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FLAMMABILITY OF POLYSTYRENE-CLAY NANOCOMPOSITES

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Introduction

Research in the area of condensed phase flame retardants for polymers usually builds upon existing technologies, such as metal hydroxides (alumina, magnesium hydroxide) or phosphorus based materials. However, these materials tend to weaken mechanical properties while improving flammability resistance. No major new flame retardant (FR) technology has emerged in this area for quite some time.

Polymer-clay nanocomposites have generated a great deal of interest lately due to improved mechanical and thermal properties.¹ Also, they have improved flammability resistance while maintaining good mechanical properties, a key advantage over existing condensed phase flame retardants.² Recent work in our laboratory in this area has shown that polymer-clay nanocomposites have greatly reduced heat release rates.² Further, we have observed polymers which normally do not char, or leave any carbonaceous residue upon burning, produce char in the presence of clay. Previously, we had investigated the flammability properties of polystyrene copolymers with phosphates and the ability to crosslink via Friedel-Crafts chemistry.³ The research presented here combines Friedel-Crafts technology with clay to obtain an improved flame-resistant polystyrene.

Experimental²

Polystyrene nanocomposites were made on a B&P twin screw extruder at 190 °C and 300 RPM. Two types of polystyrene were used, Dow Styron 612 (PS) and a modified polystyrene from Marquette University (PS-Mrqt). These two polymers were combined to form a 50/50 by mass blend. 8 mass% clay (dimethyl di(hydrogenated tallow) ammonium treated montmorillonite, A-MMT) was added to this 50/50 blend. The Marquette modified polystyrene was a copolymer of styrene and 10% 4-vinylbenzyl alcohol. 10 mass% 2-Ethylhexyl diphenyl phosphate was added to this copolymer. The polystyrene-clay nanocomposites were analyzed by transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), and X-ray diffraction (XRD). Flammability was evaluated by the Cone Calorimeter.

XRD data was collected at ambient temperatures using CuK radiation with a 0.02 2 θ step size and a 2 s count time. Bright field TEM images of polystyrene-clay nanocomposites were obtained at 120 kV, under low-dose conditions, with a Philips 400T electron microscope. Polystyrene-clay nanocomposites were ultramicrotomed with a diamond knife at 23 °C to give ~70 nm thick sections. The sections were transferred from water to carbon-coated Cu grids of 200 mesh. TGA data was collected from 30 to 700 °C at 10 °C/min under N₂ using a TA Instruments SDT 2960. Cone Calorimeter experiments were performed at an incident heat flux of 50 kW/m² using the cone heater.⁴ Peak heat release rate (HRR), mass loss rate (MLR), specific heat of combustion (H_c), specific extinction area (SEA, a measure of smoke density), ignition time (t_{ign}), carbon monoxide yield, carbon dioxide yield, and specific heat of combustion data are reproducible to within \pm a fraction of 10 % when measured at 50 kW/m² flux. The Cone data reported here are the average of three replicated experiments. The standard uncertainties (one sigma) are shown as error bars on the plots of the Cone data.

Results and Discussion

We sought to evaluate polystyrene-clay nanocomposites with several flame retardancy mechanisms available for possible synergistic effects. By using the Marquette University modified polystyrene, poly(styrene-co-4-vinylbenzylalcohol, PS-Mrqt), we obtained the benefits of the Friedel-Crafts FR approach (2-ethylhexyl diphenyl phosphate + PS-Mrqt) and the nanocomposite FR approach. We believed that the Friedel-Crafts approach,

which increases char yield, would act with the nano-dispersed clay to lower the heat release rate (HRR) further.

The copolymer group (4-vinylbenzyl alcohol), has the further advantage of giving better clay dispersion than normal polystyrene. The alcohol group, being polar, can better wet the surface of the clay, and should allow better dispersion of the clay. XRD analysis (Fig. 1) of the 8 mass% A-MMT in a 50/50 blend of PS/PS-Mrqt material showed that there was an increased distance between clay layers (d-spacing). This increased d-spacing was larger than the d-spacing observed for PS + 8 mass% A-MMT sample (Fig. 1). The XRD data, combined with TEM analysis showed the material to be a well-dispersed intercalated nanocomposite. (Fig. 2, 3). This indicates that the PS-Mrqt material, with its polar groups, helps to give a more intercalated polymer-clay nanocomposite.

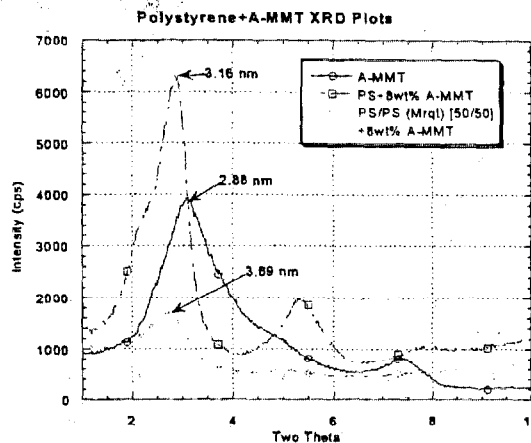


Figure 1. XRD plots of PS/A-MMT Blends

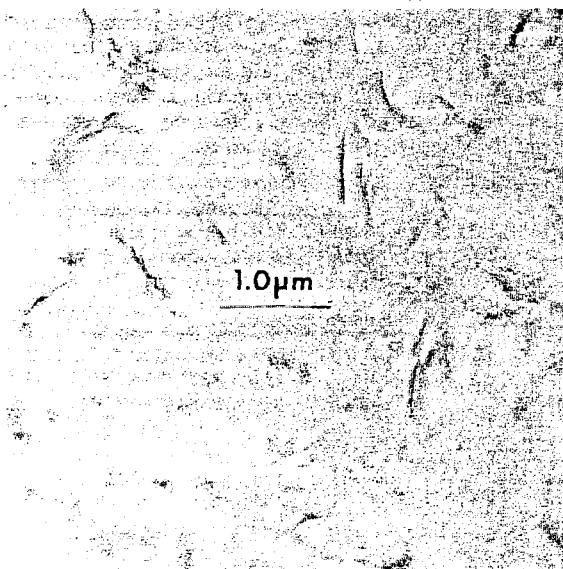


Figure 2. Low magnification TEM image of 8 mass% A-MMT in 50/50 PS/PS-Mrqt blend.

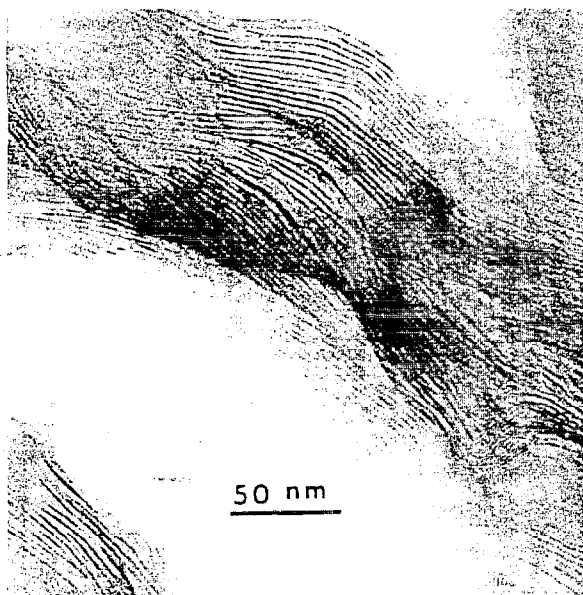


Figure 3. High magnification TEM image of 8 mass% A-MMT in 50/50 PS/PS-Mrqt blend.

Data from the cone calorimeter (Fig. 4) showed that the Friedel-Crafts approach (50/50 PS/PS-Mrqt + phosphate blend) had an approximately 50% lower peak HRR when compared to pure PS. Addition of A-MMT to this blend lowered the peak HRR by another 27%. Pure PS + A-MMT lowers the peak HRR by 70%. This gives the impression that A-MMT alone gives more of a reduction in HRR than the PS-Mrqt + A-MMT combination does. However, since no pure PS-Mrqt + A-MMT blend was made, this is not a fair comparison. The cone calorimeter data shows that the Friedel-Crafts effect significantly lowers the peak HRR, and the addition of nanodispersed A-MMT lowers the peak HRR further, indicating at least a cooperative flame retardant effect. Specifically, the two flame retardant mechanisms (Friedel-Crafts and nanodispersed clay) do not counteract each other, but the effect is neither strictly additive or synergistic.

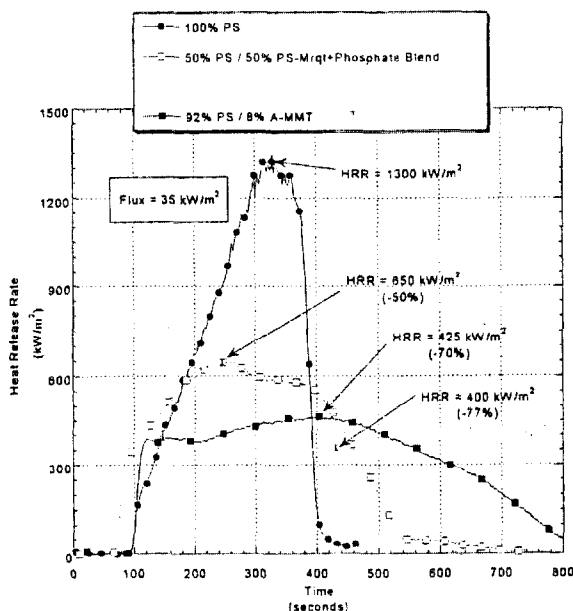


Figure 4. HRR data for PS+A-MMT samples.

Conclusions

Upon blending A-MMT with a 50/50 blend of PS and PS-Mrqt, an intercalated polymer-clay nanocomposite. The cone calorimeter data indicates that the clay did help lower the HRR for the final product. Further, the addition of the clay increased the total burn time for the material. Based upon these observations, it appears that clay nanocomposites compatible with the Friedel-Crafts flame retardant mechanism provided by PS-Mrqt material, but the improvement is not a pure synergistic one. There is an improvement in flammability, specifically a reduction of the peak HRR when the PS-Mrqt material is combined with nanodispersed A-MMT. However, the reduction provided by the Friedel-Crafts mechanism combined with the nanodispersed clay is not as impressive as the nanodispersed clay alone in PS. The real advantage to the PS-Mrqt system comes from improved dispersion of the clay in the polymer which may help mechanical properties.

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References

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- (1) (a) Giannelis, E. P. *Advanced Materials* 1996, 8, 29. (b) Kojima, Y.; Usuki, A.; Kawasumi, O. *J. Mater. Res.* 1993, 8, 1185. (c) Wang, P.; Pinnavaia, T. J. *Chem. Mater.* 1998, 10, 1820. (d) Burnside, S.; Giannelis, E. P. *Chem. Mater.* 1995, 7, 1597. (e) Lee, J.; Takekoshi, S.; Giannelis, E. P. *Mat. Res. Soc. Symp. Proc.* 1997, 457, 513.
- (2) (a) Gilman, J. W.; Kashiwagi, T.; Brown, J. E. T.; Lomakin, S.; Giannelis, E. P.; Manias, E. *Proceedings of 43rd Inter. SAMPE S And Exib.* 1998, 1053. (b) Gilman, J. W.; Kashiwagi, T.; Nyden, J. E. T.; Jackson, C. L.; Lomakin, S.; Giannelis, E. P.; Meeks, E. *Chemistry and Technology of Polymer Additives*. Blackwell Science, 1999, 249-265. (c) Gilman, J. W. *App. Clay Sci.* 1999, 13, 31. (d) Morgan, A. B.; Gilman, J. W.; Kashiwagi, T.; Jackson, C. L. *Flame Ret. Chem. Assoc. Proc.* March 12-15 2000, 25. (e) Gilman, J. W.; Harris, R. H.; Jackson, C. L.; Morgan, A. B.; Brassell, L. D.; Hunter, D. L. *PMSE Prep.* 2000, 82, 276.
- (3) Gilman, J. W.; Wilkie, C. A.; Wang, Z. *Polymer Degradation and Stability* 1999, 66, 373.
- (†) Certain commercial equipment, instruments, materials, service companies are identified in this paper in order to specify adequate experimental procedure. This in no way implies endorsement or recommendation by NIST.
- (4) Babrauskas, V. *Fire and Materials* 1995, 19, 243.