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A novel comparative study of different layered silicate clay types on exfoliation process and final nanostructure of trifunctional epoxy nanocomposites

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Abstract

The effect of three different organically modified layered silicate clays (Nanomer I.30E, Cloisite 30B and Nanofil SE 3000) on the exfoliation process and on the thermal properties and nanostructure of cured trifunctional epoxy resin based nanocomposites was studied. Optical microscopy showed that the best and poorest qualities of clay distribution in the epoxy matrix were obtained with Nanofil SE 3000 and Nanomer I.30E, respectively. However, the isothermal differential scanning calorimetry scans show that, of the three systems, it is only the Nanomer clay that promotes intra-gallery reaction due to homo- polymerisation, appearing as an initial rapid peak prior to the cross-linking reaction. This rapid intra- gallery reaction is not present in the curing curve for the Cloisite and Nanofil systems. This fact im- plies that the fully cured nanostructure of the Cloisite and Nanofil system is poorly exfoliated, which is confirmed by small angle X-ray scattering which shows a scattering peak for these systems at around 2.53^0, corresponding to about 3.5 nm d-spacing.

1. Introduction

Thermoset epoxy resin is known to display superior properties, including high stiffness, for industrial applications such as coatings and adhesives [1e7]. However, there is an important limitation in the use of these thermoset materials because of their low toughness or impact properties [1e7]. As a consequence, many researchers have investigated procedures for the improvement of epoxy toughness or the modification of its impact strength.

An improvement in the toughness of epoxy resin can be achieved by the addition of a second phase, such as liquid rubber or elastomer, as well as inorganic fillers such as silica [3,4]. Although all these methods help to modify the impact properties, they generally lead to a decrease in some of the other desirable properties, such as the glass transition temperature. Using fibers as reinforcement is considered as an alternative way to increase the toughness of epoxy resin [3,4].

Nowadays, the main focus area is to use a nanofiller as a new type of reinforcement for the epoxy matrix [5,8]. Among the different kinds of nanofiller, layered silicate clays are recognized as potential materials to promote epoxy toughness because of their availability, plate-like morphology and low-cost [1,6,7,9,10].

The highest value of the toughness in epoxy-clay systems can be obtained when their nanostructures are highly exfoliated. The degree of exfoliation of the nanostructure can be optimized if the intra-gallery reaction occurs before the extra-gallery reaction, even if the mechanisms by which exfoliation takes place may not be well understood. It can be appreciated that the separation of the clay layers will be severely inhibited if the surrounding matrix has already formed a rigid three-dimensional network structure [11]. There are many factors which play a role in achieving a desirable balance between the intra- and extra-gallery reactions: the preparation of the epoxy-clay mixture [12] [13], including the mixing procedure and the resulting dispersion of the clay in the resin, the cure schedule [13,14], the nature of the curing agent [15], and the clay type and its characteristics.

To date, there are many reports in which the study the effect of a specific clay on the epoxy matrix, typically diglycidyl ether of bisphenol-A (DGEBA) [16e27]. In contrast, less attention has been paid to study of the effect of different types of clay on the epoxy

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system; a few comparative results can be found concerning the thermal behavior and the quality of the final nanostructure for different types of clay, and their effects on the mechanical properties and exfoliation process in epoxy based nanocomposites, typically DGEBA based nanocomposites [28e31].

Therefore, the objective of this work is to investigate the effects of three different clay types on the exfoliation process and nanostructure of cured polymer layered silicate nanocomposites based on a tri-functional epoxy resin. For this purpose, we initially studied the influence of the clay on properties such as the thermal degradation and basal spacing of the clay in uncured resin/clay mixtures in order to obtain better interpretation of the experimental results which were obtained in the second stage of our work. In the second stage, we studied the exfoliation process and isothermal cure behavior of systems with a curing agent. The exfoliation process was inferred from differential scanning calorimetry (DSC) measurements, and the resulting nanostructure was determined by small angle X-ray scattering (SAXS) and also by transmission electron microscopy (TEM).

2. Materials and methods

The epoxy resin, TGAP, with trade name Araldite MY0510 (Huntsman Advanced Materials) and an epoxy equivalent between 95 and 106 g eq^{-1}, the curing agent, 4,4-diamino diphenyl sulphone (DDS), with trade name Aradur 976-1 (Aldrich), were used without further purification. The three different types of clay were: natural montmorillonite modified by octadecyl ammonium ion (primary ammonium ion), with trade name Nanomer I.30E (Nanocor Inc.); natural montmorillonite modified with a quaternary ammonium salt, with trade name Cloisite 30B (Southern Clay Products, Inc.); and organically modified nanodispersible layered silicate with secondary ammonium salt based on natural bentonite, with trade name Nanofil SE 3000 (Rockwood Additives, Inc).

First, the TGAP was mixed with each of the clays separately by mechanical mixing at about 300 rpm at 5 mass% clay with respect to TGAP mass for a period of 3 h. Then, the curing agent, DDS, in a proportion of 52 mass% with respect to the epoxy resin, giving a slight excess of epoxy relative to the stoichiometric ratio as recommended by the resin manufacturer, was added to TGAP/clay mixture. The mixture was finally degassed under vacuum at room temperature.

The calorimetric experiments were carried out using a conventional differential scanning calorimeter (DSC), DSC821e (Mettler-Toledo), and a temperature modulated DSC technique, TOPEM® (DSC823e, Mettler-Toledo), both being equipped with intra-cooling and with STARe software for data evaluation. Small sample quantities of the TGAP/clay/DDS mixture (6e10 mg for DSC and 10e15 mg for TOPEM®) were placed in sealed aluminum pans and the experiments were performed under a flow of dry nitrogen gas at 50 mL min^{-1}. All the samples were cured isothermally at 165 ^{0}C for 2 h, followed by a non-isothermal scan, from 50 ^{0}C to 300 ^{0}C at 10 ^{0}C min^{-1} in the conventional DSC or from 100 ^{0}C to 290 ^{0}C at 2 ^{0}C min^{-1} in TOPEM®. The temperature of 165 ^{0}C was selected as previous work with the TGAP/Nanomer/DDS system had shown this to be within the optimum range for isothermal cure [14]. The vitrification time during the isothermal scan and the glass transition temperature, T_g, of the fully cured nanocomposite were both determined by TOPEM®, the T_g being determined from a second non-isothermal scan [32].

A thermogravimetric analyzer (TGA) (TGA/DSC 1, Mettler-Toledo) was used to determine the thermal stability and mass loss characteristics of the TGAP/clay mixtures. The samples of mass approximately 8 mg were placed in alumina (aluminium oxide) crucibles and were heated from 40 ^{0}C to 600 ^{0}C with a rate of 10 ^{0}C min^{-1} under a dry nitrogen gas atmosphere (200 mL min^{-1}).

A Leica DME polarizing transmission optical microscope was used to examine the size of the clay agglomerations and the quality of the clay dispersion in the epoxy matrix before adding the curing agent.

The final nanostructure was characterized by Transmission Electron Microscopy (TEM), using a Jeol JeM-2010 high resolution transmission electron microscope with a resolution of 0.18 nm at 200 kV, and by small angle X-ray scattering (SAXS), using a Bruker D8 Advanced diffractometer, measurements being taken in a range of 2q ¼ 1^0 to 8^0 with copper Ka radiation (l ¼ 0.1542 nm).

3. Results and discussion

3.1. TGAP/clay mixture behavior

Fig. 1 shows the basal spacing of the different types of layered silicate clays: Nanomer I.30E, Cloisite 30B and Nanofil SE 3000. This basal spacing, which is determined by SAXS, is the interlayer distance of the organically modified clay platelets before the addition of the epoxy resin and the intercalation of the epoxy resin into the clay galleries. These peaks in the SAXS pattern correspond to the d-spacings of the pure clays, as shown in Table 1. Although these pure clays have different d-spacings, in the fresh mixture of TGAP/clay they have approximately the same d-spacing, which is about 3.5 nm irrespective of clay type, as shown in Fig. 2.

In order to compare the behavior of the TGAP with the different types of clay before adding any curing agent to the mixture, the thermal analytical techniques of DSC and TGA were used. In the non-isothermal DSC scan of pure TGAP, as shown in Fig. 3, an exothermic peak appears at high temperature (around 330 ^{0}C), corresponding to the TGAP homopolymerization reaction, which is thermally activated. Likewise, the non-isothermal DSC scans of the TGAP/clay mixtures for the Cloisite and Nanofil systems also show a homopolymerization peak at about 330 ^{0}C, approximately the same temperature as for the TGAP alone. On the other hand, in the Nanomer system this peak occurs at the slightly lower temperature of about 300 ^{0}C. This means that the TGAP homopolymerization is somewhat accelerated due to the catalytic effect of the anion ion in the Nanomer structure. In contrast, for both Cloisite and Nanofil systems, no noticeable effect on the TGAP homopolymerization can be found. Moreover, because the Nanomer can promote TGAP homopolymerization at a lower temperature before thermal degradation, it is expected that more TGAP monomer can participate in the homopolymerization reaction before the TGAP starts to degrade, which leads to the TGAP being more thermally stable, in agreement with the results of the TGA analysis presented immediately below.

The TGA traces are shown in Fig. 4. The degradation behavior is complex for all systems, with multiple steps implying multiple degradation mechanisms. Nevertheless, some interesting differences between the various systems can be identified. First, for example, a significant reduction in mass begins at about 200 ^{0}C for the TGAP without any clay and for the TGAP/Nanofil system, while this onset occurs at a noticeably higher temperature of about 250 ^{0}C for the systems with Nanomer and Cloisite, implying greater thermal stability for these latter systems. Thus, the degradation of the Nanomer system, for example, occurs consistently at temperatures at least 50 ^{0}C higher than those for the TGAP resin alone. Second, for all systems, there is a marked reduction in the rate of mass loss at approximately 330 ^{0}C, the temperature at which the exothermic peak corresponding to the epoxy homopolymerization reaction was noted in Fig. 3. Interestingly, this reduction in the rate of mass loss is the least marked for the Nanofil system, for which the exothermic peak in Fig. 3 was also the smallest. This effect of
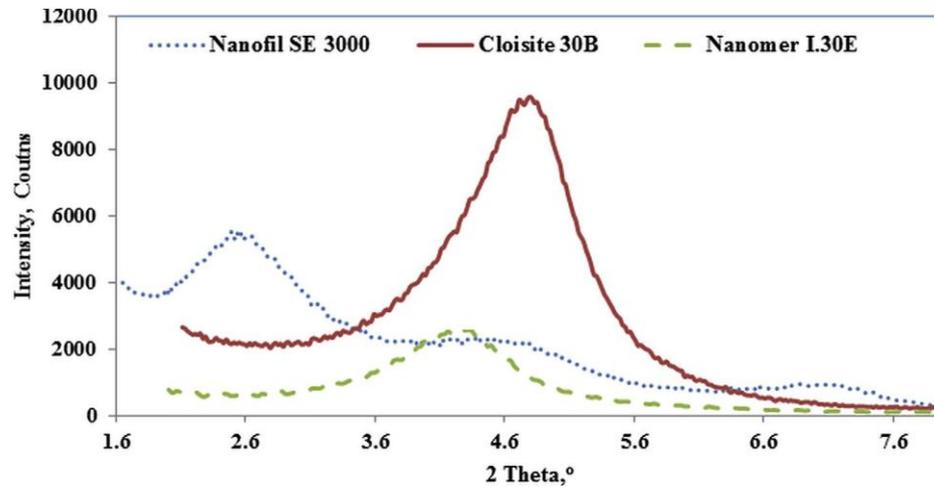
Fig. 1. SAXS patterns for the different types of layered silicate clays: Nanomer I.30E, Cloisite 30B and Nanofil SE 3000.

Table 1
Values of the *d*-spacing that were obtained from the SAXS patterns for different layered silicate clays.

Clay type	Peak double angle: 2q,⁰	*d*-spacing, nm
Nanomer I.30E	4.2	2.1
Cloisite 30B	4.7	1.8
Nanofil SE 3000	< 2:5	< 3:4
	4:7	3:7 / average 3:6
	7:1	3:7

homopolymerization on the rate of mass loss has been observed previously in a bifunctional DGEBA epoxy/clay system [33], where the effect is even more pronounced.

However, there is also a further point to be considered, namely the quality of the clay dispersion in the resin. This plays an important role in respect of the ability, or otherwise, of the clay layers to be exfoliated during the cure of the nanocomposite. In other words, good dispersion of the clay in the epoxy matrix helps to improve the exfoliation degree, whereas poorly dispersed clay, in which there are many large clay agglomerations, not only inhibits the penetration of the epoxy monomer into the clay galleries but also decreases the accessibility of the curing agent to resin.

Therefore, the size and number of the clay agglomerations in the fresh resin/clay mixtures were examined by means of optical microscopy, and the results are shown in Fig. 5. In principle, the clay particles are of the order of a few microns in the lateral dimension, but it is evident that in all these samples there are many agglomerations that are larger than this, and a small number have sizes even up to 20 or 30 mm. However, the presence of these microparticles in the resin/clay mixtures does not detract from the denomination of the resulting material as a nanocomposite, since the curing reaction required to produce the fully cured nanocomposite induces not only separation of the clay layers (exfoliation) but also an overall reduction in the size of these agglomerations, as evidenced by TEM of the cured nanocomposites [12,13]. Nevertheless, there always remain some aggregates in the final nanocomposite, and hence the material is never fully
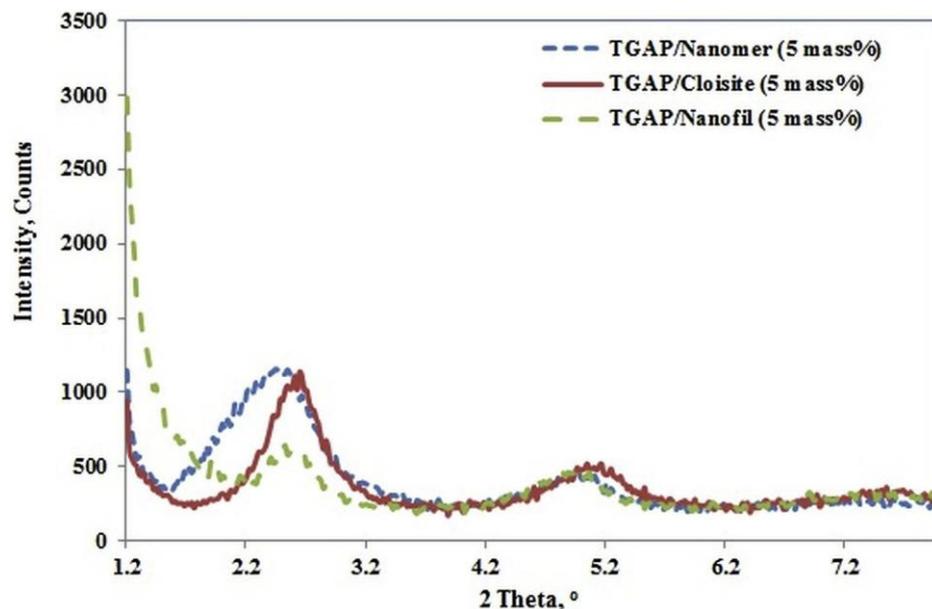

Fig. 2. SAXS patterns for the three different layered silicate clays (5 mass %) after intercalation of the TGAP epoxy resin.
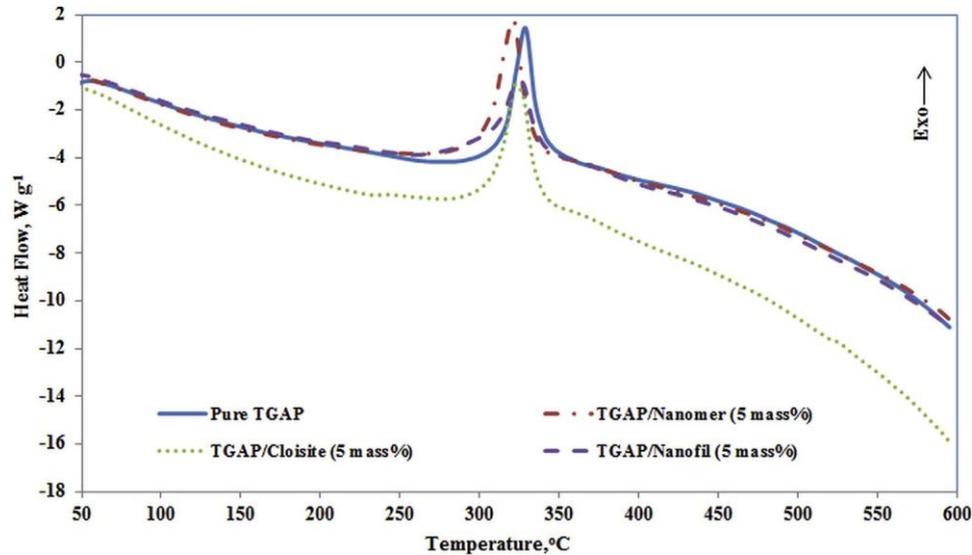
Fig. 3. DSC non-isothermal scan for the TGAP/clay (5 mass %) mixtures with different clays; heating rate is 10 ^{0}C min^{-1}.
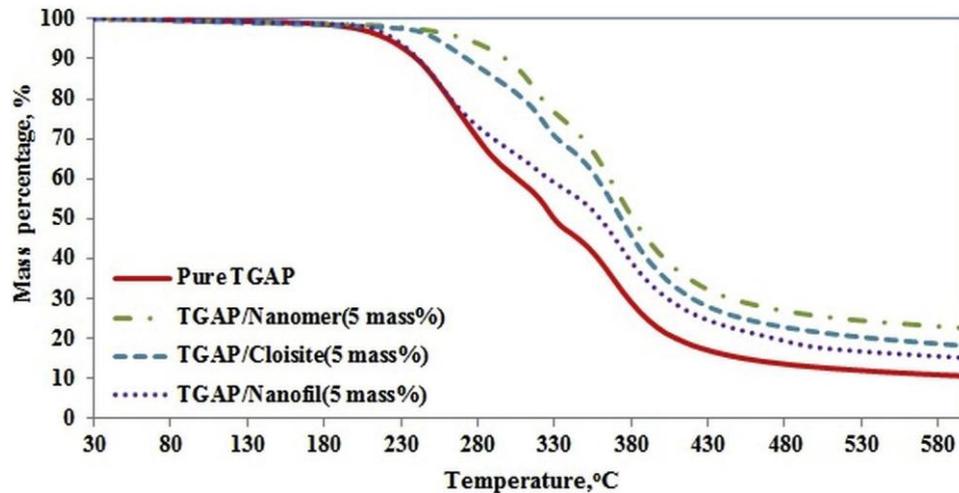

Fig. 4. TGA thermogram of the TGAP epoxy and the different TGAP/clay mixtures with 5 mass% clay content; heating rate is 10 ^{0}C min^{-1}.

exfoliated. It is for this reason that it is common to refer to a "degree of exfoliation", without ever quantifying the degree. The existence of these aggregates remains one of the major challenges for polymer layered silicate nanocomposites.

From a purely visual inspection of Fig. 5, some small differences can be identified. In particular, the most uniform dispersion occurs for the Nanofil system, for which the clay particles are all of approximately the same size and are rather evenly dispersed. In comparison, the Nanomer system shows a large proportion of very small particles, but also some agglomerations that are significantly larger, and appears to show the poorest distribution. The Cloisite system lies between these two extremes. Despite this result, it is not correct to anticipate that the cured Nanofil nanocomposite would show the most highly exfoliated nanostructure. The clay dispersion is just one aspect that is important in the overall fabrication process; in addition, the interaction between the exfoliation mechanism for the intercalated resin/clay mixture and the curing reaction must be considered and, finally, the nanostructure needs to be confirmed by other techniques such as SAXS and TEM. These aspects are discussed in the next sections.

3.2. Study of the TGAP/DDS/clay system

The intercalated TGAP/clay mixtures, for which the d-spacings are shown in Fig. 2 and the clay dispersions are shown in Fig. 5, were mixed with the DDS curing agent, according to the procedure described in an earlier section. All the mixtures were cured isothermally at 165 ^{0} C for 2 h in the DSC, and the isothermal cure curves are shown in Fig. 6. For the TGAP/Nanomer system, two exothermic peaks can be clearly identified: the first peak, very sharp and occurring very early in the isothermal cure, can be associated with the intra-gallery reaction; the second peak, much broader and showing the typical bell-shape of epoxy cure, can be associated with the extra-gallery reaction [14]. The first peak is related to the homopolymerization reaction that occurs between the clay galleries, and which is catalyzed by the ammonium ion of the organically modified clay; the second, and much larger, peak is ascribed to the cross-linking reaction between the TGAP and DDS in the bulk of the sample. In contrast, at the same isothermal cure temperature of 165 ^{0} C, neither the TGAP/Cloisite nor the TGAP/Nanofil system shows such a first peak, and just displays the broad
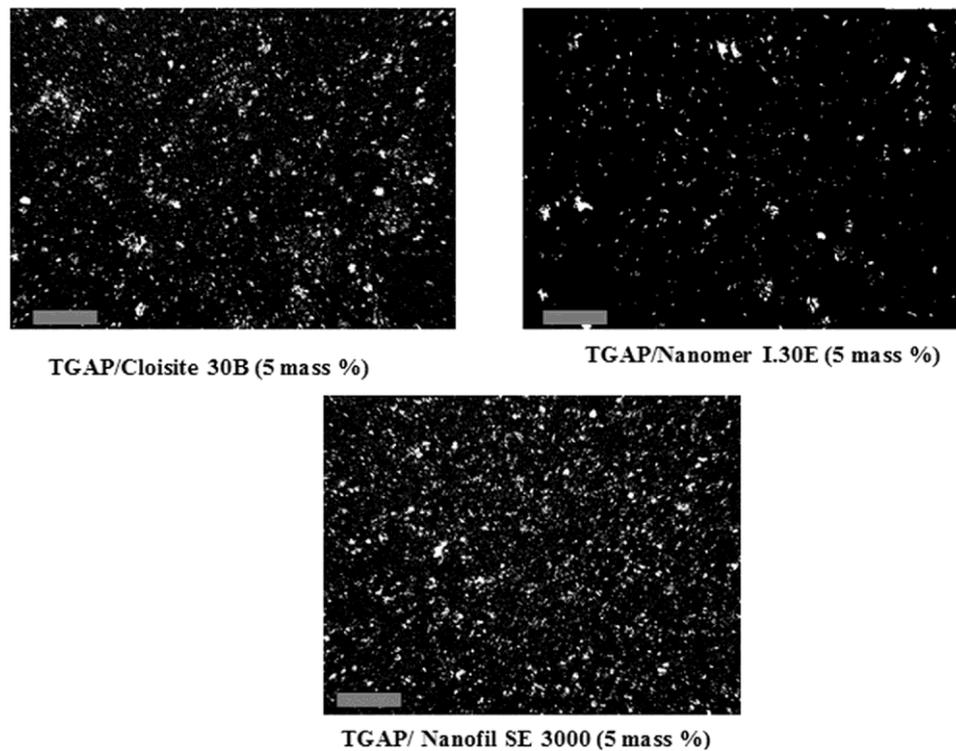
Fig. 5. Optical microscopy images of clay dispersion in the epoxy resin after 3 h mechanical mixing. Scale bar is 100 mm.
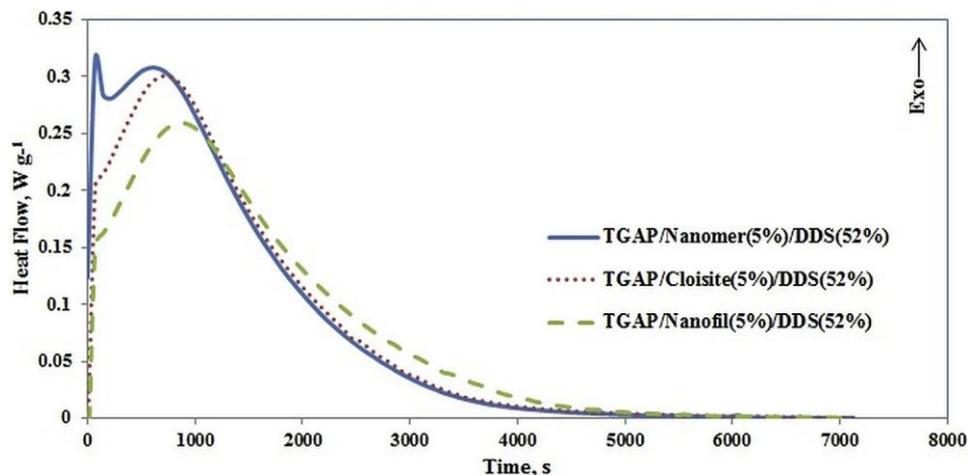

Fig. 6. Isothermal DSC scan at 165 ^{0}C for 2 h for TGAP/clay (5 mass %)/DDS (52 mass %) system for different clay types.

bell-shaped peak that is attributed to the extra-gallery cross-link-ing reaction. The implication of this is important. For exfoliation to occur, the reaction within the clay galleries must occur before the bulk cross-linking reaction inhibits any further clay layer separa-tion. This is clearly occurring in the TGAP/Nanomer system, whereas both intra- and extra-gallery reactions are occurring simultaneously in the other clay systems. One would anticipate, therefore, a better degree of exfoliation in the TGAP/Nanomer system. These results are consistent with those obtained in the non-isothermal DSC scans of the TGAP/clay mixtures without DDS, shown in Fig. 3, where it was seen that it is the TGAP/Nanomer system for which the homopolymerization reaction occurs at the lowest temperature.

Another feature that can be highlighted is the effect of the different types of clay on the main peak, namely the TGAP-DDS cross-linking reaction. It can be seen from Fig. 6 that the peak for this reaction shifts to shorter times, depending on the clay used: the Nanomer system peaks at the shortest time, and the Nanofil system at the longest time. Therefore, the Nanomer clay can accelerate the extra-gallery reaction as well as intra-gallery reac-tion during the curing procedure.

Furthermore, there is another consequence that should be considered. Among these different nanocomposites, the lowest glass transition temperature for fully cured nanocomposite, as shown in Fig. 7, was found for the Nanomer system. This is attrib-uted to the amount of intra-gallery TGAP homopolymerization that takes place during the isothermal scan, which provides indirect evidence for the occurrence of an enhanced exfoliation process in
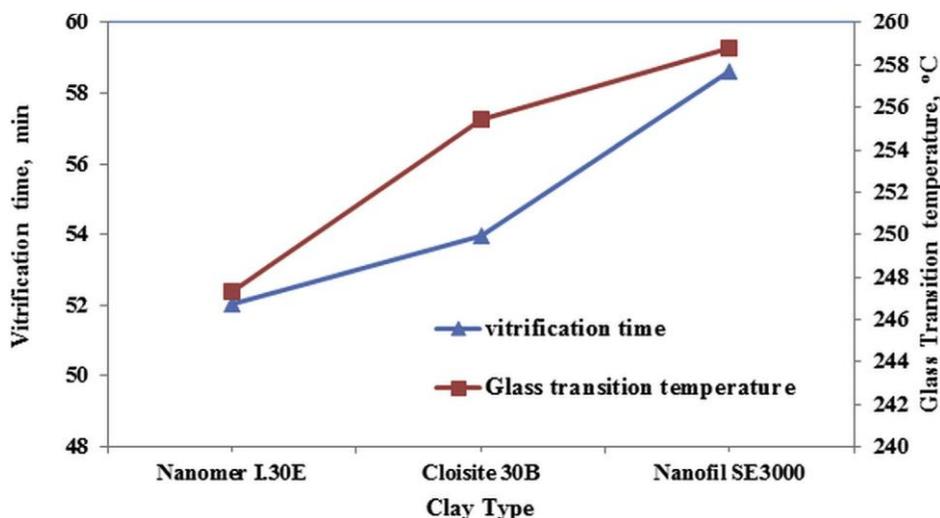
Fig. 7. The glass transition temperature and the vitrification time for the three different epoxy nanocomposites, all with 5 mass % clay and 52 mass % DDS: TGAP/Nanomer/DDS, TGAP/Cloisite/DDS and TGAP/Nanofil/DDS, cured isothermally at 165 ^{0}C for 2 h.

this system during the isothermal cure. The argument is as follows. As a consequence of the interaction of the Nanomer clay and the epoxy resin, a greater proportion of the TGAP takes part in the homopolymerization reaction within the clay galleries and, therefore, the number of epoxy groups that participate in the cross-linking reaction with the DDS decreases. This can lead to a final nanocomposite structure which is less cross-linked for the Nanomer system and, as a consequence, the glass transition temperature of the fully cured epoxy/Nanomer nanocomposite is lower than for either of the other epoxy/clay systems studied here. Moreover, the lowest value for the vitrification time is also obtained for the Nanomer system. This result is related to the catalytic nature of the montmorillonite modifier, namely primary ammonium ion, which results in the initiation of the cross-linking reaction in a shorter time.

Both of these observations, related to the glass transition temperature and the vitrification time in epoxy/clay nanocomposite systems, are in good agreement with our earlier work [12e14]. However, it should not be assumed that there is a direct relationship between the glass transition temperature and the exfoliation process. Although exfoliation requires the intra-gallery reaction to proceed, and this reaction is predominantly epoxy homopolymerisation, which results in a reduction in the glass transition temperature, the relationship is considerably more complex. For example, the glass transition temperature will also reduce if the epoxy-amine cross-linking reaction is off-stoichiometric, without implying any increase in the degree of exfoliation. Such effects have been discussed in more detail in other work [13,14,23,34].

On the other hand, the study by DSC of nanocomposite systems, in particular the analysis of the reaction kinetics, does provide important complementary evidence regarding the nanostructure development. Indeed, in some cases, calorimetric studies of the reaction can obviate the necessity for nanostructural analysis of the cured nanocomposite by SAXS and TEM, since they can demonstrate that the relationship between the intra- and extra-gallery reaction rates is not favorable for exfoliation. Examples of this have been given in earlier publications [11,13,15,35,36].

The above study by DSC of the isothermal curing process of the TGAP/clay systems with DDS, in which different types of clay are used, has shown that the TGAP/Nanomer system can enhance the intra-gallery reaction with respect to the other systems studied. It is necessary now to confirm this observation by more direct nanostructural observations. Accordingly, the SAXS scattering curves are shown in Fig. 8, where it can be seen that no scattering peaks occur for the Nanomer system, at least for d-spacings up to about 8 nm, indicating that for the Nanomer clay there is no regular layer separation in the cured nanostructure, which is a prerequisite for the existence of an exfoliated nanostructure [14].

In contrast, a small shoulder can be detected in the SAXS patterns for the Cloisite and Nanofil systems at a double angle of around 2.53^{0}, corresponding to about 3.5 nm d-spacing, which indicates that, for these systems, there remain some clay layers in close and systematic register. The TEM images also confirm that the final nanostructures of these latter systems, for example the TGAP/ Nanofil/DDS (5 mass%) sample, as shown in Fig. 9, is poorly exfoliated in comparison with the TGAP/Nanomer nanocomposites, for which the extensive degree of exfoliation has been demonstrated previously on numerous occasions, for example Figs. 7e9 in References [12e14] respectively. Numerous agglomerations can be seen in the left hand image of Fig. 9. At higher magnification, shown in the right hand image of Fig. 9, a d-spacing of approximately 2.8 nm can be measured for these agglomerations, which is in agreement with the SAXS results shown in Fig. 8.

4. Conclusions

The Nanomer system presents the best possibility for achieving a highly exfoliated epoxy-clay nanocomposite rather than the Cloisite and Nanofil systems. This can be related to the first rapid peak in the isothermal DSC scan, which corresponds to the intra-gallery reaction and which appears before the bulk cross-linking reaction; this sequence is necessary in order to promote exfoliation. This is in accord with the SAXS data, where no scattering peak can be detected. Although the initial dispersion, as evidenced by optical microscopy, appears to be best for the Nanofil system, the rapid intra-gallery reaction is not present during isothermal cure of this system. This is again consistent with the SAXS patterns, which show evidence of continued layer stacking in the cured nanocomposite. For the Cloisite system, the quality of the initial dispersion of the clay in the resin is intermediate between those for the Nanofil and Nanomer systems and, similar to Nanofil, there is no rapid intra-gallery reaction during isothermal. Consequently, SAXS shows the persistence of significant layer stacking in the cured Cloisite samples. It can be concluded, therefore, that the
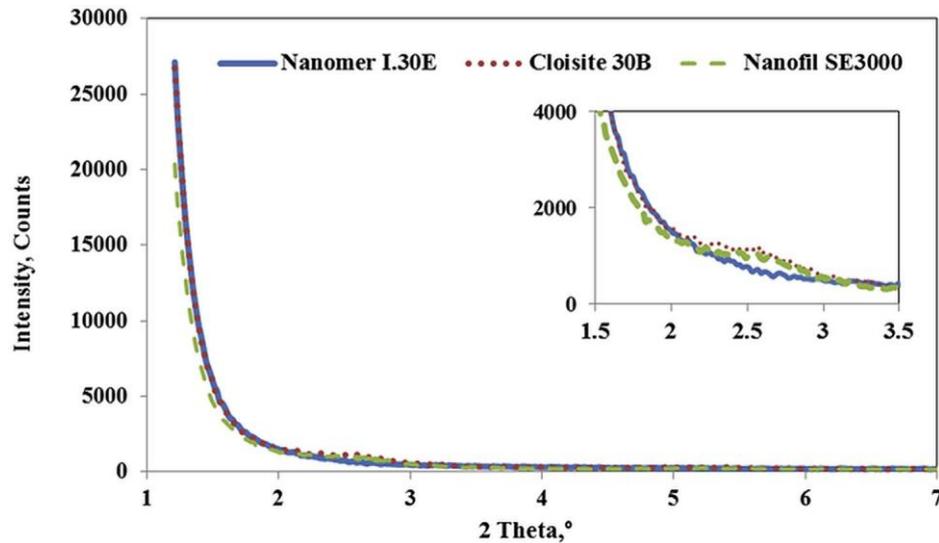
Fig. 8. SAXS diffractograms for the three different nanocomposites, all with 5 mass % clay and 52 mass % DDS: TGAP/Nanomer/DDS, TGAP/Cloisite/DDS and TGAP/Nanofil/DDS, cured isothermally at 165 ^{0} C for 2 h.
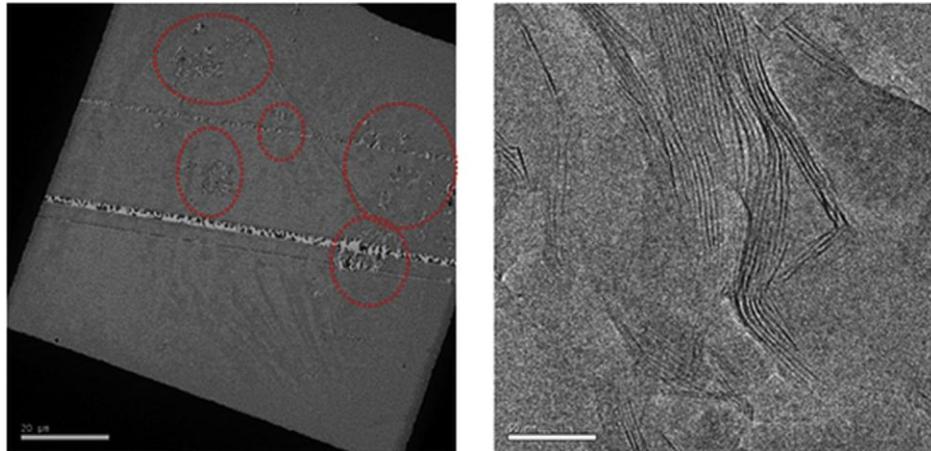

Fig. 9. TEM images for the TGAP/Nanofil (5 mass %)/DDS (52 mass %) system cured isothermally at 165 ^{0} C for 2 h; the scale bar for the left image is 20 mm and for the right image is 50 nm.

enhancement in the degree of exfoliation depends on the type of clay in TGAP nanocomposites, and that this can be associated with the appearance of a sharp peak in the isothermal DSC scan, indicative of a rapid intra-gallery reaction.

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