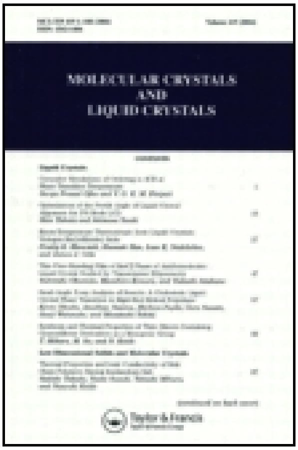

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Nanocomposites Based on Liquid Crystalline Resins

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Nanocomposites Based on Liquid Crystalline Resins

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The intercalation and exfoliation of liquid crystalline resins (LCRs) in the presence of organophilic montmorillonite were investigated. Their properties were compared with those of pristine resin, as well as with those of nanocomposites based on a commercial epoxy resin containing the same amounts of nanoclays. It was demonstrated that the dispersion of inorganic fillers has a detrimental effect on thermal and mechanical properties if a liquid crystalline (LC) matrix is used. In particular, tensile strength of LC nanocomposites is reduced with the increasing amount of organoclay, which, somehow, disturb the molecular order in the liquid crystalline resin.

Keywords: epoxy resins; liquid crystals; nanocomposites

INTRODUCTION

Nanostructured hybrid organics–inorganic composites have attracted considerable attention on the basis of both scientific research and applications [1,2]. Depending on the type of inorganic filler used,

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different types of nanocomposites can be obtained. In particular, polymer layered silicate nanocomposites belong to a class where the reinforcing phase, in the shape of platelets, has only one nanolevel dimension. From a structural point of view, two types of polymer layered silicate are possible: *intercalated nanocomposites*, consisting of a regular array of polymer into the clay galleries with fixed interlayer spacings, and *exfoliated nanocomposites* where 1 nm thick layers are individually dispersed in the polymeric matrix, forming a monolithic structure at the microscale. The most commonly used layered clay in the synthesis of nanocomposites is montmorillonite, which is obtained from bentonite. Since it is usually difficult to get an effective dispersion of inorganic clays in a polymer, compatibilising agents are required, such as alkylammonium ions. These latter can be easily exchanged with the ions situated in the galleries between the silicate layer and, due to the presence of non-polar alkyl chains, they make the diffusion of the polymer easier into the galleries.

In the early 90s, researchers from Toyota discovered the possibility of synthesizing a nanostructure from a polymer and an organophilic silicate. Their new material, based on polyamide 6 and organophilic layered silicate, showed great improvement in mechanical properties, barrier properties and heat distorsion temperature. These improvements were obtained at very low loading of layered silicate (4% wt.).

Following the pioneering work of Toyota researchers, the scientific and industrial work has been successfully extended to the other polymer systems, such as, epoxies [3–12], polyimides, polysiloxanes [13], elastomers [14], as well as other thermoplastics [1,15].

Epoxy resin is one of the most widely used polymeric materials, finding wide applications in the electronic and aerospace industry. Recent investigations of polymer nanocomposites have demonstrated substantial improvements in overall performance, including dimensional stability. Layered silicate-epoxy nanocomposites afford new opportunities to design composites with unique properties, so that great attention has been paid to these novel materials.

In previous papers, some of the authors described the superior properties obtainable by synthesizing liquid crystalline epoxy resins, consisting in tridimensional network based on rigid-rod mesogenic epoxy monomers [16–26]. In particular, a higher fracture resistance was detected compared to that of conventional resins, so that LC epoxy resins have been proposed as matrices for advanced composites. In this work, the effect of layered montmorillonite clay on properties of LC epoxy resins has been studied. The properties of LC nanocomposites were then compared to those of a commercial epoxy-based nanocomposites, obtained by adding the same content of montmorillonite and the same curing agent. This was done in order to ascertain the influence of the presence of smectite clay on a resin possessing liquid crystalline features. Few articles appeared in the scientific literature on liquid crystal/clay mineral composites [27–30]. M. Kawasumi and his co-workers prepared liquid crystal clay composites based on two-frequency addressing low-molecular liquid crystal and organized clay minerals to be used as electro-optical devices [27,28]. JC. P. Gabriel and his colleagues [29] described a lyotropic liquid-crystalline lamellar phase comprising an aqueous dispersion of planar solid-like sheets in which all the atoms involved in a layer were covalently bonded. These systems could be used to measure residual dipolar couplings for the structure determination of biomolecules by liquid-state NMR. Jin-Hae Chang and his researchers [30] synthesized nanocomposites based on a thermotropic LC polyester. Liquid crystallinity, morphology and thermo-mechanical behaviour were examined with increasing organoclay content from 0 to 6%wt. They found a significant improvement in properties with the introduction of increasing loading of clays. Up to now, no paper has been yet published on the preparation and characterization of nanocomposites based on LC epoxy resins.

EXPERIMENTAL

Materials

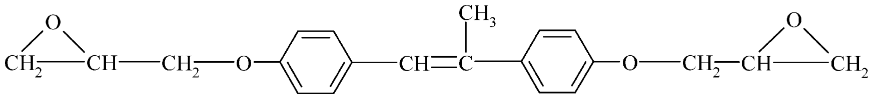
Octadecylammonium-functionalized montmorillonite C18-MMT (Nanomer I.30E) was provided by Nanocor and used as received. Montmorillonite is a layered clay mineral composed of aluminosilicate whose chemical composition is $[(Mg_{0.33}Al_{1.67})Si_4O_{10}(OH)_2]Na_{0.33}$. The dimension of the unit layer is ~ 10 Å in thickness, about 1000 Å in width and in length.

It has exchangeable cations between the layer, which are sodium cations. Therefore, the surface of the montmorillonite can be modified by exchanging sodium cations for organic onium ions such as octadecylammonium cations.

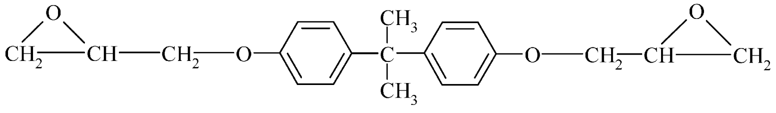
The LC epoxy monomer used for the formation of the pristine epoxy resin and the epoxy-clay nanocomposite was a diglycidyl ether of α-methylstilbene (DOMS).

The commercial epoxy resin was a diglycidyl ether of bisphenol A (DER332), purchased from Dow Chemicals, with an epoxy equivalent weight (EEW) of 171–175.

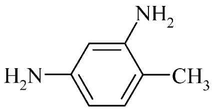
The curing agent was an aromatic diamine, the 2,4-diaminotoluene (DAT) supplied by Aldrich.



diglycidyl ether of α-methylstilbene (DOMS)



diglycidyl ether of bisphenol A (DER332)



2,4-diaminotoluene (DAT)

FIGURE 1 Chemical structures of epoxy monomers and curing agent.

The chemical structures of epoxy monomers and curing agent used are given in Figure 1.

Preparation of Pristine Resins

The LC epoxy monomer, the diglycidyloxy-α-methylstilbene (DOMS), was synthesized, according to the procedure reported in literature [17]. DOMS is a monotropic liquid crystal: it melts at T = 130°C to an isotropic liquid, and exhibits nematic phase formation at cooling, in a temperature range between 95 and 60°C.

DOMS was cured in the presence of the stoichiometric amount of DAT, in order to form the DOMS-DAT cross-linked network. The curing schedule was:

120 min at T = 130°C for cure;
30 min at T = 180°C for post-cure.

These conditions were chosen by taking into account the best compromise between the melting temperature of DOMS and the optimal conditions to make the reacting DOMS-DAT system form liquid crystalline domains upon cure [31].

The same procedure was used for the preparation of DER332-DAT pristine resin.

We will refer to the two pristine resins as DOMS-DAT and DER-DAT, respectively, later on.

A differential scanning calorimetry analysis of the samples confirmed that they were completely cured.

Preparation of Epoxy-clay Nanocomposites

For the preparation of nanocomposites the *in-situ* polymerisation approach has been carried out. According to this method the organoclay is swollen in the molten monomer and then the curing agent is added for curing reaction.

In this procedure the epoxy monomer and organoclay were ground together in a mortar. The mixed powder was then heated at $T = 130°C$, under stirring, for 15 min. The curing agent DAT was added to the molten mixture and let to mix homogeneously under stirring for few seconds. The mixture was then poured between two glass plates (previously treated with a surfactant (Surfasil®, Pierce)) and let to react at the same conditions used for pristine resins ($T_{cure} = 130°C$, $t_{cure} = 120\,min$; $T_{post-cure} = 180°C$; $t_{post-cure} = 30\,min$). Two different weight percents of organophilic nanoclays were chosen for nanocomposites, 2% and 5% wt., respectively, so that four nanocomposite samples were obtained for this study:

DOMS – DAT + 2% wt. nanoclay (DOMS-DAT2nc),
DOMS – DAT + 5% wt. nanoclay (DOMS-DAT5nc),
DER332 – DAT + 2% wt. nanoclay (DER-DAT2nc),
DER332 – DAT + 5% wt. nanoclay (DER-DAT5nc).

Characterization

Calorimetric analyses were carried out using a TA Instruments DSC model 2920, and N_2 was used as the purge gas. In the dynamic experiments, a heating rate of 10°C/min was used.

Optical anisotropy of the monomer and the cured resin was observed using a Reichter-Jung optical microscope (model Polyvar), under crossed polarized light. Crossed polarizers were used for the identification of liquid crystalline phases across the samples. The temperature was controlled using a Linkam model TH600 hot stage.

WAXS studies were performed by means of a PW 3020/00 Philips diffractometer ($Cu - K_\alpha$ Ni-filtered radiation) equipped with holder for sample spinning; the high voltage was 40 KV and the tube current was 30 mA. A standard sample was used to determine the instrumental broadening. Dynamic mechanical analyses were performed with a TA Instruments DMA (model 2980), using standard clamps in a fixed mode at 1 Hz. The heating rate was 5°C/min. The glass-to-rubbery transition temperatures of cured samples were recorded as the peak of the $\tan\delta$.

The morphology of fractured surfaces after mechanical tests was observed using a scanning electron microscope (SEM) Hitachi model S-2300. Prior to the examination, the surface was coated with a thin gold layer in order to improve the conductivity and prevent charging.

An electro-mechanical dynamometer INSTRON 4204 was used for mechanical testing on both neat cured samples and joints. The tensile strength of samples was tested according to the ASTM D1708-02a (Standard Test Method for Tensile Properties of Plastics By Use of Microtensile Specimens)

RESULTS AND DISCUSSION

Synthesis and Characterization of Pristine LC Resin

DOMS is a monotropic liquid crystal: when the DOMS monomers slowly cool from a melting temperature of 130°C to temperatures between 95 and 60°C, nematic LC domains form. At temperatures higher than 95°C these nematic LC domains are not present, and only isotropic state is observed. Nevertheless, when the monomer is cured in the presence of aromatic amines, as soon as its molecular weight begins to build up upon curing, even at temperatures higher than 95°C, the LC domains evolve and maintain the LC characteristics. DOMS was cured in such a way that enough time was given for the LC monomer to form LC domains before extensive cross-linking took place. In curing the DOMS-DAT systems the conditions adopted were 120 min at $T = 130°C$ for cure, and 30 min at $T = 180°C$ for post-cure. These conditions were expected to produce LC morphologies in the matrix, since at the curing temperature a sufficient time was given for the reacting pre-polymer to form LC domains. If higher curing temperature was chosen, DOMS-DAT cross-linked quickly and minimum time was allowed for the LC monomer to align and form LC domains. In the cured system the formation of a smectic structure has been evidenced by X-ray diffraction analysis [31].

Figure 2 reports the X-ray diffraction pattern of cured DOMS-DAT, in the 2θ range between 0 and 10°, showing a peak at $2\theta = 4.4°$

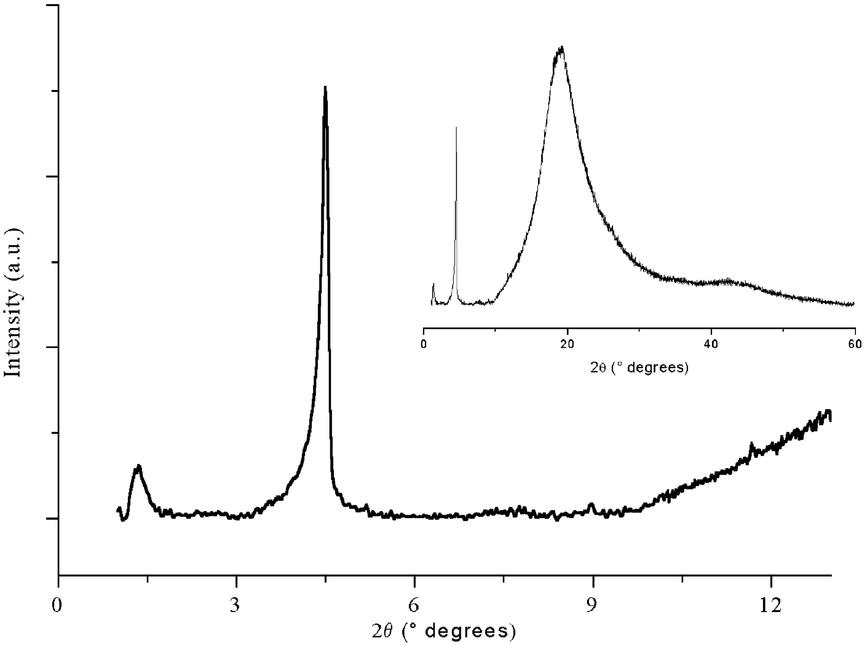


FIGURE 2 X-ray pattern of cured pristine resin DOMS-DAT in the 2θ range between 0 and 12°, and in the 2θ complete range, up to 60° (small frame).

(d-spacing = 20.0 Å) characteristic of the distance between the smectic planes in the resin. The small peak at $2\theta = 1.4°$ (d-spacing = 64.5 Å) is likely to correspond to a long distance order between smectic planes. Furthermore, a diffuse scattering peak at $2\theta = 18.5°$ (d-spacing = 4.8 Å) is also evident in the pattern, which is typical of aligned LC polymers.

By inducing a liquid crystalline phase during crosslinking of DOMS-DAT system, a smectic thermoset forms, which will maintain its liquid crystalline structure over a wide range of temperature, up to thermal decomposition. Due to the presence of well oriented LC domains within the sample, it is characterized by an improved fracture resistance with respect to the commercial epoxy resins [32].

Characterization of Organophilic Montmorillonite (C18-MMT)

Figure 3 shows the X-ray diffraction pattern of C18-MMT in the 2θ region of 0–30°. There is a peak at $2\theta = 3.9°$, which is assigned to the (001) lattice spacing (d – spacing = 22.8 Å) of organophilic montamorillonite, in which long chain alkylammonium ions have been

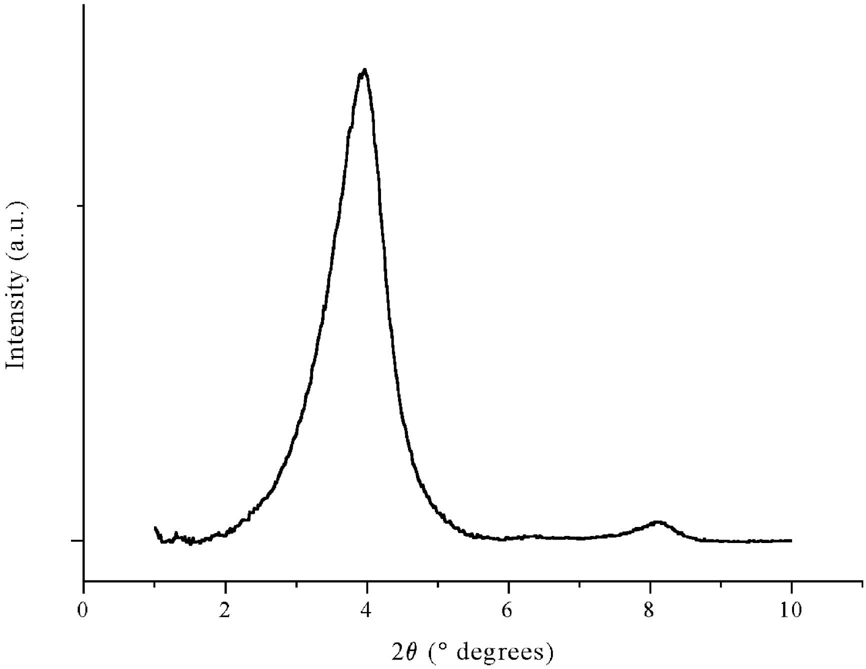


FIGURE 3 X-ray pattern of alkylammonium-functionalized montmorillonite.

intercalated. Moreover, at $2\theta = 8.1^\circ$ (d-spacing = 10.9 Å) a second, flat peak appears corresponding to the interlayer distance of the unmodified inorganic montmorillonite, which are still present in the clay used.

On the basis of the XRD results obtained for the earlier studied systems of montmorillonite when simple alkylammonium ions with a C12–C18 carbon chain are ion-exchanged for the inorganic cations in smectite clay, they might form monolayer (13.7 Å), bilayers (17.7 Å), pseudotrimolecular layers (21.7 Å) and paraffinic structure (>22 Å) [33–35]. Therefore, the octadecylammonium chain exchanged in the montmorillonite used for this study are able to give rise to a typical paraffin structure.

Preparation and Characterization of Nanocomposites

Prior to curing with 2,4-diaminotoluene (DAT), the epoxy monomers were melted and mixed with organoclay at T = 130°C for 15 min, in order to make the epoxy resins disperse into galleries of clay. The systems were then cured in the presence of DAT, according to the same procedure adopted for pristine resins: $T_{cure} = 130°C$, $t_{cure} = 120\,min$; $T_{post\text{-}cure} = 180°C$; $t_{post\text{-}cure} = 30\,min$.

The procedure followed is known as *in-situ* polymerisation [1] This method is composed of two steps. The first step consists in the intercalation, or diffusion, of monomer molecules into clay galleries, induced by the high surface energy of the clay, which attract the polar resin molecule. This leads to an increase of clay *d*-spacing [36]. In the second step, curing reaction of the monomer occurs. This causes adjacent clay layers to move from each other to reach an equilibrium separation distance with no apparent interlayer interactions. At the same time, cure outside the clay galleries occurs, until gel point is reached. Therefore, the appropriate balance between inter- and extra-gallery reaction, together with the resin and amine diffusion, are the key factor to control the organoclay delamination [37,38].

Figure 4 shows the X-ray diffraction patterns of DOMS-DAT resin loaded with the 2 and 5% wt. of nanoclay, in the 2θ range between 0 and 10°. In the case of DOMS-DAT2nc (Fig. 4a), there is no diffraction peak at $2\theta = 3.9°$, indicating that the clay was exfoliated. On the other hand, the X-ray diffraction pattern of DOMS-DAT5nc (Fig. 4b) is typical of an intercalated nanocomposites, indicating that the loading of nanoclay is at limit.

In particular, the pattern in Figure 4b shows a peak at $2\theta = 2.5°$ (d-spacing = 35.1 Å), corresponding to the interplanar spacing between silicate layers after intercalation of resin. This latter could probably be attributed to a new ordered smectic phase of the cured resin, arranged between the silicate layers. More precisely, at a spacing between two silicate layers of 35.1 Å corresponds a two-fold distance between two smectic layers in the resin.

X-ray diffraction patterns of DER-DAT2nc and DER-DAT5nc do not show any evidence of peaks at 2θ smaller than 3.9°, indicating that the clay was exfoliated without regular repeat distance between the layers. It is considered that a large amount of the Biphenol-A based monomer can enter into the gallery and the intra-gallery polymerization can occur at comparable rate to extra-gallery polymerization. Consequently, the galleries continue to expand when the degree of polymerisation increases and an exfoliated nanocomposite is formed.

Different degree of intercalation and exfoliation have been thus obtained by using the LC and the commercial epoxy monomer. Similar results have recently been reported for various epoxy-based systems [39]. The mechanism of organoclay exfoliation in epoxy-layered silicate nanocomposites has been the focus of various studies and it was

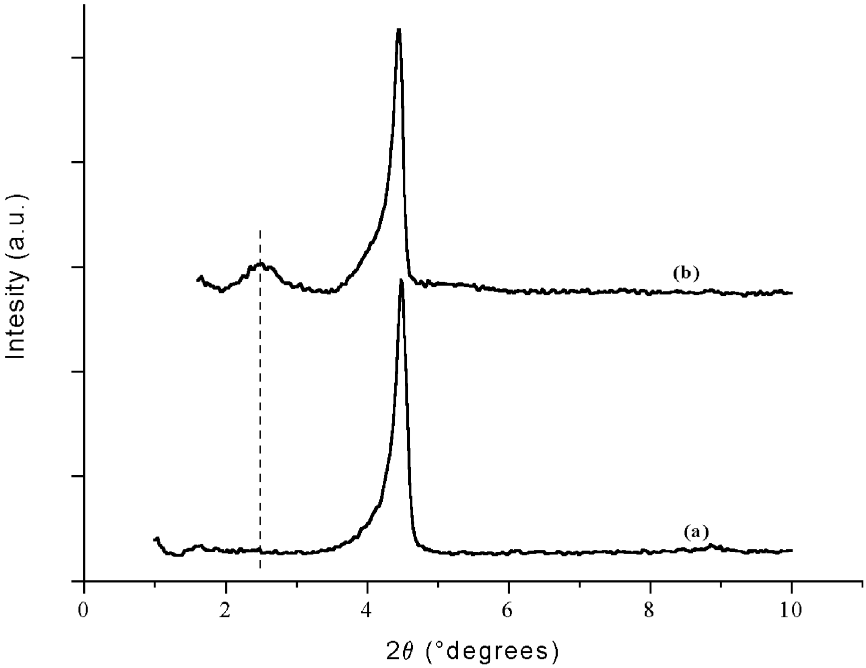


FIGURE 4 X-ray pattern of (a) DOMS-DAT2nc and (b) DOMS-DAT5nc nanocomposites.

pointed out that control of intra-gallery and extra-gallery reaction is the key to overcome the attractive forces between the silicate layers and achieving exfoliation.

The structure and chemistry of the epoxy resins are clearly of importance in determining the equilibrium between inter- and extra-gallery reactions and hence the final morphology and service-life properties of resulting nanocomposites.

The improved organoclay delamination with the DER-DAT based nanocomposites may be related to a number of aspects, one being that the lower viscosity at the curing temperature, or enhanced molecular mobility, improves mass transfer into the clay galleries, and may shift the equilibrium between inter- and extra-gallery reaction toward a higher reaction rate between the clay galleries in the DER-DAT systems. On the other hand, in the case of DOMS-DAT systems, it can be hypothesized that insufficient diffusion of the material in the intra-gallery regions was responsible for the rapid rate of extra-gallery cross-linking in comparison to the slower intra-gallery diffusion and, thus, for the limited exfoliation. Similar results were obtained by In-Joo Chin and co-workers [40] who demonstrated that an excess amount of curing agent resulted dominantly in the extra-gallery crosslinking of the resin.

To further understand the influence of the organo-functionalized silicate platelets on polymerization reaction in the resins differential scanning calorimeter on pure epoxy monomers and their mixture with 5% wt. of clays has been carried out. The thermograms indicate that spontaneous clay epoxide polymerization process takes places at the onset temperature of 203°C in the DER/MMT-C18 (5% wt.) mixture, whereas, in absence of clay, self-polymerization of DER occurs at such a high temperature that decomposition takes place before polymerisation reaction occurs.

DSC thermograms obtained for DOMS/MMT-C18 (5% wt.) and pure DOMS also indicated that the epoxide polymerization occurs at lower temperatures ($T_{onset} = 201°C$) in the presence of clay. Moreover, DOMS resin is able to give homopolymerization at lower temperatures with respect to the DER system and even in absence of catalytic clays ($T_{onset} = 370°C$ for homopolymerization of DOMS). As expected, the polymerization-delamination temperatures are very dependent on alkylammonium catalytic effect [2,41].

Thermogravimetric analyses in N_2 atmosphere provided additional information on the properties of epoxy-clay nanocomposites. The onset temperature for thermal decomposition was taken as the temperature at which the materials experienced a 5% loss in weight. Data obtained are represented in Figure 5.

From the TGA curves it was found that, in the case of DER-DAT systems, thermal stability of nanocomposites was not greatly compromised by the presence of organophilic montmorillonite, whereas, big differences could be observed between DOMS-DAT pristine resin and its DOMS-DAT2nc and DOMS-DAT5nc nanocomposites.

As mentioned by Gu and Liang [33], there are two main factors which have opposite influence on the thermal stability of epoxy-clay nanocomposites. Firstly, it has been proved that the presence of organoclay decreases the epoxy reactivity and, thus, lower crosslinking density of the cured resins is observed. A longer polymer chains among the crosslinking points is less thermally stable than a shorter chain. The second factor, which has an opposite influence of the first one, is due to the good barrier to gases of the silicate layers, so that they can insulate the underlying material and slow the mass loss rate of decomposition products. For this reason, exfoliated composites have better barrier properties than intercalated ones. In the case of DER-DAT composites, owing to the homogenous exfoliation within the

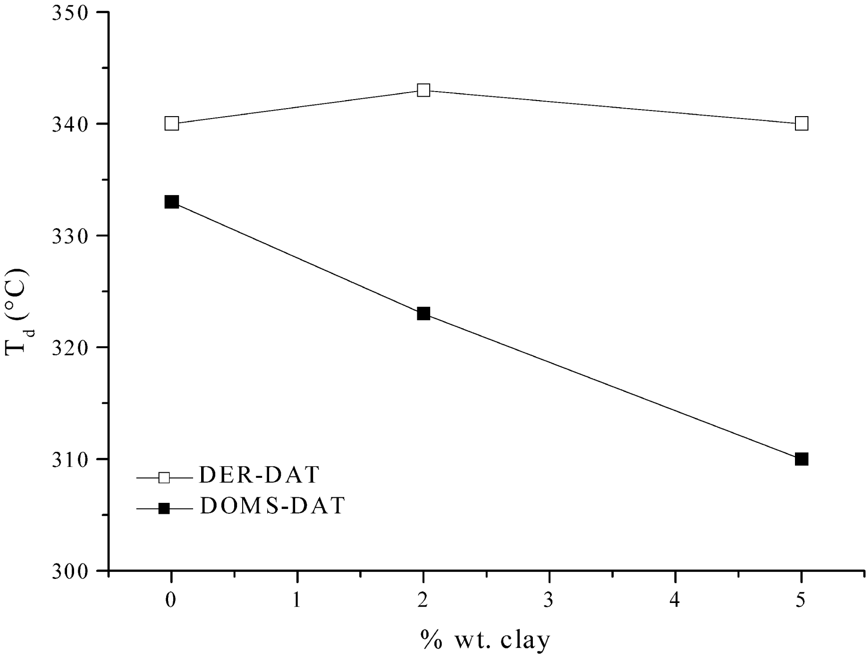


FIGURE 5 Decomposition temperatures (T_d) versus clay percent in DOMS-DAT and DER-DAT based systems.

samples, the second factor prevails, while in the DOMS-DAT based systems the lower crosslink density is dominant.

These hypotheses are confirmed by glass transition temperature (T_g) evaluation.

The T_g's of nanocomposites and neat resins were investigated using DMA. The T_g was taken as the temperature location of the tan δ peak at 1 Hz in DMA measurements. Curves are shown in Figures 6 and 7 for DER-DAT and DOMS-DAT based system, respectively. T_g values are reported in Table 1, together with the tensile strength test results.

The first important evidence in comparison of the tan δ curves of the two DER-DAT and DOMS-DAT based cured systems is that the first is characterized by a single tan δ peak, whereas the second exhibits also a marked shoulder at lower temperatures. This may be attributed to the particular biphasic structure which characterizes the liquid crystalline resins, which, in turn, is strongly affected by the mechanism of curing reaction. In previous papers [31] it has been demonstrated that during the curing reaction of mesogenic epoxy monomers, a grow-

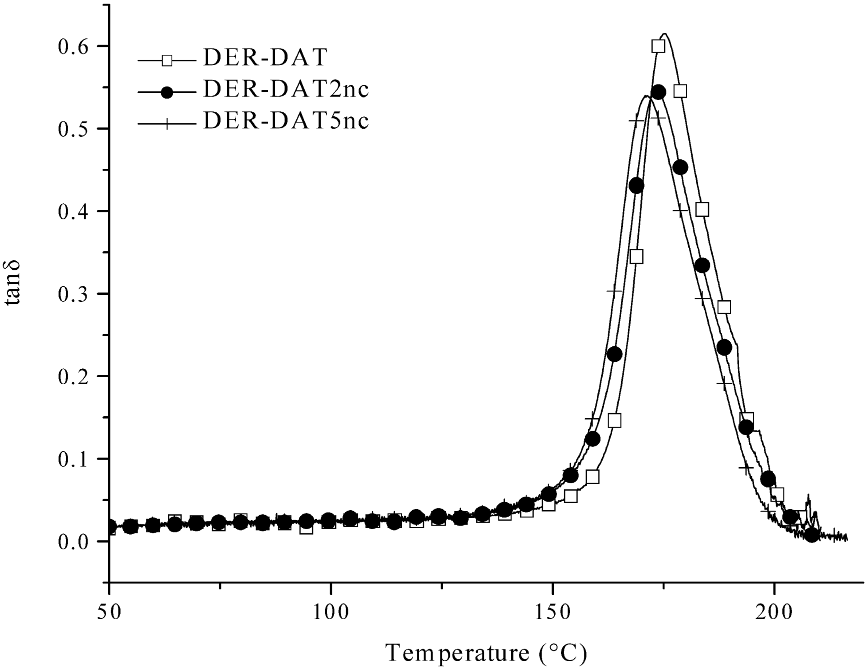


FIGURE 6 Tanδ curves for (a) DER-DAT, (b) DER-DAT2nc, (c) DER-DAT5nc.

ing "pre-polymer" forms. As soon as the pre-polymer reaches the critical dimensions, it is able to generate a liquid crystalline phase, which separates from the reaction mixture, initially characterized by a single isotropic phase. As a result, the cured LC resin is characterized by a "multidomain" structure, in which anisotropic regions are embedded in an isotropic matrix. In the absence of magnetic, electrical or mechanical fields, able to orient the sample before cure, the different domains are randomly oriented [22]. The resulting system is heterogeneous in its structure, however two phases tend to appear. The biphasic system generated is thus characterized by a double T_g: one, at lower values, can be ascribed to the resin portions cured in the LC state and the other one to the part of the resin cured in the isotropic phase. This particular configuration is responsible also for a high fracture resistance and a slow, stable, crack propagation. It is thought that the high toughness of the LC phase results from the isolated fracture of individual domains, thus producing microscopic defects and voids near and around the crack tip, which are responsible for an extensive plastic deformation [18].

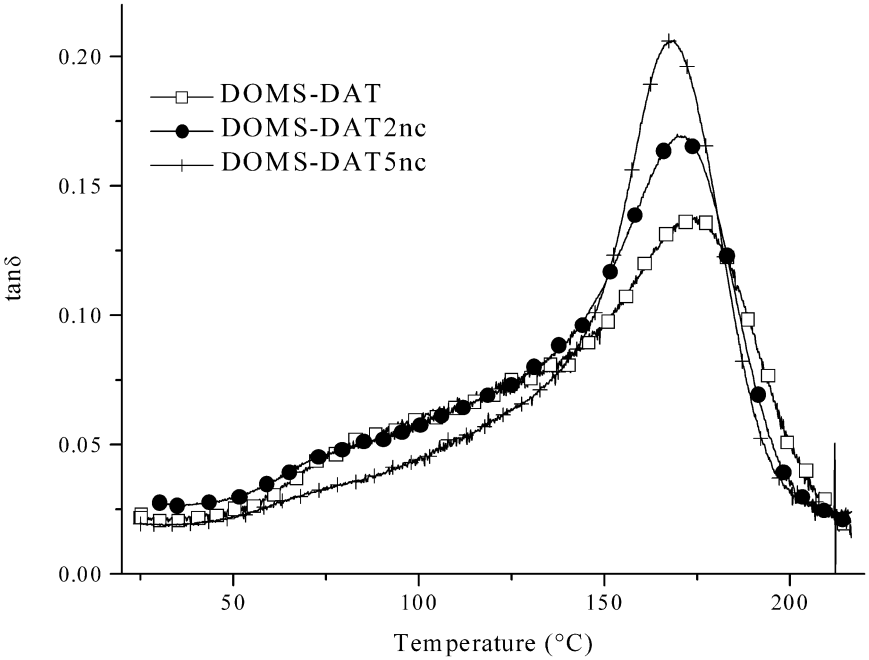


FIGURE 7 Tanδ curves for (a) DOMS-DAT, (b) DOMS-DAT2nc, (c) DOMS-DAT5nc.

Relatively small changes in glass transition temperatures were observed for the nanocomposites in comparison to the pristine epoxy polymer. Only in the case of DOMS-DAT5nc the decreasing in T_g is significant in comparison to the pristine DOMS-DAT resin (see Table 1).

T_g is likely affected not just by the degree of cure, but also by the presence of clay, with the mechanism not fully understood. Becker and co-workers [38] observed a reduced T_g with clay loading and explained it as due to a number of factors, such as changes in reaction chemistry (epoxy homopolymerization and reduced cross-link density) thermal degradation of surface modifier, or a plasticizing effect of unreacted resin, or hardener, or quaternary ammonium chloride. Jonghyun Park et al. [42] found that quaternary ammonium ions, apart from catalysing epoxy curing reactions, are capable of plasticizing cross-linked epoxy chains, the effect of which was observed in terms of reduction in glass transition temperatures. Wei-Bing Xu and his co-workers [44] explained the reduced T_g with an increase of the free volume. When the organoclay was added into the epoxy, the

TABLE 1 Glass Transition Temperatures (T_g) and Max Tensile Strength (σ_{max}) Values of DER-DAT and DOMS-DAT Pristine Resins and their Nanocomposites

System	T_g (°C)	σ_{max} (MPa)
DER-DAT	175	41 ± 2
DER-DAT2nc	173	42 ± 1
DER-DAT5nc	171	54 ± 2
DOMS-DAT	176	66 ± 4
DOMS-DAT2nc	169	49 ± 3
DOMS-DAT5nc	169	39 ± 1

free volume of highly cured epoxy was increased; the segmental mobility within the polymer increased, leading to lower T_gs.

The reaction of epoxy resin in the presence of montmorillonite containing $[H_3N(CH_2)_{17}CH_3]^+$ group results in the polymerization of the epoxide and the delamination of the clay structure. The acid catalytic role of the onium ions is verified by the fact that this kind of polymerisation-delamination reaction occurs even in the presence of H^+, NH_4^+ exchanged forms of the clay according to the reaction [41]. Once again, the higher extent of homopolymerization in the DOMS-DAT based systems is responsible for the lower values of T_gs.

Tensile strength tests results are reported in Table 1 and reported in Figure 8. From these data it can be inferred that, in the case of DOMS-DAT systems, with increasing the nanoclay loadings a decreasing in tensile strength occurs, leading to a 40% reduction in the strength at rupture in the case of DOMS-DAT5nc.

This result has been obtained in several other cases reported in the literature [45,46]. The losses of tensile strength, encountered when increasing the content of organophilic layered silicates, may indicate that network density is not homogeneous. As proposed by other groups [1], it is very likely that the cure rate of bulk epoxy resin and epoxy resins intercalated in between silicate layers are different, thus causing internal stresses which account for reduced resistance against large mechanical strains. Moreover, a perturbation of the liquid rystalline order is likely to be induced by the presence of lamellar clay.

In the case of nanocomposites containing DER-DAT matrices the increase in the clay content induces a slight improvement of the tensile strength properties. This is also a result reported in some cases in the literature [40]. However, the significant evidence is that DOMS-DAT pristine resin is characterized by a highest maximum strength in comparison with the nanocomposites obtained from the

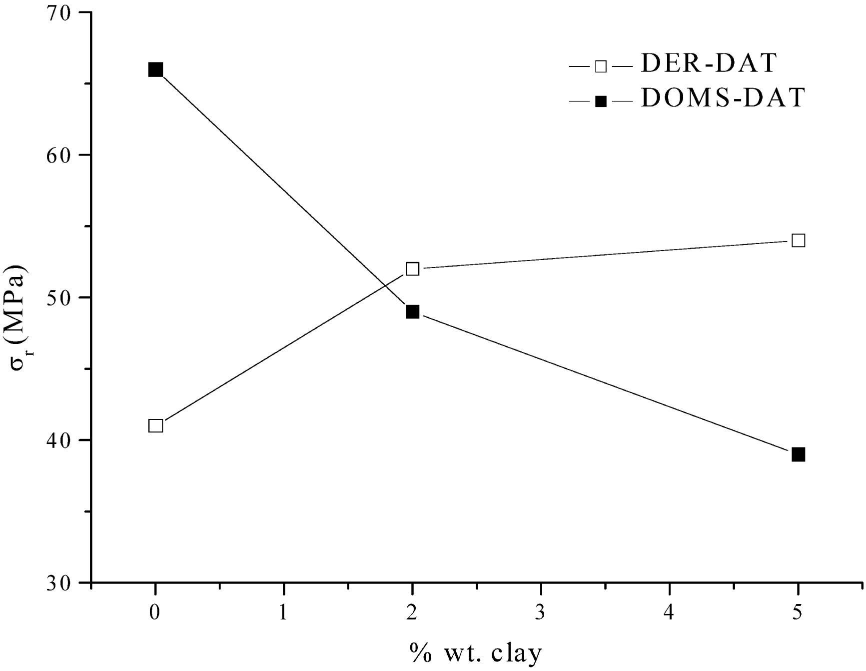


FIGURE 8 Tensile strength results for DER-DAT and DOMS-DAT based nanocomposites.

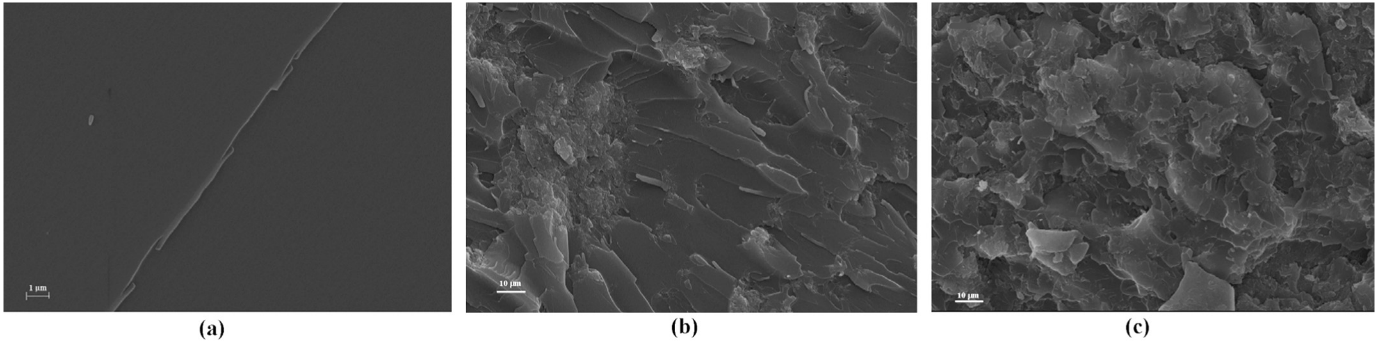
commercial resin. This is a confirmation of the superior mechanical properties of liquid crystalline resins [22].

Improvement of tensile strength requires optimisation of cure condition, especially with respect to advancement and which can take place at silicate surface.

Figures 9 and 10 show the SEM micrographs of fractured surfaces of DER-DAT and DOMS-DAT and their nanocomposites, revealing a mirror-like fracture only in the case of DER-DAT, in all the other cases a very inhomogeneous surface is well detected.

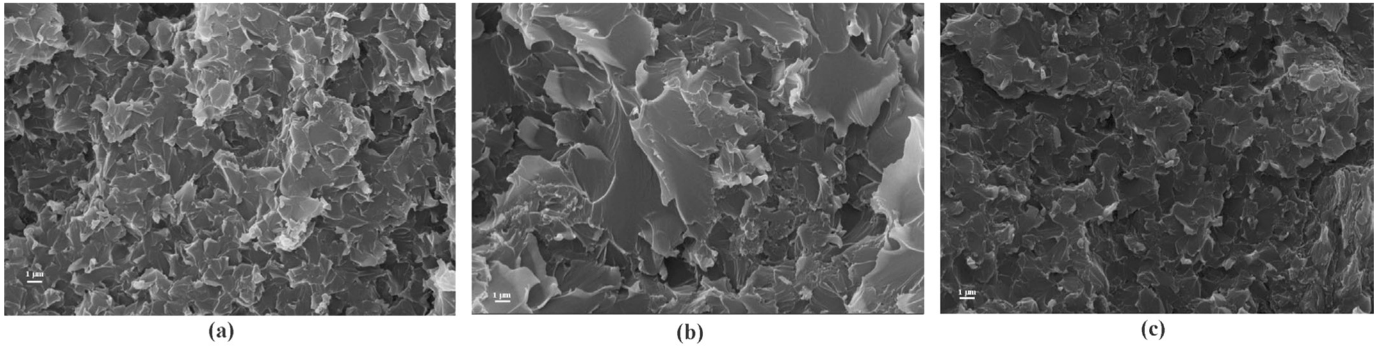
CONCLUSION

The intercalation and exfoliation behaviours of liquid crystalline resins (LCRs) in the presence of organophilic montmorillonite were investigated. Their properties were compared with those of pristine resin, as well as with those of nanocomposites based on a commercial epoxy resin, cross-linked with the same curing agent and containing



(a) (b) (c)

FIGURE 9 SEM micrographs of surface fracture of pristine (a) DER-DAT, (b) DER-DAT2nc and (c) DER-DAT5nc.



(a) (b) (c)

FIGURE 10 SEM micrographs of surface fracture of pristine (a) DOMS-DAT, (b) DOMS-DAT2nc and (c) DOMS-DAT5nc.

the same amounts of nanoclays. From the experimental data it was inferred that:

- T_gs decrease with increasing organoclay loading. The reduced temperature indicates a possible lower cross-link density, due to the homopolymerization reaction catalysed by the octadecylammonium ions exchanged in the clay galleries, or an increase in the free volume around the clay particles, or a plasticising effect of alkylammonium chains, unreacted epoxy monomers and curing agent molecules.
- Decomposition temperatures T_d decrease significantly in DOMS-DAT systems, whereas in the DER-DAT based nanocomposites the values keep almost constant. The detrimental effect of organoclay on thermal stability in the DOMS-DAT nanocomposites is likely to be due to the presence of low-crosslink density parts in the samples, which, in turn are related to the large homopolymerization extent which occurs in the presence of alkylammonium ions exchanged in the clay. In the case of DER-DAT based nanocomposites, the effect of self-polymerization is compensated by the barrier properties of clay platelets, which are more effectively dispersed in the DER-DAT matrix.
- Tensile strength is reduced of 40% with increasing the loading of clay in the DOMS-DAT nanocomposites, in comparison with the pristine resin. This has been ascribed to the "perturbation" to which the LC phases is subjected with the introduction of lamellar silicates. In the case of DER-DAT nanocomposites tensile strength properties were slightly improved, indicating that the homogeneous dispersion of clay within the polymeric matrix is effective. However, maximum strength of DOMS-DAT pristine resin was still higher than the DER-DATnc5 loaded with the 5%wt. of nanoclay. This confirmed the better properties that LCRs exhibit in comparison with the commercial resins.

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