Effect of Nanoclay Content on Mechanical Behaviour of TGDDM Epoxy Nanocomposites

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ABSTRACT

Nanocomposites based on tetruglycidyldiamino diphenylmethane (TGDDM) cured by diethyltoluene diamine (DETDA) reinforced with 1-20 phr of a commercial nanoclay, Nanomer I30E, were prepared. The effect of clay nanoparticle loading on the compression modulus of the nanocomposite was investigated. The level of exfoliation of the nanoclay was measured by small angle X-ray scattering and confirmed by transmission electron microscopy. The modulus of the nanocomposites increased progressively with increasing clay content with the 20 phr nanocomposite showing a 50% increase in modulus compared with the pure resin. The Tg of the cured nanocomposites measured by DSC decreased progressively with increased nanoclay loading.

Keywords: nanocomposites, epoxy, nanoclay, compressive modulus, glass transition temperature.

1 INTRODUCTION

Nanoscale materials have become of considerable interest for particulate reinforcement of polymers. In particular, nanoclay particles are very attractive because of their special structure and properties. Materials made by incorporating nanoclay into epoxy resin matrices have shown a significant improvement in properties, such as mechanical strength, barrier performance, and thermal stability, even at quite low clay loadings. Uniform dispersion of the nanoclay layers in the resin at the nanoscale is however required [1-4]. Two types of nanocomposite reinforced with nanoclay are possible: intercalated or exfoliated [5-8]. The nanoclay loading significantly affects the degree of exfoliation as well as the average distance between the separated nanoclay layers. The improvement in the mechanical properties of epoxy nanocomposites has been explained variously in terms of the ability for both internal and external stress dispersion in the network [9], the homogeneous distribution of nanoclay layers [10, 11], the stable interfacial region close to the nanoclay surface [12], the degree of cross-linking [13], and the stiffness of the particle acting as “network node” [14, 15]. A change in Tg is also observed in nanocomposite reinforced with nanoclay and this has been attributed to factors, such as changes in chain flexibility [14, 16], adsorbed moisture and the residual organics acting as a plasticizer [17, 18], and changes in the degree of cross-linking [19]. The flexibility of the chain is undoubtedly the most important factor influencing Tg. It is a measure of the ability of a chain to rotate about the constituent chain bonds; hence a flexible chain has a low Tg whereas a rigid chain has a high Tg [20].

In this study, the effect of nanoclay content on the mechanical behavior as well as thermal properties of a TGDDM epoxy-clay nanocomposite reinforced with a commercially available montmorillonite clay was investigated.

2 EXPERIMENTAL

2.1 Materials

The epoxy resin used was Araldite® LY568- a tetruglycidyldiamino diphenylmethane (TGDDM) obtained from Ciba Speciality Chemicals. The curing agent was Ethacure 100 supplied by Albemarle Corporation. This is a mixture of two diethyltoluene diamine (DETDA) isomers, containing 74-80% 2,4 isomer and 18-24% 2,6 isomer. The nanoclay used was Nanomer I30E from Nanocor, a montmorillonite clay modified with octadecyl ammonium ions.

2.2 Sample preparation

Oven dried nanoclay in amounts from 1-20 parts per hundred of resin (phr) were dispersed in a volume of neat epoxy resin using a high shear force stirrer (20,000 rpm) with a metal stirring disc at 70°C for 1 hour. Following mixing, the mixture was degassed in a vacuum chamber at 70-80°C for minutes. A stoichiometric concentration of DETDA was then added to the mixture of epoxy and nanoclay, and the mixture again degassed in the vacuum chamber at 80°C. The mixture was finally poured into moulds and cured at 110°C for 1 hour, then at 155°C for 2 hours and then at 195°C for 1 hour.

2.3 Characterization

Small-angle X-ray scattering (SAXS) measurements were carried out with a Philips X’pert X-ray diffraction
system using CuKα radiation with a wavelength of 1.5418740Å. An accelerating voltage of 45 kV was used with a current of 40 mA. A scanning range from 0.5 - 7.0° was used with a step size of 0.01°. The time per step was 3 seconds. Transmission electron microscope images were obtained using a Philips CM-200 field emission transmission electron microscope operating at 200 kV. The TEM samples were prepared as thin sections about 50 - 70 nm in thickness using an ultra-microtome (Reichert Ultracut E) equipped with a 45° sharp-edged glass knife. Prior to examination they were mounted on 200-mesh copper grids coated with carbon. Compression samples 6 mm in diameter and 12 mm high were tested on an Instron 1185 Screw at a cross-head speed of 2 mm/min. A Dupont Differential Scanning Calorimeter/Thermal Analyser was used to study the cure reaction and measure the glass transition temperature using ramp speeds of 2°C/min and 20°C/min respectively. The measurements were made using a nitrogen atmosphere at a flow rate of 10ml/min and. The analysis was carried out from 10°C to 240°C.

3 RESULTS AND DISCUSSION

3.1 Effect of surfactant on curing behaviour

The released energy of the curing reaction recorded using DSC is shown for some selected nanoclay additions in Figure 1.

![Exothermal curves for curing reaction of TGDDM/DETDA with various I30E nanoclay loadings.](image)

Table 1: Peak and onset temperatures of nanocomposites with various nanoclay contents.

<table>
<thead>
<tr>
<th>Nanoclay content in nanocomposites (phr)</th>
<th>Onset temperature (°C)</th>
<th>Peak temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>122.98</td>
<td>166.05</td>
</tr>
<tr>
<td>1</td>
<td>119.49</td>
<td>165.49</td>
</tr>
<tr>
<td>2.5</td>
<td>111.85</td>
<td>165.15</td>
</tr>
<tr>
<td>7.5</td>
<td>93.95</td>
<td>160.58</td>
</tr>
<tr>
<td>10</td>
<td>91.55</td>
<td>159.02</td>
</tr>
</tbody>
</table>

With increased nanoclay content, the exothermal peak temperature shifted to the left, indicating that the energy required for the curing reaction of the system decreased progressively with increasing nanoclay content, as shown in Table 1.

The shift in both the exothermal peak and the onset temperatures to lower values is attributed to the catalytic effect of the octadecylamine surfactant on the I30E nanoclay in the curing reaction, leading to a decrease in the energy required for epoxy ring opening polymerization. The catalytic effect becomes stronger with increasing nanoclay content since the surfactant concentration in the resin is increased hence the decrease with increasing clay loading.

3.2 Morphology

The distance between the layers of nanoclay, as measured by SAXS, varied with clay loadings as indicated in Figure 2. For a diffraction angle larger than 0.75°, no peaks were observed with nanoclay contents from 1 to 5 phr, indicating that the d-spacing of the nanoclay layers was greater than 120 Å, consistent with the nanoclay particles being fully exfoliated. However, with further increase in the clay loading the distance between the nanoclay layers decreased, being only 70-80 Å for the composites with 7.5-12.5 phr of nanoclay. These nanocomposites were not considered to be fully exfoliated, and are therefore referred to as pre-exfoliated nanocomposites.

![Small angle X-ray diffraction spectra for nanocomposites with varying I30E nanoclay contents.](image)
Just as the presence of the octadecylamine surfactant on the nanoclay surface had a catalytic effect on the curing reaction, it is considered that it also accelerated the cross-linking of the epoxy resin in the spaces between the layers of nanoclay so that the platelets were continuously forced to separate after the curing agent was added, as previously proposed [5, 21]. The surfactant being on the surface of the added clay particles, as well as between the individual layers, would be expected to accelerate the reaction at the surface of the particles also. At low nanoclay loadings this acceleration would be much less pronounced than between the layers because of the comparatively smaller surface area. However with increased nanoclay loading the extrapolonymerization reaction would become progressively more accelerated and this may then limit expansion of the nanoclay layers. This would account for the progressive reduction in interlayer spacing observed here.

### 3.3 Compression modulus

The compressive modulus of the nanocomposites increased progressively with increased nanoclay content, Figure 4. The modulus increased from a value 2352 MPa for the pristine resin to 3030 MPa at a loading of 10 phr of nanoclay eventually attaining a value of 3517 MPa at a loading of 20 phr of nanoclay. These values corresponded to improvements of almost 30% for 10 phr nanoclay and 50% for 20 phr nanoclay additions, Figure 5.

It is evident from Figure 5 that the improvement in modulus varies in an essentially linear manner with nanoclay content. However the values for the two lowest clay loadings seem anomalously high. This may indicate that the better exfoliation produced with the lower clay loadings has provided more effective reinforcement for the volume fraction of clay used. This in turn would suggest that the level of cross linking within the resin-filled galleries between the clay layers was increased in the better exfoliated composites. It is noted that the wider the galleries between the clay layers, the easier would be the access of the hardener to the resin in the galleries. It may be that in the composites with thinner interlayer spacings (ie, those with high clay loadings) insufficient hardener was able to penetrate into the galleries to provide full cross-linking of the resin.

### 3.4 Thermal properties

An increase in modulus in polymers is usually also accompanied by an increase in the glass transition temperature of the material. However, to the contrary the $T_g$ of the nanocomposites decreased progressively with clay content as shown in Figure 6.

The decrease in the $T_g$ of the nanocomposites with increased nanoclay content is considered to be, at least in part, due to the presence of the octadecylamine surfactant. As this was an aliphatic amine with long linear chains, the chains would be very flexible and have low thermal stability [15]. Since the concentration of surfactant in the resin would increase with increased nanoclay content the $T_g$ would also be expected to decrease. A decrease in the level of cross linking in the clay galleries would also contribute to a decrease in $T_g$. 

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Figure 3: TEM images of nanocomposites with (a) 2.5 phr, (b) 7.5 phr, (c) 12.5 phr and (d) 20 phr of nanoclay.

Figure 4: Compressive modulus of nanocomposites based on TGDDM/DETDA/I30E system. Error bars indicate one standard deviation.

Figure 5: Percentage improvement in modulus for nanocomposites with varying nanoclay contents.
4 CONCLUSIONS

A strong relationship was observed between the nanoclay content and the properties of nanocomposites based on TGDDM cured by DETDA. The compressive modulus of the nanocomposite increased progressively with increasing nanoclay content, giving an increase of 50% at a nanoclay content of 20 phr. The marked improvement in the modulus is considered to be the result of effective separation of the individual clay layers permitting good penetration of the epoxy resin into the interlayer galleries. While the modulus increased with increasing clay content, the glass transition decreased. The decrease in $T_g$ is attributed, at least in part, to the presence of increasing amounts of surfactant.

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