

ON THE EFFECT OF MONTMORILLONITE IN THE CURING REACTION OF EPOXY NANOCOMPOSITES

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The procedure for the fabrication of epoxy-based polymer layered silicate nanocomposites is important in respect of the nanostructure that is developed. To further our understanding of this, the influence of an organically modified clay (montmorillonite, MMT) on the curing kinetics of an epoxy resin has been studied by differential scanning calorimetry. Clay loadings of 10 and 20 mass% are used, and isothermal as well as dynamic cures have been investigated. For both cure schedules the effect of the MMT is to advance the reaction. Kinetic analysis yields values for the activation energy, but shows that the reaction cannot be described simply by the usual autocatalytic equation. The glass transition of the cured nanocomposites is lower than that for the cured neat resin, a result that is attributed to homopolymerisation taking place in addition to the epoxy–amine reaction.

Keywords: cure kinetics, DSC, glass transition, montmorillonite, nanocomposite

Introduction

The industrial importance of polymer layered silicate (PLS) nanocomposites is widely recognised, and recent excellent reviews have summarised their fabrication, properties and applications [1–3]. Within this broad classification of PLS nanocomposites, those based upon thermosetting polymers are of special interest in view of their potential for enhancing mechanical properties such as stiffness and toughness without compromising their density, which is a typical requirement of the aerospace industry. The fabrication of such nanocomposites, and in particular those based upon epoxy resin, the thermosetting system used in the present work, follows the *in situ* polymerisation route, which involves a sequence of stages. First, the epoxy resin is mixed with the required amount of organically modified clay, in the course of which the resin penetrates into the galleries between the silicate layers of the clay, causing an expansion of the layer separation in a process known as intercalation. Next, the required amount of cross-linking agent is added to the resin/clay mixture, and finally the mixture is subjected to a cure schedule in order to achieve a fully cured nanocomposite, in which, ideally, the clay layers are fully exfoliated.

Although this procedure may appear simple, the nanostructure and properties of the final product can depend significantly on the details associated with each of the stages in the fabrication process. In particular, it is generally accepted that optimum properties of the nanocomposite are obtained only if the silicate layers are exfoliated and homogeneously distributed throughout the cross-linked epoxy matrix. This ‘ideal’

situation should be contrasted with two other possible morphologies [1, 4]: (i) what has been termed a phase-separated microcomposite, in which the resin does not intercalate into the galleries of the clay, and hence the clay tactoids are not intimately bound to the resin matrix and (ii) an intercalated nanocomposite, in which the clay layer separation does not progress significantly beyond that obtained after the intercalation stage in the fabrication procedure. In practice, what is often likely to occur is a combination of the three morphologies, namely phase-separated microcomposite, intercalated nanocomposite and exfoliated nanocomposite, with the optimum situation being when the last of these is dominant.

However, the actual mechanisms by which exfoliation occurs are not well defined, while it is known that the occurrence, or otherwise, of exfoliation is influenced by a variety of factors, including the organic modification of the clay, the procedure for mixing the resin and clay, the reactivity of the resin and cross-linking agent, and the cure schedule. In the present paper we examine the last of these factors by a calorimetric analysis of the cure reaction, under various conditions, of a single resin/clay/hardener system containing different proportions of the organically modified clay.

Experimental

Materials and methods

The clay used is a commercial organically modified montmorillonite (MMT), Nanomer I.30E from Nano-

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cor Inc., in which the organic modifier is octadecylamine. The epoxy resin is a commercial diglycidyl ether of bisphenol-A (DGEBA), Epon 828 (Shell Chemicals), with an epoxy equivalent in the range 185–192 g eq⁻¹ and a viscosity in the range 11000–15000 mPa s, and the cross-linking agent is a polyoxypropylene diamine, Jeffamine D-230 (Huntsman Corporation).

Mixtures of resin and clay, with 10 and 20 mass% clay content, were prepared by simple mixing using a mechanical stirrer at a temperature of approximately 40°C, followed by degassing under vacuum at room temperature. The intercalation of the resin into the clay galleries was verified by small angle X-ray scattering, examples being shown in Figs 1a and b for the modified clay and the 10 mass% resin/clay mixture, respectively, which show that the *d*-spacing increases from 2.09 nm for the original modified clay to 3.59 nm for the 10 mass% resin/clay mixture. A more extensive study (to be published elsewhere) shows that there is no systematic dependence of the *d*-spacing of the resin/clay mixtures on the clay content.

Differential scanning calorimetry (DSC) experiments were performed using a Mettler-Toledo DSC821^e equipped with a sample robot and Haake EK90/MT intracooler. The temperature and heat flow scales were calibrated with indium. For all experiments, sample masses of about 7 to 8 mg were prepared, and a dry nitrogen gas flow of 50 mL min⁻¹ was used. All data was captured using the STAR software system.

The preparation of the samples for testing in the DSC followed a well-defined protocol in order to capture as much as possible of the heat flow due to the reaction in the early stages. This is important because, as will be demonstrated later, one effect of the clay is to advance the curing reaction, and to such an extent

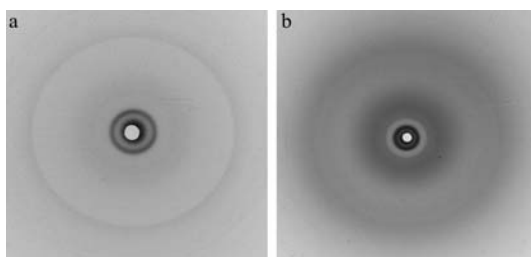


Fig. 1 Small angle X-ray scattering patterns for: a – the modified clay, showing strong scattering at an angle of $2\theta=4.22^\circ$, equivalent to a *d*-spacing of 2.09 nm, and an outer ring at $2\theta=19.72^\circ$, equivalent to a *d*-spacing of 0.45 nm and corresponding to scattering from the (110) planes of the clay layers; b – the 10 mass% resin/clay mixture, showing strong scattering at an angle of $2\theta=2.45^\circ$, equivalent to a *d*-spacing of 3.59 nm, weaker scattering at twice this angle and half this *d*-spacing, and an outer ring at a *d*-spacing of 0.45 nm, from the (110) planes in the clay layers

that even at room temperature a significant part of the reaction can occur before the sample is inserted into the calorimeter unless adequate precautions are taken to avoid this happening. Accordingly, the procedure adopted here was to mix the diamine with the resin/clay mixture freshly for each sample to be tested, and then rapidly to weigh out the required sample mass in an aluminium crucible and transfer it immediately to the DSC and start the experiment. The diamine was mixed in a stoichiometric proportion with the resin, for which the compositions of the sample without any clay (EPJ) and of those with 10 and 20 mass% clay (NEPAJ10 and NEPAJ20, respectively) are given in Table 1.

Table 1 Proportions of epoxy, diamine and montmorillonite in nanocomposite preparation

Sample	MMT% in resin/clay	Sample composition/mass%		
		epoxy	Jeffamine	MMT
EPJ	0	76.0	24.0	0
NEPAJ10	10	70.1	22.1	7.8
NEPAJ20	20	63.8	20.2	16.0

For isothermal and dynamic DSC cure experiments, the furnace of the calorimeter was preheated to the isothermal cure temperature or to the start temperature for the dynamic cure, respectively, before inserting the sample. Isothermal cure experiments were performed at temperatures between 70 and 100°C for all samples, with additional temperatures of 110°C for EPJ and 60°C for NEPAJ20, and for cure times sufficiently long for the heat flow to return to a horizontal baseline. All isothermal experiments were followed first by a dynamic scan at 10 K min⁻¹ up to 280°C to determine the glass transition temperature, T_g , of the cured (or partially cured) sample and to measure any residual heat of cure, and then by a further dynamic scan to determine the T_g of the ‘fully cured’ nanocomposite. Dynamic cure experiments were performed at heating rates of 2.5, 5, 10, 15 and 20 K min⁻¹ over a temperature range from 25 to 280 or 290°C, and were followed by a second scan at 10 K min⁻¹ to determine the T_g of the cured nanocomposite.

Data analysis

The kinetic analysis of the chemical reaction of curing is based on the following fundamental equation:

$$d\alpha/dt=k(T)f(\alpha) \quad (1)$$

which describes the time (*t*) dependence of the degree of cure, α . The rate constant, $k(T)$, is considered to have an Arrhenius temperature dependence, with an activation energy *E* and a pre-exponential factor *A*:

$$k(T)=A\exp(-E/RT) \quad (2)$$

while the function $f(\alpha)$ can take one of several forms. In the present work, we use the empirical two-parameter autocatalytic model (Šesták–Berggren equation):

$$f(\alpha)=\alpha^m(1-\alpha)^n \quad (3)$$

where m and n are the kinetic exponents of the reaction.

The heat flow, ϕ , generated by the curing reaction and measured by the DSC is assumed to be proportional to the rate of cure:

$$\phi=(d\alpha/dt)\Delta H \quad (4)$$

where ΔH is the total heat of cure. This last is evaluated either from dynamic DSC cure experiments or from isothermal experiments taking into consideration any residual heat evolved in a subsequent dynamic scan.

A variety of methods have been developed over the years for the determination of the kinetic parameters from the isothermal and dynamic cure experiments. One problem in this is the strong correlation between the activation energy E and the pre-exponential factor A , which does not permit the satisfactory use of the usual multiple regression algorithms unless at least one of these kinetic parameters is known [5, 6]. This problem can be resolved, however, by determining the activation energy by the isoconversional method. Combining Eqs (1) and (2) we can obtain the following logarithmic expression:

$$\ln(d\alpha/dt)_\alpha=\ln[Af(\alpha)]-E_\alpha/RT \quad (5)$$

where the subscript α indicates the value at a given degree of conversion. Assuming that the kinetic model $f(\alpha)$ is not dependent on the heating rate or the temperature, an activation energy E_α can be evaluated from the slope of $\ln\phi$ vs. the reciprocal of the temperature. This method can be applied both for isothermal and non-isothermal data.

Once the activation energy has been determined, the pre-exponential factor A and the parameters of the model (m and n in the case of the autocatalytic model of Eq. (3)) are evaluated by an analytical method developed by Málek [5], which has been successfully applied to the curing of epoxy resins [7]. This method can be applied to both isothermal and dynamic experiments, and provides a means for assessing which of the various kinetic models is the most appropriate for describing the experimental data.

Results and discussion

Figure 2 shows some typical isothermal cure data, comparing the heat flow as a function of time for cure at 70°C for the three systems: EPJ, NEPAJ10 and

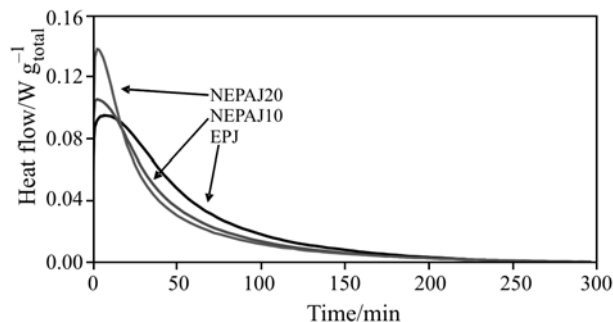


Fig. 2 Heat flow as a function of time for the isothermal cure at 70°C of the epoxy and diamine without clay (EPJ) and for the resin/clay/diamine mixtures with 10 mass% (NEPAJ10) and 20 mass% (NEPAJ20) clay

NEPAJ20. From the values of the heat flow as a function of the degree of conversion for each of the isothermal temperatures studied, the logarithm of heat flow vs. reciprocal temperature can then be plotted, as shown in Fig. 3 for NEPAJ10. From these data the activation energy (E_α) is calculated according to Eq. (5) for each isoconversional value of α , and the results obtained for the three systems studied here are shown in Fig. 4.

It is assumed in the kinetic analysis that E_α remains constant throughout the reaction, but there is a clear trend of decreasing E_α as α increases for the system without clay and for the 10 mass% clay sample. Although we do not pursue this aspect further here,

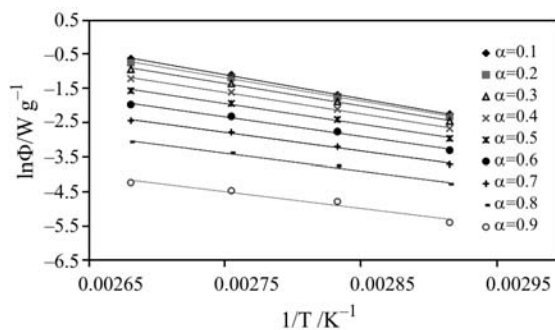


Fig. 3 Logarithm of heat flow (ϕ) as a function of reciprocal temperature for NEPAJ10 cured isothermally at 70, 80, 90 and 100°C

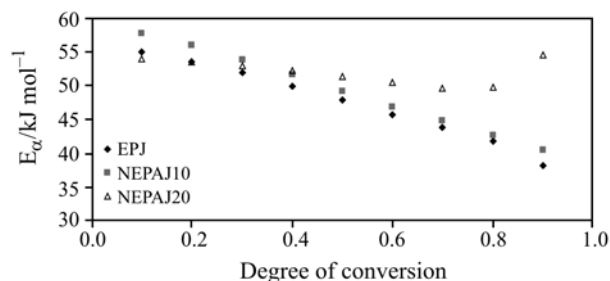


Fig. 4 Activation energy vs. degree of conversion for isothermal cure experiments

we note that this may be related to the occurrence of two kinetic processes simultaneously, not only an autocatalytic process as described by Eq. (3) but also a reaction order process, such that the reaction rate $d\alpha/dt$ can be written [8]:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (6)$$

On the other hand, the sample with 20 mass% clay shows a very different kind of behaviour. The addition of clay to the epoxy/diamine system clearly advances the isothermal cure reaction, as can be seen by the reduction in the peak time in Fig. 2 for the samples with clay compared with EPJ, which can be explained by the catalytic action of the octadecylammonium ions in the modified clay. Besides this, though, it is also important to bear in mind that the clay promotes a homopolymerisation reaction [9], which has a higher activation energy [10], while the presence of a clay content as large as 20 mass% could also result in a physical impediment to the cross-linking reaction.

Similar results are obtained from the dynamic cure schedules. For example, Fig. 5 shows the heat flow curves for dynamic cure at 20 K min^{-1} of the three different systems. In the same way as for the isothermal cure, it can be seen that the effect of the addition of clay is to advance the reaction, inasmuch as the peak temperature decreases as the proportion of clay increases. The activation energy can be calculated from these data by plotting the logarithm of the heat flow vs. the reciprocal of the temperature corresponding to any given degree of cure for each of the five heating rates used here. Such a plot is shown in Fig. 6, from which E_a is calculated from the slope. The values of E_a obtained in this way are shown as a function of α in Fig. 7. Here it can be seen that, after the initial stage of cure up to about $\alpha=0.2$, E_a remains relatively constant up to degrees of cure of about 0.6 or 0.7, after which a significant increase in activation energy is observed. Once again, similar to the isothermal case for NEPAJ20, we believe that the increase in E_a towards the end of the reaction is related to the occurrence of a

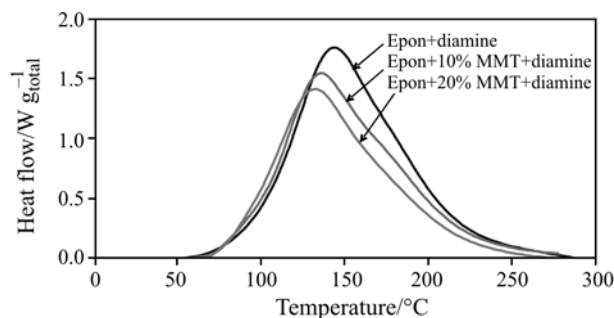


Fig. 5 Heat flow as a function of temperature for dynamic cure at 20 K min^{-1} of the three systems (EPJ, NEPAJ10 and NEPAJ20)

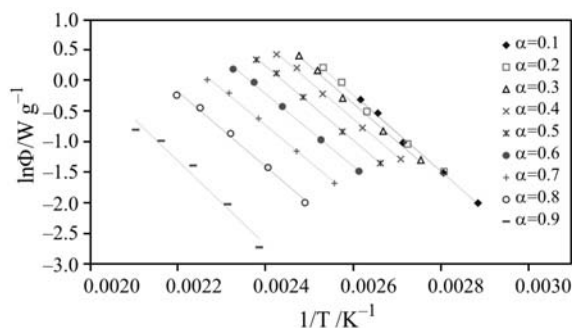


Fig. 6 Logarithm of heat flow (ϕ) as a function of reciprocal temperature for NEPAJ10 cured dynamically at 2.5, 5, 10, 15 and 20 K min^{-1}

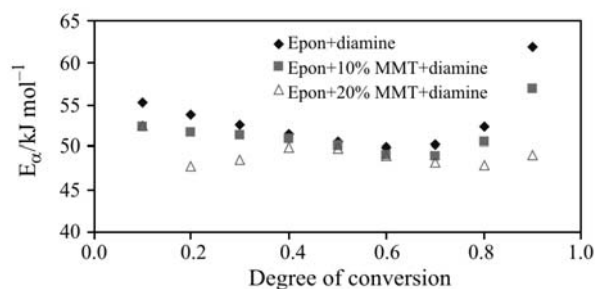


Fig. 7 Activation energy vs. degree of conversion for dynamic cure experiments

homopolymerisation reaction; in the present instance, the increase in E_a is less marked the greater is the MMT content because the clay facilitates the reaction through the action of the onium ion.

In fact, the existence of a more complex reaction than can be described by a simple autocatalytic model is suggested by other aspects of these results. Málek's method [5, 6] for the determination of the kinetic parameters requires the evaluation of two functions, $y(\alpha)$ and $z(\alpha)$, which are invariant with respect to the heating rate or isothermal temperature but are sensitive to changes in $f(\alpha)$. The function $y(\alpha)$ permits the evaluation of the kinetic exponent n as the slope of a plot of $\ln[\phi_{\text{exp}}(E/RT)]$ vs. $\ln[\alpha^{m/n}(1-\alpha)]$, while the ratio m/n can be determined from the maximum value of $y(\alpha)$ as a function of α . Although the details are not shown here, such a plot does not yield a single straight line, but instead shows two distinct linear regions with significantly different values of n , with the change in slope occurring in the range $0.5 < \alpha < 0.6$ and being more marked in the presence of MMT.

The same conclusion can be reached from a closer examination of the curves in Fig. 5. Here it can be seen that the high temperature flank of these broad bell-shaped cure curves displays a kind of shoulder, indicative of a change in the reaction kinetics in this region. To show this more clearly, Fig. 8 combines the experimental data for the dynamic cure of the three systems at a rate of 2.5 K min^{-1} with the fit of the theoretical

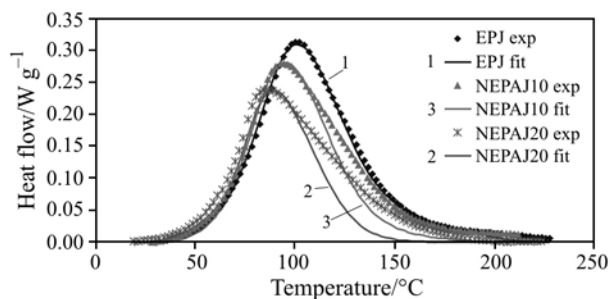


Fig. 8 Comparison of experimental and theoretical curves for dynamic cure at 2.5 K min^{-1} of EPJ, NEPAJ10 and NEPAJ20. Data points represent experimental results; full lines represent fit of theoretical model

model based on Eqs (1) to (4). The fit is adjusted, as far as is possible, to the lower temperature flank and peak of each curve. While a reasonably good fit is obtained for the whole of the cure curve for EPJ, the sample without any clay, there are significant deviations from the theoretical model for both of the samples with clay, and more so the greater is the clay content. Moreover, the deviation begins for degrees of conversion in the range 0.5 to 0.6, as observed above.

These results are interpreted in terms of the complexity of reactions occurring throughout the cross-linking process. According to Cole *et al.* [10], the process starts with the reaction of the primary amine, which is usually completed by about $\alpha=0.6$, and this is accompanied by the reaction of the secondary amine which continues until about $\alpha=0.8$. Finally, and generally towards the end of the cure process, there is etherification via the secondary amine, catalysed by the tertiary amines, as well as etherification via cationic homopolymerisation initiated by the onium ion of the organically modified MMT. These various reactions are not sequential, but can instead occur simultaneously over a certain range of α , and this is probably what is happening in the present case in order to produce the change in slope in the analysis following Málek's method and the shoulder in the dynamic cure curves.

The understanding of the cure kinetics is of great importance in the overall fabrication process of nanocomposites. For example, in the present instance we have fabricated nanocomposites using a stoichiometric ratio of epoxy and diamine, as indicated in Table 1. However, if a significant part of the cure reaction occurs via homopolymerisation catalysed by the onium ion of the clay, then there will be excess amine for the remaining epoxy groups and the reaction will be off stoichiometric. One effect of this will be to reduce the glass transition temperature, T_g , of the cured nanocomposite, and this is indeed what is observed in the present systems. Figure 9a shows that the T_g of the cured system decreases as the MMT content increases, by about 5°C per 10 mass% of MMT. At the

same time, the heat of reaction also appears to reduce with increasing MMT content, as shown in Fig. 9b, and this could be attributed to the difference in the heat of reaction for those reactions occurring via the primary and secondary amines compared with those occurring via homopolymerisation, as has been reported by other authors [11, 12].

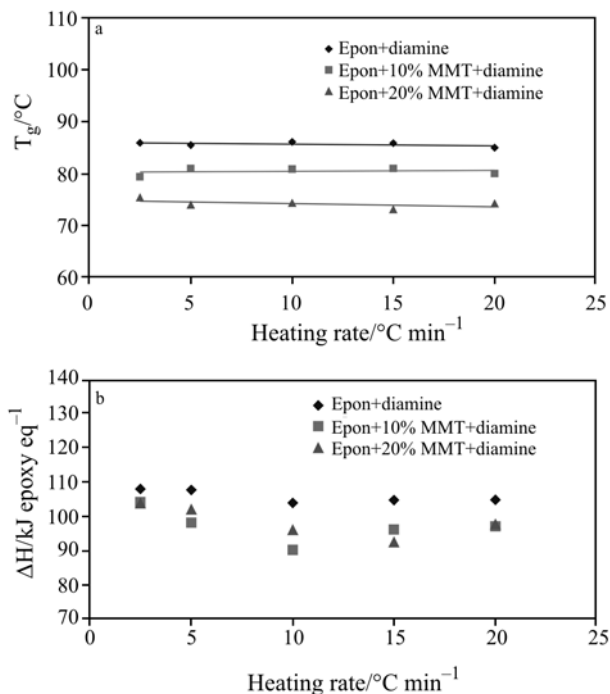


Fig. 9 Dependence of the a – glass transition temperature and b – heat of reaction on the heating rate in dynamic cure for the three systems studied: EPJ, NEPAJ10 and NEPAJ20

Finally, the cure schedule also has an important influence on the development of the nanostructure in the cured nanocomposite. This can be seen, for example, from a comparison of the small angle X-ray scattering patterns obtained on cured samples after dynamic cure at different rates. Figure 10 shows these patterns for NEPAJ10 cured dynamically at 20 K min^{-1} (Fig. 10a) and at 2.5 K min^{-1} (Fig. 10b). Both display significant scattering at angles smaller than the resolution of the instrument, equivalent to d -spacings greater than about 8 nm, which implies a significant amount of exfoliation. The important distinction between the two patterns, though, is that for the faster heating rate there remains a significant presence of intercalated (and not exfoliated) clay, with a d -spacing of 1.42 nm, while the nanocomposite obtained at the slower heating rate appears to be fully exfoliated, since the X-ray pattern shows no evidence of any remaining intercalated layers. The interesting observation that the d -spacing of 1.42 nm for the nanocomposite cured at the faster heating rate is less than that of the intercalated

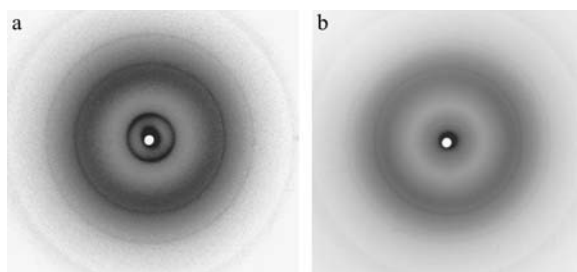


Fig. 10 Small angle X-ray scattering patterns for NEPAJ10 cured dynamically at different rates; a – 20 K min^{-1} , showing strong scattering at d -spacings greater than about 8 nm, a strong ring at 1.42 nm, and the usual scattering at 0.45 nm; b – 2.5 K min^{-1} , showing only strong scattering at d -spacings greater than about 8 nm, and the usual scattering at 0.45 nm

resin/clay mixture from which it is derived (3.59 nm), and indeed is less than that for the modified clay alone (2.09 nm), is believed to be at least in part a consequence of the complexity of the curing reaction, and is the subject of a separate paper currently in preparation.

Conclusions

The curing reaction, in the presence of a stoichiometric amount of diamine, of mixtures of epoxy resin and organically modified clay has been studied by DSC in both isothermal and dynamic modes. It is shown that the onium ion of the organically modified MMT catalyses the curing reaction, causing it to advance with respect to the curing of the neat epoxy/diamine system for both isothermal and dynamic cures. An attempt to fit a simple autocatalytic model to the curing reaction kinetics shows that the reaction is more complex than can be accommodated by such a model, and identifies two distinct regions with different kinetics, with the change occurring for a degree of cure between 0.5 and 0.6, approximately. This change is associated with the relative activities of reactions involving primary amines and secondary amines and with those involving etherification. The etherification

reaction is responsible for the reduction in T_g which is observed to occur in systems with MMT, and is also considered to be the likely cause of the decrease in the heat of reaction that is seen in the curing of the nanocomposites compared with that of the neat resin.

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