Mechanism of Exfoliation of Nanoclay Particles in Epoxy−Clay Nanocomposites

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Received September 19, 2002

ABSTRACT: The mechanism of nanoclay exfoliation was investigated in epoxy−clay nanocomposites system. The elastic force exerted by cross-linked epoxy molecules inside the clay galleries was found responsible for exfoliation of clay layers from the intercalated tactoids. Complete exfoliation of clay galleries was observed under the conditions of slow increase of complex viscosity and fast rise of storage modulus. It was observed that faster intragallery polymerization, though expedited the exfoliation process, was not necessary for exfoliation. It was also observed that clays containing hydroxylated quaternary ammonium ions and quaternary ammonium ions with no polar functional groups produced exfoliated structures equally easily, provided the ratio of storage modulus to complex viscosity was maintained above 2−4 1/s. Both higher curing temperature and the presence of organically modified clay particles accelerated the formation of gels, and the gel time presented an upper bound of time available for exfoliation.

Introduction

Filled polymeric materials offer a variety of useful properties; of special interest are those filled with nanosize clay particles. Nanoclay-filled polymeric systems offer many new and greatly improved properties over pristine polymers, which cannot be matched by filled systems of micron-sized particles, such as talc, glass fibers, and glass beads.[1−13] Much improved tensile and thermal properties,[1−9] heat distortion temperature,[1−6] resistance to flammability,[12] and reduced permeability to small molecules[5,10,11] and solvent uptake[13] have been reported in the recent literature. A common observation emerging from these studies is that the magnitude of improvement strongly depends on the state of dispersion of the clay particles in the polymer.

Sodium montmorillonite type layered silicate clays, very popular in the development of polymer nanocomposites, are available as micron size *tactoids*, which consists of several hundred individual platy particles of dimensions 1 μm × 1 μm × 1 nm, held together by electrostatic forces with a gap of approximately 0.3 nm between two adjacent particles.[14] Consequently, the tactoids must be broken down to the scale of individual particles in the dispersion process to obtain true nanocomposites, which has been a difficult task and forms an active area of research in recent literature.[1−36]

Two major steps are involved in clay particle dispersion in polymers—intercalation and exfoliation.[1−5,20] In the intercalation step, the spacing between individual clay layers, called *d-spacing*, increases from their intrinsic values as polymer chains or monomer molecules diffuse into the clay galleries, facilitated by the treatment of clay particles with organic modifiers, such as hydrophobic quaternary alkylammonium ions. In an intercalated state, the clay layers remain parallel to each other, and a new intensity peak in wide-angle X-ray diffraction (WAXD) patterns characterizes the increased *d*-spacing. In exfoliation, the individual clay particles are separated from the intercalated tactoids and are dispersed in the matrix polymer with no apparent interparticle interactions. Processing flows, such as those encountered in extrusion and molding, may impart orientation to the clay particles in both intercalated and exfoliated states. A fully exfoliated system 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. Transmission electron microscopy (TEM) is often used to show the relative separation of the clay particles in exfoliated state.

Many methods have been used in the recent past to produce intercalated and exfoliated structures in polymer−nanoclay composites, e.g., in situ polymerization of monomers,[1−11,28] melt blending,[13,22,29−31] and solution blending using polar organic solvents.[17,21] In this work, nanoclay particles were combined with monomeric epoxy, which was later polymerized to develop nanocomposites in situ.

The epoxy−nanoclay system has served as a test bed for many studies on intercalation and exfoliation of clay structures.[7−11,15,16,18,19,21,25,26,34,35] The role of the speed of epoxy curing,[7−9,16] the relative importance of intragallery and extragallery polymerization rates,[18,19] and the use of polar solvents[21] was investigated. It was found that faster intragallery polymerization produced exfoliated clay structures; the individual clay layers were pushed out of the tactoids by gradual diffusion of monomeric epoxy into the clay gallery. The absence of intensity peak in WAXD in fully cured system under certain conditions of curing, curing agent, clay type, and epoxy type supported these observations. Table 1 summarizes the observations of a representative set of studies to date on epoxy−nanoclay systems. It was argued that faster intragallery polymerization resulted from the catalytic activity of the organic modifier, quaternary alkylammonium ions, present inside the clay gallery.[16,18,19,21] The speed of diffusion of curing agents and curing temperatures were also shown to influence the degree of exfoliation.[18,19] Chin et al.[19] used a time-resolved small- and wide-angle X-ray diffraction setup and showed that exfoliated clay structures with layer

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10.1021/ma021509c CCC: $25.00

Table 1. Summary of Results to Date on Epoxy−Clay Systems

epoxy	curing agent	clay; organic modifier	curing condition	observation; gallery height	ref
Epon 828	*m*-phenylenediamine	montmorillonite; $CH_3(CH_2)_3NH_3^+$	75 °C, 2 h; 125 °C, 2 h	intercalation; 1.66 nm	9
Epon 828	*m*-phenylenediamine	montmorillonite; $CH_3(CH_2)_{15}NH_3^+$	75 °C, 2 h; 125 °C, 2 h	exfoliation	9
Epon 828	*m*-phenylenediamine	montmorillonite; $CH_3(CH_2)_{15}N(CH_3)_3^+$	75 °C, 2 h; 125 °C, 2 h	intercalation; 3.65 nm	9
Epon 828	*m*-phenylenediamine	hectorite; $CH_3(CH_2)_{15}N(CH_3)_3^+$	75 °C, 2 h; 125 °C, 2 h	exfoliation	9
Epon 828	*m*-phenylenediamine	vermiculite; $CH_3(CH_2)_{15}N(CH_3)_3^+$	75 °C, 2 h; 125 °C, 2 h	intercalation; 4.0 nm	9
Epon 828	Jeffamine D230	montmorillonite; $CH_3(CH_2)_{17}NH_3^+$	75 °C, 3 h	exfoliation	18
Epon 828	Amicure PACM	montmorillonite; $CH_3(CH_2)_{17}NH_3^+$	75 °C, 3 h	intercalation; 3.7 nm	18
Epon 828	3,3′-dimethylmethylenediamine	montmorillonite; $CH_3(CH_2)_{17}NH_3^+$	75 °C, 3 h	intercalation; 4.0 nm	18
Epon 828	Amicure PACM	montmorillonite; $CH_3(CH_2)_{17}NH_3^+$	160 °C, 3 h	exfoliation	18
Epon 828	3,3′-dimethylmethylenediamine	montmorillonite; $CH_3(CH_2)_{17}NH_3^+$	120 °C, 3 h	exfoliation	18
Epon 862	Epi-Cure Curing agent W	montmorillonite; 10A (Southern Clay)	121 °C, 3 h; 177 °C, 3 h	intercalation; 3.2 nm	36
Araldite MY720	Ethacure 100 (DETDA)	montmorillonite; octadecylammonium		exfoliation	26
DGEBA E-51	diethylenetriamine (DETA)	montmorillonite; $CH_3(CH_2)_{15}N(CH_3)_3Br$	70 °C, 2 h; 120 °C, 2 h	intercalation; 3.1 nm	35
DGEBA E-51	diethylenetriamine (DETA)	montmorillonite; $CH_3(CH_2)_{15}N(CH_3)_3Br$	140 °C, 2 h	intercalation; 3.1 nm	35
DGEBA E-51	diethylenetriamine (DETA)	montmorillonite; $CH_3(CH_2)_{15}N(CH_3)_3Br$	120 °C, 2 h	intercalation; 3.1 nm	35
DGEBA E-51	Tung oil anhydride (TOA)	montmorillonite; $CH_3(CH_2)_{15}N(CH_3)_3Br$	80 °C, 3 h	exfoliation	35
DGEBA E-51	Tung oil anhydride (TOA)	montmorillonite; $CH_3(CH_2)_{15}N(CH_3)_3Br$	120 °C, 2 h	exfoliation	35
DGEBA	(*p*,*p*′-diaminodiphenyl)methane (DDM)	montmorillonite; $CH_3(CH_2)_{17}N(CH_3)_3^+$	80 °C, 2 h	intercalation; 3.5 nm	34
DGEBA	(*p*,*p*′-diaminodiphenyl)methane (DDM)	montmorillonite; $CH_3(CH_2)_{17}N(CH_3)_3^+$	200 °C, 2 h	intercalation; 3.3 nm	34
DGEBA	(*p*,*p*′-diaminodiphenyl)methane (DDM)	montmorillonite; $CH_3(CH_2)_{17}NH_3^+$	80 °C, 2 h	exfoliation	34

spacing as high as 20 nm can be obtained when extragallery epoxy polymerization is substantially slowed down by using much lower than stoichiometric quantities of amines.

Although these observations qualitatively explain many features of clay exfoliation, some critical issues are still unanswered. For example, if exfoliation of the clay layers is caused by diffusion of epoxy molecules into clay galleries, the *d*-spacing between all pairs of clay layers should increase and assume a Gaussian distribution. Moreover, the *d*-spacing should increase continuously during the curing process until gelation occurs. However, it was observed that *d*-spacing increased from an intercalated state to an exfoliated state only after curing was continued for a specified period of time, indicating that the transition might have taken place suddenly or over a very short period of time. As we shall see later, our own study revealed that exfoliation of clay galleries was possible only under certain conditions of curing, even though faster intragallery polymerization rates were maintained in all cases. Therefore, mechanisms other than the disparity of rates between intra- and extragallery polymerization must be invoked in order to explain exfoliation phenomena in epoxy−nanoclay systems.

The Mechanism of Clay Exfoliation. In this paper we investigated the hypothesis that the elastic forces developed in the clay galleries during epoxy curing is responsible for exfoliation of the clay structures. Our hypothesis is based on the theory of polymer recoiling. Polymer chains, in this case cross-linked epoxy molecules, store more energy to recoil with growing molecular weight, i.e., with the extent of curing. This energy can be expressed in terms of the values of storage modulus of cross-linking epoxy molecules.[38−41] The adjacent layers of clay particles holding the polymerizing epoxy molecules within them, however, prevent recoiling of the cross-linked epoxy chains due to (1) electrostatic attractive forces between the quaternary ammonium ions and the negatively charged clay particles and (2) the van der Waals forces between the organic fragments of the quaternary ammonium ions. Consequently, the cross-linked epoxy chains cannot relax, and its conformational entropy gradually increases to a critical point whereby the attractive forces balance the entropic elastic forces. Beyond this critical point, the elastic forces outweigh the attractive forces and adjacent clay layers move away from each other. However, the viscous force offered by the extragallery epoxy must be overcome for eventual separation of the clay layers.

The cross-linking epoxy molecules undergo recoiling process in all cases of curing speed but have longer times available to change conformation and relax when the rate of curing is slow. Under faster curing conditions, however, cured epoxy chains have very little time to experience stress relaxation and, therefore, store much more elastic energy than the chains produced under slow curing conditions. This is true for both intra- and extragallery epoxy molecules.

The relaxation process of curing epoxy chains and the possibility of whether the clay layers can be pushed out of the tactoids to yield exfoliated structures depend strongly on how the viscosity of extragallery epoxy molecules evolves with time, as the extragallery epoxy offers viscous resistance to separation of clay layers. Therefore, clay layer exfoliation is difficult if the viscosity of the epoxy rises faster.

We now have all the force components operating on a pair of adjacent clay layers (see Figure 1). The sum of viscous force and attractive forces arising due to electrostatic attraction and van der Waals force work against exfoliation, while elastic force due to conformational entropy work for clay layer separation. If the elastic force overcomes the attractive forces and viscous force, exfoliation of clay occurs; otherwise, intercalated clay structures, with cross-linked epoxy molecules in them, are retained in the cured system. It is worthwhile to mention that exfoliation in an uncured system is not expected as the magnitude of the entropic force responsible for separating the clay layers is small due to small size of the epoxy monomers intercalating the clay galleries.

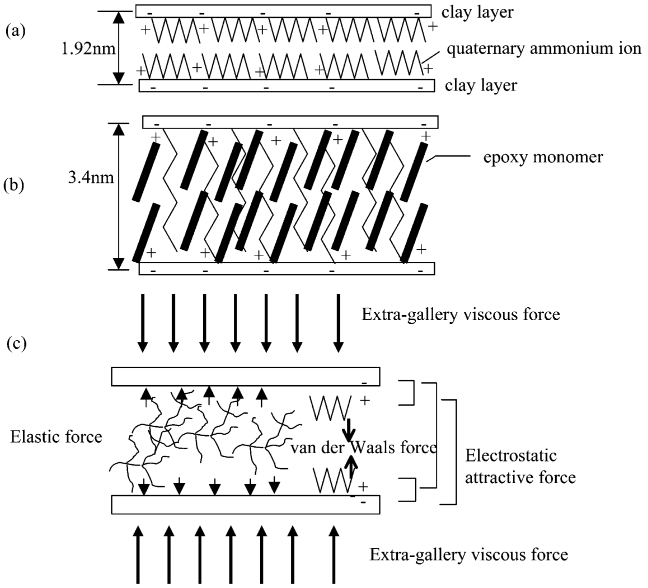

Figure 1. Schematic illustration of the intercalated state and exfoliation process showing the forces acting on a pair of clay layers: (a) organically modified clay, clay 3; (b) epoxy-intercalated state; (c) forces acting on a two-particle tactoid.

Vaia and Giannelis[41,42] presented a comprehensive treatment of the forces responsible for intercalation of clay galleries by molten thermoplastic polymer chains. These authors considered total entropy change as the sum of entropy gain by surfactant upon clay gallery expansion and loss of entropy due to polymer chain confinement. The relevance of this scenario to the present study can be drawn to explain epoxy and amine intercalation process. However, this study differs from those of Vaia and Giannelis[41,42] in that major entropic forces are generated here in the curing step, the theoretical treatment of which is not available in the literature.

The separation of clay particles from the tactoid structures begins with the outermost clay layers. The attractive forces between adjacent clay layers originate from the attractive and the repulsive energy among the neighboring atoms. The potential energy of an ion within an ionic solid is not the same as the potential energy of a simple pair of ions as there are many similar and dissimilar neighbors. Such differences in energy between the ionic solid and ion pairs can be interpreted in terms of Madelung constant, which is the ratio of potential energy of an ion within three-dimensional solids and the energy between a single pair of ions.[43−45] The inner layers have a higher ionic bonding energy than the surface layers,[43] as shown schematically in Figure 2. Consequently, the surface layers can be separated more easily than the inner layers and the exfoliation process should begin with the separation of surface layers away from the tactoids. Thus, while the outermost gallery expands to an exfoliated gallery height, the adjacent interior galleries remain in their intercalated state, until their turn for exfoliation comes. Full exfoliation results if all layers are separated from all tactoids.

A relevant question about the role of stiffness of the clay layers on eventual separation can be discussed here. It is widely accepted that clay layers are not infinitely stiff and, therefore, can bend, as has been observed in the literature. Therefore, the eventual separation of clay layers will greatly depend on the relative position in reference to the location along the tactoids; e.g., the edges may bend more and cause larger separation than the center. These finer points, although relevant, were not explored in detail in this study.

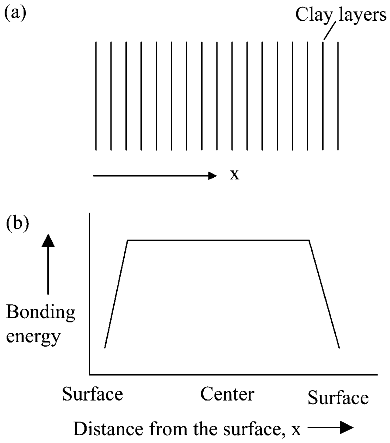

Figure 2. Schematic diagram showing the relationship between the ionic bonding energy and the location of the layers in the tactoid: (a) tactoid, (b) variation of bonding energy along the thickness of the tactoid.

An indirect evidence of reduction in the size of tactoids, which is a kinetic effect, is obtained from the observation that the peaks in WAXD do not move gradually to values of 2θ lower than 1.5° but rather reduce to smaller heights with increasing curing times. A recent study[29] proposed similar arguments to explain exfoliation of clay particles while melt compounding in polyamide 6; the polymer chains in this case were assumed to diffuse into the space between the clay particles to exert entropic elastic forces.

The gradual removal of clay layers from the tactoids cannot continue forever as 3-D epoxy networks are formed at the gel point, and the viscosity rises sharply to very large values. At this stage, relaxation of epoxy molecules is slowed down considerably due to the large viscosity of the surrounding chains and large values of shear stresses acting against the movement of the clay layers. Thus, the gel point provides an upper bound of time available for complete exfoliation of all tactoids. A fully exfoliated system results if all clay layers in all tactoids are exfoliated before the gel point. The gel point, on the other hand, is a strong function of curing temperature, curing agent, the nature of epoxy molecules, and even the nature of filler particles[46,47] and can be delayed or accelerated with proper choice of the ingredients.

The exfoliation mechanism proposed above was tested in this work using epoxy−nanoclay systems by considering two types of epoxy molecules—one aliphatic and one aromatic—and three curing agents, which offered latitude in varying the rates of intra- and extragallery polymerization of epoxy and the magnitude of storage modulus and viscosity during curing. In addition, the treatment on nanoclay particles was varied to include two types of quaternary ammonium ions, one of which is known for its catalytic effects on epoxy polymerization.

Experimental Section

Materials. *Nanoclay.* Cloisite 30B (clay 1), supplied by Southern Clay Products (Gonzales, TX), with methyl, tallow, bis(2-hydroxyethyl) quaternary ammonium ion as the cation-exchange resin was used after removal of typically 2 wt % of inherently present moisture. Sodium montmorillonite, Cloisite

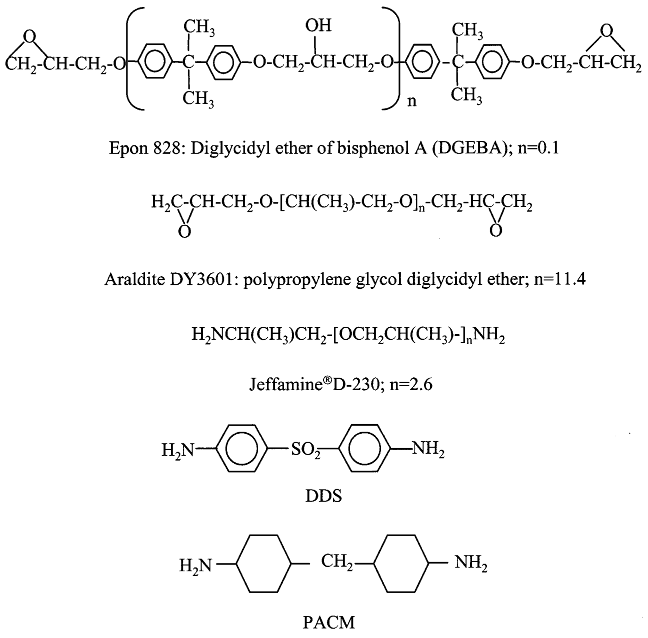

Figure 3. Chemical structures of Epon 828, Araldite DY3601, Jeffamine D230, Amicure PACM, and DDS.

Na$^+$ (clay 2), obtained from Southern Clay Products was also treated in our laboratory with *n*-hexadecylamine hydrochloride as the cation-exchange resin to produce treated clay, henceforth referred to as clay 3. A 5.66 g sample 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. About 15 g of clay 2 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 was detected in the filtrate by one drop of 0.1 N $AgNO_3$ solution. The treated clay was dried at 100 °C in the vacuum oven for 24 h, by which time all moisture was removed and a constant weight was obtained. The cation exchange equivalent (CEC) of clay 1, clay 2, and clay 3 was found to be respectively 90, 0, and 129 mequiv/g of clay.

Epoxy Resins. Two epoxy resins, one aromatic and one aliphatic, were chosen for the study. 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, poly(propylene glycol glycidyl ether), in the form of Aradite 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 epoxide equivalent weights, Epon 828 produced cross-linked epoxy networks much more rapidly and provided much higher values of shear modulus than Araldite DY3601.

Curing Agents. The curing agents were all diamine type (tetrafunctional) to facilitate rapid cross-linking of epoxy molecules. One aliphatic diamine curing agent, Jeffamine D230 of Huntsman Corp. (Houston, TX), and two cycloaliphatic polyamines, Amicure PACM (bis(*p*-aminocyclohexyl)methane) of Air Products (Cleveland, OH) and HT976 DDS (benzenamine, 4,4′-sulfonylbis) of Ciba (Tarrytown, NY), were used. Figure 3 shows the structures of the epoxy molecules and the curing agents used. The molecular weights of these curing agents were closer to each other, e.g., 225 g/g mol for Jeffamine D230, 198 g/g mol for PACM, and 248 g/g mol for DDS, such that they offered very small variation in molecular diffusivity values.

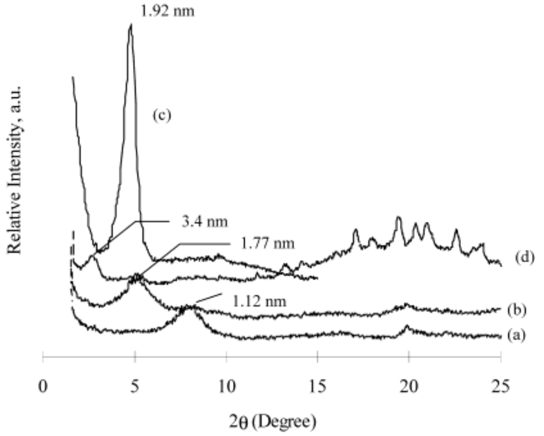

Figure 4. Characteristic *d*-spacing in clay galleries: (a) Cloisite Na$^+$ (clay 2); (b) Cloisite 30B (clay 1); (c) clay 3; (d) clay 1 and clay 3 swelled by Epon 828.

Preparation of Clay−Epoxy Nanocomposites. Organically modified clay particles, clay 1 and clay 3, were separately intercalated by epoxy by stirring the ingredients at 80 °C for 6 h with a magnetic stirrer, and the resulting mixture was dried in a vacuum oven at 80 °C for 30 min. A stoichiometric amount of suitable curing agent was 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 for 5 min at 60 °C.

The curing temperature and total curing times were varied to suit the curing agent; e.g., materials containing Jeffamine D230 and PACM were cured at 50−125 °C up to 5 h, while those with DDS were cured at higher temperatures, e.g., at 160−200 °C for up to 2 h. The aliphatic epoxy system was cured with Jeffamine D230 and PACM at 125 °C for 12 h.

Cure Kinetics Using DSC. Epoxy-curing agent and epoxy-curing agent−clay mixtures were cured isothermally under a nitrogen environment in a Dupont differential scanning calorimeter (DSC), model DSC-2910, to obtain the cure curves. The temperature was raised from room temperature to the desired curing temperature at a rate of 50 °C/min.

Rheological Measurements. The rheological properties of epoxy mixtures, with and without clay, during curing were measured using a RMS-800 Rheometrics rheometer with 25 mm parallel plate setup under oscillatory shear flow. The values of storage modulus and complex viscosity were recorded. The gel time was 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.

Curing of Epoxy in the Presence of Quaternary Ammonium Ions. Epoxy monomer and solid, dry *n*-hexadecylamine hydrochloride were mixed at 60 °C for 20 min using a magnetic stirrer, and a stoichiometric amount of the curing agent was added and mixed further for approximately 5 min at 60 °C. The epoxy:quaternary ammonium ion ratio in the mixture was maintained at a desired level. These mixtures were cured in a RMS800 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

WAXD Study. Figure 4 shows representative X-ray patterns of various materials. It is clear that the

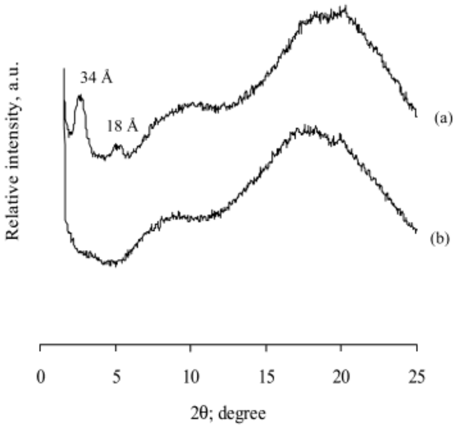

Figure 5. WAXD patterns showing (a) intercalated and (b) exfoliated clay structures obtained by curing Epon 828−5 wt % clay 1 mixtures using Jeffamine D230 respectively at 50 °C for 5 h and at 100 °C for 2 h.

respective quaternary ammonium ions increased the *d*-spacing in treated clay from 1.12 to 1.77 nm in clay 1 and to 1.92 nm in clay 3 (Figure 4b,c). The *d*-spacing further increased to 3.4 nm due to swelling of both clay 1 and clay 3 by epoxy (Figure 4d).

Although nanocomposites were prepared by first intercalating clay with epoxy, it was found that changing the sequence of addition of curing agent and epoxy did not have much influence on the exfoliation behavior. A more relevant question, however, was the ratio of epoxy and curing agent inside the clay galleries, which was difficult to determine, even if a stoichiometric ratio was maintained on an overall basis (including extra- and intragallery). A clay−amine mixture produced by mixing clay 1 and PACM at 60 °C for 5 min was examined by WAXD to reveal an increase of gallery height from 1.77 nm (clay 1) to 2.3 nm, which indicates the presence of amines inside the galleries. Grim[4] also indicated that montmorillonite type of clay has affinity for polar molecules, such as amines and alcohols. Separate experiment with Jeffamine D-230, however, did not reveal increase of gallery height. Jeffamine D-230 molecules are linear and packed inside the galleries without exerting entropic forces, while the bulky cyclohexane rings of PACM produced entropic forces, causing layer separation.[41,42] The clay gallery height further increased to 3.4 nm as amine-intercalated clay was mixed with epoxy at 80 °C as was originally observed (Figure 4d).

Three possibilities existed for the epoxy-to-amine ratio inside the galleries: (a) less than 1, (b) greater than 1, and (c) equal to 1. Only one of these possibilities was true in this case for all three curing agents, keeping in mind the closeness of their molecular weights. Therefore, the results presented in this paper refer to the same initial ratio of epoxy to amine inside the galleries before curing. It is worthwhile to note that the epoxy-to-amine ratio of much less than 1 and much greater than 1 would not generate high molecular weight epoxy network and would not lead to exfoliation of clay galleries.

Curves a and b of Figure 5 represent respectively partially and fully exfoliated clay structures produced by curing epoxy with Jeffamine D230 respectively at 50 °C for 5 h and at 100 °C for 2 h. If the sample is not fully exfoliated, as in Figure 5a, two X-ray peaks are obtained—one at $2\theta = 2.6°$ and the other at $2\theta = 5.0°$, corresponding to *d*-spacing of respectively 3.4 and 1.77 nm. Figure 6 presents TEM pictures showing the clay layer separation of about 10 nm in fully exfoliated structures (Figure 6a). In the intercalated state (Figure 6b), the clay tactoids remained mostly intact, in corroboration with the WAXD patterns of Figure 5. A low-magnification TEM image is provided in Figure 6c to show that clay particles were dispersed in epoxy to the scale of tactoids before curing and produced exfoliated structures upon curing with the same spatial distribu-

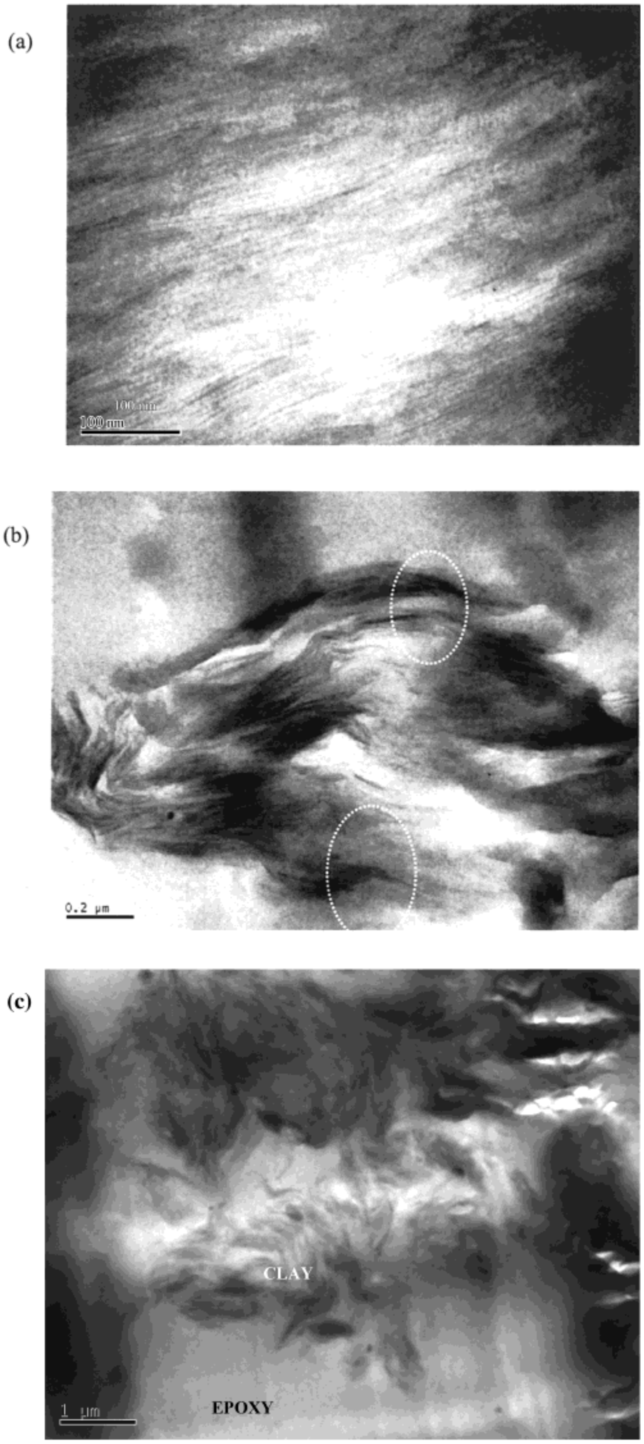

Figure 6. TEM image of an epoxy−clay composite containing 5 wt % clay 3: (a) exfoliated clay structure, cured with Jeffamine D230 at 100 °C for 3 h; (b) intercalated clay structure cured with PACM at 75 °C for 3 h. (c) Low-magnification image at the condition of (a) showing spatial distribution of exfoliated clay aggregates.

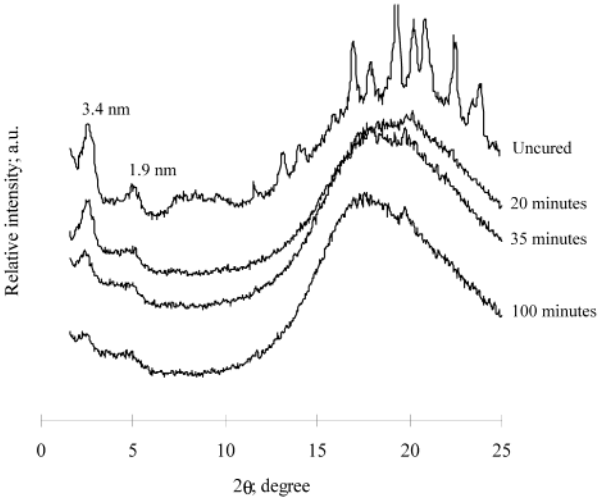

Figure 7. Changes in X-ray peaks at different curing times. Epon 828−clay 3 mixture cured at 180 °C using DDS. Clay content 5 wt %.

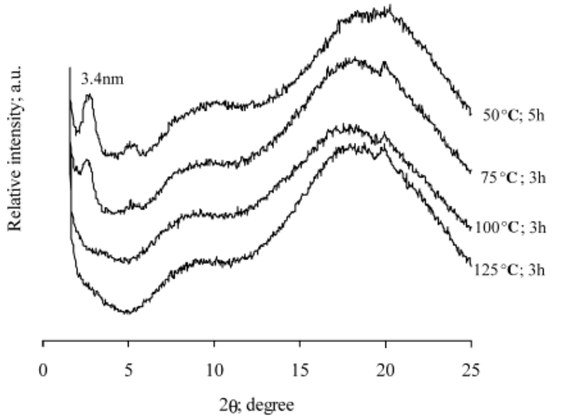

Figure 8. WAXD patterns obtained after curing epoxy at various curing conditions. Epon 828−clay 1 mixture cured with Jeffamine D230. Clay content was 5 wt %.

tion as in the uncured system. No shear-induced disordered exfoliated structures were obtained as curing was carried out under quiescent conditions.

It was observed in all cases that the positions of 2θ peaks did not change with curing, but their height reduced with the degree of curing, as is shown in Figure 7 for various curing times at a curing temperature of 180 °C for the DDS-cured system. Such reduction in peak height indicates that the epoxy-swelled tactoids with peak height of 3.4 nm lost many clay layers due to exfoliation. The same trend was observed for curing with PACM and Jeffamine D230 and with clay 1.

The effect of curing temperature on the state of exfoliation of clay structures is presented in Figure 8. A few similarities between Figures 7 and 8 are readily apparent. The peak height at $2\theta = 2.6°$ (3.4 nm) decreased for both higher curing temperature and at longer curing times. Also, the peaks at $2\theta = 5.0°$ (1.77 nm) disappeared with curing. In view of these, it can be concluded that both curing temperature and curing time dictate the state of exfoliation of clay structures, as was reported in recent literature.[7−9,16,18,19] Nevertheless, the complete state of exfoliation of clay was achieved only under certain conditions of curing times and curing temperatures; one such case is seen in Figure 8 for a curing temperature of 125 °C and a curing time of 3 h. Table 2 summarizes the observations gleaned from several conditions of curing.

Table 2. Summary of WAXD Study[a]

curing agent	clay type	curing temp, °C	curing time, h	time for first increase of storage modulus, s	exfoliation observed?
DDS	clay 1	140	2	8500	no
DDS	clay 1, 3	160	2	2240	no
DDS	clay 1	180	2	1140	no
DDS	clay 1, 3	200	2	530	yes
D230	clay 1	50	5	5300	no
D230	clay 1, 3	75	3	1000	no
D230	clay 1, 3	100	3	370	yes
D230	clay 1, 3	125	3	60	yes
PACM	clay 1, 3	75	3	533	no
PACM	clay 1, 3	100	3	390	yes
PACM	clay 1, 3	125	3	105	yes

[a] In all cases Epon 828−5 wt % clay mixtures were used.

The fact that peak location (e.g., at 5.0° and 2.6°) did not change with time in Figures 7 and 8 can lead us to infer that exfoliation process cannot be explained on the basis of the diffusion of epoxy and curing agents. If diffusion of epoxy into the galleries dictates the exfoliation process, the height of all galleries, whether at the surfaces or in the interior, should increase gradually, and their height distribution should follow a Gaussian behavior. However, the results presented in Figures 7 and 8 showed that the gallery height increased in steps, e.g., from 3.4 nm to greater than 6 nm; the latter value corresponds to a value of $2\theta = 1.5°$.

The influence of the nature of quaternary ammonium ions on clay exfoliation was found to be rather weak. The Jeffamine D230-cured Epon 828−clay system produced fully exfoliated clay structures with both clay 1 and clay 3, when cured at 100 °C. In view of this, most of the results presented in this paper were based on clay 3, although experiments were carried out using both types of treated clays.

Chemical Reactivity. It is evident from Table 2 that exfoliated clay structures were produced when cured at relatively higher temperatures for longer periods of time, which in turn has a direct bearing on the rate and the degree of curing. Figure 9 presents a set of cure curves obtained using different curing agents at several curing temperatures. As expected, the degree of curing depended strongly on the nature of curing agents and increased with curing temperature. For example, Jeffamine D230 provided the slowest curing at 50 °C and the fastest at 125 °C. Of all the conditions studied, the rate of curing was the highest with PACM at 125 °C, followed by Jeffamine D230 at 125 °C and DDS at 200 °C; in the case of PACM, the degree of curing reached 90% in approximately 15 min. Accordingly, exfoliated structures for Jeffamine D230 and PACM-cured systems were obtained for curing temperatures of 100 °C or above and for DDS-cured systems at 200 °C or above. These observations indicate that higher conversion is useful for production of fully exfoliated clay structures.

Let us now examine whether the argument presented above holds true for partially exfoliated systems. Figure 10 compares WAXD peaks of two partially exfoliated systems, cured respectively with Jeffamine D230 and PACM at 75 °C. The rate of curing with PACM was higher than with Jeffamine D230 (Figure 9b,c). However, the degree of exfoliation was found to be higher for the Jeffamine D230-cured system as the peak height at $2\theta = 2.6°$ (3.4 nm) is lower than the PACM-cured

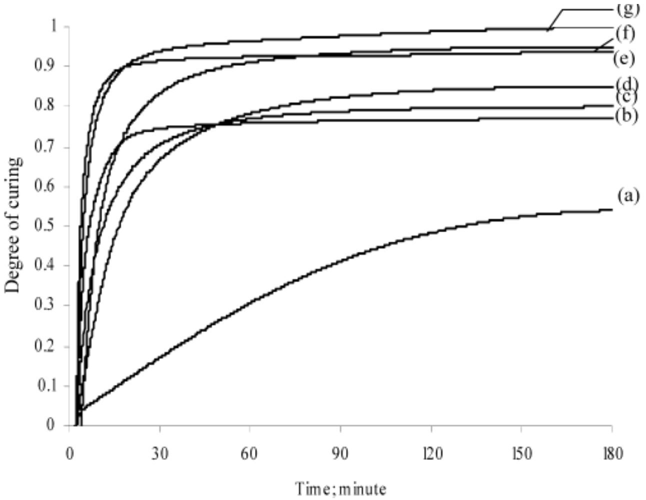

Figure 9. Cure curves of Epon 828 cured with three curing agents at different curing temperatures for 3 h: (a) Jeffamine D230 at 50 °C, (b) PACM at 75 °C, (c) Jeffamine D230 at 75 °C, (d) DDS at 180 °C, (e) PACM at 125 °C, (f) DDS at 200 °C, (g) Jeffamine D230 at 125 °C.

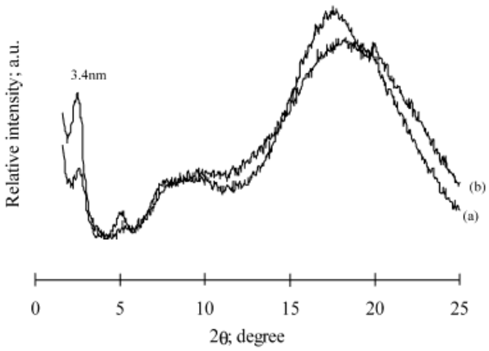

Figure 10. WAXD patterns of sample specimens cured with (a) Jeffamine D230 and (b) PACM at 75 °C. The samples contained 5 wt % of clay 3.

system. Therefore, it can be inferred that the degree of exfoliation cannot be interpreted entirely using the reactivity data.

Role of Diffusivity of Curing Agent. Curing agents, small molecules themselves, are capable of diffusing into clay galleries during mixing and curing and therefore may influence the exfoliation phenomena. The curing agents considered in this study were of similar molecular weight and, therefore, offered very similar molecular diffusivity at the same curing temperature. Consequently, in each case, the molecules of the curing agent were expected to diffuse into clay galleries in the mixing step and, therefore, not play any role in exfoliation. The above statement is supported by considering an example, where two different curing temperatures were used to intentionally alter the rates of diffusion, but no differences in the extent of exfoliation were observed, e.g., in the case of Epon 828−clay 1 mixtures cured respectively with DDS at 180 °C and Jeffamine D230 at 100 °C (see Table 2). The diffusivity of DDS was expected to be higher at 180 °C than that of Jeffamine D230 at 100 °C. Nevertheless, fully exfoliated structures were produced in the latter case.

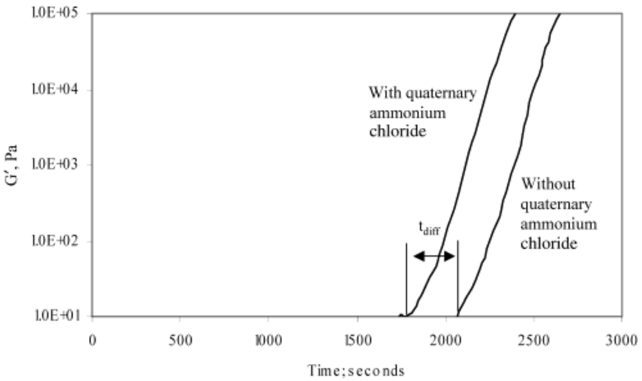

Figure 11. Epon 828 cured with DDS in a parallel plate rheometer showed much more rapid increase of storage modulus in the presence of hexadecylammonium chloride at 180 °C.

Table 3. Values of t_{diff} for Epon 828

curing agent	curing temp, °C	t_{diff}, s
Jeffamine D230	75	680
	100	133
	125	35
PACM	75	260
	100	88
	125	43
DDS	160	895
	180	268
	200	93

Intra- and Extragallery Polymerization Rates. The presence of organic modifiers gives rise to differences in intra- and extragallery polymerization rates.[16,18,19,21] A faster intragallery polymerization rate originates from the acceleration of epoxy curing reactions due to the acidity of the organic modifiers inside the galleries.[16] An indication of this was obtained in this study from the different values of shear modulus measured in oscillatory shear flow while curing epoxy with and without the presence of quaternary ammonium chloride. The time required for the onset of sharp rise of storage modulus substantially decreased in the presence of quaternary ammonium ions (Figure 11). The difference between the times taken for the onset of storage modulus rise in systems with and without quaternary ammonium chloride, t_{diff}, is presented in Table 3. The values of t_{diff} reduced with the increase of curing temperature for all curing agents, signifying that the rise of storage modulus becomes more dependent on the curing temperature at high values than the catalytic effects of the quaternary ammonium chloride.

In view of Figure 11 and Table 3, it can be inferred that, in all cases of treated clay, the intragallery polymerization rates were faster than the extragallery polymerization rates. Such faster rates can be attributed to the catalytic effects of the quaternary ammonium ions, originally observed by previous researchers.[16,18,19] Despite such differences in the rate of polymerization between intra- and extragallery, exfoliation was observed to occur only in some selected cases (see Tables 1 and 2).

One might argue that exfoliation is possible only in cases with lower viscosity, as lower viscosity promotes higher rates of diffusion of epoxy molecules and curing agents into the galleries. In addition, lower viscosities offer lower viscous resistance against separation of clay layers from the rest of the clay tactoids. However, an example shows that such is not the case. Epoxy cured with DDS at 180 °C offers much less viscosity at the beginning of curing than epoxy cured with Jeffamine D230 at 100 °C, although full exfoliation was obtained only in the case of Jeffamine D230-cured system (see Figure 12).

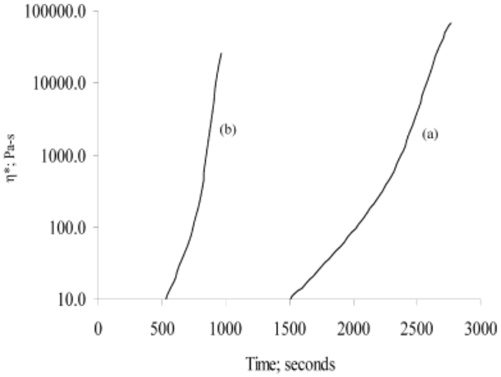

Figure 12. Epoxy cured with (a) DDS at 180 °C offered much less viscosity early in the curing period than epoxy cured with (b) Jeffamine D230 at 100 °C.

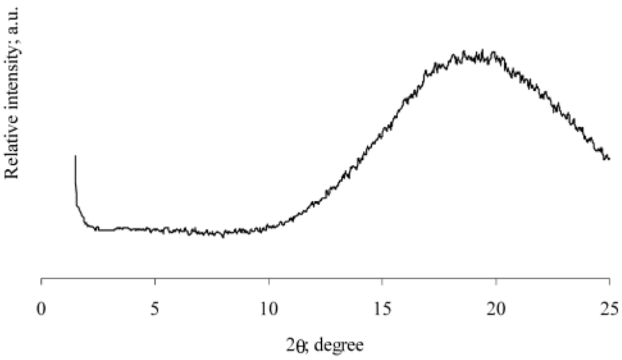

Figure 13. WAXD patterns showing fully exfoliated structures in epoxy−clay systems with intra- and extragallery polymerization rates matched. Clay content 5 wt % clay 3.

In another set of experiments, the intra- and extragallery polymerization rates were matched by mixing epoxy/clay/curing agent with desired amounts of organic modifier, hexadecylamine hydrochloride. Epon 828 was mixed with organically modified clay, clay 3 at 80 °C for 6 h, followed by mixing with curing agent Jeffamine D230 and organic modifier at 60 °C for an additional 5−10 min. The concentration of the organic modifier in extragallery epoxy was maintained at the same level as intragallery, and the rates of intra- and extragallery polymerization were matched. The mixture was cured at 125 °C for 3 h to produce the composite material. The WAXD patterns of the cured material, presented in Figure 13, shows fully exfoliated clay structures after curing. It is worthwhile to refer to Table 2 and reiterate that fully exfoliated clay structures were also obtained under the same conditions though with faster intragallery polymerization rate. Therefore, a disparity between the rates of intra- and extragallery polymerization is not a necessary condition for achieving fully exfoliated clay structures.

Relationship among Viscosity, Storage Modulus, Reaction Speed, and Exfoliation. The observations on exfoliation behavior presented in Table 2 can now be explained using the storage modulus and shear viscosity data presented in Figure 14. The data were generated by taking the values of storage modulus and viscosity at various times during curing of epoxy in a RMS-800 rheometer with a parallel plate setup and oscillatory shear flow at a frequency of 5 rad/s and a strain of 5%. Note that no clay was used.

Although the values of complex viscosity (η^*) and storage modulus (G') are interrelated, the magnitude of each can be useful. For example, for the same curing agent, Jeffamine D230, epoxy samples cured at 125 °C showed almost 400 times higher value of storage modulus (9220 vs 26 Pa) when compared to that cured at 50 °C for the same value of dynamic viscosity of 1000 Pa·s (see curves 50D and 125D in Figure 14). Therefore, the elastic force available for separation of adjacent clay layers in samples cured at 125 °C was about 400 times higher than cured at 50 °C, although the viscous force was the same. Consequently, a fully exfoliated clay structure was obtained in the former case, while the WAXD patterns presented in Figure 5a show a largely intercalated clay structures. It is worthwhile to mention here that the speed of curing of epoxy at 125 °C was almost 100 times faster than at 50 °C, as measured from the slope of the cure curves in Figure 9, and a higher value of storage modulus resulted in the former due to faster chain growth and lesser time for relaxation of growing chains. Another example is found where Jef-

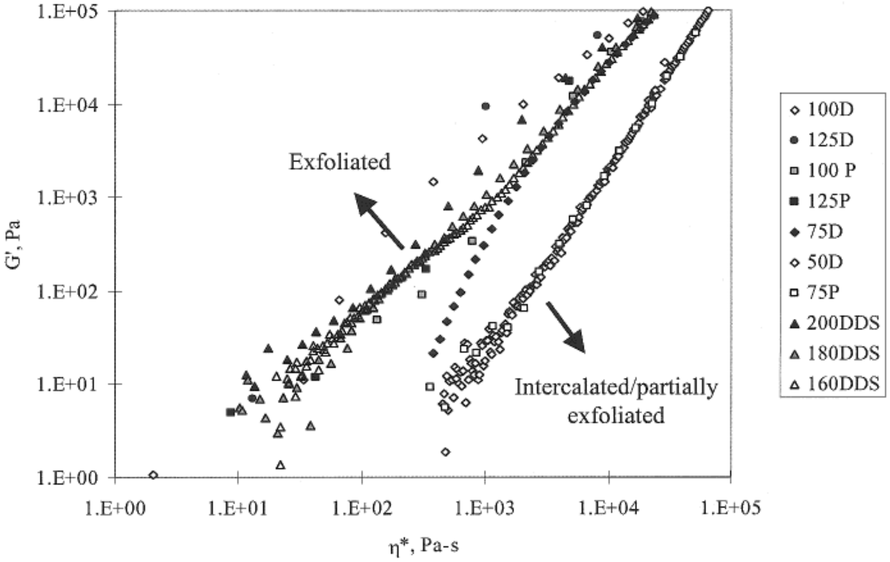

Figure 14. Relationship between storage modulus and viscosity taken at various stages of curing of Epon 828 in a RMS800 rheometer. The legends 50D, 75D, 100D, and 125D represent curing with Jeffamine D230 at respectively 50, 75, 100, and 125 °C; 75P, 100P, and 125P represent PACM-cured system at 75, 100, and 125 °C, while 160DDS, 180DDS, and 200DDS represent DDS-cured epoxy at 160, 180, and 200 °C.

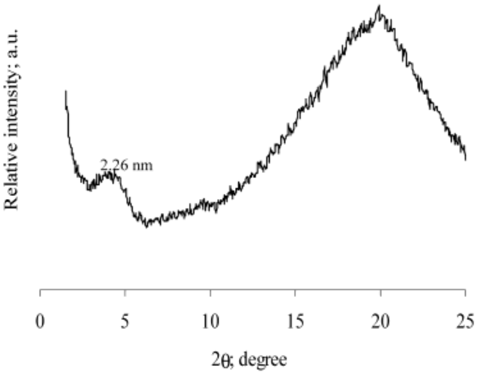

Figure 15. WAXD pattern of cured Araldite 3601–clay 3 mixture at 125 °C for 12 h with PACM. Clay content was 5 wt %.

famine D230-cured material showed almost 10 times higher storage modulus (456 vs 41 Pa) than PACM-cured material for the same value of dynamic viscosity, 1000 Pa·s (see curves 75D and 75P in Figure 14), but only partially exfoliated clay structures were obtained in both cases (Figure 10).

Figure 14 also lists the observations of Table 2 that complete exfoliation was possible only under certain conditions of curing. It can be inferred from Figure 14 that complete exfoliation was possible only when the ratio of shear modulus to complex viscosity was greater than 2–4 1/s, while partially exfoliated/intercalated structures resulted when the ratio was much less than 1 1/s.

The rationale for not using clay to generate the data of Figure 14 was to separately study how the viscosity of extragallery epoxy increased with curing. The values of storage modulus, one would expect from epoxy–clay systems, would be much larger than those presented in Figure 14, first due to clay content and second due to exfoliated structures. Nevertheless, the values of 2–10 1/s of the ratio of shear modulus to complex viscosity for exfoliation presented conservative estimates of the relative importance of storage modulus and were useful in explaining the trends.

Further evidence that elasticity of cross-linking epoxy was responsible for exfoliation of clay structures, the aliphatic epoxy, Araldite DY3601, was cured with Jeffamine D230 and PACM at 125 °C for 6 h in a RMS800 rheometer, and the evolution of storage modulus and complex viscosity was noted. The values of storage modulus and complex viscosity of fully cured system were found to be very low, in the range of 1–5 Pa for storage modulus and 5 Pa·s for complex viscosity. The WAXD patterns of clay structures (Figure 15) in Araldite DY3601 cured with Jeffamine D230 and PACM at 125 °C for 12 h showed the presence of intercalated tactoids with a *d*-spacing of 2.26 nm, although under the same curing conditions fully exfoliated clay structures were obtained with Epon 828.

A set of experiments was carried out where the intragallery polymerization rate was intentionally slowed down with the use of slow curing epoxy, Araldite DY3601, while the faster curing epoxy, Epon 828, was used as the extragallery epoxy. Clay particles (clay 3) were first mixed with Araldite DY3601 and the curing agent (Jeffamine D230) to yield a material with clay content as high as 20 wt %. The clay structure was found to be intercalated by the molecules of DY3601 as tested by WAXD with a *d*-spacing of 2.26 nm. A small amount of this mixture was hand-mixed with Epon 828 and a requisite amount of the same curing agent to yield an epoxy–clay composite containing 4 wt % clay. The WAXD patterns presented in Figure 16a still show peaks at $2\theta = 2.6°$ and 5.0°, which are Epon 828-intercalated clay peaks. Therefore, complete exfoliation of the clay structures was not possible due to slow rise of elasticity inside the clay galleries.

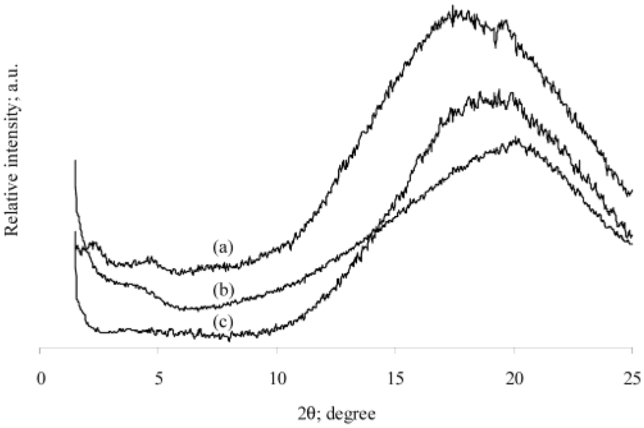

Figure 16. WAXD patterns of cured epoxy–clay 3 mixtures cured with Jeffamine D230 at 125 °C for 3 h: (a) Araldite DY3601 inside the gallery, Epon 828 outside the gallery; (b) Epon 828 inside the gallery, Araldite DY3601 outside the gallery; (c) Epon 828 inside and outside the gallery to match intra- and extragallery polymerization rates. Clay content: 4 wt % in (a, b), 5 wt % in (c).

In another experiment, the treated clay (clay 3) was first intercalated with faster curing epoxy Epon 828, and a small amount of the resultant mixture containing about 20 wt % of clay was dispersed in slower curing Araldite DY3601. The requisite amount of the same curing agent, Jeffamine D230, was mixed as well. In this manner, the intragallery polymerization rate was intentionally designed to be faster than extragallery polymerization rate, and the WAXD pattern of these materials presented in Figure 16b shows complete exfoliation of the clay structures. In the same way, an epoxy–clay system was prepared to offer the same rate of polymerization, both inside and outside the clay galleries. Epon 828 was mixed with 5 wt % clay 3 and thoroughly dried *n*-decylamine hydrochloride, and the mixture was cured with Jeffamine D230 at 125 °C for 3 h. A fully exfoliated clay structure again resulted as shown in Figure 16c. Therefore, faster intragallery polymerization expedites exfoliation of clay galleries but is not a requirement for exfoliation.

Table 4 lists the values of storage modulus and complex viscosity at gel point obtained for Epon 828 cured without clay and with clay 3 and in the presence of *n*-hexadecylammonium chloride. In this case, the gel point was defined as the time at which the value of loss tangent reached a value of unity for a strain of 5% and a frequency of 5 rad/s. Other definitions of gel points can be also used,[48,49] but the current definition was used only for comparison of the trends observed. It is evident that gel time and the values of storage modulus and complex viscosity dramatically reduced with curing temperature. In addition, the presence of both *n*-hexadecylammonium chloride and clay particles expedited gelation, although gelation was much more rapid at 100 and 125 °C in the presence of clay 3 purportedly due to exfoliation of clay particles (Figure 17). PACM caused the fastest gelation, in 100 s, followed by

Table 4. Gel Time (t_{gel}) Obtained Using a RMS800 Rheometer; Epon 828 Cured with Jeffamine D230 Separately without Clay, with 5 wt % Clay 3, and with Hexadecylammonium Chloride

	no clay			with clay 3		with hexadecylammonium chloride		
curing temp, °C	75	100	125	100	125	75	100	125
t_{gel}, s	3670	893	226	367	126	2990	760	191
complex viscosity η*, Pa·s	20500	3400	1200	10700	4770	21300	3610	1218
storage modulus, Pa	77000	12000	3000	36000	17600	83900	12200	2800

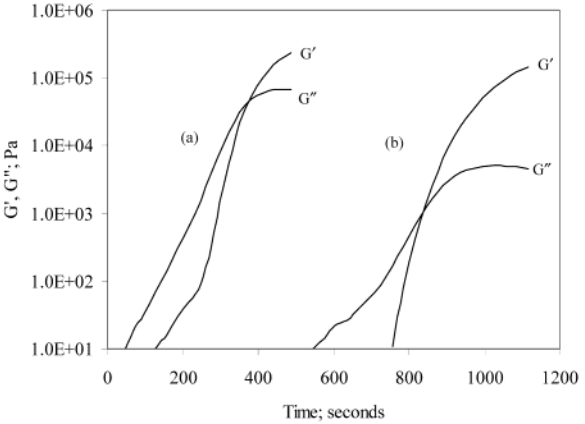

Figure 17. Changes of storage modulus (G') and loss modulus (G'') for curing of Epon 828 with Jeffamine D230 at 100 °C: (a) with 5 wt % clay 3, (b) without clay.

Jeffamine D230, in 226 s when Epon 828 was cured at 125 °C. Thus, the time available for complete exfoliation of clay structures was a little less than 4 min for the Jeffamine D230-cured system at 125 °C, while the presence of clay 3 accelerated gelation to about 2 min (Figure 17). A detailed investigation on the role of clay content and organic treatment of clay on gel time and the values the complex viscosity and storage modulus at gel point is being conducted in our laboratory, and the results will be reported in a future publication.

One question that comes to mind is why only the elasticity originating inside the galleries are being considered in our effort to explain exfoliation mechanism. The elasticity of epoxy, curing outside the galleries, also increases with curing, but the confinements to growing chains by the layers of clay are not present. Consequently, cross-linking epoxy chains outside the galleries relax gradually until the gel point is reached, by which time the chains form 3-D networks and relax over a long period of time.

Conclusions

The results presented shed light on the role of elastic force as the primary force behind clay layer exfoliation in epoxy−nanoclay systems. The elastic force exerted by the cross-linking epoxy molecules inside the clay galleries pushed out the outermost clay layers from the tactoids against the opposing forces arising from electrostatic and van der Waals attraction and shear, the latter due to motion of clay sheets during exfoliation. Exfoliation continued until the extragallery epoxy turned into a gel; the formation of gels, on the other hand, was expedited by higher curing temperature and the presence of clay particles. Exfoliated structures were produced even when the rates of intra- and extragallery curing reactions were matched, which obviates the requirement that intragallery polymerization must be faster. It was found in this study that complete exfoliation of clay structures can be produced if the ratio of shear modulus to complex viscosity is maintained at or above 2−4 1/s, such that elastic forces inside the galleries outweigh the viscous forces offered by the extragallery epoxy.

Acknowledgment. This research was partially supported by National Science Foundation CAREER grant (DMI-0134106) to S.C.J. The authors thank Doug Hunter of Southern Clay for providing clay particles and anonymous reviewers for suggesting improvements.

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MA021509C