Enhanced thermal properties of PS nanocomposites formed from inorganic POSS-treated montmorillonite

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Abstract

We have prepared polystyrene/clay nanocomposites using an emulsion polymerization technique. The nanocomposites were exfoliated at up to a 3 wt% content of pristine clay relative to the amount of polystyrene (PS). We used two different surfactants for the montmorillonite: the aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS) and the ammonium salt of cetylpyridinium chloride (CPC). Both surfactants can intercalate into the layers of the pristine clay dispersed in water prior to polymerization. Although the *d* spacing of the POSS-intercalated clay is relatively smaller than that of the CPC-intercalated clay, PS more easily intercalates and exfoliates the POSS-treated clay than the CPC-treated clay. IR spectroscopic analysis further confirms the intercalation of POSS within the clay layers. We used X-ray diffraction (XRD) and transmission electron microscopy (TEM) to characterize the structures of the nanocomposites. The nanocomposite prepared from the clay treated with the POSS containing surfactant is exfoliated, while an intercalated clay was obtained from the CPC-treated surfactant. The molecular weights of polystyrene (PS) obtained from the nanocomposite is slightly lower than the virgin PS formed under similar polymerization conditions. The value of T_g of the PS component in the nanocomposite is 8 °C higher than the virgin PS and its thermal decomposition temperature (21 °C) is also higher significantly. The presence of the POSS unit in the MMT enhances the thermal stability of the polystyrene.
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1. Introduction

Nanoclay-filled polymeric systems offer the prospect of greatly improving many of the properties of their mother polymers. In the recent literature, there have been reports of nanoclay-filled polymeric systems that display significant improvements in tensile and thermal properties [1–9], heat distortion temperatures [1–6], and resistance to flammability [12] and reduced permeability to small molecules [5,10,11] and reduced solvent uptake [13]. A common observation emerging from these studies is that the magnitude of improvement depends strongly on the state of dispersion of the clay layers in the polymer matrix.

The nanocomposite typically comprises the organically modified clay and the mother polymer. Montmorillonite (MMT), which is an aluminosilicate mineral with sodium counterions present between the layers, is the most commonly used clay. The space between these clay layers is referred to as the clay gallery. To make this inorganic clay compatible with organic polymers, the sodium counterions are usually ion-exchanged with an organic ammonium or phosphonium salt to convert the material into hydrophobic ammonium- or phosphonium-treated clays. The nanocomposites may be prepared either by a blending process (either melt blending or solution blending) or by an in situ polymerization process in the presence of the organically modified clay.

In this paper, we describe the preparation of two types of nanocomposites formed from cetylpyridinium chloride (CPC)- and aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS)-treated clays (Scheme 1). The PS/clay nanocomposite formed using the CPC-treated clay exhibited no significant improvements in thermal properties [14–18] in our laboratory. Major reason of choice POSS molecules are typically stable up to 300 °C, which is higher than the thermal degradation temperatures of most organic molecules. POSS consists of a rigid cubic silica core, having

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Scheme 1 structure

(left column figure)

CPC

POSS

R=i-butyl
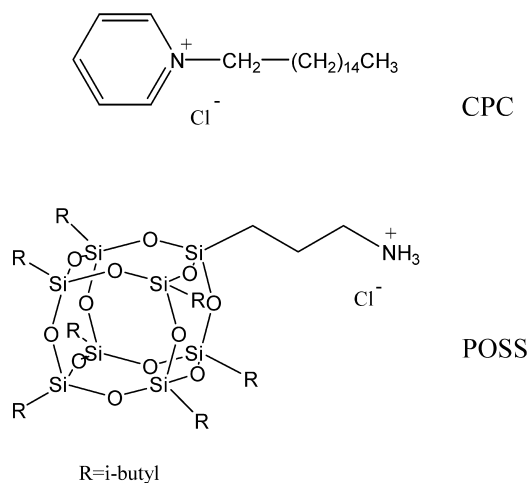
Scheme 1. Chemical structures of the surfactants used to prepare the modified clays.

0.53 nm side lengths, to which organic functional groups can be attached, at the vertices, for further reactions. POSS derivatives containing amine functional groups can play the role of surfactants for the treatment of clay; the thermal stability of the resulting nanocomposite is enhanced.

PS/clay nanocomposites were prepared through emulsion polymerization by suspending the surfactant-treated clay in styrene monomer. IR spectroscopic analysis confirmed the existence of POSS in the intercalated clay samples. We used both X-ray diffraction (XRD) and transmission electron microscopy (TEM) to characterize the clay structure. The properties of these PS/clay nanocomposites were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and gel permeation chromatography (GPC).

2. Experimental

2.1. Materials

Most of chemicals used in this study, including monomeric styrene, chemically pure acetone, methanol, tetrahydrofuran, and potassium hydroxide (KOH) were acquired from the Aldrich Chemical Co., Inc. The styrene monomer was purified by removing the inhibitor with the aid of an inhibitor-removal column, which was also acquired from Aldrich. Sodium dodecyl sulfate (SDS) and hydrochloride acid were both obtained from Curtin Matheson Scientific, Inc. Potassium persulfate ($K_2S_2O_8$) and aluminum sulfate [$Al_2(SO_4)_3$] were acquired from Fisher Scientific Co., USA. Cetylpyridinium chloride (CPC) was obtained from Acros Organics, USA. Aminopropyl-isobutyl polyhedral oligomeric silsesquioxane (POSS) was obtained from Hybrid Plastics, Inc. Pristine Na-MMT was provided by Telekal Co., Taiwan.

2.2. Preparation of CPC-modified clays

The organically modified clay was obtained by combining sodium montmorillonite (5 g) and the desired quantity (1, 1.5, 2, or 2.5 g) of the ammonium salt (CPC), as previously described [19].

2.3. Preparation of POSS-modified clays

The prewashed clay (1 g) and water (50 ml) were placed into a 100 ml two-neck round-bottom flask and stirred continuously for 4 h. POSS (0.4 g) in THF (1 ml) was placed into another flask and then 10% hydrochloric acid (1 ml) was added and then stirring for 1 h. This POSS solution was then added into the suspended clay and the mixture was stirred overnight. The mixture was filtered, washed several times with deionized water, and then dried overnight in a vacuum oven at room temperature.

2.4. Preparation of polystyrene/clay nanocomposites

Emulsion polymerization was performed as follows. A suspension of clay (0.3 g) in deionized water (40 ml) was stirred for 4 h at room temperature. A solution of surfactant (CPC or POSS; 0.12 g) was added and the mixture was stirred for 4 h. KOH (0.02 g) and SDS (0.4 g) were added into the solution and the temperature was raised to 50 °C. Styrene monomer (10 g) and $K_2S_2O_8$ (0.05 g) were added slowly to the flask. Polymerization was performed at 50 °C for 8 h. After cooling, 2.5% aqueous aluminum sulfate (10 ml) was added to the polymerized emulsion, followed by dilute hydrochloric acid (10 ml), with stirring. Finally, acetone was added to break down the emulsion completely. The polymer was washed several times with methanol and distilled water and then dried overnight in a vacuum oven at 80 °C. Similar procedures were employed to prepare virgin polystyrene.

2.5. Instrumentations

IR spectroscopy was performed on a Nicolet Avatar 320 FTIR Spectrophotometer; 32 scans were collected at a spectral resolution of $1 \, cm^{-1}$. Infrared spectra of the organic-modified clay were obtained using the conventional KBr pellet method. XRD spectra were collected on an M18XHF-SPA X-ray diffraction instrument (MacScience Co., Japan), using Co Kα radiation; Bragg's law ($\lambda = 2d \sin \theta$) was used to compute the spacing. TEM images of the composites were obtained at 100 kV using a Hitachi H-7500 Electron Microscope. The sample was ultramicrotomed at room temperature using a glass knife on a Leica Ultracut UCT Microtome to give 100 nm-thick sections. The contrast between the layered silicates and the polymer phase is sufficient for imaging and, therefore, no heavy metal staining was required prior to imaging. Thermogravimetric analyses were performed on a TA Instruments
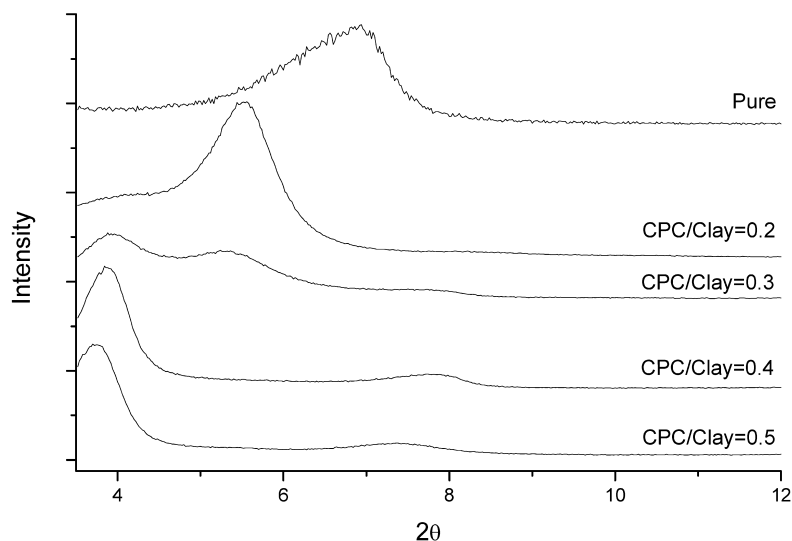
Fig. 1. XRD spectra of materials featuring various ratios of the organic ammonium salt.

Thermal Analyzer under a 40 ml/min flow of nitrogen gas at a scan rate of 20 °C/min from 30 to 800 °C. A Du-Pont (DSC-9000) differential scanning calorimeter (DSC) was used to measure the glass transition temperature (T_g) of the PS/clay. The sample was preheated at a scan rate of 20 °C/min from 30 to 200 °C and then cooled quickly to 30 °C from the melt of the first scan. The second scan rate was 20 °C/min from 30 to 200 °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. Molecular weights and molecular weight distributions were characterized by GPC using a Waters 510 HPLC-equipped with a 410 Differential Refractometer, a UV detector, and three Ultrastyragel columns (100, 500, and 10^3 Å) connected in series in order of increasing pore size—using THF as an eluent at a flow rate of 0.4 ml/min. The molecular weight calibration curve was obtained using polystyrene standards.

3. Results and discussion

This study focused on comparing nanocomposites prepared using two different surfactant-modified clays. The CPC surfactant is an ammonium salt that contains a long aliphatic chain. The POSS surfactant is an ammonium salt that features a cube-like cage structure containing seven isobutyl groups located at the corner positions. Scheme 1 displays the structures of these two ammonium salts, CPC and POSS, used to prepare the modified clays. Conventional surfactants, such as CPC, are unstable at high temperatures. Thus, we expected that nanocomposites prepared from the POSS surfactant would possess better thermal stabilities relative to those formed using the CPC surfactant.

3.1. X-ray diffractions

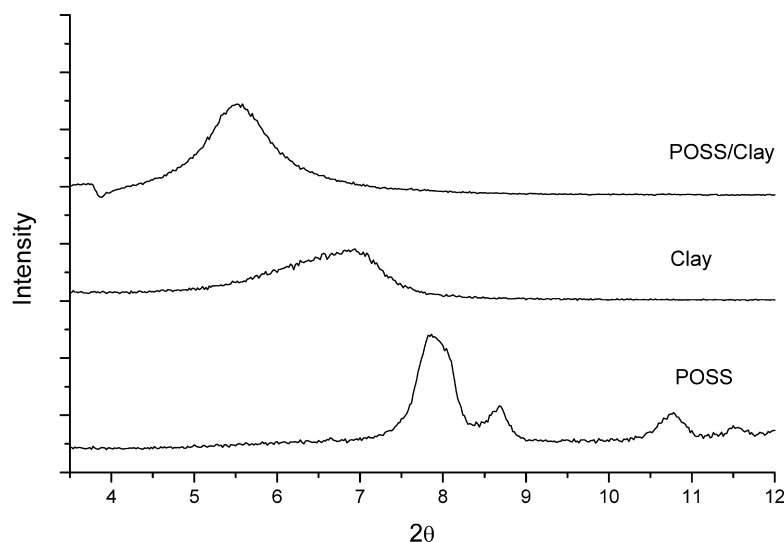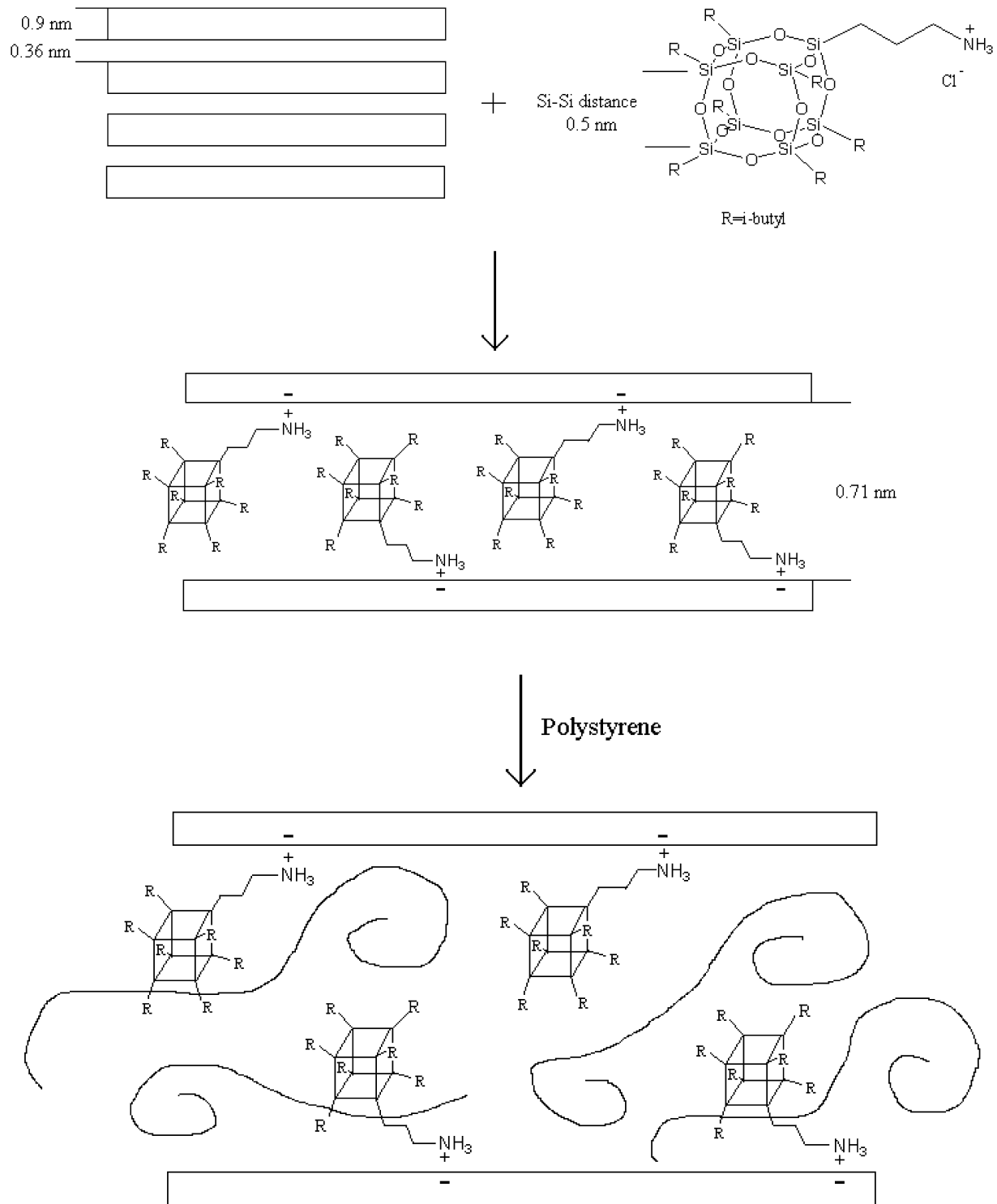We used XRD to characterize the layered structures of

Fig. 2. X-Ray powder diffraction patterns of pure POSS, pure clay, and intercalated clay.

Scheme 2. Schematic drawing of the clay intercalated by the POSS and polystyrene.

the modified clays and polymer/clay nanocomposites, since changes in 2θ indicate changes in the gallery distance of the clay. Fig. 1 shows XRD patterns of organic-modified clays containing different CPC/clay ratios. The basal space indicates the interlayer spacing of the silicate layers, which is calculated from the peak position using the Bragg equation.

The pristine clay has this peak at 6.94°, which corresponds to a basal space of 1.26 nm. The insertion of the CPC surfactant between the galleries of the clay increases the d spacing as the CPC/clay ratio increases. When the CPC/clay ratio is greater than 0.4, the d spacing remains constant, which implies that oversaturation of the surfactant has
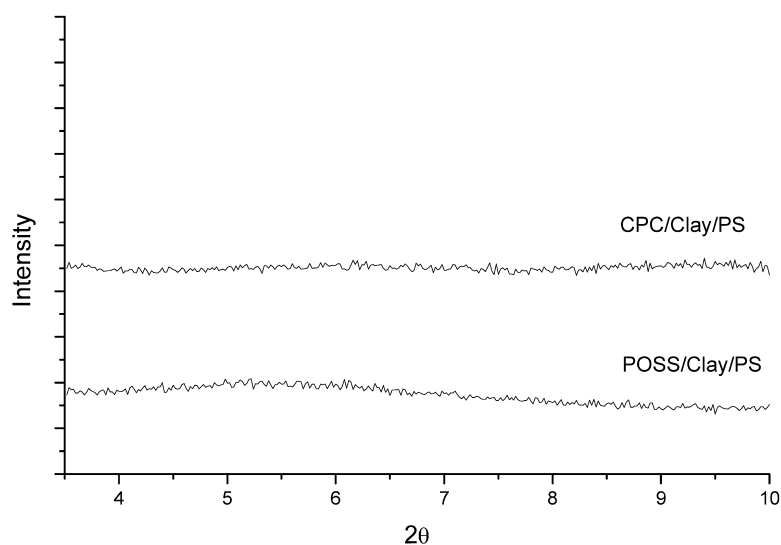
Fig. 3. XRD spectra of the two surfactant-containing nanocomposites, indicating the degree of exfoliation.

occurred. This result indicates that the CPC surfactant becomes successfully intercalated into the galleries of the clay nanoparticles.

Fig. 2 shows the XRD results of the POSS-intercalated clay. The pure POSS surfactant has characteristic diffraction peaks at 7.9 and 8.8° that arise from aggregation of the POSS. When the POSS surfactant is inserted between the galleries of the clay, the d spacing is increased from 1.26 nm for the pristine clay to 1.61 nm for the POSS surfactant-intercalated clay, which indicates that the POSS surfactant has indeed been intercalated successfully into the galleries of the clay. This d spacing is relatively smaller than that of the CPC-treated clay, but it does not affect the clay intercalation or exfoliation within the PS matrix. The POSS is known to interact with PS to promote intercalation and exfoliation [20]. This result agrees well with the TEM result that indicated that the degree of clay exfoliation of the POSS-treated nanocomposite is even greater than that of the CPC-treated material. The POSS surfactant-intercalated clay (POSS/Clay) exhibits only one diffraction peak; no peak was detected to arise from the aggregation of POSS. The POSS surfactant-intercalated clay is presented schematically in Scheme 2. The interlamellar distance indicated in the figure is calculated by the expression: $\Delta d = d$ spacing - thickness of one platelet (~ 1.0 nm). In the case of the clay intercalated with POSS surfactant, the distance between two adjacent clay plates is 0.71 nm which is close to the particle size of the POSS. The R group (isobutyl group) of the POSS experiences van der Waals interactions with the styrene monomer, and thus allows the styrene monomer can polymerize within the galleries of the clay.

The formation of a true polymer/clay nanocomposite requires the insertion of the polymer between the layers of the clay. There are two terms used to describe the general classes of nanocomposites: intercalation and exfoliation

(also called delamination). In the case of intercalation, polymer chains are inserted between galleries of the clay, and the spacing between the galleries is increased. On the other hand, in the case of exfoliation, these individual silicate layers are distributed randomly such that they no longer interact with the cations. Characterizing the formation of a nanocomposite requires measurement of the d spacing by XRD and the use of TEM to determine the actual distribution of platelets within the polymer matrix. The formation of an exfoliated structure usually results in the complete loss of registry between the clay layers so that no peak can be observed by XRD. The most likely occurrence is the formation of a mixture of exfoliated and intercalated structures; this phenomenon requires detection by TEM.

Fig. 3 shows the XRD results for CPC/Clay/PS and POSS/Clay/PS nanocomposites. No peak is detected for the nanocomposites from both the CPC- and POSS-treated clays, which suggests that they have exfoliated structure. TEM is still required, however, to observe the true structure and distribution of the silica platelets. There is an angle detecting limit for the XRD detector which is unable to detect the diffraction angle less than 3.5°.

3.2. TEM measurements on the nanocomposites

Fig. 4 shows TEM images of two nanocomposites prepared from the CPC- and POSS-modified clays. The layers of platelets observed for these CPC-treated nanocomposites are, in fact, an intercalated structure. For the POSS-treated nanocomposite, each clay layers is isolated and evenly distributed within the PS matrix, which implies that a full exfoliation is formed that is consistent with the XRD data.
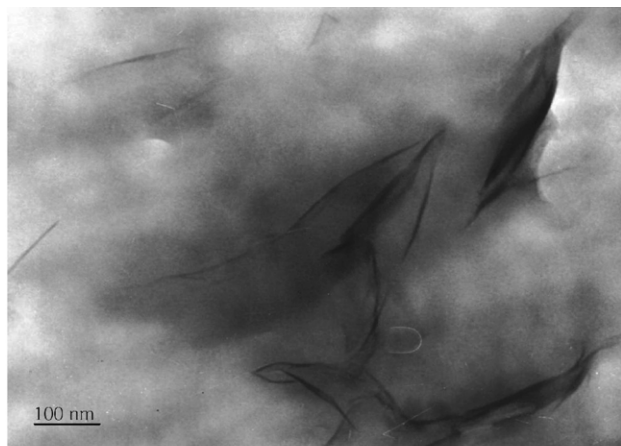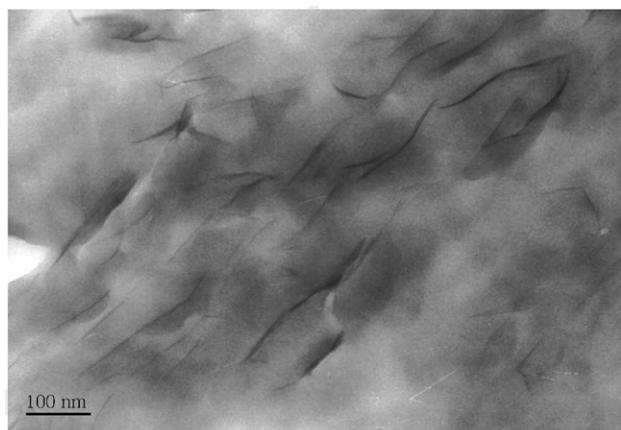
Fig. 4. TEM micrographs of (a, top) the CPC-treated nanocomposite and (b, bottom) the POSS-treated nanocomposite.

3.3. Infrared spectroscopy

IR analysis further confirms the existence of the POSS in the intercalated clay sample. Figure 5 shows the IR spectra of pure POSS, pure clay, and the POSS-treated clay. The pure clay exhibits a strong absorbance at 1040 cm^{-1} for the
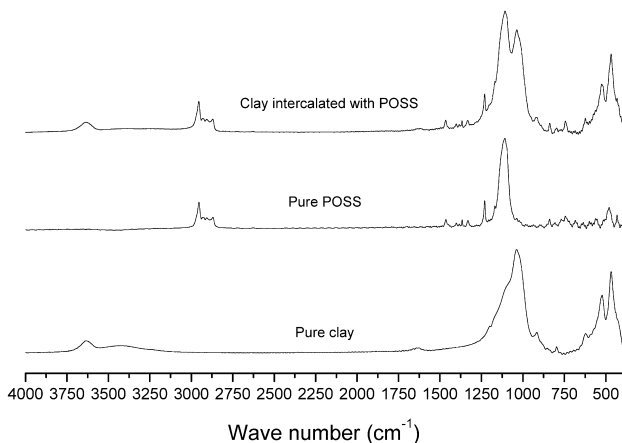

Fig. 5. IR spectra of pure clay, pure POSS, and intercalated clay.

Table 1
Results of TGA and DSC for polystyrene nanocomposites

Sample	T_g, (°C)[a]	$T_{0.05}$, (°C)[b]	$T_{0.5}$, (°C)[c]	Char at 600 °C (%)
PS	100	390	424	0
CPC/Clay/PS	102	408	424	2.9
POSS/Clay/PS	108	411	446	2.8

[a] Glass transition temperature (T_g).
[b] 5% Degradation temperature ($T_{0.05}$).
[c] 50% Degradation temperature ($T_{0.5}$).

Si–O–Si bond in montmorillonite silicate. The pure POSS surfactant exhibits characteristic absorption peaks for its C?H bonds at 2950–2800 cm^{-1}, the Si–C bonds at 1230 cm^{-1}, and the Si–O–Si bonds of the cage structure at 1109 cm^{-1}. The POSS-treated clay possesses all of the characteristic peaks of pure POSS and pure clay, which is an indication that the POSS surfactant is intercalated into the host galleries of the clay. This result is consistent with XRD data.

3.4. Analyzing glass transition temperatures

Fig. 6 shows the DSC thermograms for the virgin PS and surfactant-modified clay nanocomposites. The T_g of the virgin PS is 100 °C while the values of T_g for the CPC/clay and POSS/clay nanocomposites are 102 and 108 °C, respectively. The presence of the clay layer tends to retard PS chain movement near its value of T_g. The better-dispersed clay nanocomposite (POSS/clay) retards chain movement more effectively than does the CPC/clay-modified nanocomposite.

3.5. Molecular weights of the nanocomposites

Table 2 lists the molecular weights of PS in nanocomposites under similar emulsion polymerization conditions. The virgin PS has higher average molecular weights (M_n and M_w) and a lower polydispersity index (PDI) than the two nanocomposites. It has been reported [21] that clay may act as additional micelles that are responsible for the observed lower molecular weight.

3.6. Characterization by TGA

Fig. 7 shows the TGA traces of pure clay, clay treated

Table 2
Molecular weights of polystyrene nanocomposites

Sample	M_n ($\times 10^3$)[a]	M_w ($\times 10^3$)[b]	PDI (M_w/M_n)[c]
PS	26.1	31.8	1.22
CPC/Clay/PS	22.5	30.8	1.37
POSS/Clay/PS	21.9	31.1	1.42

[a] Number-average molecular weights (M_n).
[b] Weight-average molecular weights (M_w) were determined by GPC.
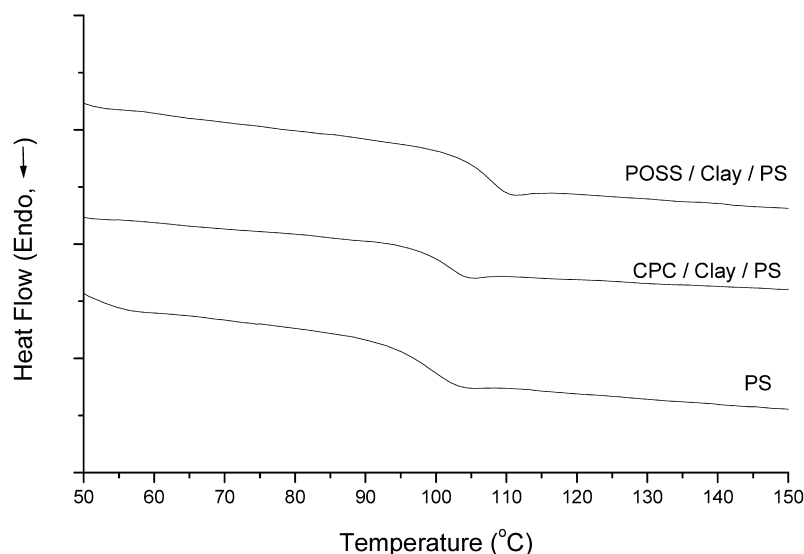[c] Polydispersity index, M_w/M_n.

Fig. 6. DSC curves for determining the glass transition temperature of the nanocomposites.

with the POSS, and clay treated with the CPC. As expected, the inorganic montmorillonite silicate possesses exceptionally high thermal stability. The total weight loss of the pristine clay is only 5.7% up to 800 °C, which corresponds to three different types of water present in the montmorillonite clay [22]. In contrast, the surfactant-intercalated clays are more easily decomposed. Both CPC- and POSS-modified clays begin to decompose at much lower temperatures than the pure clay. The modified clays possessing identical component weight ratio (surfactant/ clay = 0.4) give different temperatures of the 5% weight loss. The POSS-modified clay decomposes at a higher temperature of 386 °C while the CPC-modified clay decomposes at 278 °C. The POSS-intercalated clay is relativity more thermally stable than the CPC-intercalated clay. Thermal decompositions and removal of surfactants are responsible for the observed weight losses of these

intercalated clays. This result also agrees well with the IR result that suggested that the clay indeed contains the organic surfactant.

Fig. 8 shows TGA thermograms of nanocomposites and polystyrene. Both of the surfactant-modified PS nanocomposites display higher decomposition temperatures than the virgin PS. The onset of thermal decomposition for the nanocomposites is shifted to higher temperatures. The POSS-intercalated clay nanocomposite is the most thermally stable one among these three samples. The nanocomposite prepared from clay/POSS displays a 21 °C increase in the decomposition temperature for 5% weight loss relative to virgin PS; the clay/CPC nanocomposite is 18 °C higher. Table 1 summarizes the TGA results for the nanocomposites. The highest temperature of 50% weight loss is observed for the POSS-intercalated clay nanocomposite. In the case of the CPC-intercalated clay
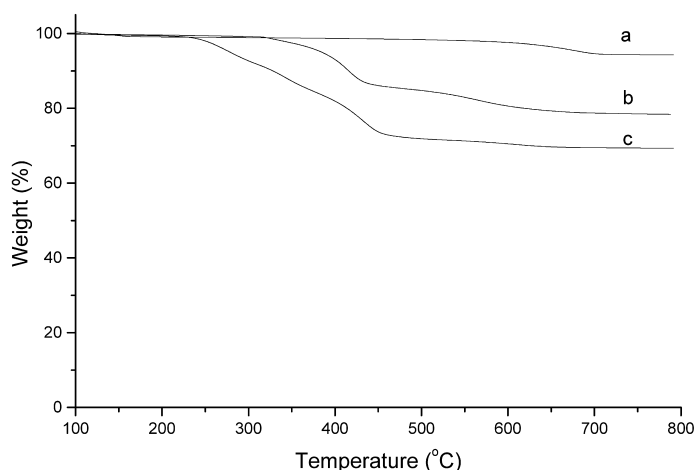

Fig. 7. TGA traces of (a) pure clay, (b) clay intercalated with the POSS, and (c) clay intercalated with CPC.
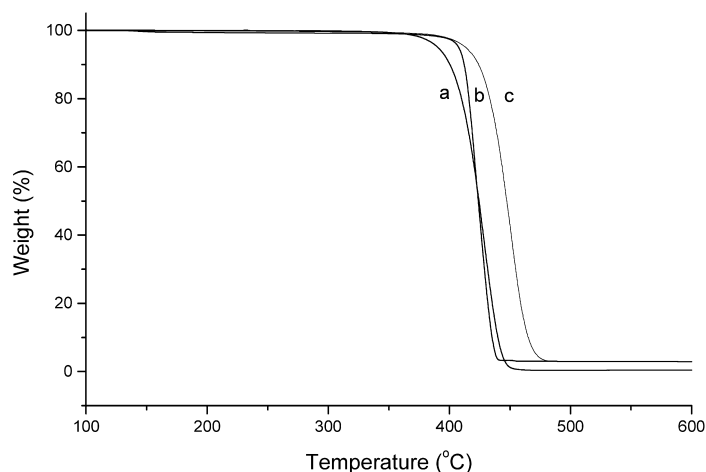
Fig. 8. TGA curves for the nanocomposites under a nitrogen atmosphere: (a) pure PS, (b) the nanocomposite formed with CPC, and (c) the nanocomposite formed with POSS.

nanocomposite, the temperature of 50% weight loss is actually the same as that for the virgin polystyrene. Therefore, the nanocomposite prepared from CPC-modified clay exhibits no improvement over the virgin PS, but, in the contrast, the nanocomposite prepared with POSS-modified clay has an improved thermal stability.

4. Conclusions

We have prepared polystyrene/clay nanocomposites that have (a) an exfoliated structure when derived from POSS treatment and (b) an intercalated forms when treated with CPC. The intercalation of surfactants into montmorillonite clay nanoparticles was confirmed by XRD and FTIR spectroscopy. Results of XRD indicated that the d spacing increased from 1.26 nm for pristine clay to 1.61 nm for the POSS-intercalated clay. TGA of the nanocomposites suggests that the onset of thermal degradation occurs at a higher temperature for the nanocomposite formed from POSS than for either the virgin PS or the nanocomposite derived from CPC treatment. It appears that the presence of the POSS in the clay enhances the thermal stability of polystyrene. Surfactant-modified clays give PS having lower molecular weights (M_n and M_w) and a higher MW distribution (polydispersity index, PDI) relative to the virgin PS formed under similar emulsion polymerization conditions. The glass transition temperatures of the nanocomposites incorporating CPC or POSS are higher than that of the virgin PS.

Acknowledgements

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