The mechanical properties and fracture behaviour of epoxy-inorganic micro- and nano-composites

A. J. KINLOCH*, A. C. TAYLOR
Department of Mechanical Engineering, South Kensington Campus, Imperial College London, London, SW7 2AZ, UK
E-mail: a.kinloch@imperial.ac.uk
E-mail: a.c.taylor@imperial.ac.uk
Published online: 12 April 2006

Hybrid materials have been formed using an epoxy polymeric matrix and a range of inorganic particles, including mica and organically-modified montmorillonites ('organoclays'), with various concentrations of the silicate modifier up to about 30 wt.% depending upon the viscosity increase induced by the presence of the silicate. Wide-angle and small-angle X-ray scattering plus transmission electron microscopy were used to identify the morphologies produced, which included particulate, intercalated and ordered exfoliated. The modulus of these composites increased with the weight fraction of silicate. The morphology had a small effect on the measured modulus; the nano-composites with the ordered exfoliated microstructure showing the highest values of the modulus for a given volume fraction of silicate. The fracture toughness, $K_c$, and the fracture energy, $G_c$, initially increased as the weight fraction of the silicate was increased, but then decreased at relatively high concentrations. The measured moduli and toughnesses were compared to theoretical predictions. The measured moduli values showed very good agreement with the predicted values, whilst the agreement for values of the measured fracture energy, $G_c$, with the predicted values, based upon a crack deflection toughening mechanism, were less convincing. Indeed, analysis of the fracture surfaces using scanning electron microscopy showed that the main toughening effect of the silicate particles is due to plastic deformation of the epoxy matrix around the particles.

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1. Introduction

In recent years the concept of forming hybrids using polymers and inorganic materials has received a significant amount of attention. Many claims for the potential of these organic/inorganic hybrids have been made [1], but for some combinations of materials little experimental data has been produced. Many of these studies have used surface-treated silicates, or organoclays, to produce layered-silicate nano-composites, e.g. [2, 3]. A nano-composite is defined as a composite where one of the components has a dimension in the nanometre range [3]. The addition of inorganic filler to a polymer matrix can greatly increase its stiffness, especially for thermoplastic materials in the rubbery region. However, thermosetting polymers have attracted less attention, and much of the work that has been done using these materials has employed elastomeric epoxies, e.g. [4, 5]. Some studies have used rigid thermosets, e.g. [6–8], and high-functionality epoxies [9, 10]. However, though various authors have studied the properties of epoxy-silicate nano-composites [11–15], there have generally been few studies comparing the properties of thermoset nano- and micro-composites [16–18].

The present paper is concerned with the mechanical properties and fracture behaviour of epoxy-inorganic micro- and nano-composites and discusses how the morphology of the inorganic particles can affect the mechanical and fracture properties of the nano-composites produced. This morphology is typically described as ‘particulate’ (or conventional), ‘intercalated’ or ‘exfoliated’, as identified by wide-angle X-ray scattering (WAXS) [19, 20]. These microstructures are shown schematically in Fig. 1. In an intercalated nano-composite, polymer chains enter the galleries between the clay platelets.

* Author to whom all correspondence should be addressed.

DOI: 10.1007/s10853-005-5472-0
and increase the measured spacing. For an exfoliated structure, the clay platelets are pushed further apart, and the spacing becomes too large to measure using WAXS. Note that an exfoliated structure may be ordered or disordered as shown in Fig. 1. For a particulate structure, the particles remain unchanged.

2. Experimental

2.1. Materials

The epoxy used was a diglycidylether of bisphenol A, DGEBA, (AY105, Huntsman, UK) cured using an amine hardener, polyoxypropylenediamine, (Jeffamine D230, Huntsman, UK). A range of inorganic particles was used, as shown in Table I, comprising unmodified and organically-modified silicates. Mica is a platy potassium aluminium silicate, and was supplied with no surface treatment. The other particles are all montmorillonite (a smectite clay). These clays were supplied either untreated (Cloisite Na$^{+}$) or with an organic surface treatment. Three surface-treated clays were used—Cloisite 25 A is treated with dimethyl, hydrogenated tallow, 2-ethylhexyl quaternary ammonium, and Cloisite 30B is treated with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium. Finally, Nanomer I30E is treated with octadecylamine.

Plates of epoxy composite, 6 mm thick, were produced as follows. The epoxy was poured into a beaker, the inorganic particles were added and the mixture was stirred using a spatula. The beaker was placed in a vacuum oven at 75$^\circ$C, and the entrapped air was removed from the resin. The vacuum was then released, and the mixture was left in the oven for 24 h. After this time the mixture was stirred and a stoichiometric amount of hardener added. The mixture was stirred again and poured into a release-coated steel mould. The mould was placed in an oven, and the epoxy was cured for 3 h at 75$^\circ$C followed by 12 h at 110$^\circ$C [21]. The plate of epoxy was removed after cooling and machined to produce tensile dumbbell and fracture specimens according to the relevant standards [22–24].

Note that the addition of the silicates increased the viscosity of the epoxy resin and hence there was a maximum percentage inclusion of silicate, above which the viscosity of the resin was too high to be able to cast the plates to make the test specimens. For the Cloisite 30B and 25A, a maximum of 15 wt.% of silicate could be used. The maximum addition of Nanomer I30E was 10 wt.%, and of Cloisite Na$^{+}$ was 20 wt.%. For the mica-modified epoxy, 30 wt.% of silicate could be used.

2.2. Mechanical and fracture testing

The tensile specimens were tested in compliance with the standards [22, 24] at a constant displacement rate of 1 mm/min, using a clip-on extensometer to measure the strain within the gauge length. The Young’s modulus was calculated for each of the four replicate samples. Note that the tensile strength is not quoted, as this parameter is highly dependent upon the surface finish of the specimens, for brittle materials such as these.

The fracture specimens were tested at a constant displacement rate of 1 mm/min. Both compact tension (CT) and single-edge notch bend (SENB) tests were performed. Four replicate samples were used in each case and the fracture toughness, $K_c$, was calculated. The machined notch was sharpened by drawing a new razor blade across the notch tip prior to testing [23]. Note that the data produced were compared to data from specimens where a natural crack had been tapped into the specimen, and the $K_c$ values using both techniques were found to be identical within experimental error. (The tapping technique is more difficult and results in many broken SENB specimens, hence the drawing technique was preferred.) Also there was no significant difference between the data from the CT and the SENB test geometries.

<table>
<thead>
<tr>
<th>Silicate</th>
<th>Supplier</th>
<th>Surface treatment</th>
<th>Particle diameter</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica R120</td>
<td>Minelco, UK</td>
<td>None</td>
<td>50 $\mu$m</td>
<td>15</td>
</tr>
<tr>
<td>Cloisite Na$^{+}$</td>
<td>Southern Clay Products, USA</td>
<td>None</td>
<td>25 $\mu$m</td>
<td>4</td>
</tr>
<tr>
<td>Cloisite 25A</td>
<td>Southern Clay Products, USA</td>
<td>2MHTL8</td>
<td>10 $\mu$m</td>
<td>4</td>
</tr>
<tr>
<td>Cloisite 30B</td>
<td>Southern Clay Products, USA</td>
<td>MT2EtOT</td>
<td>10 $\mu$m</td>
<td>4</td>
</tr>
<tr>
<td>Nanomer I30E</td>
<td>Nanocor, USA</td>
<td>Octadecylamine</td>
<td>10 $\mu$m</td>
<td>4</td>
</tr>
</tbody>
</table>

Notes: 2MHTL8: Dimethyl, hydrogenated tallow, 2-ethylhexyl quaternary ammonium; MT2EtOT: Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium; Particle diameter and aspect ratio measured using laser light scattering.