Macromolecules **2003,** *36,* 8391−8397

Effect of Plasticization of Epoxy Networks by Organic Modifier on Exfoliation of Nanoclay

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Received June 23, 2003

ABSTRACT: Plasticization of cross-linked epoxy networks by hydrocarbon chains of quaternary ammonium ions and its effect on exfoliation behavior of nanoclay particles in mixtures of aromatic and aliphatic epoxies were investigated. It was found that quaternary ammonium ions, apart from catalyzing epoxy curing reactions, are capable of plasticizing cross-linked epoxy chains, the effect of which was observed in terms of large reduction in glass transition temperature and lowering of the values of storage modulus of cured epoxy networks. The effect of plasticization on storage modulus was found to be small for aromatic epoxy and large for aliphatic epoxy. As a consequence, the aromatic epoxy−clay system produced complete exfoliation of clay galleries, while the systems with mixtures of aliphatic and aromatic epoxy resulted in intercalated systems, even though the extent of curing of epoxy was the same in all cases.

Introduction

The properties of polymer−clay nanocomposites are determined by their morphologies, e.g., the shape of clay, the size of clay particles, and the degree of dispersion in the polymer.[1−4] The best properties are obtained when the clay particles are in fully exfoliated state and are well-dispersed. Several methods have been used in the recent past to produce exfoliated clay−polymer nanocomposites, e.g., in-situ polymerization of monomers,[1−10] melt blending,[11−15] and solution blending using polar organic solvents.[16,17]

In-situ polymerization methods have been used to produce an array of polymer−clay nanocomposites, e.g., polyamides,[1−5] epoxies,[6−10] polyurethanes,[17] cyanate esters,[18,19] and poly(methyl methacrylate).[20−23] Nanocomposite preparation by the in-situ polymerization method is composed of two steps:[1−4,17−24] intercalation and exfoliation. In intercalation step, monomer molecules are allowed to diffuse into clay galleries, leading to an increase of *d* spacing. In this case, the intensity peaks in wide-angle X-ray diffraction (WAXD) patterns appear at lower values of 2θ than the clay itself. In addition, the intercalated clay layers remain parallel to each other with strong interlayer interactions. In the exfoliation step, large polymer molecules, formed by polymerization of the monomer, exert entropic forces on adjacent clay layers. If the magnitude of this entropic force is larger than the sum of forces opposing separation of clay layers, adjacent clay layers move from each other to reach an equilibrium separation distance with no apparent interlayer interactions.

The role of entropic force on exfoliation of organically treated clay particles in the epoxy−clay nanocomposite system was recently studied by our group.[25] It was shown that the entropic or elastic force originating inside clay galleries and measured in terms of storage modulus is responsible for exfoliation, as it pushes out the outermost clay layers in tactoids against the opposing forces composed of electrostatic and van der Waals attraction and viscous force offered by the extra-gallery epoxy. An illustration of the forces operating on a pair of adjacent clay layers is presented in Figure 1. The exfoliation of clay layers continues with the separation of the outermost clay layers from tactoids until all galleries are exfoliated or the cross-linked epoxy turns into a gel or a glass, whichever occurs earlier. A fully exfoliated system, in this case, is characterized by the absence of intensity peaks in WAXD patterns, e.g., in the range $1.5° \leq 2\theta \leq 10°$, which corresponds to a *d* spacing of at least 6 nm, which can be verified by transmission electron microscopy (TEM). As curing reactions of epoxy are carried out under quiescent conditions, there is no external shear force acting on clay particles. Consequently, the clay particles remain parallel even in an exfoliated state.

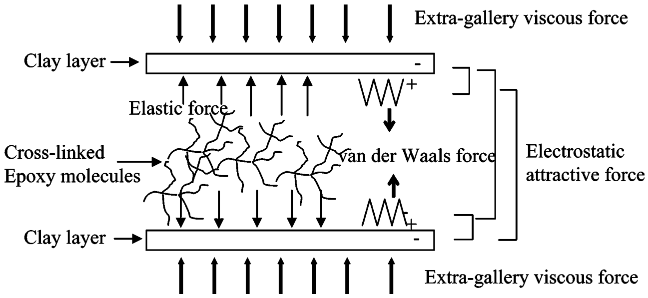

Figure 1. Schematic illustration of forces acting on a pair clay layers during intercalation and exfoliation.

In our previous studies,[25] we also found that the ratio of storage modulus (G') of intragallery epoxy and the complex viscosity (η^*) of extra-gallery epoxy is useful in determining whether the conditions of epoxy curing are conducive to exfoliation. Exfoliated structures result for higher values of G'/η^*, while lower values indicate intercalation, even though the intragallery polymerization rate is faster than extra-gallery in all cases. In an aromatic epoxy−nanoclay system, values of G'/η^* in the range 2−4 1/s produced exfoliation, while those less than 1 1/s produced intercalated structures.[25]

In this paper, results are presented to delineate the role of quaternary ammonium ions as potential plasti-

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10.1021/ma0303465 CCC: $25.00

cizers of cross-linked epoxy networks and its ramification on exfoliation behavior of nanoclay particles. The work was based on a hypothesis that cross-linked epoxy networks inside the clay galleries will not develop sufficiently large values of storage modulus G', if they are heavily plasticized by the hydrocarbon chains of the quaternary ammonium ions. Consequently, the separation of clay layers will be hindered, as lower values of G' mean much lower entropic forces inside the galleries. The magnitude of G'/η^*, however, will be strongly dependent on the nature of the quaternary ammonium ions and on the nature of epoxy monomer and the curing agents. Although the possibility of plasticization of polymer chains by quaternary ammonium ions was invoked in a recent study[27] to explain higher values of elongation at break in the clay–thermoplastic polyurethane system, its effect on exfoliation of nanoclay has not been investigated.

In this study, as a first approximation, a mixture of appropriate amounts of quaternary ammonium chloride, epoxy, and amine emulated the intragallery composition. After obtaining good understanding of plasticization effects, epoxy–clay nanocomposites were prepared, and the exfoliation behavior was analyzed in light of the trends observed using approximated intragallery composition.

Experimental Section

Materials. *Nanoclay*. CloisiteNa^+ (clay 1) obtained from Southern Clay Products was treated in our laboratory with *n*-hexadecylamine hydrochloride as the cation-exchange resin to produce organically treated clay, henceforth referred to as clay 2. Clay 2 was synthesized by the following method: 5.66 g of hexadecylamine, $CH_3(CH_2)_{15}NH_2$, obtained from Aldrich was dissolved in 150 mL of ethanol. The solution was added to 21 mL of 1.0 N hydrochloric acid solution in distilled water for preparation of an aqueous solution of *n*-hexadecylamine hydrochloride, $CH_3(CH_2)_{15}NH_3^+Cl^-$. About 15 g of clay 1 was dispersed in *n*-hexadecylamine hydrochloride solution by vigorous stirring for 6 h at 70 °C. A white precipitate formed, which was isolated by filtration and washed several times with hot water/ethanol 50:50 by volume mixture until no trace of chloride ions was detected in the filtrate by one drop of 0.1 N $AgNO_3$ solution. The treated clay thus produced (clay 2) was dried at 100 °C in a vacuum oven for 24 h, by which time all moisture was removed. The cation-exchange capacity (CEC) of clay 2 was found to be 129 mequiv/g of clay using thermogravimetric analysis.

The quaternary ammonium chloride salt was isolated in solid state by evaporation of the aqueous solution of hexadecylamine hydrochloride, which was dried thoroughly to remove the last traces of moisture and saved for later use.

Epoxy Resins. Two epoxy resins, one aromatic and the other aliphatic, were chosen. The aromatic epoxy, diglycidyl ether of bisphenol A (DGEBA) in the form of Epon 828 of Shell Chemical (Houston, TX), offered epoxide equivalent weight of 178–190, viscosity of 11–15 Pa s, and specific gravity of 1.15 at 25 °C. The aliphatic epoxy, polypropylene glycol glycidyl ether, in the form of Araldite DY3601 of Vantico (Brewster, NY), was used with epoxide equivalent weight of 385–405, viscosity of 0.42–0.52 Pa s, and specific gravity of 1.03 at 25 °C. As evident from the value of epoxide equivalent weights, Epon 828 is capable of producing cross-linked epoxy networks much more rapidly and can provide much higher values of storage modulus than Araldite DY3601 in fully cured state with the same curing agent. In view of this, Epon 828 and Araldite DY3601 were mixed in different proportions to deliberately obtain different levels of storage modulus and shear viscosity values. As will be seen later, these two epoxies also differed in the extent of plasticization by the hydrocarbon chains of the quaternary ammonium chloride. In this study the weight ratio of Epon 828:Araldite DY3601 was varied between 100:0, 90:10, 70:30, 50:50, 30:70, 10:90, and 0:100.

Curing Agents. Two curing agents—one aromatic diamine and the other aliphatic diamine—were used. Both curing agents were tetrafunctional. The aromatic diamine, DDS (benzenamine, 4,4′-sulfonylbis) made by Ciba (Tarrytown, NY) with trade name HT976 and the aliphatic diamine curing agent, Jeffamine D230 of Huntsman Corp. (Houston, TX), were obtained respectively in solid and liquid forms at room temperature. The molecular weights were respectively 225 and 248 g/mol for DDS and Jeffamine D230.

Preparation of Clay–Epoxy Nanocomposites. All materials were dried in a vacuum oven at 80 °C for 48 h. First, the organically modified clay 2 was intercalated by epoxy by stirring the ingredients at 90 °C for 6 h with a magnetic stirrer, and the resulting mixture was dried in a vacuum oven at 80 °C for 30 min. This time period was found to be suitable for production of intercalated clay, as the *d* spacing increased from 1.92 to 3.4 nm. A stoichiometric amount of suitable curing agent was then added to the epoxy–clay mixture, and the ingredients were mixed further for approximately 5 min at 60 °C. The resultant mixture was degassed in a vacuum oven for approximately 5 min at 60 °C and cured in an aluminum mold. The curable epoxy mixtures without the clay were prepared by mixing the ingredients (epoxy and curing agent) for 5 min at 60 °C.

The curing temperature and the total curing times used in this study were 125 °C and 3 h for Jeffamine D230 and 200 °C and 3 h for DDS. These curing conditions produced fully exfoliated clay (clay 2) galleries in Epon 828, reported in an earlier study.[25]

Cure Kinetics and Glass Transition Temperature. The speed of curing of epoxy was evaluated with and without the use of quaternary ammonium chloride. For this purpose, binary mixtures of epoxy and curing agent and ternary mixtures of epoxy, curing agent, and quaternary ammonium chloride were prepared and cured isothermally under a nitrogen environment in a Dupont differential scanning calorimeter (DSC), model DSC-2910, to obtain the cure curves so as to judge the influence of quaternary ammonium ions on the extent of curing. The ternary mixtures contained 90 parts by weight of epoxy, 10 parts by weight of quaternary ammonium chloride, and a stoichiometric amount of curing agent. In each case, the reaction mixtures were dried in a vacuum oven thoroughly to remove the traces of moisture. The temperature was raised from room temperature to the desired curing temperatures, e.g., 125 °C for Jeffamine D230 and 200 °C for DDS, at a rate of 50 °C/min, and kept at the curing temperature for 3 h. The glass transition temperatures (T_g) of cured epoxy specimens were determined after completion of the curing step. A scan rate of 20 °C/min and temperature in the range −100 to 250 °C were used.

Rheological Measurements. The rheological properties, such as the values of G' and η^* of curing epoxies, were measured using an RMS-800 Rheometrics rheometer with 25 mm parallel plate setup under oscillatory shear flow at the desired curing temperature. The values of storage modulus G', loss modulus G'', complex viscosity η^*, and loss tangent tan δ were recorded for mixtures with and without quaternary ammonium chloride. The gel time, taken as the time for crossover of the values of loss and storage modulus at a strain of 5% and a frequency of 5 rad/s, were also determined.

Rheological Properties in the Presence of Quaternary Ammonium Chloride. Epoxy monomers and solid, thoroughly dried *n*-hexadecylamine hydrochloride salt were mixed at 90 °C for 20 min using a magnetic stirrer, and a stoichiometric amount of the curing agents was added and mixed further for approximately 5 min at 60 °C. The ratio of epoxy to quaternary ammonium chloride in the mixture was maintained at a desired level, so as to match the amount of quaternary ammonium ions present inside the clay galleries. For example, 90 parts by weight of epoxy, 10 parts by weight of quaternary ammonium chloride, and a stoichiometric amount of curing agent were mixed together. These mixtures were

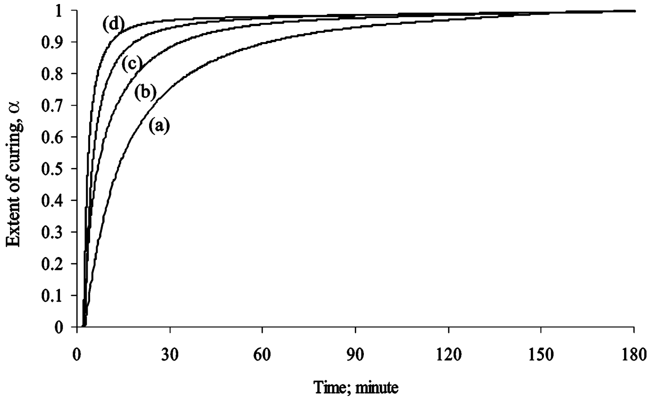

Figure 2. Cure curves of epoxies with and without quaternary ammonium chloride. Mixtures were cured using Jeffamine D230 at 125 °C for 3 h. (a) Araldite DY3601 without the quaternary ammonium chloride, (b) Araldite DY3601 with the quaternary ammonium chloride, (c) Epon 828 without the quaternary ammonium chloride, and (d) Epon 828 with the quaternary ammonium chloride.

cured in an RMS800 rheometer at a strain of 5% and a frequency of 5 rad/s at 125 °C for mixtures containing Jeffamine D230 and at 200 °C for mixtures containing DDS. The measurements were carried out until the torque values reached the limit of the transducer of the rheometer.

Wide-Angle X-ray Diffraction and TEM. One-dimensional, wide-angle X-ray diffraction patterns were obtained by using a Rigaku X-ray diffractometer with wavelength $\lambda = 1.54$ Å (Cu), a tube voltage of 50 kV, and tube current of 150 mA. The scanning range was varied from $2\theta = 1.5°$ to 25° with a rate of 5°/min. The sample specimens for transmission electron microscopy were prepared by microtoming in a Reichert Ultracut Microtome at room temperature and inspected using a transmission electron microscope (TEM) model TACNAI-12 by FEI.

Results and Discussion

Catalytic Effect on Epoxy Curing. Figure 2 presents the degree of curing as a function of time obtained in each case from DSC following a method described elsewhere.[28,29] It is evident from comparison of curves a and b or c and d that both the rate and the extent of curing (α) were higher in the presence of quaternary ammonium chloride. The extent of curing, however, reached approximately 97% in 3 h in all cases. It can be concluded from Figure 2 that the quaternary ammonium chloride increased the rate of epoxy curing substantially for both Epon 828 and Araldite 3601 as reported earlier by Lan et al.[8] In this context, faster intragallery curing should provide faster rise of storage modulus, G', inside the galleries.

Kamal[29] proposed an empirical equation to describe the extent of curing of epoxide groups, α:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^2(\alpha + B) \qquad (1)$$

where k is the rate constant and B, a dimensionless quantity, contains the initial concentrations of the catalyst and epoxy monomer and the rate constants of catalyzed and noncatalyzed epoxy−amine reactions. Table 1 lists the values of k calculated from the data of Figure 2 using eq 1. It is clearly evident that the conversion of epoxide groups took place approximately at twice the rate in the presence of quaternary ammonium chloride. In addition, the fastest conversion occurred for the Jeffamine D230-cured Epon 828 system.

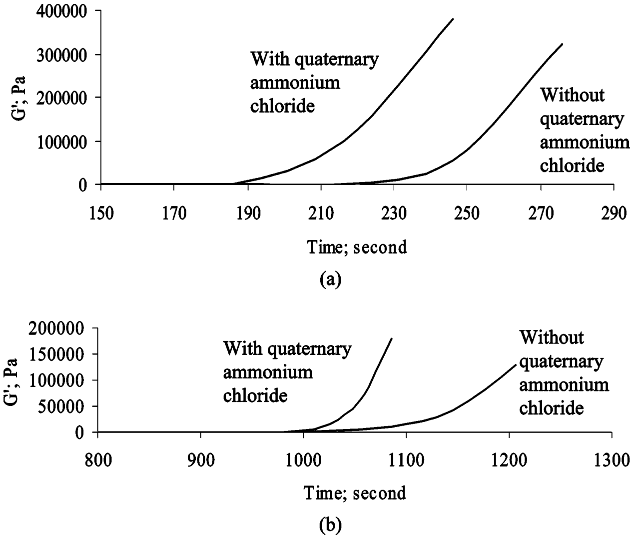

Figure 3. Growth of storage modulus in Epon 828 cured with (a) Jeffamine D230 at 125 °C and (b) DDS at 200 °C in the presence of quaternary ammonium chloride.

Table 1. Reaction Rate Constant k from Eq 1

		k, min^{-1}	
	curing agent	Epon 828	Araldite DY3601
with quaternary ammonium chloride	Jeffamine D230	0.55	0.23
	DDS	0.12	0.08
without quaternary ammonium chloride	Jeffamine D230	0.24	0.09
	DDS	0.08	0.05

Figure 3 shows that the onset of sharp rise of storage modulus occurred much earlier in the presence of quaternary ammonium chloride for both Jeffamine D230- and DDS-cured systems. For example, in Figure 3a, a value of storage modulus of 10^5 Pa was reached in ∼216 s in the presence of quaternary ammonium chloride, while it took ∼276 s to reach the same value in the absence of quaternary ammonium chloride. The same value of storage modulus was reached in the DDS-cured system (Figure 3b) in ∼1090 and ∼1180 s, respectively, with and without the use of quaternary ammonium chloride.

The trends observed in Figures 2 and 3, however, cannot be generalized to conclude that higher value of storage modulus would always result when epoxy is cured in the presence of quaternary ammonium chloride. Figure 4a shows that Jeffamine D230-cured mixtures of Epon 828/Araldite DY3601 show a reversal of trend for a 50:50 composition by weight (curves iii). For this mixture, the rise of storage modulus was more rapid for the system without quaternary ammonium chloride. Separate experiments with DSC for this epoxy mixture revealed that the conversion of epoxide groups still occurred at a much faster rate in the presence of quaternary ammonium chloride. The same was found to be true for the DDS-cured system, although the reversal of G' vs time behavior now occurred at much lower loading of aliphatic epoxy, e.g., at aromatic to aliphatic epoxy ratio of 90:10, as presented in Figure 4b. An immediate conclusion from the trends observed in Figure 4 would be to suspect if the quaternary ammonium chloride plasticized the cross-linked epoxy network. If yes, a relevant question to ask is why such plasticization behavior is apparent in the case of mix-

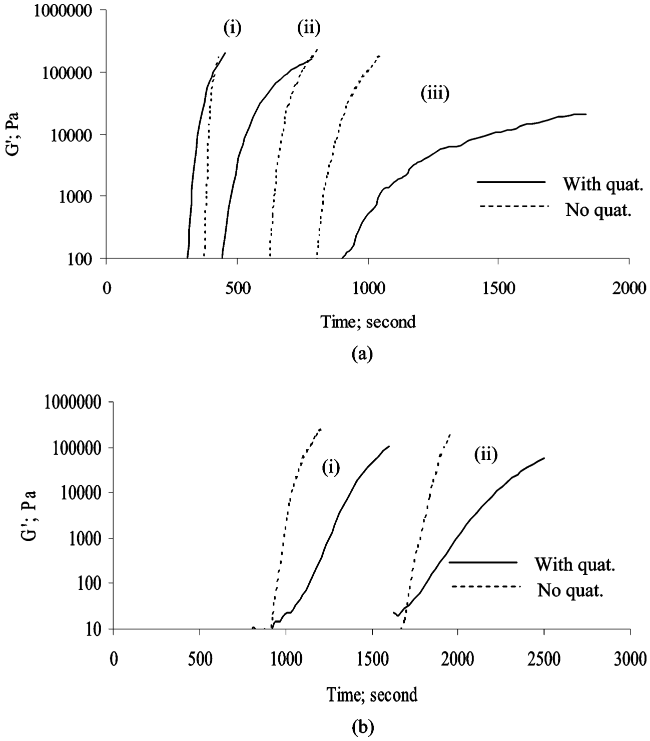

Figure 4. Growth of storage modulus of epoxy mixtures cured with (a) Jeffamine D230 at 125 °C and (b) DDS at 200 °C in the presence of quaternary ammonium chloride. The composition of Epon 828 and Araldite DY3601 in parts by weight are as follows: (a) (i) 90:10, (ii) 70:30, (iii) 50:50 and (b) (i) 90:10 and (ii) 70:30.

Table 2. Storage Moduli *G′* (Pa) of Cured Aradite DY3601 at Room Temperature (29 °C) with 4% Strain

	with quaternary ammonium chloride		without quaternary ammonium chloride	
freq, rad/s	Jeffamine D230-cured	DDS-cured	Jeffamine D230-cured	DDS-cured
5	3.78	4.87	4.34	28.12
50	33.90	41.95	35.73	1271.80

tures of aromatic and aliphatic epoxy, as in Figure 4 and not observed in the case of aromatic epoxy as in Figure 3.

Plasticization by Quaternary Ammonium Chloride. To investigate the issues of plasticization by quaternary ammonium chloride, Araldite DY3601 was cured in an RMS-800 parallel plate rheometer under quiescent conditions for 3 h at 125 and 200 °C respectively with Jeffamine D230 and DDS. The cured material appeared as low-viscosity liquid, instead of a glassy polymer obtained in the case of Epon 828, the modulus of which was also low and fell below the lower limit of the transducer of the rheometer at the curing temperature. To obtain comparative values of *G′* of cured Araldite DY3601, with and without quaternary ammonium chloride, the cured materials were cooled to room temperature (29 °C) and their rheological properties were measured with oscillatory shear flow at 4% strain with 0.1−100 rad/s of frequency. Table 2 shows that the values of *G′* are lower in the presence of quaternary ammonium chloride. Of the two curing agents used in this study, DDS-cured systems were worse affected. The value of storage modulus decreased by as much as 97% for the DDS-cured system from 1272 Pa at 50 rad/s without quaternary ammonium chloride to 42 Pa in the presence of quaternary ammonium chloride. This can be attributed to plasticization by the quaternary ammonium chloride, as the extent of conversion of epoxide group was the same in all cases (Figure 2). The complex viscosity of the cured materials shows Newtonian behavior, as presented in Figure 5. Again, the effect of plasticization can be seen due to the presence of quaternary ammonium chloride. For example, the DDS-cured system without quaternary ammonium chloride (curve d) offered an order of magnitude higher viscosity than the one with quaternary ammonium chloride (curve c).

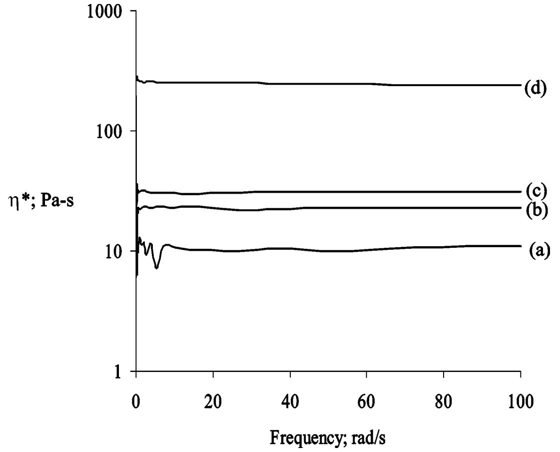

Figure 5. Complex viscosity of cured Araldite DY3601 at 4% strain and frequency range of 0.1−100 rad/s. (a) Jeffamine D230 cured with quaternary ammonium chloride, (b) Jeffamine D230 cured without quaternary ammonium chloride, (c) DDS cured with quaternary ammonium chloride, and (d) DDS cured without quaternary ammonium chloride.

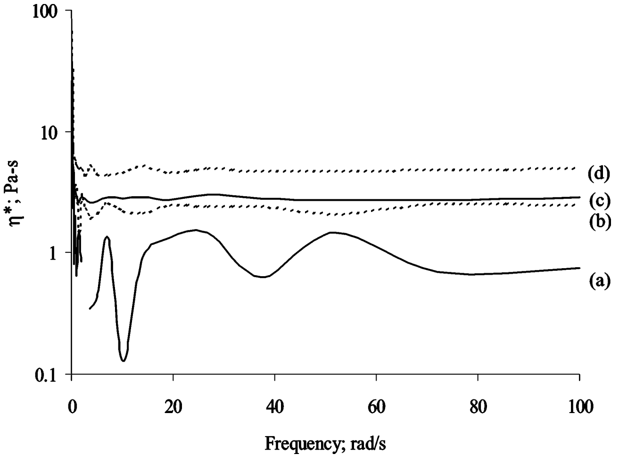

Figure 6. Complex viscosities of Araldite DY3601 cured with Jeffamine D230 at 125 °C for 40 min and DDS at 200 °C for 65 min under 4% strain and frequency range of 0.1−100 rad/s. (a) Jeffamine D230 cured with quaternary ammonium chloride, (b) Jeffamine D230 cured without quaternary ammonium chloride, (c) DDS cured with quaternary ammonium chloride, and (d) DDS cured without quaternary ammonium chloride.

A relevant question is whether such plasticization occurs throughout the curing process, thereby preventing or delaying the formation of gels. To determine this, rheological measurements were carried out after curing of Araldite DY3601 for 40 min using Jeffamine D230 and 65 min using DDS. Figure 6 shows that the value of complex viscosity was low in each case, following the same trend, as in Figure 5; that is, the system with quaternary ammonium chloride offered much less viscosity again due to plasticization. Therefore, the plas-

Table 3. Glass Transition Temperatures of Cured Epoxy

		T_g, °C	
	curing agent	Epon 828	Araldite DY3601
with quaternary ammonium chloride	Jeffamine D230	73	−48
	DDS	159	−44
without quaternary ammonium chloride	Jeffamine D230	87	−46
	DDS	197	−38

ticization effects were apparent in the Araldite 3601 system throughout the curing period.

The Epon 828 system was also affected by plasticization, although not apparent in Figure 3. Table 3 presents the glass transition temperatures of various cured systems determined by DSC. It is readily apparent that the DDS-cured Epon 828 system exhibits a drop in T_g values by almost 40 °C due to the presence of quaternary ammonium chloride, while the Araldite DY3601 system shows a drop of only 6 °C. The extent of such drop in T_g, however, was less in the Jeffamine D230-cured system, for example, 15 °C for Epon 828 and 2 °C for Araldite DY3601. Therefore, the quaternary ammonium chloride plasticized both Epon 828 and Araldite DY3601. The large drop in T_g observed in the DDS-cured system can be attributed in part to generation of smaller molecules by decomposition of quaternary ammonium chloride, as the curing temperature of 200 °C was in the neighborhood of decomposition temperature of quaternary ammonium chloride.[30−32] However, this point was not explored further in this study.

A point to note here is that the reduced values of T_g in the cured epoxy system can be mistakenly attributed to incomplete curing of epoxy molecules. A recent study[26] reported reduction in T_g in epoxy−nanoclay systems, attributing such reduction to incomplete curing of epoxy molecules.

Since plasticization in the fully cured Epon 828 system was apparent from the reduction in the values of T_g and not from G' vs time plots as in Figure 3, the values of G' were plotted as a function of α, the extent of curing, as in Figure 7, to reveal clearly the effect of plasticization in the Epon 828 system. The time axis in Figure 3 was converted to α using the data of Figure 2, assuming that the degree of curing was a function of temperature and was not affected by plasticization. It is now evident from Figure 7 that for the same degree of curing and, therefore, for the same degree of cross-linking density the Epon 828 system with quaternary ammonium chloride (curve b) offered much less elasticity than the one without quaternary ammonium chloride (curve a). Thus, plasticization also affected the values of storage modulus in the Epon 828 system, although it was not apparent in Figure 3 due to much faster curing rate brought about by the quaternary ammonium chloride.

Figure 8 presents plots of the loss tangent as a function of the extent of curing α for the DDS-cured Epon 828 system, from which the effect of plasticization on gelation can be inferred. Assuming gelation took place when tan δ reached a value of 1, i.e., at the crossover of G' and G'' values, it is clear that the presence of quaternary ammonium chloride in epoxy prevented gelation until a higher conversion was reached, $\alpha_{gel} = 0.768$ vs 0.817. In view of this, one can argue that long hydrocarbon chains of the quaternary ammonium chloride extends into the epoxy network and prevents formation of infinite epoxy networks until a higher gel conversion is reached.

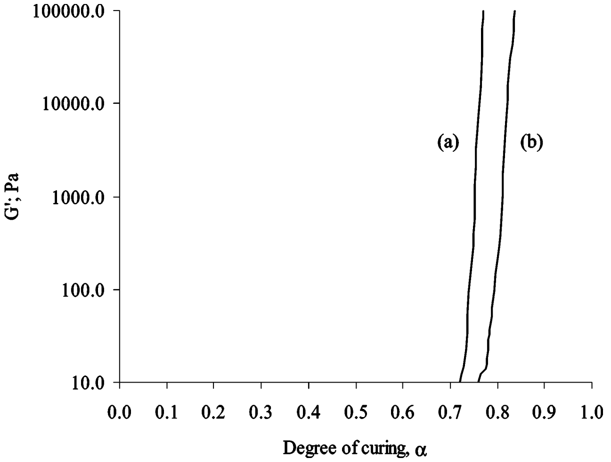

Figure 7. Growth of storage modulus in Epon 828 cured with DDS at 200 °C: (a) without quaternary ammonium chloride; (b) with quaternary ammonium chloride.

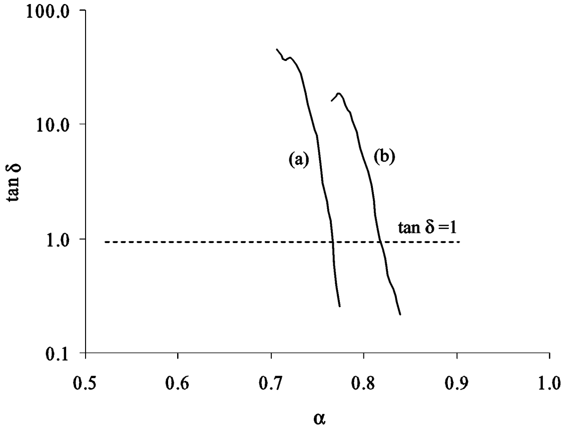

Figure 8. Loss tangent of Epon 828 cured with DDS at 200 °C: (a) without quaternary ammonium chloride; (b) with quaternary ammonium chloride.

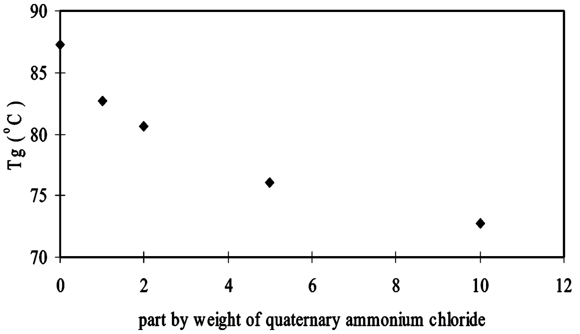

Figure 9. T_g of completely cured Epon 828 as a function of parts by weight of quaternary ammonium chloride mixed with 100 parts by weight of epoxy and stoichiometric amount of curing agent. Epon 828 was cured with Jeffamine D230 at 125 °C for 3 h.

Figure 9 presents further evidence that the reduction of T_g of cured epoxy in the presence of quaternary ammonium chloride was due to plasticization and not due to reduced degree of curing. In this case, various amounts of quaternary ammonium chloride were mixed with 100 parts by weight of epoxy and the mixtures cured with stoichiometric amounts of curing agent. The values of T_g of cured epoxy gradually decreased with the increase of quaternary ammonium chloride content,

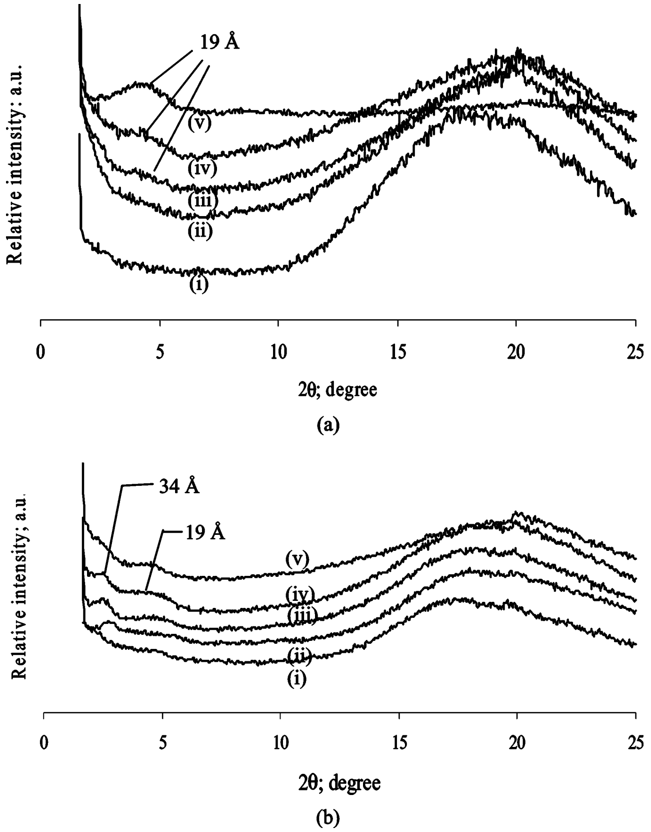

Figure 10. WAXD patterns of cured epoxy mixtures (aromatic and aliphatic epoxies)–clay composites containing 4 wt % clay 2: (a) cured with Jeffamine D230 at 125 °C for 3 h, composition of aromatic and aliphatic epoxies in parts by weight are (i) 100:0, (ii) 70:30, (iii) 50:50, (iv) 30:70, and (v) 10:90 and (b) cured with DDS at 200 °C for 3 h; composition of aromatic and aliphatic epoxies in parts by weight are (i) 100:0, (ii) 90:10, (iii) 70:30, (iv) 50:50, and (v) 10:90.

Table 4. T_g of Jeffamine D230-Cured Epon 828 at 125 °C for 3 h with 5 or 10 wt % of Clay 1 and Clay 2 Evaluated by DSC

clay type	wt % of clay	T_g, °C (onset)	T_g, °C
clay 1	0	82	87
	5	82	88
	10	84	88
clay 2	5	80	85
	10	79	83

although complete curing was achieved faster with higher concentration of quaternary ammonium chloride as in Figure 2.

Table 4 shows that T_g of the organically treated clay (clay 2)–epoxy nanocomposite was slightly lower than that of the sodium montmorillonite clay–epoxy nanocomposite. The values of T_g remained almost unchanged with the addition of clay 1, while a reduction by 4 °C was observed in the presence of clay 2. One can attribute this to the plasticization effect by quaternary ammonium chloride present in clay 2. Note that clay 2 particles were fully exfoliated under this curing condition, thereby exposing a large fraction of extra-gallery cross-linked epoxy molecules to the hydrocarbon chains of the quaternary ammonium ions.

Exfoliation as a Function of Composition of Epoxy Mixture. The competition between the plasticization effect and the catalytic effect of quaternary ammonium chloride on curing rate made a great impact on exfoliation behavior of clay particles in cured epoxy–clay systems. Figure 10 shows WAXD patterns of cured epoxy–clay nanocomposites containing 4 wt % clay 2. The clay (clay 2) peaks with *d* spacing of 19 Å remained in Jeffamine D230-cured epoxy mixtures containing aliphatic epoxy with a weight ratio over 50:50, as in Figure 10a, curves iii–v. In DDS-cured epoxy mixtures, on the other hand, the intercalated clay peaks at 19 Å and epoxy-intercalated peaks at 34 Å are seen in systems with an aliphatic to aromatic epoxy ratio over 10:90, as in Figure 10b, curves ii–v. In all other cases, exfoliated epoxy–clay nanocomposites were obtained. These results corroborate our findings of Figure 4. It was observed in Figure 4 that, in mixtures containing aliphatic epoxy, the values of G' did not rise sharply due to plasticization by the quaternary ammonium chloride.

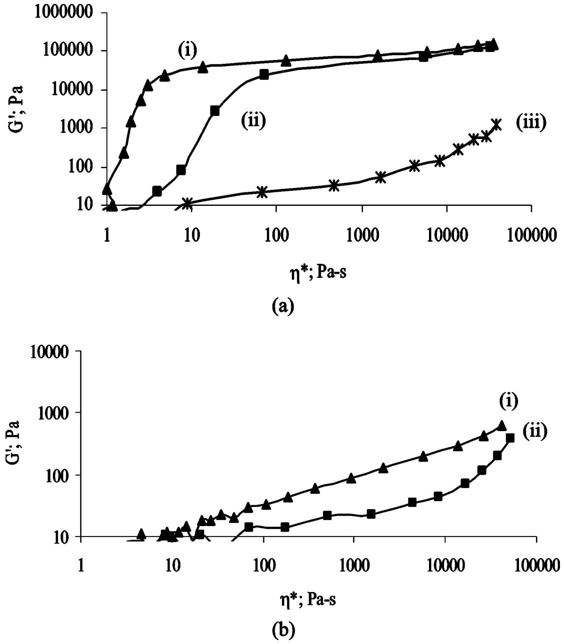

Figure 11. Plot of G' vs η^* of epoxy mixtures during curing by (a) Jeffamine D230 at 125 °C and (b) DDS at 200 °C. The compositions of aromatic epoxy and aliphatic epoxy in parts by weight are (a) (i) 90:10, (ii) 70:30, (iii) 50:50 and (b) (i) 90:10, (ii) 70:30.

The ratio of the values of intragallery G' and extra-gallery η^* can shed some light on the exfoliation behavior observed in Figure 10. For this purpose, we plotted the values of G' obtained in the presence of quaternary ammonium chloride and η^* obtained without quaternary ammonium chloride, both cured for the *same time period*, as presented in Figure 11. The ratio G'/η^* now represents the relative values of storage modulus of the cross-linking epoxy molecules inside the galleries and the viscous forces offered by the extra-gallery cross-linking epoxy molecules. It was observed from transmission electron micrograph (TEM) images (Figure 12) and WAXD patterns that exfoliated composites were produced only in cases where the G'/η^* ratio was high, e.g., 1000 1/s in Figure 11a, curve i, and 100 1/s in Figure 11a, curve ii. On the other hand, only intercalated clay composites were produced in cases with low (<1 1/s) values of G'/η^*, e.g., ~0.01 in Figure 11a, curve iii. The same observation can be made for DDS-cured system in Figure 11b, curves i and ii, as the values of G'/η^* were of the order of 0.1 and 0.01, respectively, and exfoliation was not observed.

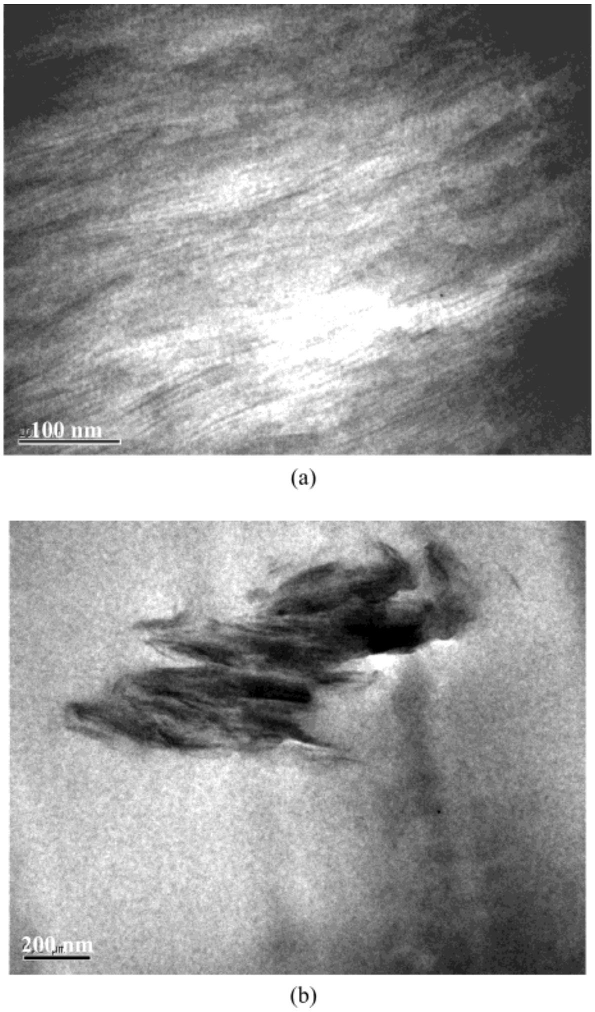

Figure 12. TEM images of epoxy–clay composites. (a) Exfoliated clay structure produced by curing of Epon 828 with Jeffamine D230 at 100 °C for 3 h with 5 wt % clay 2. (b) Intercalated clay structure produced by curing of 90:10 parts by weight of aromatic and aliphatic epoxies using DDS at 200 °C for 3 h with 4 wt % clay 2.

Conclusions

This study investigated two effects of quaternary ammonium ions in epoxy–clay nanocomposite systems: the catalytic effect on curing rate of epoxy and plasticization of epoxy networks by long hydrocarbon chains present in quaternary ammonium ions. It was found that the degree of exfoliation of the clay–epoxy system was a strong function of the ratio of storage modulus of intragallery cross-linking epoxy molecules and viscosity of extra-gallery cross-linking epoxy molecules. The competition between faster curing of epoxy due to catalytic effect of quaternary ammonium ions and lowering of storage modulus due to plasticization by hydrocarbon chains of quaternary ammonium ions affected the ratio G'/η^* and, therefore, the exfoliation behavior.

The effect of plasticization was seen to be present in both aliphatic and aromatic epoxy and was found to be a strong function of the nature of curing agent. However, in aromatic epoxy systems, the effect of plasticization could not deter complete exfoliation, as the effect of higher curing speed of epoxy on the value of storage modulus was much stronger than the effect of plasticization. The presence of aliphatic epoxy, however, deterred complete exfoliation, first due to inherently low values of storage modulus and second due to plasticization. The plasticization effect was found to be stronger in the DDS-cured epoxy systems, which can be partially attributed to decomposition of hydrocarbon chains of quaternary ammonium ions.

Acknowledgment. This research was supported by National Science Foundation in the form of CAREER grant to S.C.J.

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MA0303465