

Synthesis of Exfoliated PS/Na–MMT Nanocomposites via Emulsion Polymerization

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Exfoliated PS/Na–MMT nanocomposites were obtained up to 3 wt % of clay without modifying clay organically and DBS–Na affected the degree of exfoliation of silicate layers. The feed rate of monomers also had an effect on polymerization, and it was a key to controlling the total monomer concentration and maintaining a certain polymerization rate inside the clay. As the amount of AMPS increased, it was easy to enlarge and exfoliate the clay layers. The onset degradation temperature of the nanocomposites was higher than that of pure PS without clay and shifted toward a higher temperature as the amount of pristine Na–MMT increased. Through the NMR spectrum, the end-tethered material on silicate layers was AMPS and styrene. The storage modulus of A0.3STD3% had the 100% higher value than that of A0.3STD0%. The image of exfoliated nanocomposites was shown by TEM.

Introduction

Polystyrene (PS) is one of the most mass-productive and commercialized polymers, and its homopolymer and copolymers are being produced by various methods such as solution polymerization and emulsion polymerization. Hence, PS/clay nanocomposites may have huge applicability, so many people have been focusing on the PS/clay nanocomposites with various methods described in the next phrases. The clay in nanocomposites has been intercalated by *in situ* polymerization^{1–6} and melt intercalation⁷ of PS using organically modified silicate, and recently exfoliated by a few researchers.^{8–11} Fu and Qutubuddin⁸ modified pristine montmorillonite (Na–MMT) with vinylbenzylidemethylidodecylammonium chloride (VDAC)⁹ by cation exchange between sodium ions in clay galleries and onium, dispersed its particle in styrene monomer, and polymerized. Another similar work¹⁰ was performed to obtain the exfoliated PS/clay nanocomposites, using the layered silicate modified with protonated amine-terminated PS. Weimer and co-workers¹¹ obtained the delaminated PS/silicate nanocomposites by anchoring a living free radical polymerization initiator into silicate layers followed by bulk polymer-

ization. So far, most research on PS/silicate nanocomposites have used organically modified layered silicate,^{12–23,30} while Kim and co-workers³² used pristine Na–MMT and obtained the intercalated PS/Na–MMT nanocomposite by emulsion polymerization.

This paper will show the method of delaminated hydrophobic polymer/clay nanocomposites without any alkylammoniums. The hydrophilicity of pristine Na–MMT impedes the formation of delaminated morphology with hydrophobic polymers including polystyrene. So we

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adopt the reactive surfactant, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS),²⁴⁻²⁶ with an amido and sulfonic group in its molecule, which was used to synthesize the exfoliated PMMA/Na-MMT nanocomposite.^{29,33} In addition to AMPS, dodecylbenzenesulfonic acid sodium salt (DBS-Na) is also used. We investigate the effects of AMPS content, DBS-Na addition, and feed rate of styrene on the synthesis of a hybrid, especially on the degree of exfoliation of clay layers.

Experimental Section

Materials. Pristine Na-MMT (Kunipia-F) with the cation-exchange capacity (CEC) of 119 mequiv/100 g was provided by Kunimine Co. and dispersed in deionized water (Na-MMT/water = 5 g/145 g) for 24 h at ambient temperature before use. Styrene, 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS), and dodecylbenzenesulfonic acid sodium salt (DBS-Na) were purchased from Aldrich Chemical and used as received. Potassium persulfate (initiator: Junsei), *n*-hexane (nonsolvent: Junsei), and lithium chloride (Junsei) except tetrahydrofuran (THF: Fluka, HPLC grade) were pretreated with the same method as described in the other paper.²⁷

Synthesis of Polystyrene/Na-MMT Nanocomposites. *First Stage.* An aqueous clay dispersion with 5 g of styrene, a certain amount of AMPS, and 20 g of initiator solution (KPS/water = 1 g/99 g) were charged into a 1-L four-neck reactor equipped with a baffle stirrer, a reflux condenser, a nitrogen inlet, and a rubber septum. The deionized water was added to reach the total amount of 200 g. The solution was stirred at 200 rpm for 1 h under nitrogen gas at an ambient temperature. Then, the reactor temperature was raised to 65 °C and kept at that temperature for 1 h.

Second Stage. After the first stage, 5 g of DBS-Na solution (DBS-Na/water = 5 g/45 g) was injected into the solution through a septum, and then 15 g of styrene was fed into the reactor at two feed rates (0.08 and 0.16 cm³/min) via a glass syringe using a syringe pump. When only AMPS is used, the injection step of DBS-Na solution is omitted. When the monomer feeding was finished, 5 g of KPS solution was injected through a septum and the solution was stirred for additional 4 h at 85 °C to polymerize residual monomers. Samples were collected from the reactor, freeze-dried for 5 days, and further dried under a high vacuum at 100 °C for 1 day.

Polymer Recovery. Polymer recovery by THF extraction or reverse ion exchange with LiCl²⁷ in THF was carried out by the procedure mentioned in detail in our previous work.²⁹ The composite with 3 wt % of Na-MMT was extracted to separate unbound polymers from the composite with a Soxhlet extractor using THF, and the residual clay was reverse ion-exchanged to retrieve molecules bound or end-tethered on the clay layers.

Characterization. FT-IR, X-ray, ¹H NMR, GPC, TGA, and TEM were used to obtain the data in the same way as in our previous paper.^{29,33} The column of GPC was calibrated with five standard polystyrene samples. The molecules end-tethered²⁹ or bound on silicate layers were obtained by reverse ion exchange and their molecular weights were measured by Tandem MS, JMS HX-110/110A from JEOL Co. with FAB+ (fast atom bombardment) ion mode, using nitrobenzyl alcohol as a matrix at 0.6 °C.

Tan δ and storage modulus (E') were obtained by a Rheometric Scientific DMTA4 using a dual cantilever bending mode from 30 to 170 °C with a heating rate of 4 °C/min under 0.01% of deformation at 1 Hz of frequency. Samples were molded into 10 × 20 × 1.3 mm size at 140 °C for 4 min under 3000 psi of pressure. The glass transition temperature, T_g , was determined from the maximum in the tan δ vs temperature scan.

Basal spaces between clay layers in an aqueous clay dispersion with styrene and AMPS were measured before the polymerization because it would offer a lot of crucial information on the exfoliation behavior of silicates during polymerization. The clay dispersion containing 3 wt % of Na-MMT was poured into three 100-mL beakers into which styrene, AMPS, and a mixture of AMPS and styrene were added with the same ratio as described in the first stage. The mixture was stirred for 1 h to measure X-ray diffraction patterns.

Results and Discussion

In the sample code A#ST#%, A stands for AMPS, S for styrene, and T for pristine Na-MMT. The number following A means the weight of AMPS (g) and the number following T is the weight percent of clay relative to monomer. Since all samples contain 20 g of styrene, the number is not given after S. In the sample code A#STD#%, the last number following TD is the weight percent of clay relative to monomer and the letter D means DBS-Na is added. The number for DBS-Na content is not given because 0.5 g of DBS-Na is fixed.

The FT-IR spectrum of a nanocomposite (A0.3ST3%) is omitted for simplicity but the assignments of characteristic peaks of AMPS, Na-MMT, and polystyrene (PS) are listed as follows. A0.3ST3% has very clear peaks describing Si-O stretching at 1034 cm⁻¹ from Na-MMT and a very small peak of S=O stretching at 1369 cm⁻¹ from AMPS. Those of PS occurred at around 3080–3020 cm⁻¹ (aromatic CH stretching), 2920–2847 cm⁻¹ (aliphatic stretching), and 1490–1450 cm⁻¹ (CH₂ bending). For AMPS, 3036, 1661, and 1371–1244 cm⁻¹ are assigned for N-H stretching, C=O stretching, and S=O stretching, respectively.

Figure 1a shows the XRD patterns taken from the nanocomposites without DBS-Na. All samples were extracted with THF for 12 h to remove surfactants or oligomers. A0.3ST1% shows a broad trace of a diffraction pattern, which is considered as a partially exfoliated state. A very weak and broad peak around 5.6° for A0.3ST3% and a strong diffraction peak around 6.0° for A0.3ST5% suggest the intercalation of the PS chains into the gallery of silicate layers. The basal spacing, d_{001} , of silicate layers at a peak position is calculated from Bragg's law. The basal spacing of pristine Na-MMT is 1.14 nm. The d_{001} spacings of A0.3ST3% and A0.3ST5% are calculated at 1.58 and 1.47 nm, respectively.

Figure 1b shows X-ray diffraction patterns of pristine Na-MMT and the nanocomposites obtained by adding DBS-Na as a stabilizer of particles after the first-stage polymerization was completed. A0.3STD5% and A0.3STD10% show obvious peaks at about 6° in 2 θ angles, indicating the formation of intercalated nanocomposites. On the other hand, A0.3STD3% shows a trace of a diffraction pattern and can be viewed as a partially exfoliated PS/Na-MMT nanocomposite. A0.3STD1% does not show the (001) plane reflection peak in Figure 1b. The absence of diffraction peaks demonstrates that the clay is exfoliated or delaminated in a PS matrix. But the A0.3STD series, which were not extracted with THF, have no X-ray peaks except A0.3STD10%. It indicates that the layer interaction of silicates in A0.3STD3–10% still exists and the surface charge of silicates was not compensated by PS.

TEM image in Figure 2 also confirms an exfoliated morphology developed in the A0.3STD1% nanocompos-

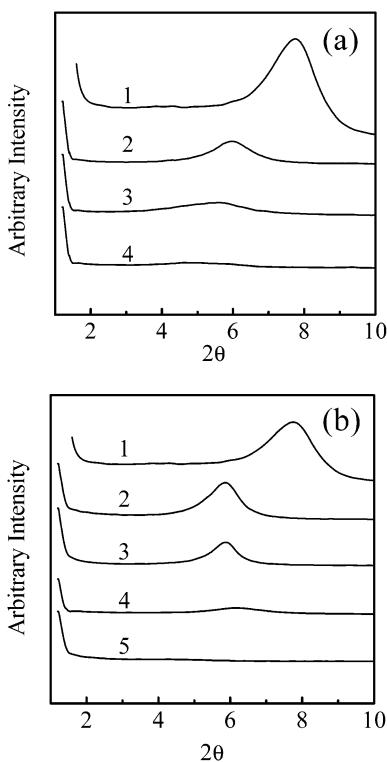


Figure 1. X-ray diffraction patterns of (a) A0.3ST and (b) A0.3STD series: (a-1) pristine Na-MMT given as a reference, (a-2) A0.3ST5%, (a-3) A0.3ST3%, (a-4) A0.3ST1%, (b-1) pristine Na-MMT, (b-2) A0.3STD10%, (b-3) A0.3STD5%, (b-4) A0.3STD3%, and (b-5) A0.3STD1%. All samples were extracted with THF for 12 h in a Soxhlet extraction apparatus and compressed into a disk shape. The character D next to T means that DBS-Na is added.



Figure 2. TEM micrograph of A0.3STD1%.

ite. The light regions represent PS, and the dark bands stand for the individual Na-MMT layers. Most MMT layers are randomly dispersed in the PS matrix, and a bundle of layers are located in the middle of left side, but these are not in Bragg condition to diffract. This disordered microstructure suggests that the nanocomposite has the exfoliated morphology.

Figure 3 shows the effect of the feed rate of monomers on the A0.3STD series. At the feed rate of $0.08 \text{ cm}^3/\text{min}$, X-ray diffraction patterns of the A0.3STD series shift to higher angle positions than those at the feed rate of

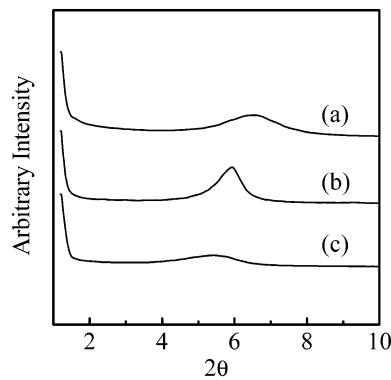


Figure 3. X-ray diffraction patterns of (a) A0.3STD10%, (b) A0.3STD5%, and (c) A0.3STD1%, with $0.08 \text{ cm}^3/\text{min}$ of monomer feed rate. All samples were extracted with THF for 12 h in a Soxhlet extraction apparatus and compressed into a disk shape.

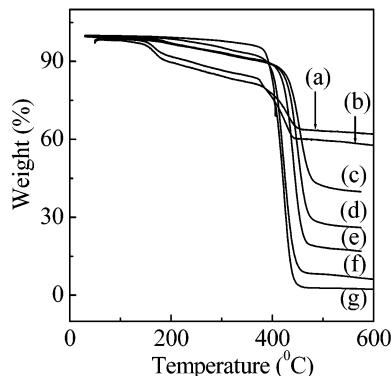


Figure 4. Thermal gravimetric curves for the A0.3ST series: (a) A0.3ST3%, (b) A0.3ST1%, (c) A0.3STD10%, (d) A0.3STD5%, (e) A0.3STD3%, (f) A0.3STD1%, and (g) A0.3STD0%, under N_2 .

$0.16 \text{ cm}^3/\text{min}$ in Figure 1b. If we assume that, after the first stage of polymerization, the emulsion particles containing clays are at interval 3,^{28,31} it is called a monomer starved state.³¹ Monomers will be consumed competitively in two regions of an emulsion particle: One is the hydrophilic gallery of silicate layers and the other is the hydrophobic exterior of the clay particle surrounded by DBS-Na. When the feed rate of styrene is low, most monomers will polymerize in the hydrophobic exterior rather than in the hydrophilic gallery of silicate layers and most clays are hardly exfoliated. As a result, even A0.3STD1% fails in the exfoliation of silicate layers, showing a peak at 5.4° in 2θ angle when compared with that in Figure 1b-5. The others also show the intercalated state in Figure 3.

The thermal decomposition behaviors of the A0.3STD series and the A0.3ST series prepared are given in Figure 4. Weight loss at about 180°C attributes to the decomposition of AMPS. In Figure 4c-g, the onset degradation temperatures of the A0.3STD series are higher than pure PS and shift toward higher temperature as the amount of pristine Na-MMT increases. The nanocomposite with 10 wt % of clay shows a 40°C increase in decomposition temperature at 20% weight loss. This figure explains that DBS-Na, a conventional surfactant, has increased the yield of PS because the residual amounts of A0.3ST1% and A0.3ST3% at 600°C are 58 and 62%, which are corresponding to 42.3 and 43.3% yields, but the residual amounts of A0.3STD1%

Table 1. Molecular Weights of Polystyrene Recovered from Nanocomposites

samples	Mn	Mw	PDI	yield (%) ^c	d_{001} spacing (nm)
A0.3ST1%	29 000	65 000	2.25	42.3	exfoliated
A0.3ST3%	31 000	109 000	3.47	43.3	1.58
A0.3STD0%	45 000	193 000	4.30	100.0	
A0.3STD1%	56 000	265 000	4.67	98.2	exfoliated
A0.3STD5%	87 000	346 000	3.95	81.2	1.47
A0.3STD10%	73 000	215 000	2.93	72.4	1.47
A1.0STD3%	72 000	294 000	4.07	95.0	partially exfoliated
A2.5STD3%	30 726	67 000	2.21	74.3	exfoliated
E ^a A0.3STD3%	256 000	3.75	88.3	partially	
		68 000			exfoliated
R ^b A0.3STD3%	312 ^b				

^a E and R stand for the polymer recovery by THF extraction and by reverse ion exchange after THF extraction, respectively.

^b Molecular weight obtained from Tandem MS analysis using the FAB+ ion method. ^c Yields of nanocomposites were calculated by residual amounts in TGA measurement using the pure polymer for the calculation base.

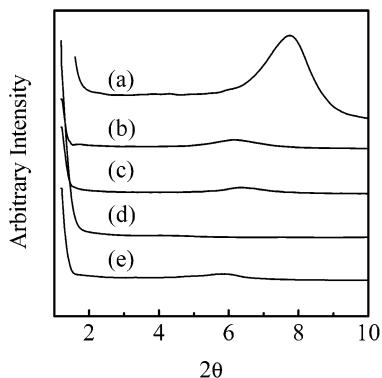


Figure 5. X-ray diffraction patterns according to the amount of AMPS, reactive surfactant (a) pristine Na-MMT, (b) A0.3STD3%, (c) A1STD3%, (d) A2.5STD3%, and (e) A2.5T3%. All samples were extracted with THF for 12 h in a Soxhlet extraction apparatus and compressed into a disk shape.

and A0.3STD3% are 5.1 and 16.9%, showing 98.2 and 88.3% yields (refer to Table 1). DBS-Na added at the second stage will be adsorbed on the surface of growing particles and attract monomers or oligomeric radicals from the aqueous medium to the growing particles, resulting in high yield near or in the galleries of the silicates and delamination state or widening of the basal spacing.

Figure 5 shows the XRD patterns of nanocomposites prepared with different amounts of amphiphilic AMPS. In each case, clay content is fixed at 3 wt % for comparison. The exfoliated state is obtained in A2.5STD3%. A1STD3% and A0.3STD3% can be explained as partially exfoliated nanocomposites forming small stacks of clay layers dispersed well in the polymer matrix, while 2.5STD3% shows the exfoliation of clay. The increase of AMPS has an effect on widening and exfoliating the clay layers. When a large amount of AMPS exist in the galleries of silicate layers with styrene, which will be shown in Figure 6d, polymerization will occur, widening the gap between silicate layers. We can infer that a perfectly exfoliated form can be obtained by polymerization of styrene and AMPS inside the clay.

In Figure 6, the XRD patterns of pristine Na-MMT dispersed in water are shown under various conditions to investigate the degree of intercalation of AMPS, styrene, and both of them into the clay layers before

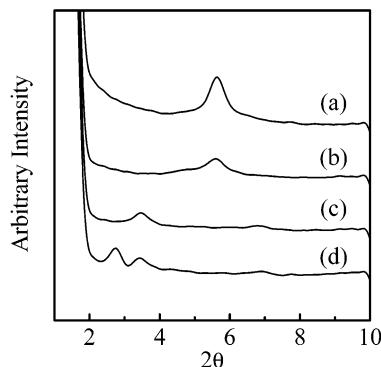


Figure 6. X-ray diffraction patterns of water dispersions of pristine Na-MMT under various conditions: (a) the dispersion of Na-MMT in water, (b) with styrene, (c) with AMPS, and (d) with both AMPS and styrene.

the reaction occurs. The peak for Na-MMT appears at a 2θ of 5.7° corresponding to the basal space of 1.55 nm. The peak for Na-MMT with styrene occurred at 5.6°, which indicates that hydrophobic styrene monomers rarely penetrate into the galleries of clay layers. In the case of the dispersion of Na-MMT with AMPS in water, two peaks are shown at 3.4° and 6.8° with d_{001} and d_{002} spacing of MMT, respectively. It means that AMPS is intercalated into the clay layers. When both AMPS and styrene are added into the dispersion of Na-MMT, one additional peak appears at 2.7° with the basal space of 3.27 nm. This result indicates that styrene monomers are intercalated into the clay layers as well as AMPS. It is recognized from Figure 6b that styrene monomers alone are difficult to intercalate when they are added and AMPS facilitates styrene intercalate into the clay layers.

Molecular weights of PS are summarized in Table 1. The A0.3STD series have much higher molecular weights than the A0.3ST series. It also confirms that DBS-Na enhances the polymerization of monomers as mentioned earlier. After the reverse ion exchange of EA0.3STD3%, the molecular weight of the precipitated part by *n*-hexane is only 312, corresponding to oligomers that were trapped in and end-tethered on the silicate layers during the first stage of the reaction in the presence of clay. We have proposed a mechanism of exfoliation of Na-MMT with amphiphilic AMPS in our previous paper.²⁹ Hydrogen ion, H^+ , will dissociate from the sulfonic acid group of AMPS and move to nitrogen to form a protonated amido portion and exchange with sodium ions on silicates. The sodium dissociated from silicates will associate with sulfate ion of AMPS to form sulfonic acid sodium salt, which is a surface-active material. AMPS has a vinyl group which will polymerize by a radical initiator. The molecules tethered on clay layers may be terminated by the radicals during polymerization, or clay layers hinder further polymerization, so they show small molecular weights.

Figure 7 represents the NMR spectra of A0.3STD0%, the polymer recovered from A0.3STD3% by extraction with THF, and the molecules obtained from A0.3STD3% by reverse ion exchange after THF extraction. The peaks of solvent, THF, are shown at 3.58 and 1.73 δ . In Figure 7a,b, the peaks of the phenyl group of PS are observable in the range of 6.4–7.2 δ . Methylene and methine groups of PS are found at 1.4 and 1.9 δ , respectively. The peaks for AMPS are not discernible since the

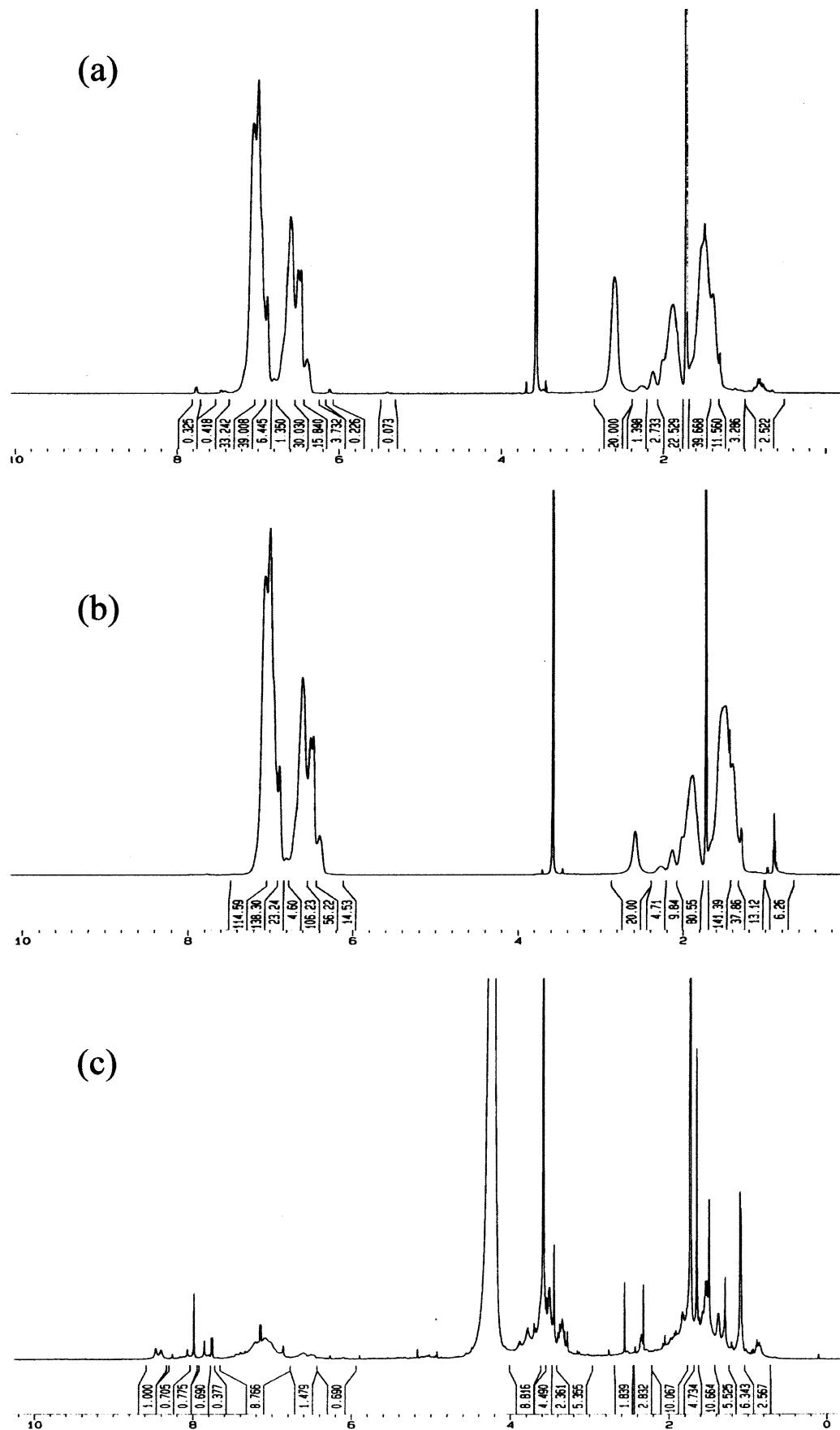


Figure 7. ^1H NMR spectra of (a) A0.3STD0%, using THF as a solvent without TMS, (b) polystyrene recovered from A0.3STD3% by extraction with THF by a Soxhlet extraction apparatus for 5 days, and (c) polymer obtained from A0.3STD3% by reverse ion exchange with THF/LiCl, after THF extraction with a Soxhlet apparatus for 5 days.

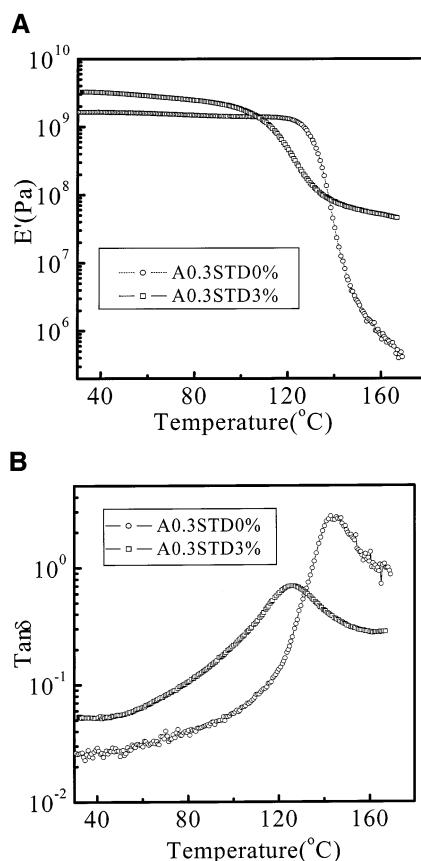


Figure 8. (a) Storage modulus, (b) $\tan \delta$ of A0.3STD0% and A0.3STD3%, on temperature with DMA scans.

amount of AMPS is much smaller than that of styrene in polymer. The methylene group of DBS-Na shows the peak at $2.6\ \delta$. NMR peaks of A0.3STD0% and the polymer recovered from A0.3STD3% by extraction with THF are very similar to the typical spectrum of PS. By the NMR spectrum of Figure 7c, the molecules end-tethered on silicate layers show the peaks for a phenyl group in styrene around $7.1\text{--}8.0\ \delta$ and the peaks for methylene and methyl groups of AMPS at 3.3 and $1.4\text{--}1.5\ \delta$. According to the peak areas, the ratio of AMPS and styrene is about 1:1.

Figure 8 shows DMTA results of PS (A0.3STD0%) and PS/Na-MMT nanocomposite (A0.3STD3%). Storage moduli, E' , are shown in Figure 8a, describing that A0.3STD3% has the 100% higher value of dynamic modulus than A0.3STD0% at $30\ ^{\circ}\text{C}$ and keeps the higher value up to $100\ ^{\circ}\text{C}$. Glass transition temperatures are obtained from the peak temperature of $\tan \delta$

in Figure 8b. A0.3STD3% has a lower glass transition temperature than A0.3STD0%. This lower T_g of A0.3STD3% might be attributed to the existence of small molecules with the molecular weight of 312 in clay layers.

Conclusions

We considered the effects of DBS-Na, AMPS, and feed rate of styrene on the synthesis of PS/Na-MMT nanocomposites. When PS/Na-MMT nanocomposites were prepared with AMPS only, A0.3STD1% and A0.3STD3% show very weak and broad peaks at around 5.6° . On the other hand, for PS/Na-MMT nanocomposites prepared with AMPS and DBS-Na, A0.3STD3% shows a trace of a diffraction considered as a partially exfoliated PS/Na-MMT nanocomposite, and A0.3STD1% does not show the (001) plane reflection peak. At a slow feed rate of $0.08\ \text{cm}^3/\text{min}$, X-ray diffraction patterns of the A0.3STD series shift to higher angle positions than those at the feed rate of $0.16\ \text{cm}^3/\text{min}$. Increasing AMPS enhanced the state of exfoliation in the nanocomposites because A1STD3% and 2.5STD3% show the exfoliation of clay. Clay dispersions in water explain the interaction between styrene and Na-MMT. When both AMPS and styrene are added into the dispersion of Na-MMT, two peaks are shown at 2.7° and 3.4° . These results indicate that AMPS facilitates styrene to intercalate into the clay layers. DBS-Na added at the second stage attracts monomers or oligomeric radicals from the aqueous medium to the growing particles, resulting in high yield near or in clay galleries and delamination state or widening of the basal spacing. The increase of AMPS has an effect on the widening and exfoliating of the clay layers. The onset degradation temperatures of the A0.3STD series are higher than that of pure PS and shift toward higher temperature as the amount of pristine Na-MMT increases. The nanocomposite with 10 wt % clay shows a $40\ ^{\circ}\text{C}$ increase in decomposition temperature at 20% weight loss. The storage modulus of A0.3STD3% has a 100% higher value of the dynamic modulus than that of A0.3STD0% at $30\ ^{\circ}\text{C}$. Exfoliated PS/Na-MMT nanocomposites were obtained up to 3 wt % clay without modifying clay organically.

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