

The Effects of Promoter and Curing Process on Exfoliation Behavior of Epoxy/Clay Nanocomposites

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ABSTRACT: The effects of a catalyst and coupling agent as well as a curing process on exfoliation behavior of $\text{CH}_3(\text{CH}_2)_{15}\text{NH}_3^+$ -montmorillonite clay in an anhydride-cured epoxy-clay system have been investigated by XRD, DSC, and TEM. The results have shown that the organoclay is easily intercalated by the epoxy precursor during the mixing process, and the clay galleries continue to expand during the curing process, but the Na^+ -montmorillonite clay is not intercalated during either the mixing or the curing process. The results also suggest that in the cured system without any promoter although partial exfoliated clay layers have already formed, an amount of the intercalation structure still remains. Although addition of a promoter or coupling agent into the cured system significantly lowers the maximum reaction temperature, and during the curing process the layered organoclay can be gradually broken into nanoscale structures, in which no d_{001} diffraction peaks are observed, the complete exfoliation is achieved at gel time or before. The possible mechanism for the complete exfoliation is discussed on the thermodynamic and kinetic point of view. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 808–815, 2000

Key words: epoxy resin; layered silicate; nanocomposite; promoter; coupling agent

INTRODUCTION

The dispersed phase in conventional composites is on a macroscopic (μm)-length scale, while for nanocomposites it is on a nanometer-length scale. Owing to this structural aspect, the dispersed phase has a large specific surface area and strong interaction with the matrix. Also, owing to the two-dimensional homogeneity and the high aspect ratios of the nanoscale clay layers, typically in the range 200–2000, nanocomposites can ex-

hibit lighter weight dimensional stability and a certain degree of strength, stiffness, heat resistant, and barrier properties with far less clay loading than that used in conventional filled polymer composites. Hence, they have attracted considerable attention from both the scientific and practical point of view.

The *in situ* polymerization of monomer in the clay galleries, or so-called intercalate polymerization, is one of very useful methods to prepare high-performance properties of polymer-clay nanocomposite materials.^{1–4} This approach has been successfully employed to prepare thermoplastic nanocomposites.^{5–12} Thereafter, this revolutionary nanocomposite chemistry has also been

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extended to the thermosetting systems, such as polyimide and epoxy.^{13–16} Due to several influences, two types of nanocomposites would possibly be formed: intercalated, exfoliated, or sometimes a combination of both hybrids. However, only the exfoliated state, in which silicate nanolayers are delaminated and individually dispersed in the polymer matrix, may maximize interfacial contact between the organic and inorganic phases, and leads to a dispersion homogeneously; as a result, the nanocomposite with optimum performance properties can be obtained. The epoxy–clay nanocomposites can be readily prepared from either solution mixing or directly mixing without any solvent as a swelling agent.^{13,15–19} Pinnavaia et al.¹⁷ have shown that the extent of organoclay layer exfoliation in the epoxy matrix is mainly determined by the chain length and the acidity of the gallery organic cations. Long-chain alkylammonium ions allow more epoxy precursors to be accommodated in the gallery that may be a prerequisite to achieve layer exfoliation upon an intragallery reaction. Onium ions with bronsted acidity catalyze an intragallery curing reaction at a rate that is comparable to the extragallery reaction. Therefore, the clays with acidic onium ions facilitate clay exfoliation and the formation of an exfoliated nanocomposite. Not long after, they¹⁸ have noted that even if by using onium ion chain lengths as short as three carbon atom, exfoliated clay nanocomposites can also be formed as long as all of the inorganic exchangeable cations have been replaced by alkylammonium ions after being subjected to several ion exchange reactions. Those results should manifest that the nature of organoclay including the ability to accommodate reactants and intragallery catalytic polymerization, plays an decisive role for balance of the intra- and extragallery polymerization rates and for exfoliation behavior; therefore, selecting a suitable catalyst that can be adsorbed by intergallery surfaces may be favorably reactive toward nanocomposite formation. Moreover, the curing processes of the thermosetting resins involve a multistep proceeding from a reaction fluid, elastomer (gelled rubber), and finally crosslinking solid, and at various stages the reaction mechanism changes from kinetic to diffusion control and the material vitrifies from an elastic gel to gelled glass. Due to the complexities involved that might influence the exfoliation behavior of the clays in the thermosetting matrix, work in this area must be deeply studied, especially the question of at which stage a complete exfoliation will be taken place

must be clearly understood. For this reason, in this article, the effects of curing process and addition of a catalyst and coupling agent into anhydride-cured epoxy–clay systems on exfoliation behaviors of $\text{CH}_3(\text{CH}_2)_{15}\text{NH}_3^+$ –montmorillonite are investigated by XRD, DSC, and TEM. The possible mechanism for complete exfoliation is also discussed as to the thermodynamic and kinetic point of view.

EXPERIMENTAL

Materials

Epoxy resin E-51, the diglycidyl ether of bisphenol A (denoted EP) with a molecular weight of 390, used in this study was a commercial product and purchased by Tianjin Synthesized Resin Factory (China). Methyltetrahydrophenol anhydride (MeTHPA), used as a curing agent, was produced by Shanghai Reagents Third Factory (China), CP. *N,N*-dimethylbenzylamine (DMBA) was used as a catalyst or promoter. γ -Glycidoxypropyltrimethoxysilane (denoted 560) was a coupling agent. Source clay Na^+ –montmorillonite (Na^+ -Mont) was obtained from China. Organoclay (16-Mont) was prepared by an ion-exchange reaction of Na^+ -Mont with *n*-hexadecylammonium chromide containing a small amount of onium ions with a shorter alkyl chain.

Preparation of Clay/EP Mixtures and Composites

To a 250-mL three-necked round-bottom flask the stoichiometric mixtures of epoxy resin and clays were added and magnetically stirred at 75°C for 30 min, then the temperature was raised to 225°C and stirred for another 1 min. The resulting mixtures still maintained at a liquid state during the mixing processes.

The curing agent (MeTHPA) with or without any catalyst (DMBA) was added into the clay/EP mixture in a beaker at 50°C, mixed thoroughly by stirring, then degassed in a vacuum desiccator, and cast into a Teflon mold. The composite samples were cured by a two-stage method as a received curing process (unless stated otherwise), i.e., first precured at 80°C for 2 h, followed post-cured at 160°C for 3 h. The concentration ratio of EP and MeTHPA was fixed at 100 : 80 by weight for composites without any catalyst, and EP : MeTHPA : DMBA = 100 : 80 : 2 for composites with a catalyst. For composites with a catalyst

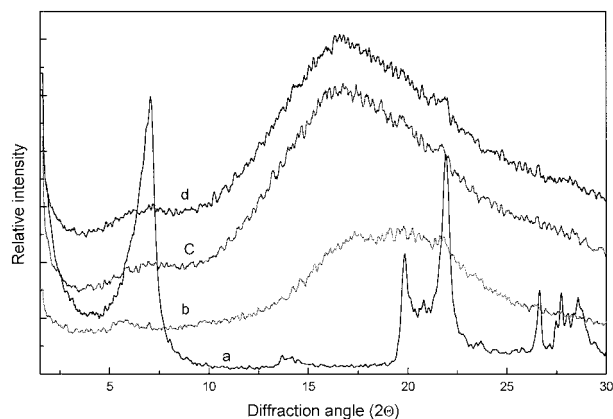


Figure 1 XRD patterns of epoxy containing 3% Na⁺-montmorillonite clay mixtures and composites: (a) pristine clay, (b) mixed at 225°C, (c) b mixture cured at 80°C 50 min, (d) b mixture cured at 80°C for 2 h, then 160°C for 3 h.

and coupling agent, the coupling agent was 2% of the total epoxy resin weight.

Measurement

The changes in basal spaces of the layered clays in mixture and composite samples were detected by XRD. X-ray diffraction patterns were recorded by monitoring the diffraction angle 2θ from 1.5° to 40° on a Japan D/max-RB 12-kW diffractometer using Cu K α radiation at a generator voltage of 40 kV and a generator current of 100 mA. The scanning speed and the step size used were at 2°/min and 0.02°, respectively. The cured block samples embedded in a capsule were microtomed with a glass knife. The resulting ultrathin sections supported on a copper grid were observed with a Hitachi H-800 transmission electron microscope (TEM) operated at an acceleration voltage of 100 kV. Differential scanning calorimeter (DSC) were conducted on Perkin-Elmer DSC-7 thermal analyzer at a heating rate of 20°C/min for dynamic scanning.

RESULTS AND DISCUSSION

Figure 1 represents the XRD patterns of epoxy/Na⁺-montmorillonite pristine clay mixtures and their composites. It can be seen that the [001] diffraction peak of the pristine clay appears at $2\theta = 7.06^\circ$, with basal spacing of 1.25 nm. Although there is no change at any of the diffraction positions, either in the mixtures or in the cured sys-

tems with the clay loading of 3 and 5%, indicating that even if the heat release by crosslinking reaction of extragallery has taken place, epoxy monomers hardly overcome the electrostatic attraction between the negatively charged silicate layers, and replace the exchangeable ions on clay layers, where no interlayer expansion is observed and only a conventional particle composite is formed.

By treating the clay with alkylammonium ions, however, the organic cations replace the inorganic cations and the original hydrophilic clay becomes an oilphilic organoclay; hence, the epoxy precursors can be absorbed by intragallery and pushes the layers apart. As shown in Figure 2, the diffraction peak of organoclay is located at $2\theta = 4.66^\circ$. The basal spacing of 1.9 nm is about 0.9 nm large than that observed with a dry montmorillonite. By comparison, with a sharp diffraction peak of pristine clay, an additional shoulder peak appears at $2\theta = 6.1^\circ$ near the main peak, corresponding to an interlayer separation of ~ 0.45 nm. Because the van der Waals diameter of a methyl group is about 0.4 nm,²⁰ it then can be deduced that the organoclay used is mainly a double-layer complex with the alkyl chain lying parallel to the silicate surface, while a small part of it is a single-layer complex with a short-alkyl chain. Also, the results in Figure 2 clearly show the diffraction peaks appearing at the same location with the same basal spacing of 3.5 nm for all of the mixtures, with loading in the range of 1–7%, and the secondary reflections are at about 5.0°, suggesting the clay tactoids have been expanded or intercalated by epoxy resin when mixed ether at 80°C or at elevated temperature of 225°C. As is well

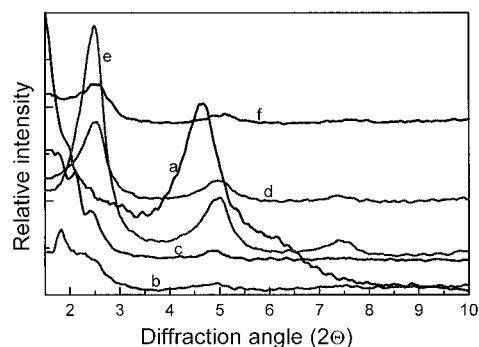


Figure 2 XRD patterns of epoxy mixtures with loading in the range 1–9% CH₃(CH₂)₁₅NH₃⁺-montmorillonite clay mixed at different temperatures for various periods of time: (a) organoclay, (b) 1%, 1 min at 225°C, (c) 3%, 1 min at 225°C, (d) 5%, 1 min at 225°C; (e) 7%, 1 min at 225°C; (f) 9%, 2 h at 80°C.

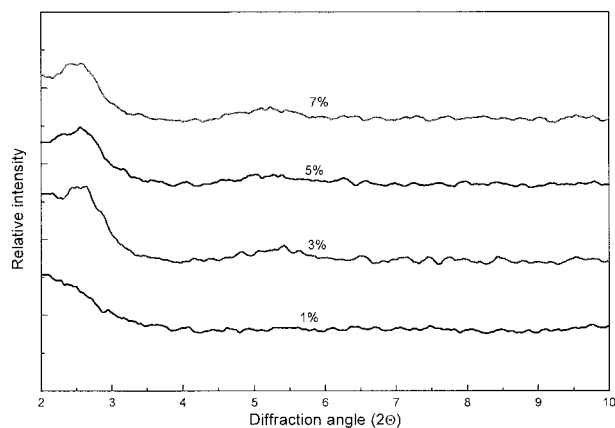


Figure 3 XRD patterns of acid-cured epoxy without any BDMA nanocomposites containing 1–7% organoclay.

known, the extent of clay expansion upon an organic molecule adsorbed is determined by the molecular size or chain length and the spatial arrangement of that in the silicate layer. For the *n*-hexadecylammonium ion used in this example, assuming the chain adopts a *trans-trans* configuration, then the basal spacing (or the extent of clay expansion) may be calculated from the following equation: $d_{001} = (n - 1) \times 1.26 + dc + dm$ (in Å), where *n* is the number of carbon atom, 1.26 is a length per carbon bond in the chain direction, and *dc* and *dm* are the basal spacing of dry clay and the van der Waals diameter of the methyl end group (0.4 nm), respectively. Clearly, the observed basal spacing (3.5 nm) nearly agree with the corresponding calculated values (3.2 nm) for epoxy/organoclay mixture systems. This indicates that the alkyl chain is completely extended perpendicular to the silicate surface and an intercalation complex with a “brush” configuration is formed. This is owing to the affinity of organoclay with the epoxy resin. Even with the steric hin-

drance of alkyl chains absorbed on opposite inter-layer surfaces, the entropy repulsion may occur. This will lead layered clays to expand further; thus, additional diffraction peaks may appear at lower angles with basal spacing of ~5 nm, corresponding to a distance of the order of twice the alkyl chain length, as observed in the mixtures at loading or below 3%.

Figure 3 shows the XRD patterns of epoxy/organoclay-cured systems without any promoter DMBA. It can be seen that by a two-stage curing process, the composite containing 1% clay does not exhibit a diffraction peak. The absence of Bragg scattering indicates that the clay tactoids have been completely exfoliated by the curing process and the composites with loading in the range 3–7%; however, they still retain an amount of intercalation clays, although there are dramatically decreases in the intensity of clay reflections when compared to the XRD of the corresponding mixtures, indicating that only an appropriate amount of intercalation clays have been transformed into exfoliation clays. A possible reason for this is that as the mixtures are cured at 80°C in the first stage, the curing rate for the systems without any promoter is too slow (the gel time is of 280 min, as shown in Table I), and within a period of 2 h, with the help of the protonated onium ions alone, the reaction extent or the release of the reactive heat in the gallery is too low to overcome the van der Waals attractive energy between the silicate layers and alkyl chains. This then restricts a large amount of silicate layers to continue to expand, while at the second stage curing process at 160°C the viscosity of the systems (which have been subjected to curing process at the first stage), increases rapidly to inhibit more epoxy and curing agents to migrate into the gallery space and then extragallery reaction will be faster than the intragallery reaction. As a re-

Table I Gelling Time of Epoxy and Epoxy/Organoclay Composites with Promoter

Sample (clay wt %)	t_g at 80°C (min)	t_g at 100°C (min)	t_g at 120°C (min)	t_g at 140°C (min)	t_g at 185°C (min)	Activation Energy (kJ/mol · K)
0	71.17	17.55	5.98	1.75		17.66
1	61.67	14.43	4.80	1.30		18.49
3	48.33	11.52	3.30	1.00		18.67
5	41.13	10.82	2.82	1.00		17.88
7	14.53	4.75	1.48	0.45		16.75
5 Without BMDA	280.0				1.68	

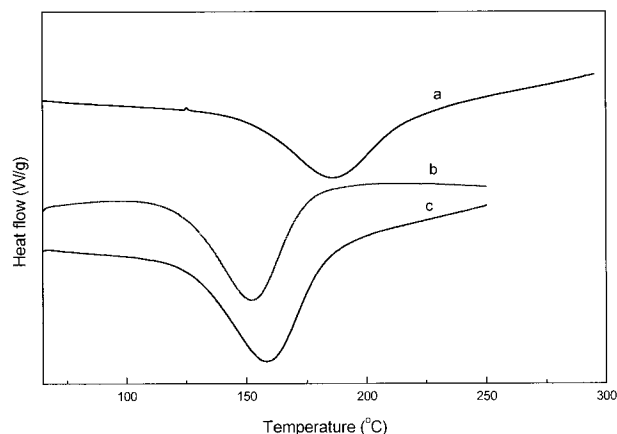


Figure 4 DSC curves of various acid-epoxy-5% $\text{CH}_3(\text{CH}_2)_{15}\text{NH}_3^+$ -montmorillonite clay mixtures: (a) without any BDMA, (b) with BDMA, (c) with BDMA and a coupling agent.

sult, some of the clay layers cannot be completely exfoliated, and intercalated clay nanocomposite structures tend to form. From DSC curves in Figure 4 it also can be seen that in cured epoxy-clay systems without any promoter, the temperature at which the maximum reaction heat arrived is 186°C, which is 30°C higher than in the systems with a promoter. If the mixtures with loading clays of 3 and 5% are cured at nearly the peak maximum temperature, 185°C for 1 h, the exfoliation behavior can be greatly improved, as shown in Figure 5.

Figure 6 illustrates the XRD patterns of cured epoxy-clay systems with a promoter, DMBA. The composites with 1–5% clay loading exhibit no

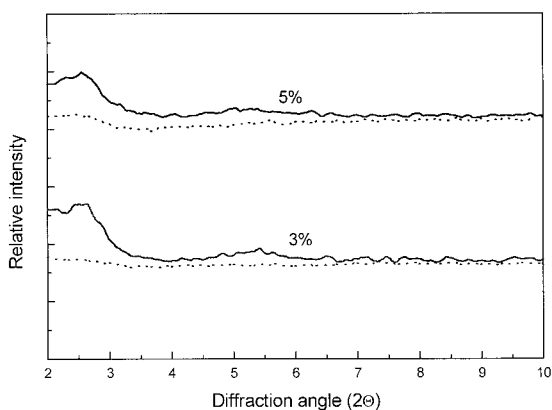


Figure 5 XRD patterns of epoxy nanocomposites with 3 and 5% clay cured by acid without any BDMA. (—) cured by received curing process, (···) cured at 185°C for 1 h.

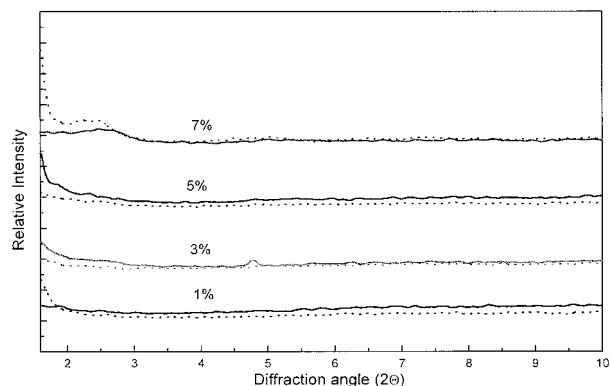


Figure 6 Comparison of XRD patterns for acid-epoxy/clay nanocomposites cured with and/or without the coupling agent.

Bragg scattering, indicating that the clay layers have been completely exfoliated by the catalyzation curing process and exfoliated nanocomposites are formed. This is true, as can be revealed by TEM observation for the composite with loading 5 wt % of organoclay (shown in Fig. 7). The clay layer separation is of 8.0 nm, even up to 15.0 nm. Thus, the addition of a suitable promoter will lower the peak maximum temperature and

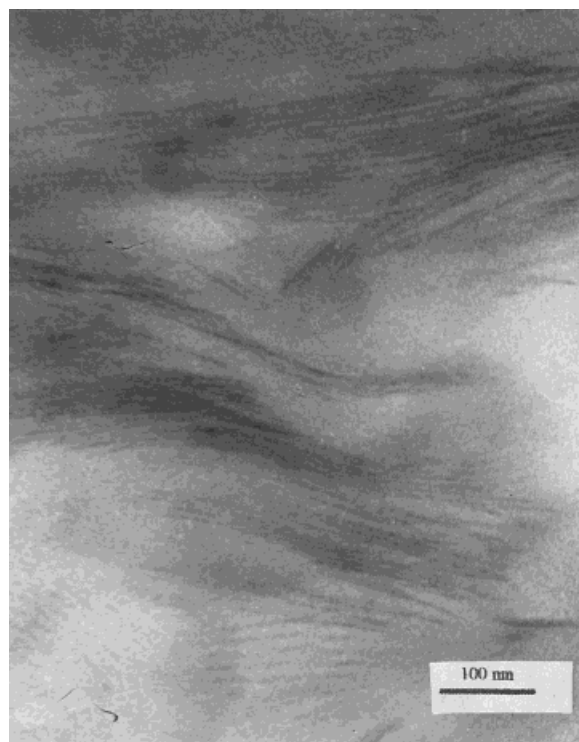


Figure 7 TEM photograph of an epoxy-5% $\text{CH}_3(\text{CH}_2)_{15}\text{NH}_3^+$ -montmorillonite clay nanocomposite.

quickly release the reaction heat of the intergallery, although the gelling time of the extragallery resin is simultaneously shortened, maybe a large amount of heat has been released at 80°C before resin hardening, where then an exfoliated nanocomposite will be formed. The gelling times, as a function of curing temperatures, are listed in Table I. It can be shown that for each system with the same loading, the greater the temperature, the shorter the gelling time, which follows the Arrhenius equation. In addition, the gelling time decreases with increasing the clay loading. Apparently, when the gelling time of a cured system is significantly shortened, the reaction may heat release before the gel point is enough for complete exfoliation to occur. As observed for the 7 wt % composite sample, the gelling time is relatively shorter (about 15 min at 80°C). Although the intensity of clay dramatically reflects a decrease compared with the corresponding mixtures, the amount of the clay still retains an intercalated structure. It should be noted, however, that the addition of a promoter is provided, which must be adsorbed by the intergallery; otherwise, complete exfoliation may not occur. DMBA is a nucleophilic reagent that can be adsorbed by the intragallery due to an affinity of organic cations with it.

The results of cured epoxy–clay systems with a promoter and coupling agent are included for comparison in Figure 6. Because the coupling agent can also be adsorbed by clay surfaces, and further lowers the peak maximum temperature (Fig. 5), it favors the cyclic anhydride to open and reacts with the epoxy. Consequently, the exfoliation behavior can be improved. As observed in Figure 6, the diffraction peak for a 7 wt % composite with a coupling agent shifts toward a slightly lower angle when compared to that in the composite without a coupling agent.

The catalysts can accelerate more reaction heat of the intragallery to release, and the polymerization can occur at a rate that is comparable to extragallery polymerization, which thus favors a complete exfoliation formation of the clay. But the curing processes of the thermosetting resins are more complexed than that of thermoplastics. During the curing proceeding the resin transformation from a reaction fluid to a crosslinking solid, the viscosity of the system will significantly increase. This might make the intragallery diffusion more restrictive, and it becomes more difficult to achieve a complete exfoliation of the clay tactoids. Therefore, the studies of the curing pro-

cess on exfoliation behavior, especially at which stage the organoclays are completely exfoliated, are important to prepare exfoliated nanocomposites. Figure 8(a) and (b) represent the XRD as a function of curing time at 80°C for epoxy–clay systems with a loading of 3 and 5% clay, respectively. It can be found that the diffraction peaks of intercalation still remained within a period of 20 min, while after 50 min the clays are completely exfoliated. The results indicate that the complete exfoliation of clay tactoids occurs at gelling time or before, as shown by Table I. This is consistent with the results of epoxy-18 alkylammonium montmorillonite systems, as reported previously.¹⁶

From the discussion above, for thermosetting nanocomposites there are two principles for predicting to the complete exfoliation of clay tactoids.

The first is thermodynamic principle: the free energy change, ΔG , for complete exfoliation is separable into independent enthalpy (ΔH) and entropy (ΔS) terms. They both are the sum of terms contributed by polymer and silicate clay, respectively, as following

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

for polymer matrix

$$\Delta G_c = \Delta H_c - T\Delta S_c$$

for silicate clay

The total free energy change, ΔG_t , is

$$\begin{aligned} \Delta G_t &= (\Delta H_m + \Delta H_c) - T(\Delta S_m + \Delta S_c) \\ &= \Delta H_t - T\Delta S_t \end{aligned}$$

When monomers or polymers penetrate into the gallery, they are situated in a restrained state, which inhibits intercalation, where the configurational or entropic change term, ΔS_m , is negative, namely entropy loss. In contrast, the expansion of the gallery by monomers or polymers causes the entropic change term of the clay gallery to be positive, namely entropy gain, which will compensate the entropy loss associated with the monomer or polymer confinement. If the entropy gain is large or equal to the entropy loss, the total enthalpy will determine whether or not exfoliation takes place, that is, as long as the release heat produced by intragallery polymerization,

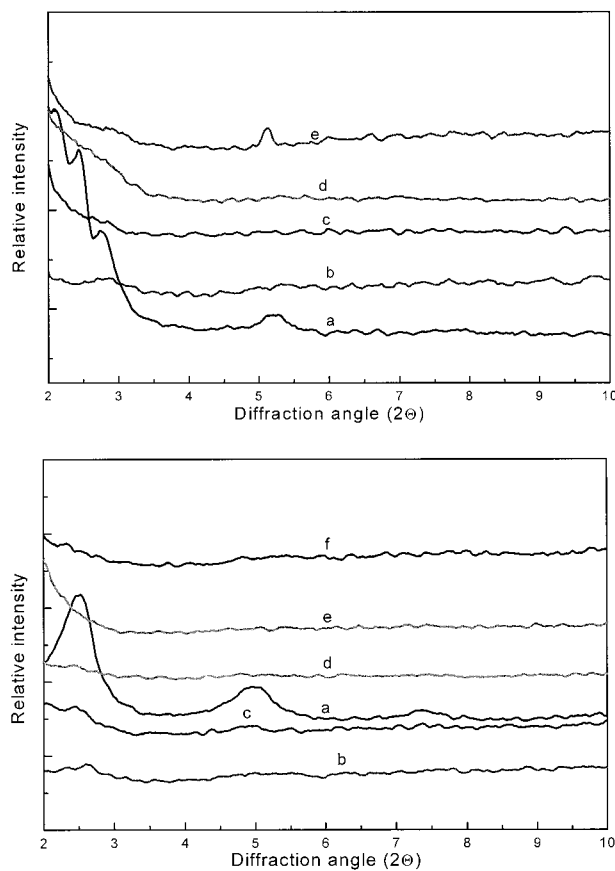


Figure 8 (a) XRD patterns of epoxy-3% clay nanocomposite cured with different curing processes: (a) mixture; (b), (c), and (d) cured at 80°C, for 20 min, 50 min and 80 min, respectively; (e) the received curing process. (b) XRD patterns of epoxy-5% clay nanocomposite cured with different curing processes: (a) mixture; (b), (c), and (d) cured at 80°C, for 20 min, 50 min and 2 h, respectively; (e) d sample postcured at 160°C for 1 h; (f) cured by the received curing process.

ΔH_m (at constant pressure), is larger than the van der Waals attractive energy (endothermic ΔH_c) at a distance above 8 nm (no Bragg scattering can be exhibited in XRD pattern), the complete exfoliation of the clay layers will take place spontaneously, which is the necessary condition for complete exfoliation. This can be shown in the instance of many composites with a promoter, on the contrary, as in the conventional composites with pristine clay and intercalated composites without any promoter.

The second is kinetic principle: when the reaction rate of the intragallery is comparable to the extragallery, but the gelling time of the system is significantly shortened, as long as the gel point is

arrived at the viscosity increases rapidly to inhibit more epoxy, and the curing agent migrates into the gallery space. Then the release heat is not large to enough, and as a result, some of the clay layers cannot be completely exfoliated, and then the intercalated clay nanocomposite structures tend to be formed. This is the fulfilled condition. As shown in the instance of intercalated nanocomposite containing 7% organoclay with a promoter.

In other words, the complete exfoliation condition is that the heat of the intragallery polymerization released before the gel point requires larger than the van der Waals attractive energy between the interlayer, i.e., $\Delta H_m(t \leq t_g) \gg \Delta H_c$. This consideration must be confirmed in further studies.

CONCLUSION

The organoclay is easily intercalated by the epoxy precursor during the mixing process, but the pristine clay is not even through the curing process. Addition of a suitable catalyst and coupling agent provided that it can be adsorbed by intergallery surfaces may be a favorable reaction toward the nanocomposite formation. The complete exfoliation is achieved at gelling time or before. The possible condition for complete exfoliation is that the heat of the intragallery polymerization released before the gel point requires larger than the van der Waals attractive energy between the interlayers.

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