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Enhanced thermal properties of PS nanocomposites formed from montmorillonite treated with a surfactant/cyclodextrin inclusion complex

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Abstract

We have prepared polystyrene/clay nanocomposites using an emulsion polymerization technique. The nanocomposites were exfoliated at 3 wt% content of pristine clay relative to the amount of polystyrene (PS). We employed two surfactants for the montmorillonite: cetylpyridinium chloride (CPC) and the CPC/α-CD inclusion complex. Prior to polymerization, each surfactant intercalates into the layers of the pristine clay dispersed in water. The inclusion complex was characterized by X-ray diffraction, ^{13}C CP/MAS NMR spectra, and ^{1}H NMR spectroscopy, and TGA. X-ray powder patterns of the CPC/α-CD complex indicate that the α-CDs units form channels. The ^{13}C CP/MAS NMR spectrum of the complex suggests that a CPC chain is included in the channel formed by the α-CDs. The ^{1}H NMR spectra of the complexes indicate that the stoichiometry of the complexes is 1:2 (i.e. one CPC molecule and two α-CD units). The TGA reveals that the inclusion complex has higher thermal stability relative to the virgin CPC. We employed both X-ray diffraction (XRD) and transmission electron microscopy (TEM) to characterize the structures of the nanocomposites. The value of T_g of the PS component in the nanocomposite is 6 °C higher than that of the virgin PS and its thermal decomposition temperature is 33 °C higher. The CPC/α-CD-treated clay is more effective than is virgin CPC-treated clay at enhancing the thermal stability of polystyrene.

Keywords: Nanocomposite; Cyclodextrin; Montmorillonite

1. Introduction

A number of extensive investigations into the intercalation of organic alkylammonium cations into montmorillonite clay have been reported [1–3]. Most of these intercalating agents have been low-molecular-weight alkyammonium salts, amino acids, and diamine salts [4–6]. Typically, intercalation results in a widening of the clay basal spacing to within the range 19–40 Å, which correlates linearly with the molecular size of the intercalating agent [3,4,7]. These intercalated smectic clays may be exfoliated by using a polymer to form nanocomposites [8]. Nanocomposites offer the prospect of vastly improved properties relative to their mother polymers. There have been reports that suggest that nanoclay-filled polymeric systems display significant improvements in their tensile and thermal properties [9–17], heat distortion temperatures [9–14], resistance to flammability [20], reduced permeability to small molecules [13,18,19], and reduced solvent uptake [21]. 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.

To date, cyclodextrins (CDs) have never been reported as surfactants for intercalating in clay. CDs comprise a series of α-1,4-linked cyclic oligosaccharides consisting of six (α-CD), seven (β-CD), eight (γ-CD) or more glucose units; their shapes resemble hollow truncated cones. The cavities of CDs are hydrophobic because they contain no hydroxyl groups; thus, CDs have the ability to include hydrophobic molecules within their cavities. Since the discovery of CDs, a large number of their inclusion complexes with various low-molecular-weight compounds have been prepared and characterized [22]. In this study, we have examined whether including a surfactant within CD channels improves its thermal stability.

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In this paper, we describe the preparation of two types of nanocomposites formed from clays treated with either cetylpyridinium chloride (CPC) or the CPC/α-CD inclusion complex. The PS/clay nanocomposite formed using the CPC-treated clay exhibited no significant improvements in its thermal properties [23–27]. We found that CPC, a linear aliphatic surfactant, is able to form a crystalline complex with cyclodextrin. Including CPC within CD channels improves the thermal stability of the virgin CPC.

We prepared PS/clay nanocomposites through emulsion polymerization by suspending the surfactant-treated clay in styrene monomer. The formation of a complex between α-CD and CPC was studied quantitatively; we confirmed the stoichiometry of the inclusion complex from the ^{1}H NMR spectrum. X-ray powder patterns of the CPC/α-CD complex indicated that the guest surfactant chain resides within the channels provided by the orderly stacked α-cyclodextrin molecules. We used solid-state ^{13}C NMR spectroscopy to measure the structure of the CPC chain within its the inclusion complex with α-CD, and both X-ray diffraction (XRD) and transmission electron microscopy (TEM) to characterize the structure of the clay. The properties of these PS/clay nanocomposites were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

Most of chemicals used in this study, including monomeric styrene, 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 hydrochloric 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). α-Cyclodextrin was obtained from Tokyo Kasei Kogyo co. (Japan); pristine Na-MMT was provided by Telekal Co. (Taiwan).

2.2. Preparation of inclusion complex

CPC (5.59 mmol) in water (80 mL) was mixed at room temperature with a saturated solution of α-CD (16.8 mmol) in water (80 mL). The mixture was stirred at 70 °C for 8 h and then it was left to stand at room temperature overnight. The mixture became turbid and the complex was obtained as a white crystalline precipitate. The precipitated product was collected by centrifugation and dried in a vacuum oven at 70 °C. The complex was then washed several times with water to remove any uncomplexed α-CD and CPC. Finally, the powder was dried in a vacuum oven at 60 °C for 24 h.

2.3. Preparation of surfactant-modified clays

A suspension of pre-washed sodium montmorillonite (Na-MMT, 5 g) in distilled water (250 mL) was stirred overnight in a 500-mL, two-neck, round-bottom flask. The surfactant (CPC or CPC/α-CD inclusion complex; 2 g), which was dissolved in 10 mL of 1 N HCl solution, was then added dropwise at room temperature to the stirred aqueous solution. After stirring the mixture for 3 h, the white precipitate was filtered, washed with water until no chloride ion could be detected by an aqueous $AgNO_3$ solution, 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 CPC/α-CD inclusion complex; 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 the emulsion down completely. The polymer was washed several times with methanol and distilled water and then dried overnight in a vacuum oven at 80 °C. A similar procedure was employed to prepare the virgin polystyrene.

2.5. Instrumentations

X-ray diffraction 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 diamond knife on a Leica Ultracut UCT Microtome to give 70-nm-thick sections. The contrast between the layered silicates and the polymer phase was sufficient for imaging and, therefore, no heavy metal staining was required prior to imaging. ^{1}H NMR spectra of the complex were recorded at 500 MHz on a Varian 500 NMR Spectrometer (USA). Chemical shifts of the complex were referenced to the signal for DMSO at $\delta = 2.50$ ppm. ^{13}C CP/MAS NMR spectra were measured on a Bruker DSX400WB NMR spectrometer (Germany) using a sample spinning rate of 5.4 kHz at room temperature. The spectra were acquired using a 3.9-μs proton 90° pulse, a 3-ms contact time, and a 3-s repetition time. TGA were performed

on a TA Instruments Thermal Analyzer under a flow of nitrogen gas (40 mL/min) at a scan rate of 20 °C/min from 30 to 800 °C. A Du-Pont (DSC-9000) DSC was used to measure the glass transition temperature (T_g) of the PS/clay nanocomposites. 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.

3. Results and discussion

In this study, we focused on comparing nanocomposites prepared using two surfactant-modified clays. The CPC surfactant is an ammonium salt containing a long aliphatic chain that can be include within the cavity of α-CD to form an inclusion complex. Two surfactant, CPC and CPC/α-CD inclusion complex, are used to prepare the modified clays. Conventional surfactants, such as CPC, are thermally unstable at high temperatures. Thus, we expected that nanocomposites prepared from the CPC/α-CD surfactant would possess greater thermal stabilities relative to those formed using the conventional CPC surfactant alone.

3.1. X-ray diffraction

We employed X-ray diffraction (XRD) to characterize the layered structures of the modified clays and polymer/-clay nanocomposites. Changes in the value of 2θ reflect changes in the gallery distance of the clay. In addition, X-ray diffraction can also be used to detect whether the CPC units are included within the cavities of α-CD units. Fig. 1 shows the X-ray diffraction patterns of pure α-CD, the inclusion complex, and its intercalated clay. The most prominent peak for the CPC/α-CD inclusion complex appears at 19.7° (2θ), which indicates that the inclusion complex is indeed formed from CPC units included within the CD channels [28]. We also observe that the CPC/α-CD inclusion complex pattern is similar to that of the PEO/α-CD inclusion complex [29]. This finding provides strong evidence that the CPC/α-CD inclusion complex had a channel-type structure. Furthermore, the XRD pattern of the clay intercalated by the inclusion complex indicates a diffraction peak at 19.7°, which implies that the inclusion complex remains present in the gallery of the clay. Scheme 1 displays clay intercalated by CPC/α-CD inclusion complexes. We calculated the interlamellar distance indicated in this figure by using the following expression: $\Delta d = d$ spacing − thickness of one platelet (ca. 10 Å). In the case of the clay intercalated with the inclusion complex, the distance between two adjacent clay plates is 42.2 Å which is a value close to that expected for two layers of CPC.

Fig. 2 shows the XRD results of the surfactant-intercalated clay. The pristine clay exhibits a peak at 6.14°, which corresponds to a basal space of 1.43 nm. The insertion of the CPC surfactant between the galleries of the clay increases the d spacing from 1.43 to 2.27 nm. This result indicates that the CPC surfactant is intercalated successfully into the galleries of the clay nanoparticles. Furthermore, the d spacing of the clay intercalated clay by the inclusion complex is increased to 5.12 nm; i.e. the d spacing caused by the inclusion complex is substantially higher than that cause by CPC alone. We believe that this finding can be explained by considering that the linear aliphatic chain within the CPC/α-CD cannot bend within the galleries of the clay and, therefore, the d spacing of clay intercalated by the CPC/α-CD inclusion complex is significantly higher than that formed using pure CPC.

Fig. 3 shows the XRD patterns for polymer/clay

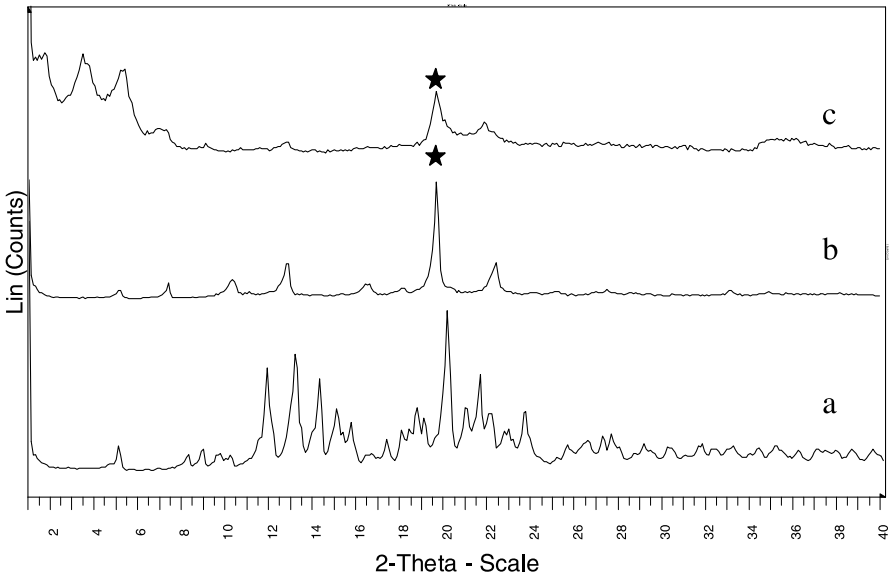
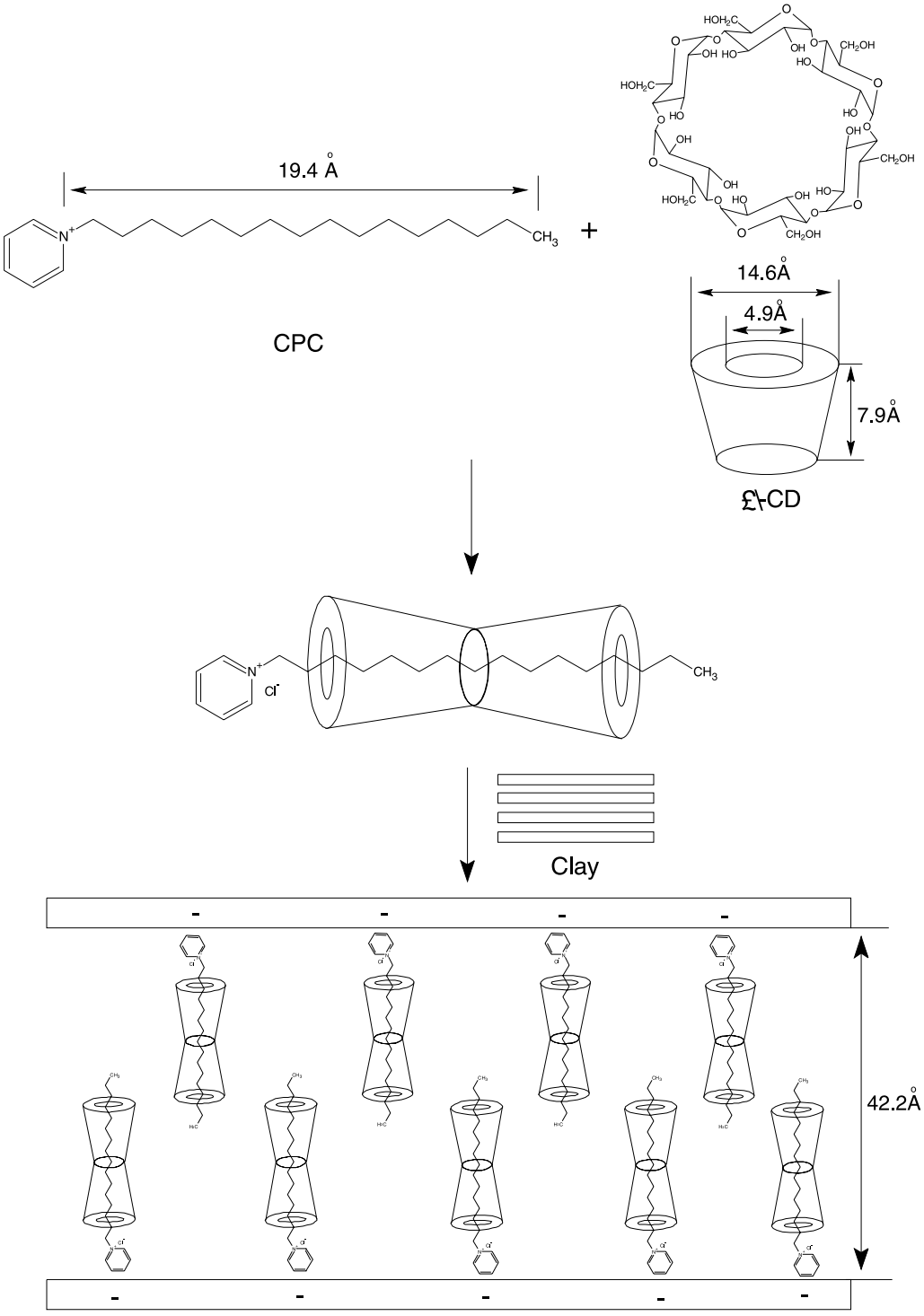


Fig. 1. X-ray diffraction patterns of (a) α-CD, (b) the CPC/α-CD inclusion complex, and (c) clay intercalated by the CPC/α-CD inclusion complex.



Scheme 1. Schematic representation of clay intercalated by the CPC/α-CD inclusion complexes.

nanocomposites. We detected no peak for the nanocomposites prepared from the CPC- and CPC/α-CD-treated clays, which implies that they all possess exfoliated structures. Because there is a limit to the angle of detection when using XRD, it is impossible to detect diffraction angle below 1°. Thus, it was still necessary to observe the true structures and distributions of the silica platelets through the use of TEM.

3.2. TEM Characterization

Figs. 4 and 5 show TEM images at two magnifications of the nanocomposites prepared from the CPC- and CPC/α-CD-treated clays. These images indicate the dispersion of the clay layers within the polymer. In Fig. 4, we observe that the clay platelets of the CPC-treated nanocomposite are

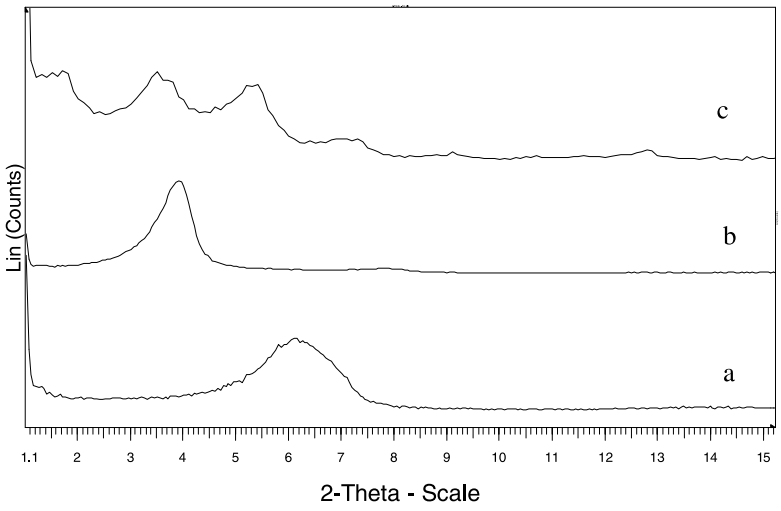


Fig. 2. X-ray diffraction patterns of (a) pure clay, (b) the CPC-intercalated clay, and (c) the CPC/α-CD intercalated clay.

mainly exfoliated, but in certain regions they are more concentrated and intercalated. Fig. 5 shows an image of the CPC/α-CD-treated nanocomposite: essentially all of the clay layers are isolated and evenly distributed within the PS matrix, which implies that a full exfoliation has occurred; this conclusion is consistent with the finding of the XRD data.

3.3. Stoichiometry of the complex

We isolated the complex by centrifugation, washed it with water to remove and uncomplexed CD and CPC, and the dried the sample in a vacuum oven at 70 °C. We used ^{1}H NMR spectroscopy to investigate the stoichiometry of this complex. Fig. 6 show the ^{1}H NMR spectrum of the inclusion complex formed between α-CD and CPC in DMSO. By comparing the value of the integrals of selected peaks of α-CD (C1H) and CPC (the ethyl group, a), we obtained an α-CD/CPC ratio of 2. The estimated length of the alkyl tail of the CPC unit is roughly equal to the length of two α-CD molecules, so the theoretically predicted result agrees well with the experimental result.

3.4. Solid state ^{13}C NMR spectroscopic analysis

Solid state ^{13}C NMR spectroscopy [e.g. ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectroscopy] provided additional information concerning the structure of the α-CD complex. Fig. 7 shows the ^{13}C CP/MAS NMR spectra of α-CD, the CPC/α-CD complex, and the clay intercalated by the inclusion complex. The resonances of the C(1) and C(4) nuclei of the pure α-CD result in multiple lines because of asymmetric

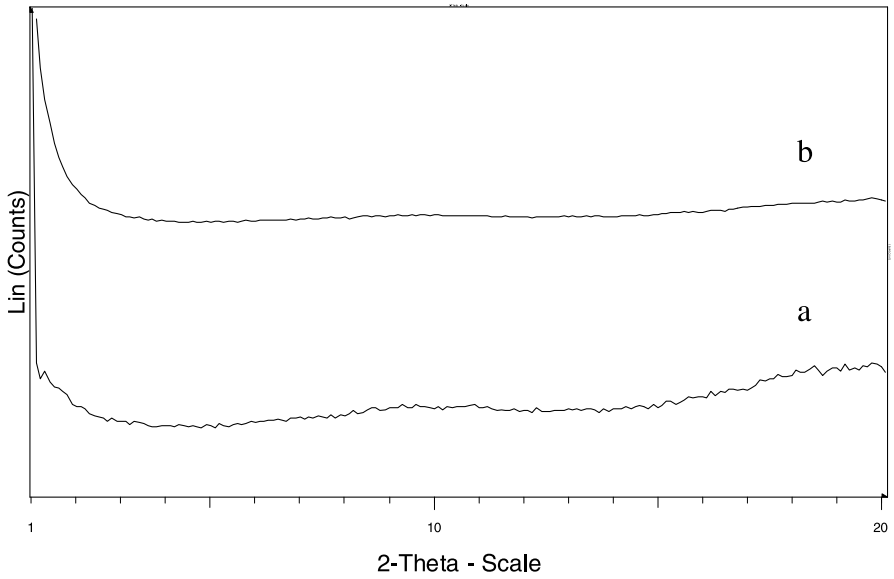


Fig. 3. WAXD analysis of PS nanocomposites prepared by emulsion polymerization: (a) CPC treatment; (b) CPC/α-CD treatment.

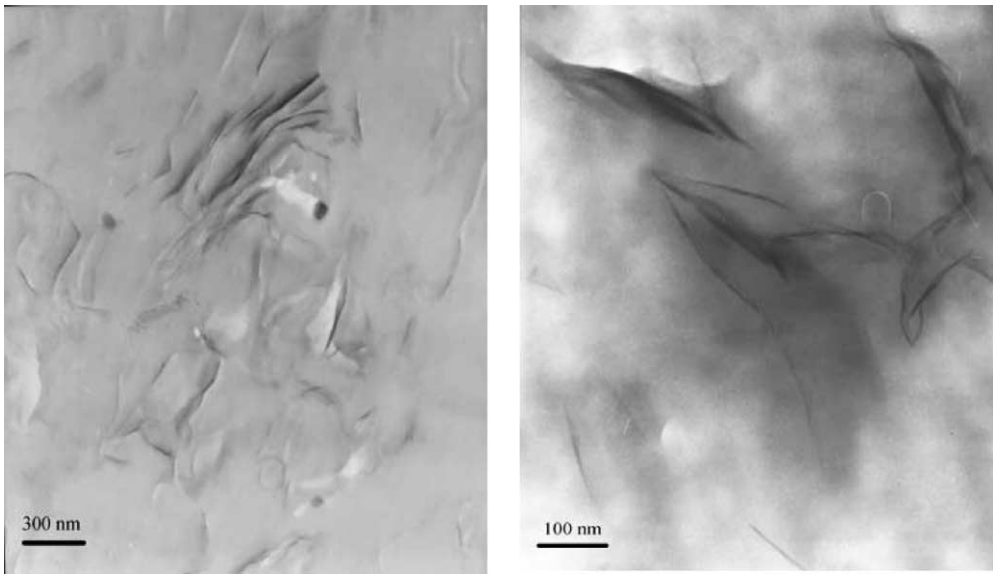


Fig. 4. TEM images of the CPC-treated nanocomposite at low (left) and high (right) magnifications.

glucopyranosyl conformations. In contrast, the signals of the C(1) and C(4) nuclei of the CPC/α-CD complex appear as sharp singlets, which implies that the α-CD unit adopts a symmetric cyclic conformation upon complexation. The solid state ^{13}C NMR spectra provide evidence that α-CD forms a channel-type complex with CPC. The signals of the clay intercalated by the inclusion complexes also appear as sharp singlets, which indicate that the inclusion complexes of the intercalated clay exist within the gallery of the clay. The peaks recorded from the intercalated clay are, however, relatively broad when compared with the other signals. Inserting the inclusion complex within the gallery of the clay decreases the spin–spin relaxation time (T_2) and, thus, results in a greater width at half-height.

3.5. Glass transition temperatures

Fig. 8 shows the DSC thermograms for virgin PS and surfactant-modified clay nanocomposites. Table 1 summarizes the results of DSC measurements. The glass transition temperature (T_g) of the virgin PS is 100 °C and the values of T_g of the CPC/clay and inclusion complex/clay nanocomposites are 102 and 106 °C, respectively. The presence of the clay layers tends to retard movement of the PS chain and, thus, it results in a higher value of T_g. The better-dispersed clay nanocomposite (i.e. that of the inclusion complex-intercalated clay) retards chain movement more effectively than that of the CPC/clay-modified nanocomposite.

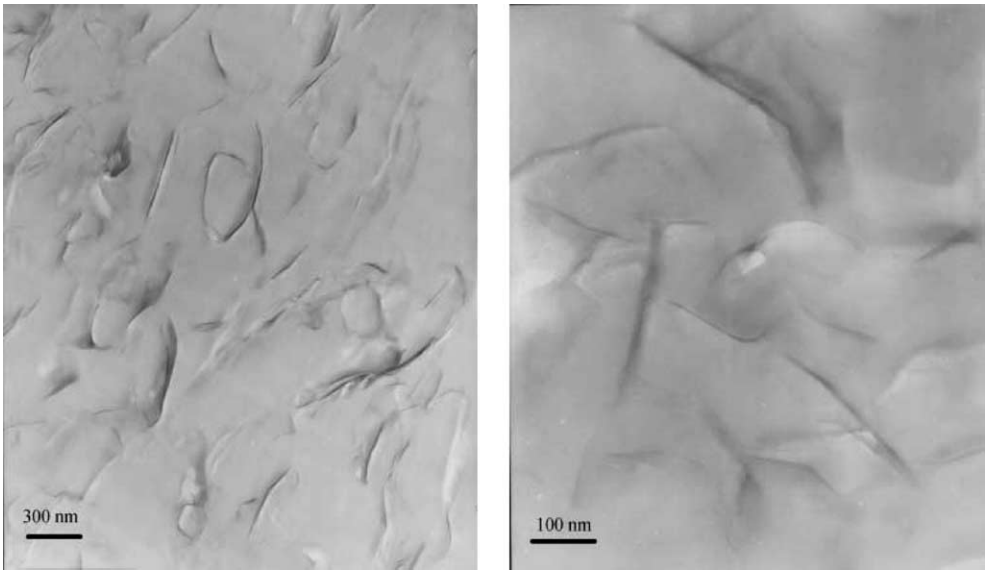


Fig. 5. TEM images of CPC/α-CD-treated nanocomposite at low (left) and high (right) magnifications.

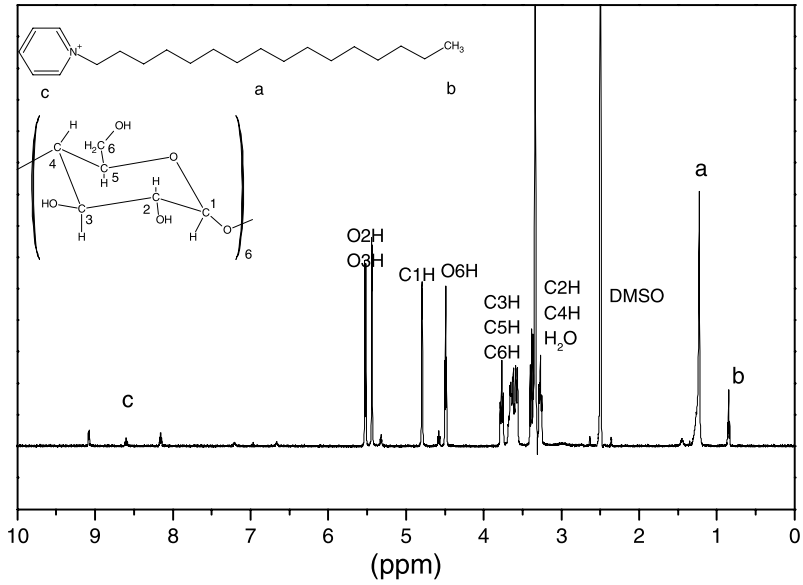


Fig. 6. ^{1}H NMR spectrum (500 MHz) of the CPC/α-CD complex in DMSO-d_6.

Table 1
Results of TGA and DSC data for the polystyrene nanocomposites

Sample	Clay content (%)	T_g (°C)[a]	$T_{0.05}$ (°C)[b]	$T_{0.5}$ (°C)[c]	Char at 600 °C (%)
PS	0	100	390	424	0
CPC/Clay/PS	3	102	408	424	2.9
α-CD/CPC/Clay/PS	3	106	423	452	5.8

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

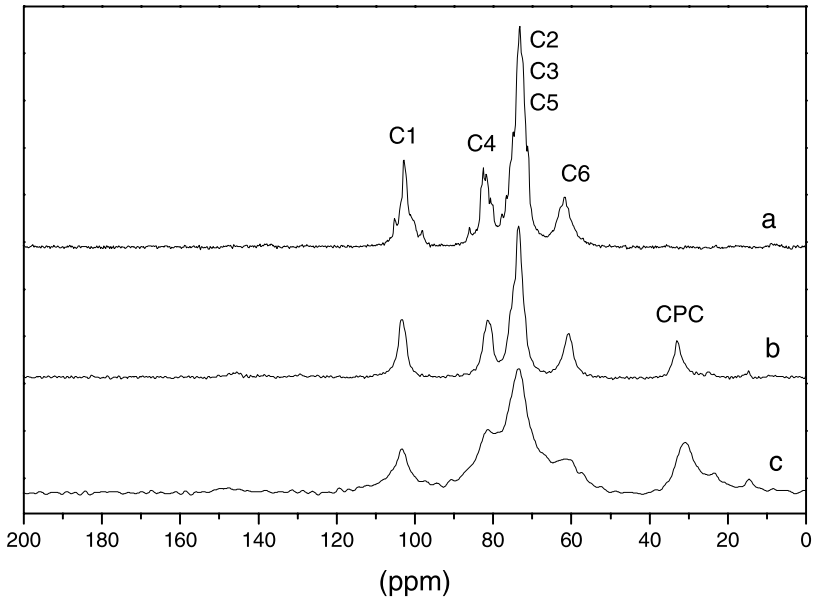


Fig. 7. ^{13}C CP/MAS NMR spectra of (a) α-CD, (b) CPC/α-CD, and (c) CPC/α-CD intercalated clay.

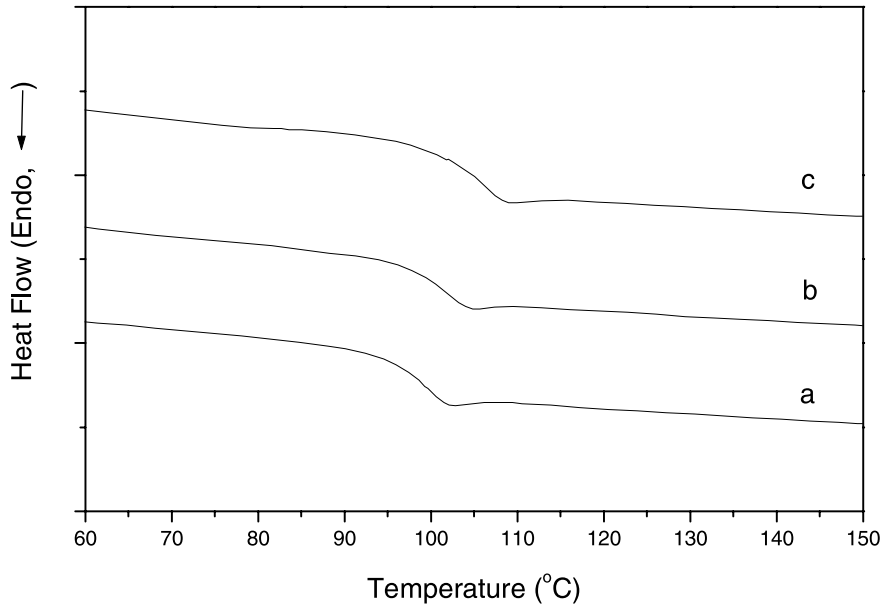


Fig. 8. DSC curves for determining the glass transition temperature of (a) PS, (b) the nanocomposite formed using CPC, and (c) the nanocomposite formed using CPC/α-CD.

3.6. Characterization by TGA

Fig. 9 shows TGA traces of pure CPC and the CPC/α-CD inclusion complex. The CPC/α-CD inclusion complex decomposes at a higher temperature (284 °C) than the pure CPC (220 °C). Thus, the formation of an inclusion complex between CPC and α-CD improves the thermal stability of the CPC surfactant. The mechanism for the enhancement in thermal property is that the presence of the α-CD is able to protect the CPC from earlier decomposition.

Fig. 10 shows TGA thermograms of the nanocomposites and pure polystyrene. The two surfactant-modified PS nanocomposites display higher decomposition temperatures than does the virgin PS with the CPC/α-CD-intercalated clay nanocomposite being the most thermally stable among the three samples. The nanocomposite prepared from the CPC/α-CD-intercalated clay exhibits a 5% weight loss temperature that is 33 °C higher than that of the virgin PS. TEM micrograph of the CPC-intercalated clay nanocomposite is a mixture of intercalated and exfoliated structures. The 5% weight loss temperature of the CPC-intercalated clay nanocomposite is 18 °C higher than the virgin PS. Table 1 summarizes the TGA results for these nanocomposites. The nanocomposite containing α-CD will obviously

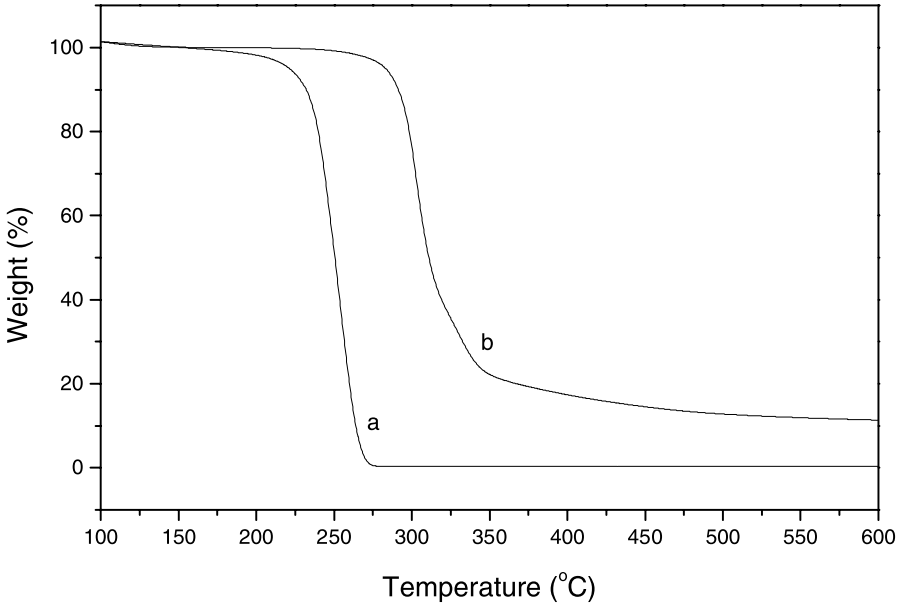


Fig. 9. TGA curves of (a) pure CPC and (b) the CPC/α-CD inclusion complex.

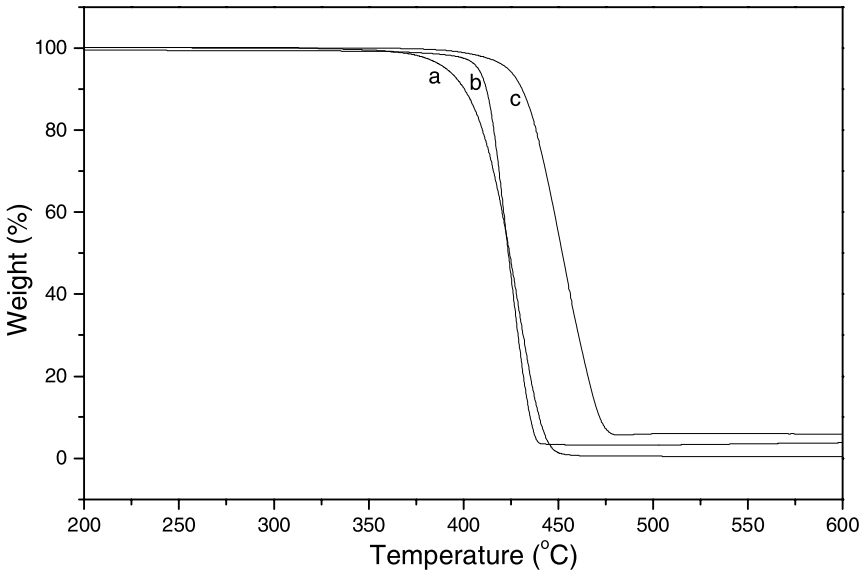


Fig. 10. TGA curves of the nanocomposites recorded under nitrogen atmospheres: (a) pure PS, (b) the nanocomposite formed using CPC, and (c) the nanocomposite formed using CPC/α-CD.

have a larger char yield. It will be more meaningful to prove that the weight loss of PS itself is improved by the presence of α-CD. We also observed that the highest temperature for 50% weight loss occurred for the CPC/α-CD-intercalated clay nanocomposite. Because the CPC-intercalated clay nanocomposite possesses a 50% weight loss temperature that is the same as that of virgin polystyrene, it is clear that this nanocomposite offers no substantial improvements over the virgin PS. In contrast, the nanocomposite prepared from the CPC/α-CD-modified clay displays improved thermal stability.

4. Conclusions

We have prepared polystyrene/clay nanocomposites that have (a) a mainly exfoliated structures with some portions intercalated when treated with CPC and (b) a fully exfoliated structure when treated with CPC/α-CD. We confirmed the existence of an inclusion complex between CPC and α-CD by XRD and ^{13}C CP/MAS NMR spectroscopic analyses. The ^{1}H NMR spectra of the complexes demonstrate that the stoichiometry of the complexes is 1:2 (one CPC molecule to two α-CD units). TGA revealed that the inclusion complex possesses increased thermal stability relative to that of the virgin CPC. We used XRD to confirm that intercalation of surfactants occurred into the montmorillonite clay nanoparticles. Our XRD data indicated that the *d* spacing after treatment with the inclusion complex was higher than that after treatment with the pure CPC surfactant. The results of TGA indicated that the onset of thermal degradation occurred at a higher temperature for the nanocomposite formed from CPC/α-CD than it did for either the virgin PS or the nanocomposite derived after treatment with CPC. Thus, it appears that the presence of the CPC/α-CD complex in the clay enhanced the thermal stability of polystyrene. The glass transition temperatures of the nanocomposites were slightly higher than that of the virgin PS.

Acknowledgements

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References

[1] Pinnavaia TJ. Science 1983;220:365.
[2] Zanetti M, Lomakin S, Camino G. Macromol Mater Eng 2000;279:1.
[3] Giannelis EP. Appl Organomet Chem 1998;12:675.
[4] Theng BK. G Formation and properties of clay–polymer complexes. New York: Elsevier; 1979.
[5] Alexandre M, Dubois P. Mater Sci Eng 2000;28:1.
[6] LeBaron PC, Wang Z, Pinnavaia TJ. Appl Clay Sci 1999;15:11.
[7] Vaia RA, Ishii H, Giannelis EP. Chem Mater 1993;5:1694.
[8] Usuki A, Kojima Y, Kawasumi M, Okada A, Fukushima Y, Kurauchi T, Kamigaito O. J Mater Res 1993;8:1179.
[9] Okada A, Kawasumi M, Usuki A, Kojima Y, Kurauchi T, Kamigaito O. Mater Res Soc Symp Proc 1990;171:45.
[10] Okada A, Kawasumi M, Kuraurchi T, Kamigaito O. Polym Prepr 1987;28:447.
[11] Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O. J Polym Sci Part A: Polym Chem 1993;31:983.
[12] Usuki A, Kojima Y, Kawasumi M, Okada A, Fukushima T, Kurauchi T, Kamigaito O. J Mater Res 1993;8:1179.
[13] Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O. J Polym Sci Part A: Polym Chem 1993;31:2493.
[14] Okada A, Usuki A. Mater Sci Eng 1995;3:109.
[15] Lan T, Pinnavaia T. J Chem Mater 1994;6:2216.

[16] Lan T, Pinnavaia TJ. Chem Mater 1994;6:573.
[17] Lan T, Kaviratna PD, Pinnavaia TJ. Chem Mater 1995;7:2144.
[18] Messersmith P, Giannelis EP. J Polym Sci Part A: Polym Chem 1995; 33:1047.
[19] Messersmith P, Giannelis EP. Chem Mater 1994;6:1719.
[20] Gilman JW, Jackson CL, Morgan A, Harris R, Manias E, Giannelis EP, Wuthenow M, Hilton D, Phillips SA. Chem Mater 2000;12:1866.
[21] Burnside SD, Giannelis EP. Chem Mater 1995;7:1597.
[22] Bender ML, Komiyama M. Cyclodextrin chemistry. Berlin: Springer-Verlag; 1978.
[23] Tseng CR, Wu JY, Lee HY, Chang FC. Polymer 2001;42:10063.
[24] Tseng CR, Lee HY, Chang FC. J Polym Sci Part B: Polym Phys 2001; 39:2097.
[25] Wu HD, Tseng CR, Chang FC. Macromolecules 2001;34:2992.
[26] Tseng CR, Wu JY, Lee HY, Chang FC. J Appl Polym Sci 2002;85: 1370.
[27] Tseng CR, Wu HD, Wu JY, Chang FC. J Appl Polym Sci 2002;86: 2492.
[28] Cristian CR, Constantin L, Alan ET. Macromolecules 2001;34:1318.
[29] Hua J, Goh SH, Valiyaveettil S. Macromolecules 2002;35:1399.