

Preparation and Characterization of Polystyrene–Clay Nanocomposites by Free-Radical Polymerization

CHEN-RUI TSENG,¹ JENG-YUE WU,² HSIN-YI LEE,³ FENG-CHIH CHANG¹

¹ Institute of Applied Chemistry, National Chiao-Tung University, Hsin-Chu, Taiwan, 30043

² Department of Chemical Engineering, National Chung-Hsing University, Tai-Chung, Taiwan

³ Synchrotron Radiation Research Center, Hsin-Chu, Taiwan

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ABSTRACT: The polymerizable cationic surfactant, vinylbenzyltrimethylammonium chloride (VBDEAC), was synthesized to functionalize montmorillonite (MMT) clay and used to prepare exfoliated polystyrene–clay nanocomposites. The organophilic MMT was prepared by Na⁺ exchanged montmorillonite and ammonium cations of the VBDEAC in an aqueous medium. Polystyrene–clay nanocomposites were prepared by free-radical polymerization of the styrene containing intercalated organophilic MMT. Dispersion of the intercalated montmorillonite in the polystyrene matrix determined by X-ray diffraction reveals that the basal spacing is higher than 17.6 nm. These nanocomposites were characterized by differential scanning calorimetry (DSC), transmission electron micrograph (TEM), thermal gravimetric analysis (TGA), and mechanical properties. The exfoliated nanocomposites have higher thermal stability and better mechanical properties than the pure polystyrene. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1370–1377, 2002

Key words: clay; polystyrene;

INTRODUCTION

Polymer nanocomposites are a new class of material with at least one ultrafine phase dimension, typically a few nanometers. Nanocomposites possess unique properties that are not shared by conventional composites primarily because of large interfacial area per unit volume. Exfoliated polymer–clay nanocomposites are especially desirable for property improvement due to the homogeneous dispersion of clay and great interfacial area between polymer and clay. The efficiency

of clay to enhance properties of the polymer is primarily determined by the degree of clay dispersion within the polymer matrix. The hydrophilic nature of the clay surface impedes its homogeneous dispersion in the organic polymer phase. However, the clay in the polymer–clay hybrid can be dispersed well at the nanometer scale through insertion of polymer chains into the silicate interlayers of the clay when the clay is pretreated by a suitable surfactant. The impregnation of a clay by a vinyl monomer such as methyl methacrylate,^{1–4} acrylonitrile,^{5,6} or styrene^{7–11} followed by free-radical polymerization has recently been investigated.

Intercalated polystyrene–clay nanocomposites have been prepared by several researchers. Kato et al.⁷ reported the intercalation of polystyrene in stearyltrimethylammonium cation exchanged montmorillonite (MMT). Akeelah and Moet⁸ pre-

Correspondence to: F.-C. Chang (changfc@cc.nctu.edu.tw).

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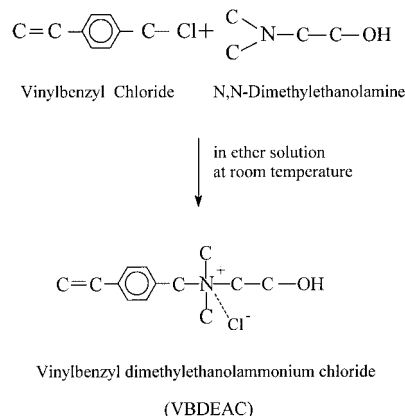
pared intercalated polystyrene-clay nanocomposites using acetonitrile solvent in which the sodium ions of the MMT were ion exchanged with vinylbenzyltrimethylammonium ions, and an intercalated polystyrene-clay nanocomposite with the basal spacing of 1.72–2.45 nm was obtained. Doh and Cho¹¹ reported on the synthesis of intercalated polystyrene containing dispersed organophilic MMT that exhibited higher thermal stability relative to the pure polystyrene (PS) or the PS-pristine-MMT composite. It has also been reported that polymer-clay nanocomposites can be prepared through melt intercalation.^{12,13} As is well known, polymer chains can be intercalated into the layered silicates of the clay by either inserting an appropriate monomer and subsequent polymerization or directly inserting polymer chains from the solution or the melt.¹⁴ Blends of thermoplastic polymers with montmorillonite have been extensively studied because a small amount of well-dispersed clay in a polymer matrix can significantly improve its mechanical properties, optical properties, and magnetic behavior, particularly with nylon 6-clay hybrids.^{15–17} The incompatibility of clay layers with the organic monomer phase impedes the clay from being dispersed homogeneously in the polymer matrix, and results in poorer properties for the nanocomposites. The surfactant for nylon 6-clay hybrids should contain two reactive groups: one suitable for reaction with the polymer, and the other capable of reacting with the clay.

In the present investigation, the intercalation of cation exchanged montmorillonite using vinylbenzyl dimethylethanolammonium chloride (VBDEAC) and/or cetyl pyridium chloride (CPC) has been investigated. The objective of the present work is directed toward polystyrene in montmorillonite interlayers and the characterization of the thermal and mechanical properties of these novel organic-inorganic nanocomposites.

EXPERIMENTAL

Materials

Montmorillonite “Kunipia F” (clay) was supplied by the Kunimine Co. of Japan. This clay mineral bears exchangeable sodium ions with cation exchange capacity (CEC) of ca. 119 mEq per 100 g. Cetyl pyridium chloride (CPC), cationic surfactant, was purchased from Sigma with purity greater than 99%. The polymerizable cationic sur-



Scheme 1 The Synthetic route for VBDEAC by reacting vinylbenzyl chloride and N,N-dimethylethanamine.

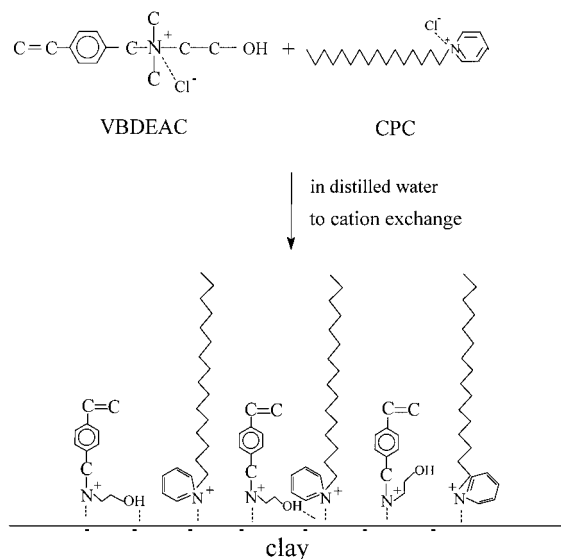
factant, vinylbenzyl dimethylethanolammonium chloride (VBDEAC), was prepared by the reaction of vinylbenzyl chloride with 2-dimethylethanamine in ether solvent for 24 h at room temperature. The precipitate was filtered, washed with ether, freeze dried, and kept in a vacuum oven at room temperature for 24 h. The synthetic route for VBDEAC is shown in Scheme 1.

Preparation of Organophilic Clay Mineral

The mixture of 1g sodium montmorillonite, 0.39 g CPC, or 0.28 g VBDEAC, and 50 mL distilled water was placed in a 100-mL beaker, which gives equivalent ratios of clay : CPC or clay : VBDEAC = 1 : 1. The structure of this organically modified clay, denoted as “clay-(VBDEAC/CPC),” is presented in Scheme 2, where the ratio of VBDEAC/CPC is 10/0, 7/3, 5/5, 3/7, or 0/10 by equal cation exchange capacity with the clay : surfactant = 1 : 1. The mixture was stirred vigorously for 8 h, and then filtered, washed, freeze dried, and kept in a vacuum oven at room temperature for 24 h.

Preparation of Polystyrene/montmorillonite Hybrids

The clay or the clay-(VBDEAC/CPC) was added into styrene monomer and polymerization initiated at 60°C for 48 h using benzoyl peroxide (BPO). After polymerization, the solvent was removed in a vacuum oven at 60°C for 24 h. Exfoliated polystyrene-clay nanocomposites of this study were achieved in two stages: the preparation of the intercalated clay-(VBDEAC/CPC) by a cation exchange process, and the free-radical polymerization of the styrene monomer within the



Scheme 2 The structure of organically modified clay with VBDEAC/CPC = 5/5 by cation exchange capacity.

clay-(VBDEAC/CPC) interlayers to yield PS/clay nanocomposites as shown in Scheme 3.

Characterization

Infrared Spectra

Infrared spectra were obtained at a resolution of 1.0 cm^{-1} with a FTIR (Nicolet AVATAR 320 FTIR spectrometer, USA) at 30°C ranging from $4000\text{--}400\text{ cm}^{-1}$. The frequency scale was internally calibrated using a He-Ne laser and 32 scans were single-averaged to reduce the noise.

X-ray Diffraction

X-ray diffraction spectra were collected on a X-ray diffraction instrument (M18XHF-SRA., MacScience Co., Japan) using $\text{CoK}\alpha$ radiation. The basal spacing or d_{001} -spacing of the samples were calculated using the Bragg's equation ($\lambda = 2d\sin\theta$).

Transmission Electron Microscope (TEM)

TEM micrographs were taken from a microtomed section of PS/clay hybrids of 60–100-nm thickness mounted in epoxy using a TEM (JEM-2000FX, JOEL Co., Japan) with an acceleration voltage of 100 kV.

Thermal Properties

Thermal properties of the hybrid were measured by differential scanning calorimetry (DSC) with

an average weight of 5–10 mg on a DSC instrument model DSC 910s from TA Co. of USA. The sample was heated in nitrogen flow to 200°C for 5 min at a scanning rate of $10^\circ\text{C}/\text{min}$ and then cooled to room temperature; heating was repeated with the same heating rate. The glass transition temperature (T_g) of the PS was based on the second scanning. Thermal gravimetric analysis (TGA) was carried out using a Seiko SSC-5200 Thermogravimetric Analyzer from Seiko Co., Japan. Samples of about 10 mg mass were heated to 500°C using a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen flow.

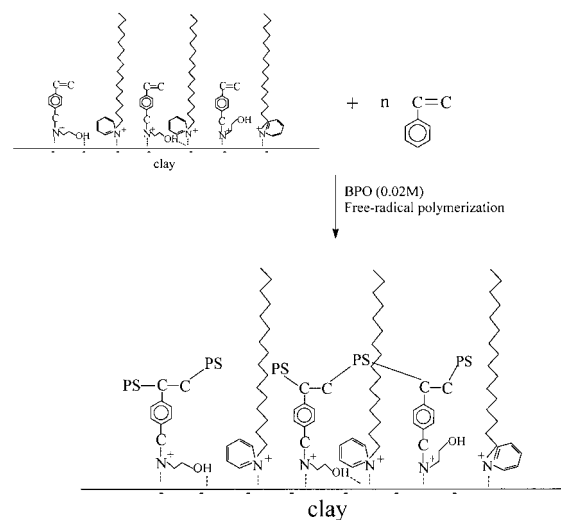
Mechanical Properties

Flexural properties were performed according to the ASTM D790 standard method using an Instron Universal Testing Machine Model 4201 with the pressdown rate of 1.2 mm/min. Notched Izod impact strength was measured on a pendulum-type hammer TMI43-1 from the TMI Co. of USA according to the ASTM D256 method at room temperature.

RESULTS AND DISCUSSION

Structure of the VBDEAC

Evidence of the VBDEAC structure was verified by FTIR analysis. Figure 1 illustrates IR spectra of the vinylbenzyl chloride, 2-dimethylethano-



Scheme 3 Free-radical polymerization of styrene in the present of clay-[VBDEAC/CPC] intercalate to yield PS/clay nanocomposite.

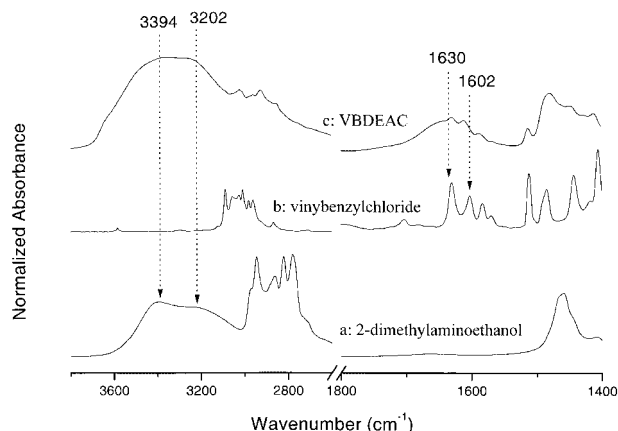


Figure 1 IR spectra ranging from 3800 to 1400 cm^{-1} of (a) 2-dimethylethanolamine; (b) vinylbenzyl chloride; and (c) VBDEAC.

amine, and VBDEAC where both characteristic absorptions of vinylbenzyl chloride and 2-dimethylethanolamine can be found. The appearance of 3202 and 3394 cm^{-1} peaks ($-\text{OH}$ stretching) in Figure 1(a) and (c) is due to characteristic frequencies of the 2-dimethylethanolamine. The 1400–1600 cm^{-1} absorbance is characteristic of the C–H stretching of vinylbenzyl chloride and 2-dimethylethanolamine as shown in Figure 1(a) and (b). The characteristic bands of the aromatic ring, contributed by styrene units, are observed at 1630 and 1602 cm^{-1} [Fig. 1(b) and (c)]. Evidence of these characteristic absorption bands being found suggests that the VBDEAC was successfully prepared by the reaction of vinylbenzyl chloride with 2-dimethylethanolamine.

Dispersibility of Clay in PS/Clay Nanocomposites

The structure of MMT consists of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge-shared octahedral sheet of aluminum hydroxide. Stacking of the layers of clay particles is held by weak dipolar or van der Waals forces.¹⁸ Figure 2 shows the X-ray diffraction patterns of the original clay and clay-(VBDEAC/CPC) with different VBDEAC/CPC ratios. The original clay contains the basal reflection that is characteristic of the unintercalated repeat distance at $d = 1.2$ nm ($2\theta = 7.1^\circ$) as shown in Figure 2(a). The basal spacing of the intercalated clay-VBDEAC was determined to be 1.56 nm [Fig. 2(b)]. Because the basal spacing of the clay without any adsorbed cation is 1.2 nm, the VBDEAC surfactant layer thickness in the interlay-

ers of the clay would account for 0.36 nm. This result indicates that the VBDEAC is indeed intercalated into interlayers of the clay. Two peaks can be seen in the clay-(VBDEAC/CPC = 5/5) with $d = 1.61$ and 2.06 nm, as shown in Figure 2(d), corresponding to the intercalation of the clay-VBDEAC [Fig. 2(b)] and the clay-CPC [Fig. 2(f)], respectively. The reflection shifts progressively toward a lower angle with increasing CPC content in the clay-(VBDEAC/CPC).^{7,8} The basal spacing of clay-(VBDEAC/CPC = 3/7) is 2.17 nm [Fig. 2(e)], and the corresponding thickness contribution of the VBDEAC/CPC = 3/7 surfactant mixture layer in the interlayers of the clay is about 0.97 nm, which is identical to that of the clay-CPC [Fig. 2(f)].

The use of the VBDEAC/CPC surfactant mixture to promote basal spacing of clay interlayers is primarily due to the exchange with the interlayer cations. The intercalation is considered as the result of a balance between the interlayer cohesive force and the attractive force required to increase the interlayer distance. The VBDEAC/

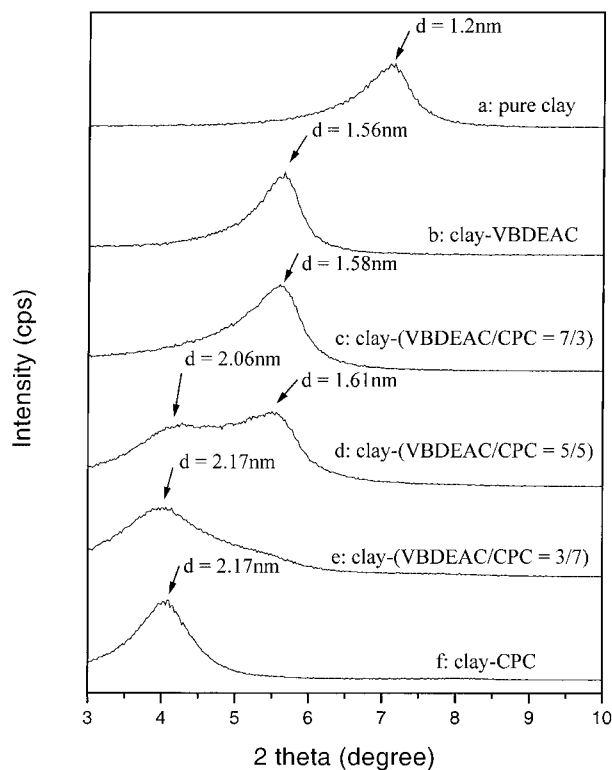


Figure 2 X-ray diffraction patterns ranging from $2\theta = 3$ to 10° for (a) pure clay; (b) clay-VBDEAC; (c) clay-(VBDEAC/CPC = 7/3); (d) clay-(VBDEAC/CPC = 5/5); (e) clay-(VBDEAC/CPC = 3/7); and (f) clay-CPC.

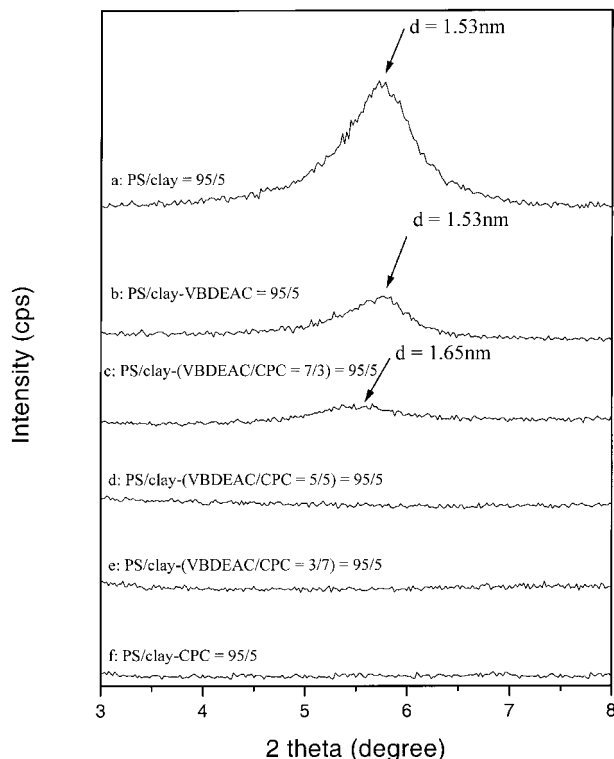


Figure 3 X-ray diffraction patterns ranging from $2\theta = 3$ to 8° for (a) PS/clay = 95/5; (b) PS/clay-VBDEAC = 95/5; (c) PS/clay-(VBDEAC/CPC = 7/3) = 95/5; (d) PS/clay-(VBDEAC/CPC = 5/5) = 95/5; (e) PS/clay-(VBDEAC/CPC = 3/7) = 95/5; and (f) PS/clay-CPC = 95/5.

CPC accommodates the intercalated clay by the organic cation, and renders the hydrophobic silicate surface organophilic. After cation exchange by a surfactant, the resultant clay surface becomes hydrophobic. This organoclay formed can be dispersed more easily in the organic media, and subsequent polymerization is used for the preparation of PS/clay nanocomposites. Further evidence of clay dispersibility in the PS matrix can also be obtained from X-ray diffraction patterns. Figure 3 presents X-ray diffraction patterns for PS/clay-(VBDEAC/CPC) = 95/5 hybrids with various VBDEAC/CPC ratios ranging from $2\theta = 3$ – 8° . The X-ray diffraction pattern of the PS/clay = 95/5 hybrid with untreated clay has the distance of $d = 1.53$ nm [Fig. 3(a)], which is close to the PS/clay-VBDEAC hybrid [Fig. 3(b)]. This result indicates that VBDEAC chains alone cannot intercalate into the clay layers to effectively promote the insertion of styrene monomers.¹⁴ The distance of the VBDEAC-treated silicate layer is not long enough to be intercalated by the styrene monomer. The basal space of the clay interlayer

increases progressively with the increase of the CPC content in the PS/clay-(VBDEAC/CPC) nanocomposite. No apparent peak can be observed in the measured range for composites of clay-(VBDEAC/CPC = 5/5, 3/7 and 0/10), as shown in Figure 3(d)–(f), an indication of severe clay exfoliation in the polystyrene matrix. Results from Figure 3(d)–(f) strongly suggest that the clay appears to be delaminated and dispersed completely within the PS matrix after polymerization when the clay is pretreated with a suitable VBDEAC/CPC surfactant mixture.

During the cationic exchange process, the intercalated CPC space facilitates diffusion of styrene molecules between the clay-(VBDEAC/CPC = 5/5 and 3/7) layers prior to the onset of polymerization. Figure 4(a) and 4(b) present X-ray diffraction patterns for clay-(VBDEAC/CPC = 5/5 and 3/7) in the PS/clay-(VBDEAC/CPC) = 95/5 ranging from $2\theta = 0.5$ – 2.5° . The X-ray diffraction pattern of the PS/clay-(VBDEAC/CPC = 3/7 and 5/5) nanocomposites have the distance of $d = 9.6$ and 17.6 nm [Fig. 4(b) and (a)]. Although the basal spacing of clay-(VBDEAC/CPC

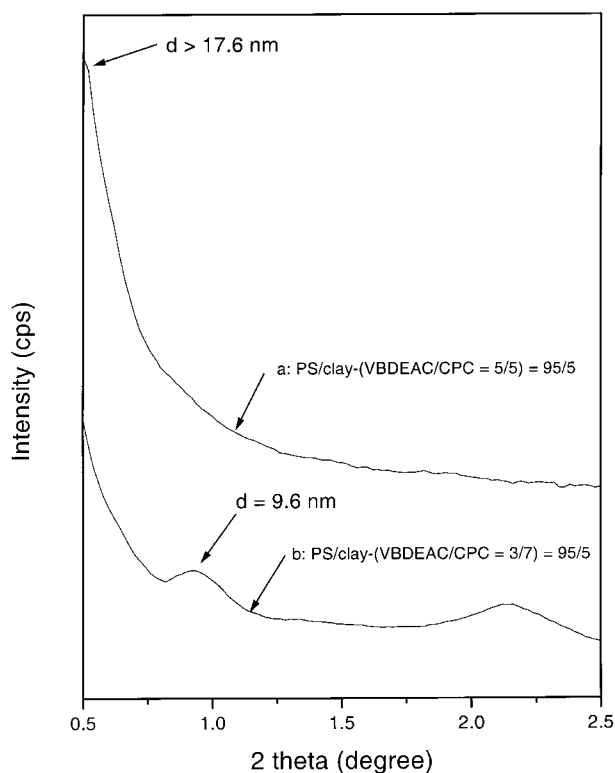


Figure 4 X-ray diffraction patterns ranging from $2\theta = 0.5$ to 2.5° for (a) PS/clay-(VBDEAC/CPC = 5/5) = 95/5; and (b) PS/clay-(VBDEAC/CPC = 3/7) = 95/5.

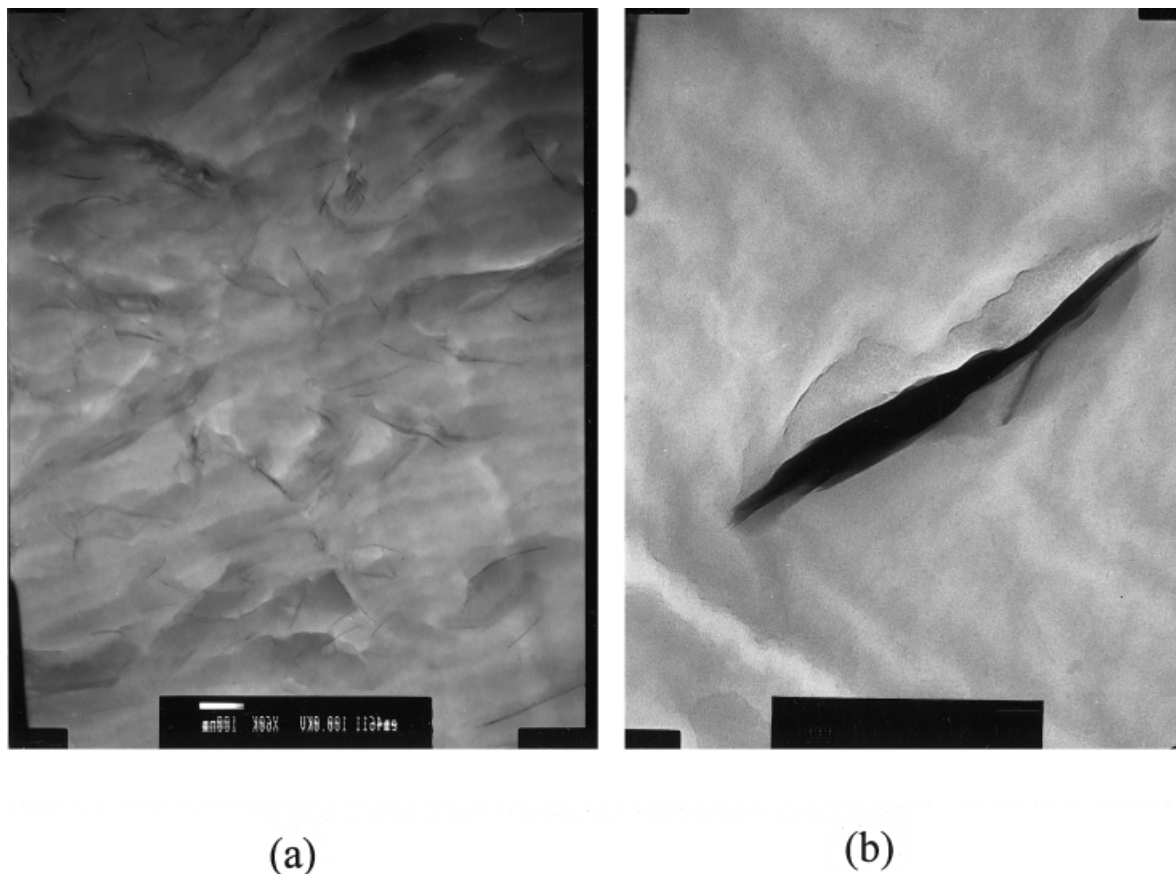


Figure 5 TEM micrographs for (a) PS/clay-(VBDEAC/CPC = 5/5) = 95/5; and (b) PS/clay = 95/5 hybrid obtained from free-radical polymerization.

= 5/5) is lower than that of clay-(VBDEAC/CPC = 3/7) (Fig. 2), there is better exfoliation of the clay in the polystyrene matrix from the former. This phenomenon can be interpreted the stronger interaction between the styrene and VBDEAC. The result suggests that the VBDEAC surfactant has stronger interaction and better swelling ability with styrene monomer than that of the CPC surfactant. Presumably, the polymerization of PS propagating chains in clay interlayers were swollen by the styrene molecules because of the sufficiently attractive force between the styrene and intercalated polystyrene propagating chains.

Figure 5(a) and (b) show TEM micrographs of PS/clay-(VBDEAC/CPC = 5/5) = 95/5 and PS/clay = 95/5 hybrids after free-radical polymerization, respectively. Figure 5(a) shows the clay layers (dark lines) are randomly distributed within the PS matrix. Figure 5(b) reveals that the untreated clay within the PS matrix is in the range of few tenths to 100 nm, indicating that the layers of clay are unintercalated.¹⁹ These observations correlate well with their respective XRD patterns.

Thermal Properties

To investigate the effect of VBDEAC/CPC ratios in the clay layers on molecular mobility of PS chains in terms of its T_g , DSC study for pure PS and PS/clay-(VBDEAC/CPC) hybrids has been carried out, and results are shown in Figure 6. The glass transition temperature (T_g) of the polystyrene matrix remained nearly unchanged by adding 5 wt % of the untreated clay [Fig. 6(a) and (b)]. The T_g of PS/clay-(VBDEAC/CPC) = 95/5 hybrid increases with increasing CPC content, as shown in Figure 6(c)-(f). This result indicates that the portion of intercalated PS chain segments within the silicate galleries tends to retard the segmental motion of the PS matrix and results in a T_g increase.

Figure 7 shows TGA thermograms for various PS/clay-(VBDEAC/CPC) nanocomposites. Evidently, thermal decomposition temperatures of PS/clay-(VBDEAC/CPC = 7/3, 5/5, 3/7, and 0/10) hybrids [Fig. 7(b)-(e)] shift to a level significantly higher than that of the PS/clay composite [Fig.

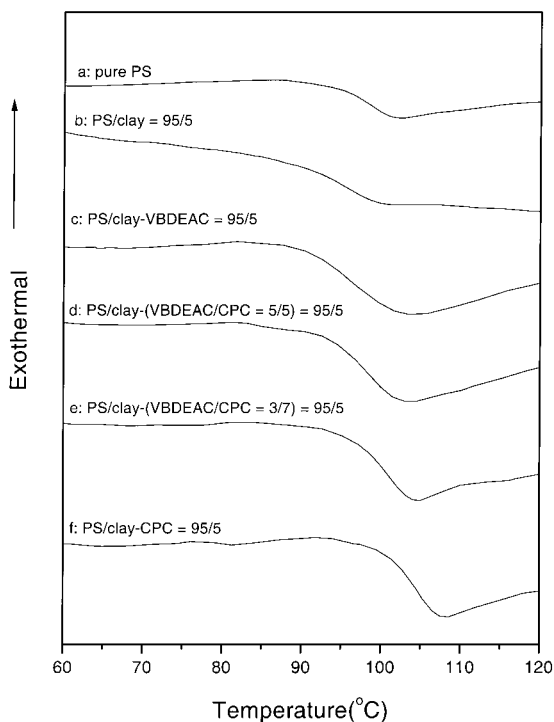


Figure 6 DSC thermogram of (a) pure PS; (b) PS/clay = 95/5; (c) PS/clay-VBDEAC = 95/5; (d) PS/clay-(VBDEAC/CPC = 5/5) = 95/5; (e) PS/clay-(VBDEAC/CPC = 3/7) = 95/5; and (f) PS/clay-CPC = 95/5.

7(a)], indicating thermal stability enhancement of the PS matrix by the intercalated PS chains and the exfoliated clay.¹¹ Results from the TGA thermograms indicate that the thermal insulation effect of the clay depends on the content of the intercalated PS chains. Incorporating CPC and VBDEAC/CPC surfactant mixture renders the surface of the clay more hydrophobic, which lowers the interfacial tension between the clay and PS molecules by adding the surfactant mixture. The exfoliated clay resists thermal degradation of these PS nanocomposites due not only to its stable structure, but also to the restriction on thermal motion of PS chains.

Mechanical Properties

Mechanical properties of pure PS, PS/clay = 95/5, and PS/clay-(VBDEAC/CPC = 5/5) = 95/5 hybrids are summarized in Table I. The hybrid with untreated clay, PS/clay = 95/5, does not give any significant improvement in flexural modulus over the pure PS. The flexural modulus of the PS/clay-(VBDEAC/CPC) hybrid increases to almost twice that of the PS or the PS/clay. This significant

enhancement in modulus can be attributed to the clay exfoliation resulting in a greater clay-matrix interfacial area, and thus effectively retards plastic deformation. The flexural strength is also improved with the addition of clay, especially for the VBDEAC/CPC pretreated clay. Similar to the trend of the flexural modulus, the enhancement of impact strength is most significant for the hybrid containing the VBDEAC/CPC pretreated clay. Better clay distribution and higher interfacial adhesion between the dispersed clay and the PS matrix by VBDEAC/CPC surfactant are responsible for the observed significant improvement in the impact strength.

CONCLUSIONS

VBDEAC, a cationic surfactant with a polymerizable group, was synthesized for the preparation of exfoliated polystyrene-clay nanocomposites. The VBDEAC surfactant was successfully prepared by the reaction of vinylbenzyl chloride with

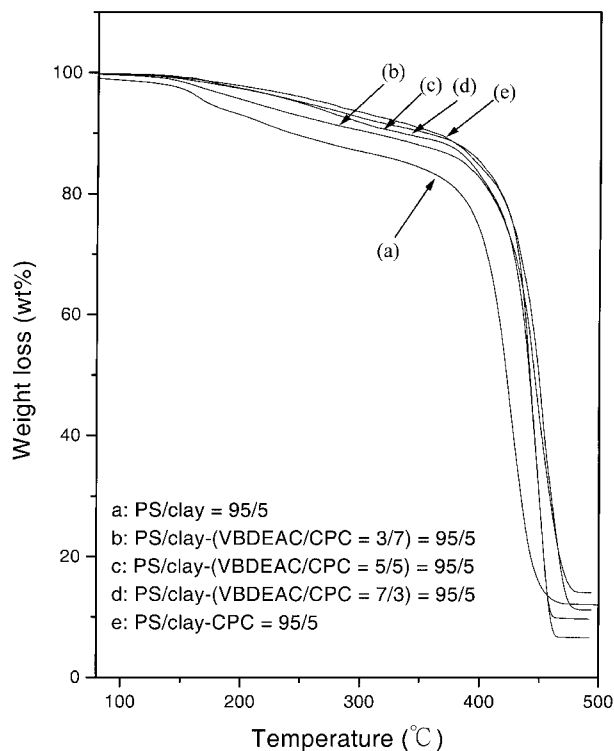


Figure 7 TGA thermogram of weight loss as a function of temperature for (a) PS/clay = 95/5; (b) PS/clay-(VBDEAC/CPC = 7/3) = 95/5; (c) PS/clay-(VBDEAC/CPC = 5/5) = 95/5; (d) PS/clay-(VBDEAC/CPC = 3/7) = 95/5; and (e) PS/clay-CPC = 95/5.

Table I Effect of the Clay-[VBDEAC/CPC] and Pure Clay on the Mechanical Properties of PS/Clay Hybrids

Composition	Clay Content (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Impact Strength (J/M)
PS	0	2.32	6.7	23.4
PS/clay	5	2.35	13.5	25.1
PS/clay - [VBDEAC/CPC = 1/1]	5	4.67	16.7	34.8

2-dimethylethanolamine. Experimental results indicated that the clay delaminated within the PS matrix when the clay was pretreated with the VBDEAC/CPC surfactant mixture. Relative to the pure PS, the PS containing exfoliated clay showed higher T_g and higher thermal degradation temperature. This finding suggests that PS segments confined within the silicate galleries of the clay tend to retard the segmental motion of the PS matrix.

The PS nanocomposite containing clay-(VB-DEAC/CPC = 5/5) significantly promotes higher flexural modulus, flexural strength, and impact strength than the pristine PS. This result further confirms that the better dispersibility and increased interfacial adhesion of the clay with PS matrix are responsible for mechanical property improvements.

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