Synthesis and Properties of Polystyrene–Montmorillonite Nanocomposites by Suspension Polymerization

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ABSTRACT: Organophilic montmorillonite was prepared using ion-exchange method between sodium ions in clay layers and stearyltrimethyl ammonium chloride in the various solvents, including deionized water, ethanol, acetone, and toluene. The montmorillonite has the largest d_{001} spacing, as determined by X-ray diffraction in toluene, than the other solvents considered. Ethanol can completely wash out the overexchanged stearyltrimethyl ammonium chloride among layers of montmorillonite. However, deionized water is the preferred ion-exchange solvent. The thermal stability of organophilic montmorillonite was investigated by high-resolution thermogravimetric analysis (TGA). Polystyrene–montmorillonite nanocomposites were obtained by suspension free radical polymerization of styrene in the dispersed organophilic montmorillonite. X-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed that montmorillonite had been exfoliated. 5.0 wt % of clay in the synthesized nanocomposite was found to be the optimum content that improved both thermal and mechanical properties over those of pure polystyrene under the experimental conditions applied. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 101–109, 2004

Key words: polystyrene; nanocomposites

INTRODUCTION

Polymer composites have been extensively used in transportation, construction, and electronics products. They provide many advantages. Importantly, they offer unusual combinations of stiffness and strength, which are difficult to obtain separately from individual components. Recently, the polymer family of nanocomposites has attracted a deepening interest of various scientists. A nanocomposite is characterized by the size of its particles, and is a dispersed phase with particles of smaller than 100 nm. Consequently, nanocompsites have relatively large surface areas and interact strongly with a polymer matrix. Therefore, the nanocomposites possess unique properties that are not typically shared by their traditional composite counterparts.

Montmorillonite is a clay mineral that consists of stacked silicate sheets whose thickness is approximately 1.00 nm. Its crystal structure is comprised of two-dimensional layers formed by fusing two silica tetrahedral sheets with an edge-shared octahedral sheet of either aluminium or magnesium.[1] Stacking these layers generates van der Waals gaps or galleries. The galleries are occupied by cations, typically sodium ions and/or calcium ions, which balance the charge deficiency, which is generated by isomorphous substitution within the layers, for example, of tetrahedral Si^{4+} by Al^{3+} or octahedral Al^{3+} by Mg^{2+}. Because these cations are not structural, they can be easily replaced by other positively charged atoms or molecules, and are called exchangeable cations.[2] In contrast to pristine layered silicate, which contains alkali metal and alkali earth change-balancing cations, organically modified layered silicates contain alkyl ammonium or phosphonium cations.[3,4] The presence of these organic modifiers in the galleries changes the originally hydrophilic silicate surface into an organophilic one. The modified layered silicates may be engineered to optimize their compatibility with a given polymer according to the functionality, packing density, and length of the organic modifiers, the modified layered silicates. Montmorillonite can be neutralized and bonded either by substitutions within the lattice or, more commonly, by cations in the layer region. The extent of substitution depends on the structure on the montmorillonite. In the tetrahedral plane, the extent of substitution may reach 15.0%; in the octahedral plane, complete substitute may occur. Typical cation exchange capacities of montmorillonite are 70–120 mEq per 100 g.[4] When organic cations are incorporated into the surface of the clay, they strongly affect the thermal behavior of the clay material.

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Several useful polymer–clay nanocomposites have been produced, such as nylon–clay hybrids,[5,6] poly-(methyl methacrylate)–clay hybrids,[7–9,18] and polypropylene–clay hybrids.[10–12] These polymer-layered silicate nanocomposites exhibit drastic improvements in mechanical and thermal properties, generally attributed to the uniform dispersion of the clay silicate layers in the polymer matrix. Several attempts have been made to prepare polystyrene–clay nanocomposites.[13–15] A common technique involves impregnating clay in styrene monomer followed by polymerization. Akelah and co-worker reported forming a polystyrene nanocomposite using acetonitrile.[13] They made clay organophilic by ion-exchange with a vinylbenzyltrimethyl ammonium chloride compound. Polystyrene–clay intercalated nanocomposites with a maximum d_{001}-spacing of 2.54 nm were obtained. Giannelis developed a new method for producing polystyrene–clay by melt intercalation.[14] Recently, Xaoan and Sted developed a new swelling agent, vinylbenzyldimethyldodecyl ammonium chloride, for intercalation clay, and then added azobis(isobutyronitrile) to initiate polymerization from the swelling agent with styrene monomer.[15] Zhu and coworker prepared the polymer–clay nanocomposite of styrene and methyl methacrylate by bulk, solution, suspension, and emulsion polymerization.[18] The exfoliated polystyrene–clay nanocomposites were obtained and exhibited mechanical properties superior to than those of pure polystyrene. Polystyrene–clay nanocomposites have a much lower peak heat release rate (PHRR) than the virgin polymer.[19]

In the present study, organophilic montmorillonite was prepared with stearyltrimethyl ammonium chloride in various different solvents, including deionized water, ethanol, acetone, and toluene. The styrene monomers were dispersed in the water phase using the dispersant poly(vinyl alcohol), and then the polystyrene–clay nanocomposites were generated by suspension polymerization between the organophilic montmorillonite silicate layers with a free radical initiator. Montmorillonite is understood to be entirely dispersed into the polystyrene matrix to achieve polystyrene–clay nanocomposites. The synthesized nanocomposites exhibit thermal and mechanical properties better than those of the pure polymer. The phase transfer was elucidate with TMA (thermal mechanical analyzer). The structure, synthesis, and properties of such composites are discussed.

EXPERIMENTAL

Material

Purified sodium montmorillonite (CEC = 95 mEq/100 g), from Southern Clay Products Inc., was used to synthesize polystyrene–clay nanocomposites. The swelling agent of stearyltrimethyl ammonium chlo-ride (SAC) was obtained from Akzo Nobel Chemical Inc. Poly(vinyl alcohol) (PVA, M_W = 77,000–79,000), benzyl peroxide (BPO), and styrene were purchased from Aldrich Co. Ltd.. All materials were used without further treatment. Toluene, acetone, and ethanol were received from Fluka Co. Ltd., and were distilled before use.

Preparing organophilic montmorillonite

Sodium montmorillonite (10.0 g) was added to 600 mL of solution of stearyltrimethyl ammonium chloride and concentrated orthophosphoric acid (0.5 mL). The mixture was stirred vigorously at 80°C for 24 h. (When acetone was used as the solvent, the reaction temperature was 30°C.) A white precipitate was isolated by filtration, and washed five times with the reaction solvent. The organophilic montmorillonite was then collected after it was dried *in vacuo* for 8 h.

Preparing polystyrene–montmorillonite nanocomposites (suspension polymerization)

The dispersion agent, PVA, (0.4 g), was dissolved in 400 mL of deionized water at 80°C, and the initiator BPO was then added. The molar ratio of BPO to styrene was 1 to 200. The organophilic montmorillonite was mixed with the styrene monomer at room temperature. The styrene solution was then added into the PVA solution and stirred. The reaction temperature was maintained at 80°C. After 8 h of suspension polymerization, the particle products were isolated by filtration and then washed with deionized water. The polystyrene–clay nanocomposites were obtained by drying *in vacuo* overnight.

Instrument

X-ray diffraction (XRD) was performed using CuK$_\alpha$ (radiation at 30 kV and 20 MA). The Fourier Transform Infrared (FTIR) spectrum of the sample was obtained using a Perkin–Elmer 1650 that cast on potassium bromide (KBr). The decomposition temperature (T_d) was measured using a TA2950 thermal gravimetric analyzer (TGA), with a heating rate of 5°C/min to 600°C in an environment of nitrogen. The dimensional change of the nanocomposites was measured using a TA2940 thermal mechanical analyzer (TMA), with a heating rate of 5°C/min to 200°C in air. The mechanical properties were determined by a TA 2980 dynamic mechanical analyzer (DMA), at 1-Hz frequency with a heating rate of 5°C/min to 200°C in air. TGA, TMA, and DMA, involved only a single analytical step, and the error of the instrument was 0.1%. The scanning electron micrograph (SEM) images of the nanocomposites were recorded using a JSM-5400LV,

TABLE I
Preparation Organophilic Montmorillonite via Different Solvents[a]

No.	solvent (600 mL)	$2\theta_{max}$ (degree)	d_{001} spacing (nm)	T_1[b] (°C)	T_2[c] (°C)	Leftover[d] (wt %)
Na-1	—	6.25	1.41	—	—	90.9
Sa-1	DI-water	4.80	1.84	164.8	312.3	74.2
Sa-2	acetone	4.95	1.78	188.8	307.6	77.0
Sa-3	ethanol	5.90	1.50	229.8	—	81.3
Sa-4	toluene	3.90	2.26	256.4	354.4	72.8

[a] Cloisite $Na^{\oplus}$ clay = 10.0 g (CEC = 95 mEq/100 g), reaction time = 24 h, reaction temperature = 80°C (acetone at 30°C).
[b] T_1 = first-onset decomposition temperature of swelling agent.
[c] T_2 = second-onset decomposition temperature of swelling agent.
[d] Leftover weight percent at 1000°C.

JEOL, at an acceleration voltage of 20 kV. The transmission electron micrograph (TEM) of nanocomposites was obtained from JEM-100LX, JEOL, at an acceleration voltage of 120 kV.

RESULTS AND DISCUSSION

Organophilic montmorillonite

A high temperature is required when polymer–clay nanocomposites are prepared using either *in situ* polymerization or melt intercalation. However, if the processing temperature at which polymer–clay nanocomposites are synthesized exceeds the thermal stability threshold of the organophilic clay, then decomposition occurs. The onset decomposition temperature of organophilic clay, therefore, is meaningful in the process of forming polymer–clay nanocomposites. Because the degradation is very sensitive to the organic interface in the layered silicate, understanding the upper processing temperature and environment of these nanocomposites is quite important. To understand how the ion-exchange environment influences the thermal stability and structure of organophilic montmorillonite, four solvents, including deionized water, acetone, ethanol, and toluene, for ion exchange with an SAC swelling agent, were used to prepare the organophilic montmorillonites, which were then examined and compared to each other.

Table I summarizes the XRD results. The distances between the silicate layer can be calculated by Bragg's law ($n\lambda = 2d\sin\theta$, d = layer distances). The wavelength (λ) of the X-ray was 1.5418 Å using CuK_α radiation. The measured d_{001}-spacing of pristine montmorillonite is 1.4 nm ($2\theta = 6.25°$). The organophilic montmorillonite exchanged using toluene as the solvent had the largest d_{001}-spacing ($2\theta = 3.9°$, d_{001} = 2.26 nm) but still exhibited pristine montmorillonite peaks at 6.25° and 7.10°. As observed from the XRD results, nonreactive sodium montmorillonite remains present in organomontmorillonite exchanged in tolu-ene, perhaps because ion-exchange cannot easily proceed between sodium cations and SAC in toluene. However, ethanol is a very good solvent, which can wash out the overexchanged organic modifier. However, the d_{001} spacing of organophilic montmorillonite only increases 0.1 nm after it is swelled by SAC in the ethanol.

Figure 1 plots the derivative thermogravimetric analysis (DTG) curves of organophilic montmorillonite prepared in the various solvents. The evolution of water from sodium montmorillonite was considered in two regions.[16] The free water and interlayer water evolution region is in the temperature range 40–300°C, and the structural water evolution region is in the temperature range 500–1000°C, wherein the bonded OH group undergoes dehydroxylation. However, the DTG curve of organically modified montmorillonites in Figure 1 is more conveniently considered pass through four regions under the experimental conditions used in this study. The free water region is below 200°C. The region in which organic substances evolve ranges from 200 to 500°C. The structural water region is in the temperature range from 500 to 800°C. Organic carbon reacts in some yet unknown way between 800 and 1000°C. The release of organic species from organophilic montmorillonite is a two-step process, due to difference between the occurrence of the organic modifier, the overexchanged organic modifiers and the bonded organic modifiers of between the clay layers. As indicated by the DTG curve for the organic-modified montmorillonite samples (Fig. 1), before the first DTG peak, the derivative weight loss was flat (in a steady state). Accordingly, the temperature at which the derivative weight loss was 0.001%/°C more than the value at the plateau was considered to be the first onset of decomposition temperature (T_1). The temperature at which the derivative weight loss between the first and second weight loss peaks was lowest was considered to be the second onset decomposition temperature (T_2). Table I sum-
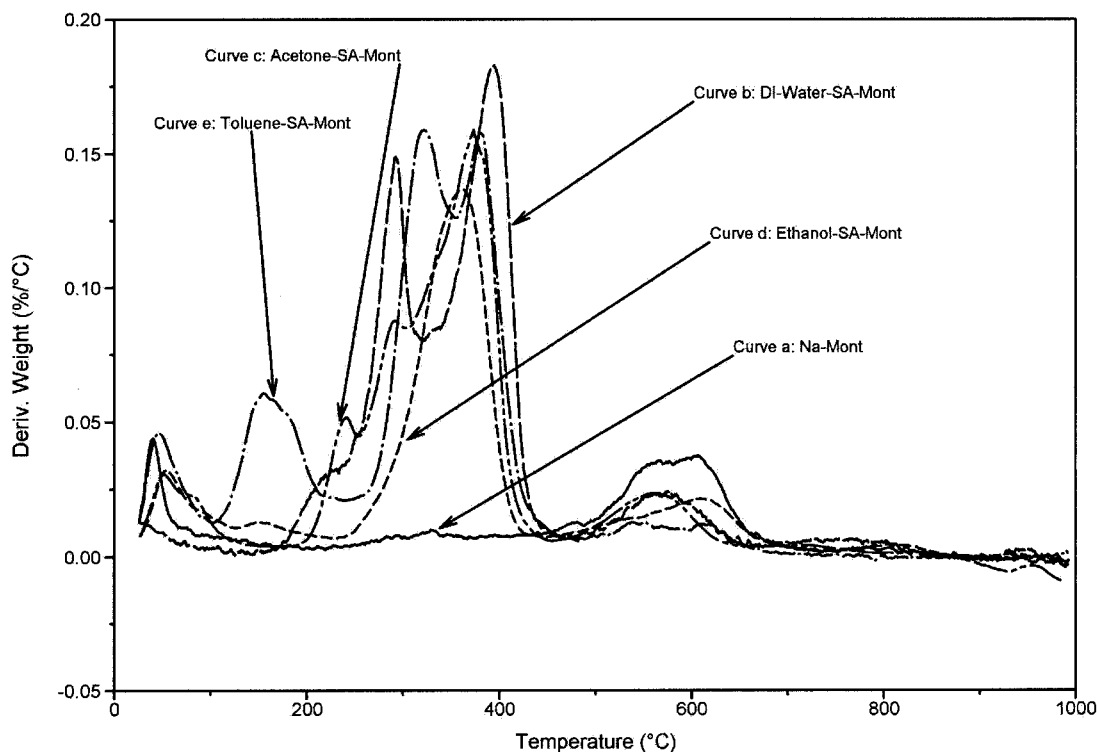
Figure 1 The DTG curves of (a) sodium montmorillonite and organophilic montmorillonite by using different solvents of (b) deions water, (c) acetone, (d) ethanol, and (e) toluene.

marizes the results. For the organophilic montmorillonite prepared in the deionized water, the first onset decomposition temperature was 164°C, similar to that of the swelling agent SAC. For the organophilic montmorillonite prepared in toluene, approximately 5% weight is lost in the temperature range from 110 to 210°C. The aromatic solvent toluene is believed to penetrate the clay layer and remain there even after drying. Organophilic montmorillonite prepared in toluene had the highest T_1 and T_2 ($T_1 = 256.4$°C, $T_2 = 354.4$°C), perhaps because the organic modifier can completely enter the clay layers, generating less overexchanged organic modifier. When ethanol is used as the solvent, only one organic decomposition peak is observed between 200 to 400°C, because all the overexchanged organic modifiers were dissolved and washed out by ethanol. Consequently, only bonded organic modifiers are present in the organophilic montmorillonite. The decomposition mechanism of organic modified montmorillonite has been discussed elsewhere.[17]

Zhu and coworker[19] published TGA/FTIR studies. The XRD results shown in Figure 2. After heating to 300°C for 1 h, the d_{001} spacing of sample Sa-1 declined to 1.4 nm (from curve a to curve b); and after heat treatment at 500°C, all the organic modifiers were decomposed and the layer distances restored to those of pristine sodium montmorillonite (curve c).
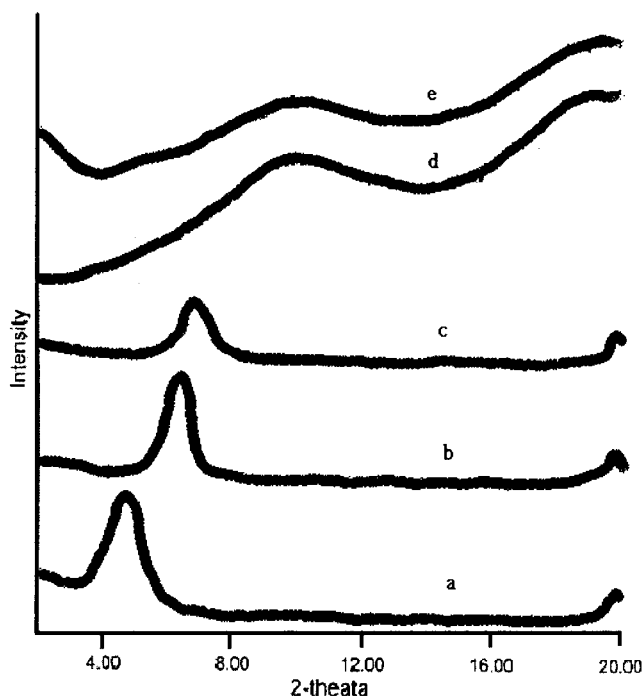

Figure 2 The XRD curves of (a) organophilic montmorillonite [by SAC], (b) organophilic montmorillonite heat to 300°C, (c) organophilic montmorillonite heat to 500°C, (d) polystyrene, and (e) polystyrene–montmorillonite nanocomposite.
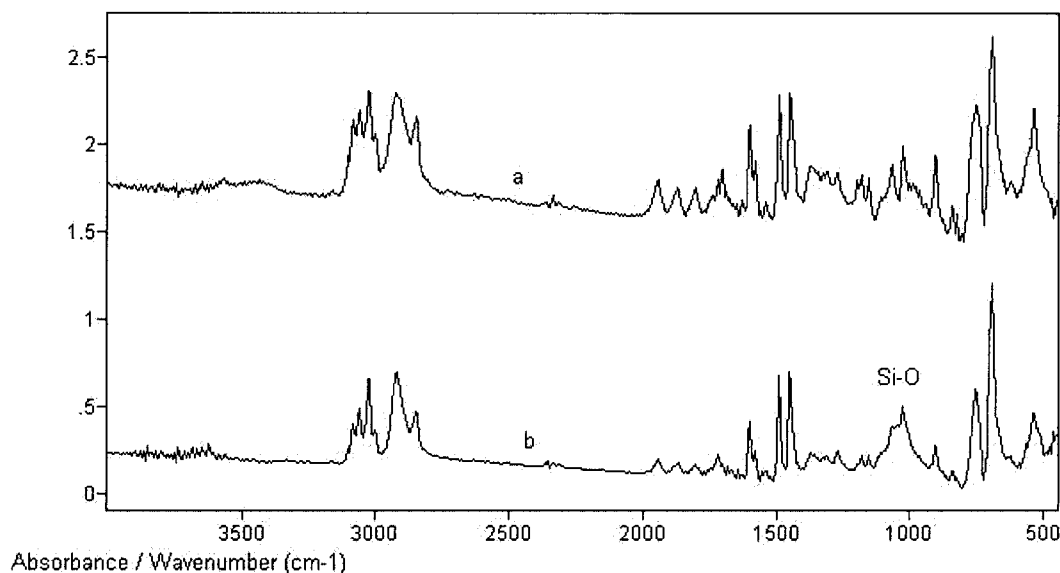
Figure 3 The FTIR spectrum of (a) polystyrene, and (b) polystyrene–montmorillonite nanocomposite.

The d_{001} spacing of the organophilic montmorillonite is a rather important factor in the following polymer–clay synthesis process, and a larger d_{001} is preferred for the polymerization. Deionized water was used as the solvent in preparing organophilic montmorillonite in the following synthesis step, because it has a relatively high d_{001}. Although the organophilic montmorillonite prepared in toluene yielded the largest d_{001} spacing obtained using any solvent examined, the very early decomposition peak at 100°C, which suggests some uncertainty in the synthesized composite products, implies that deionized water actually was a safer choice for the present study.

clay peak, implying that polystyrene is present in silicate sheets for the PS–Mont nanocomposite.

Table II lists the results for PS–Mont nanocomposites that contain various amounts of organophilic montmorillonite. When montmorillonite was added in styrene polymerization, both the yield and activity increased. However, after the organophilic montmorillonite contents were increased to 2.0 g, the products became gel-like, and the yield and activity clearly declined because montmorillonite has a chain transfer termination effect in the formation of the PS chain. The montmorillonite layers restrict the propagation of the PS chains and the molecular weight declines. The

Polystyrene–montmorillonite nanocomposites

Suspension polymerization was used to synthesize polystyrene–montmorillonite (PS–Mont) nanocomposite. The PVA is a dispersion agent that can surround styrene, BPO, and organophilic montmorillonite in deionized water. Polymerization proceeded within the PVA vacuole, and the PS–clay nanocomposite is the pearl-shape product. Figure 3 displays the FTIR spectra of structures of both pure PS (curve a) and PS–Mont nanocomposite (curve b) prepared by suspension polymerization. The absorption bands from 3200 to 3000 cm^{-1} are associated with unsaturated C—H vibration in the phenyl ring of PS and the out-of-plane vibration modes of the phenyl ring are 760, 700, and 542 cm^{-1}. The PS–clay retains O—H and Si—O vibrations at 3650 and 1030 cm^{-1}. Figure 2 presents the XRD pattern of PS—Mont nanocomposite (curves c and d). PS–Mont nanocomposite yields no

TABLE II
Preparation Polystyrene Nanocomposite via Different Amounts of Montmorillonite[a]

No.	Mont.[b] [SA-1(g)]	Yield[c] (%)	act.[d] ($\times 10^3$)	Mont.[e] (wt %)	T_d[f] (°C)
PS-1	—	82.7	2.15	—	402.7
PSC-1	0.5	92.5	2.46	2.5	418.3
PSC-2	1.0	89.0	2.42	5.2	422.2
PSC-3	1.5	89.0	2.48	7.5	423.5
PSC-4	2.0	78.8	2.24	11.1	416.4

[a] DI-water = 400 mL, PVA = 0.4 g, styrene = 0.2 mol, BPO = 1.0 mmol, reaction temperature = 80°C, reaction time = 8 h.
[b] The amount of organophilic montmorillonite in the reaction.
[c] Yield% = (g product)/(g styrene + g clay).
[d] Activity = (g product)/(mol BPO × h).
[e] Montmorillonite contents = (g clay)/(g product).
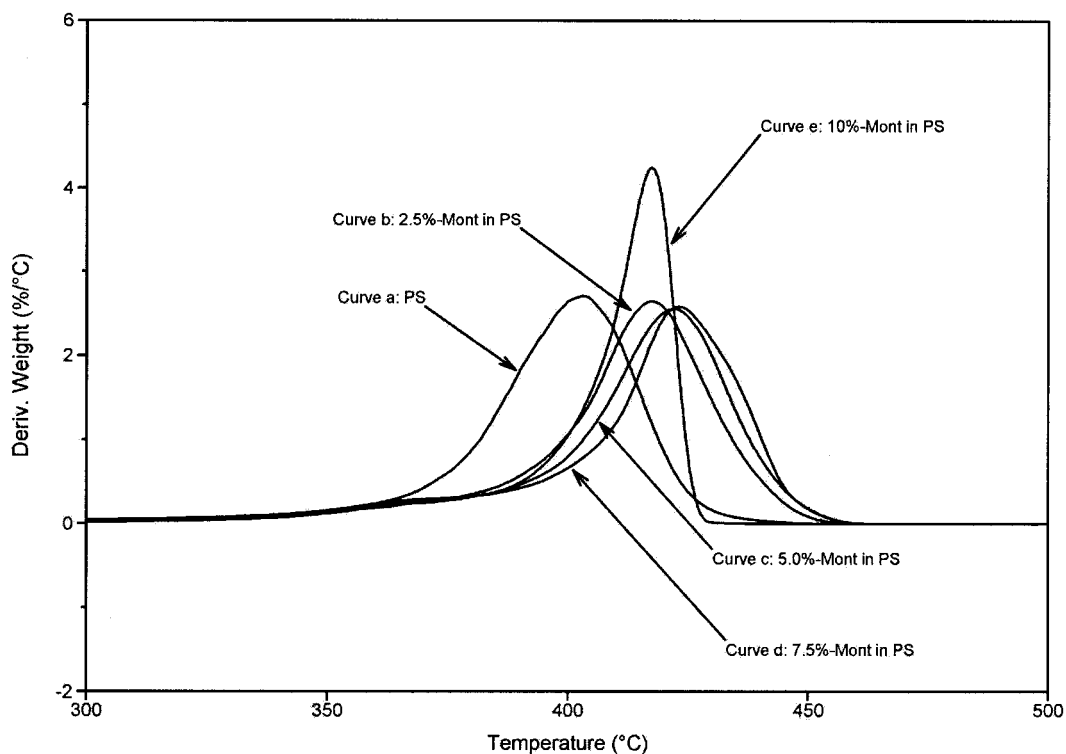[f] T_d = maximum decomposition temperature in the HDTG curve.

Figure 4 The DTG curves of (a) polystyrene and polystyrene–montmorillonite nanocomposite with different clay contents (b) 2.5wt %, (c) 5.0 wt %, (d) 7.5 wt %, and (e) 10.0 wt %.
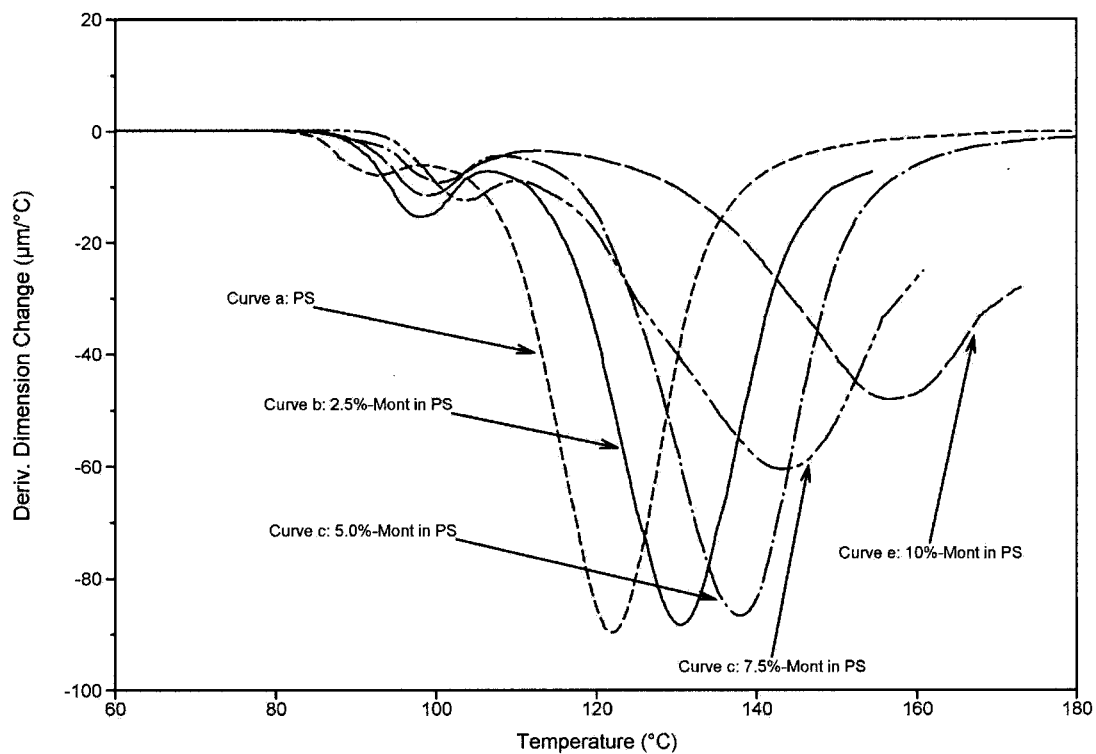

Figure 5 The TMA curves of (a) polystyrene and polystyrene–montmorillonite nanocomposite with different clay contents (b) 2.5 wt %, (c) 5.0 wt %, (d) 7.5 wt %, and (e) 10.0 wt %.
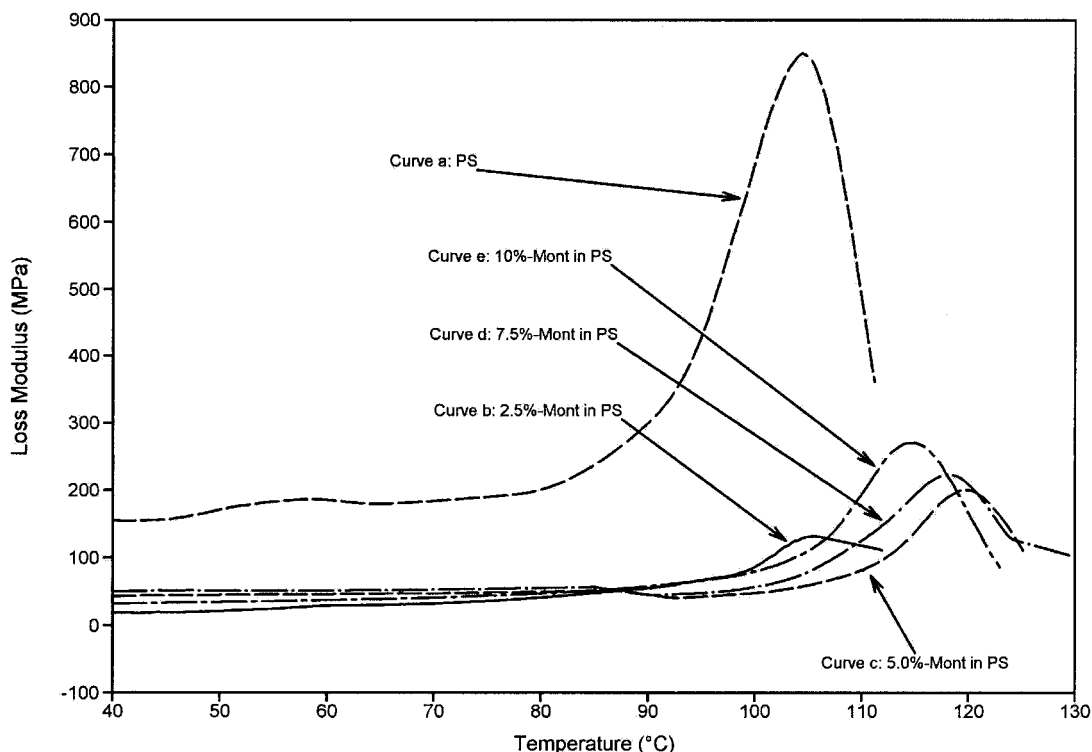
Figure 6 The loss modulus curves of (a) polystyrene and polystyrene–montmorillonite nanocomposite with different clay contents (b) 2.5 wt %, (c) 5.0 wt %, (d) 7.5 wt %, (e) 10.0 wt %.

grams of clay output in column 5 exceed the grams of clay input in column 2. Figure 4 displays DTG curves of PS and PS–Mont nanocomposites. The PS–Mont has a higher maximum decomposition temperature peak than that of PS. A higher clay content in the nanocomposite corresponds to a higher decomposition temperature of the nanocomposite. Again, the decomposition temperature of the nanocomposite with 7.5 wt % montmorillonite (curve e) was lower than those of the 2.5wt % (curve b) and 5.0 wt % montmorillonite (curve c), implying that 5.0 wt % montmorillonite is the maximum proportion content in the nanocomposite for improving thermal stability. TMA results shown in Figure 5 also verify the above observation. The dimensions changed because of phase transfer, which in the nanocomposite depends on the organophilic montmorillonite content. As the content of organophilic montmorillonite in the PS–Mont nanocomposites increased, the temperature of dimensional change also clearly increased, from 121°C for the homopolymer (curve a) to 130°C for the nanocomposite with 2.5 wt % organophilic montmorillonite (curve b), 139°C for the nanocomposite with 5.0 wt % organophilic montmorillonite (curve c), 145°C for the nanocomposite with 7.5 wt % organophilic montmorillonite (curve d), and 158°C for the nanocomposite with 10.0 wt % organophilic montmorillonite (curve e). The dispersion of silicate sheets in the PS matrix can increase the yielding tem-

perature, causing the dimensional change to require more heat energy. The results show that the thermal stability of PS–Mont nanocomposites exceeds that of PS homopolymer.

The mechanical properties of the synthesized nanocomposites were examined by dynamic mechanical analysis. Figure 6 shows the loss modulus results of polystyrene and various PS–Mont nanocomposites. The loss modulus of nanocomposites is much higher

Magification=66000 (0.66mm=10nm)

Figure 7 The TEM photograph of polystyrene–montmorillonite nanocomposite [clay contents = 5 wt %].
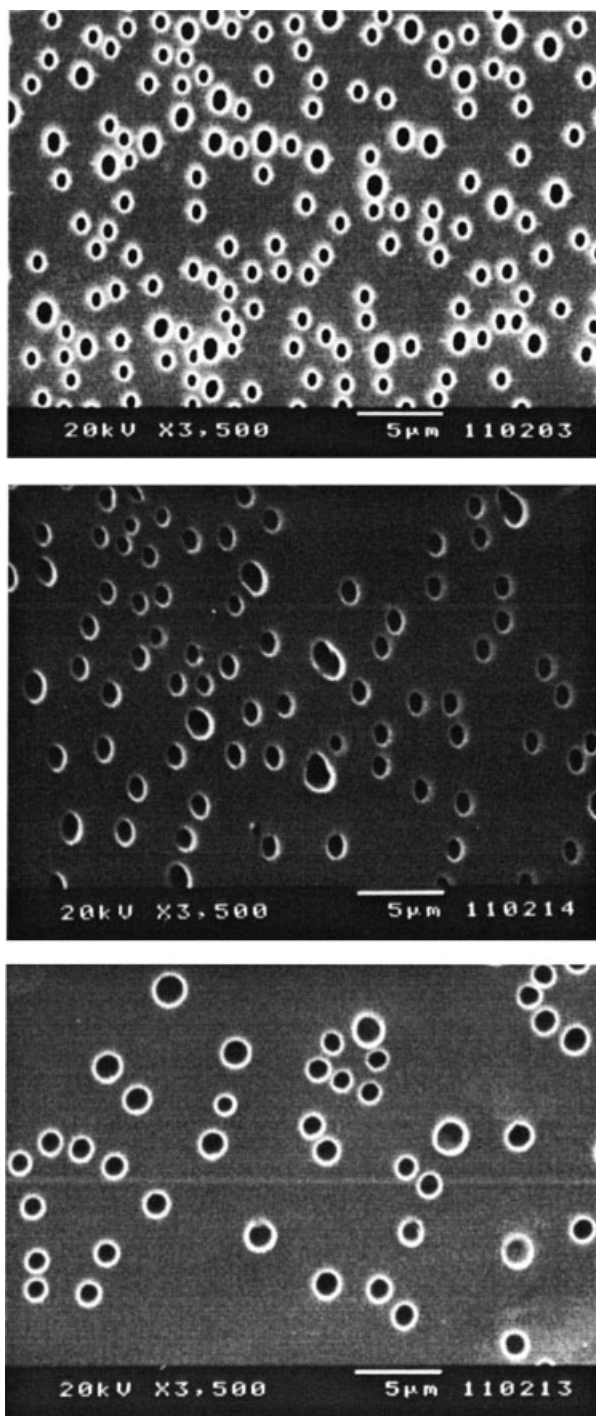
Figure 8 The SEM photographs of (a) polystyrene, (b) polystyrene–montmorillonite nanocomposite [clay content = 2.5 wt %], and (c) polystyrene–montmorillonite nanocomposite [clay content = 5.0 wt %] treatment with THF.

than that of pure PS (curve a). When the organophilic clay amount was 5.0 wt % (curve c), a maximum loss modulus peak was observed at 119°C, due to the phase transition in the PS material. The loss modulus of nanocomposites declines slightly as clay loading

increases beyond 5.0 wt %, perhaps because the organophilic montmorillonite dispersion in the PS affects the diffusion of the initiator molecules and the silicate sheets block chain propagation during polymerization.

Figure 7 shows a TEM picture of PS–Mont nanocomposite that contains 5.0 wt % organophilic clay. The dark lines are the intersections of the silicate sheets. The silicate sheets of clay are homogenously dispersed in the polystyrene matrix because of swelling by the organic modifier that further undergoes exfoliation during suspension polymerization. PS–Mont nanocomposites also have been proven to exhibit excellent barrier properties. The lump samples of PS–Mont were immersed into THF solvent for 2 min and then the surface of each sample was examined by SEM. The SEM pictures [Figs. 8(a)–(c)] indicate that the PS–Mont nanocomposites are much more effectively prevent the THF solvent from penetrating into matrix than PS. The holes are caused by THF penetration, and the PS–Mont [Figs. 8(b) and (c)] had fewer holes than the pure polystyrene [Fig. 8(a)]. The number of holes in the PS–Mont surface decreased as the clay content increased. The silicate sheets of clay provide a good solvent barrier that increases the application of such polymers in electronic and packing materials.

CONCLUSIONS

The solvent affects the synthesis of organophilic montmorillonite with SAC. Toluene can provide fine dispersion of the montmorillonite, and ethanol can wash the overexchanged organic modifiers. However, these solvents have impurities and low d_{001} spacing problems. Deionized water is preferred in the ion-exchange process. Polystyrene–montmorillonite nanocomposites were synthesized by suspension polymerization. XRD, TEM, and SEM results showed the polystyrene was exfoliated into the silicate layers, and was finely dispersion in the polystyrene matrix. The preliminary results indicated that the polystyrene nanocomposites were more thermally stable and had better mechanical properties than pure polystyrene material. The optimum organophilic montmorillonite content that yields the best improvement in both thermal stability and mechanical properties of a nanocomposite is 5.0 wt % under the experimental conditions applied herein.

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