Comparative results between three protocols for achieving highly exfoliated epoxy-clay nanocomposites[*)]

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Abstract: Three different methods of fabricating polymer layered silicate (PLS) nanocomposites based upon a tri-functional epoxy resin are compared in respect of the nanostructure and impact energy of the cured nanocomposites. The three methods are designed to maximise the amount of intra-gallery reaction that takes place during cure, and this paper examines separately the effects of: (i) increasing the isothermal cure temperature; (ii) preconditioning the resin/clay mixture; and (iii) incorporating an initiator of homopolymerisation within the clay galleries. It is shown that each of these methods increases the degree of exfoliation in the cured nanocomposite, and that this improved nanostructure correlates also with an increase in the impact energy.

Keywords: PLS nanocomposites, exfoliation, epoxy resin, homopolymerisation, differential scanning calorimetry.

Porównanie wysoko eksfoliowanych nanokompozytów żywicy epoksydowej z krzemianami wytwarzanych trzema metodami

Streszczenie: Trzema różnymi metodami wytwarzano nanokompozyty na bazie trójfunkcyjnej żywicy epoksydowej napełnianej warstwowymi glinokrzemianami (PLS). Analizowano ich strukturę i wytrzymałość na uderzenie. Porównano efekt uzyskiwany na drodze: (i) zwiększania temperatury izotermicznej reakcji sieciowania żywicy, (ii) wstępnego kondycjonowania sporządzonej mieszaniny żywicy z glinokrzemianem i (iii) prowadzenia reakcji w obecności inicjatora homopolimeryzacji. Wykazano, że każda z ww. metod prowadzi do wzrostu stopnia eksfoliacji usieciowanych nanokompozytów, a zmiany w strukturze znajdują potwierdzenie w zwiększeniu ich udarności.

Słowa kluczowe: nanokompozyty PLS, eksfoliacja, żywica epoksydowa, homopolimeryzacja, różnicowa kalorymetria skaningowa.

The idea of obtaining significant reinforcement of polymers at low filler contents by the incorporation of nanoclays has been rather widely investigated since the original conception by the Toyota research group in the early 1990's [1]. In order to accomplish the desired improvement in mechanical properties of these nanocomposites, it is necessary for the clay layers to be separated and dispersed homogeneously throughout the polymer matrix, in a process referred to as exfoliation, which creates a very large polymer-clay interfacial area [2]. For epoxy-clay nanocomposites, this process of exfoliation begins with the intercalation of the resin monomer into the clay galleries, and the subsequent crosslinking reaction is supposed to lead to the desired exfoliated nanostructure. However, achieving a highly exfoliated nanostructure in these epoxy layered silicate nanocomposites has proven difficult, and it is common to refer to „partial" exfoliation or to consider the nanostructure to be exfoliated when the *d*-spacing of the clay layers cannot be detected by Small Angle X-ray Scattering (SAXS), which normally implies layer separations greater than about 8 nm. One problem is related to the relative rates of reaction of the resin in the intra- and extra-gallery regions of the clay. It is generally recognized that, in order to maximise the degree of exfoliation, the intra-gallery reaction should occur before the extra-gallery reaction [3, 4], but this does not occur naturally for nanocomposites based upon DGEBA epoxy and organically modified montmorillonite (MMT) cured with a diamine [5]. One possibility for overcoming this problem is to precondition the intercalated epoxy-clay mixture [6, 7] before adding the curing agent and effecting the crosslinking reaction; this preconditioning procedure results in a homopolymerisation reaction taking place within the clay galleries. On the

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other hand, it transpires that, during the isothermal cure of such nanocomposite systems based upon a tri-functional epoxy resin cured with a diamine, two distinct reactions occur: the first is the epoxy homopolymerisation reaction taking place within the clay galleries, while the second is the bulk crosslinking reaction in the extra-gallery regions [8]. This system therefore affords a mechanism for improved exfoliation in these epoxy-clay nanocomposites, and we present here the results of three different ways in which the intra-gallery reaction can be promoted. These are:

(a) preconditioning of the resin-clay mixture;

(b) selection of the isothermal cure temperature;

(c) incorporation of an initiator of cationic homopolymerisation within the clay galleries.

The procedures involved in each of these protocols and the nanostructures and properties obtained are the subject of this paper.

EXPERIMENTAL PART

Materials

The epoxy resin was triglycidyl *p*-aminophenol, TGAP (Araldite MY0510, Huntsman Advanced Materials), with diaminodiphenyl sulphone, DDS (Aradur 976-1, Huntsman Advanced Materials), as the curing agent. The organically modified clay (MMT) was Nanomer I.30E (Nanocor Inc.). The initiator was a boron trifluoride monoethylamine complex, BF_3·MEA (Sigma Aldrich), which is known to be an efficient initiator for the homopolymerisation of epoxy resins [9].

Preparation of samples

For the „standard" preparation of the epoxy-clay nanocomposites, mixtures of TGAP and 2 wt % or 5 wt % MMT were first mixed mechanically for approximately 4 h. For the preconditioning procedure, these mixtures were then stored either at room temperature (*RT*) or at higher temperatures (40 °C, 60 °C, 80 °C) using a thermostatic bath. After storage for selected periods of time at each temperature, the epoxy equivalent (*EE*) was determined by titration and the glass transition temperature, T_g, of the mixture was determined by differential scanning calorimetry (DSC). For the curing of the final nanocomposite, the required amount of DDS was added to the TGAP/MMT mixture, according to the measured *EE* of the resin and to give an excess epoxy ratio (1:0.85 molar).

To incorporate the initiator into the system, BF_3·MEA and MMT were first mixed together in various proportions (to give 0.5 wt % and 1 wt % for BF_3·MEA, and 2 and 5 wt % for MMT, both with respect to the TGAP content in the final nanocomposite) using acetone as a solvent, which was subsequently removed by evaporation at room temperature over a period of about one day. The resulting mixture, ground to a fine powder, was then dispersed in the TGAP by high shear mechanical mixing (Polytron, PT1200C, Kinematica AG) at room temperature. This TGAP/MMT/BF_3·MEA mixture was then heated on a hot-plate to 80 °C and the DDS was added.

Methods of testing

All samples were degassed under vacuum at room temperature for 10—15 min before scanning them in the DSC. The calorimetric experiments were carried out using a conventional DSC (DSC821e, Mettler-Toledo) with a flow of dry nitrogen gas at 50 cm^3/min.

The impact tests were performed using a Zwick Izod impact tester 5110 according to ASTM D4508-05 (2008) on rectangular samples, 25 × 12 × 2.5 mm, with a hammer of energy 0.545 J.

The nanostructure of the cured samples was observed by Transmission Electron Microscopy (TEM) on ultra-microtomed sections using a Jeol JeM-2010 high resolution transmission electron microscope. The fracture surfaces of the impact samples were observed using a Scanning Electron Microscope (SEM, Jeol 5610).

RESULTS AND DISCUSSION

Preconditioned samples

Samples of TGAP/MMT/DDS prepared according to the standard procedure described above and then cured isothermally display two peaks in the DSC curves, as shown in Fig. 1. The first peak, which is very rapid, is assigned to the intra-gallery homopolymerisation reaction of the epoxy resin catalysed by the onium ion of the MMT, while the second peak is associated with the crosslinking reaction of the TGAP with the DDS. The reason why the first peak can be assigned to the intra-gallery reaction is evident when the cure curve for the preconditioned sample is compared, as shown also in Fig. 1. Here it can be seen that the effect of preconditioning, in this case for 112 days at *RT*, is to eliminate the first peak and reduce the heat of reaction, measured as the area under the cure curve. This is because a homopolymerisation reaction occurs within the clay galleries during the preconditioning process, in which both the *EE* and the T_g of the mixture increase [6, 7]. Consequently, for preconditioned samples no further intra-gallery reaction will occur when the DDS is added and the sample is cured isothermally at 150 °C, and the heat of reaction will be reduced because some epoxy groups will have already reacted during preconditioning.

The occurrence of the intra-gallery reaction before the crosslinking reaction is important for exfoliation. It is clear, therefore, that preconditioning the TGAP-clay mixture before adding the curing agent helps to promote the intra-gallery reaction and hence should be beneficial for exfoliation. TEM images show that the preconditioning procedure does indeed improve the final nanostructure

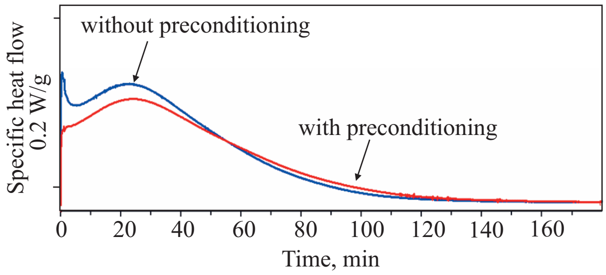

Fig. 1. Isothermal cure of TGAP/MMT(5 wt %)/DDS at 150 °C, with and without preconditioning, as indicated, exothermic direction is upwards

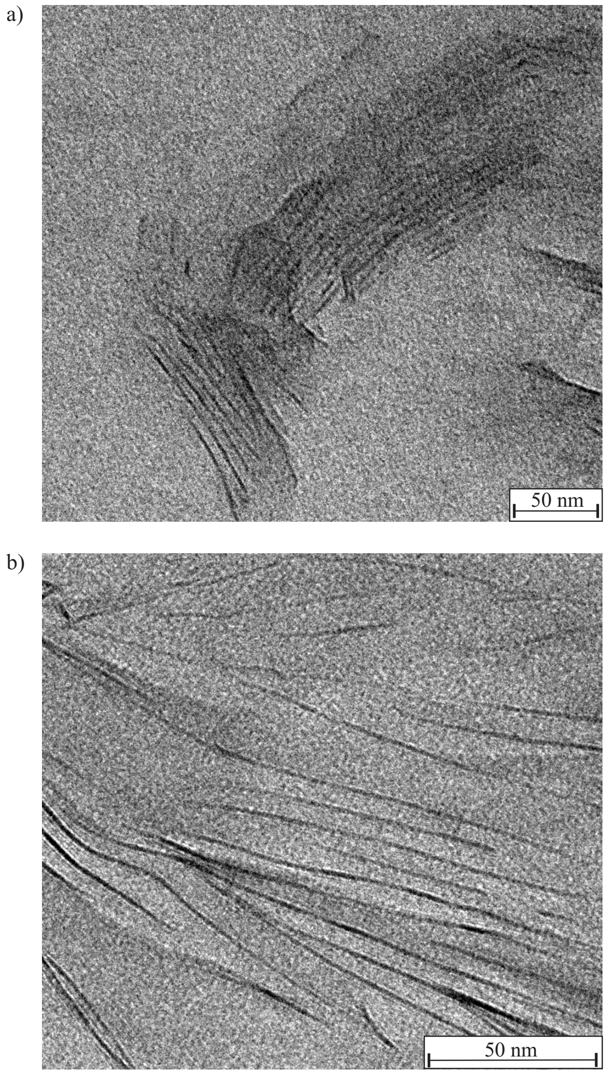

Fig. 2. TEM micrographs of cured TGAP/MMT(5 wt %)/DDS nanocomposites: a) without preconditioning, b) with preconditioning

by producing a greater layer separation and a more random dispersion of the clay layers, as illustrated in Fig. 2.

Isothermal cure temperature

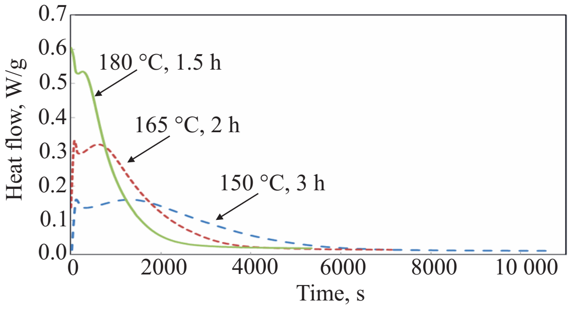

Fig. 3. DSC scans for a TGAP/MMT(5 wt %)/DDS mixture prepared by the standard procedure and cured isothermally at the temperatures indicated

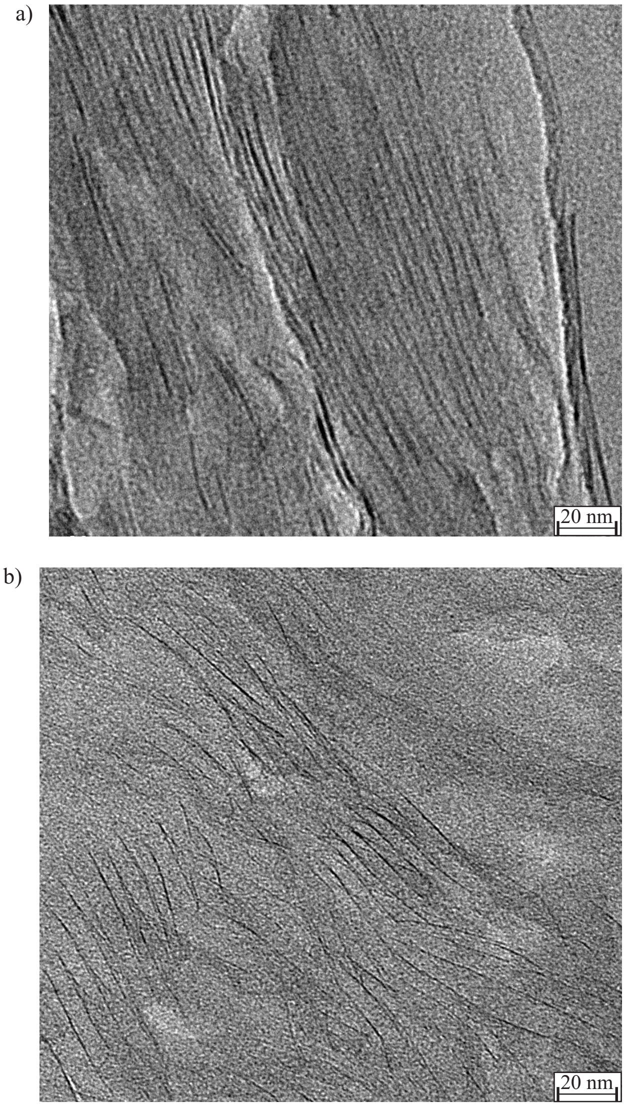

Fig. 4. TEM images for TGAP/MMT(5 wt %)/DDS nanocomposites cured isothermally at the different temperatures indicated: a) cured at 120 °C for 16 h, b) cured at 180 °C for 1.5 h

The effect of the isothermal cure temperature for TGAP/MMT/DDS mixtures prepared by the standard method has been investigated, and is illustrated in Fig. 3. It can be seen that, in each case, there is a very rapid first (intra-gallery) reaction, followed by the broader bell-shaped peak corresponding to the crosslinking reaction. As the isothermal cure temperature increases, the crosslinking reaction moves to shorter times, as expected, while the magnitude of the intra-gallery reaction increases. This latter effect can be quantified by deconvolution of the overall curve into two peaks and determining the area under the first peak, which corresponds to the amount of homopolymerisation reaction that has taken place [10]. For example, for the samples and cure schedules in Fig. 3, the approximate extent of reaction within the clay galleries at the different cure temperatures is as follows: 33 % at 150 °C, 50 % at 165 °C, and 76 % at 180 °C.

The greater extent of the homopolymerisation reaction that takes place at the higher cure temperature would imply that a greater degree of exfoliation would be expected for cure at 180 °C in comparison with cure at 120 °C. This is indeed the case, as illustrated in Fig. 4, where the TEM micrographs show significantly greater layer separations for the higher cure temperature. The same effect was observed by Becker et al. [11] for both DGEBA- and TGAP-based nanocomposites.

Initiator of cationic homopolymerisation

The intra-gallery homopolymerisation reaction can also be promoted by the inclusion of $BF_3 \cdot MEA$ as an initiator within the clay galleries. Firstly, the $BF_3 \cdot MEA$ is intercalated into the clay galleries by the procedure described earlier. The presence of the $BF_3 \cdot MEA$ within the clay galleries is verified by SAXS, which in fact shows that the *d*-spacing decreases, from 2.1 nm for the organically modified MMT to 1.3 nm, which is attributed to the interchange of the monoethylamine of the BF_3 complex with the octadecyl ammonium salt of the MMT. This should be compared with an increase in the *d*-spacing to 3.5 nm when the TGAP is intercalated into the MMT [8].

The curing agent, DDS, is then added and the system is cured. Here, the cure schedule must be selected carefully in order to separate the two reactions: the intra-gallery homopolymerisation reaction, now initiated by the $BF_3 \cdot MEA$, and the extra-gallery crosslinking reaction with the DDS. This involves a two-stage schedule. First,

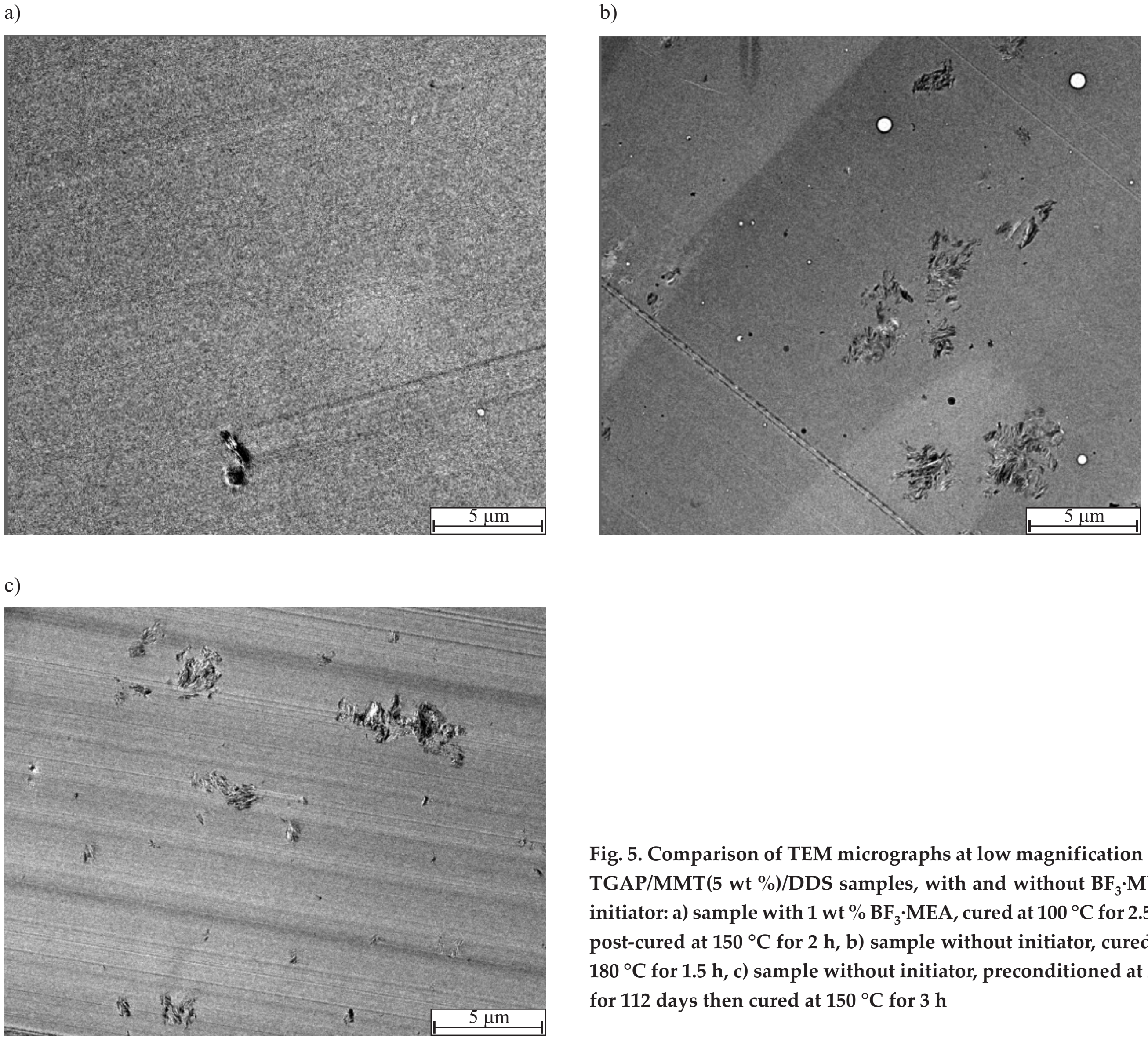

Fig. 5. Comparison of TEM micrographs at low magnification for TGAP/MMT(5 wt %)/DDS samples, with and without $BF_3 \cdot MEA$ initiator: a) sample with 1 wt % $BF_3 \cdot MEA$, cured at 100 °C for 2.5 h, post-cured at 150 °C for 2 h, b) sample without initiator, cured at 180 °C for 1.5 h, c) sample without initiator, preconditioned at *RT* for 112 days then cured at 150 °C for 3 h

the system is cured isothermally at a relatively low temperature, 100 °C or 110 °C, during which the intra-gallery reaction proceeds, allowing the clay layers to separate without any significant crosslinking occurring in the extra-gallery regions. This is followed by an isothermal post-cure at a higher temperature to allow the crosslinking reaction to proceed.

An illustration of the effect of this procedure on the nanostructure can be seen in Fig. 5. Here, TEM images at low magnification are shown in order to demonstrate how the incorporation of the BF_3·MEA into the system results in a significantly better dispersion of the clay in the matrix of epoxy resin. Only a single aggregate can be seen in Fig. 5a for the sample with initiator, whereas several agglomerations, often somewhat larger, can be seen for the other samples in Figs 5b and 5c.

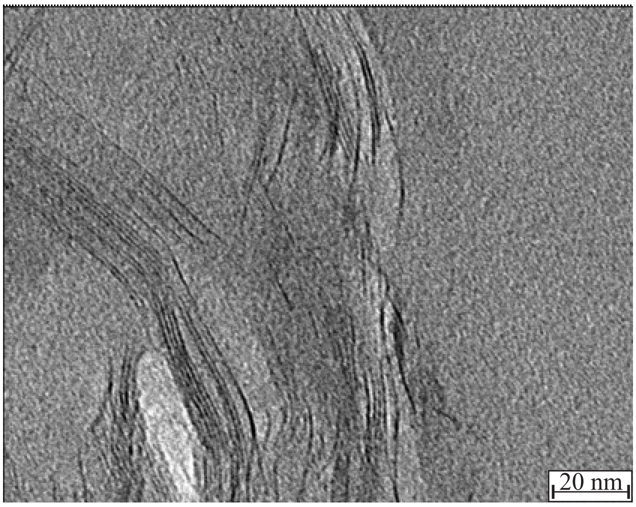

Fig. 6. TEM micrograph of TGAP/MMT(5 wt %)/DDS/BF_3 nanocomposite post-cured at 150 °C

The low magnification TEM images in Fig. 5 serve to illustrate the improved dispersion of the clay when the procedure involving the BF_3·MEA initiator is used. Nevertheless, within the small agglomeration of Fig. 5a, for example, there still remains some layer stacking in the clay, as shown in Fig. 6, though this occurs to a much smaller extent than in the other preparations. Here it is evident that there are some regions in which the *d*-spacing is as small as 1.3 nm, the spacing of the clay intercalated with BF_3·MEA before the addition of the TGAP.

Impact tests

Although it can be deduced from the TEM images shown above that these three preparation procedures lead, to a greater or lesser extent, to an enhanced degree of exfoliation in the final nanostructure of the cured nanocomposite, these images each nevertheless represent only a small selected part of the overall nanostructure. In this respect it is interesting in addition to determine a bulk property, such as the impact strength, which is strongly dependent on the nanostructure. To this end, the effects of the preparation procedures described above on the impact energy of cured nanocomposites with 2 wt % MMT are collected in Table 1.

Table 1. Values of the impact strength of epoxy-clay nanocomposites with 2 wt % MMT

Formulation	Impact strength, kJ/m^2	Standard deviation
Reference	1.40	±0.18
TGAP/MMT/DDS, 150 °C	1.60	±0.20
TGAP/MMT/DDS, 180 °C	1.70	±0.38
TGAP/MMT/DDS, preconditioned at 40 °C	2.10	±0.33
TGAP/MMT/DDS/BF_3 (0.5 wt %)	2.34	±0.24

The reference material is TGAP cured with DDS without any clay reinforcement; it is evident that the addition of clay increases the impact strength for all the preparation methods used, but that the increase is greater for some than for others. For the standard preparation, isothermal cure at 180 °C increases the impact strength slightly more than does isothermal cure at 150 °C, as anticipated from both the DSC and TEM results, the former showing that more intra-gallery reaction occurs (ref. Fig. 3) while the latter shows that the *d*-spacing is greater (ref. Fig. 4) the higher is the isothermal cure temperature. An even greater increase in the impact energy, 50 % relative to the reference, is obtained when the TGAP/MMT mixture is preconditioned, in this case for 56 days at 40 °C, before curing with the addition of the DDS. This procedure ensures an extensive amount of intra-gallery reaction, which leads to an improved degree of exfoliation (ref. Fig. 2), in accordance with these impact results. The greatest increase in impact energy, by nearly 70 % relative to the reference, is afforded by the procedure involving the incorporation of BF_3·MEA, in this case in a proportion of 0.5 wt %, into the clay galleries. This procedure promotes the intra-gallery reaction, which was shown to lead to fewer and smaller aggregates in the cured nanocomposite (ref. Fig. 5), in accordance with these impact results.

The fracture surfaces after impact, for the same samples as those for which the impact energies were presented in Table 1, have been observed by SEM, and the results are shown in Fig. 7 at a magnification of ×50. The reference sample, TGAP/DDS without any clay (Fig. 7a), shows the typical rather brittle fracture surface, with only a few striations where the crack velocity has increased. The amount of striations in Fig. 7b, for the TGAP/MMT/DDS sample cured isothermally at 150 °C, is significantly greater, and the characteristic parabolic

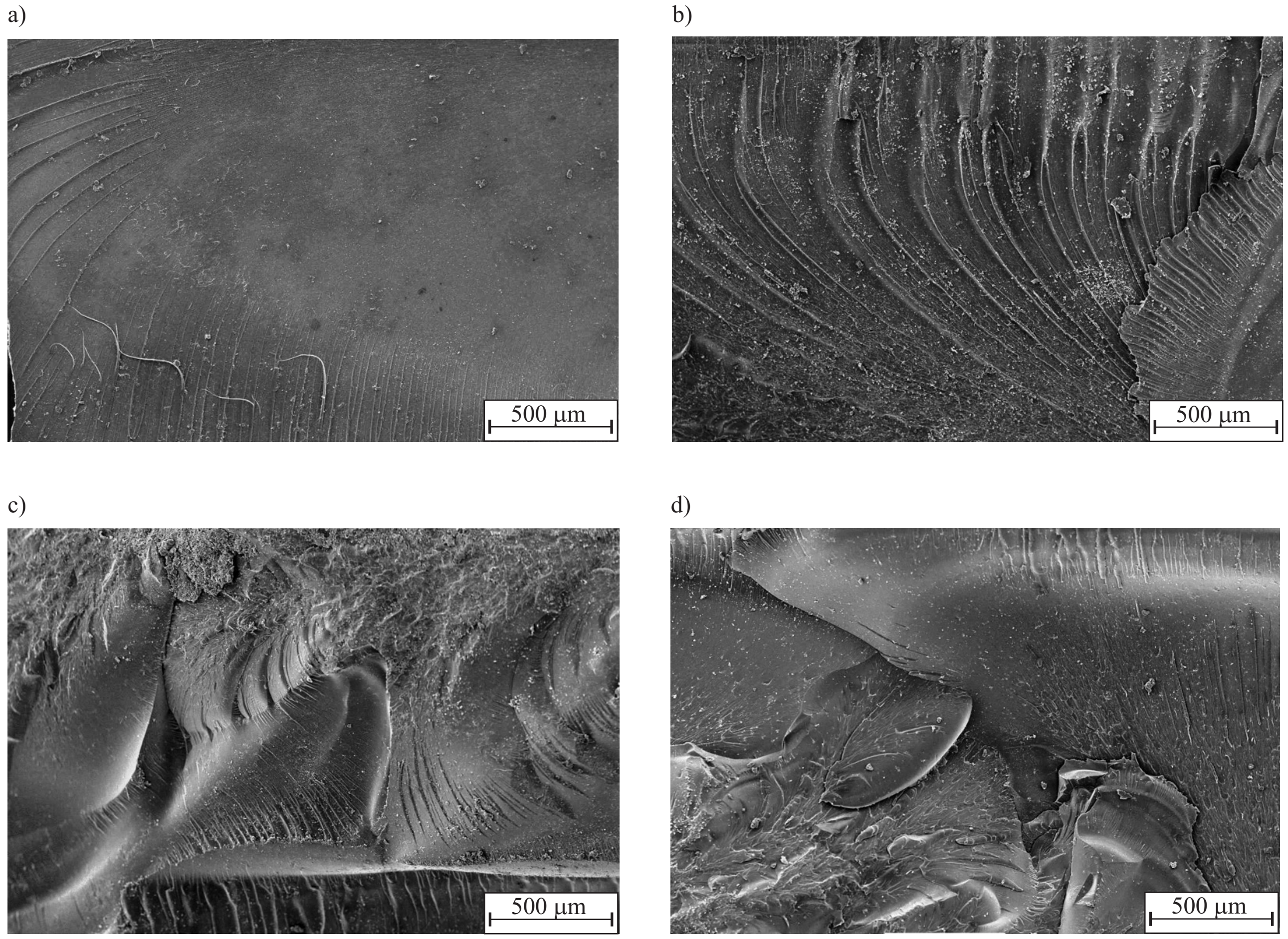

Fig. 7. SEM micrographs of the fracture surfaces of 2 wt % MMT nanocomposite samples after impact testing: a) reference, TGAP/DDS without any clay, b) TGAP/MMT/DDS cured at 150 °C, c) TGAP/MMT/DDS preconditioned 56 days at 40 °C, d) TGAP/MMT/DDS/BF_3

shape associated with the divergence of the crack from one plane to another can be seen. The overall appearance, though, is of an essentially planar fracture in both Figs 7a and 7b. On the other hand, the fracture surfaces seen in Figs 7c and 7d, for the preconditioned sample and the sample in which the BF_3·MEA initiator was used, respectively, both show a generally much rougher surface. This is consistent with the significantly higher values of impact energy listed in Table 1 for these samples.

CONCLUSIONS

The effect on the nanostructure and properties of three different preparation procedures for the fabrication of polymer layered silicate (PLS) nanocomposites based upon a trifunctional epoxy, TGAP, has been investigated: preconditioning of the resin-clay mixture before curing; isothermal cure at different temperatures; incorporating an initiator of cationic homopolymerisation into the clay galleries before intercalation of the epoxy resin and curing. All these procedures promote the occurrence of the homopolymerisation reaction within the clay galleries, which occurs before the bulk crosslinking reaction, and which hence leads to improved exfoliation. The improved nanostructure is observed by TEM and results also in an increase in the impact energy of the cured nanocomposites. The most effective procedure is to incorporate the initiator, a BF_3·MEA complex, into the clay galleries, and represents an important protocol for the achievement of highly exfoliated PLS nanocomposites.

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REFERENCES

[1] Kojima Y., Usuki A., Kawasumi M., Okada A., Kurauchi T., Kamigaito O.: *J. Polym. Sci., Part A* **1993**, *31*, 983. http://dx.doi.org/10.1002/pola.1993.080310418

[2] Alexandre M., Dubois P.: *Mater. Sci. Eng.* **2000**, *28*, 1. http://dx.doi.org/10.1016/S0927-796X(00)00012-7

[3] Kornmann X., Lindberg H., Berglund L.A.: *Polymer* **2001**, *42*, 4493. http://dx.doi.org/10.1016/S0032-3861(00)00801-6

[4] Chin I-J., Thurn-Albrecht T., Kim H-C., Russell T.P., Wang J.: *Polymer* **2001**, *42*, 5947. http://dx.doi.org/10.1016/S0032-3861(00)00898-3

[5] Montserrat S., Román F., Hutchinson J.M., Campos L.: *J. Appl. Polym. Sci*. **2008**, *108*, 923. http://dx.doi.org/10.1002/app.27297

[6] Tolle B.T., Anderson D.P.: *J. Appl. Polym. Sci*. **2004**, *91*, 89. http://dx.doi.org/10.1002/app.13150

[7] Pustkova P., Hutchinson J.M., Román F., Montserrat S.: *J. Appl. Polym. Sci*. **2009**, *114*, 1040. http://dx.doi.org/10.1002/app.30697

[8] Hutchinson J.M., Shiravand F., Calventus Y.: *J. Appl. Polym. Sci*. **2013**, *128*, 2961. http://dx.doi.org/10.1002/app.38452

[9] Matejka L., Chabanne P., Tighzert L., Pascault J.P.: *J. Polymer Sci., Part A* **1994**, *32*, 1447. http://dx.doi.org/10.1002/pola.1994.080320806

[10] Shiravand F., Hutchinson J.M., Calventus Y.: *Polym. Eng. Sci*. **2014**, *54*, 51. http://dx.doi.org/10.1002/pen.23540

[11] Becker O., Cheng Y-B., Varley R.J., Simon G.P.: *Macromolecules* **2003**, *36*, 1616. http://dx.doi.org/10.1021/ma0213448

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