

# Homopolymerization Effects in Polymer Layered Silicate Nanocomposites Based Upon Epoxy Resin: Implications for Exfoliation

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**ABSTRACT:** Exfoliation of polymer layered silicate nanocomposites based upon epoxy resin has previously been reported to be enhanced by allowing some homopolymerization of the resin to occur, catalyzed by the onium ion of the organically modified clay, before the addition of the cross-linking agent and the curing of the nanocomposite. In this work we examine the effects of homopolymerization induced by pre-conditioning the resin/clay mixtures by storing them at various temperatures, from room temperature to 100°C, prior to curing. It is found that pre-conditioning results in similar increases in both the epoxy equivalent (EE) and the glass transition temperature ( $T_g$ ) of the resin as a consequence of homopolymerization, with a linear relationship between

EE and  $T_g$  that depends on the pre-conditioning temperature. This is attributed to two different homopolymerization reaction mechanisms, activated monomer (AM) and activated chain end (ACE), the former dominating at high temperature and the latter at low temperature. The effects of these homopolymerization reactions on the network and nanostructure of the nanocomposite are discussed, the important aspect emerging being that the ACE mechanism is the one that most significantly enhances the exfoliation process. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1040–1047, 2009

**Key words:** PLS nanocomposites; homopolymerization; montmorillonite; epoxy resin

## INTRODUCTION

It is generally accepted that the optimum nanostructure for polymer layered silicate (PLS) nanocomposites is one in which the clay layers are fully exfoliated, implying that the silicate platelets are completely separated from their original ordered stacking arrangement, and are distributed uniformly throughout the polymer matrix. This exfoliated nanostructure should be distinguished from an intercalated structure, in which the clay layers are somewhat separated by the penetration of the polymer into the clay galleries, but where the layer stacking order persists.<sup>1–3</sup> In practice, a nanostructure with characteristics of both exfoliation and intercalation is usually obtained, with the extent of exfoliation dependent on the details of the nanocomposite prepara-

tion method. Any procedure which could enhance the degree of exfoliation would have tremendous potential for advancing the industrial application of these nanocomposite materials.

In this work, we investigate one such possibility in the case of PLS nanocomposites prepared by in-situ polymerization with epoxy resin as the matrix material. This is based upon the original observation by Benson Tolle and Anderson<sup>4</sup> that prolonged storage at room temperature of a mixture of epoxy resin and organically modified montmorillonite (MMT) before adding the cross-linking agent and curing the nanocomposite led to a dramatic enhancement of the development of exfoliation as identified by Small Angle X-ray Scattering (SAXS). We subsequently used various thermal analytical techniques to investigate such storage of resin/clay mixtures, a process referred to as pre-conditioning,<sup>5</sup> and attributed the resulting effects to a homopolymerization reaction of the epoxy monomer catalyzed by the onium ion of the organically modified MMT.

In fact, some years earlier Wang and Pinnavaia<sup>6</sup> had noted that, instead of crosslinking the epoxy using a curing agent,<sup>7</sup> a new type of epoxy-based PLS nanocomposite could be prepared by homopolymerization of diglycidyl ether of bisphenol A (DGEBA) epoxy resin in the presence of an

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organically modified MMT clay. On heating samples in the differential scanning calorimeter (DSC) at 20 K/min they found that the onset temperature for homopolymerization of the epoxy/clay mixture was more than 100°C less than that for the epoxy resin alone, and that this reaction transformed the mixture into a polyether-clay nanocomposite in the form of a highly expanded powder, as observed also by others.<sup>8,9</sup> The absence of diffraction peaks in the SAXS patterns indicated that the clay layer separation had been increased beyond that measurable by this technique, while transmission electron micrographs (TEM) were considered to display an exfoliated nanostructure, though the original stacking arrangement can still be seen.

The promotion of homopolymerization in epoxy-based PLS nanocomposites would therefore appear to provide an interesting possibility for the attainment of a well-exfoliated structure. However, not only do all of these studies<sup>6,8,9</sup> as well as others,<sup>10</sup> initiate the homopolymerization reaction by increasing the temperature, which can approach that at which significant degradation occurs, but also the final powder texture is not desired. In contrast, Benson Tolle and Anderson<sup>4</sup> and Hutchinson et al.<sup>5</sup> have demonstrated that a homopolymerization reaction takes place in these resin/clay mixtures even at room temperature. Of course, the reaction takes place more slowly and does not proceed to completion, but the advantage is that when, after this preconditioning, the crosslinking agent is added, the process of exfoliation is enhanced.<sup>4</sup> The mechanism of clay exfoliation is still open to debate, but it is clear that the reaction kinetics plays an important role,<sup>11,12</sup> which is intimately linked with any pre-conditioning treatment of the resin/clay mixture. The purpose of this work is therefore to investigate the homopolymerization reaction that takes place during the pre-conditioning of epoxy resin/clay mixtures at several temperatures between room temperature and 100°C.

## EXPERIMENTAL

Two resins of DGEBA type were used, DER 331 and DER 332 (Dow Chemical Company), differing in their viscosities and epoxy equivalents: respectively, 11,000–14,000 mPa·s and 182–192 g/eq for DER 331 and 4000–6000 mPa·s and 172–176 g/eq for DER 332, according to the manufacturer's literature. The clay was octadecyl onium ion modified MMT, Nanomer I.30E (Nanocor), and the curing agent was a polyetheramine, Jeffamine D-230 (Huntsman). The epoxy/clay mixtures were prepared with an MMT concentration of five parts per hundred resin (phr) by weight, by simple and solvent mixing. Simple mixing involves 6 h in an ultrasonic bath after first mechanically mixing the resin and clay, followed by

degassing under vacuum at room temperature (RT). For solvent mixing, the MMT was first dispersed in acetone, and then the appropriate amount of resin was added and mixed for 1 h in an ultrasonic bath. The mixture was then degassed under vacuum and left at RT to evaporate the acetone. Complete elimination of the solvent was considered to have occurred when the glass transition temperature  $T_g$  of this mixture had returned to the same value as that for samples prepared by simple mixing.

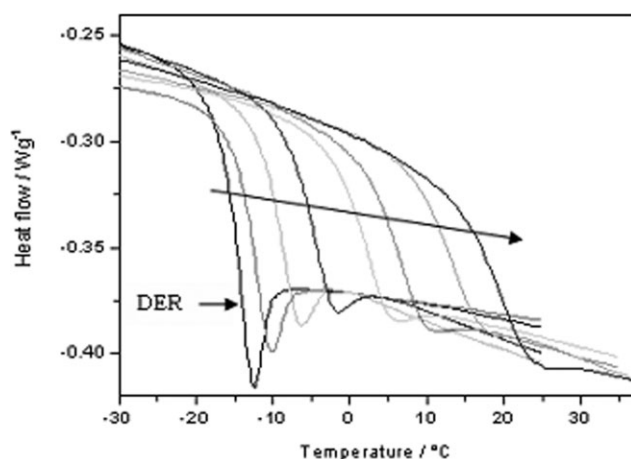
All epoxy/clay mixtures were pre-conditioned by placing them in thermostatic baths at 100°C, 80°C, 60°C or RT for various periods of time up to 4 months and more. As a function of pre-conditioning time and temperature, the epoxy equivalent (EE) for each pre-conditioned mixture was determined by titration,<sup>13</sup> and the glass transition temperature was determined by DSC. For this last, a Mettler-Toledo DSC821e calorimeter equipped with a sample robot and Haake EK90/MT intracooler was used, with a heating rate of 10 K/min over a temperature range from –70 to 25°C and for samples with mass between 8 and 10 mg.

The intercalation of the epoxy resin into the galleries of the layered clay was checked by measuring the *d*-spacing by SAXS. X-ray patterns were recorded on film under vacuum at RT, and molybdenum disulfide ( $d = 0.6147$  nm) was used for calibration. A modified Statton camera (W. R. Warhus, Wilmington, DE) using a pinhole collimator with Ni-filtered copper radiation of wavelength 0.1542 nm was used. All samples were studied within sealed quartz capillaries.

After pre-conditioning for the selected time at each temperature, a stoichiometric amount of curing agent according to the measured EE was added to the epoxy/clay mixture, and the cure kinetics was studied by DSC. For each cure experiment, a fresh mixture of resin/clay with the stoichiometric amount of curing agent was prepared. For comparison, DSC scans were also made to determine the cure kinetics of resin/clay samples without pre-conditioning and for the resin without clay. The cure kinetics was studied under non-isothermal conditions over the temperature range from –10 to 290°C for heating rates between 2 and 15 K/min, and under isothermal conditions at 70, 80, 90, 100, and 110°C. To verify complete cure, the glass transition and any residual heat of cure were evaluated from second heating scans at 10 K/min. More details of the experimental procedure are described elsewhere.<sup>12</sup>

## RESULTS

Figure 1 shows a typical set of DSC traces on a resin/clay mixture prepared by simple mixing using resin DER 331 and pre-conditioned at 100°C for the times indicated. It can clearly be seen that the  $T_g$  of



**Figure 1** DSC scans at 10 K/min to determine the glass transition temperature of DER 331 and of resin/clay samples prepared by simple mixing and pre-conditioned at 100°C for the following times: 3, 26, 47, 70, 82, 97, and 110 days. Arrow indicates direction of increasing pre-conditioning time. Exothermic heat flow direction is upwards and heat flow is normalized to the total sample mass.

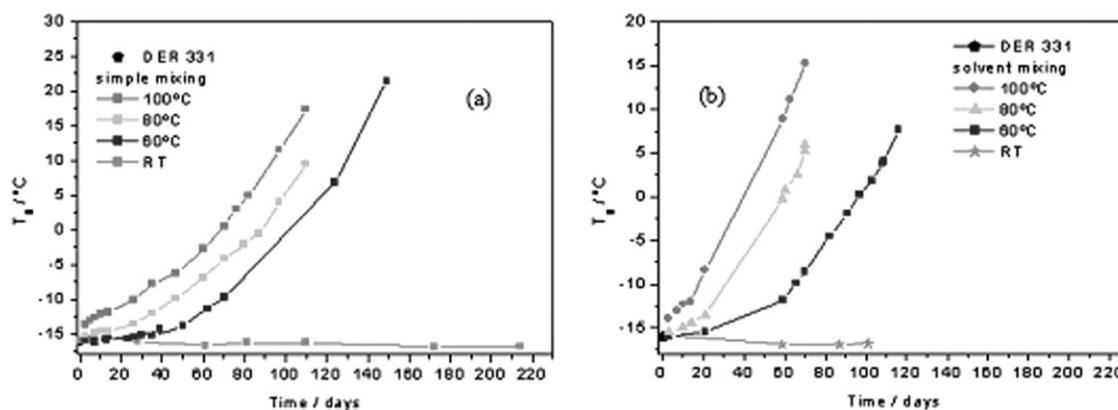
the mixture increases with increasing pre-conditioning time, and that the transition becomes wider and displays a reduced endothermic overshoot, indicative of a broadening of the relaxation time distribution.

The  $T_g$  is determined as the mid-point temperature between the glassy and rubbery asymptotes, and is plotted as a function of pre-conditioning time in Figure 2 for the different pre-conditioning temperatures and preparation methods, and for resin/clay mixtures based upon DER 331. Within the timescale used here, pre-conditioning at RT has no noticeable effect on  $T_g$ . On the other hand, for pre-conditioning temperatures in the range 60–100°C there is a steep increase in  $T_g$ , the increase being more rapid the higher is the pre-conditioning temperature and for mixtures prepared by solvent mixing. Similar results were obtained also

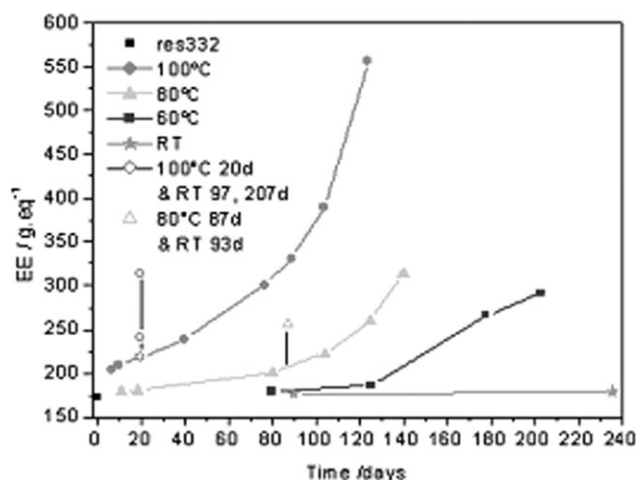
for epoxy/clay mixtures based upon DER 332 and prepared by simple mixing, the main difference being that the pre-conditioning effect on  $T_g$  occurs more slowly for DER 332 than for DER 331. For example, pre-conditioning simple mixtures at 100°C for 100 days results in an increase in  $T_g$  to about 12.5°C for DER 331, but only to about 5°C for DER 332, with even more pronounced differences being observed at lower pre-conditioning temperatures.

In parallel with the determination of the glass transition temperatures, the EE of the same pre-conditioned mixtures was evaluated by titration, and the dependence of EE on pre-conditioning time at the different temperatures is shown in Figure 3 for the case of resin/clay mixtures based upon DER 332 prepared by simple mixing. A similar trend to that found for  $T_g$  can be seen. There is no noticeable effect for pre-conditioning at RT, but at the higher pre-conditioning temperatures the EE increases with increasing pre-conditioning time, and more so the higher is the pre-conditioning temperature. The increase in EE implies a reduction in the amount of epoxy groups, and is a direct measure of the amount of homopolymerization that has taken place during the pre-conditioning.

The similar trends for both  $T_g$  and EE as a function of pre-conditioning time and temperature suggest that there might be a simple relationship between these two measurements, and this is indeed what transpires. Figure 4 shows that there is an excellent linear relationship between EE and  $T_g$  over the ranges of values covered here. An increase in  $T_g$  as the EE increases, in other words as the amount of homopolymerization increases, is clearly to be expected, though one might not a priori anticipate a linear relationship. What is particularly interesting, though, is the observation that there is a different linear relationship for each of the different pre-conditioning temperatures. This implies that the amount of homopolymerization that occurs during pre-



**Figure 2** Dependence of glass transition temperature on time of pre-conditioning at temperatures indicated for resin/clay mixtures based on DER 331 and prepared by (a) simple mixing and (b) solvent mixing. The lines are drawn to guide the eye.

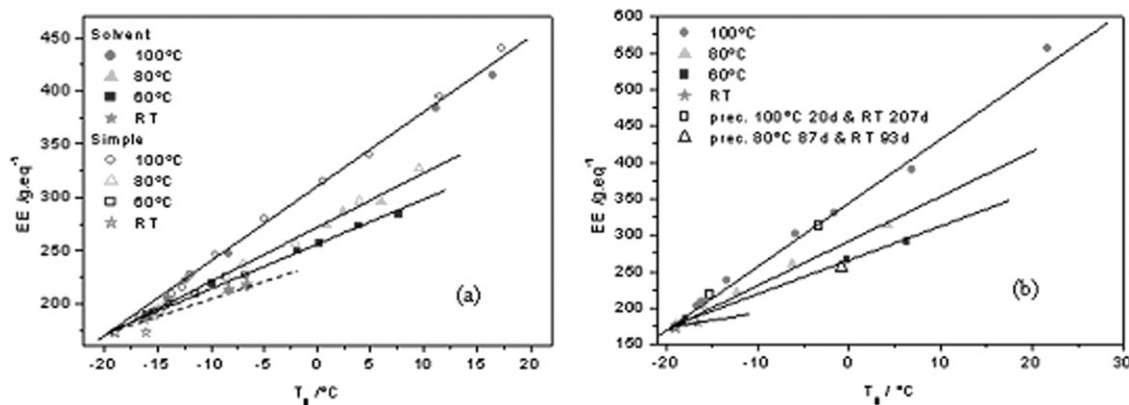


**Figure 3** Dependence of epoxy equivalent (EE) on pre-conditioning time at temperatures indicated for resin/clay mixtures based on DER 332 and prepared by simple mixing. The lines are drawn to guide the eye.

conditioning, as identified by the EE, is insufficient on its own to define the network structure and its properties, in particular  $T_g$ . Instead, different network structures appear to be formed when homopolymerization takes place at different temperatures, with lower pre-conditioning temperatures leading to higher  $T_g$  networks. Furthermore, this occurs for both types of preparation method, simple and solvent mixing, as can be seen in Figure 4(a). Thus, even though the pre-conditioning effect is more rapid for the resin/clay mixtures prepared by solvent mixing (Fig. 2), the relationship between EE and  $T_g$  is independent of the preparation method, implying that the same network structure is formed in both cases but that the process takes place more rapidly when the solvent method is used to prepare the mixture.

It is also interesting to observe that the pre-conditioning rate at RT, which is effectively zero within the timescale used here (240 days maximum), can be accelerated by initiating the reaction at a higher temperature. This is shown by the open symbols in Figures 3 and 4(b). In Figure 3, the lowermost open circle represents the EE value ( $\sim 220$  g/eq) for a resin/clay mixture pre-conditioned for 20 days at  $100^\circ\text{C}$ , for which the corresponding  $T_g$  value is approximately  $-15^\circ\text{C}$ , indicated by the lower open square in Figure 4(b). If the temperature of this pre-conditioned mixture is then reduced to RT and the pre-conditioning continues at RT for further periods of 97 and 207 days, the EE value is found to rise to  $\sim 240$  and  $\sim 315$  g/eq, respectively, as indicated by the other open circles in Figure 3, while the  $T_g$  increases to  $\sim -3.5^\circ\text{C}$  for the latter, indicated by the upper open square in Figure 4(b). This increase in both EE and  $T_g$  that occurs on pre-conditioning at RT for 207 days, after initiation at  $100^\circ\text{C}$ , is much larger than the effectively zero change that takes place when the pre-conditioning occurs only at RT for a similar period of time (238 days, see Fig. 3). In fact, in this case where the RT pre-conditioning for a period of 207 days is preceded by an initiation period of 20 days at  $100^\circ\text{C}$ , the relationship between EE and  $T_g$  falls exactly on the line for pre-conditioning at  $100^\circ\text{C}$ , as indicated in Figure 4(b) by the upper open square, the lower open square representing the effect of the prior initiation period of 20 days' pre-conditioning at  $100^\circ\text{C}$ . Thus, after initiation at  $100^\circ\text{C}$ , the same network structure with the same relationship between EE and  $T_g$  is being formed during pre-conditioning at RT as is formed during pre-conditioning at  $100^\circ\text{C}$ , albeit at a slower rate.

Similar behavior is observed when the homopolymerization is initiated by pre-conditioning at the lower temperature of  $80^\circ\text{C}$  for 87 days, leading to



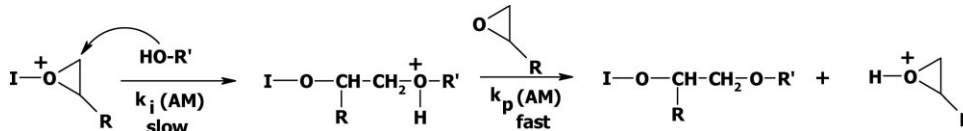
**Figure 4** Relationship between epoxy equivalent (EE) and glass transition temperature in resin/clay mixtures pre-conditioned at the temperatures indicated: (a) DER 331, filled symbols for solvent mixing, open symbols for simple mixing, for symbol \* refer to text; (b) DER 332, filled symbols for simple mixing, for open symbols refer to text. The lines are drawn to guide the eye.

values of EE of  $\sim 205$  g/eq and  $T_g$  about  $-14^\circ\text{C}$ , and then continuing the pre-conditioning at RT. After 93 days at RT, the EE has increased to  $\sim 255$  g/eq, as indicated by the open triangle in Figure 3, and  $T_g$  has increased to about  $-1^\circ\text{C}$ , as indicated by the open triangle in Figure 4(b). Once again, this represents an increase in both EE and  $T_g$  that would not have occurred at RT without the prior initiation at  $80^\circ\text{C}$ . In contrast to what happens after initiation at  $100^\circ\text{C}$ , however, the subsequent pre-conditioning at RT in this case does not lead to the same relationship between EE and  $T_g$  as for pre-conditioning at  $80^\circ\text{C}$ . The difference is indicated by the open triangle in Figure 4(b) lying significantly to the right of the line for  $80^\circ\text{C}$  pre-conditioning. This implies that after initiation at  $80^\circ\text{C}$ , the RT pre-conditioning

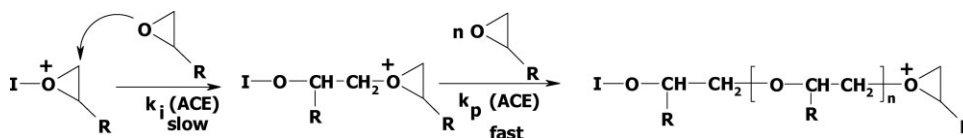
results in a different network structure, with a higher  $T_g$  for a given EE value, from that produced by pre-conditioning at  $80^\circ\text{C}$ .

## DISCUSSION

The apparently different homopolymerization processes that are occurring during pre-conditioning at increasing temperatures, giving rise to network structures with decreasing glass transition temperatures for the same extent of reaction as measured by the EE, are believed to be the result of different mechanisms of propagation in cationic polymerization. These have been designated as activated monomer (AM)



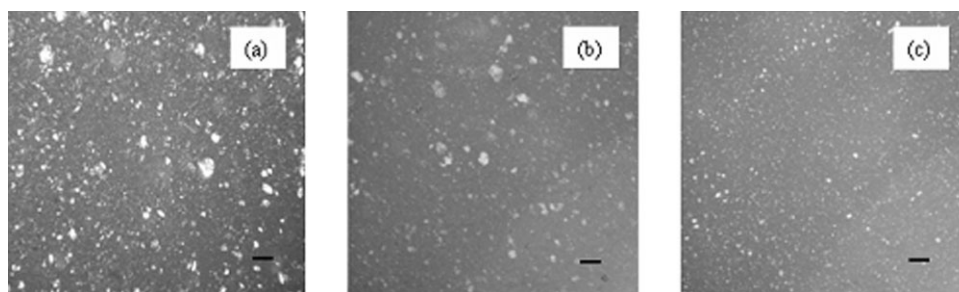
and activated chain end (ACE) mechanisms.<sup>14–17</sup>



According to Matejka et al.<sup>15</sup>, polymerization by the AM mechanism is slower because the repeating reaction step  $k_i$  (AM) is slower than the propagation step  $k_p$  (ACE) in the ACE mechanism. The AM mechanism can result in a certain number of short chains, or even in some crosslinking not taking place, which could introduce a plasticizing effect.<sup>17</sup> Hence less crosslinking in the network structure and a lower value of  $T_g$  would be expected of the AM mechanism, and it is the dominant mechanism at the higher pre-conditioning temperatures. In contrast, the ACE mechanism results in a greater degree of crosslinking and a higher value of  $T_g$ , and is the dominant mechanism at lower pre-conditioning temperatures. The acceleration of the RT pre-conditioning by initiation at higher pre-conditioning temperatures can be explained on the basis of these mechanisms. At the higher temperature, the AM mechanism creates numerous short chains, which persist when the resin/clay mixture is then pre-conditioned at RT, such that the ACE propagation reaction then gives rise to a faster homopolymerization than would have occurred in the presence of the rel-

atively few chains that would have been present without the initiation step at the higher temperature.

A further illustration of this initiation effect is afforded by some earlier experiments on resin/clay mixtures, using a DGEBA resin of different provenance (Epon 828, Shell Chemicals, EE = 185 – 192 g/eq, viscosity 11,000 – 15,000 mPa·s) with the same 5 phr by weight of Nanomer I.30E clay. This mixture was mechanically mixed for 1.5 h at  $50^\circ\text{C}$ , rather than RT, not for the purposes of pre-conditioning (about which we were unaware at the time) but simply to reduce the viscosity and improve the dispersion of the clay in the resin. After this simple mixing procedure, the resin/clay mixture was then stored at RT. While studying the effects of pre-conditioning with resins DER 331 and DER 332, we measured also the  $T_g$  and EE for the Epon 828 mixture after storage at RT for 34 and 37 months, and the results are plotted as the symbols \* in Figure 4(a). It can be seen that the RT pre-conditioning has been accelerated by the very short initiation period of 1.5 h at  $50^\circ\text{C}$ , and that the slope of the dashed line corresponding to RT pre-conditioning is consistent with the trend shown by the lines for higher pre-conditioning temperatures.



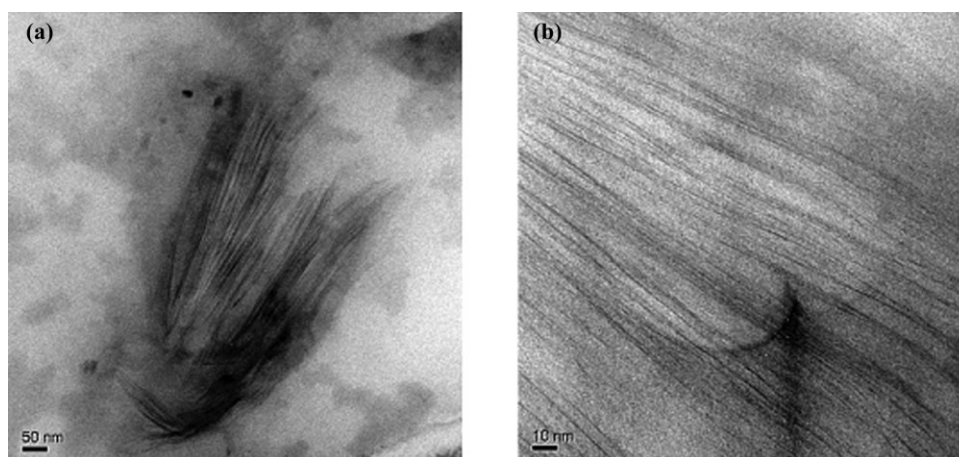
**Figure 5** Optical micrographs of simple mixture of resin with 5 phr modified clay: (a) without pre-conditioning; (b) after pre-conditioning 28 days at 100°C; and (c) after about 3 years at RT. Scale bar is 100  $\mu\text{m}$ .

The more rapid pre-conditioning observed for solvent mixing compared with simple mixing can be explained by physical rather than chemical effects. It is known that solvent preparation of resin/clay mixtures leads to a much better dispersion of the clay in the resin,<sup>5</sup> which has a significant effect on the cure kinetics and the nanostructure development.<sup>18,19</sup> The better dispersion implies an easier access of the resin to the modified clay layers, where it is the onium ion which acts as a catalyst of the homopolymerization reaction. Although the reaction proceeds more rapidly in the solvent prepared mixtures, for any given pre-conditioning temperature both solvent and simply mixed samples will experience the same homopolymerization mechanism, thus giving a unique relationship between EE and  $T_g$  for each pre-conditioning temperature [Fig. 4(a)].

The dispersion of the clay in the resin is crucially important in the development of an optimum nanostructure for the cured nanocomposite, and the effect of pre-conditioning at RT on the quality of the dispersion is interesting. Simple mixing of the epoxy resin with 5 phr by weight of the modified clay gives a rather poor dispersion<sup>5</sup> in which there are agglomerations, which can be as large as 100  $\mu\text{m}$ , as

shown in Figure 5(a). After pre-conditioning for 28 days at 100°C, the dispersion is noticeably better [Fig. 5(b)]. The effect of pre-conditioning at RT, however, is to produce a significantly better dispersion [Fig. 5(c)], even though the amount of homopolymerization that has taken place can be seen from Figure 4(a) to be less than that after 28 days at 100°C, for which a value of EE of  $\sim 225$  g/eq is observed (Fig. 3). The effect of pre-conditioning appears similar to that occurring in the polymerization filling technique,<sup>20</sup> whereby in-situ polymerization of olefins catalyzed directly from the surface of carbon nanotubes allows for a complete deaggregation of these fillers.

During curing of these pre-conditioned resin/clay mixtures, the dispersion of the clay aggregates is improved still further, as illustrated by the transmission electron micrograph in Figure 6(a), which shows a typical aggregate with dimensions of almost 1  $\mu\text{m}$  in length, the original clay layer longitudinal dimension, and about 500 nm in the transverse direction. At higher magnification within an aggregate [Fig. 6(b)] it is clear that although there is an overall increase in the clay layer  $d$ -spacing, from about 3.5 nm in the freshly intercalated resin/clay



**Figure 6** Transmission electron micrographs of cured nanocomposite prepared from resin/clay mixture pre-conditioned at RT for about 3 years.

**TABLE I**  
**Glass Transition Temperatures of Cured Nanocomposites**

Sample or pre-conditioning treatment	$T_g/^\circ\text{C}$	
	Isothermal	Non-isothermal
none	$85.9 \pm 0.7$	$82.3 \pm 0.5$
$100^\circ\text{C}/28$ days	$83.4 \pm 1.1$	$80.3 \pm 1.3$
RT / 3 years	$93.8 \pm 1.0$	87.1
without clay	–	$85.6 \pm 0.6$

mixture, as determined by SAXS,<sup>5</sup> the nanostructure is far from being fully exfoliated.

The importance of there being different mechanisms operating as a function of the pre-conditioning temperature lies also in the resulting network structure and its properties. In fact, pre-conditioning at RT appears to be the most interesting in this respect. This is very clearly seen from the values of  $T_g$  observed for resin/clay mixtures cured with the stoichiometric amount of diamine, which are given in Table I. For example, a simple mixture based on DER 331 and pre-conditioned at  $100^\circ\text{C}$  for 28 days has a  $T_g$  value in the range  $83.4 \pm 1.1^\circ\text{C}$  after isothermal cure and  $80.3 \pm 1.3^\circ\text{C}$  after non-isothermal cure, with no systematic effect of the particular cure conditions (i.e., isothermal cure temperature, or heating rate for non-isothermal cure), while the same mixture without pre-conditioning has  $T_g$  values in the ranges  $85.9 \pm 0.7^\circ\text{C}$  and  $82.3 \pm 0.5^\circ\text{C}$ , respectively. Thus, pre-conditioning at  $100^\circ\text{C}$  reduces the  $T_g$  of the cured nanocomposite. On the other hand, the Epon 828 mixture pre-conditioned for about 3 years at RT has a  $T_g$  of  $87.1^\circ\text{C}$  after non-isothermal cure, which not only is greater than the  $T_g$  of the nanocomposite made from the same mixture without pre-conditioning, but also is greater than the  $T_g$  of the cured resin without any clay ( $85.6 \pm 0.6^\circ\text{C}$ ),<sup>18</sup> in contrast to the usual observation that  $T_g$  decreases with the addition of clay.<sup>18</sup>

Even more remarkable, though, is the effect on this pre-conditioned Epon 828 mixture of an isothermal cure at low temperature after heating from ambient at a slow rate. For the preparation of bulk samples for the measurement of mechanical properties, the pre-conditioned Epon 828 mixture with the stoichiometric amount of diamine calculated according to the measured EE was placed in a mold and heated slowly (5 K/min) in an air circulating oven to  $70^\circ\text{C}$ , at which temperature it was cured isothermally for 2 h. After cooling slowly to RT, the plaque was removed from the mold and a small amount was cut off for the determination of  $T_g$ . A DSC scan from 25 to  $120^\circ\text{C}$  at 10 K/min showed a  $T_g$  of  $67.6^\circ\text{C}$ , indicative of vitrification, and hence only partial cure, during isothermal cure at  $70^\circ\text{C}$ . A sec-

ond DSC scan from 25 to  $250^\circ\text{C}$  revealed some residual cure, and a third scan showed a  $T_g$  of  $93.8^\circ\text{C}$  for the fully cured sample. The plaque was subsequently replaced in the oven and postcured at  $120^\circ\text{C}$  for 6 h. A DSC scan on a small amount taken from this fully cured plaque showed a  $T_g$  of  $92.8^\circ\text{C}$ . A similar experiment in which the sample was first cured at RT for 20 h before post-curing showed a  $T_g$  of  $94.8^\circ\text{C}$  for the fully cured nanocomposite. These  $T_g$  values for the cured nanocomposite fabricated from a resin/clay mixture pre-conditioned for a long time at RT are remarkable, and indicate that a quite different process seems to be occurring during pre-conditioning at RT compared with higher temperatures.

## CONCLUSIONS

The pre-conditioning of mixtures of epoxy resin and clay by storage at various temperatures for periods of time up to 4 months and more leads to homopolymerization of the resin catalyzed by the onium ion of the organically modified clay. Both the EE and the glass transition temperature ( $T_g$ ) of the resin increase with increasing pre-conditioning time, the increase being more rapid the higher is the temperature and for the solvent preparation method. The relationship between EE and  $T_g$  is linear, and independent of the preparation method of the resin/clay mixture, but depends on the pre-conditioning temperature in a systematic way. This is attributed to different reaction mechanisms, the active monomer mechanism predominating at high temperatures and the ACE mechanism predominating at low temperature, which result in different network structures. The effect of pre-conditioning at room temperature is particularly interesting, as it leads to a much improved dispersion of the clay in the resin and, after cure, to a significant increase in the  $T_g$  of the cured nanocomposite under certain curing conditions.

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