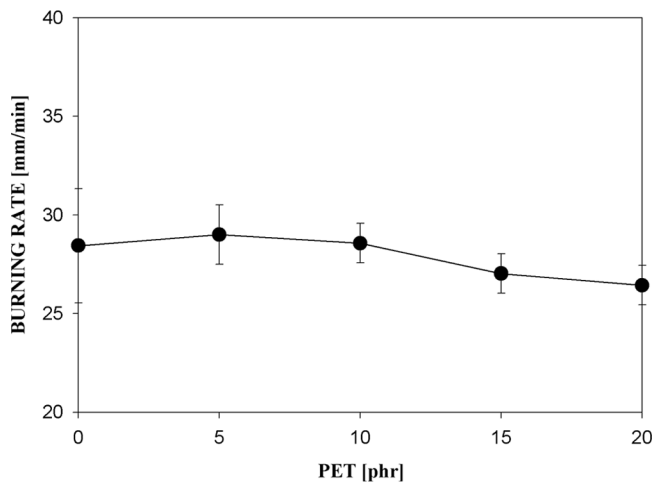


FIGURE 2 HIPS-PET system. Burning rate as a function of PET concentration.

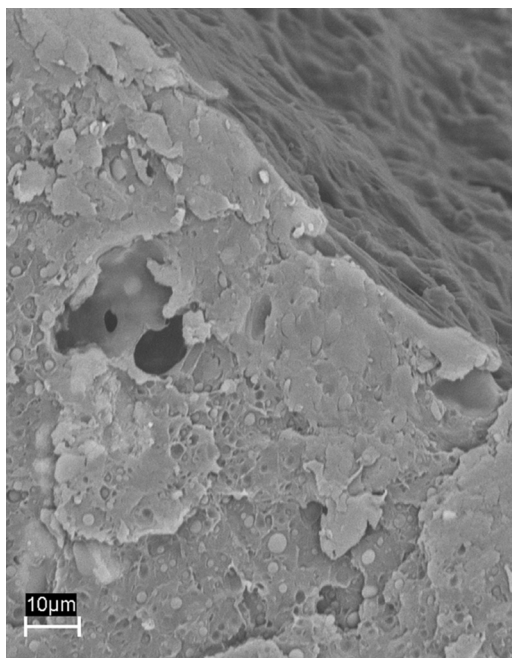


FIGURE 3 HIPS-PET system. Micrograph of a fractured surface showing domains of PET in the HIPS matrix.

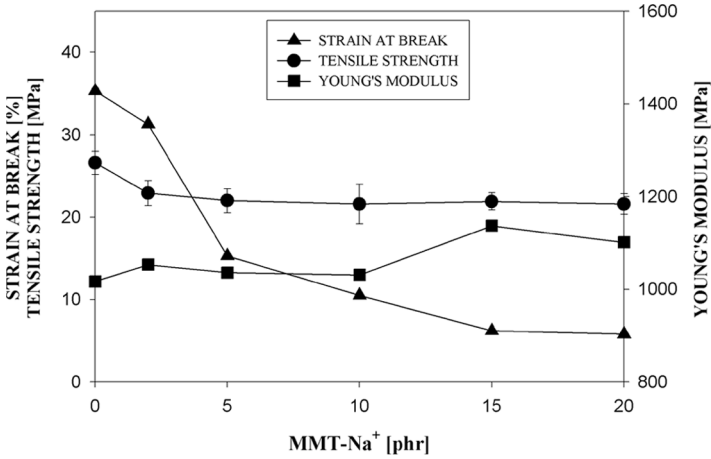


FIGURE 4 HIPS-clay system. Mechanical properties as functions of montmorillonite content.

and Young's modulus are not substantially influenced by the clay content in the HIPS-clay blend. On the contrary, a large decrease is observed in the strain at break, especially at high contents (around 15–20 phr). In the HIPS-PET-clay blend, besides the large decrease in the strain at break, the Young's modulus increases above the value of the system without clay. These results show that this blend becomes

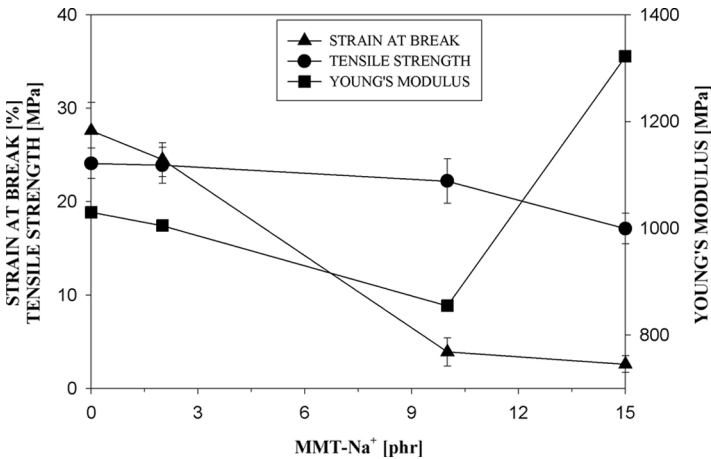


FIGURE 5 HIPS-PET-clay system. Mechanical properties as functions of montmorillonite content.

quite rigid at high clay contents, and as compared to the usual behavior of nanocomposites, the clay is acting here as a filler.

Nonetheless, the rate of combustion is indeed affected by clay content in the nanocomposite systems. As shown in Figure 6, the addition of clay increases the burning rate in the HIPS-clay blend, but in the HIPS-PET-clay system, a comparatively large decrease is observed for clay concentrations larger than 15 phr. This positive behavior of the HIPS-PET-clay system is attributed to the presence of the nanoparticles at the interface between the PET microspheres and the HIPS matrix. Indeed, the morphology of the HIPS-PET mixture indicates that this is a quite incompatible system in which a large interfacial tension induces a defined interface between both polymers. The clay nanoparticles are also quite incompatible with HIPS, but more compatible with PET. It is likely that the particles prefer the PET phase and the interface between the polymers. Consequently, the nanoparticles help in the formation of the char layer during combustion of the PET spheres. The char layer acts as a barrier to energy transfer and mass loss, and the layer thickness increases with clay content.

The increase in the burning rate observed in the HIPS-clay blend in Figure 6 shows that in this case the nanoparticles do not help in the formation of the barrier layer. As mentioned, clay particles acting as fillers dispersed in a single highly flammable polymer phase behave

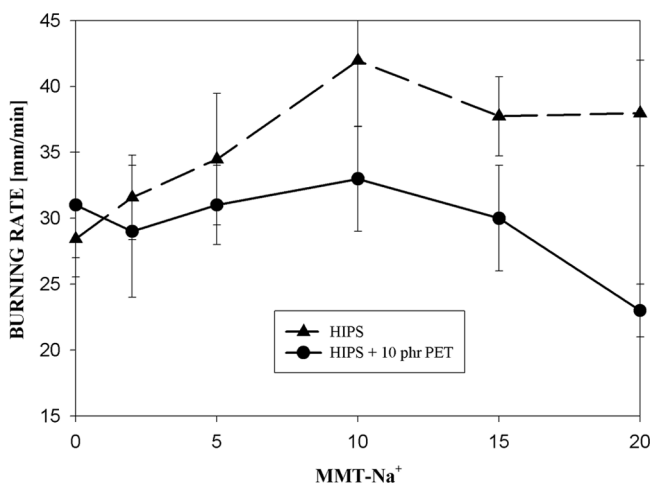


FIGURE 6 HIPS-clay and HIPS-PET-clay systems. Burning rate as a function of clay content.

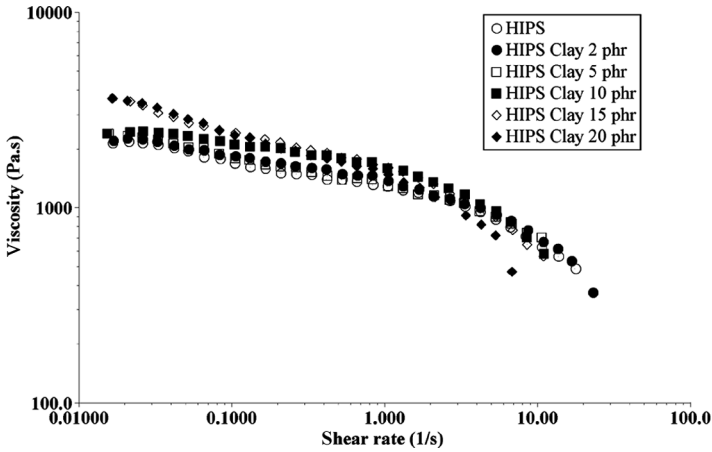


FIGURE 7 HIPS-clay systems. Shear viscosity as a function of shear rate.

according to a different mechanism as the material is burned. The crucial point in this system is the absence of an interface in which the nanoparticles can accommodate. Here we propose that the viscosity of the polymer is largely reduced as the temperature rises due to combustion, but also this reduction is promoted by the presence of nanoparticles. It has been shown that nanoparticles induce orientation and disentanglement of polymer chains [14,15], increasing chain mobility. The falling viscosity increases the flow rate of the polymer to the combustion region and consequently, the rate of combustion increases. This mechanism is enhanced as clay particle concentration increases, up to saturation at large enough clay content, as observed in Figure 6. This scheme is substantiated by the rheological data presented below.

In Figure 7, the shear viscosity of the HIPS-clay systems is plotted against shear rate. At low shear rates the viscosity of the mixtures tends to a Newtonian plateau. Mixtures with relatively high clay content exhibit considerably higher viscosity, but at moderate shear rates they present lower viscosity. As the concentration of the clay particles increases, the shear-thinning behavior is more accentuated, confirming that, in fact, the presence of nanoparticles increases polymer mobility, inducing orientation and disentanglement of chains.

As reported elsewhere [16], clay concentration affects the viscosity behavior as a function of temperature. Figure 8 depicts the system structure represented by the complex viscosity, in which the larger values correspond to the system with higher clay content. The sudden rise in the viscosity indicates the decomposition or degradation

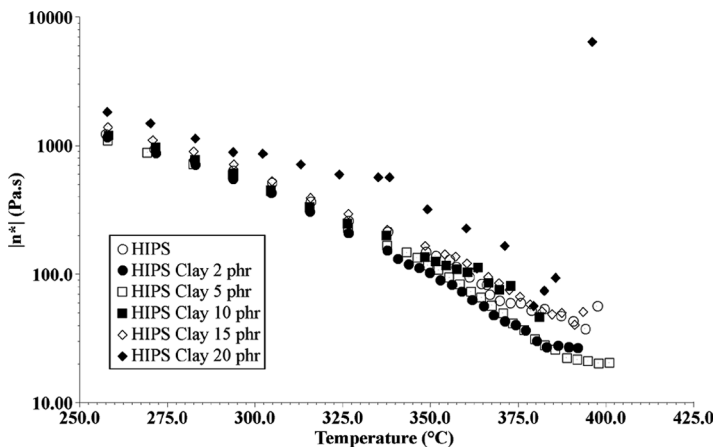


FIGURE 8 HIPS-clay systems. Complex viscosity as a function of temperature.

temperature. While the HIPS begins the decomposition process at 395°C, that in HIPS with 15 phr decreases to 391°C and reaches 380°C with the largest clay concentration.

The shear-thinning behavior is more accentuated in the HIPS-PET-clay systems, as shown in Figure 9, and again, the blend with the

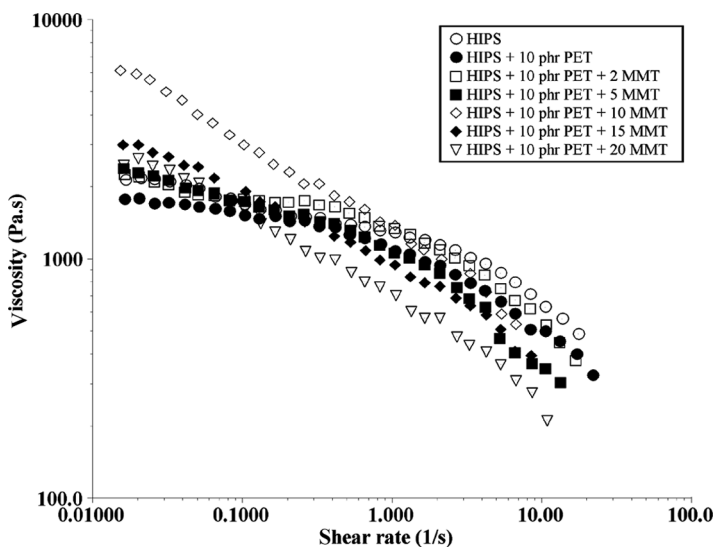


FIGURE 9 HIPS-PET-clay systems. Shear viscosity as a function of shear rate.

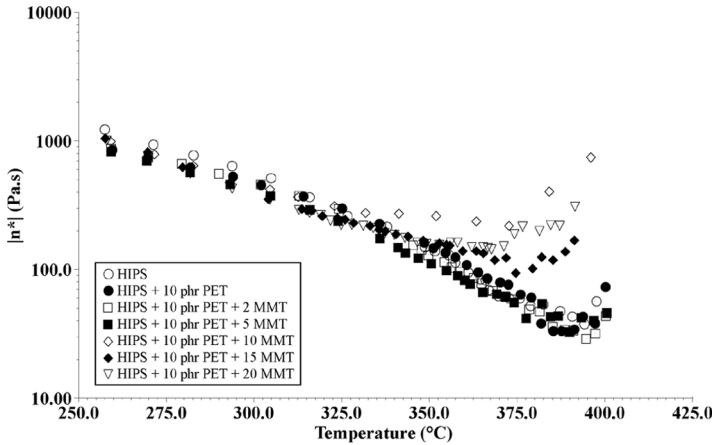


FIGURE 10 HIPS-PET-clay systems. Complex viscosity as a function of temperature.

largest clay concentration attains lower viscosities at relatively high shear rates. However in small quantities, the presence of PET is important to the rheological properties of the final blend, as observed in the drastic decrease of the viscosity as the shear rate grows, larger than in the systems without PET. The complex viscosity as a function of temperature in the HIPS-PET-clay systems is shown in Figure 10. The shifts in the degradation temperature are larger than those in the HIPS-clay systems of Figure 8. With respect to the HIPS degradation temperature (395°C), with 15 phr of clay the degradation temperatures diminish to 375°C and to 367°C with 20 phr. These drastic temperature shifts indicate that the primary stable carbon layer is indeed formed at lower temperatures, so the global effect is a diminution of the rate of combustion as the temperature rises. In fact, in this system there is a polymer-polymer interface in which clay nanoparticles are concentrated and formation of the char layer is easier than in the case of the HIPS-clay blend, where a polymer-polymer interface does not exist. Research into mechanisms by which the rate of combustion diminishes due to the formation of the insulated carbon layer in nanocomposites is still ongoing.

CONCLUSIONS

Montmorillonite nanoparticles have a negative influence when mixed with HIPS, because the rate of combustion of HIPS increases and the

strain at break diminishes. The proposed explanation suggests that clay particles have a small affinity with the HIPS matrix and act as fillers. Rheological properties are affected by the particles, especially at relatively high concentrations. The shear-thinning behavior of the mixtures is more accentuated as particles' concentration increases, and the decomposition temperature diminishes. As a consequence, the flow of polymer to the condensed region is enhanced and the burning rate increases.

With a 10 phr of PET content in the HIPS matrix, the morphology study shows that the blend is composed of microspheres of PET which do not influence the mechanical properties nor the rate of combustion of HIPS. This indicates a large interfacial tension that reflects incompatibility of the mixture. The addition of clay nanoparticles to the HIPS-PET system brings about a lower rate of combustion, especially at relatively high particle concentration. The shear-thinning behavior of the viscosity is more drastic and the decomposition temperature is reduced more with respect to that of HIPS. This is a positive effect, since a char layer is formed at lower temperatures, preventing further combustion and diminishing the burning rate. The mechanism proposed suggests that clay particles stay at the interface between both polymers, since the interfacial tension of the clay particles with HIPS is larger than that with PET. The clay particles in the PET microspheres then promote the formation of the carbonaceous layer that leads to a diminishing burning rate.

REFERENCES

- [1] Rios-Guerrero, L., Kesskkula, H., and Paul, D. R., *Polymer* **41**, 5415 (2000).
- [2] Donald, A. M. and Kramer, E. J., *J. Appl. Polym. Sci.* **27**, 3729 (1982).
- [3] Krevelen Van, D. W. (1990). *Properties of Polymers*, third ed., Elsevier, Netherlands, pp. 641–652.
- [4] Grand, A. F. and Wilkie, C. A. (2000). *Fire Retardancy of Polymeric Materials*, Marcel Dekker Inc, New York, pp. 47–65.
- [5] Utevski, L., Scheinker, M., Georlette, P., and Shoshana, L., *J. Fire. Sci.* **15**, 375 (1997).
- [6] Yang, C. and Sheen, B., *J. Appl. Polym. Sci.* **37**, 3185 (1989).
- [7] Gilman, J., *Appl. Clay. Sci.* **15**, 31 (1999).
- [8] Zhu, J. and Wilkie, C., *Polym. Int.* **49**, 1158 (2000).
- [9] Porter, D., Metcalfe, E., and Thomas, M., *Fire. Mat.* **24**, 45 (2000).
- [10] Zanetti, M., Camino, G., Canavese, D., Morgan, A., Lamelas, F., and Wilkie, C., *Chem. Mat.* **14**, 189 (2002).
- [11] Hu, Y., Wang, S., Ling, Z., Zhuang, Y., Chen, Z., and Fan, W., *Macrom. Mater. Eng.* **288**, 272 (2003).
- [12] Morgan, A., *Polym. Adv. Technol.* **17**, 206 (2006).

- [13] Lyon, R. and Janssens, M., Polymer Flammability, Report No. DOT/FAA/AR-05/14, U.S. *Department of Transportation Federal Aviation Administration Office of Aviation Research, Washington, DC, USA*. **20591** (2005).
- [14] Lim, Y. and Park, O., *Macrom. Rapid. Commun.* **21**, 231 (2000).
- [15] Castillo-Tejas, J., Alvarado, J., and González-Alatorre, G., *J. Chem. Phys.* **123**, 054907 (2005).
- [16] Sanchez-Olivares, G., Sanchez-Solis, A., and Manero, O. *Int. J. Polym. Mater.* **57**, 245 (2008).

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