Intra- and Extra-Gallery Reactions in Tri-Functional Epoxy Polymer Layered Silicate Nanocomposites

John M. Hutchinson, Fatemeh Shiravand, Yolanda Calventus

Departament de Màquines i Motors Tèrmics, ETSEIAT, Universitat Politècnica de Catalunya, Colom 11, 08222 Terrassa, Spain
Correspondence to: J. M. Hutchinson (E-mail: hutchinson@mmt.upc.edu)

ABSTRACT: Achieving a high degree of exfoliation in epoxy-based polymer layered silicate (PLS) nanocomposites is crucial to their successful industrial application, but has hitherto proved elusive. In this work, a system is presented which shows significant promise in this respect. The isothermal cure of PLS nanocomposites based upon a tri-functional epoxy resin (TGAP) has been studied by DSC, and displays two exothermic peaks. The first peak, very rapid, relates to a homopolymerization reaction within the intra-gallery regions, while the second peak reflects the bulk crosslinking reaction. The occurrence of the intra-gallery reaction before the bulk reaction enhances the degree of exfoliation in the cured nanocomposite. Furthermore, pre-conditioning the resin/clay mixture before adding the curing agent and effecting the isothermal cure also allows a greater extent of intra-gallery reaction to occur before the extra-gallery epoxy-amine reaction. Consequently, this system results in a high degree of exfoliation, as revealed by transmission electron microscopy. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The mechanism of organo-clay exfoliation in epoxy layered silicate nanocomposites has been the focus of various studies.[1–6] In particular, it has been suggested[1,3,7–10] that control of the relative rates of the intra- and extra-gallery reactions is the key to overcoming the attractive forces between the silicate layers and hence to achieving full exfoliation. Nevertheless, it has thus far proved extremely difficult in practice to obtain a fully exfoliated nanocomposite, despite some claims to have achieved this objective.[11–14] As a consequence, it is common either to refer to a partially exfoliated nanostructure or to consider the structure to be exfoliated when the *d*-spacing is larger than that detectable by small angle X-ray scattering (SAXS), even in situations in which transmission electron microscopy (TEM) clearly shows layer stacking.[9,15–18] The question therefore still remains of how progress can be made toward achieving in practice a nanostructure which, if not fully exfoliated, then at least has a greater degree of exfoliation than has hitherto been described.

One possibility is to "pre-condition" the mixture of epoxy resin and organically modified clay.[5,6,10,19] This involves leaving the mixture, at ambient or higher temperature, for a length of time before adding the curing agent and curing the nanocomposite. The effect of this is to allow a homopolymerization reaction, catalyzed by the onium ion of the organically modified clay, to take place within the clay galleries. This procedure has been shown to improve the subsequent exfoliation which takes place during cure,[5,6] but also improves the dispersion of the clay in the resin, which is another key aspect as regards the degree of exfoliation that can ultimately be achieved in the nanocomposite.[10,19]

The reason why pre-conditioning is effective in respect of the exfoliation is related to the supposed requirement that, during the curing process of the nanocomposite, the extra-gallery reaction should occur after the intra-gallery reaction. If the extra-gallery reaction occurs first, then the network formed in the bulk of the nanocomposite prevents further nanostructural development in the clay galleries, with the result that reduced clay layer separations, smaller even than those in the clay before intercalation of the resin, can be observed as a consequence of the shrinkage that occurs during the extra-gallery cure process. Since the reaction that occurs during pre-conditioning takes place before the addition of any curing agent, it necessarily occurs within, or close to the surfaces of, the clay particles, and hence promotes the intra-gallery reaction.

We present here an epoxy–clay system in which the different reactions, intra-gallery and extra-gallery, can be clearly separated, and hence for which the effects of pre-conditioning can be clearly demonstrated. In particular, we show that a significantly improved nanostructure can be achieved in this way.
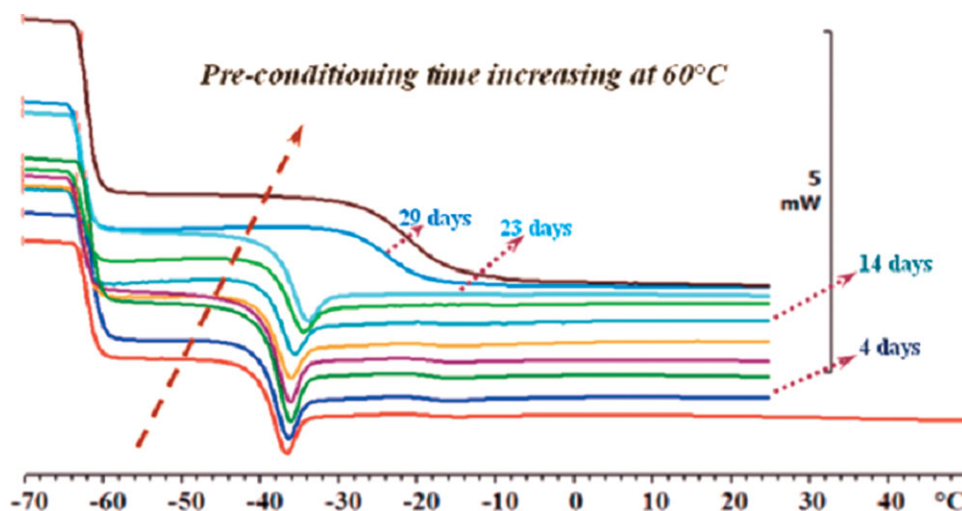
Figure 1. DSC scans showing change of glass transition temperature of TGAP/MMT (5 wt %) mixtures during pre-conditioning at 60°C for storage times indicated. Endothermic direction is upwards. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

The epoxy resin, tri-glycidyl *para*-amino phenol (TGAP), with trade name Araldite MY0510 (Huntsman Advanced Materials, Basel, Switzerland) and an epoxy equivalent (EE) between 95–106 g/eq, the curing agent, 4,4-diamino diphenyl sulfone (DDS), with trade name Aradur 976-1 (Sigma-Aldrich Química, S.A., Madrid, Spain), and the organically modified montmorillonite (MMT), with trade name Nanomer I.30E (Nanocor, Hoffman Estates, IL), were used without further purification.

Preparation of Epoxy-Clay Nanocomposites. Mixtures of TGAP epoxy resin and 2 wt % or 5 wt % MMT were first prepared in glass beakers using a mechanical mixer with a speed of ∼ 200 rpm for approximately 4 h, and were then stored either at room temperature (RT) or at higher temperatures (40°C, 60°C, 80°C) using a thermostatic bath (Techne, Stone, UK, TE-8D or TU-16D). After storage for selected periods of time at each temperature, the EE was determined by titration[6,20] and the glass transition temperature, T_g, of the mixture was determined by differential scanning calorimetry (DSC) in a scan from −70°C to 25°C at 10 K min^{-1} using a sample of 8–10 mg mass. For the curing of the final nanocomposite, the required amount of DDS was added to the pre-conditioned TGAP/MMT mixture, according to the measured EE of the resin and to give an excess epoxy ratio (1 : 0.85 mole ratio).[21,22] The DDS was added and mixed by hand for 5–7 min at 80°C on a hot-plate, and the mixture was then immediately degassed under vacuum at room temperature for 10–15 min.

Differential Scanning Calorimetry and TOPEM®. DSC experiments were carried out using a conventional calorimeter, DSC821e (Mettler-Toledo, Schwerzenbach, Switzerland), and a temperature modulated DSC technique, TOPEM® (DSC823e, Mettler-Toledo), both being equipped with STAR^e software and intra-cooling. Small sample quantities (6–10 mg for DSC and 10–15 mg for TOPEM®) were placed in sealed aluminum pans and the experiments were performed under a flow of dry nitro-

gen gas at 50 mL/min. The heat of reaction was determined by carrying the reaction isothermally to completion at the different selected cure temperatures. The first scans of both DSC and TOPEM® for each isothermal cure temperature provided the curve of heat flow versus cure time, from which the isothermal (partial) heat of cure was obtained. The TOPEM® experiments additionally gave the frequency independent specific heat capacity, c_{p0}, as a function of cure time, from which the vitrification time, t_v, at each isothermal cure temperature was determined as the time at which the sigmoidal decrease in c_{p0} occurred.

After the isothermal cure was completed, the sample was cooled rapidly either in the DSC to 50°C or in TOPEM® to 100°C. It was then heated at a rate of 10 K min^{-1} from 50°C to 300°C in the DSC in order to determine the residual heat of reaction (ΔH_{res}), and at 2 K min^{-1} from 100°C to 290°C in TOPEM® in order to determine the glass transition temperature of the fully cured sample.[22] The sum of the isothermal heat of cure and the residual heat was taken to represent the total heat of the reaction (ΔH_{tot}).

Optical Microscopy. To examine the size and the quality of the dispersion of the clay aggregates in the epoxy/clay mixtures, prepared as described above and before adding the curing agent, a Leica DME polarizing transmission optical microscope was used.

Small Angle X-Ray Scattering and Transmission Electron Microscopy. SAXS and TEM were both used to determine the nanostructure of the cured nanocomposites. X-ray diagrams were obtained using a Bruker D8 Advanced diffractometer, measurements being taken in a range of $2\theta = 1°$ to $8°$ with copper Kα radiation ($\lambda = 0.1542$ nm). The TEM was carried out with a Jeol Jem-2010 HRTEM electron microscope with an acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

Epoxy Equivalent and Glass Transition Temperature

Epoxy/clay mixtures prepared with 2 wt % and 5 wt % clay were pre-conditioned at several temperatures (RT, 40°C, 60°C,
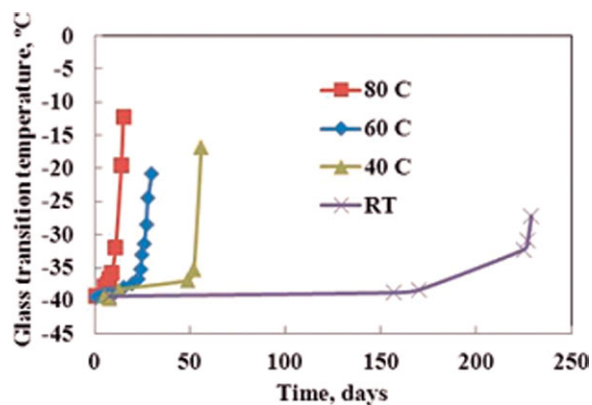
Figure 2. T_g versus pre-conditioning time for TGAP/MMT (5 wt %) mixtures at different storage temperatures, as indicated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

80°C) for various periods of time up to solidification. A typical set of DSC results for a sample with 5 wt % MMT and pre-conditioned at 60°C is shown in Figure 1.

It can clearly be seen that T_g increases with increasing pre-conditioning time and that there is a rather abrupt change between 23 and 29 days; the transition becomes wider and displays a reduced endothermic overshoot, indicative of a broadening of the relaxation time distribution. If the mid-point temperature between the glassy and rubbery states is considered as the glass transition temperature, then T_g can be plotted as a function of the pre-conditioning time, as shown in Figure 2. For pre-conditioning temperatures in the range from 40°C to 80°C, T_g can be seen to increase rapidly after an "initiation period" which becomes longer as the pre-conditioning temperature decreases. Between pre-conditioning at 40°C and RT there is a rather abrupt increase in the initiation period, though even at RT there appears to be a similar rapid increase in T_g once the initiation period is passed.

In parallel with the determination of the glass transition temperature, the EE of the TGAP/MMT mixture was evaluated by titration, and Figure 3 shows the dependence of the EE on the
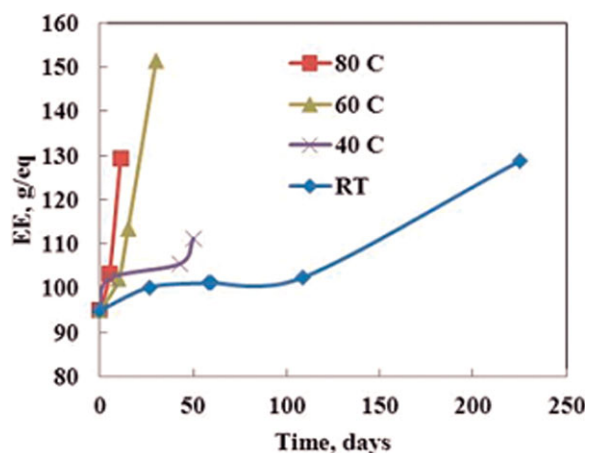
pre-conditioning time for different storage temperatures. A similar trend to that found for T_g can be seen, namely a rapid increase in the EE after a relatively short initiation period for pre-conditioning temperatures between 40°C and 80°C, but a much longer initiation period for pre-conditioning at RT.

The changes in T_g and EE with pre-conditioning time imply that the TGAP monomer is converted to TGAP polymer by a homopolymerization reaction, catalyzed by the onium ion of the organically modified MMT, the EE measurement showing how much homopolymerization has taken place during pre-conditioning. This same interpretation was made for the pre-conditioning of a bi-functional epoxy, diglycidyl ether of bisphenol-A (DGEBA), in mixtures with the same organically modified MMT, where a linear relationship between EE and T_g was observed.[6] A schematic illustration of the various reactions that may occur during the crosslinking of an epoxy nanocomposite has been given previously (see Figure 9 in Ref. 10, for example), where in particular the functional group involved in the homopolymerization and the repeat unit of the resulting homopolymer are shown.

In the present case of the tri-functional epoxy resin TGAP, however, the relationship between EE and T_g, illustrated in Figure 4 for the pre-conditioning temperature of 60°C, shows two distinct and approximately linear regions, which intersect at the pre-conditioning time of 23 days. This is the pre-conditioning time at which the abrupt change in the DSC traces occurs, as seen in Figure 1.

Repetition of this procedure for different pre-conditioning temperatures gives similar results to those found for 60°C, as follows. There are two linear regions in the dependence of EE on T_g, intersecting at a pre-conditioning time at which the mixture first becomes sticky, associated with the gel time. With further pre-conditioning time beyond gelation, the viscosity increases and eventually leads to the mixture becoming solid at room temperature, at which time it is no longer possible to use the mixture for the preparation of a nanocomposite, as the curing agent cannot now be incorporated. As regards the practical
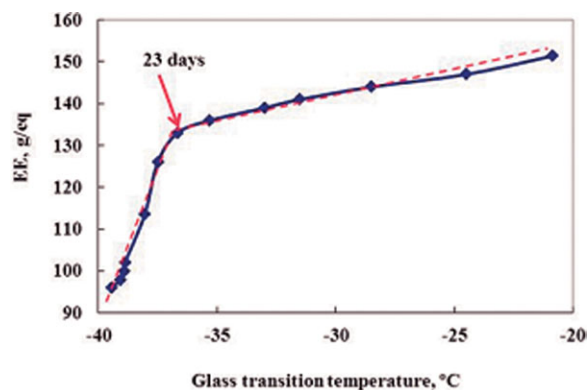

Figure 3. EE versus pre-conditioning time for TGAP/MMT (5 wt %) mixtures at different storage temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. EE versus T_g for TGAP/MMT (5 wt %) mixture at 60°C storage temperature. The dashed lines are drawn to guide the eye. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
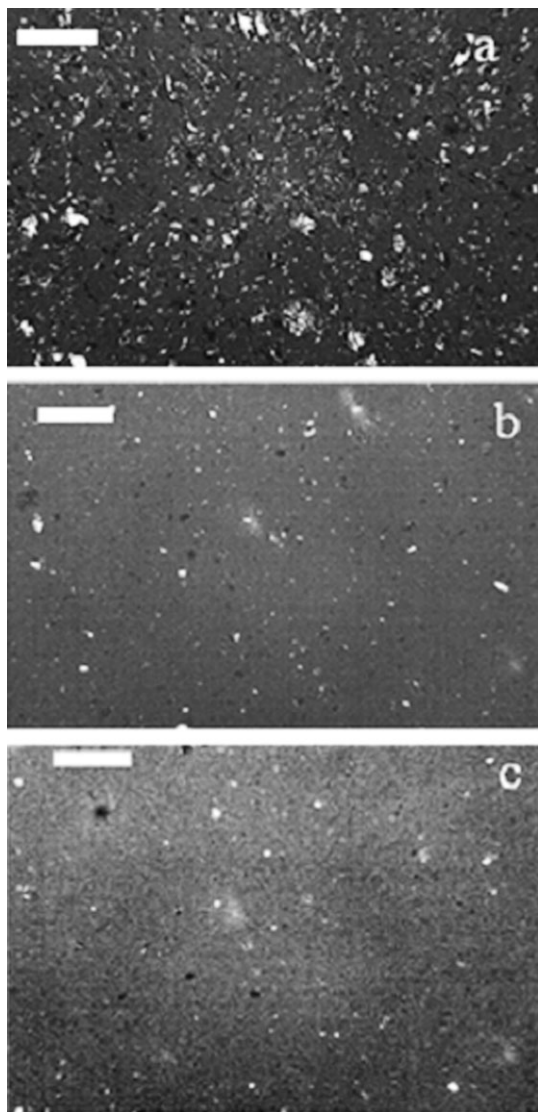
Figure 5. Optical micrographs of dispersion of clay in resin for: (a) 5 wt % MMT after mechanical mixing for ~ 4 h at RT; (b) 5 wt % MMT after pre-conditioning 232 days at RT; (c) 2 wt % MMT after 163 days at RT. Scale bar is 100 μm.

processing of epoxy-clay nanocomposites by this pre-conditioning route, in a future work it would be interesting to investigate the dependence of the viscosity on the pre-conditioning temperature and time. For the present, we note that the gel and solidification times, respectively, for the 5 wt % mixture at each pre-conditioning temperature are: RT, 225 days, 238 days; 40°C, 56 days, 60 days; 60°C, 23 days, 30 days; 80°C, 14 days, 15 days.

Dispersion of Clay in Epoxy Resin
Polarizing transmission optical microscopy was used to investigate how the quality of the dispersion of MMT in the TGAP resin was influenced by the clay content and by the different pre-conditioning treatments (temperature and time). Figure 5(a) shows the dispersion after mixing TGAP/MMT (5 wt %) for 4 h at RT, where considerable clay agglomeration can be seen (the white particles represent the clay agglomerations). Despite the presence of these agglomerations, however, SAXS shows that the clay has been intercalated with the epoxy resin, the d-spacing increasing from 2.1 nm for the organically modified clay to 3.1 nm in the intercalated state.

Samples with this quality of dispersion were then pre-conditioned at different temperatures until gelation, and typical results are shown in Figure 5(b, c) for 5 and 2 wt % MMT contents, respectively. The dispersion of the clay in the resin improves significantly with pre-conditioning, with the largest particle size after pre-conditioning being approximately the same in both cases, of the order of 10–15 μm, though with fewer particles for the 2 wt % content. An important difference, however, is that the improved dispersion is achieved in a significantly shorter time for the lower clay content. As will be shown later, the dispersion shown here, before curing, further improves significantly after curing as a result of the nanostructural changes that take place during cure.

Cure Kinetics
The above observed effects of pre-conditioning on the glass transition temperature, EE, and dispersion of the clay in the resin can now be used to interpret the effects of pre-conditioning on the isothermal cure kinetics and resultant nanostructure of these nanocomposites. For this purpose, samples were first pre-conditioned until gelation (change in linear dependence of
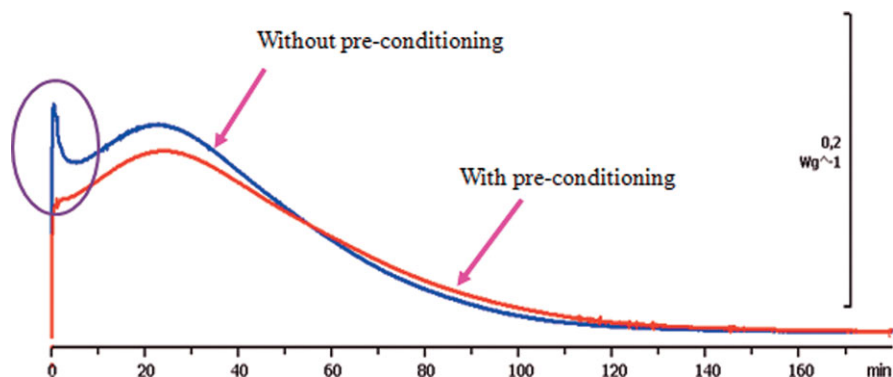

Figure 6. Isothermal cure by DSC at 150°C of two TGAP/MMT (5 wt %) mixtures, one without pre-conditioning and one pre-conditioned at RT for 112 days, as indicated. Curing agent was DDS. The first peak, resulting from the intra-gallery reaction, is highlighted. Exothermic direction is upwards. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Summary of Results for TGAP/MMT (2 wt %) Mixtures, Pre-conditioned at Different Temperatures, and Cured with DDS Isothermally at 150°C for 3 h

Pre-conditioning temperature (°C)	No	RT	40	80
Pre-conditioning time (days)	No	63	56	12
Epoxy equivalent (g eq^{-1})	95	100.3	114.9	129.4
T_g of TGAP/MMT (°C)	−40.3	−39.4	−35.55	−25.6
Heat of reaction, 1st scan (J g^{-1})	507.5	503.3	470.0	451.4
Vitrification time, 1st scan (min)	93.1	99.4	82.7	117.2
Time of peak, 1st scan (min)	25.6	26.1	17.5	14.0
Residual heat, 2nd scan (J g^{-1})	111.0	109.9	71.2	64.3
Total heat of reaction (J g^{-1})	618.5	613.1	542.1	515.3
T_g fully cured (°C)	254.7	253.1	231.9	231.1

EE on T_g, as shown in Figure 4) at each temperature, and then the required amount of curing agent, calculated according to the EE for that pre-conditioning time and temperature, was added and the sample was cured isothermally in the DSC at one of four different temperatures (120°C, 150°C, 165°C, 180°C) for a time that depended on the cure temperature. A parallel experiment of isothermal cure by TOPEM also gave the vitrification time.[22,23] Subsequently, a second non-isothermal scan was made in the DSC to determine the residual heat of reaction, and by TOPEM to determine the glass transition temperature of the fully cured nanocomposite.[22] A typical result is shown in Figure 6, for the particular case of isothermal cure for 3 h at 150°C for two samples: one without pre-conditioning, and one which has been pre-conditioned for 112 days at RT.

It can clearly be seen that the cure of the sample that has not been pre-conditioned consists of two reactions: the first (highlighted) is a very rapid reaction, for which only the post-peak part of the reaction is observed, while the second overlaps partly with first reaction and corresponds to the reaction of the TGAP with DDS. On the other hand, the pre-conditioned sample does not show this first reaction, instead showing a single exothermal peak. Furthermore, the area under the pre-conditioned cure curve is slightly smaller, because the homopolymerization reaction occurring during pre-conditioning means that some of the epoxy groups have already reacted before the addition of the DDS.

More important, though, is the non-appearance of the first, very rapid, reaction in the cure of the pre-conditioned samples. This is the result of the homopolymerization reaction that has taken place within the clay galleries during pre-conditioning. Furthermore, this initial rapid reaction does not occur for the TGAP/DDS reaction in the absence of clay.[22] The obvious conclusion is that this rapid reaction is a homopolymerization reaction taking place within the clay galleries. The importance of this is that it demonstrates that, for the TGAP/MMT/DDS system without pre-conditioning, the intra-gallery reaction occurs before the extra-gallery reaction, which is a necessary condition for there to be significant exfoliation of the nanocomposite. Consequently, for the TGAP system there are two possibilities for achieving exfoliated nanocomposites: (i) by pre-conditioning the TGAP/MMT mixture, which allows for an intra-gallery reaction to take place before the addition of the crosslinking agent; and (ii) directly by isothermal cure without pre-conditioning, since there is an intra-gallery reaction which occurs before the extra-gallery reaction of TGAP with DDS.

In the latter case, the isothermal cure temperature is an important parameter controlling the relative contributions of intra-gallery and extra-gallery processes to the overall reaction. Furthermore, there is some overlap between the initial and main reactions, so that the homopolymerization reaction within the clay galleries is not complete before the extra-gallery reaction

Table II. Summary of Results for TGAP/MMT (5 wt %) Mixtures, Pre-conditioned at Different Temperatures, and Cured with DDS Isothermally at 150°C for 3 h

| Pre-conditioning temperature (°C)	No	RT	40	80
Pre-conditioning time (days)	No	60	45	11
Epoxy equivalent (g eq^{-1})	95	101.2	110	130.4
T_g of TGAP/MMT (°C)	−40.3	−39.3	−37.9	−31.9
Heat of reaction, 1st scan (J g^{-1})	503.4	467.5	464.8	452.4
Vitrification time, 1st scan (min)	87.1	100.8	82.7	91.6
Time of peak, 1st scan (min)	22.	25.7	15.2	10.4
Residual heat, 2nd scan (J g^{-1})	106.4	110.2	90.0	34.6
Total heat of reaction (J g^{-1})	609.8	586.7	554.8	496.0
T_g fully cured (°C)	251.9	250.2	248.3	233.9
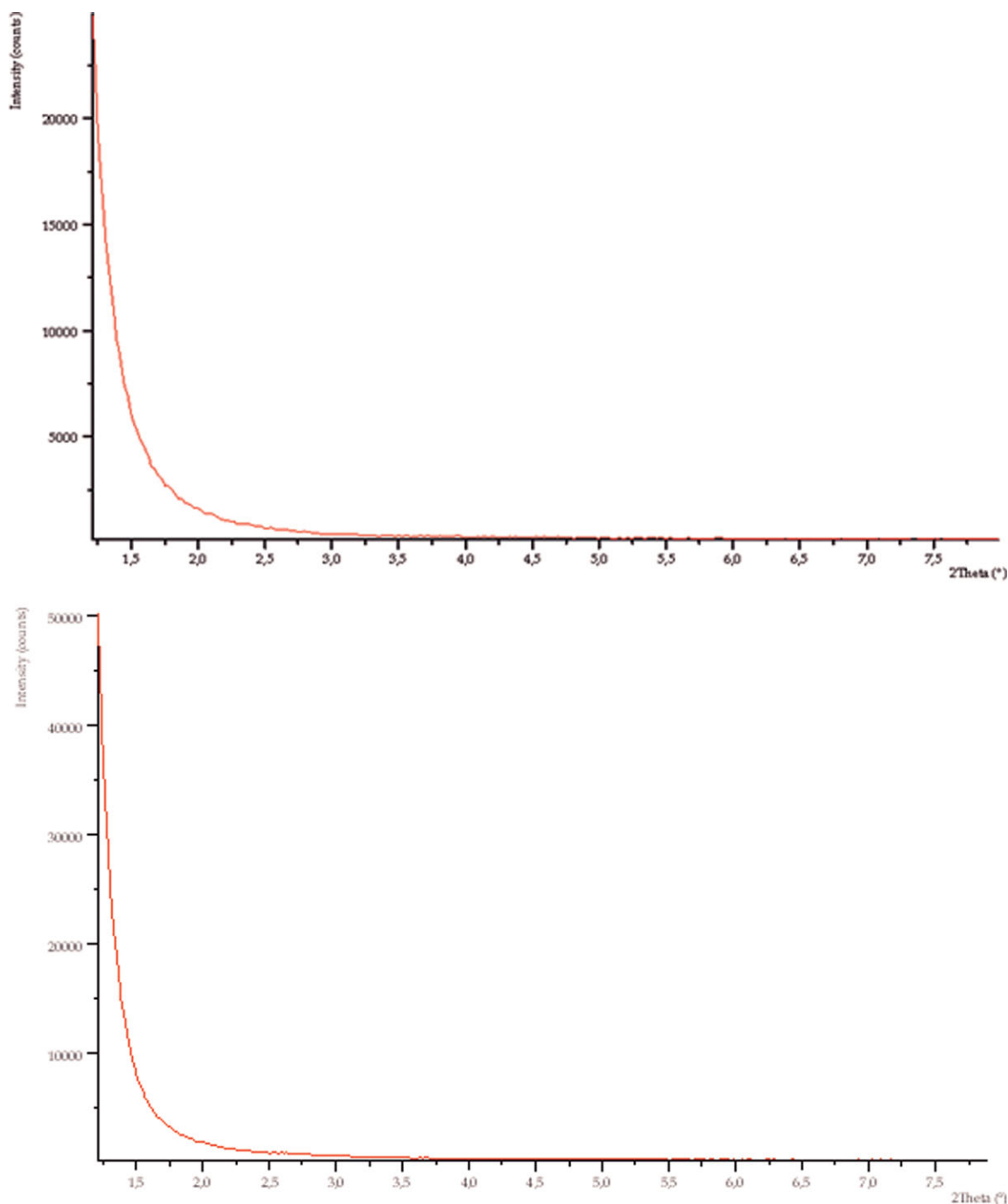
Figure 7. SAXS diffractograms for TGAP/MMT (5 wt %) samples pre-conditioned for 225 days at RT (upper diagram) or 62 days at RT (lower diagram), and then cured at 150°C for 3 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

begins, which will have an influence on the exfoliation procedure. The deconvolution of the cure curve into two separate peaks is therefore another important part of the analysis. These aspects will be considered in detail in a separate publication.

The above situation for TGAP nanocomposites is in direct contrast to that observed earlier for DGEBA nanocomposites, where this very rapid initial reaction does not occur.[10] With DGEBA, therefore, the intra-gallery reaction does not occur naturally before the bulk extra-gallery reaction. Hence, in order to promote the intra-gallery reaction and maximize the exfoliation in the DGEBA/MMT system, it is necessary to follow the pre-conditioning route. Unfortunately, however, homopolymerization at RT in the DGEBA system is significantly slower than for the TGAP/MMT system, and so the procedure is less practicable.[6]
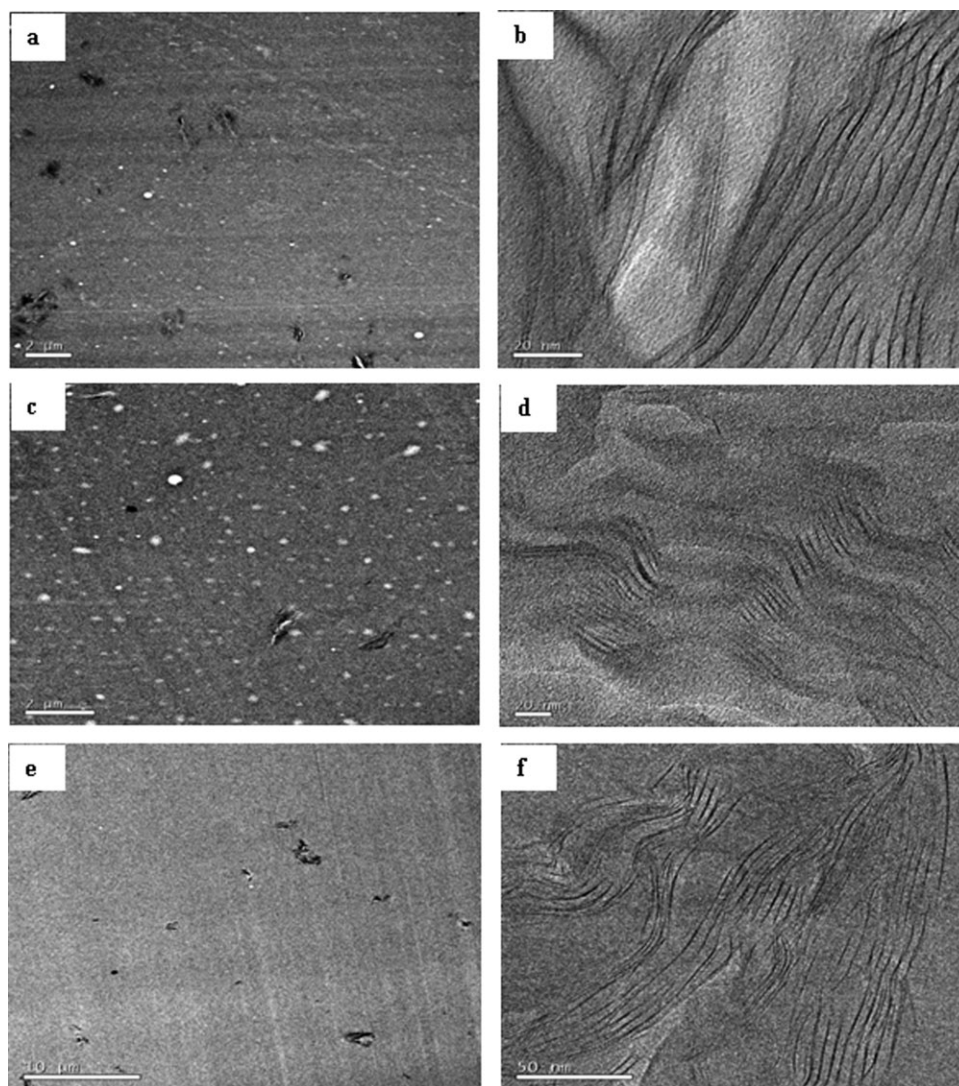
Figure 8. TEM images after pre-conditioning TGAP/MMT (2 wt %) at: (a, b) RT; (c, d) 40°C; (e, f) 80°C, followed by curing at 150°C for 3 h.

The results for all the important parameters related to the isothermal cure, the second non-isothermal scan, and the final nanocomposite are collected in Table I for TGAP/MMT (2 wt %) mixtures pre-conditioned and then cured isothermally with DDS at 150°C. Here it can be seen that the total heat of reaction decreases for samples pre-conditioned to gelation at increasing temperature, which is consistent with the observed increase in both EE and glass transition temperature as the sample homopolymerizes during pre-conditioning. Similar conclusions were also obtained from the results of TGAP/MMT (5 wt %) system, which are shown in Table II.

The final glass transition temperature of the fully cured system decreases with increasing pre-conditioning temperature under these conditions. The fully cured T_g should not, however, be taken as an indication of the degree of exfoliation. There are two reaction processes occurring here: the homopolymerization reaction within the clay galleries, which may occur either during pre-conditioning or in the initial stages of isothermal cure, and the TGAP/DDS reaction. These lead to different network structures and hence different glass transition temperatures. It is usually considered that the homopolymerization reaction leads to a less dense network structure, and hence to a lower T_g for the fully cured system; this is consistent with the observed reduction of T_g with increasing pre-conditioning temperature, shown in Tables I and II, for which the increasing EE is indicative of a greater amount of homopolymerization the higher is the pre-conditioning temperature. Rather than using the final glass transition temperature as an indicator of whether or not exfoliation has taken place in the nanocomposite, it is necessary instead to use SAXS and TEM to identify the nanostructure for the nanocomposites prepared with and without pre-conditioning.

Nanostructural Analysis

The nanostructure of the cured nanocomposites, both with and without pre-conditioning, was investigated by SAXS. Typical results are shown in Figure 7 for samples pre-conditioned at RT for 225 days and 62 days before being cured isothermally at 150°C for 3 h. For all pre-conditioning conditions, the SAXS
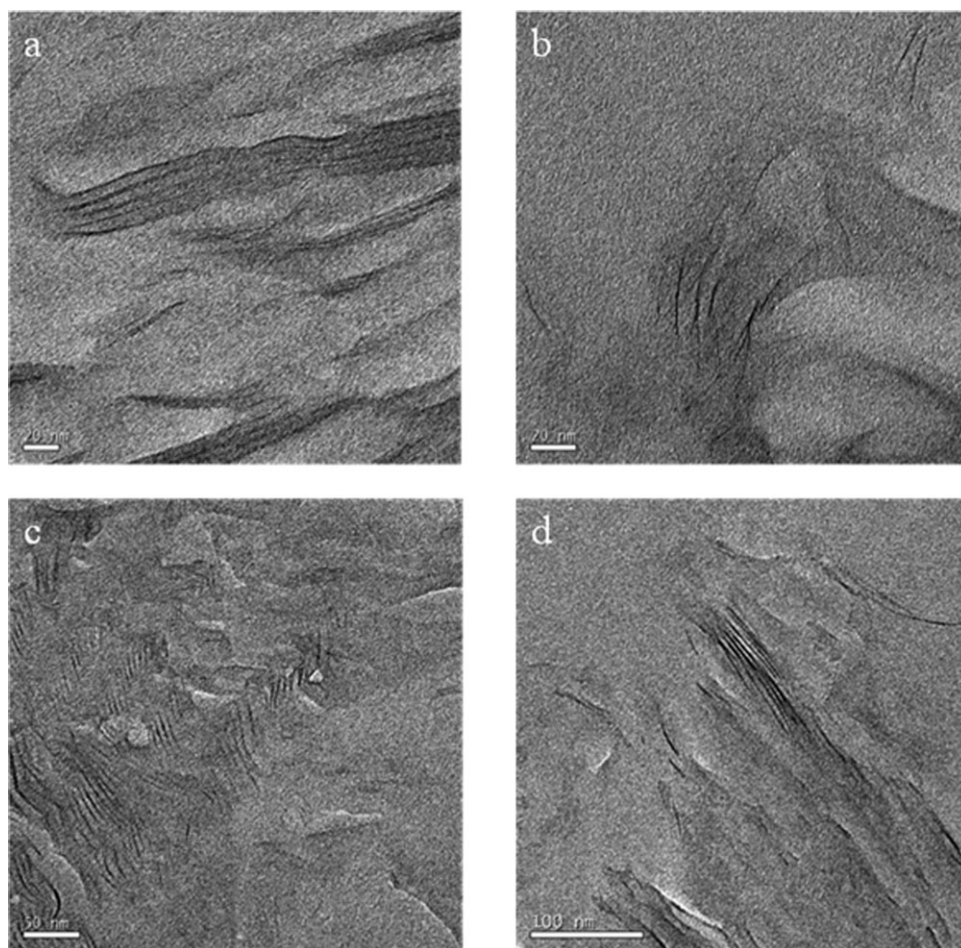
Figure 9. TEM micrographs for TGAP/MMT(2 wt %) samples cured isothermally for 3 h at 150°C after pre-conditioning: (a) for 105 days at RT; (b) for 225 days at RT; (c) for 54 days at 40°C; (d) 12 days at 80°C.

results were similar, showing no diffraction peaks in the low angle range, which is indicative of layer separations greater than about 8 nm, the limit at low angles for the equipment used here. This is a necessary requirement for exfoliation, but is not sufficient as there may be layer stacks with d-spacings greater than this value, and so these SAXS results must be supplemented by TEM.

The TEM micrographs for samples with 2 wt % MMT content which had been pre-conditioned at RT, 40°C, and 80°C for the times listed in Table I before being cured isothermally for 3 h at 150°C are shown in Figure 8. Here, in the low magnification images [Figure 8(a,c,e)], the dark regions represent small clay agglomerations (the small white circles are holes in the substrate material). These are representative of the whole of the ultra-microtomed section, and it can be seen that these agglomerations have a maximum equivalent diameter of the order of 2 μm. This is considerably smaller than the typical size of agglomeration in the TGAP/MMT mixture before curing (see Figure 5), which implies that the curing process has significantly modified the nanostructure, not just in exfoliating the clay layers but also in improving the dispersion of the clay, as was noted previously for elastomeric epoxy-clay nanocomposites.[24]

If one of the agglomerations seen in each of Figure 8(a,c,e) at low magnification is observed at higher magnification, the clay nanostructures are those seen in Figure 8(b,d,f), respectively. Clearly there still remains some layer stacking, but it is generally rather irregular, and the minimum spacing is approximately 8 nm, consistent with the lack of any scattering in the SAXS results. Similar nanostructures were observed for different regions of these (and other) pre-conditioned samples. For example, Figure 9 shows several further TEM micrographs of representative nanostructures for the TGAP/MMT(2 wt %) nanocomposites cured for 3 h at 150°C after pre-conditioning under the following conditions: 105 days at RT [Figure 9(a)], 225 days at RT [Figure 9(b)], 54 days at 40°C [Figure 9(c)], 12 days at 80°C [Figure 9(d)].

We believe that the clay is completely exfoliated in the regions between these small agglomerations, and that complete exfoliation throughout the whole sample would require the elimination of these small agglomerations. It appears as if the higher pre-conditioning temperatures are better than pre-conditioning at RT in this respect, though the effect is not dramatic. Furthermore, since, as observed above, the isothermal cure process induces significant nanostructural changes, it seems likely that
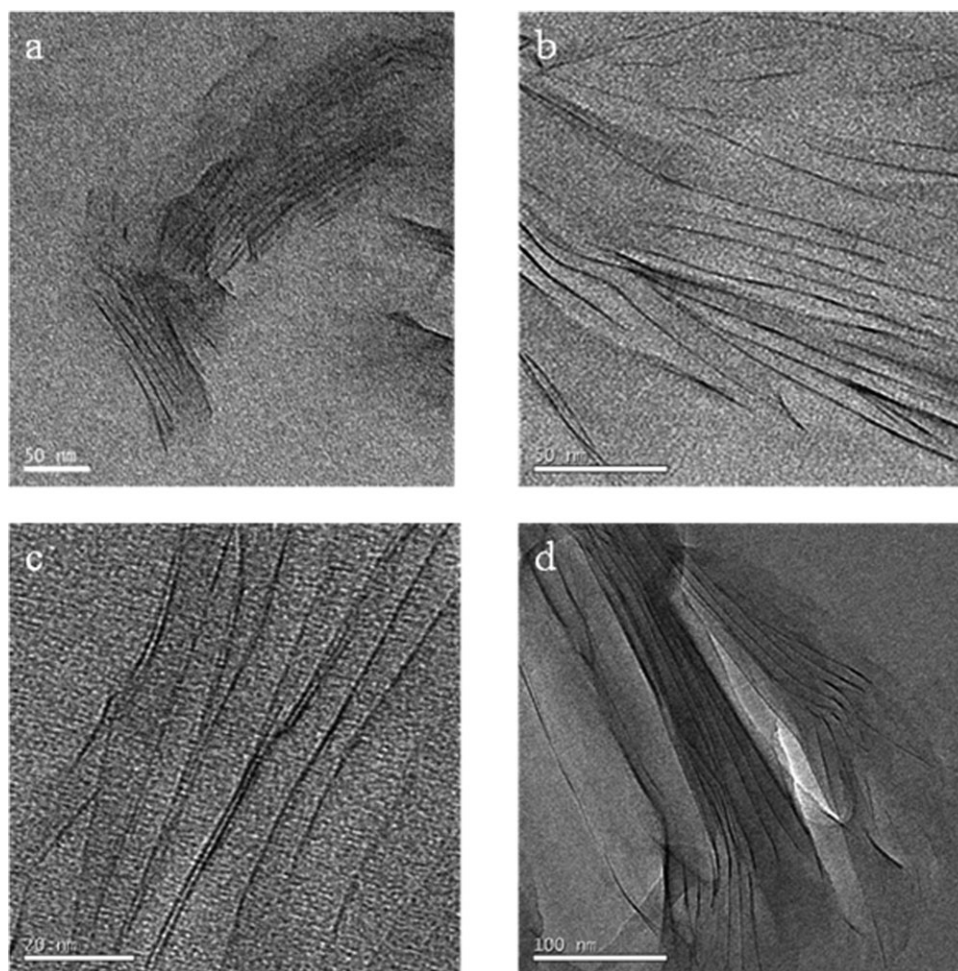
Figure 10. TEM images of TGAP/MMT (5 wt %) mixtures cured for 3 h at 150°C: (a) without pre-conditioning; (b, c) after pre-conditioning 63 days at RT; (d) after pre-conditioning 112 days at RT.

an additional parameter worth investigating is the isothermal cure temperature; this is currently under study, and will be reported in a separate publication.

The effect of pre-conditioning is clear. In Figure 10 we make a comparison, for a nanocomposite with 5 wt % MMT content, of the nanostructure obtained without any pre-conditioning [Figure 10(a)] with that obtained after pre-conditioning the TGAP/MMT mixture for 63 days at RT (cf., Table I) [Figure 10(b, c)] and after 112 days at RT, all samples being cured isothermally for 3 h at 150°C. It is clear that the pre-conditioning has a significant effect on the nanostructure; even though the intra-gallery reaction occurs first for the sample without pre-conditioning, there remains some layer stacking, whereas the clay layers are rather well disassociated in the pre-conditioned samples. The conclusion is that pre-conditioning is an effective means of promoting the reaction within the clay galleries, which ultimately is required for exfoliation to be achieved in the cured nanocomposite.

CONCLUSIONS

The isothermal cure of polymer layered silicate (PLS) nanocomposites based upon the highly reactive tri-functional epoxy resin TGAP displays two exothermic reactions: the first reaction is very rapid, and is attributed to the homopolymerization reaction in the intra-gallery regions, while the second is the cross-linking reaction with the curing agent. This is confirmed by the observation that pre-conditioned samples show only a single exothermic peak, the crosslinking reaction. The occurrence of this rapid intra-gallery reaction results in improved exfoliation in the cured nanocomposite. On the other hand, the pre-conditioning of mixtures of organically modified MMT and the epoxy resin is shown to improve both the dispersion of the clay in the resin and the subsequent exfoliation of the clay when the nanocomposite is cured. The pre-conditioning occurs by a homopolymerization process within the clay galleries, and is characterized by a different behavior from that observed earlier for a bifunctional epoxy resin, DGEBA: instead of a linear relationship between EE and T_g, the TGAP/MMT system displays an abrupt change in this relationship at a time corresponding to gelation of the mixture. Pre-conditioned samples, after curing with DDS, show a significantly better degree of exfoliation, as identified by TEM, than do samples not pre-conditioned, because pre-conditioning allows a greater extent of intra-gallery reaction to occur before the extra-gallery reaction. The overall conclusion is that,

even in the present system for which the intra-gallery reaction occurs before the extra-gallery reaction, for high degrees of exfoliation it is essential to maximize the intra-gallery reaction, and that pre-conditioning is the most effective means of achieving this end.

ACKNOWLEDGMENTS

REFERENCES

1. Lan, T.; Kaviratna, P. D.; Pinnavaia, T. *J. Chem. Mater.* **1995,** *7*, 2144.

2. Wang, Z.; Pinnavaia, T. *J. Chem. Mater.* **1998,** 10, 1820.

3. Park, J. H.; Jana, S. C. *Macromolecules* **2003,** *36*, 2758.

4. Kong, D.; Park, C. E. *Chem. Mater.* **2003,** *15*, 419.

5. Benson Tolle, T.; Anderson, D. P. *J. Appl. Polym. Sci.* **2004,** *91*, 89.

6. Pustkova, P.; Hutchinson, J. M.; Román, F.; Montserrat, S. *J. Appl. Polym. Sci.* **2009,** *114*, 1040.

7. Chin, I.-J.; Thurn-Albrecht, T.; Kim, H.-C.; Russell, T. P.; Wang, J. *Polymer* **2001,** *42*, 5947.

8. Kornmann, X.; Lindberg, H.; Berglund, L. A. *Polymer* **2001,** *42*, 4493.

9. Chen, C.; Curliss, D. *J. Appl. Polym. Sci.* **2003,** *90*, 2276.

10. Montserrat, S.; Román, F.; Hutchinson, J. M.; Campos, L. *J. Appl. Polym. Sci.* **2008,** *108*, 923.

11. Chen, C.; Benson Tolle, T. *J. Polym. Sci. Part B: Polym. Phys.* **2004,** *42*, 3981.

12. Chen, B.; Liu, J.; Chen, H.; Wu, J. *Chem. Mater.* **2004,** *16*, 4864.

13. Wang, K.; Wang, L.; Wu, J.; Chen, L.; He, C. *Langmuir* **2005,** *21*, 3613.

14. Wang, K.; Chen, L.; Wu, J.; Toh, M. L.; He, C.; Yee, A. F. *Macromolecules* **2005,** *38*, 788.

15. Brown, J. M.; Curliss, D.; Vaia, R. A. *Chem. Mater.* **2000,** *12*, 3376.

16. Becker, O.; Cheng, Y.-B.; Varley, R. J.; Simon, G. P. *Macromolecules* **2003,** *36*, 1616.

17. Velmurugan, R.; Mohan, T. P. *J. Mater. Sci.* **2004,** *39*, 7333.

18. Mohan, T. P.; Ramesh Kumar, M.; Velmurugan, R. *Polym. Int.* **2005,** *54*, 1653.

19. Hutchinson, J. M.; Montserrat, S.; Román, F.; Cortés, P.; Campos, L. *J. Appl. Polym. Sci.* **2006,** *102*, 3751.

20. Norme Française Enregistré. Composés d'époxydes, determination de l'equivalent époxyde, NF T 51-522, AFNOR, September **1975**.

21. Varley, R. J.; Hodgkin, J. H.; Hawthorne, D. G.; Simon, G. P. *J. Appl. Polym. Sci.* **1996,** *60*, 2251.

22. Hutchinson, J. M.; Shiravand, F.; Calventus, Y.; Fraga, I. *Thermochim. Acta* **2012,** *529*, 14.

23. Fraga, I.; Montserrat, S.; Hutchinson, J. M. *J. Therm. Anal. Calorim.* **2008,** *91*, 687.

24. Lipinska, M.; Hutchinson, J. M. *Compos. Sci. Technol.* **2012,** *72*, 640.