

Synthesis of Na⁺-Montmorillonite/Amphiphilic Polyurethane Nanocomposite via Bulk and Coalescence Emulsion Polymerization

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ABSTRACT: Polyurethane/clay nanocomposites have been synthesized using Na⁺-montmorillonite (Na⁺-MMT)/amphiphilic urethane precursor (APU) chains that have hydrophilic polyethylene oxide (PEO) chains and hydrophobic segments at the same molecules. Nanocomposites were synthesized through two different crosslinking polymerization methods. One is UV curing of melt mixed APU/Na⁺-MMT mixtures; the other is coalescence polymerization of APU/Na⁺-MMT emulsions. These two kinds of composites had intercalated silicate layers of Na⁺-montmorillonite by insertion of PEO chains in APU chains, which was confirmed by X-ray diffraction measurement and transmission electron microscopy. These composite films also showed improved mechanical properties compared to pristine APU films. Al-

though the two kinds of nanocomposites exhibited the same degree of intercalation and were synthesized based on the same precursor chains, these nanocomposite films had the different mechanical properties. Nanocomposites synthesized using APU/Na⁺-MMT emulsions, having microphase-separated structure, had greater tensile strength than those prepared with melt-mixed APU/Na⁺-MMT mixtures. Location of intercalated Na⁺-MMT by PEO chains at the oil-water interface also could be confirmed by rheological behavior of the APU/Na⁺-MMT/water mixture. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3130–3136, 2003

Key words: polyurethane; clay; nanocomposite; microphase-separated structure

INTRODUCTION

Inorganic particles such as clay, SiO₂, and TiO₂ are widely used as reinforcement materials for host polymers. Among these inorganic materials, clay has been receiving special attention in the field of nanocomposites because of its submicroparticle size and intercalation properties. Nanocomposites containing intercalated clay particles exhibit improved moduli, decreased gas permeability, and enhanced heat resistance, which makes clay a useful filler in polymer polymeric composites.^{1–9}

The synthesis of clay/polymer nanocomposites has been done mainly by two approaches: (1) insertion of a suitable monomers and subsequent polymerization^{10–14} and (2) direct insertion of polymer chains using solution or melt mixing.^{15–18} For hydrophilic polymers, such polyelectrolytes and polyethylene oxide, these polymers or monomers can be easily inserted between silicate layers, forming intercalated or exfoliated clay composites, because those hydrophilic polymers are easily inserted between silicate layers containing the cations Na⁺ or Ca⁺.^{19–22} For organic nonpolar polymers, however, their insertion into montmorillonite should be done through modifying

the clay surface by the exchange of the interlayer cations' long-chain alkyl ammonium salts (lipophilization).^{1–3,14,21,23–25} The degree of intercalation, and properties of composites synthesized using lipophilized clay, strongly depend on the nature and the chain length of alkyl ammonium salts. So, most clay/polymer composites have been prepared using lipophilized clay through intercalative polymerization and melting mixing.

In this work, we present the synthesis of clay/amphiphilic polyurethane nanocomposites not using lipophilized clay but using a Na⁺-type montmorillonite. Since, as generally used, polyurethane (PU) does not have a hydrophilic moiety that can be inserted into a silicate layer of Na⁺-type montmorillonite, clay/PU composites had been synthesized through mixing PU with lipophilized clay or poly(ϵ -caprolactone)/clay composites.^{26–29} However, amphiphilic polyurethane (APU) precursor chains, used in this study, have hydrophilic segments (polyethylene oxide) and hydrophobic segments in the same chains, so we expect that polyethylene oxide in amphiphilic polyurethane precursor chains can be inserted between silicate layers; as a consequence, clay/PU composites can be synthesized without lipophilization. So, we propose a new synthetic method of clay/organic polymer composites based on amphiphilic polymer chains without using lipophilization. According to our previous reports,^{30–34}

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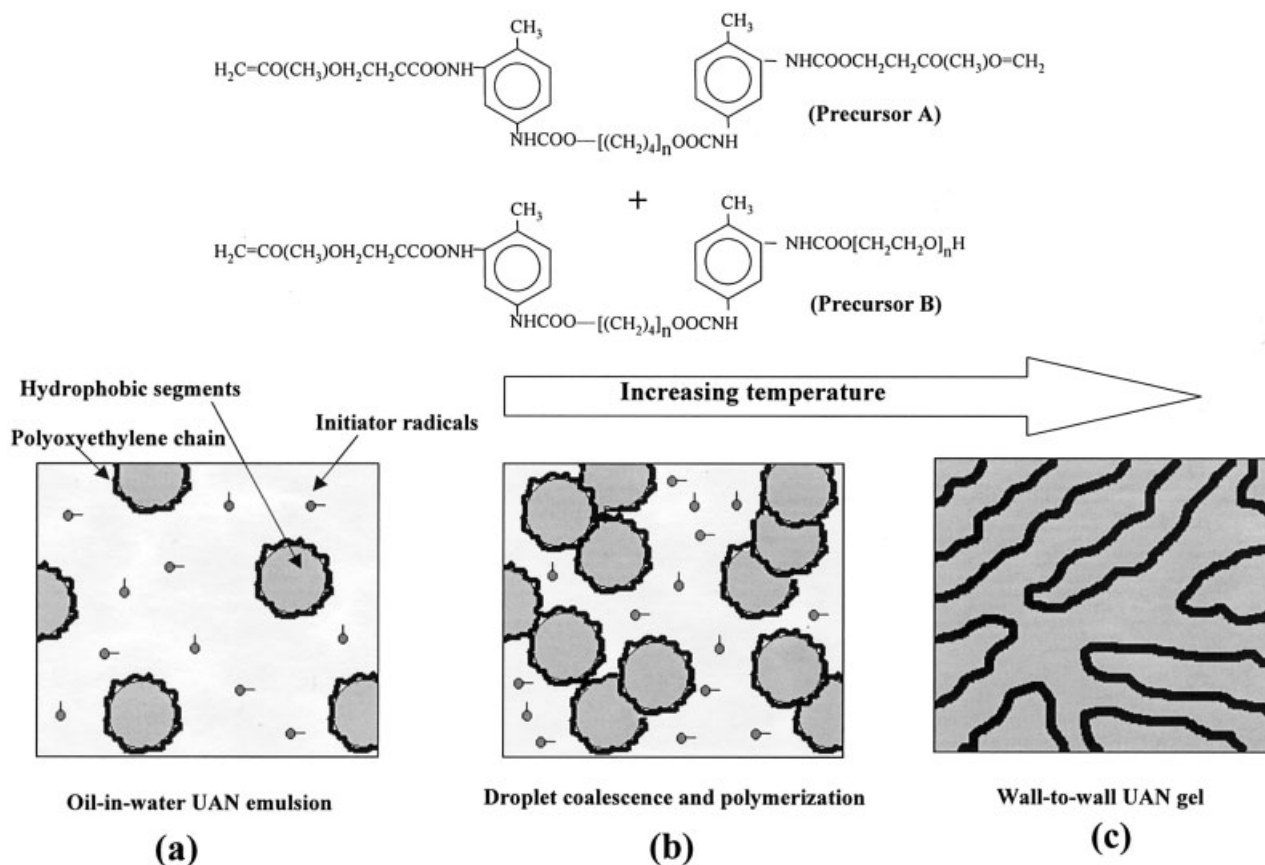


Figure 1 Schematic figures of structure of APU chains and gelation mechanism from O/W emulsion of UAN to wall-to-wall gels.

the degree of microphase separation in APU chains is largely changed by the types of solvent used, so crosslinked APU films synthesized using different solvents exhibited very different mechanical properties and swelling behavior. To demonstrate the effect of the microstructure of crosslinked APU films on the mechanical property of composite films, we used two different synthetic methods for the clay/APU composites. One is ultraviolet (UV) curing of APU/clay mixture without using any solvent, and the other is coalescence polymerization of APU/clay emulsions. We shall first describe morphological differences in the two types of amphiphilic polyurethane networks examined by atomic force microscopy (AFM) and their tensile property, and discuss it in relation to the different microstructures anticipated for these networks. Finally, the intercalated structure of clay/APU composites will be confirmed by X-ray scattering experiment and transmittance electron microscopy (TEM) measurement.

EXPERIMENTAL

Materials

Commercial sodium montmorillonite (Na⁺-MMT) produced by Southern Clay Products Inc. (USA), was used

as received. In the synthesis of APU precursor chains, poly(tetramethylene glycol) (PTMG, $M_w = 1000$, Hysung BASF), 2,4-toluene diisocyanate (TDI, Junsei Chemical Co., Japan), 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co., USA), and polyethylene glycol (PEG, $M_w = 600$, Aldrich Chemical Co.) were used. Potassium persulfate (KPS, Wako Pure Chemicals Co., Japan) and (1-hydroxycyclohexyl)-phenylmethanone (Ciba-Geigy Chemical Co., Switzerland, Irgacure 184) were used as a water-soluble initiator and photoinitiator, respectively. PTMG and polyethylene glycol (PEG, $M_w = 2000$) were dried and degassed at 80°C and 3–5 mm Hg for 2 days.

Synthesis of APU chains and APU networks^{30–34}

As illustrated in Figure 1, APU chains used in this study are a mixture of precursor chains A and B having both a polyethylene oxide (PEO) chain end group and reactive vinyl groups. These chains are synthesized by the reaction of PEG with the residual isocyanate groups of urethane acrylate chains through a three-step synthetic process. The molar ratio of PTMG/TDI/2-HEMA/PEG used in the synthesis of APU precursors was 2.0/1.0/1.2/0.8. The polystyrene

equivalent weight average molecular weight, obtained using the above formulation, is 4750 g/mol with a polydispersity of 1.7. Characterization of synthesized APU chains was carried out using nuclear magnetic resonance (NMR) and infrared (IR) spectra, as reported in our previously published articles.^{30–34}

APU networks were synthesized through crosslinking polymerization of APU chains at two different conditions. One was UV curing of the APU chain without the use of any solvents. The other was a rapid coalescence polymerization of APU emulsions. For the synthesis of UV-cured APU films, Irgacure 184 (3 wt %), photoinitiator and APU chains were first mixed and coated on the glass frame. UV curing of APU chains was carried out for 5 min (UV Lamp; 450W, Ace Glass Co.). For the preparation of crosslinked films, using APU emulsions,^{32,33} distilled deionized (DDI) water (15 g) was first slowly added into the melted APU precursor chains (6 g) while vigorous stirring (380 rpm) to obtain a very fine oil-in-water emulsion. Then, APU emulsions containing water-soluble initiator, KPS (0.5 wt %) were poured into silicone-packed molds and crosslink polymerized for 4 h at 65°C. In the course of polymerization, low-viscosity liquid, APU emulsions were converted to cheese-like solids. After the completion of polymerization, the APU gel films obtained were immersed in an acetone-water mixture for purification. The gelation mechanism of APU emulsions at elevated temperature was reported at our previous article in detail.³²

Synthesis of PU/clay nanocomposites

Clay/APU composite films were also prepared with two different methods. One was UV curing of bulk-mixed APU/clay mixture and the other was polymerization of APU/clay emulsions. For UV-cured composite films, synthesized APU chains and photoinitiator were first placed in a reaction vessel equipped with mechanical stirrer, and Na⁺-MMT was added and mixed for 12 h. The weight ratio of APU/Na⁺-MMT was 98/2, 97/3, and 95/5. Then these mixtures were drawn on glass plates and placed under reduced pressure to remove air bubbles. After that, these mixtures were cured in air by irradiating with a static UV lamp (450 watt UV lamp, Ace Glass Co.,) for 5 min and postcured at 60°C for 2 h.

For the synthesis of APU/clay composite films based on APU/clay emulsions, emulsification of APU/clay mixture was carried out prior to crosslinking polymerization. To prepare oil-in-water emulsions of APU/Na⁺-MMT mixtures, DDI water (16 g) was added dropwise into a mixture (7 g) of APU chains and Na⁺-MMT, in a reaction vessel equipped with a mechanical stirrer. Water-soluble initiator, KPS (0.005 g), was added to the APU/Na⁺-MMT emulsions, which were then poured into silicone-packed molds

(20 × 20 × 0.5 cm) to carry out crosslinking polymerization. Like APU emulsions, as temperature increased to 60°C, APU/Na⁺-MMT emulsions rapidly aggregated in the course of crosslinking polymerization; as a consequence, the oil-in-water emulsion becomes a wall-to-wall gel film. This film was washed with excess acetone and dried under reduced pressure for 1 day.

Measurements

AFM (Digital Instruments, Inc., NanoScope III) was used to examine the surface topology. AFM was operated with silicon probes in the tapping mode. The AFM-E piezoelectric scanner scanned a surface area 10 × 10 mm². The spring constant of the silicon cantilever was 50 N/m. In the tapping mode, the cantilever, on which the tip was mounted, was oscillated at a frequency of ca. 250 kHz.

X-ray scattering experiments for the dried composite films were conducted with a Rigaku D/Max-2200 (copper radiation, 40 kV, 100 mA, a nickel filter). Tensile properties were measured on an Instron machine according to ASTM D903-93. The test was carried out at 5 mm/min speed. Viscosity change with water concentration was measured by a Brookfield Synchroelectric Viscometer with spindle LVT no. 1-4 at constant temperature (35°C) and shear rate. A TEM (JEM 100CX, JEOL), applying an acceleration voltage of 100 kV, was used to clarify the nanostructure of composite films.

RESULTS

Figure 2 shows the X-ray diffraction (XRD) patterns for Na⁺-MMT clay as well as for Na⁺-MMT clay/PMUA composites prepared at different conditions. For Na⁺-MMT/APU composite films prepared using UV curing (curve c of Fig. 2), the *d*-spacing value of the silicate layer increased from 11 Å (Na⁺-MMT) to 32 Å (Na⁺-MMT/PU composites), indicating that the silicate layers of MMT clay are intercalated by the insertion of PEO chains in APU chains through just mixing of Na⁺-MMT with APU precursor chains in the bulk state.

As presented in Figure 3, tensile strength and elongation of Na⁺-MMT/APU composites is greater than pristine UV-cured APU film. As the weight fraction of Na⁺-MMT clay increases in composites, tensile strength and elongation of clay/APU composites increases at the same time.

Figure 4 represents tensile properties of the composite films and neat APU films prepared using APU emulsion and APU/Na⁺-MMT emulsion, respectively. Like UV-cured APU/Na⁺-MMT composite films, these composite films exhibited greater tensile properties than pristine APU film. As the weight frac-

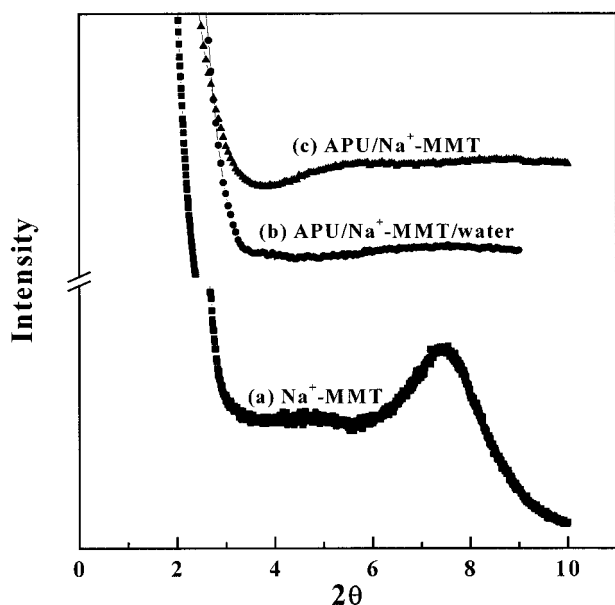


Figure 2 X-ray diffraction angle patterns of (a) \blacksquare -, Na⁺-MMT; (b) \bullet -, APU/Na⁺-MMT composites film synthesized with APU/Na⁺-MMT emulsions; (c) \blacktriangle -, UV-cured APU/Na⁺-MMT composites.

tion of Na⁺-MMT clay in the composite increases, the composite films showed an increase of tensile strength and decrease of elongation.

XRD patterns for composite films, synthesized through rapid coalescence polymerization of Na⁺-MMT/APU emulsions, also indicate that silicate lay-

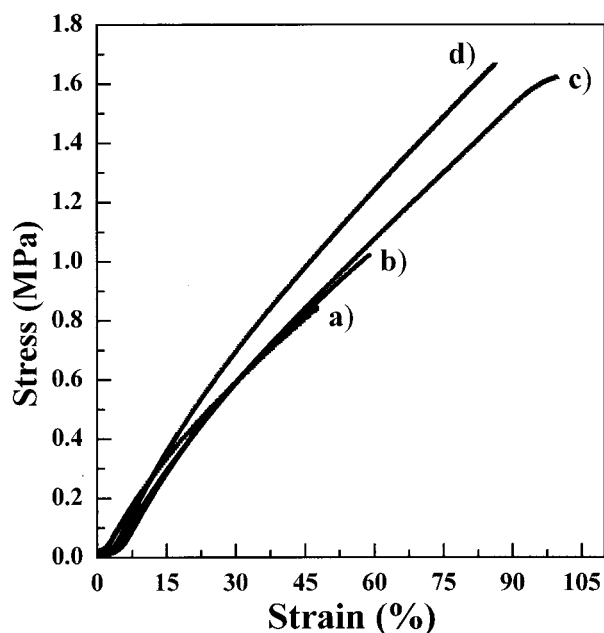


Figure 3 Stress-strain curves for (a) UV-cured APU film; (b) UV-cured APU/Na⁺-MMT (weight ratio of 98/2) composites film; (c) UV-cured APU/Na⁺-MMT (weight ratio of 97/3) composites film; (d) UV-cured APU/Na⁺-MMT (weight ratio of 95/5) composites films

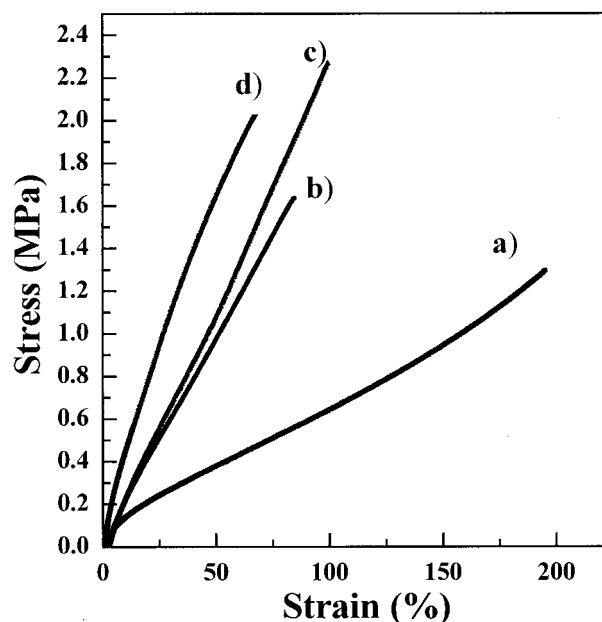


Figure 4 Stress-strain curves for APU films synthesized with APU/Na⁺-MMT emulsions; (a) 0 wt % of Na⁺-MMT; (b) 2 wt % of Na⁺-MMT; (c) 3 wt % of Na⁺-MMT; (d) 5 wt % of Na⁺-MMT.

ers of Na⁺-MMT were intercalated and dispersed in the APU matrix (curve b of Fig. 2). Even though these two kinds of composites were prepared using very different procedures (bulk polymerization and rapid coalescence emulsion polymerization), XRD results show that these two Na⁺-MMT/APU composites have the same degree of intercalation. This result indicates that intercalation of silicate layers is independent of the mixing medium such as bulk or aqueous phase.

Figure 5 presents a TEM of Na⁺-MMT/APU composites films. Dark line corresponds to the intercalated silicate layer dispersed in the APU matrix, indicating the intercalation of Na⁺-MMT by insertion of PEO chains in APU chains.

DISCUSSION

Effect of hydrophilic/hydrophobic microphase separation on mechanical properties

It has been reported that mechanical properties of crosslinked urethane acrylate films strongly depend on the degree of microphase separation between hard and soft segments or between hydrophilic and hydrophobic segments.³⁵⁻³⁸ The higher microphase separation between two different segments is, the greater are the tensile strength and elongation of crosslinked films, because phase-separated domains act as physical filler and strengthen association of each segments.

Pristine APU gel films exhibited very different mechanical properties, even though these APU films

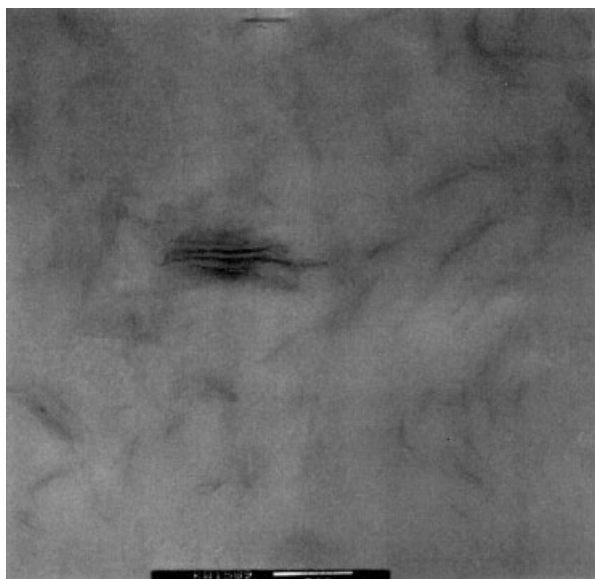


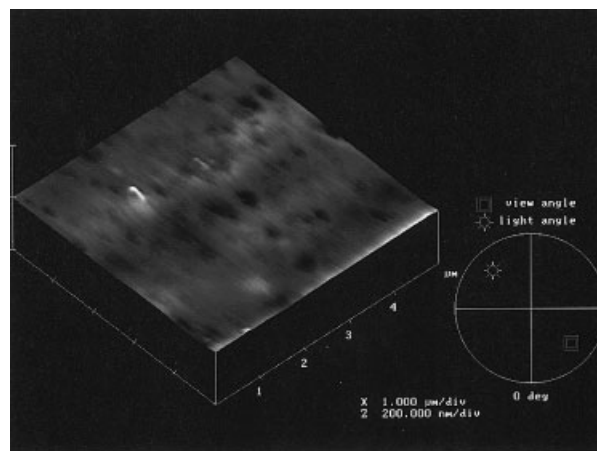
Figure 5 TEMs of APU/Na⁺-MMT composite film.

were synthesized using the same precursor chains. For tensile properties, film synthesized using coalescence polymerization of APU emulsion (curve a of Fig. 4) showed higher tensile strength and elongation than the one synthesized through UV curing of bulk APU chains (curve a of Fig. 3). This result may be due to the difference of microstructure between these two crosslinked films.

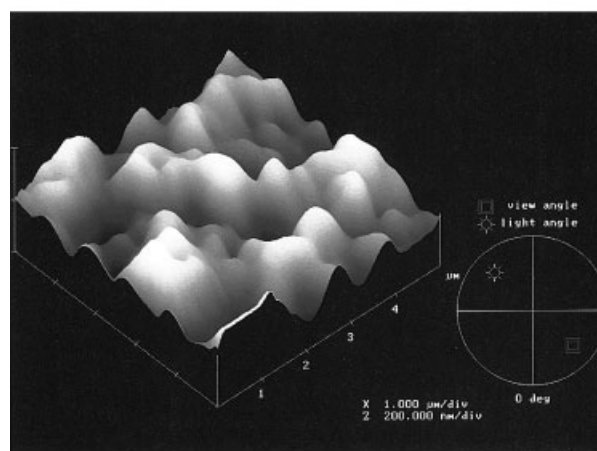
As illustrated at Figure 1, APU chains were comprised of PEO terminal groups (hydrophilic segment) and polytetramethylene glycol-based chains (hydrophobic segment). In the absence of water, the degree of phase separation between hydrophilic PEO chains and hydrophobic polytetramethylene oxide based segments is relatively small, so UV-cured APU films have a relatively homogeneous network structure. However, it can be expected that APU gel films, prepared using APU emulsions, have a highly microphase-separated network. On mixing APU chains with water, hydrophilic polyoxyethylene chains are separated from hydrophobic segments and orient toward the water phase to form oil-in-water (O/W) emulsion having nanosized APU particles [see Fig. 1(a)]. At elevated temperature, however, aggregation of APU nanoparticles and crosslinking polymerization occur simultaneously, because of the dramatic decrease in hydrophilicity of polyoxyethylene chains and polymerization of APU occurs at the same time by increasing temperature [see Fig. 1(b)]. As a consequence, APU emulsions are converted to wall-to-wall gel film having a highly microphase-separated network structure [see Fig.1(c)]. So, the higher tensile strength and elongation of APU gel films, synthesized using APU emulsions, can be interpreted as due to their highly microphase separated structure.

Figure 6 shows AFM image of the surface of two kinds of APU gel films. Even though these gel films were synthesized using the same APU chains, these films showed very different surface morphology depending on the preparation conditions. The surface image of APU gel film, prepared using O/W APU emulsions, is like that of immiscible polymer blends, whereas UV-cured APU gel film has an almost homogeneous flat surface. Also, the surface of APU gel film, synthesized using APU emulsion, is rougher [Surface mean roughness (R_a) = 42.034 nm] than that of UV-cured UAN gel [(R_a) = 1.386 nm] film. This result can support our assumption that APU gel film prepared using APU emulsions has a highly phase-separated network structure.

Unlike conventional polyurethane composites, which showed that the increase of tensile strength is accompanied by a sacrifice of elongation, UV-cured



(a)



(b)

Figure 6 Atomic force microscopy image of dried APU gel films (a) UV-cured APU gel film; (b) APU gel film synthesized with APU emulsions.

APU/Na⁺-MMT composite films showed, with the increase of tensile strength, improvement in elongation as well as with the increase of weight fraction of Na⁺-MMT in composite films. This result also can be interpreted as due to the increase of degree of hydrophilic/hydrophobic microphase separation through insertion of PEO chains of APU into silicate layers of Na⁺-MMT. In the course of APU/Na⁺-MMT mixing, PEO chains in APU chains are phase separated to insert a silicate layer of Na⁺-MMT, causing the increase in degree of hydrophilic/hydrophobic microphase separation. As a consequence, tensile strength and elongation of APU film are improved at the same time by dispersion of intercalated Na⁺-MMT phases in the APU matrix, as well as increased hydrophilic/hydrophobic microphase separation of APU networks.

In Figures 3 and 4, at the same weight ratio of Na⁺-MMT in the composite film, APU/Na⁺-MMT film prepared using APU emulsions exhibited higher tensile strength than the film prepared by UV curing of the APU/Na⁺-MMT mixture. Since these composite films were synthesized with the same precursor chain and Na⁺-MMT particles, this result may be due to the synergistic effect of microphase-separated structure and dispersion of intercalated Na⁺-MMT. In other words, the microphase-separated structure of APU/Na⁺-MMT film could be strengthened by intercalated silicate layers of Na⁺-MMT particles.

Unlike UV-cured APU/Na⁺-MMT composite films, the composite films, synthesized using Na⁺-MMT/APU emulsion mixtures, exhibited a decrease in elongation with the increase of weight ratio of Na⁺-MMT. This result can be also interpreted as due to the synergistic effect of microphase-separated structure and dispersion of intercalated Na⁺-MMT. Rigidity of the APU networks was enhanced too much by this synergistic effect, and as a consequence, elongation of the composite films was decreased by dispersion of intercalated Na⁺-MMT.

Location of Na⁺-MMT at W/O interface

It has been reported that clay can enhance stability of emulsions because clay can locate at a W/O interface, preventing droplets from aggregation and coalescence.³⁹⁻⁴¹ So, it can be thought that silicate layers of Na⁺-MMT particles are located at the W/O interface during emulsification of APU/Na⁺-MMT mixtures. In our previous articles, we reported that phase-separated PEO chains of APU chains formed interconnected domains, causing an increase of viscosity of APU/water mixtures.³² This peculiar behavior could be confirmed by monitoring change of viscosity of the APU/water mixture with the increase of weight fraction of water.³²

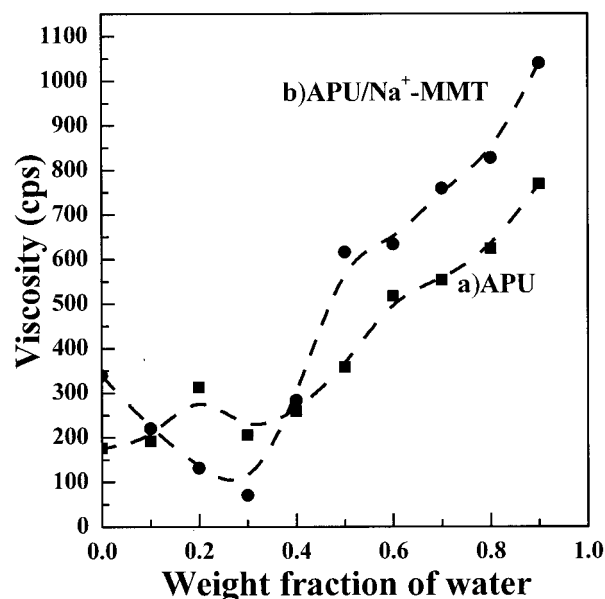


Figure 7 Viscosity plotted against water concentration at the same shear rate: (a) \blacksquare , APU; (b) \bullet , APU/Na⁺-MMT.

Figure 7 presents the change in viscosity of APU and APU/Na⁺-MMT mixtures as a function of volume fraction of water. Viscosity of APU chains at first decreased, due to the solubilization of water by PEO chains, then its viscosity increased with the increase of volume fraction of water, due to formation of associated PEO chains through hydrophilic/hydrophobic microphase separation. As the weight fraction of water increases, degree of microphase separation of PEO chains of APU chains is increased, to increase the formation of associated PEO domains, causing the increase nonviscosity of APU/water mixtures. A detailed mechanism for viscosity behavior of APU emulsions has been reported earlier.³²

At the same weight fraction of water, the APU/Na⁺-MMT mixture showed a greater increase of viscosity than for the APU/water mixture (curve b of Fig. 7). This result can be interpreted in terms of the location silicate layers of Na⁺-MMT at the W/O interface and insertion of PEO chains between silicate layers of Na⁺-MMT. On mixing of the APU/Na⁺-MMT mixture with water, hydrophilic/hydrophobic microphase separation and insertion between silicate layers of PEO chains occur at the same time. These microphase-separated PEO chains, containing intercalated silicate layers, strengthen the associated structure, causing a greater viscosity of the APU/Na⁺-MMT/water mixtures than the APU/water mixtures. Consequently, greater tensile strength of APU/Na⁺-MMT composite films prepared using APU emulsions can be explained by the strengthened microphase-separated structure of APU networks by location of intercalated silicate layer of Na⁺-MMT.

CONCLUSIONS

Polyurethane/clay nanocomposites have been synthesized using Na⁺-montmorillonite (Na⁺-MMT)/amphiphilic urethane precursor (APU) chains. XRD patterns showed that two kinds of nanocomposites had intercalated silicate layers of Na⁺-MMT in their matrix. Mechanical property of APU films can be improved by dispersed Na⁺-MMT particles, as well as induced hydrophilic/hydrophobic microphase separation of APU films. Since nanocomposites synthesized using APU/Na⁺-MMT emulsions had a highly microphase-separated structure, tensile strength of such a composite was greater than that of film prepared with melt-mixed APU/Na⁺-MMT mixtures. Rheological behavior of APU/Na⁺-MMT/water mixtures showed the location of intercalated Na⁺-MMT by PEO chains at the O/W interface, which also influenced mechanical properties of nanocomposite films.

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References

- Lebaron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl Clay Sci* 1997, 15, 11.
- Giannelis, E. P. *JOM (March)* 1992, 28.
- Giannelis, E. P. *Adv Mater* 1996, 8, 29.
- Ruiz-Hitzky, E.; Aranda, P. *Adv Mater* 1990, 2, 545.
- Ruiz-Hitzky, E.; Aranda, P. *Chem Mater* 1992, 4, 1395.
- Garces, J. M.; Moll, D. J.; Bicerano, J.; Fibiger, R.; McLeod, D. G. *Adv Mater* 2000, 12, 1835.
- Carrado, K. A.; Xu, L. *Chem Mater* 1998, 10, 1440.
- Ishida, H.; Campbell, S.; Blackwell, J. *Chem Mater* 2000, 12, 1260.
- Krishnamoorti, R.; Vaia, R. A.; Giannelis, E. *Chem Mater* 1996, 8, 1728.
- Laus, M.; Francescangeli, O.; Sandrolini, F. *J Mater Res* 1997, 12, 3134.
- Okamoto, M.; Morita, S.; Taguchi, H.; Kim, Y. H.; Kotaka, T.; Tateyama, H. *Polymer*, 2000, 41, 3887.
- Fournaris, K. G.; Karakassides, M. A.; Petridis, D. *Chem Mater* 1997, 11, 2372.
- Chen, G.; Liu, S.; Zhang, S.; Oi, Z. *Macromol Rapid Commun* 1999, 21, 746.
- Noh, M. H.; Lee, D. C. *J Appl Polym Sci* 1999, 74, 2811.
- Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. *Macromolecules* 1999, 28, 8080.
- Vaia, R. A.; Giannelis, E. *Macromolecules* 1997, 30, 7990.
- Burnside, S. D.; Giannelis, E. *Chem Mater* 1995, 1597.
- Fukushima, Y.; Okada, A.; Kawasumi, M.; Kurauchi, T.; Kamigaito, O. *Clay Miner* 1988, 5, 422.
- Wu, J.; Lerner, M. M. *Chem Mater* 1993, 5, 835.
- Hild, A.; Sequaris, J. M.; Narres, H. D.; Schwuger, M. *Colloid Surf A* 1997, 23-124, 515.
- Lan, T.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 2216.
- Carrado, K.; Xu, L. *Chem Mater* 1998, 10, 1440.
- Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater Res* 1993, 8, 1179.
- Wang, M. S.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 468.
- Shi, H.; Lan, T.; Pinnavaia, T. J. *Chem Mater* 1996, 8, 1584.
- Chen, T. K.; Tien, Y. I.; Wei, K. H. *Polymer* 2000, 41, 1345.
- Chen, T. K.; Tien, Y. I.; Wei, K. H. *J Polym Sci Polym Chem* 1999, 37, 2225.
- Wang, Z.; Pinnavaia, T. J. *Chem Mater* 1998, 10, 3769.
- Zilg, C.; Thonmann, R.; Mulhaupt, R.; Finter, J. *Adv Mater* 1999, 11, 49.
- Kim, J. Y.; Cohen, C. *Macromolecules* 1998, 31, 3542.
- Kim, J. Y.; Kim, C. H.; Yoo, D. J.; Suh, K. D. *J Polym Sci, Polym Phys* 2000, 38, 1903.
- Kim, J. Y.; Suh, K. D. *Colloid Polym Sci* 1996, 274, 1025.
- Suh, K. D.; Kim, J. Y.; Kim, J. L. *J Appl Polym Sci* 1997, 65, 821.
- Kim, J. Y.; Suh, K. D. *Macromol Chem Phys* 1996, 197, 2429.
- Kim, B. K.; Lee, K. H.; Jo, N. J. *J Polym Sci, Polym Chem* 1996, 34, 2095.
- Lee, K. H.; Kim, B. K. *Polymer* 1996, 37, 2251.
- Koshihara, K.; Hwang, K. S.; Foley, S. K.; Yarusso, D. J.; Cooper, S. L. *J Mater Sci* 1982, 17, 1447.
- Lin, S. B.; Tsay, S. Y.; Speckhard, T. A.; Hwang, K. K. S.; Jezerc, J. J.; Cooper, S. L. *Chem Eng Commun* 1984, 30, 251.
- Yan, Y.; Masilyah, J. H. *Colloid Surf A* 1993, 75, 123.
- Yan, N.; Masilyah, J. H. *Colloid Surf A* 1995, 96, 229.
- Yan, N.; Masilyah, J. H. *J Colloid Interf Sci* 1994, 168, 386.