

Intercalation of Epoxy Resin in Organically Modified Montmorillonite

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ABSTRACT: Various methods of preparation of epoxy resin/clay mixtures, before the addition of the crosslinking agent and curing to form epoxy-based polymer layered silicate (PLS) nanocomposites, have been investigated to determine their effect on the nanostructure. Organically modified montmorillonite clay was used, and the mixtures were prepared by both simple mixing and solvent-based methods. X-ray diffraction shows that intercalation of the resin into the clay galleries occurs for all clay loadings up to 25 wt % and for both preparation methods, but the dispersion of the clay in the resin, observed by optical microscopy, is significantly better for the solvent preparation method. Differential scanning calorimetry (DSC) shows that the intercalated resin has the same molecular mobility as the extra-gallery resin, but suggests that the intercalated resin does not penetrate completely into the galleries. Pro-

longed storage of the resin/clay mixtures at room temperature leads to changes in the DSC response, as well as in the response to thermogravimetry, which are interpreted as resulting from homopolymerization of the epoxy resin, catalyzed by the onium ion in the modified clay. This confirms and explains the earlier observation of Benson Tolle and Anderson (J Appl Polym Sci 2004, 91, 89) that "conditioning" of the resin/clay mixtures at ambient temperature has a significant effect when the crosslinking agent is subsequently added, and indicates that the preparation method has important consequences for the nanostructure development in the PLS nanocomposites. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3751–3763, 2006

Key words: nanocomposites; resins; dispersions; differential scanning calorimetry (DSC); cationic polymerization

INTRODUCTION

It is widely considered that the optimum structure in polymer layered silicate (PLS) nanocomposites in general, and in particular here for those based upon epoxy resins, is the one in which silicate layers in the clay are fully exfoliated.^{1,2} The first stage in this process of exfoliation is the intercalation of the resin into the galleries of the organically modified clay, which results in an increased separation of the clay layers to give a *d*-spacing for (001) reflections of 3–4 nm, as can be identified by peaks in intensity obtained by small angle X-ray scattering (SAXS). Following the addition of an appropriate crosslinking agent in the required proportion, the curing reaction can be accompanied by the simultaneous exfoliation of the clay layers such that the SAXS peaks broaden, decrease in intensity, and shift to larger *d*-spacing, eventually disappearing when the nanostructure is

presumed to be exfoliated. Absence of (001) reflections, though, does not guarantee a fully exfoliated structure,³ which should be verified by transmission electron microscopy (TEM).

However, it is clear from results presented in the literature (e.g., see Refs. 3–9) that this procedure does not always result in exfoliation. There are many factors that can influence the outcome, including resin type, curing agent, clay type and modification treatment, as well as cure temperature and time. In particular, it is often considered to be of primary importance that the intragallery cure reaction rate be greater than the intergallery rate for exfoliation to occur,^{3–5,9–12} though there remains some doubt about the actual molecular mechanisms involved.

Furthermore, in addition to the simple procedure of directly mixing the resin and the clay, which in itself can be subject to many variations, such as the use of a magnetic stirrer, high shear mixing and/or an ultrasonic bath, or mixing at ambient or elevated temperature, there have been a number of reports that the preparation of the resin/clay mixture by first dispersing the clay in a liquid (so-called solvent or slurry type preparations), before the addition of the resin, can improve the dispersion of the clay in the nanocomposite as well as facilitating its exfolia-

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tion.^{6,13–17} Finally, it appears also that the time interval between the preparation of the resin/clay mixture and the addition of the curing agent can have an important influence on the rate at which exfoliation takes place; Benson Tolle and Anderson¹⁸ call this process “preconditioning,” and find that it has an effect on both the morphology and the properties of the nanocomposite.

To achieve their full potential as advanced engineering materials, the morphology development in these epoxy PLS nanocomposites must be better understood before the structure–property relationships can be established. As an illustration of the uncertain situation that exists at present, consider the effect of clay content on the glass transition temperature, T_g , of PLS nanocomposites based upon diglycidyl ether of bisphenol-A (DGEBA) epoxy resin crosslinked with a diamine. According to Liu et al.,¹⁹ the T_g of the cured nanocomposites decreases with increasing clay content, by about 10°C for a 4 wt % clay concentration. On the other hand, Feng et al.²⁰ reported an approximately linear increase in T_g with increasing clay content, by 6°C for a 10 wt % concentration, Ratna et al.²¹ found a much larger increase of T_g , by as much as 20°C for a clay content of 5 wt %, Dean et al.²² reported a similarly large increase of T_g of 19°C, which remains constant for clay contents of 2, 4, and 6 wt %, while Jan et al.²³ found that T_g first increases dramatically, by 25°C to 27°C depending on the clay type, for a clay content of 0.5 wt %, and then decreases gradually, by 3°C or so, as the clay content increases up to 3 wt %. Apart from the results obtained by Liu et al.,¹⁹ all these data indicate an increase in T_g when clay is added and the resin is cured with a diamine. Strangely, when the DGEBA resin is cured with a tetramine the majority of data show a decrease, or no significant change, in T_g of the nanocomposites in comparison with the resin cured in the absence of clay. For example, for such systems, Brown et al.²⁴ found that T_g decreases by about 8°C (for Cloisite 30B), or by 10–20°C (for Cloisite 6A), or remains essentially constant (for Cloisite 25A), for clay contents up to 25 wt %, while Miyagawa et al.¹⁵ reported only a small increase, by less than 2°C, for clay contents up to 10 wt %. For anhydride cured DGEBA epoxy resin, more complex variations of T_g with clay content are observed,^{25,26} but with an overall increase in T_g for the nanocomposites in comparison with the resin cured in the absence of clay.

Such an uncertain situation does not only apply to the glass transition temperature of PLS nanocomposites. Similar observations can be made with respect to the tensile strength of cured PLS nanocomposites based upon DGEBA epoxy resin and montmorillonite. For example, the tensile strength has been reported to increase with clay content up to 4 wt %²⁷ or 5 wt %, ²⁸ to remain constant,²⁹ to decrease up to

5 wt %¹⁶ or up to 10 wt %, ³⁰ to increase for clay contents up to 2.5 wt % and then to decrease,³¹ or to decrease for clay contents up to 2 wt %³² or 4 wt %, ²² and then to increase for higher clay loadings.

From this brief survey of the literature, it is evident that there are many factors that can determine the structure and properties of nanocomposites. The example illustrated above, which relates to the glass transition temperatures of nanocomposites, shows that even for the same epoxy resin (DGEBA) and curing agent (diamine) differences of almost 40°C can be found for the effect of clay content on T_g , while even greater variations can be observed when other curing systems are studied. These discrepancies are clearly not trivial. As a consequence, the relationship between properties (in our examples T_g and tensile strength) and structure (as identified here by clay content) is not a simple one. In particular, much can depend on the first step in the fabrication process, namely the procedure adopted for the preparation of resin/clay mixtures. Accordingly, we present here the results of a detailed study, mainly, but not entirely, by thermal analytical techniques, of this preparation procedure, which leads to the intercalation of the epoxy resin in the galleries of the modified clay.

EXPERIMENTAL

Materials

A commercial organically modified montmorillonite (MMT), supplied by Nanocor, Inc. (Arlington Heights, IL), was used in this study. This organoclay has the trade name Nanomer I.30E, and is an octadecylammonium-treated MMT with a density of approximately 1.7 g/cm³ according to the manufacturer's literature.

The epoxy resin used (Epon 828, Shell Chemicals [Resolution Performance Products, Houston, Texas]) is based upon DGEBA and has a density of 1.16 g/cm³ and a viscosity of 110–150 Poise (11,000–15,000 mPa s) at 25°C. The epoxide equivalent weight is in the range 185–192 g/eq. For the few samples of resin/clay mixtures that were partially cured, the crosslinking agent used was a diamine, Jeffamine D-230 from Huntsman Corp (Salt Lake City, Utah).

Preparation of resin/clay mixtures

A number of different methods were used for preparing the mixtures of epoxy resin and clay. In the simplest procedure, about 1 g of the modified clay was mixed directly with the amount of epoxy resin to give the required weight percentage of clay, as a proportion of the total, in the final mixture. The mixing process was effected either by hand, by mechanical stirrer, or by the use of the Polytron (Model PT1200C, Kinematica AG, Lucerne, Switzerland), a high-shear

mixer with controllable speed between 5000 and 25,000 rpm, and took place either at room temperature or at temperatures up to 75°C, and was followed by degassing in a vacuum oven.

An alternative was the solvent preparation method, adopted in various forms by different groups,^{6,13–17} whereby the modified clay was first mixed with acetone (approximately 30 mL of acetone for 1 g of clay) using the Polytron, for 40 min, before adding the epoxy resin and continuing the mixing with the Polytron for a further 40 min. These solvent prepared mixtures were left uncovered in 100-mL glass beakers so that the majority of the solvent could evaporate, and were then degassed in a vacuum oven at room temperature to ensure the complete elimination of the solvent.

A number of resin/clay mixtures with clay contents from about 5 wt % up to more than 25 wt % were prepared by the different procedures outlined above. All resin/clay mixtures were then stored in desiccators prior to their study by the various thermal analytical techniques described below.

Optical microscopy

The dispersion of the clay in the resin was observed using a Leica polarizing transmission optical microscope.

Small angle X-ray scattering (SAXS)

The intercalation of the resin in the clay galleries was investigated by SAXS. X-ray diagrams were recorded on film under vacuum at room temperature, and molybdenum disulphide ($d = 0.6147$ 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 for these experiments. All samples were studied within sealed quartz capillaries.

Thermogravimetry

A Mettler Toledo thermogravimetric analyzer (TGA), model TG50-M3, was used to compare the thermal stability and weight loss characteristics of the resin/clay mixtures and of the epoxy resin. Samples of about 5 mg were placed in alumina crucibles and heated at 10 K/min from 40°C to 600°C under a dry nitrogen gas flow (200 mL/min).

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC821e equipped with an intracooler and robot sample placer, and the data was analyzed using the STAR software. These DSC experiments were used to investigate the glass

transition of the resin/clay mixtures for comparison with that of the resin alone, and also to study the homopolymerization reaction of the epoxy resin that takes place under circumstances described later. For the former, samples of about 10 mg were sealed in standard aluminum pans with a hole in the lid, and the standard procedure was to cool the sample from 25°C to –70°C at –10 K/min, stabilize at –70°C for 20 min, and then to perform the heating scan at 10 K/min from –70°C to 25°C, with a flow of dry nitrogen at 50 mL/min throughout. For the latter, samples of about 5 mg were heated to various temperatures in the range 150–225°C, representing a temperature interval just prior to the first significant weight loss identified by a complete TGA scan, and the glass transition temperature was then measured by scanning at 10 K/min in the DSC over a suitable temperature range. All glass transition temperatures were evaluated as the midpoint temperatures determined using the Mettler Toledo STAR software.

RESULTS AND DISCUSSION

Optical microscopy

The dispersions obtained by the different preparation methods were compared by examining, in the polarizing optical microscope, a drop of each mixture placed on a glass slide and spread between the slide and a cover slip. Typical dispersions for the simple mixing method and the solvent preparation method are shown in Figure 1(a, b), respectively. It is immediately apparent that a much better dispersion is achieved with the solvent preparation method. The sample prepared by the simple mixing method has a large number of agglomerations of the order of 30–40 μm in size, with the largest being of the order of 80 μm , whereas that prepared by the solvent method has the majority of agglomerations only of the order of 5–10 μm , while the largest are only about 20 μm . This is not likely to affect the characterization of the samples by X-ray diffraction or by DSC, since the process of intercalation is expected to occur independently of the size of the clay agglomerations. On the other hand, the dispersion is expected to have a significant effect on some properties of the cured nanocomposites if these agglomerations remain after crosslinking, and particularly on ultimate properties such as fracture strength and toughness.

X-ray characterization

The SAXS data obtained for the resin/clay mixtures prepared by the simple mixing method and by the solvent and slurry methods are shown in Table I.

The d -spacing for the modified clay (R0) of 2.09 nm, although it is slightly smaller than other values reported in the literature,^{10,21,33–38} which fall in the range 2.26 nm to 2.5 nm, for the same commercial

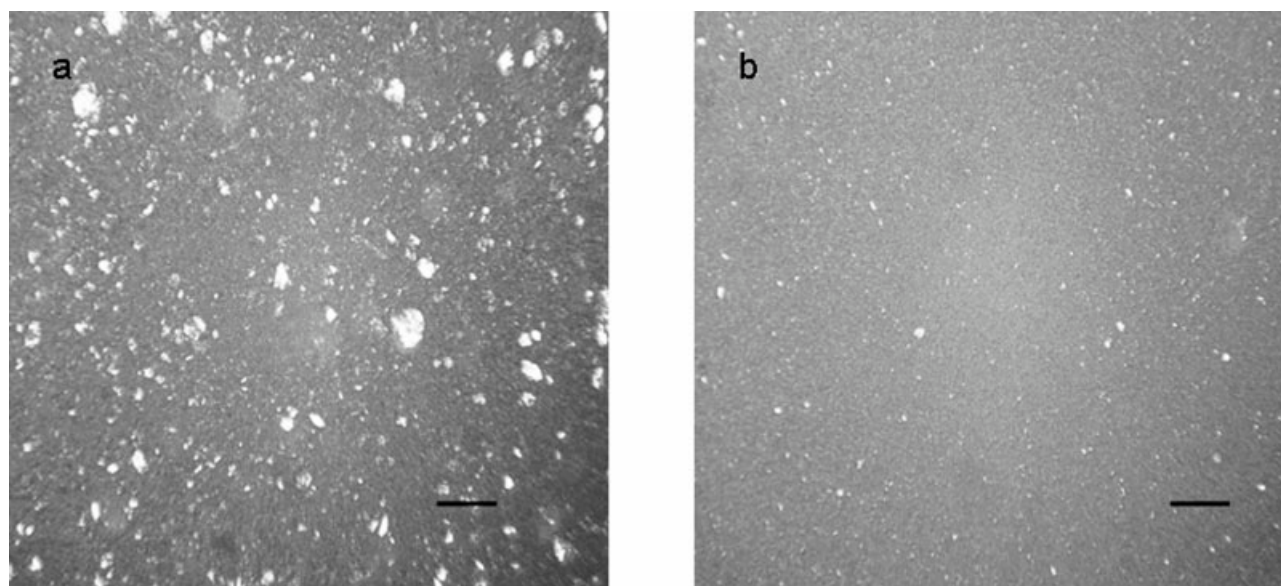


Figure 1 Optical micrographs of the dispersion of montmorillonite in epoxy resin, 4.9 wt % loading: (a) using simple mixing method, (b) using solvent method. Scale bar is 125 μm .

product (Nanomer I.30E), can be seen to increase for all the resin/clay mixtures based upon Nanomer I.30E presented here, indicating that the resin has intercalated into the clay galleries, irrespective of whether the samples are prepared by the simple mixing method or by the solvent method. Indeed, these intercalated d -spacings are close to the theoretical maximum spacing of 3.74 nm calculated⁴ for the vertically oriented octadecyl cation.

For the solvent-prepared samples, there appears to be a small reduction in the d -spacing as the clay content is increased, while degassing at 100°C for 24 h (sample R10) rather than at room temperature gives a somewhat larger spacing, which might be attributed to some homopolymerization taking place at this elevated temperature, catalyzed by the modified clay, a possibility that is discussed further below. The use of 100°C for the vacuum oven temperature follows the procedure recommended by Miyagawa et al.,¹⁵ but after observing the results for sample R10 subsequent samples were degassed at lower temperature.

A small amount of resin/clay mixture was taken from samples R1, R2, and R3, and a stoichiometric amount of the diamine curing agent was mixed in by hand for the purposes of examining the kinetics of the curing reaction by DSC, though these results are not reported here as the study of the curing reaction kinetics and of the properties and morphology of the cured nanocomposites are the subjects of future papers. These resin/clay mixtures plus curing agent are denoted as samples R1*, R2*, and R3*, respectively, and were observed to harden very rapidly at room temperature, presumably as a result of the catalytic action of the modified clay. These sam-

ples are referred to as semicured, as the curing reaction will have proceeded only until the glass transition temperature of the sample reached approximately room temperature, at which point the structure will have vitrified, with a dramatic reduction in the crosslinking reaction rate thereafter. A small portion of each of these samples was examined by SAXS and no peaks were observed, suggesting that exfoliation had taken place, even though the samples were only partially cured. It appears that for this epoxy resin and clay system the processes of intercalation and exfoliation occur rather easily. As an illustration of the differences between the nanostructures of the resin/clay mixtures without any curing agent and of the semicured samples after addition of the curing agent and partial curing at room temperature, the SAXS diagrams for samples

TABLE I
Composition and d -Spacing for Resin/Clay Mixtures

Sample code	wt % clay	d -Spacing (nm)	Comments
R0	100.0	2.09	Nanomer I.30E
R1	10.0	3.59	Hand-mixed
R2	10.0	3.75	Mechanically stirred
R3	10.0	3.77	Polytron
R4	10.0	not measured	Mechanically stirred
R5	10.0	not measured	Mechanically stirred
R1*, R2*, R3*	10.0	no peaks	Semi-cured
R7	4.9	3.93	Solvent, degas RT
R12	10.0	3.67	Solvent, degas RT
R9	14.3	3.70	Solvent, degas RT
R10	19.1	4.18	Solvent, degas 100°C
R13	20.1	3.64	Solvent, degas 75°C
R11	25.1	3.51	Solvent, degas RT
R14	28.2	3.52	Solvent, degas 75°C

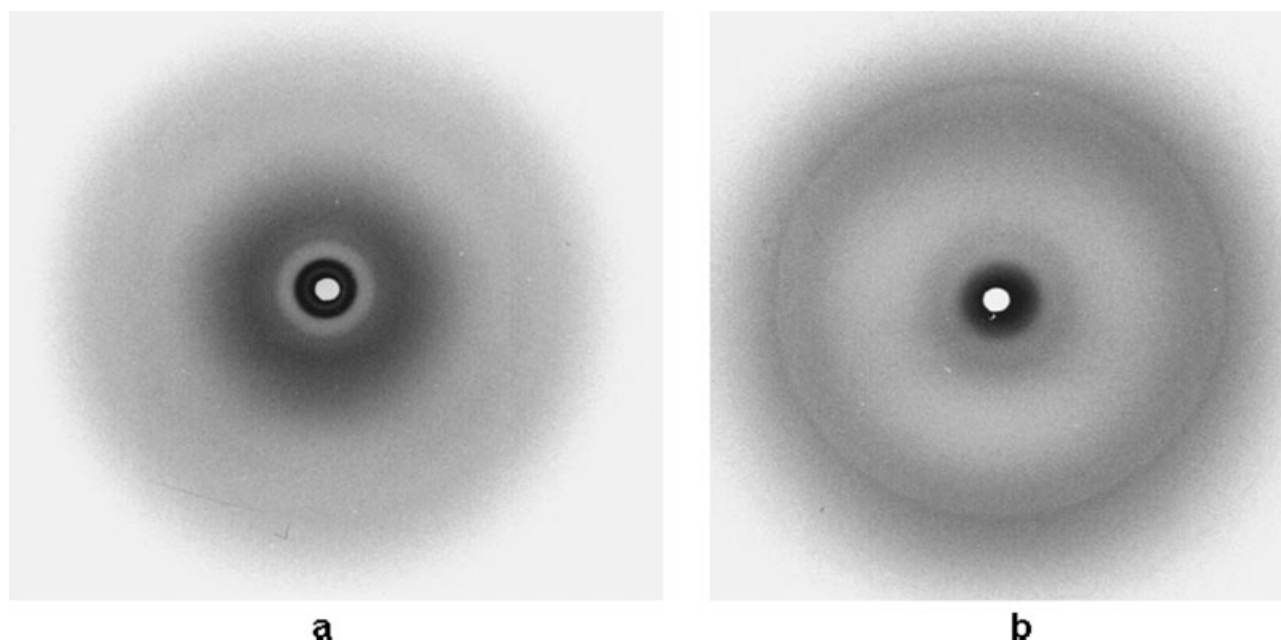


Figure 2 SAXS scattering patterns for resin/clay samples: (a) sample R3, before addition of curing agent; (b) sample R3*, after addition of curing agent and partial cure at room temperature.

R3 and R3* are shown in Figure 2. In Figure 2(a), the simple resin/clay mixture shows an intense ring, towards the center of the diagram, which corresponds to a spacing of 3.77 nm; this intense ring is not apparent for the semicured sample in Figure 2(b).

Thermogravimetry

The weight loss as a function of temperature determined by TGA for various samples is shown in Figure 3. The resin alone shows a two-step degradation process, with the maximum rate of weight loss for the first step occurring at about 265°C and accounting for (~ 20% of the weight loss, while for the second step this occurs at about 380°C and relates to the remaining 80% weight loss. According to Grassie et al.,^{39,40} the early stages of degradation, at about 280°C and corresponding to the first step observed here, consist of isomerization of the epoxy groups and subsequent C—O bond scission, liberating acrolein, allyl alcohol, and acetone as the principal volatile products. Subsequently, homopolymerization of the epoxy resin reduces the rate of weight loss before the second stage of degradation begins.

For the 10 wt % resin/clay mixtures, whether mixed manually, mechanically or by the Polytron, the stabilization of the weight loss occurs almost immediately after the first stage of degradation is initiated, and levels off at a much higher percentage of the original weight than for the resin alone, as illustrated in Figure 3 for the sample R3. This difference between the weight loss behavior of the resin/clay

mixture and of the resin alone is a result of the catalytic effect of the organically modified clay, which promotes the homopolymerization of the resin. Not only is the weight loss for this first step significantly less for the resin/clay mixtures than for the resin alone, amounting to only about 3%, but also the second, and major, degradation step is delayed until higher temperatures, with the maximum rate of weight loss occurring at around 425°C in comparison with 380°C for the resin alone.

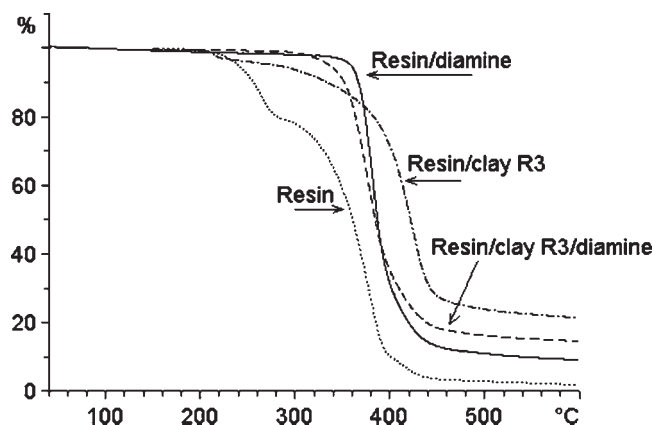


Figure 3 Percentage weight as a function of temperature for Epon 828 resin, both without curing agent (dotted line) and after curing (full line), and for resin/clay mixture R3, both without curing agent (dash-dotted line) and after curing with stoichiometric ratio of diamine (dashed line). Although only the curves for the resin/clay mixture R3 are shown here, those for the other two mixtures, R1 and R2, are essentially identical to those for R3.

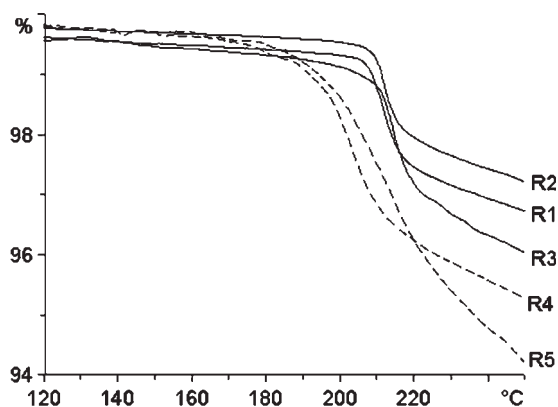


Figure 4 Initial weight loss by TGA for 10 wt % resin/clay mixtures: R1, R2, and R3 (full lines) after conditioning at room temperature for about 8 weeks; R4 and R5 (dashed lines) immediately after preparation.

Furthermore, the first degradation step in these resin/clay mixtures is also influenced by the time that elapses between the preparation and the testing of the mixture, a process referred to as "conditioning" by Benson Tolle and Anderson,¹⁸ as can be seen by reference to Figure 4. The degradation of resin/clay samples R1, R2, and R3 was investigated after about 8 weeks had elapsed between their original preparation and their testing by TGA, whereas samples R4 and R5 were tested immediately after preparation. The conditioned samples show an even smaller, and more abrupt, weight loss in a temperature range between 10°C and 20°C higher than for the unconditioned samples. Thus the process of conditioning at room temperature appears to have a similar effect on the degradation behavior to that of homopolymerization, and we believe that homopolymerization is indeed what is happening in the resin, even at ambient temperature, when catalyzed by the onium ion in the clay.

When a stoichiometric amount of the diamine crosslinking agent is added to the resin/clay mixtures, and they are then subjected to analysis by TGA, the crosslinking process is initiated and takes place during the heating (refer to Fig. 3). As a consequence, there is no first step in the degradation process, as homopolymerization now does not take place, but instead the degradation occurs in a single step which now shows a maximum rate of weight loss at about 400°C, and appears very similar to the degradation of the resin cured with diamine in the absence of clay. It is clear that both the cured resin and the cured nanocomposites have higher thermal stability than the resin/clay mixtures up to at least 350°C, and higher thermal stability than the resin alone over the whole temperature range. On the other hand, the resin/clay mixtures exhibit less percentage weight loss than do either the cured resin or the cured nanocomposites for temperatures greater

than about 380°C, which might be explained by the fact that the addition of the diamine reduces the proportion of the clay in the mixture or nanocomposite.

Differential scanning calorimetry

DSC scans on the resin and on the 10 wt % resin/clay simple mixtures (R1, R2, and R3), shortly after preparation, are shown in Figure 5. The heat flow is calculated per gram of mixture, but when it is calculated per gram of resin, by dividing the curves for the resin/clay mixtures by 0.9, then all the curves superpose to a very good approximation. This means that both the glass transition temperature, T_g , and the change in specific heat capacity, ΔC_p , of the epoxy resin are not affected by the presence of the clay in the mixtures, even though the resin has clearly intercalated into the clay galleries, as evidenced by SAXS and the results in Table I. On the other hand, it might have been anticipated that the restriction of the resin by its confinement in the clay galleries would have led to an increase in the glass transition temperature for the resin/clay mixtures. The implication of this result is either that insufficient resin has penetrated into the galleries to have a significant effect, or that the molecular mobility of the resin is in fact not reduced by its confinement within the 2–3 nm spacing between the layers of the clay.

Some clarification on this point is afforded by the DSC scans on mixtures prepared by the solvent method. Figure 6 shows several DSC scans on a solvent-prepared sample, R11, with a clay loading of 25.1 wt %, but before the evaporation of the solvent. For these scans, the sample was placed in the aluminum crucible of the DSC without degassing and shortly after mixing the resin into the clay/acetone suspension. The first scan, corresponding to the lowest curve in Figure 6, was made in the usual way by cooling at -10 K/min to -70°C , stabilizing at -70°C for 10 min, and then scanning at 10 K/min. Two step-like

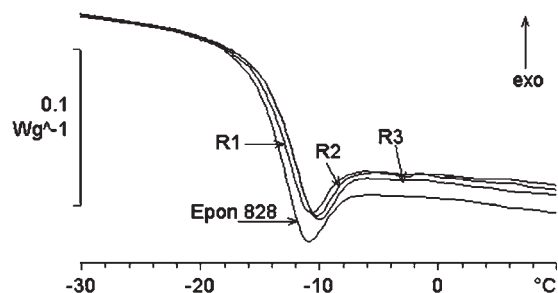


Figure 5 Part of DSC scans from -70°C to 25°C at 10 K/min for epoxy resin and for 10 wt % resin/clay mixtures prepared by simple mixing methods and tested shortly after preparation: R1, manually; R2, stirred mechanically; R3, using Polytron. The specific heat flow scale bar is determined per gram of mixture.

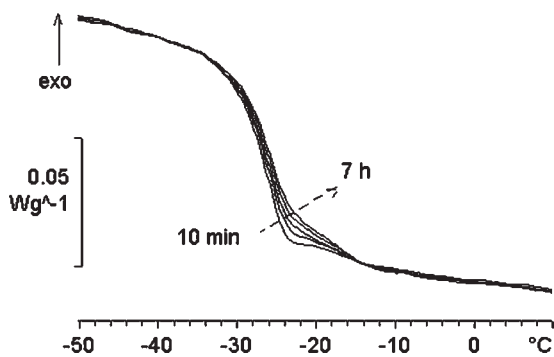


Figure 6 Parts of successive DSC scans from -70°C to 25°C at 10 K/min of a single solvent-prepared sample, R11 (25.1 wt % clay), stored for increasing lengths of time at -70°C between each scan: 10 min, 1 h, 2 h, 4 h, and 7 h. The specific heat flow scale bar is calculated per gram of mixture.

changes in the heat flow can be seen, corresponding to two glass transitions: the larger step is believed to reflect the glass transition of the "bulk resin," outside the clay galleries, and has a midpoint at about -27.5°C and a ΔC_p of 0.482 J/gK , while the smaller step, at higher temperature, is believed to correspond to the glass transition of the resin intercalated in the clay galleries, with a midpoint of about -16°C and a ΔC_p of 0.048 J/gK . The separation of the single glass transition response for the simple mixtures in Figure 5 into two distinct glass transitions, lower and upper, for the solvent-prepared samples is considered to result from the different plasticizing effects of the acetone on the bulk and intercalated resin, respectively. The bulk resin is easily accessed by the solvent, and the plasticization of the resin is evident in a reduction of the glass transition temperature from about -14°C to about -27.5°C . On the other hand, the restriction imposed by the clay galleries does not permit the same degree of plasticization to occur for the intercalated resin, for which the T_g reduces only to about -16°C .

Following this first scan, the same sample was then cooled again to -70°C , stored at this temperature for a period of time, and then scanned at 10 K/min to identify these two glass transitions. This was repeated for periods of time of 1, 2, 4, and 7 h at -70°C , with the successive curves shown in Figure 6. The gradual elimination of solvent that takes place by evaporation results in a reduction in the plasticization of the bulk resin, and a consequent increase in the lower glass transition temperature, which is seen to merge gradually with the upper glass transition of the intercalated resin.

It is interesting to estimate the relative proportions of bulk and intercalated resin from the ΔC_p values for the two glass transitions of sample R11 in Figure 6, using the first scan (lowest curve) for these purposes. These are found as $\Delta C_p(\text{bulk}) = 0.482\text{ J/gK}$ and $\Delta C_p(\text{intercalated}) = 0.048\text{ J/gK}$, giving a total

$\Delta C_p = 0.530\text{ J/gK}$. Thus the relative proportions of bulk resin and intercalated resin estimated in this way are 90.9% and 9.1%, respectively.

On the other hand, the relative proportions of bulk and intercalated resin can also be estimated from the dimensions of the intercalated nanostructure, and by making some assumptions about the intercalation of the resin in the clay. The large clay loading of 25.1 wt % was deliberately used to emphasize the effect of the intercalated resin. Taking the manufacturers' data for the densities of the resin and clay, $\rho_{\text{resin}} = 1.16\text{ g/cm}^3$ and $\rho_{\text{clay}} = 1.7\text{ g/cm}^3$, it is possible to convert this clay loading into a volume percentage as 18.6 vol % of clay and 81.4 vol % of resin. If we consider 100 cm^3 of resin/clay mixture, then the initial volume of clay is 18.6 cm^3 and of resin is 81.4 cm^3 . When the resin intercalates into the clay galleries, the d -spacing increases from 2.09 nm to 3.51 nm. Since the clay laminate thickness is approximately 1.0 nm (e.g., Ref. 1), this implies that the gallery dimension increases from 1.09 nm to 2.51 nm when the resin penetrates. Thus the initial gallery volume, containing no resin, is $1.09/2.09 \times 18.6 (= 9.7)\text{ cm}^3$, which increases to $2.51/2.09 \times 18.6 (= 22.3)\text{ cm}^3$ after intercalation. If the increase of 12.6 cm^3 in gallery volume, from 9.7 to 22.3 cm^3 , involves complete penetration of the resin, then the proportion of intercalated resin would be $12.6/81.4 = 15.5\%$, since the total volume of resin remains constant at 81.4 cm^3 . This is a significantly greater proportion of intercalated resin than is estimated from the ΔC_p values (9.1%). The implication of this is that during intercalation the resin does not penetrate completely into the galleries. Indeed, if the clay tactoids are assumed to be circular, and the resin penetrated uniformly around the circumference of these tactoids, then the 9.1% proportion of intercalated resin estimated from the ΔC_p values implies penetration to a depth of only about one third of the radius of the clay particles. This could have important consequences in respect of the curing and exfoliation process, since it is widely assumed that the curing reaction must take place more rapidly within the clay galleries than in the bulk resin if exfoliation of the clay is to be successful.

The results presented in Figure 6, in which two glass transitions appear, relate to solvent-prepared resin/clay mixtures scanned in the DSC before the evaporation of the solvent. It is important to note, though, that after complete evaporation of the solvent the DSC traces for the resin/clay mixtures return to being essentially identical to that of the resin alone, and to those observed for the resin/clay mixtures prepared by the simple mixing method (Fig. 5) when they are scaled for the clay content. As an illustration of this, Figure 7 shows the DSC scans for solvent-prepared mixtures with 5 wt % (R7), 10 wt % (R12), and

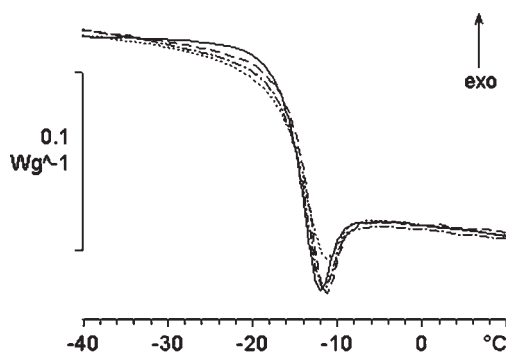


Figure 7 Parts of DSC scans from -70°C to 25°C at 10 K/min for resin/clay samples prepared by the solvent method, for comparison with the scan for the resin alone: Epon 828 (full line); R7 (4.9 wt % clay, dashed line); R12 (10.0 wt % clay, dash-dotted line); R11 (25.1 wt % clay, dotted line). The specific heat flow scale bar is calculated per gram of resin.

25 wt % clay (R11) after complete evaporation of the solvent. In this figure, the specific heat flow has been scaled per gram of resin, from which it can be seen that the curves for all the clay contents superpose upon each other, and also upon the curve for the resin alone, to a very good approximation. The small differences between the response of the resin and of the mixtures, particularly that of sample R11 which has the greatest clay content, is probably due to a small amount of homopolymerization occurring during storage of the mixtures at room temperature (61, 23, and 26 days, respectively, for samples R7, R11, and R12). After elimination of the solvent, therefore, the resin again has the same molecular mobility as for the samples prepared by the simple mixing method as well as that for the resin alone, and irrespective of the clay loading, once again implying that the intercalation of the resin in the clay galleries does not influence its molecular mobility.

As a check that no structural changes had been taking place in respect of the intercalation of the resin in the clay galleries, the d -spacing of sample R3 was measured again by SAXS after it had been conditioned at room temperature for about 6 months, and it was found to be identical to the original value of 3.77 nm , with a SAXS diagram identical to that of Figure 2(a). Thus, if homopolymerization is occurring in the resin, it has no effect on the d -spacing, in agreement with the observations of Benson Tolle and Anderson.¹⁸

Homopolymerization

It has been noted above that homopolymerization of the epoxy resin may play an important role in the overall preparation process of epoxy PLS nanocomposites, particularly as it may occur to a significant extent even at ambient temperature as a result of the

reaction being catalyzed by the clay. The process of homopolymerization takes place according to the scheme illustrated in Figure 8.⁴¹ The DGEBA monomer (a) consists of two epoxy groups separated, in the simplest case of the pure monomer, by a group denoted subsequently in Figure 8 as E. The cationic polymerization process is initiated by the alkylammonium ion in the MMT, which reacts with an epoxy group to produce an oxonium ion (b). In the propagation stage (c), the oxonium ion reacts with other epoxy groups; at each step of this propagation process, the group E has another epoxy group attached, which can initiate and propagate in the same way, and it could even be possible for a branch of the growing chain to terminate on the same molecule. The end product is a highly branched and/or crosslinked polyether.

In this respect, Benson Tolle and Anderson¹⁸ found recently that storage of resin/clay mixtures for long periods of time at room temperature had a dramatic effect on the exfoliation development. For example, for a 5 wt % mixture of Epon 828 and Nanomer I.30E montmorillonite, the same resin and clay components as are used in the present work, while storage for a period of more than 16 weeks at room temperature resulted in no significant change in the d -spacing of the resin/clay mixture, which remained at $3.5 \pm 0.1\text{ nm}$, it accelerated the exfoliation process when the diamine crosslinking agent was added, such that the d -spacing after curing for 60 min at 80°C had increased to 11.0 nm in comparison to only 4.2 nm for mixtures not conditioned in this way. These authors considered it likely that "some epoxy reaction" occurs during this conditioning process, but did not believe it to be a homopolymerization reaction since such a reaction occurs at temperatures much higher than room temperature.

To better understand what processes are occurring during conditioning of these resin/clay mixtures, a combination of TGA and DSC has been applied to these samples so as to investigate the effects of heating to various temperatures within the range in which the small initial weight loss of about 3% takes place in the first stage of degradation (see Fig. 4). A sample of about 7 mg taken from mixture R4, with 10 wt % clay, was placed in an aluminum DSC crucible and heated in the TGA to a maximum temperature of 150°C , which is below the temperature at which the first stage of degradation begins. A weight loss of only 0.05 mg was observed, and no noticeable color change was seen in the sample. It was then placed in the DSC and scanned from -60°C to 150°C at 10 K/min to determine the glass transition temperature of the sample after this treatment of heating it to the temperature of 150°C . This procedure was repeated for further maximum temperatures of 185°C , 192°C , 200°C , and 225°C , which encompass the tempera-

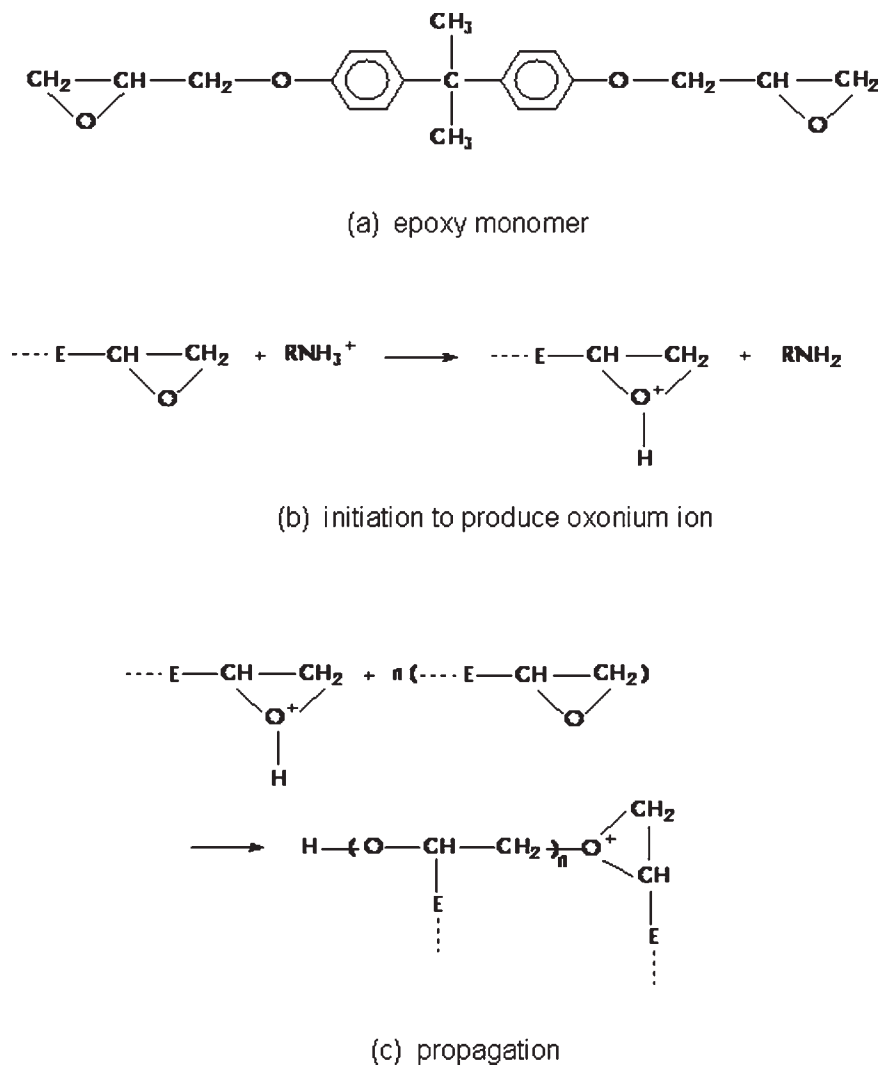


Figure 8 Stages in the cationic homopolymerization reaction of epoxy resin.

ture range in which the first stage of degradation occurs.

The results are shown in Figure 9. For the sample heated to 150°C, the T_g increases only slightly, from about -14°C for the resin alone to -12.7°C, but this small increase is nevertheless indicative of some homopolymerization having taken place. When the sample is heated to 185°C, the increase in T_g to -5.6°C is more noticeable, but it can be seen that there is a dramatic increase in T_g when the sample is heated to a temperature greater than about 190°C, which is attributed to significant homopolymerization of the epoxy. For the sample heated to 225°C, the value of T_g is 127.1°C, which is somewhat higher than the value of 102°C found by Ton-That et al.¹³ for the same Epon 828/I.30E combination, but with only 2 wt % of clay, when heated in the DSC to 250°C. This indicates that the clay loading has an effect, as would be expected, on the extent of poly-

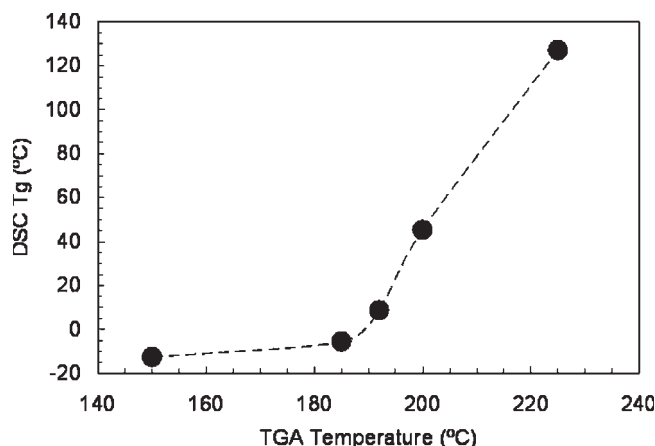


Figure 9 Dependence of glass transition temperature of 10 wt % resin/clay mixture (R4), prepared by simple mixing method, on the maximum temperature to which it was previously heated in the TGA.

merization that takes place. When epoxy resin alone is subjected to the same maximum temperature of 225°C, no change in the T_g from its original value of -14.1°C is observed, as was also noted by Ton-That et al.¹³ When the resin/clay sample was removed from the TGA after heating to 225°C, it had the appearance of a pinkish powder of very low density. This transformation from viscous liquid to powder as a result of the homopolymerization of the epoxy resin was observed earlier by Pinnavaia and co-workers,^{42,43} who proposed that delamination of the clay structure and subsequent exfoliation occurs when, following the polymerization of the preintercalated monomer, more epoxy monomer enters the clay galleries causing them to expand.

The above procedure of partially degrading the sample in the TGA prior to studying it by DSC was adopted in order not to contaminate the DSC by the degradation products. Nevertheless, to monitor the process continuously, some experiments were also conducted directly in the DSC, scanning from -60°C to 300°C at 10 K/min followed by a second scan, but using very small samples, up to only about 2 mg, to minimize the contamination of the instrument. Figure 10 shows such a DSC scan on a resin/clay sample with 5 wt % clay, together with the corresponding TGA and differential TGA scans on the same mixture. The DSC scan shows the initial T_g of the resin at about -14°C, which is followed by a complex superposition of various processes, extending from about 150°C to 280°C, roughly in the same temperature interval in which the first degradation step is seen by TGA. It is possible that the appearance of two peaks in this DSC scan may result from the superposition of a single exothermic peak due to polymerization and an endothermic peak due to degradation. In the second scan, this 5 wt % sample exhibited a T_g of 114.0°C, while a 10 wt % sample similarly studied by heating to 250°C in the DSC showed a second-scan T_g of 118.5°C, in reasonable agreement with the value of 127.1°C noted above, again suggesting that the extent

of polymerization depends on the clay loading. For all samples tested, the total enthalpy calculated from the area under the DSC trace, which may be an underestimate if an endothermic process intervenes, was 545 ± 40 J/g.

In similar DSC experiments at a heating rate of 2 K/min, Lan et al.⁴³ observed two reasonably well separated exothermic peaks for the octadecyl ammonium ion modified clay, the lower temperature peak being assigned to the polymerization of preintercalated resin, and the higher temperature peak being assigned to the polymerization of the extra-gallery resin which migrates to the clay surfaces, with the total enthalpy being of the order of 500 J/g. Comparing their 5 wt % data with the present Figure 10, and using their quoted activation energies for the low-temperature and high-temperature processes to convert the peak temperatures to those appropriate for a heating rate of 10 K/min (163.3°C and 191.6°C, respectively), it can be seen that there are significant differences. In particular, Figure 10 shows two peaks that are not separated as they are for Lan et al., as well as a slight shoulder on the low temperature flank of the lower peak, with the whole process occurring at temperatures significantly higher than for Lan et al. Instead, our results agree more closely with those of Ton-That et al.,¹³ who show a similar shoulder but only a single peak, though in the same temperature interval as that found here.

Furthermore, Lan et al.⁴³ find a linear relationship between the polymerization enthalpy associated with the low-temperature peak and the clay content, which is taken as confirmation that the low-temperature process relates to the polymerization of the preintercalated resin. In particular, for the 10 wt % clay the fraction of the total enthalpy due to intragallery polymerization is about 50%. However, a similar calculation to one made earlier for the 25 wt % clay shows that, for a resin/clay mixture with 10 wt % clay content and for the d -spacings given in Table I, even complete penetration of the resin into the galleries would account for only 6% intercalated resin. For incomplete penetration, as the DSC results on the solvent-prepared samples suggests is the case, the amount of intercalated resin would be even less. The implication is that the initial homopolymerization process does not take place only within the clay galleries, but is much more extensive, either because of the existence of onium ions not "bound" to the clay surfaces¹³ and/or because cation transfer to the epoxy group at the end of the polyether chain during homopolymerization (see Fig. 8) catalyzes the reaction with an ever increasing amount of resin.^{41,44} The small shoulder visible on the low temperature side of the peak in Figure 10, and in the work of Ton-That et al., may be related to the initial stages of this process in which the polymerization results from the onium ions themselves.

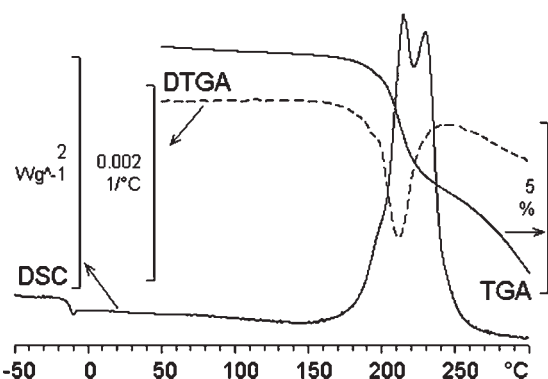


Figure 10 DSC, TGA, and differential TGA (DTGA, dashed line) scans on a 5 wt % resin/clay mixture.

In fact, the differences between the results of Lan et al. and those presented in Figure 10, in respect of the appearance of well-separated peaks or otherwise, could be attributed to the dispersion of the clay in the resin. The better is the dispersion of the clay particles, the smaller is the distance between them, and hence the more uniform will be the polymerization process on the assumption that it occurs over a much more extensive volume than the clay particles themselves. As the optical microscopy study here shows (Fig. 1), the dispersion can be significantly influenced by the preparation procedure, and it is therefore possible that this may account for the observed differences.

While it is clear that homopolymerization in resin/clay mixtures takes place at high temperatures, it is not so evident that it can take place also at ambient temperature. Indeed, Benson Tolle and Anderson¹⁸ specifically state that their observed effects of preconditioning are not, in their opinion, the result of a homopolymerization reaction in the light of the fact that such reactions take place at much higher temperatures. However, when a resin/clay mixture is stored for several months at room temperature, there is a noticeable increase in the glass transition temperature, as shown in Figure 11 for a mixture with 25 wt % clay prepared by the solvent method. Here, an abnormally large clay content was used to emphasize the effect of the clay. The two full lines show the response of a single sample taken from the resin/clay mixture, on heating in the DSC at 10 K/min, after being stored at room temperature for 78 and 92 days, in comparison with the resin alone, which is shown as the dotted line. Two differences are immediately apparent: an increase in the midpoint T_g and a reduction in the endothermic peak magnitude. The increase in T_g is small but significant, and the fact that the two conditioned responses, with only 14 days between them in comparison with the overall conditioning time of 78 days, can be superposed is consistent with a very

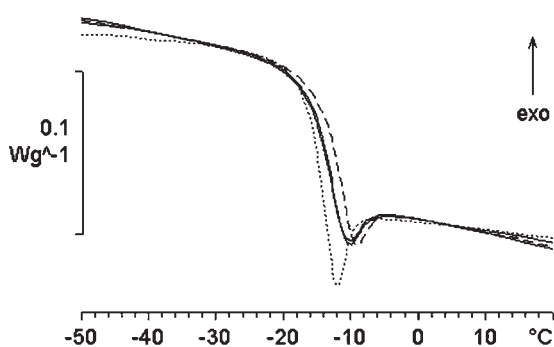


Figure 11 DSC scans at 10 K/min on a 25 wt % solvent prepared resin/clay mixture after conditioning at room temperature for 78 and 92 days (full lines) and then after a further 1 h at 75 °C immediately following the 92 days period (dashed line). The scan for the resin alone (dotted line) is also shown for reference.

slow process occurring at room temperature. The reduction in the endothermic peak height is indicative of a broadening of the relaxation time distribution, which, together with the increase in T_g , suggests that the conditioning process results in additional molecular motions with longer relaxation times. This is consistent with the occurrence of homopolymerization and increasing chain length in a limited number of molecules.

The dashed line shows how the response of the same sample changes after being heated to 75 °C for 1 h after 92 days at room temperature. The effect is qualitatively the same as conditioning at room temperature, but the process occurs much more rapidly. We believe that the nature of the changes that occur during conditioning at room temperature, and the fact that there is a qualitative continuity in the effect over a temperature range from room temperature to 75 °C, and also beyond as seen in Figure 9, is evidence for homopolymerization, catalyzed by the onium ion, occurring in the resin/clay mixtures over this whole temperature range.

Further support for this interpretation comes from some preliminary Fourier Transform Infrared (FTIR) spectroscopy studies on these resin/clay mixtures. A thin film of the mixture was spread onto a smooth surface of NaCl and was scanned in the wavenumber interval 4000–600 cm^{-1} using a Nicolet 510 type spectrophotometer with CsI optics. Homopolymerization of the epoxy resin would result in the gradual diminution of the epoxy group band at 915 cm^{-1} , but this is complicated by the fact that montmorillonite itself also has quite a strong band in exactly this region. However, it would also lead to the growth of a band in the region 1150–1000 cm^{-1} , associated with the stretching of the C—O—C ether linkages formed by the polymerization reaction, as observed by Ton-That et al.¹³ The sample R11, with 25.1 wt % of clay, after conditioning at room temperature for 7 months does indeed show a broad band in this region, which is not present in a similarly conditioned sample (R7) with only 4.9 wt % of clay.

CONCLUSIONS

The method of preparation of resin/clay mixtures using Epon 828 DGEBA epoxy and a commercially modified montmorillonite clay (Nanomer I.30E), before the addition of a curing agent to give the final epoxy PLS nanocomposites, has been shown to have an important effect on the dispersion of the clay in the resin. The best dispersion is achieved when the solvent preparation method is used. Irrespective of the dispersion, however, the resin intercalates into the clay galleries to give a separation of the clay layers of about 2.7 nm, as measured by X-ray diffrac-

tion, essentially independent of the clay content in the range 5–25 wt %. The degradation of these resin/clay mixtures occurs in two steps, the first amounting to only about 3% weight loss and being much less than that occurring in the resin alone, as a result of homopolymerization that takes place in the mixtures, catalyzed by the clay. When these mixtures are “conditioned” by leaving them at room temperature for long periods of time, this first degradation step becomes smaller and moves to higher temperature, these changes being attributed to homopolymerization, catalyzed by the onium ion, occurring even at room temperature.

Differential scanning calorimetry studies reveal that the resin/clay mixtures, for all the clay loadings studied, have a glass transition temperature and an increment in specific heat capacity that are essentially equal to those of the resin alone, indicating that the confinement of the resin in the clay galleries of dimensions less than 3 nm does not have any effect on its molecular mobility. On the other hand, for mixtures prepared by the solvent method but for which not all the solvent has been eliminated, DSC scans show two glass transitions, attributed to the different effects of plasticization of the solvent on the bulk resin and on the intercalated resin. Analysis of the magnitudes of the increments in specific heat capacity associated with each of these two transitions suggests that the transition associated with the intercalated resin is smaller than would be anticipated had the resin completely filled the clay galleries. Accordingly, it is concluded that the resin does not completely penetrate the galleries of the clay, but rather only penetrates to about one third of the radius (assuming disc-shaped clay particles), which could have important consequences for the interpretation of the effects of homopolymerization as well as for the subsequent crosslinking reaction and exfoliation process when the diamine is added and the mixture is cured.

The effects of homopolymerization were studied by combining DSC and TGA so as to determine the glass transition temperatures of resin/clay mixtures which have been partially degraded. For pretreatments up to 190°C there is a slow but steady increase in the T_g of the mixture, with a very rapid increase for higher temperatures. In the DSC traces, the exothermic peak due to homopolymerization is complicated by the superposition of an endothermic degradation process, but the appearance of the exotherm may provide information about the dispersion of the clay. It is believed that the process of homopolymerization takes place even at room temperature, under the catalytic action of the onium ions in the clay. Evidence for this is provided by the observation of an increase in T_g for resin/clay mixtures “conditioned” by storage for several months at room temperature.

Inasmuch as Benson Tolle and Anderson¹⁸ have observed that such conditioning greatly facilitates the subsequent exfoliation of the clay during curing, the process of homopolymerization that takes place in these resin/clay mixtures is of great significance.

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