

Thermal Properties of Polystyrene Nanocomposites Formed from Rigid Intercalation Agent-Treated Montmorillonite

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ABSTRACT: Polystyrene (PS)/clay nanocomposites were prepared with two different new intercalation organophilic clays, the phosphonium salt (APP) and the ammonium 4-(4-adamantylphenoxy)-1-butanamine (APB) salts, by emulsion polymerization technique. X-ray diffraction and transmission electron microscopy were performed to characterize the layered structures of APB- and APP-treated polymer-clay nanocomposites, and both resulted in exfoliated structures. Molecular weights of PS obtained from these nanocomposites are slightly lower than the virgin PS formed under similar polymerization conditions. Coefficient of thermal expansion showed approximately a 44–55% decrease for APB- and APP-intercalated clay nanocomposites relative to the pure PS. Both T_g and thermal decomposition temperature of the PS component in the nanocomposite are higher than the virgin PS, implying that the presence of clay is able to enhance thermal stabilities of the PS. ©2007 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 45: 1781–1787, 2007

Keywords: adamantane; nanocomposites; polystyrene

INTRODUCTION

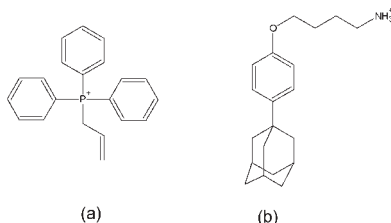
Polystyrene (PS) is one of the most mass-productive and commercialized polymers that can be produced by various methods such as solution and emulsion polymerizations. PS/clay nanocomposites possess potential applications and have been intensively investigated. The clay in PS nanocomposites can be intercalated by *in situ* polymerization^{1–6} or by melt intercalation⁷ using organically modified silicates.^{8–11} It has been reported that higher thermal stability and reduced

rate of heat release can be achieved through polymer-clay nanocomposites.^{4,12–16}

Polymer/clay nanocomposites typically comprise the organically modified clay and the mother polymer. The chemical structure of montmorillonite (MMT) consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either magnesium or aluminum hydroxide. Ion exchange of the Na⁺ and Ca⁺ in gallery cations of stacked silicates in MMT by inorganic, organic, and complex cations renders the hydrophilic-layered silicate organophilic. The modification of the gallery surfaces is usually required for intercalation of organic polymer precursors. Higher interlayer spacing allows for the subsequent exfoliating process when blending with polymer matrix. The sufficient

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Scheme 1. Structures of intercalation agent (a) APP, (b) APB.

interlayer widening is the key condition for the homogeneous dispersion of the silicate platelets within the polymer matrix.

In this article, polymer/clay nanocomposites based on two new organically modified clays are produced by emulsion polymerization. Chemical structures of these intercalation agents, allyl-triphenyl-phosphonium chloride (APP) and 4-(4-(1-adamantylphenoxy)-1-butanamine (APB), are shown in Scheme 1. In general, the intercalation agent is typically a linear aliphatic chain, possessing relatively poorer thermal stability.^{17–21} It has been reported that the use of phosphonium cation as intercalation agent is able to enhance thermal stability.^{15,22} The APB contains the rigid group of adamantane, which can be expected to improve thermal stability similar to a phosphonium cation. The phosphorus-containing compound as an intercalation agent is also expected to improve the flammable retardability of the resulting composite. In addition, the APP contains a double bond allowing for polymerization taking place within the clay gallery. In this study, PS/clay nanocomposites are prepared through emulsion polymerization by suspending the organic-treated clay in styrene monomer.

EXPERIMENTAL

Materials

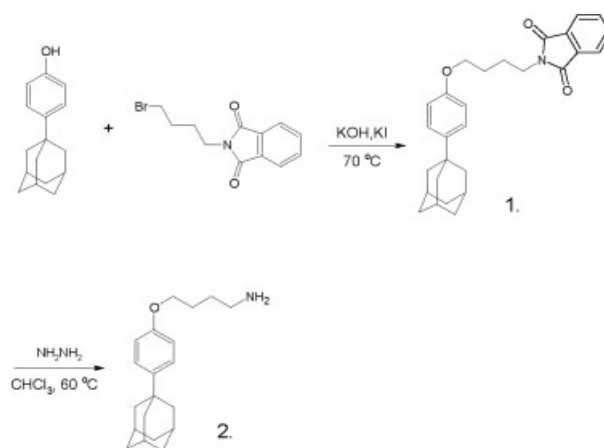
Most of the chemicals used in this study, including styrene, acetone, methanol, tetrahydrofuran, potassium iodide (KI), and potassium hydroxide (KOH) were acquired from the Aldrich Chemical. The styrene monomer was purified by removing the inhibitor using an inhibitor removal column also acquired from Aldrich. Both sodium dodecyl sulfate (SDS) and hydrochloric acid were obtained from Curtin Matheson Scientific. Potassium persulfate ($K_2S_2O_8$) and alumi-

num sulfate [$Al_2(SO_4)_3$] were acquired from Fisher Scientific, USA. Allyl-triphenyl-phosphonium chloride (APP), chloroform, and hydrazine were obtained from Acros Organics, USA. Both 4-(1-adamantyl)phenol and *n*-(4-bromobutyl)phthalimide were obtained from TCI. Pristine Na-MMT was provided by Telekal, Taiwan.

Synthesis of Intercalation Agent of APB

This APB containing a rigid group of adamantane was prepared according to the pathway shown in Scheme 2. The 4-(4-(1-adamantylphenoxy) butyl phthalimide (1) was prepared by the reaction between 4-(1-adamantyl)phenol (0.8 g, 3.5 mmol) and *N*-(4-bromobutyl)phthalimide (1.19 g, 4.2 mmol) in 50 mL of acetonitrile. Both KOH (0.5 g) and KI (0.006 g) were added with stirring and heated to 70 °C for 24 h. The solvent was removed in a rotary evaporator at 50 °C, and the resulting crude product was dissolved in ether and washed several times with distilled water. The purified product in ether solvent was dried with anhydrous sodium sulfate, followed by evaporation of the ether under vacuum to afford a yellow product (1).

A mixture containing 1 (0.438 g, 1.02 mmol), hydrazine monohydrate (0.3 g, 6 mmol), and chloroform/methanol (7:3, 10 mL) was heated overnight at 55–60 °C. After cooling to room temperature, the solid byproduct was removed by filtration. The filtrate was diluted with $CHCl_3$ (100 mL), washed with water (2×100 mL), dried over $MgSO_4$, and then concentrated. The residue was dissolved in ether (10 mL) and CH_2Cl_2 (5 mL), and a solution of methanesulfonic



Scheme 2. Preparation of intercalation agent (APB).

acid (0.1 g, 1.04 mmol) in ether (30 mL) was added. The resulting mixture was concentrated to 10 mL and placed at $-20\text{ }^{\circ}\text{C}$ overnight. The solid was collected by filtration to afford a pale yellow product (**2**).

Preparation of Modified Clays

The Na^+ -MMT (1 g) was dispersed into deionized water (50 mL) and stirred continuously for 4 h. The intercalation agent (APP or APB) was mixed in water (10 mL) was thus prepared, and 1 mL of 10% hydrochloric acid was added and stirred for 1 h. This intercalation agent solution was poured into the MMT–water solution under vigorous stirring overnight. The resulting organically modified clay was then filtered, washed thoroughly with deionized water, and dried overnight in a vacuum oven at room temperature.

Preparation of PS/Clay Nanocomposites

A 250 mL three-neck round-bottom flask containing the pristine clay (0.3 g) in deionized water (40 mL) was stirred for 4 h at room temperature. A aqueous solution of surfactant (APP or APB; 0.12 g) was poured into the clay suspension and stirred vigorously overnight. After filtration, the organically modified clay in 50 mL deionized water was stirred for 4 h. KOH (0.02 g) and SDS (0.4 g) were added into the suspension and the temperature was raised to $50\text{ }^{\circ}\text{C}$. Styrene monomer (10 g) and $\text{K}_2\text{S}_2\text{O}_8$ (0.05 g) were added slowly to the flask. The polymerization was carried out at $50\text{ }^{\circ}\text{C}$ for 8 h. After cooling, 2.5% aqueous aluminum sulfate (10 mL) was poured into the polymerized emulsion, followed by dilute hydrochloric acid (10 mL), with stirring. Finally, acetone was added to break down the emulsion completely and the resulting polymer was washed several times with methanol and distilled water and then dried overnight in a vacuum oven at $80\text{ }^{\circ}\text{C}$. Similar procedures were employed to prepare virgin PS.

Instrumentations

X-ray diffraction (XRD) spectra were collected on an M18XHF-SPA X-ray diffraction instrument (MacScience, Japan), using $\text{Co K}\alpha$ radiation. Bragg's law ($\lambda = 2d \sin\theta$) was used to compute the clay spacing. A Hitachi H-7500 transmission electron microscopy (TEM; 100 kV) was used to examine clay morphology and orientation. The

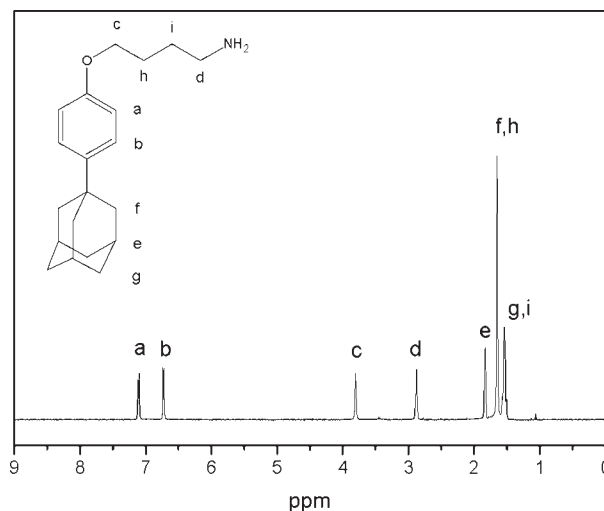


Figure 1. Proton NMR spectra of intercalation agent (APB).

sample was ultramicrotomed at room temperature using a diamond knife on a Leica Ultracut UCT Microtome to give 70-nm thick sections and mounted on carbon-coated Cu TEM grids. The measurement of sample in a DSC sample was done by cooling to $10\text{ }^{\circ}\text{C}$ quickly from the melt of the first scan. The second scan rate was $20\text{ }^{\circ}\text{C}/\text{min}$ from 30 to $150\text{ }^{\circ}\text{C}$, and the value of T_g was taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines. The coefficient of thermal expansion (CTE) was measured using a TA 2940 thermomechanical analyzer (TMA) by recording the change in the dimension of the specimens with the temperature. The specimens, in cubic form ($5 \times 5 \times 5\text{ mm}^3$), and the force applied was 0.005 N, and it was heated from 25 to $150\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$. Thermogravimetric analyses (TGA) were performed on a TA Instruments Thermal Analyzer under a 40 mL/min flow of nitrogen gas at a scan rate of $20\text{ }^{\circ}\text{C}/\text{min}$ from 30 to $800\text{ }^{\circ}\text{C}$. ^1H NMR spectroscopic analyses were performed using a Varian Unitynova-500 NMR spectrometers at 500 MHz. All of the spectra were recorded using CDCl_3 as the solvent and TMS as the external standard. Molecular weights and molecular weight distributions were characterized by gel permeation chromatography (GPC) using a Waters 510 HPLC, using THF as an eluent at a flow rate of 0.4 mL/min. The polymer chains were extracted from the clay surface using a reverse ion exchange

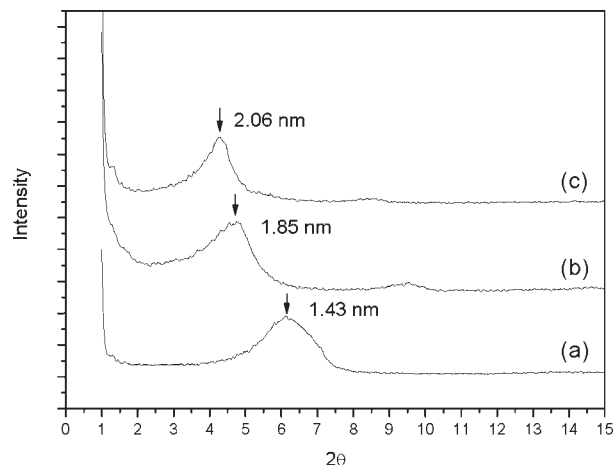


Figure 2. X-ray diffraction patterns of (a) pure clay, (b) the APP-intercalated clay, (c) the APB-intercalated clay.

reaction with LiCl/DMF to investigate the molecular weight and molecular weight distribution by GPC.

RESULTS AND DISCUSSION

Preparation of APB

^1H NMR spectrum of the APB prepared according to Scheme 2 is shown in Figure 1. Aromatic protons appear as doublet at 7.1 and 6.7 ppm. Two triplets at 3.8 and 2.9 ppm correspond to the protons of $-\text{O}-\text{CH}_2-$ and $-\text{CH}_2-\text{N}$ in butylamine group, respectively. The protons of

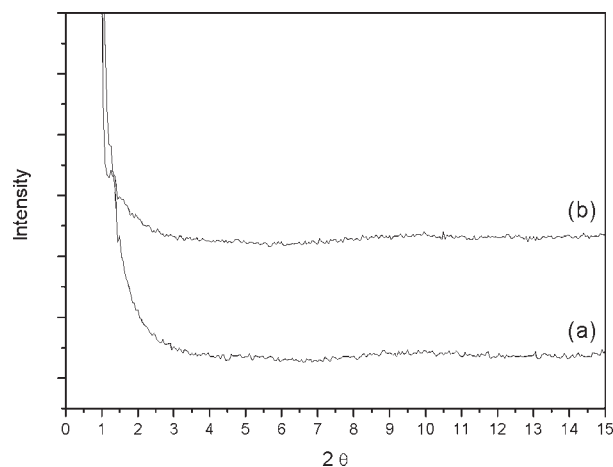


Figure 3. WAXD analysis of PS nanocomposites prepared by emulsion polymerization: (a) APB treatment; (b) APP treatment.

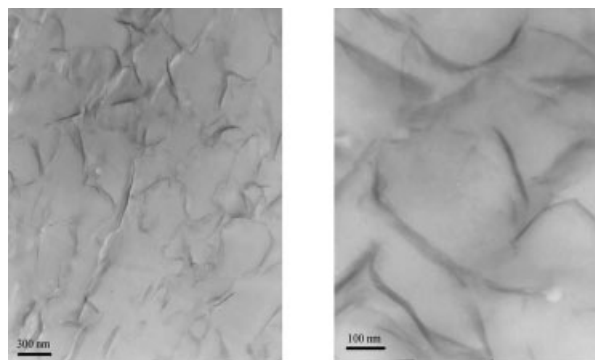


Figure 4. TEM images of the APP-treated nanocomposite at low (left) and high (right) magnifications.

adamantane (**e**) show a multiplet at 1.8 ppm. Protons of **f** and **h** (Fig. 1) overlap at 1.6 ppm, and protons of **g** and **i** also overlap at 1.5 ppm.

X-ray Diffractions

Figure 2 displays XRD patterns of the pure clay and intercalation agent-treated clays. By using the Bragg equation, $n\lambda = 2d \sin \theta$, the basal spacing values of these samples are calculated from the peak position. The d spacing value increases from 1.43 nm for the original clay to 1.85 nm for the intercalated agent of APP, indicating that the intercalation agent of APP is indeed successfully intercalated into the galleries of the clay nanoparticles. The APB intercalation agent is also inserted between the galleries of the clay, with d spacing at 2.06 nm.

In general, polymer/clay nanocomposites can be classified into two types: (1) the intercalated polymer/clay nanocomposites have layered clay dispersed in a polymer matrix with polymer

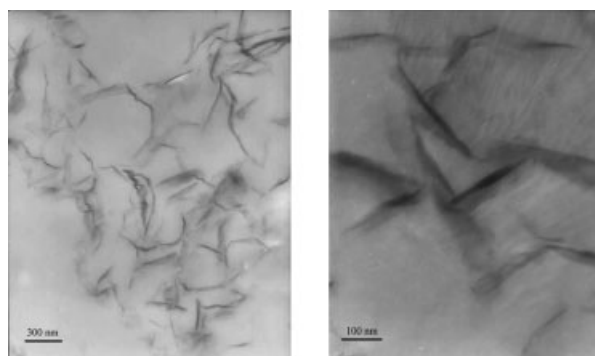


Figure 5. TEM images of APB-treated nanocomposite at low (left) and high (right) magnifications.

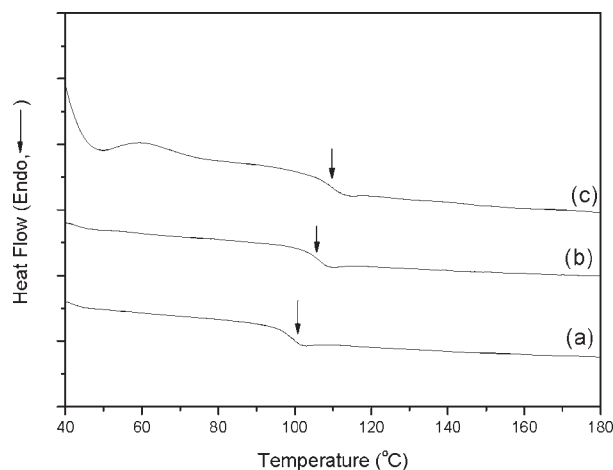


Figure 6. DSC curves for determining the glass transition temperature of (a) PS, (b) the nanocomposite formed using APP, and (c) the nanocomposite formed using APB.

chains inserted within layered galleries, (2) the fully delaminated clay platelets dispersed individually within the polymer matrix. Exfoliated clay platelets provide better contact and distribution within the polymer matrix, and thus enhance properties of the nanocomposites more effectively. Characterizing the formation of a nanocomposite requires measurement of the d spacing by XRD and TEM to identify the resulting structure of the clay platelets in polymer matrix. The formation of exfoliated clay platelets tends to be distributed in the matrix homogeneously and results in the totally disappeared XRD peak. The formation of a mixture of exfoliated and intercalated structures is also possible, which requires detection by TEM.

Figure 3 presents the XRD results for APP-Clay/PS and APB-Clay/PS nanocomposites. No XRD peak is present in the pattern of APP-Clay/PS and APB-Clay/PS, suggesting that the clay platelets are totally exfoliated. However, it is still necessary to observe the true structures

and distributions of the silica platelets based on TEM.

TEM Measurements on the Nanocomposites

Figures 4 and 5 are TEM images at two magnifications of nanocomposites of APP-Clay/PS and APB-Clay/PS, both show good dispersion and exfoliation of the clay platelets within the PS matrix. TEM result clearly shows that these clay platelets are fully exfoliated and evenly dispersed in PS matrix, which is consistent with the observation from XRD pattern.

Glass Transition Temperatures

Figure 6 displays the DSC thermograms for the virgin PS and organic-modified clay nanocomposites, and the results are summarized in Table 1. The glass transition temperature (T_g) of the virgin PS is 100 °C, while the values of T_g for the APP-clay and APB-clay nanocomposites are 107 and 109 °C, respectively. The presence of the clay layer tends to hinder movement of the PS chains and thus results in a higher value of T_g .

Molecular Weights of the Nanocomposites

Table 2 lists the molecular weights of virgin PS and PS in nanocomposites under similar emulsion polymerization conditions. The virgin PS has slightly higher average molecular weights (M_n and M_w) and a lower polydispersity index (PDI) than these two nanocomposites. It has been reported²³ that clay may act as additional micelles that are responsible for the observed lower molecular weight.

Coefficient of Thermal Expansion

The CTE was obtained from TMA. Figure 7 shows CTE values of pure PS and nanocomposites.

Table 1. Results of TGA and DSC for Polystyrene Nanocomposites

Sample	Clay (wt %)	T_g (°C)	Weight Loss Temperature (°C)		Char Yield (%)
			5 wt %	50 wt %	
PS	0	100	390	424	0
APB/clay/PS	3	109	395	452	3.2
APP/clay/PS	3	107	414	453	3.2

Table 2. Molecular Weights of PS and PS Nanocomposites

Sample	M_n^a (10^4)	M_w^b (10^4)	PDI ^c (M_w/M_n)
PS	44.1	53.4	1.21
APB/clay/PS	39.6	51.9	1.31
APP/clay/PS	41.1	51.0	1.24

^a Number-average molecular weights (M_n) and

^b weight-average molecular weights (M_w) were determined by GPC.

^c Polydispersity index, M_w/M_n .

A 44–55% decrease of CTE is observed for APB- and APP-intercalated clay nanocomposites relative to the pure PS. The results indicate that the presence of the exfoliated clay layers is able to effectively reduce CTE and improves its dimensional stability.

Characterization by TGA

Figure 8 shows TGA traces of pure APP and APB under nitrogen atmosphere. The pure APB decomposes at a higher temperature of 308 °C while pure APP decomposes at 288 °C, indicating that the APB is thermally more stable than APP. Therefore, the intercalation agent containing rigid adamantane is also considered to be thermally stable relative to most aliphatic intercalation agents.

Figure 9 shows TGA thermograms of pure PS and PS/clay nanocomposites. Both of the intercalation agent-treated clay nanocomposites display higher decomposition temperatures than the virgin PS and the results are also summarized in

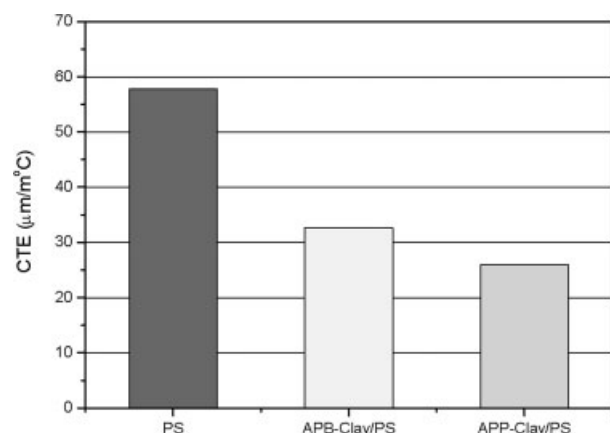
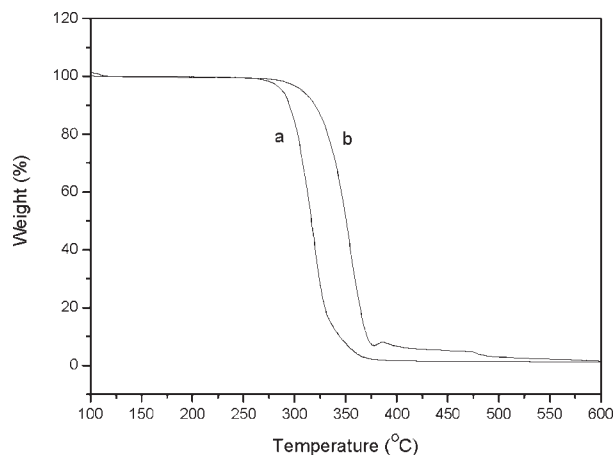
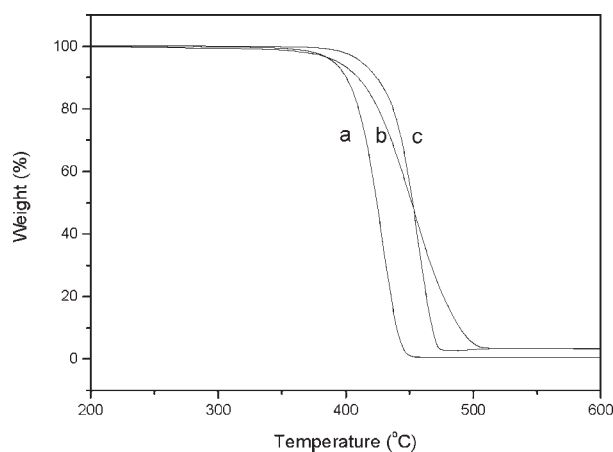
**Figure 7.** Coefficient of thermal expansion of nanocomposites.**Figure 8.** TGA curves of (a) pure APP (b) pure APB.

Table 1. The nanocomposite prepared from APP-intercalated clay displays a 24 °C higher decomposition temperature for 5% weight loss than the virgin PS, which the APB-intercalated clay nanocomposite gives only at 5 °C higher. Both nanocomposites contain inorganic clay and result in char yield as would be expected. Both adamantane and phosphonium group can enhance the thermal stability of the resulting nanocomposites.

CONCLUSIONS

In this study, we successfully synthesized intercalation agent of APB and prepared PS/clay

**Figure 9.** TGA curves of the nanocomposites recorded under nitrogen atmospheres: (a) pure PS, (b) the nanocomposite formed using APB, and (c) the nanocomposite formed using APP.

nanocomposites with a fully exfoliated structure. The intercalation of APB and APP into clay nanoparticles was confirmed by XRD. Results of XRD indicated that the d spacing increased from 14.3 Å for pristine clay to 20.6 Å for the APB-intercalated clay. TGA of the nanocomposites suggests that the onset of thermal degradation occurs at a higher temperature for the nanocomposite than for the virgin PS. It appears that the presence of the clay enhances the thermal stability of PS. The presence of the intercalation agent-treated clays slightly reduces the PS molecular weights (M_n and M_w) and increases MW distribution (PDI) relative to the virgin PS under similar emulsion polymerization conditions. The glass transition temperatures of the APP-Clay/PS or APB-Clay/PS are higher than that of the virgin PS. The polymer adding silica layer can reduce CTE and provide good dimensional stability for the nanocomposites.

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REFERENCES AND NOTES

1. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 983.
2. Usuki, A.; Koiwai, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Appl Polym Sci* 1995, 55, 119.
3. Noh, M. W.; Lee, D. C. *Polym Bull* 1999, 42, 619.
4. Doh, J. G.; Cho, I. *Polym Bull* 1998, 41, 511.
5. Okamoto, M.; Morita, S.; Taguchi, H.; Kim, Y. H.; Kotaka, T.; Tateyama, H. *Polymer* 2000, 41, 3887.
6. Zeng, C.; Lee, L. J.; *Macromolecules* 2001, 34, 4098.
7. Lim, Y. T.; Park, O. O. *Macromol Rapid Commun* 2000, 21, 231.
8. Fu, X.; Qutubuddin, S. *Mater Lett* 2000, 42, 12.
9. Fu, X.; Qutubuddin, S. *Polymer* 2001, 42, 807.
10. Hoffmann, B.; Dietrich, C.; Thomann, R.; Friedrich, C.; Mulhaupt, R. *Macromol Rapid Commun* 2000, 21, 57.
11. Weimer, M. W.; Chen, H.; Giannelis, E. P.; Sogah, D. Y. *J Am Chem Soc* 1999, 121, 1615.
12. Gilman, J. W.; Kashiwagi, T.; Giannelis, E. P.; Manias, E.; Lomakin, S.; Lichtenham, J. D.; Jones, P. In *Fire Retardancy of Polymers: The Use of Intumescence*; Le Bras, M.; Camino, G.; Bourbigot, S.; Delobel, R., Eds.; Royal Society of Chemistry: London, 1998; pp 201–221.
13. Gilman, J. W.; Kashiwagi, T.; Nyden, M.; Brown, J. E. T.; Jackson, C. L.; Lomakin, S.; Giannelis, E. P.; Manias, E. In *Chemistry and Technology of Polymer Additives*; Al-Malaika, S.; Golovoy, A.; Wilkie, C. A., Eds.; Blackwell, 1999; pp 249–265.
14. Zhu, J.; Wilkie, C. A. *Polym Int* 2000, 49, 1158.
15. Zhu, J.; Morgan, A. B.; Lamelas, F. J.; Wilkie, C. A. *Chem Mater* 2001, 13, 3774.
16. Gilman, J. W.; Kashiwagi, T. In *Polymer–Clay Nanocomposites*; Pinnavaia, T. J.; Beall, G. W., Eds.; John Wiley: New York, 2000; pp 193–206.
17. Tseng, C. R.; Wu, J. Y.; Lee, H. Y.; Chang, F. C. *Polymer* 2001, 42, 10063.
18. Tseng, C. R.; Lee, H. Y.; Chang, F. C. *J Polym Sci Part B: Polym Phys* 2001, 39, 2097.
19. Wu, H. D.; Tseng, C. R.; Chang, F. C. *Macromolecules* 2001, 34, 2992.
20. Tseng, C. R.; Wu, J. Y.; Lee, H. Y.; Chang, F. C. *J Appl Polym Sci* 2002, 85, 1370.
21. Tseng, C. R.; Wu, H. D.; Wu, J. Y.; Chang, F. C. *J Appl Polym Sci* 2002, 86, 2492.
22. Jin, Z.; Fawn, M. U.; Alexander, B. M.; Charles, A. W. *Chem Mater* 2001, 13, 4649.
23. Dongyan, W.; Jin, Z.; Qiang, Y.; Charles, A. W. *Chem Mater* 2002, 14, 3837.