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The property and formation mechanism of unsaturated polyester–layered silicate nanocomposite depending on the fabrication methods

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Abstract

The properties of unsaturated polyester (UP)/montmorillonite (MMT) nanocomposite greatly depend on the preparation procedure because of the chemical reactions and physical interactions involved. To investigate the properties and formation mechanism of UP/MMT nanocomposite, samples were prepared by two different mixing methods. The first method, simultaneous mixing, is similar to the method used for preparing the conventional unsaturated polyester and filler composite. The second method is the sequential mixing, a new approach for preparing unsaturated polyester–layered silicate nanocomposite. In the first step, pre-intercalates of the unsaturated polyester and MMT nanocomposites were prepared. In other words, mixture of the UP and organophillic-treated MMT are prepared in the first step; a styrene monomer was then added to the pre-intercalates of UP/MMT with varying mixing time. The structures of UP/MMT nanocomposite were investigated by X-ray diffraction and transmission electron microscopy. To investigate the formation mechanism of UP/MMT nanocomposite, dynamic mechanical thermal analysis, solution-rheometry and melt-rheometry were performed. The properties and formation processes depending on two methods are compared. These tests enable us to understand the mechanism of UP–silicate nanocomposite formation. Based on this mechanism, we have been able to increase the crosslinking density and the degree of dispersion in UP/MMT nanocomposite. © 2000 Published by Elsevier Science Ltd.

Keywords: Unsaturated polyester; MMT; Nanocomposite

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1. Introduction

Polymer nanocomposites, especially polymer–layered silicate nanocomposites, represent a rational alternative to conventionally filled polymers. Because of their nanometer scale dispersion, nanocomposites exhibit markedly improved properties when compared with the pure polymers or conventional composites [1]. Polymer–layered silicate nanocomposites possess several advantages such as: (a) a lighter weight compared to conventionally filled polymers, because high degrees of stiffness and strength can be realized with far less high-density inorganic material; (b) mechanical properties that are potentially superior to fiber-reinforced polymers; and (c) their outstanding diffusional barrier properties without requiring a multipolymer layered design [2].

In general, there are two methods of making nanocomposites, melt intercalation and in situ intercalative polymerization of monomers. Melt intercalation of high polymers is a powerful new approach for synthesizing polymer–layered silicate nanocomposite. This method is quite general and is broadly applicable to many commodity polymers, from essentially non-polar polystyrene, weakly polar PET to strong polar nylon [1]. The nanocomposites of thermoset polymer can be prepared by the in situ intercalative polymerization method [3]; phenol resins, epoxy resins [4,5] and unsaturated polyester resins are included in this category. These thermosetting nanocomposite materials are prepared by first swelling the various organo-modified montmorillonite (MMT) with the proper polymerizable monomers, followed by crosslinking reactions.

During swelling, the monomer diffuses from the bulk monomer into the galleries between the silicate layer. Depending on the degree of penetration of the monomer into the organo-layered silicate (OLS) structure, different types of nanocomposites can be obtained ranging from intercalated to exfoliated or delaminated. Polymer penetration resulting in finite expansion of the silicate layers produces intercalated hybrids consisting of well-ordered mutilayers composed of alternating polymer/silicate layers. Extensive polymer penetration, resulting in disorder and

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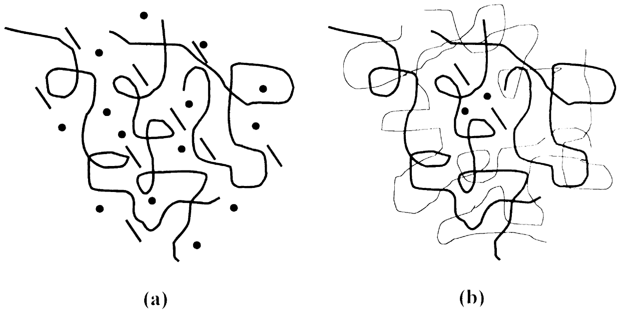

Fig. 1. Curing mechanism of UP: (a) styrene–UP solution mixture before curing; and (b) after curing. (dot, styrene monomer; bold line, uncured unsaturated polyester chain; line, polymerized-styrene chain connecting the unsaturated points of unsaturated polyester).

eventual delamination of the silicate layer, produces exfoliated hybrids consisting of individual nanometer-thick silicate layers suspended in the polymer matrix [6].

Unsaturated polyesters (UP) can be dissolved in a polymerizable monomer such as styrene monomer. A UP is a long-chain linear polymer containing a number of reactive double bonds. The styrene monomer, which also contains C and C reactive double bonds, acts as a curing agent by bridging adjacent polyester molecules at their unsaturation points. During the styrene–unsaturated polyester crosslinking copolymerization, the initiator decomposes and creates free radicals in the system. The free radicals grow and form long-chain molecules by connecting styrene monomers and unsaturated polyester molecules by both inter- and intramolecular reactions. A schematic of the growth of free radicals is shown in Fig. 1 [7].

Due to the typical curing mechanism of unsaturated polyester, the styrene monomer, unsaturated polyester linear chain and organophillic-treated MMT exist together in the nanocomposite formation system. Consequently, the behaviors of each component in the nanocomposite formation system are very important. Although research has shown experimental evidence [8] to support the formation of UP/clay nanocomposite, there have been no studies explaining the mechanism of UP/MMT nanocomposite formation. In this study, we report the properties and formation mechanism of unsaturated polyester nanocomposite by several experiments.

2. Experimental

2.1. Materials

Two different kinds of MMT were used. The Kunimine Co., provided the purified MMT under the trade name Kunipia-F. This MMT was treated in our lab with dodecyl ammonium bromide by accepted procedures [9,10]. First, 20 g of MMT was dispersed into 400 ml of water. Dodecyl methyl ammonium bromide (8.82 g) was then dissolved in 100 ml of water and in 100 ml of ethanol. It was poured into the MMT–water solution with vigorous stirring for 5–6 h at 50–70°C. The precipitates were collected and redispersed for 1 h. The solution was then filtered and freeze-dried to yield an organophilic MMT.

Southern Clay Products Inc, USA, supplied organophilic-treated MMT under the trade name of Cloisite®20A. The MMT-20A contained dimethyl dihydrogenated tallow ammonium as an organic modifier. Hydrogenated tallow is composed of C18 of 65 wt%, C16 of 30 wt% and C14 of 5 wt%.

The unsaturated polyester resin was synthesized using polyol from the glycolysis of PET. The synthetic procedure was as follows [11]: 70 g (0.365 mol/repeating unit) of PET pellets were added to 1.84 mol of propylene glycol (PG) so that the molar ratio of PET repeating unit to PG was 1:5.04. This mixture, together with 0.5 wt% zinc acetate based on PET weight as transesterification catalyst, was charged into a glass reactor. The reactor was heated for 3 h at 175°C, and then held for 5 h at 225°C. The reaction was carried out under reflux in a nitrogen atmosphere. After 8 h, the contents in the reactor were allowed to cool to room temperature. The unsaturated polyester resins were prepared by reacting the glycolized products with maleic anhydride at the fixed value of the glycolized products including free glycol to a maleic anhydride molar ratio of 1.1. The polyesterification reaction was carried out in a glass reactor equipped with a partial condenser and stirring assembly. The reactants were heated to 150°C and then held for about 24 h to complete the reaction.

The styrene monomer was obtained from Junsei Chemicals. To initiate polymerization, 1 wt% of a free-radical peroxide initiator, benzoyl peroxide (BPO) from Fluka AG, was added.

2.2. Preparation of unsaturated polyester silicate nanocomposite

There are two procedures for manufacturing the UP/MMT nanocomposite. The first step is the mixing process. In other words, the UP linear chains are mixed with styrene monomers and layered silicate. The next step is the curing process. The crosslinking reaction starts by decomposing the initiators in the curing process.

In this experiment, two different ways of mixing were used. The first, simultaneous mixing, has been used to prepare the conventional unsaturated polyester and filler composites. The unsaturated polyester chains, styrene monomers and organophillic-treated MMTs were simultaneously mixed for 3 h at 60°C. The second method, sequential mixing, is a new approach for preparing unsaturated polyester–layered silicate nanocomposites. In the first step, the pre-intercalates of the unsaturated polyester and MMT nanocomposites were prepared. In other words, the mixture of the UP and organophillic-treated MMT were prepared in the first step; then the styrene monomer was added to these pre-intercalates of UP/MMT, varying mixing

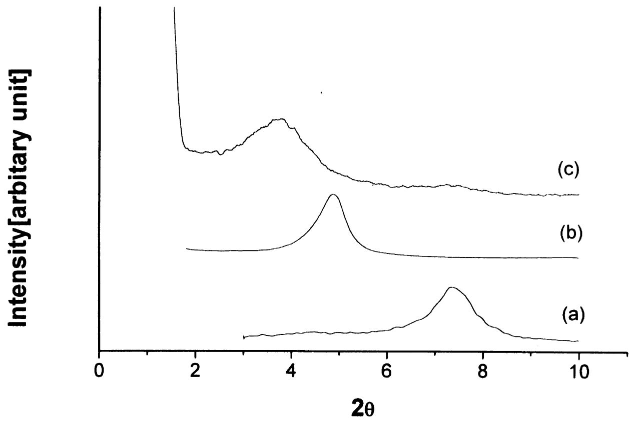

Fig. 2. XRDs of MMTs: (a) virgin MMT; (b) dodecyl ammonium-treated-MMT; and (c) dimethyl dihydrogenated tallow ammonium-treated MMT.

times of 15, 30, 60 and 180 min at 60°C. All UP–MMT–styrene mixtures contained 0.01 wt% hydroquinone as an inhibitor to prevent reaction in the mixing stage.

Finally, all mixtures were cured at 80°C for 3 h. Post-curing was also performed for 4 hours at 120°C. All UP/MMT nanocomposites contained UP of 55 wt%, styrene monomer of 40 wt% and MMT 5 wt%.

2.3. Measurements

X-ray diffraction (XRD) patterns were obtained by using a Rigaku X-ray diffractometer equipped with CuKα radiation and a curved graphite crystal monochromator. Samples were prepared by applying the pre-intercalated mixture and nanocomposite of UP/MMT in sheet form on a slide. All XRD data were collected by an X-ray generator equipment with $\lambda = 1.5406$ Å. Bragg's law, $\lambda = 2d \sin\theta$, was used to compute the crystallographic spacing, d.

Dynamic mechanical thermal analysis (DMTA) of all unsaturated polyester noncomposite materials were performed on a Rheometric Scientific™ dynamic mechanical thermal analyzer with the dual cantilever bending mode at the condition of 1 Hz, 0.01 strain and −50 to 300°C range. Samples were prepared approximately 30 mm long, 10 mm wide and 1.2–2 mm thick.

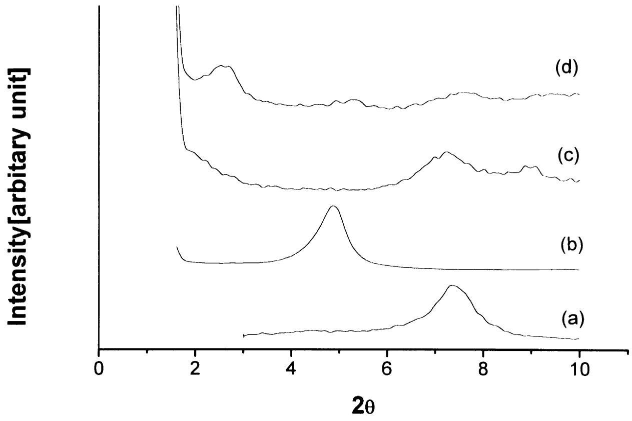

Fig. 3. XRD data for unsaturated polyester with dodecyl ammonium-treated silicate nanocomposite system. Composites were prepared using the simultaneous mixing method: (a) virgin MMT; (b) dodecyl ammonium-treated MMT; (c) virgin MMT and UP nanocomposite; and (d) dodecyl ammonium-treated MMT and UP nanocomposite.

Microscopic investigation was performed with a JEOL 2000EX transmission electron microscope (TEM) with acceleration voltage of 100 kV.

G_{N0} was measured using an Advanced Rheometric Expansion System (ARES) melt-rheometer operated at an oscillating torsion frequency of 1 Hz. G_{N0} is defined as the storage shear modulus measured after the storage shear modulus approached a specified value above the glass transition temperature. Storage shear modulus was measured at a strain amplitude of 0.01%. The sample was heated at 5°C/min with a stabilization time of 2 min before any measurement. All measurements were performed within the range 80–220°C using rectangular-shaped samples ($45 \times 10 \times 1.6$ mm^3).

The transient shear experiments for monitoring the mixing behavior of UP–styrene solution mixture were performed using a Couette cell type rheometer (ARES solution rheometer). The solution mixtures under investigation were placed in the gap between the stationary outer measuring cup surrounded by the temperature controlling bath and the rotating measuring bob. All experiments were performed at 60°C. The diameters of the cup and bob were 34 and 32 mm, respectively (i.e. gap size was 1 mm).

3. Results and discussion

XRDs of MMTs revealed different peaks with the surface modifiers shown in Fig. 2. The MMT showed a peak at 7.3°, corresponding to the (001) plane. The gallery spacing of both MMT-D (a dodecyl ammonium bromide-treated silicate) and MMT-20A (a dimethyl dihydrogenated tallow-treated silicate) is broadened. The interlayer spacing of the MMT-20A is larger than that of the MMT-D; this is because the MMT-20A contains the two longer alkylammonium chains as organic modifiers. The peaks for MMT, MMT-D and MMT-20A are shown at 7.3, 4.7 and 3.5°, respectively. These 2θ values correspond to interlayer spacing of 11.9, 18.4 and 24 Å, respectively.

Fig. 3 shows the XRD data for UP with a dodecyl ammonium bromide-treated silicate (MMT-D) nanocomposite system. This nanocomposite system was prepared using the simultaneous mixing method, which is generally used as a mixing method for conventional UP composite systems. Next, curing and post-curing were performed. Fig. 3 shows the absorption of the UP–styrene monomer from the change of the (001) spacing of the organiophillic-treated MMT layers. The MMT gallery spacing broadens from 18.40 to 31.53 Å. It is possible that the organophilic treatment of MMT facilitated this by increasing the wettability of the MMT [9,12]. However, the UP–styrene monomer did not intercalate between the layers of untreated MMT.

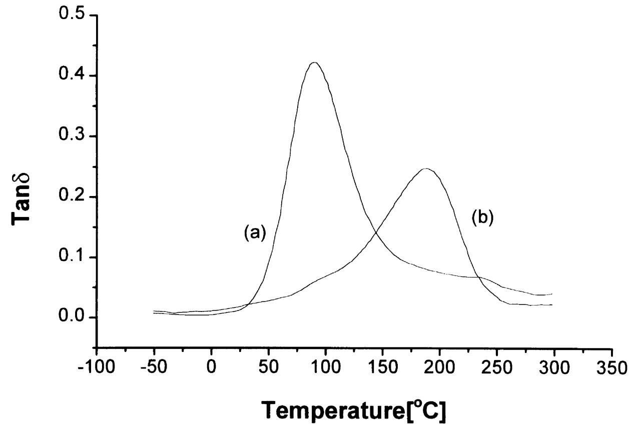

Fig. 4. tan δ of: (a) UP–dodecyl ammonium-treated silicate nanocomposite; and (b) cured virgin UP.

A sinusoidal load was applied to the sample and the real, E', and imaginary, E'', moduli were measured by DMTA. The ratio E''/E' is defined as the loss tangent or damping tan δ, which is taken as the glass transition temperature at its peak point. Fig. 4 shows tan δ of the UP–dodecyl ammonium-treated silicate nanocomposite and virgin UP-cured resin.

Generally, the thermal transitions of thermoplastic polymer/MMT nanocomposites are manifested more weakly than those of pure thermoplastic polymers [13]. DSC measurements on intercalated PEO/MMT hybrid indicate the absence of any thermal transitions corresponding to the glass or the melting transition of PEO [14]. It has been reported that glass transition of the thermoset polymer/MMT nanocomposites is higher than that of the pure thermoset polymer, for example, the glass transition of epoxy/MMT nanocomposite was elevated with an increasing MMT content [15].

However, Fig. 4 shows that the T_g of UP/MMT-D nanocomposite was lower than that of the pure cured UP. It is known that the primary factor affecting the T_g of the cured UP is the crosslinked density in the same UP resin [16,17]. Therefore, it can be concluded that UP/MMT-D nanocomposite has low crosslinking density.

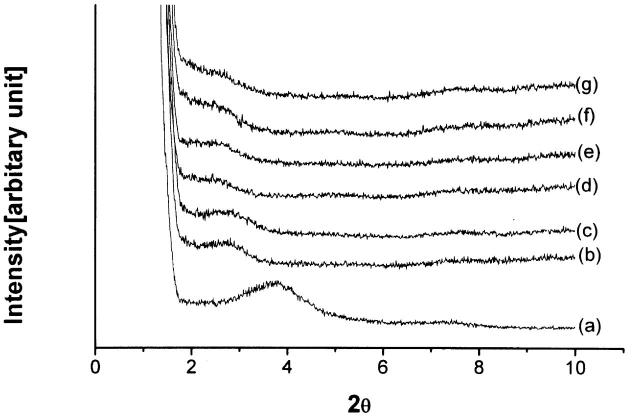

Fig. 5. XRD data of UP/MMT-20A system. This nanocomposite system was prepared using both simultaneous mixing and sequential mixing methods: (a) MMT-20A; (b) UP/MMT-20A nanocomposite using simultaneous mixing method. UP/MMT-20A nanocomposite using sequential mixing method varying mixing times of: (c) 0 min (pre-intercalates); (d) 15 min; (e) 30 min; (f) 60 min; and (g) 180 min.

As mentioned in the previous section, UP/MMT nanocomposites are formed by the following sequences. UP chains, styrene monomers and organic organophilic MMTs (O-MMTs) coexist in the mixing medium. The styrene monomers diffuse into the gallery of the O-MMTs much faster than the UP chains. Solvents and monomers have diffusion coefficients on the order of 10^{-5} (cm^2/s), while polymers have the diffusion coefficient on the order of 10^{-7} (cm^2/s) [18,19]. If the curing reaction starts in these conditions, the styrene homo-polymer is produced primarily in the interlayer of the O-MMT and the crosslinking density decreases inside and outside of the O-MMT, because the styrene monomers are concentrated on the interlayer and styrene monomers are insufficient for the crosslinking the reactive double bonds of the unsaturated polyester. For this reason, the UP/MMT nanocomposite manufactured by the conventional method has a lower T_g than that of the pure cured UP.

To verify this assumption, a new fabrication method for the UP/MMT nanocomposite was applied, and the resulting UP/MMT nanocomposite compared to conventional nanocomposites.

Fig. 5 shows XRD data for UP with a dimethyl dihydrogenated tallow-treated silicate (MMT-20A) system. Nanocomposites were prepared using either the simultaneous mixing method (a conventional mixing method) or the sequential mixing method (a novel mixing method). The UP/MMT-20A nanocomposite made from the simultaneous method shows a weak and a broad peak. This is to be expected if the silicate layers have been intercalated by polymer molecules during the mixing and crosslinking reaction of the UP. The pre-intercalate of the UP/MMT-20A nanocomposite prepared by intercalating UP chains into the O-MMTs without styrene monomers, i.e. the first stage of the sequential mixing method, shows the similar interlayer spacing and degree of the intercalation without a curing reaction. The peaks gradually disappear and the intensity of the XRD shows gradual increase in the low 2θ region with mixing time, so the peak for the UP/MMT-20A nanocomposite using the sequential mixing method with mixing time of 180 min almost disappears. The degree of intercalation of the UP/MMT-20A nanocomposite using the sequential mixing method increased with mixing time in Fig. 5.

More direct evidence for the formation of a nanocomposite is provided by TEM of an ultramicrotomed section. The TEM images in Fig. 6 display individual silicate layers apparent as dark lines. There are some irregular dispersions of the silicate layer. Some particles of the silicate layers maintained their original ordering, while some were exfoliated. As shown in Fig. 6, the TEM image of the

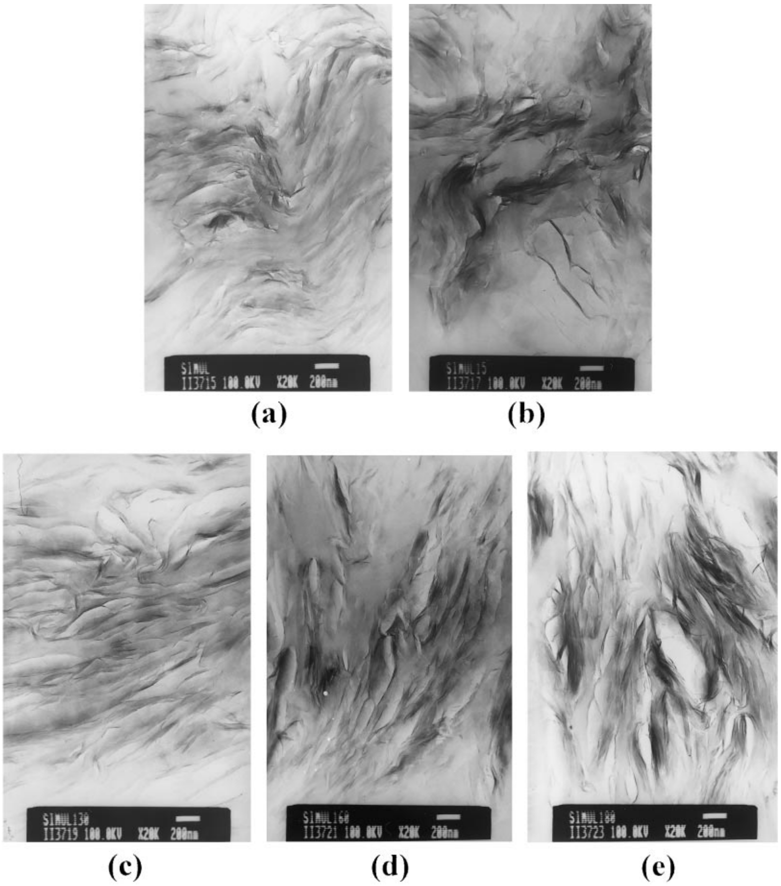

Fig. 6. TEM images of UP/MMT-20A nanocomposites using both mixing methods: (a) UP/MMT-20A nanocomposites using simultaneous mixing method. UP/MMT-20A nanocomposites using sequential mixing method, varying mixing times of: (b) 15 min; (c) 30 min; (d) 60 min; and (e) 180 min.

UP/MMT-20A composite, prepared by both mixing methods, indicates that the separation between the dispersed plates is irregular and in the broad range of 30–200 Å. The partially exfoliated and well-dispersed portion of the UP/MMT-20A composite manufactured by the sequential mixing method increases with mixing time. In the UP/MMT-20A nanocomposite using simultaneous mixing method, the dispersion of the silicate layers is higher than

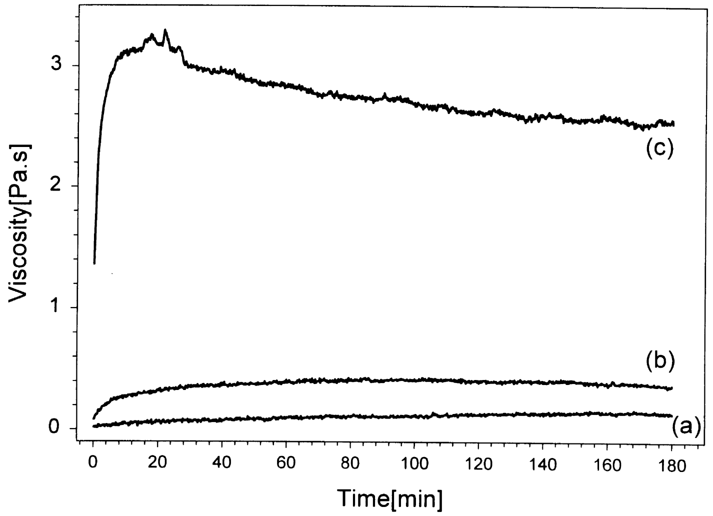

Fig. 7. Transient shear viscosity behaviors of UP/MMT-20A in mixing stage: (a) unfilled UP/styrene monomer solution mixture. UP/styrene monomers/MMT-20A solution mixture using: (b) simultaneous mixing; and (c) sequential mixing.

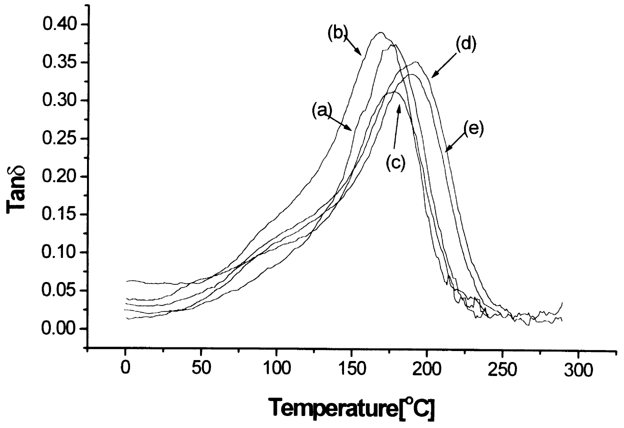

Fig. 8. Results of DMTA on samples prepared by both simultaneous and sequential mixing methods: (a) UP/MMT-20A nanocomposites using simultaneous mixing, and UP/MMT-20A nanocomposites using sequential mixing, varying mixing times of: (b) 15 min; (c) 30 min; (d) 60 min; and (e) 180 min.

in the nanocomposite prepared with the sequential mixing method with a mixing time of 15 min; however, dispersion is lower than in those using sequential mixing method.

The transient shear viscosity behaviors are shown in Fig. 7. This experiment was performed at the mixing stage before the curing reaction. For the stability of the mixture, 10 min after the solution that contains the styrene monomer, UP linear chains and organophilic MMT were mixed, and the transient shear viscosities were measured for the mixture. The viscosities of the both nanocomposite systems were higher than that of the unfilled UP system, because the nanocomposite system contains the O-MMTs of 5 wt%. Increases in viscosity were observed in the all nanocomposite systems, because the styrene monomer and the UP linear chains intercalate into the MMT interlayer from the solution mixture in the early mixing stage.

It is noteworthy that the viscosity of the solution mixture of the UP–styrene monomer depends on the UP–styrene monomer composition in the matrix and the volume fraction of the MMT intercalated with UP and styrene. The greater the amount of styrene monomer in the matrix, the lower the viscosity that is presented. The viscosity increase with the simultaneous mixing method was much higher and faster than that of the sequential mixing method; this implies that more styrene monomers diffuse into the relative empty gallery of the silicate and more quickly than in the simultaneous mixing method. On the other hand, the viscosity of the sequential mixing method system gradually increased. Because the styrene monomers diffuse into the gallery filled with the intercalated UP linear chains, the styrene monomers diffuse into the gallery more slowly and to a lesser extent. It is thought that the decrease of the viscosity after about 30 min is due to the orientation and aggregation of the primary silicate particle.

DMTA was performed on the cured samples prepared by the both simultaneous and sequential mixing methods. These experimental results are presented in Fig. 8. The T_gs of the cured UP/MMT-20A nanocomposites using sequential mixing increase with mixing time with styrene monomers. Finally, the T_g of the UP/MMT-20A nanocomposite was shifted to 190°C, which corresponds to the cured pure UP. This is because of the diffusion of the styrene monomers into the interlayer increase with mixing time. Hence, the styrene monomers, which act as a curing agent, are much more dispersed inside and outside of the silicate layers as mixing time increases, the crosslinking reaction takes place homogeneously inside and outside of the silicate layers, and the crosslinking density reach that of the cured pure UP. The T_g of the UP/MMT-20A nanocomposite using simultaneous mixing is higher than that of the composite using sequential mixing with a mixing time of 15 min, but lower than others using sequential mixing.

To determine the crosslinking density of the samples, we used a method based on the theory of rubber elasticity [20].

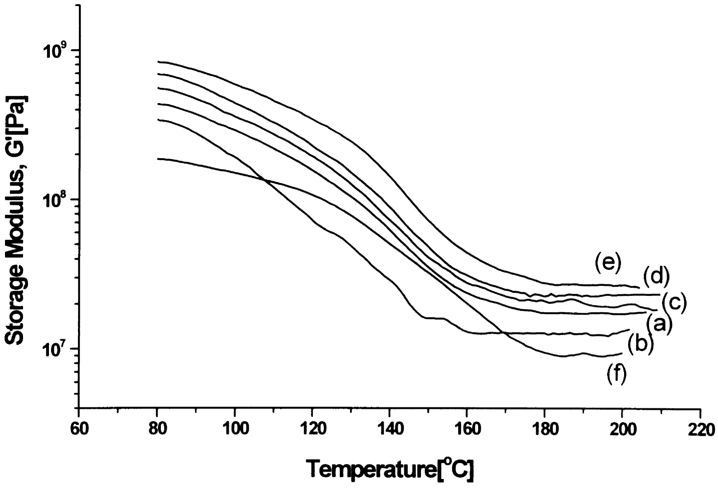

Fig. 9. Storage shear modulus, G', of the cured UP/MMT-20A: (a) UP/MMT-20A nanocomposites using simultaneous mixing; UP/MMT-20A nanocomposites using sequential mixing with varying mixing times of: (b) 15 min; (c) 30 min; (d) 60 min; and (e) 180 min. (f) The cured UP without clay.

The number-average molecular weight between crosslinks is correlated with the rubber plateau modulus [21]:

$$M_C = \frac{\rho R T}{G_{N0}} \tag{1}$$

where ρ is density at temperature T, and R is the universal gas constant. Thus crosslinking density (ν_C) can be calculated using Eq. (2), since

$$\nu_C = \frac{\rho N_A}{M_C} \tag{2}$$

where N_A is Avogadro's number.

In Fig. 9 the storage shear modulus (G') of the cured UP/MMT-20A and unfilled UP are plotted as a function of temperature. The storage modulus of UP/MMT nanocomposite is higher than that of the unfilled UP. Increase in the storage modulus is observed in the all nanocomposite system, because MMT plays a role in nanoscale reinforcement in the UP matrix. As we mentioned in the previous section, the primary factor in the T_g of the cured UP is the crosslink density. Crosslinking density is proportional to the rubber plateau modulus (G_{N0}) from Eqs. (1) and (2). The value of the rubber plateau modulus (G_{N0}) increases with increased mixing time in sequential mixing. Hence, the crosslinking density also increases with increased mixing time in sequential mixing. While the crosslinking density of UP/MMT-20A nanocomposite using simultaneous mixing shows the lowest value, excepting the nanocomposite using sequential mixing with mixing time of 15 min, all UP/MMT-20A nanocomposites demonstrate a rubbery plateau after passing the glass transition temperature. As expected, the trend of the crosslinking density is concurrent with the T_g behavior.

4. Conclusions

The structures of UP/MMT nanocomposite were investigated by XRD and TEM. To investigate the formation mechanism of UP/MMT nanocomposite, DMTA, and solution rheometry and melt rheometry were used. These results enable us to understand the mechanism of UP–silicate nanocomposite formation. The styrene monomer moves more easily than uncured UP chains. This may generate higher styrene monomer concentration in the MMT gallery than in any other part in a simultaneous mixing system. If polymerization occurs in these conditions, the total crosslinking density of the sample decreases due to the low concentration of styrene in uncured UP linear chains. According to this formation mechanism of UP–silicate nanocomposite systems, such situations are also easily understandable in the sequential mixing method. The styrene monomer diffuses to the gallery of the MMT intercalated with UP to an extent as time goes on. Therefore, it is thought that crosslinking density and T_g of UP–silicate nanocomposite increase to some extent. Hence, the styrene monomers, which act as a curing agent, are much more dispersed inside and outside of the silicate layers as mixing time increases. Therefore, the crosslinking reaction takes place homogeneously inside and outside of the silicate layers, and crosslinking density reaches the degree of crosslinking density of the cured pure UP.

These nanocomposite formation mechanisms and manufacturing processes should be carefully considered when nanocomposites are manufactured using several kinds of polymers or monomer–polymer pairs whose molecular weight differences are large. For example, there are multi-intercalating nanocomposite systems, nanocomposite systems using compatibilizers and multicomponent polymer nanocomposite systems.

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References

[1] Giannelis EP. Appl Organomet Chem 1998;12:675–80.
[2] Kirshnamoorti R, Vaia RA, Giannelis EP. Chem Mater 1998;8:1728–34.
[3] Akelah A, Moet A. J Mater Sci 1996;31:3589–96.
[4] Lan T, et al. Chem Mater 1995;7:2144–50.
[5] Lee DC, Jang LW. J Appl Polym Sci 1998;68:1997–2005.
[6] Vaia RA, Giannelis EP. Macromolecules 1997;30:7990–9.
[7] Yang YS, Lee LJ. Polymer 1998;29:1793–800.
[8] Kornmann X, et al. Polym Engng Sci 1998;38:1351–8.
[9] Hasegawa N, et al. J Appl Polym Sci 1998;67:87–92.
[10] Oh Y, et al. J Polym Sci, Part B: Polym Phys 1998;36:789–95.
[11] Suh DJ, et al. Polymer 2000;41:461–6.
[12] Kawasumi M, et al. Macromolecules 1997;30:6333–8.
[13] Granick S, editor. Polymers in confined environments Berlin: Springer, 1999.
[14] Vaia RA, et al. J Polym Sci, Part B: Polym Phys 1997;35:59–67.
[15] Kelly P, et al. J Mater Sci 1994;29:2274–80.
[16] Ma SC, et al. Polym J 1993;25:897–907.
[17] Yu TL. Polym J 1996;28:965–9.
[18] Welty JR, et al. Fundamentals of momentum, heat, and mass transfer. 3rd ed. New York: Wiley, 1984.
[19] Brandrup J, Immmergut EH. Polymer handbook. 3rd ed. New York: Wiley, 1989.
[20] Ferry JD. Viscoelastic properties of polymers. New York: Wiley, 1980.
[21] van der Sanden MCM, Meijer HEH. Polymer 1993;34:5063–72.