

Effect of Reactive Diluents on Properties of Unsaturated Polyester/Montmorillonite Nanocomposites

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ABSTRACT: Unsaturated polyester (UP)/montmorillonite (MMT) nanocomposite was prepared by using hydroxypropylacrylate (HPA) as a reactive diluent instead of conventional styrene monomer and the effect of polarity of reactive diluent on properties of nanocomposite was investigated. X-ray and mechanical test data indicated that mixing for an extended period of time is essential to enhance the physical properties of nanocomposites in the UP/Cloisite

6A system. This was attributed to the high polarity of HPA that may disturb the preintercalation of UP resin into the galleries of MMT. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 238–242, 2004

Key words: unsaturated polyester; montmorillonite; nanocomposites; diluent effect; reactive processing

INTRODUCTION

Recently, polymer–clay nanocomposites have received much attention because of their unique and enhanced physical and mechanical properties compared with those of conventional macroscale composites.¹ In our previous study, it was found that the mixing time of all uncured components does not influence the degree of dispersion of montmorillonite (MMT) in unsaturated polyester (UP) resin. However, the chemical interaction between MMT and UP resin impedes improvement of morphology of the nanocomposite. This may be attributed to the hydroxyl group of the organic modifier, residing in galleries of MMT, that causes hydrogen bonding with hydroxyl and/or carboxylic end group of UP resin, a tendency that has already been shown in several polymer nanocomposites using the melt intercalation method.²

The raw materials used for the preparation of UP resin can be divided into four groups: unsaturated acids, saturated acids, diols, and vinyl monomers. In some cases, acrylic monomers have also been used for reactive diluents in place of common styrene monomer in specific applications.³ The comonomer of acrylics such as methylmethacrylate and styrene allowed the control of thermal shrinkage of UP resin in the curing stage.⁴ However, because of the possibility that these reactive diluents may affect the preparation and various properties of the nanocomposite, further

study of the correlation between properties of diluents and the nanocomposite is required.

In this study, we attempted to prepare a UP/MMT nanocomposite using hydroxypropylacrylate (HPA) as highly polar reactive diluent, and then the effect of polarity of diluent on various properties of the nanocomposite was investigated.

EXPERIMENTAL

Materials

The UP resin was synthesized by direct esterification of three comonomers (obtained from Duksan Chemicals, Seoul, Korea): maleic anhydride, phthalic anhydride, and propylene glycol.³ The crosslinking reaction was carried out by free-radical mechanism between the reactive diluents and the carbon–carbon double bonds in the UP molecules, finally leading to the formation of a three-dimensional thermoset polymer. HPA was supplied by Aldrich Chemicals (Milwaukee, WI). Benzoyl peroxide was provided by Acros Chemicals (Morris Plains, NJ) and used as thermal initiator. *N,N*-Dimethyl-*p*-toluidine was purchased from Aldrich Chemicals and used as accelerator for the ambient-temperature curing reaction.⁵ The concentration of the accelerator was 0.1 phr.

The organically modified MMTs, Cloisite 30B (CEC = 90 meq/100 g) and Cloisite 6A (CEC = 140 meq/100 g), were supplied by Southern Clay Inc. Methyl tallow bis-2-hydroxyethyl (MT2EtOH) ammonium salt was a modifier to Cloisite 30B, where hydrogenated tallow (HT) is predominantly an octadecyl chain with smaller amounts of lower homologs (~ 65% C18; ~ 30% C16; ~ 5% C14). Cloisite 6A is known to contain a remark-

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TABLE I
Curing Behaviors of UP/Cloisite 30B Nanocomposites

MMT content (wt %)	Conversion (%)		Gel time (min)	
	30 min	120 min	30	120
0	86	87	15.2	16.7
1	86	85	15.8	16.1
3	86	87	15.7	15.4
5	87	87	16.2	15.4

ably high density of organic modifier, dimethyl dihydrogenated tallow (2M2HT) ammonium salt.

In a 1000-mL beaker were placed three comonomers. The relative compositions of UP resin calculated were PG : PA : FA = 1 : 0.3 : 0.5 by molar ratio. This solution was heated at 100°C for 1 h without agitation. After preheating of comonomers, the solution was stirred vigorously at 160°C for 1 h and at 190°C for 3 h. The synthesized UP resin was held for a few hours at 200°C, followed by acid value measurement. The synthesis was considered complete if the acid value reached 35, after which the UP resin was moved to another beaker at room temperature.

The NMR peak for maleic anhydride almost disappeared after the reaction, attributed to the extensive isomerization of maleate to fumarate during the synthesis of UP resin.

Preparation of UP/MMT nanocomposite

Amounts of 1, 3, and 5 wt % of MMT were added and preintercalated by heated UP resin for 10 min at 180°C by using mechanical mixer at the speed of 800 rpm. To investigate the capability of diffusion of diluents into the galleries of MMT, samples with 40 wt % of HPA were mixed for 30 and 120 min at 50°C with 300 rpm mixing speed, followed by the addition of 0.01 wt %

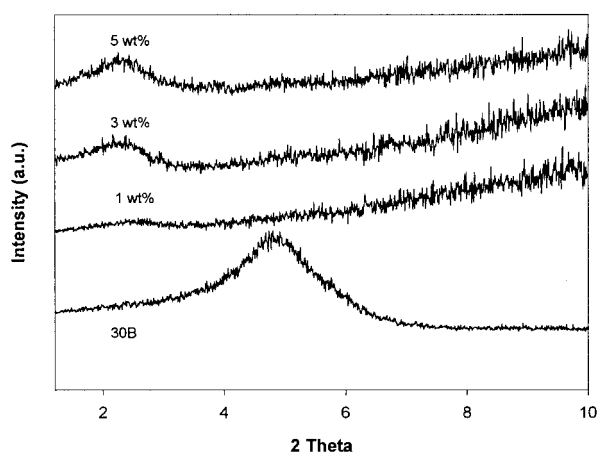


Figure 1 XRD patterns of UP/Cloisite 30B nanocomposite with various MMT contents (mixing time = 30 min).

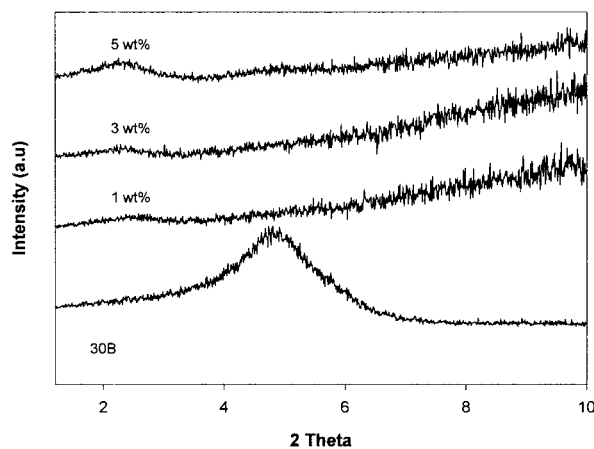


Figure 2 XRD patterns of UP/Cloisite 30B nanocomposite with various MMT contents (mixing time = 120 min).

hydroquinone as an inhibitor to prevent the reaction during the mixing stage. The 1 wt % of BPO as the free-radical initiator was added to the mixtures and well stirred for 1 h at room temperature. The 0.1 wt % of the accelerators were included and the mixtures were quickly poured into silicone molds, cured in an air-circulating oven maintained at room temperature for 3 h. After the curing schedule, the samples were postcured at 120°C for 3 h.

Measurements

The curing conversion was measured by differential scanning calorimetry (Perkin-Elmer DSC-7; Perkin Elmer Cetus Instruments, Norwalk, CT). Isothermal runs of samples were carried out at room temperature for 3 h, and then reheated from room temperature to 300°C in the scanning mode at a heating rate of 10°C/min to determine the residual reactivity (ΔH_{res}). Nonisothermal runs were also carried out in the scan-

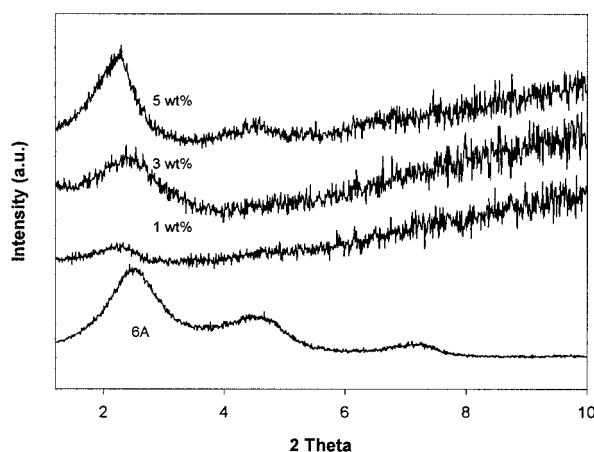


Figure 3 XRD patterns of UP/Cloisite 6A nanocomposite with various MMT contents (mixing time = 30 min).

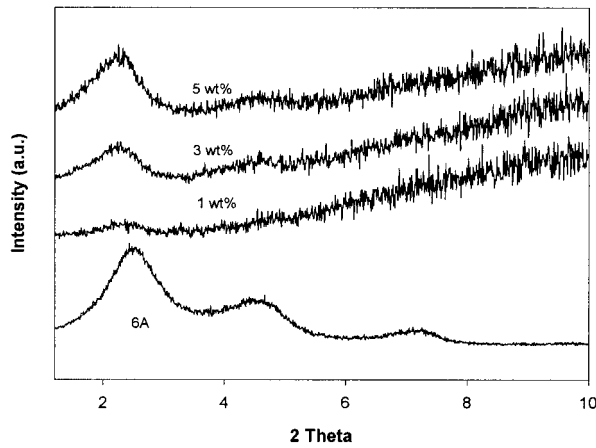


Figure 4 XRD patterns of UP/Cloisite 6A nanocomposite with various MMT contents (mixing time = 120 min).

ning mode from room temperature to 300°C to obtain the total heat of reaction (ΔH_t). The overall conversion (X) was calculated from $X = (\Delta H_t - \Delta H_{res})/\Delta H_t$.⁶ The layer spacing of the MMT was measured on a Philips X'pert-APD monochromic X-ray diffractometer (Philips, The Netherlands) with Cu- K_α radiation ($\lambda = 1.54,056 \text{ \AA}$) at a generator voltage of 35 kV and current of 25 mA. 2θ scanning was in 0.02° steps at a speed of $2^\circ/\text{min}$ from 1.5 to 10° . The gel time of UP/MMT nanocomposite was read as the crossover point of G' and G'' in rotational mode on a UDS-200 rheometer (Paar Physica Inc., Germany) with isothermal curing at room temperature. The viscoelastic properties of UP/MMT nanocomposite were measured on a UDS-200 rheometer with torsional mode under conditions of 1 Hz, 0.03% strain, at a temperature range from room temperature to 180°C. The glass-transition temperature (T_g) of the nanocomposite was taken as the

TABLE II
Viscoelastic Properties of UP/MMT Nanocomposites

MMT	Mixing time (min)	Content (wt %)	G'_{N0} (MPa)	T_g ($^\circ\text{C}$)
Cloisite 30B	—	0	3.2	62
	30	1	3.5	66
		3	4.1	63
		5	4.7	64
	120	1	3.6	62
3		4.2	63	
5		4.8	65	
Cloisite 6A	—	0	3.2	62
	30	1	2.8	57
		3	2.1	54
		5	2.7	55
	120	1	3.5	63
3		3.6	62	
5		3.5	62	

maximum $\tan \delta$ peak point during the rheological test, which was calculated from the G''/G' ratio. The flexural test was carried out for samples on an Instron model 4465 testing machine (Instron, Canton, MA) according to ASTM D790 procedures. The tensile strength was also measured by ASTM D638 on an Instron test machine. The results of two tests were taken from the mean value of those five measurements.

RESULTS AND DISCUSSION

The curing conversion of UP/Cloisite 30B nanocomposites using HPA is described in Table I. It is clear that the mixing time of uncured components does not affect the conversion of the nanocomposite.

The X-ray diffraction (XRD) patterns of the UP/Cloisite 30B nanocomposite using HPA for diluent as

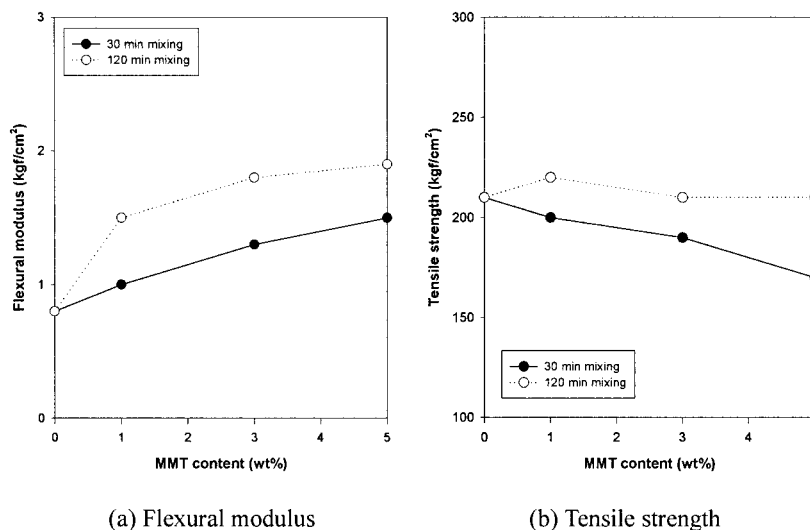


Figure 5 Mechanical properties of UP/Cloisite 30B nanocomposites with various MMT contents.

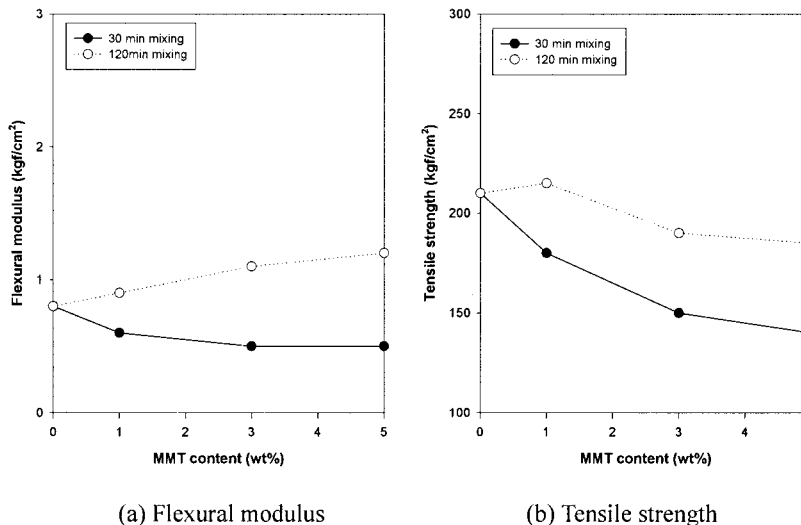


Figure 6 Mechanical properties of UP/Cloisite 6A nanocomposites with various MMT contents.

a function of MMT content for different mixing times are shown in Figures 1 and 2. It may be observed that the peak at 4.8° corresponding to the (001) plane in pristine Cloisite 30B is broadened in the nanocomposite containing 1 wt % of MMT and shifts to a lower 2θ value at 2.2° in the nanocomposite as the MMT content is increased. However, the influence of mixing time on the exfoliation of MMT cannot be observed. These results are almost identical to those of the nanocomposite with styrene monomer for reactive diluent in our previous study.

These trends were also observed in the UP/Cloisite 6A system. In Figures 3 and 4, the mixing time was not responsible for the morphology of the nanocomposites.

To confirm the correlation between polarity of reactive diluents and properties of MMT, the viscoelastic behavior of UP/MMT nanocomposites with different mixing times was investigated. As shown in Table II, there was no apparent difference of rubbery plateau modulus G_{N0} values between 30 and 120 min mixing times in the

UP/Cloisite 30B nanocomposite. On the other hand, it is observed that the modulus increased with mixing time in the case of UP/Cloisite 6A nanocomposites. It was shown that a shift of T_g values of the nanocomposites did not occur. However, these results suggest an obvious effect of the diluent's polarity on the viscoelastic property of the nanocomposite. It was hypothesized that the intercalation of HPA into the galleries of Cloisite 6A was not as easily accomplished as that into Cloisite 30B because of the polar property of HPA and the chemical interaction between HPA molecules. Therefore, most of the HPA still existed outside of Cloisite 6A, which may cause the different curing behaviors inside and outside of each layer.

Figures 5 and 6 show the mechanical properties of the nanocomposites. It may be observed that the flexural modulus and tensile strength of UP/Cloisite 30B nanocomposites are not obviously proportional to the mixing time. In the case of the UP/Cloisite 6A system, however, it is found that the flexural modulus of the nanocomposite is improved with mixing time, as

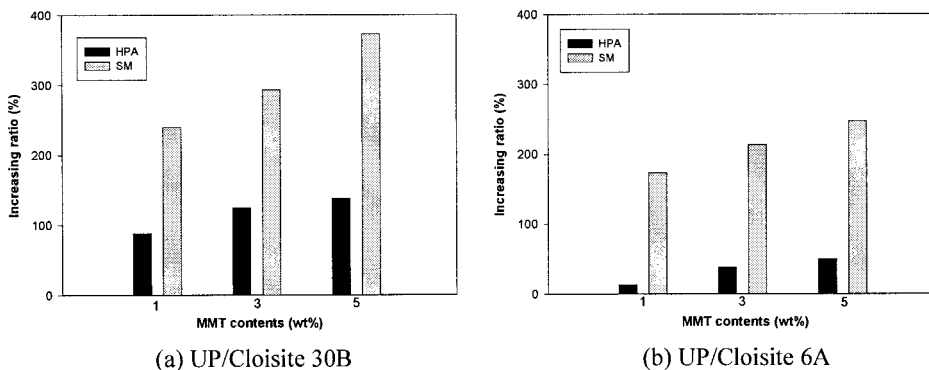


Figure 7 Enhancement ratio of flexural modulus of UP/MMT nanocomposite (mixing time = 120 min).

shown in Figure 6, which corresponds to the results of viscoelastic properties of the nanocomposite.

For a more comprehensive study of the effect of diluent on the properties of nanocomposite, Figure 7 shows the enhancement ratio (%) of flexural modulus of each nanocomposite. These values verified the relative percentage increase of the ratio of nanocomposites to pure UP thermoset resin with no MMT loading. As may be observed in Figure 7, it is clear that styrene monomer is more favorable than polar HPA for diffusion into the galleries of MMT layers, especially in the UP/Cloisite 6A system. Moreover, the high density of organic modifiers in Cloisite 6A may obstruct the swelling into the galleries of MMT.

CONCLUSIONS

In this study, the effect of polarity of a reactive diluent on the properties of UP/MMT nanocomposite was discussed. The X-ray data revealed that the polarity of diluent was not responsible for the morphology of nanocomposites regardless of MMT type. However, in the UP/Cloisite 6A system, the extended-time mixing process was necessarily required to improve the physical properties of nanocomposites. A possible mechanism that would explain these results is the high affinity between HPA molecules and the high density of organic modifier reducing the diffusion of diluent into MMT galleries. A large amount of diluent existing outside the MMT may negatively affect the physical properties of nanocomposites.

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