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Synthesis of epoxy–clay nanocomposites. Influence of the nature of the curing agent on structure

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Abstract

Epoxy–clay nanocomposites were synthesised by swelling an organophilic montmorillonite in a diglycidyl ether of bisphenol A resin with subsequent polymerisation. Three different curing agents were used: an aliphatic diamine and two cycloaliphatic diamines. The cure kinetics of these systems was evaluated by differential scanning calorimetry and the structure of the nanocomposites was characterised by X-ray diffraction and transmission electron microscopy. Successful nanocomposite synthesis was dependent not only on the cure kinetics of the epoxy system but also on the rate of diffusion of the curing agent into the galleries because it affects the intragallery cure kinetics. The nature of the curing agent influences these two phenomena substantially and therefore the resulting structure of the nanocomposite. The curing temperature controls the balance between the extragallery reaction rate of the epoxy system and the diffusion rate of the curing agent into the galleries. Thus, the choice of curing agent and curing conditions controls the extent of exfoliation of the clay in the material. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Clays have long been used as fillers in polymer systems because of low cost and the improved mechanical properties of the resulting polymer composite. All other parameters being equal, the efficiency of a filler to improve the physico-mechanical properties of a polymer system is sensitive to its degree of dispersion in the polymer matrix [1]. Until recently, clay particles could only be dispersed on the microscale. In the early 1990s, Toyota researchers [2] discovered that treatment of a montmorillonite clay with amino acids allowed dispersion of the individual 1 nm-thick silicate layers of the clay on a molecular scale in polyamide 6. Their hybrid material showed major improvements in physical and mechanical properties even at very low clay content (1.6 vol%). Since then, many researchers have performed investigations in the new field of polymer nanocomposites. This has lead to further developments in the range of materials and synthesising methods available.

There are essentially three different approaches to synthesise polymer–clay nanocomposites: melt intercalation, solution and in situ polymerisation. The *melt intercalation*

process was invented relatively recently by Vaia et al. [3]. A thermoplastic polymer is mechanically mixed with an organophilic clay at elevated temperature. The polymer chains are then intercalated between the individual silicate layers of the clay. The proposed driving force of this mechanism is the enthalpic contribution of the polymer/organoclay interactions. This method is becoming increasingly popular since the resulting thermoplastic nanocomposites may be processed by conventional methods such as extrusion and injection moulding.

In the *solution* method, the organoclay, as well as the polymer, are dissolved in a polar organic solvent [4]. The entropy gained by the desorption of solvent molecules allows the polymer chains to diffuse between the clay layers, compensating for their decrease in conformational entropy [1]. After evaporation of the solvent, an intercalated nanocomposite results. This strategy can be used to synthesise epoxy–clay nanocomposites [5] but the large amount of solvent required is a major disadvantage.

The in situ *polymerisation* approach was the first strategy used to synthesise polymer–clay nanocomposites and is a convenient method for thermoset-clay nanocomposites [6]. It is similar to the solution method except that the role of the solvent is replaced by a polar monomer solution. Once the organoclay has been swollen in the monomer, the curing

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EPON 828

n = 0 (88%); n =1 (10%); n = 2 (2%)

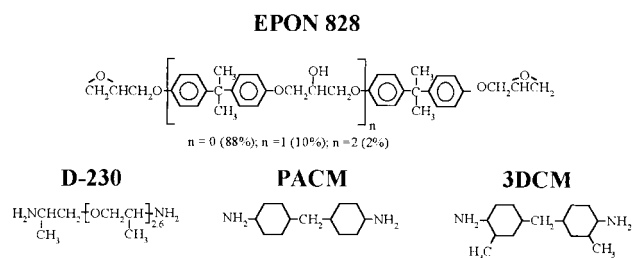**D-230**   **PACM**   **3DCM**

Fig. 1. Chemical structures of EPON 828, Jeffamine D230, Amicure PACM, and 3DCM.

agent is added and complete exfoliation occurs in favourable cases. According to our previous study [7], the polymerisation is believed to be the indirect driving force of the exfoliation. The clay, due to its high surface energy, attracts polar monomer molecules in the clay galleries until equilibrium is reached. The polymerisation reactions occurring between the layers lower the polarity of the intercalated molecules and displace the equilibrium. This allows new polar species to diffuse between the layers and progressively exfoliate the clay. Therefore, the nature of the curing agent as well as the curing conditions is expected to play a role in the exfoliation process.

Based on the work by Lan et al. [6], we conclude that a balance between the intragallery and the extragallery polymerisation rates is required in order to exfoliate the clay in epoxy systems. In the present study, we will investigate how the nature of the curing agent influences this balance.

Three different curing agents are used in combination with a diglycidyl ether of bisphenol A (DGEBA) epoxide resin. The cure kinetics of these three epoxy systems is evaluated by differential scanning calorimetry (DSC). The structure of the clay in the nanocomposites is characterised by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The reactivity and chemical structure of the curing agent have a direct effect on the extent of exfoliation of the organoclay. It is demonstrated that the choice of curing agent and curing conditions can be optimised in order to obtain a exfoliated nanocomposite with improved mechanical properties.

2. Experimental

2.1. Materials

The clay in the study was an industrially purified and organically treated montmorillonite, C18-CWC (trade name ODA-CWC) provided by Nanocor Inc. with a cation-exchange capacity of 140 meq/100 g. The epoxy resin was DGEBA, EPON 828, provided by Shell Chemicals. It was used in combination with an aliphatic diamine curing agent, Jeffamine D-230 from Huntsman Corporation and two cycloaliphatic polyamines: 3,3′-dimethylmethylenedi(cyclohexylamine) (3DCM) from BASF AB and Amicure bisparaaminocyclohexylmethane (PACM) from

Air Products. The chemical structures of the different reagents are presented in Fig. 1.

2.2. Preparation of the epoxy–clay nanocomposites

The DGEBA resin was mixed with the desired amount of organophilic clay at 75°C for 24 h. A stoichiometric amount of the curing agent was added. The mixture was outgassed in a vacuum oven for a short period of time and poured in a fluoropolymer coated steel mould. Samples synthesised with Jeffamine D-230 were cured 3 h at 75°C and post-cured 12 h at 110°C. Samples synthesised with 3DCM and PACM were cured 3 h at temperatures ranging from 60 up to 160°C and post-cured 3 h at 160°C. A DSC analysis of the samples confirmed that they were fully cured.

2.3. X-ray diffraction

Powder XRD analyses were performed using a Siemens D5000 diffractometer with Cu radiation (50 kV, 40 mA). The scanning speed and the step size were 0.08°/min and 0.02°, respectively. The nanocomposite plates produced during the moulding process had a smooth surface. Therefore, disk shaped specimens (50 mm in diameter, 2 mm thick) were cut from these plates and directly analysed by XRD.

2.4. Differential scanning calorimetry

Cure kinetics measurements were performed with a Mettler Toledo DSC 820. Dynamic scans were performed from 25 to 300°C at a heating rate of 10°C/min under argon atmosphere. Isothermal scans were followed by a dynamic scan in order to determine the residual heat of reaction. The temperature was set prior to the introduction of the sample in the chamber. The degree of cure versus time was calculated from the total heat of reaction given by the dynamic scans and partial integration of the isothermal scans versus time. The degree of cure is defined as:

$$\alpha(t) = \frac{\int_0^t H(t)\,\mathrm{d}t}{\int_0^\infty H(t)\,\mathrm{d}t} = \frac{H(t)}{H_r}$$

where $H(t)$ corresponds to the heat of reaction at the time t and H_r to the total heat of reaction.

2.5. Flexural properties

Polymer and nanocomposite samples were tested using the three-point bending experiment according to ASTM D790M-93. The sample dimensions were $80 \times 10 \times 4$ mm^3. The support span and the rate of crosshead motion were 64 mm and 1.7 mm/min, respectively. The load versus the deflection of the specimen at the midspan was recorded and flexural modulus was calculated from classical beam theory. The true clay content, which is the content of clay without alkylammonium ions, was
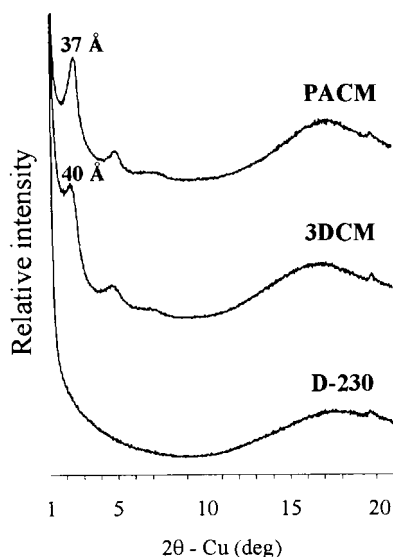
Fig. 2. XRD patterns of epoxy–clay nanocomposites cured 3 h at 75°C with three different curing agents: Jeffamine D-230, 3DCM, and PACM. The clay content is 5 wt%. The spectra are displaced vertically for clarity.

determined by weighing the samples before and after ignition at 1000°C for 2 h. The conversion from wt% to vol% was based on the densities of the polymer and the clay, respectively, 1.1 and 2.74 g/cm^3. The true clay content was used since alkylammonium ions contribute to the weight of the organophilic clay. The error made in the determination of the true clay content (wt%) by ignition was about 1%. It was related to water molecules present between the layers as well as the removal of OH groups in the layered silicate structure.

2.6. Transmission electron microscopy

The TEM specimen was cut from a nanocomposite block using an ultramicrotome, LKB 2088 Ultratome V equipped with a diamond knife. A thin specimen (100–200 nm) was cut from a mesa of about 1×1 mm^2. It was collected in a trough filled with water and placed on a 200 mesh copper grid. The nanocomposite structure was observed using a JEM-2000EX TEM at an acceleration voltage of 200 kV.

3. Results and discussion

3.1. Reaction mechanisms and effects on nanocomposite structure

Fig. 2 shows the X-ray diffractograms of epoxy–clay nanocomposites cured with three different curing agents. In each system, 5 wt% of the organophilic clay, C18-CWC, was first swollen in the DGEBA resin at 75°C for 24 h in order to allow the diffusion of the epoxy molecules between the silicate layers of the clay. During this stage, the spacing between the layers increases from 12 to approximately 34 Å as was shown in our earlier study [7]. The

curing agent was then added and the resin was cured 3 h at 75°C after initiation of the reaction with the curing agent. A nanocomposite is formed when polymerisation occurs between the clay layers. If the spacing between the layers is small so that we obtain a basal (001) reflection on the diffraction pattern, the nanocomposite is termed intercalated. If the spacing is large, X-rays cannot detect the (001) reflection, and the nanocomposite is termed exfoliated. An increase in spacing between layers is termed an increase in degree of exfoliation.

The first diffractogram was obtained with an organoclay swollen DGEBA resin cured by an aliphatic diamine, Jeffamine D-230. No (001) reflection is detectable at low angle. This is because the clay was exfoliated during the polymerisation. The distance between the clay layers is therefore too large to be detected by the X-ray analysis ($\theta < 1°$, $d > 88$ Å). Our previous study [7] confirmed exfoliation of the clay in this epoxy system by TEM. The second diffractogram was obtained using 3DCM as curing agent. Here, the clay is intercalated since (00l) reflections are observed at small angles. The average spacing between the clay layers is 40 Å. The third diffractogram was obtained using PACM as a curing agent. In this case, the (001) and (002) reflections are also clearly visible. The interlamellar spacing in this intercalated nanocomposite is about 37 Å.

These three diffractograms demonstrate that curing agents of different chemical structure lead to various degrees of exfoliation of the clay layers in the nanocomposite at a given curing temperature. The small peak appearing at large angle ($2\theta = 20°$) in all the diffraction patterns corresponds to the crystallographic planes ((110) and (020)) of the clay layers. The presence of this peak demonstrates that the XRD analysis is sensitive enough to detect the presence of the clay in the nanocomposite.

In order to clarify the effect of the curing agent on nanocomposite structure, the cure kinetics of these three epoxy systems was then investigated. Fig. 3 shows the evolution of the degree of cure versus time for the three different epoxy systems during 3 h at 75°C. The epoxy system cured with PACM shows the largest initial slope. This means that PACM is the most reactive curing agent at 75°C. The system based on the 3,3$'$-dimethyl substituted curing agent (3DCM) shows a lower reactivity. The methyl groups present in 3DCM are shielding the amine groups and the reactivity of the curing agent is lowered as compared with PACM [8] (see Fig. 1). The system cured with Jeffamine D-230 shows the lowest reactivity.

If we compare the results presented in Figs. 2 and 3, we observe a direct correlation between the reactivity of the epoxy system and the degree of exfoliation of the clay in the corresponding nanocomposite. The lower the reactivity, the higher the degree of exfoliation. Based on Fig. 3, we expect that a decrease in curing temperature of the systems based on 3DCM and PACM will lower their reactivity so that it will be closer to the reactivity of the EPON 828/Jeffamine D-230 system. If lower reactivity is the only
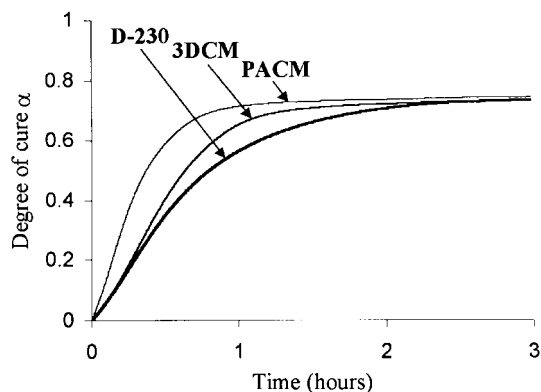
Fig. 3. Evolution of the degree of cure α as a function of time for three epoxy systems cured with Jeffamine D-230, PACM, and 3DCM for 3 h at 75°C.

factor favouring exfoliation, a lowering of the curing temperature of the systems based on 3DCM and PACM is expected to increase the degree of exfoliation of the clay.

Fig. 4 presents two series of X-ray diffraction patterns corresponding to the two epoxy/organophilic clay systems based on 3DCM and PACM. Decreasing the curing temperature from 75 to 60°C in both systems shifts both (001) reflections to higher angle, which means that the degree of exfoliation decreases in both systems. Thus, lowering the reactivity of both epoxy systems by decreasing the curing temperature does not facilitate exfoliation of the clay. Apparently, the reactivity of the epoxy system is not the only factor controlling exfoliation of the clay.

In addition to polymerisation rate of the system, the rate of intercalation of the curing agent in the clay galleries also needs to be considered. Indeed, Lan et al. [6] demonstrated that the exfoliation of the clay is not only dependent on the

reactivity of the epoxy system but also on the rate of intercalation of epoxy and curing agent. The term "rate of intercalation" corresponds to the rate of diffusion of the organic molecules between the clay layers. Indeed, if this rate is too slow, the polymerisation rate outside the layers (extragallery polymerisation) will be faster than the polymerisation rate between the layers (intragallery polymerisation) and only intercalated nanocomposites will form.

In Fig. 4, as the curing temperature is increased from 75 to 160°C, the (001) reflection is shifted to lower angle and disappears at 160°C. This increasing degree of exfoliation at higher temperatures takes place in both systems even though the system based on PACM still demonstrates a small shoulder at small angle after 3 h at 160°C. If higher curing temperature increases the reactivity of the epoxy systems, it also increases the diffusion rate of the epoxy and the curing agent between the layers, favouring the intragallery cure kinetics. This leads to the exfoliation of the clay.

We have now established that the exfoliation of the clay occurs at higher temperature in the epoxy systems cured with the cycloaliphatic diamines (3DCM, PACM) as compared with the one cured with the aliphatic diamine (Jeffamine D-230) and that it is apparently caused by a difference in diffusion rate of the curing agents. This suggests that the two cycloaliphatic diamines have a slower diffusion rate than the aliphatic diamine at a given temperature. Due to the high surface energy of the clay, diffusion of organic species between the clay layers is influenced by their polarity. However, the mobility of the organic molecules influences also the diffusion rate. The molecules of high mobility diffuse more rapidly. Therefore, we need to determine which of these factors is dominating. In order to estimate the polarity of these three curing agents, we can evaluate their solubility parameter δ, which is directly
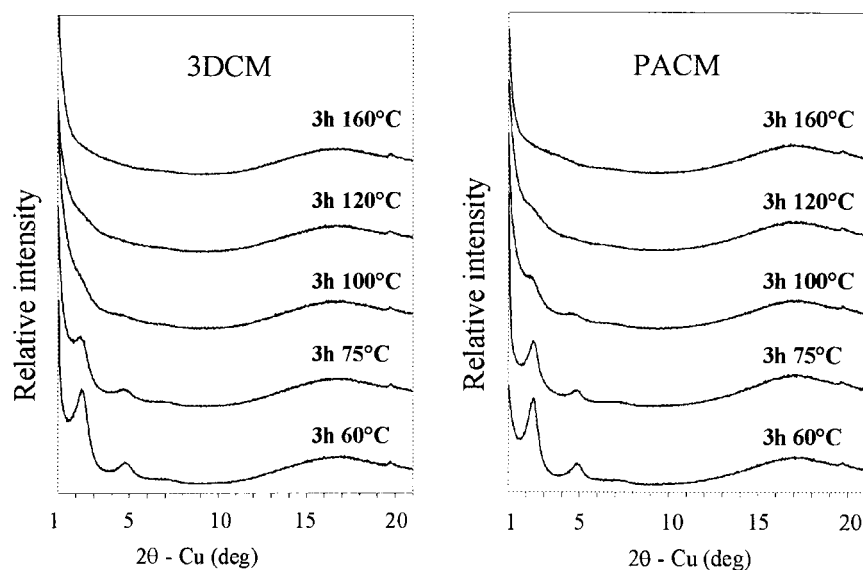

Fig. 4. XRD patterns for different curing temperatures for two epoxy systems cured with 3DCM and PACM. The clay content is 5 wt%. The spectra are displaced vertically for clarity.

Table 1
Molecular weight, density and solubility parameter of the three curing agents

	Jeffamine D-230	3DCM	PACM
Molecular weight (g/mol)	225.1	238.4	210.4
Density (g/cm^3)	0.948	0.944	0.92
Solubility parameter δ (MPa$^{1/2}$)	17.8	17.7	17.7

dependent on dispersive, permanent dipole–dipole interactions (i.e. polarity) and hydrogen bonding forces. We use the group contribution method according to Hoy's values [9]. The solubility parameter is given by:

$$\delta_i = \frac{\rho_j \sum F_i}{M_j}$$

where ρ_j is the density of the curing agent, F_i the molar attraction constant of each chemical groups i and M_j the molecular weight of the curing agent. The results are presented in Table 1.

According to Table 1, the three curing agents have similar molecular weight and almost identical solubility parameters. Even though the solubility parameter is a simplistic concept, these results indicate that the three curing agents have similar polarities. Thus, the difference in diffusion rate of the curing agents is probably not due to a difference in the polarity of the molecules. Instead, it may be related to a difference in molecular flexibility, which influences the molecular mobility and hence the diffusion rate. The aliphatic diamine has a highly flexible backbone as compared with the two cycloaliphatic diamines. This favours high molecular mobility as well as high diffusion rate between the clay layers. At low temperature, this improves the balance between intra and extragallery polymerisation so that exfoliation occurs. It would explain why 3 h at 75°C are necessary to exfoliate the clay in the epoxy system cured with the aliphatic curing agent (Jeffamine D-230), whereas 3 h at 160°C are required for similar results with an epoxy system cured with one of the two cycloaliphatic curing agents (3DCM or PACM). This illustrates that the molecular
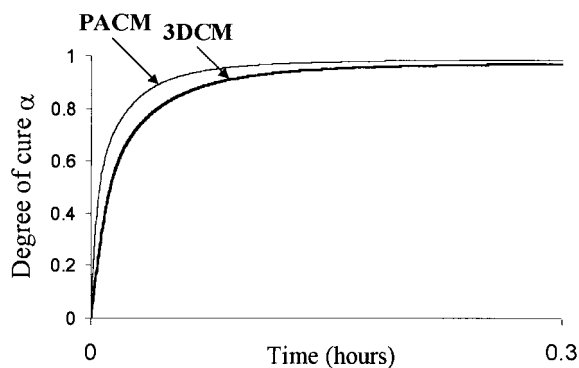

Fig. 5. Evolution of the degree of cure α of two epoxy systems cured with PACM and 3DCM at 160°C as a function of time.

mobility of the curing agent is likely to be of substantial importance in the exfoliation process.

The comparison between the two series of XRD patterns in Fig. 4 also reveals that at any curing temperature from 60 to 160°C, the degree of exfoliation of the clay is always slightly larger for the system based on 3DCM than the one based on PACM at a given curing temperature. This comes from the fact that these two curing agents have similar molecular structures and apparently matching polarities but lead to different cure kinetics. The shielding effect of the methyl groups on the amine functions in the 3DCM molecular structure decreases its reactivity. The lower reactivity of the 3DCM curing agent permits to reduce the extragallery polymerisation rate without significantly reducing the intragallery polymerisation rate favoured by the diffusion of the curing agent between the layers. This leads to a better balance between the extragallery and intragallery reaction rates so that the clay is further exfoliated.

Fig. 5 shows the evolution of the degree of cure α versus time at 160°C for these epoxy systems. The epoxy system cured with PACM shows the largest initial slope. This difference in cure kinetics might explain the presence of the slight shoulder observed for a nanocomposite cured with PACM for 3 h at 160°C (see Fig. 4). At 160°C, the extragallery polymerisation for the system based on PACM is too fast as compared with the intragallery polymerisation. Therefore, a favourable balance between the extragallery and intragallery reaction rates cannot be established and a remnant XRD-shoulder indicates the presence of non-exfoliated clay. Thus, both the diffusion rate and the reactivity of the curing agent influence exfoliation of the clay in the epoxy matrix.

3.2. Nanocomposite structure

Fig. 6 shows a transmission electron micrograph of a exfoliated nanocomposite based on the EPON 828/3DCM system obtained after curing 3 h at 160°C. Many of the features observed in this picture are similar to the ones described in our previous study of a nanocomposite cured with Jeffamine D-230 [7]. Indeed, as observed previously, the clay layers are inhomogeneously distributed and large regions of pure polymer are observed. Moreover, multiplets of non-exfoliated clay are also present.

However, one can distinguish two distinct regions in Fig. 6 that were not apparent with the nanocomposite cured with Jeffamine D-230. In region A, the interlamellar spacing is about 100 Å, whereas in region B, it is only about 60 Å. The presence of islands where the clay is only intercalated (such as the one observed in region B) might be caused by the relatively high reactivity of this epoxy system as compared with the one cured with Jeffamine D-230. Indeed, since the polymerisation occurs much more rapidly at 160°C, it is more likely that inhomogeneities will be formed during the separation of the clay layers. In the nanocomposite cured with Jeffamine D-230, the polymerisation
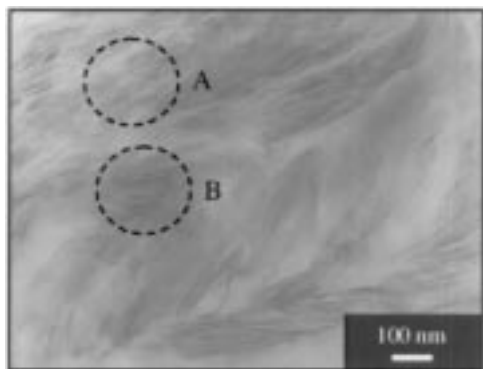
Fig. 6. Transmission electron micrograph showing the nanostructure of a exfoliated nanocomposite based on the EPON 828/3DCM epoxy system. In region A, the average interlamellar spacing is about 60 Å, whereas in region B, it is about 100 Å. The clay content is 5 wt%.

occurs more slowly and the exfoliation process is therefore more homogeneous.

3.3. Flexural properties

Fig. 7 shows the normalised moduli of exfoliated nanocomposites cured with Jeffamine D-230 and 3DCM as a function of true clay content. The flexural moduli of the epoxy systems cured with Jeffamine D-230 and 3DCM at zero clay content were, respectively, 2.95 and 2.61 GPa. For both systems, the flexural modulus increases substantially with the true clay content, despite the small amounts of clay added. Indeed, for the nanocomposite cured with Jeffamine D-230, the modulus is increased by 43% with only 4.2 vol% of clay.

A similar increase in modulus for glass bead-epoxy requires more than three times the reinforcement content [10]. The synthesis of a exfoliated nanocomposite structure allows the clay layers to more efficiently swell in the epoxy matrix leading to better dispersion and larger stiffness improvement. One likely explanation for this strong reinforcement effect is the increase in

effective volume fraction of reinforcement entities as the distance between the clay layers is increased. The relative increase in flexural modulus is larger for the nanocomposite cured with Jeffamine D-230 than for the one cured with 3DCM.

If the degree of exfoliation of the clay in the epoxy matrix is proportional to an increase of modulus of the nanocomposite, Fig. 7 suggests that a higher degree of exfoliation of the clay is achieved with an epoxy cured with Jeffamine D-230 as compared with one cured with 3DCM. Fig. 6 tends to confirm this idea, revealing the presence of islands of intercalated clay in the nanocomposite cured with 3DCM that are not present in the nanocomposite cured with Jeffamine D-230. The low reactivity and high flexibility (i.e. molecular mobility) of the Jeffamine D-230 curing agent seems to favour the intragallery reaction rate so that a good ratio between intra and extragallery polymerisation rates is obtained. This balance can be established at low temperature in the system cured with Jeffamine D-230, causing a more homogeneous exfoliation of the clay in the epoxy matrix.

4. Conclusions

The nature of the curing agent has a major effect on the synthesis of exfoliated epoxy–clay nanocomposites. The exfoliation of the organophilic clay in epoxy systems is controlled by a relative difference in reaction rates between the intragallery and the extragallery polymerisation. The curing temperature controls both the cure kinetics and the diffusion rate of the curing agent between the clay layers. By changing the cure temperature, we can therefore control the relative extent of intragallery and extragallery polymerisation. The flexibility (i.e. molecular mobility) and the reactivity of the curing agent are important parameters, which influence the balance between the extragallery and the intragallery reaction rates.

Measurements performed on two epoxy systems shows that the largest improvements in modulus with clay content are obtained for an epoxy resin cured with a an aliphatic curing agent with relatively low reactivity. In such an epoxy system, the largest extent of exfoliation was observed. The corresponding larger degree of silicate layer dispersion correlated with a higher modulus of the material.
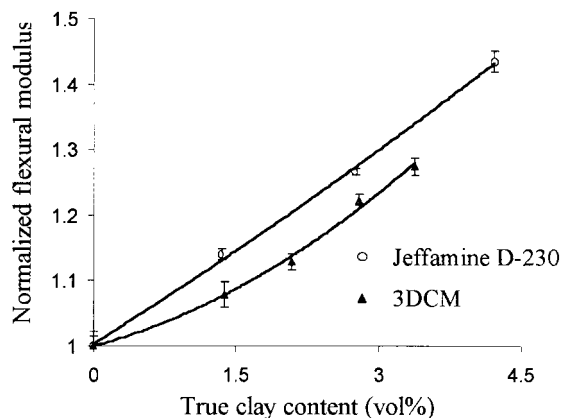

Fig. 7. Evolution of the normalised flexural moduli of exfoliated nanocomposites cured with Jeffamine D-230 and 3DCM as a function of true clay content. Solid lines are fit to data.

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