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Synthesis and characterization of PS-clay nanocomposite by emulsion polymerization

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Summary

Polystyrene-Na^+-montmorillonite(PS-Na^+-MMT) nanocomposites are prepared by a simple emulsion polymerization. The X-ray diffraction(XRD) and infrared spectroscopy (IR) analysis confirm that polystyrene(PS) macromolecules can be inserted between lamella layers and whose layer separation is consequently higher than in the polymer-free clay. The enhanced thermal properties of composites are measured by differential scanning calorimetry(DSC) and thermogravimetric analysis(TGA) thermogram and indicate that the glass transition and the decomposition onset temperature of obtained nanocomposites are found to be moved to the higher temperature region. The increased Young's modulus of the obtained nanocomposites is ascribed to the intercalation of PS in clay galleries as well as the fine dispersion of clay particles into the polymer matrix.

Introduction

In recent years, polymer-clay nanocomposite material have attracted great interests from researchers since they frequently exhibit unexpected hybrid properties synergistically derived from the two components(1-5). In most cases, the new and improved properties are derived when the dimensions of dispersed clay is less than 100nm and many techniques have been attempted for the ultrafine dispersion of clay into the polymer matrix. This is due, in great part, to the recent developments of new functionalization of smectic clays, especially Na^+-montmorillonite(Na^+-MMT)(6-9).

Montmorillonite, a smectic clay, is the hydrous alumina silicate mineral whose lamellae are constructed from an octahedral silica sheets, and exhibits a net negative charge on the lamellar surface and causes then to attach by sorbed cations (Na^+ or Ca^{2+}). Thus, in case where the interlayer is incorporated with sodium cation, the hydrophilic properties must be enhanced, which in turn leads to high degree of water swelling. Therefore, these phenomena can possibly provide an effective method for the preparation of hybrid composite intercalated with polymer in the layered silicate if an aqueous system is involved in the intercalation procedure. Accordingly, in our previous work, we successfully synthesized PMMA-clay hybrid material by using emulsion system on the basis of above mentioned phenomena.(10). In this article, we report on the synthesis and characterization of PS-clay nanocomposites whose bond strength between two components is expected to be poor than that of PMMA-clay hybrid.

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The aim of this study is to confirm whether the strongly hydrophobic PS can be intercalated into the hydrophilic silicate layers by using a simple technique of emulsion polymerization or not.

Experimental

Emulsion Polymerization : Clay purification and its Na^+-exchanging processes are followed by the method described previously(10). Purified Na^+-MMT with distilled water in a 1000mL erlenmeyer flask was sonicated with the variation of clay versus water composition from 1.32 to 10 in wt % for 1 hour with moderate agitation at 60 °C. An emulsion polymerization in which a distilled styrene monomer(SM) was dispersed in a continuous water phase with the aid of sodium lauryl sulfate was carried at 75 °C for 4 hours in the presence of potassium persulfate and sonicated Na^+-MMT. After coagulation by the addition of 10wt% aluminum sulfate solution, the reaction products were filtered and dried under reduced pressure for 2 days. A part of the pulverized products was then extracted with hot toluene for 5 days by means of the Soxhlet technique.

Characterization and Measurement : Sonication was conducted by BRANSON 3200 (Branson Ultrasonics Co., USA) sonicator at a frequency of 60 Hz. Dynamic light scattering measurement was done with 633nm wavelength light source from He-Ne laser using BrookHaven BI-9000AT autocorrelator. The content of intercalated polymer is determined by the DuPont 9900 thermogravimetric analyzer. Samples of 20mg masses were heated to 600 °C at a heating rate of 20 °C/min under nitrogen atmosphere. The average molecular mass of extracted PS was determined from size exclusion chromatography (SEC) in tetrahydrofuran(THF) using a Waters HPLC chromatography fitted with Ultrastyragel (Waters Associates) columns and both the refractive index and UV detector. The FT-IR spectra for the homopolymer and composites were recorded on a Nicolet spectrophotometer in the range of 4000-400cm^{-1}. The KBr pellet method was used. The thermal behavior of composites was observed by Dupont 2100 differential scanning calorimeter. Samples of 10mg mass were heated in nitrogen atmosphere to 150 °C at heating rate of 10 °C/min. XRD patterns were recorded by monitoring the diffraction angle 2θ from 2 to 32 degree on a Philip PW1847 X-ray crystallographic unit monitored with a Guinier focusing camera. The unit was equipped with Ni-filtered $CuK\alpha$ radiation source operated at 40KV and 20mA. The relaxation behaviors of the composites were observed by dynamic mechanical thermal analyzer (DMTA). MK-III (Polymer Laboratories Co., British) was operated at a driving frequency of 1 Hz and the temperature scanning rate was 4 °C/min. The bar type specimens were injection molded at 230 °C with dimensions of 14 mm x 12.7 mm x 3.19 mm thick. The stress-strain behaviors of the composites were described by the tensile testing. An universal testing machine(UTM, Hounsfield Co., H10K-S) operated with crosshead speed of 5mm/min was used. The dogbone specimens were molded on the Mini-Max Injection Molder (Model CS-183, Custom Scientific Instruments, Inc.) set at 230± 5 °C. The mass needed to mold a specimen was approximately 1.0g. The tests were carried out at 25 °C and 60% relative humidity.

Results and discussion

A polymerization using emulsion technique has significant advantages in obtaining a polymer-clay hybrids, as is mentioned in our previous study(10). One of the important advantages is the employment of water as a dispersion medium. Because the swelling property of Na^+-MMT is caused by hydration of water to the interlayer inorganic cation (Na^+) and which in turn leads to the insertion of micelles into the galleries of layered silicates. However, in the presence of limited amounts of water, Na^+-MMT forms gels which contain isolated silicate layers and aggregate of several layers. Therefore, lowering the size of aggregated Na^+-MMT before the polymerization reaction is considered to be an essential requirement to allow fine and homogeneous dispersion of clay particles in aqueous medium of emulsion system.

Figure 1 compares the XRD patterns taken from the Na^+-MMT sonicated and not sonicated in pure water for 1 hour. The sonicated product results in decrease of average particle diameter as much as 0.5 from 1.5μm in the range of clay/pure water ratio 0.013 ~ 0.104 and is expected to be dispersed finely in aqueous medium. As is evident from the Figure 1, the overall crystal structure of sonicated MMT is mostly equivalent to that of nonsonicated MMT, indicating that such a severe exfoliation of MMT dose not occurred during sonication in the aqueous system.

The quantities of loaded polymer from the TGA experiment are summarized in Table 1, together with the values of input ratio of styrene monomer to Na^+-MMT. Evidently, those products extracted are showing a considerable amounts of unextractable organic materials, which can be regarded as the intercalated PS. The PS loading behavior is appeared to be inversely proportional to the amounts of MMT added.

Figure 2 shows the XRD patterns of the pristine Na^+-MMT and those of purified composites in toluene for 5 days. Evidently the 001 d-spacings of the composites were found to be increased up to 1.55 nm as the increment of PS content in the composites. This result confirms that the strongly hydrophobic PS macromolecules can be inserted into the galleries of pristine silicate clay. The variations of d_{001} values are calculated and summarized in Table 1. Comparing with PMMA-clay hybrid from the same emulsion method, the increment of 001 d-spacings of the composites in all clay contents were slightly decreased. It is, therefore, proposed that strong hydrophobicity of styrene monomer makes it difficult to penetrate into the clay galleries than the MMA monomer which has polar group in its side chain.

The increment of basal 001 d-spacings of Na^+-MMT was also confirmed by TGA for the purified samples with toluene. As shown in Figure 3, there remains a considerable amounts of unextractable organic materials even after 5 days of extraction. The residual PS is regarded as the polymer intercalated between the interlayers of clay. This confinement of the polymer in the interlayer is tentatively ascribed to both the ion-induced dipole force acting between the host (clay) and the guest (PS) and the contraction of the gallery height due to the water removal from the gallery.

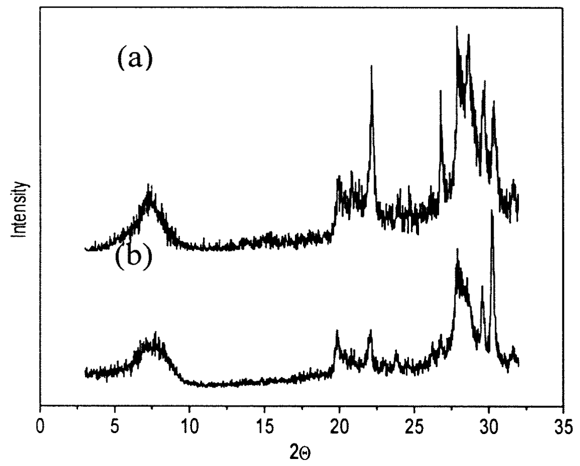


Figure 1. XRD patterns of : (a) nonsonicated MMT (b) sonicated MMT in pure water for 1hr.

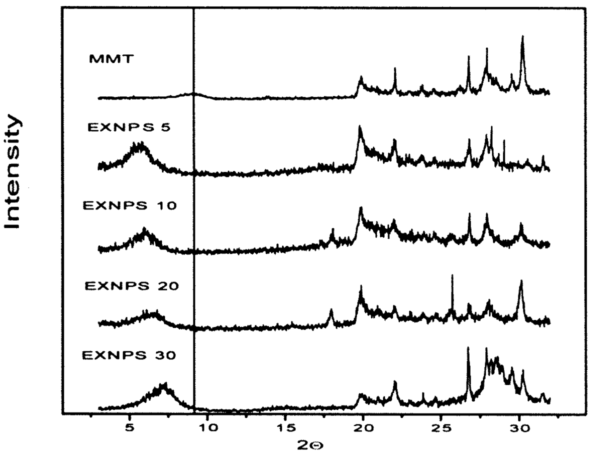


Figure 2. XRD patterns of extracted Composites (EXNPS series).

Table 1. The Input Ratio, Contents of PS in the Nanocomposites and Interlayer Distance

Sample	Input Ratio of SM / MMT (g/g)	PS Content in Product (wt%)		Interlayer Distance $d_{(001)}$ (nm)
		A[a]	B[b]	
MMT	0/100	-	-	0.98
NPS5	95/ 5	88.7	45.6	1.55
NPS10	90/10	82.8	33.9	1.46
NPS20	80/20	75.4	28.8	1.38
NPS30	70/30	65.9	21.7	1.24

a= Products not purified by extraction (NPS series)

b= Products purified by hot toluene extraction for 5 days (EXNPS series)

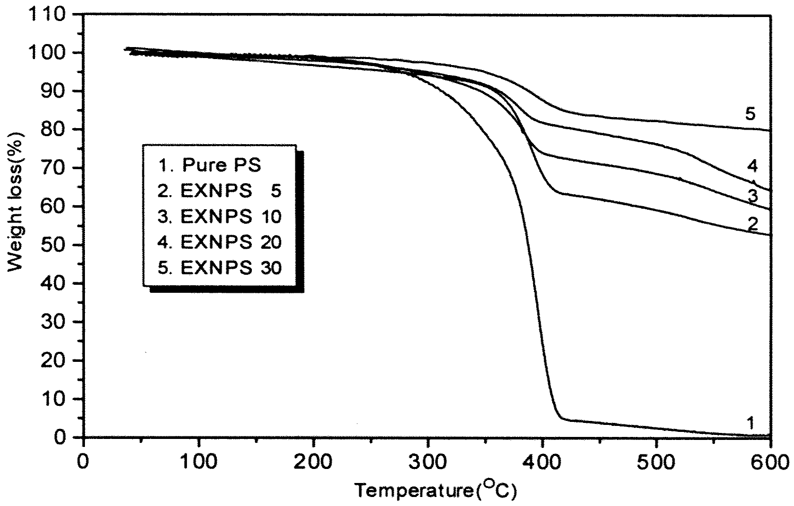


Figure 3. TGA thermogram of pure PS and extracted composites.

Table 2 shows the average molecular masses and polydispersities of PS obtained from the toluene extracts by the addition of excess methanol to the extracts. The obtained Mw values of extracted polymer are found to be in the order of 10^5 g/mol, which is comparable with that of pure PS, indicating that the clay presence in the reaction medium does not affect the average molecular mass of the polymer intercalated.

Table 2 . Average Molecular Masses and Polydispersities of PS obtained from the Composite Extracts

Sample Code	Mn × 10^{-4} (g/mol)	Mw × 10^{-4} (g/mol)	Mw / Mn
Pure PS	9.3	23.0	2.43
NPS5	9.1	22.0	2.41
NPS10	11.0	23.0	2.09
NPS20	7.9	17.0	2.15
NPS30	8.4	18.0	2.14

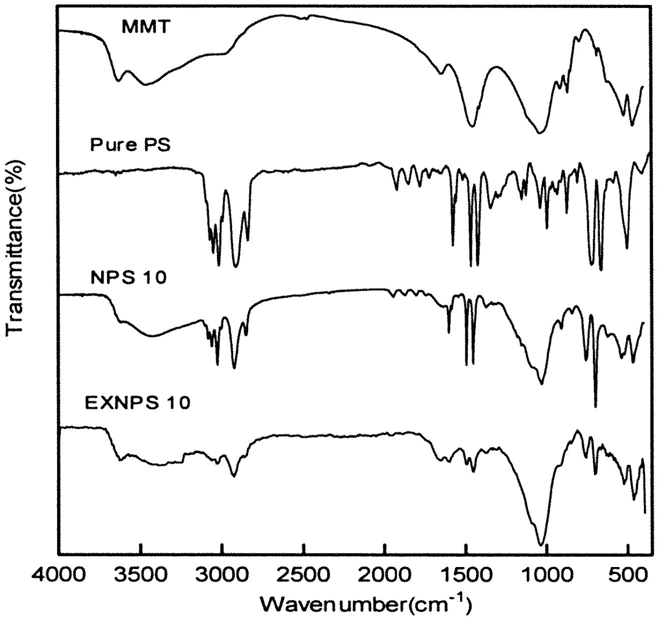
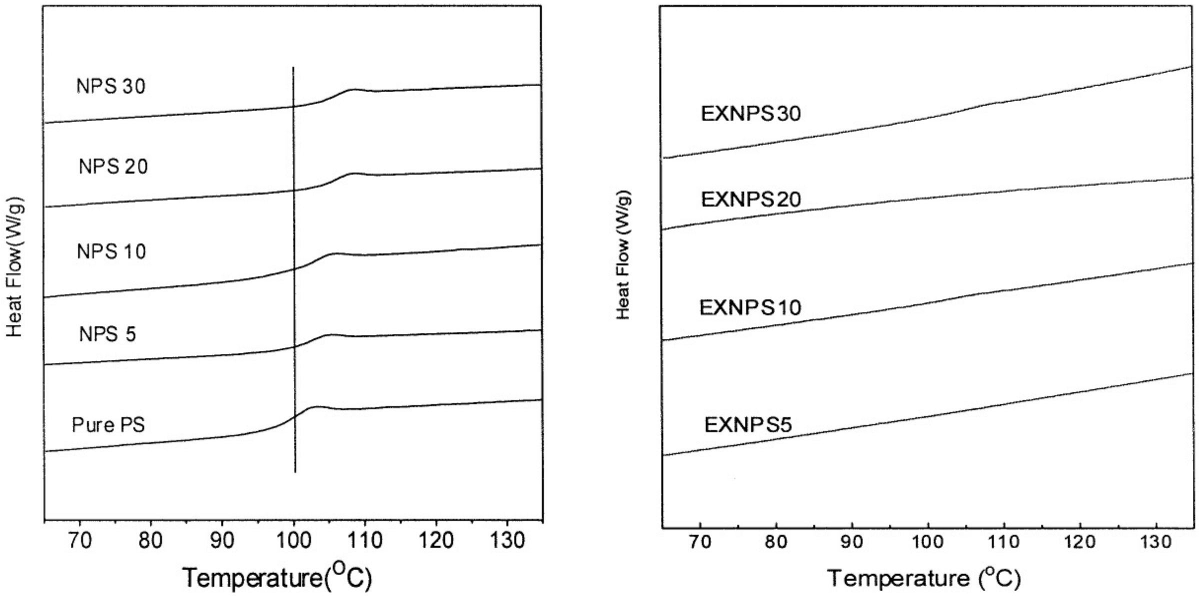


Figure 4. IR spectra of PS, MMT, unextracted nanocomposite (NPS), and extracted nanocomposite (EXNPS).

Further evidence for the intercalation can be obtained from the IR spectrum recorded for the extracted composites. The FT-IR spectra, which are shown in Figure 4, reveal the presence of characteristic peaks of both PS and MMT from the extracted and unextracted composites alike. The absorption bands at 3070, 3030 cm^{-1} (aromatic C-H stretching), 2960, 2930 cm^{-1} (aliphatic C-H stretching) are the consequences due to the characteristic frequencies of PS. The absorption bands of MMT group are also found at 3630, 1050, and those between 600-400 cm^{-1} can be associated respectively with -OH stretching of the lattice water, Si-O stretching, and Al-O stretching, and Si-O bending. The existence of PS and MMT characteristic peaks in fully extracted composite is ascribed to the polymer intercalation to the host's layer by the secondary valence forces.



(a) (b)

Figure 5. DSC thermograms of nanocomposites; unextracted (a) and extracted composites (b).

The thermal behaviors of synthesized composites are found in TGA thermogram which has been described early in Figure 3 for the polymer loading behavior. Evidently, the decomposition onset temperature of those composites shifted toward the higher temperature range than that of pure PS. In addition, all hybrid composites are found to be stable up to 330°C. The glass transition behavior of pure PS and nanocomposites are described in Figure 5(a) by DSC thermogram. The pure polymer exhibits an endotherm approximately at 100 °C corresponding to the Tg of PS and the enhancement of Tg transition of the unpurified product is found to be proportional to the amount of MMT(11). This suggests that the inorganic materials accumulate heat enough to transfer the glass transition upward.

Figure 5(b) shows the DSC thermogram of extracted composites. In this case, however, the clear transition can not be found and is ascribed to the confinement of the intercalated polymer chains within the silicate galleries that prevents the segmental motions of the polymer chains. The effect of chain confinement in the clay layers is also detailed by the DMTA testing. Shown in Figure 6 are the temperature dependencies of the tensile storage modulus, E', and tanδ of the pure PS and unextracted nanocomposite (NPS 10). The shift and broadening of the tanδ peak to higher temperatures indicate an increase in nanocomposite Tg and broadening of the glass transition temperature. Broadening and increase of Tg have been observed in the organic-inorganic nanocomposites and are generally ascribed to the restricted segmental motions near the organic -inorganic interfaces(12-14).

The benefit of clay loading in polymer reinforcement is illustrated by the tensile data in Table 3. Comparing the mechanical properties of the pure PS and nanocomposites, the improved performance is found in modulus but not in strength.

As expected, the benefit in strength for this strongly hydrophobic PS is not as great as that of PMMA-clay hybrid. This result suggests that the reduced tensile strength in nanocomposites is mainly ascribed to a poor interfacial adhesion between PS matrix and clay particles. Undoubtedly, however, the enhancement of modulus is reasonably attributed to the high resistance exerted by the MMT against the plastic deformation, together with the effects of stretching resistance of the oriented backbone of polymer chains in the galleries.

Table 3. Tensile Results of unextracted Nanocomposites and Pure PS

Sample Code	Stress at Max Load (Mpa)	Strain at Max Load(%)	Young's Modulus (Gpa)
Pure PS	28.7	2.87	1.21
NPS5	21.7	2.40	1.30
NPS10	23.4	1.63	1.91
NPS20	16.6	1.01	2.64
NPS30	16.0	2.30	1.83

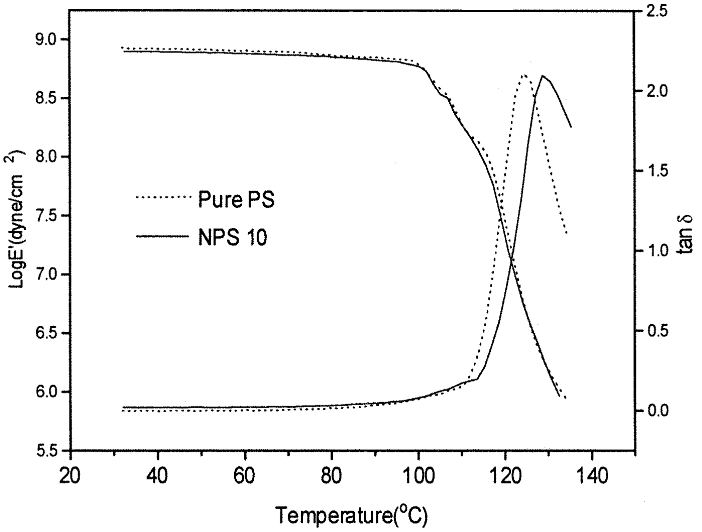


Figure 6. Temperature dependence of E' and tanδ for pure PS and unextracted nanocomposite(NPS10).

Conclusion

From the results so far obtained, it can be concluded that polymer-clay nanocomposite can be successfully synthesized using strongly hydrophobic monomer and smectic clay by a simple emulsion polymerization technique. The enhanced thermal and mechanical properties are attributed to the fixation of polymer chains into the interlayer of MMT and the restricted segmental motions near the organic-inorganic interfaces. The strong fixation of polymer to the inorganic surfaces is considered to be due to the cooperative formation of ion-induced dipole forces.

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