Toughening performance of glass fibre composites with core–shell rubber and silica nanoparticle modified matrices

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ABSTRACT

The fracture energies of glass fibre composites with an anhydride-cured epoxy matrix modified using core–shell rubber (CSR) particles and silica nanoparticles were investigated. The quasi-isotropic laminates with a central 0°/0° ply interface were produced using resin infusion. Mode I fracture tests were performed, and scanning electron microscopy of the fracture surfaces was used to identify the toughening mechanisms.

The composite toughness at initiation increased approximately linearly with increasing particle concentration, from 328 J/m^2 for the control to 842 J/m^2 with 15 wt% of CSR particles. All of the CSR particles cavitated, giving increased toughness by plastic void growth and shear yielding. However, the toughness of the silica-modified epoxies is lower as the literature shows that only 14% of the silica nanoparticles undergo debonding and void growth. The size of CSR particles had no influence on the composite toughness. The propagation toughness was dominated by the fibre toughening mechanisms, but the composites achieved full toughness transfer from the bulk.

1. Introduction

The epoxy polymers used as the matrices of fibre composites are thermosets, and hence are highly crosslinked. This makes them rather brittle, being susceptible to the initiation and propagation of delaminations, so the epoxy matrix is toughened when the composites are used as a structural material. Various approaches have been used, including the addition of rubber [1–4], thermoplastic [5,6] or ceramic [7,8] tougheners. One of the most successful approaches has been the addition of a rubber adduct such as carboxyl-terminated butadiene acrylonitrile (CTBN) which will phase-separate into micron-sized particles during curing of the epoxy polymer [1,4]. Alternatively, the addition of pre-formed core–shell rubber (CSR) particles has been shown to result in an impressive toughness improvement in bulk polymers [9–11]. These particles typically comprise a soft rubbery core inside a shell of polymethylmethacrylate. The use of CSR particles eliminates the incomplete phase separation that occurs when using liquid rubber, which leads to a reduction in the modulus and the glass transition temperature of the epoxy. For fast-curing epoxies (e.g. [12]), the formation of the epoxy network is much faster than the phase-

separation process, so CTBN rubber particles will not form properly. Further, CTBN increases the viscosity of the epoxy significantly, and thus CTBN-modified resins are less suitable for use with infusion processes than the lower viscosity CSR-modified resins. The diameter of the CTBN particles is dependent on the cure conditions, so cannot be readily controlled and will vary, especially through a thick composite component. The toughness of CTBN-modified epoxies varies with particle size [13], so this can lead to a concomitant variation in properties. Thus for many applications pre-formed CSR particles may be more suitable than phase-separating rubbers such as CTBN. The toughness of fibre-reinforced composites (FRCs) with CSR-modified matrices has been discussed by Day et al. [14] and Tsai et al. [15], but there is relatively little work in the literature that discusses these materials.

The toughening mechanisms responsible for the increased toughness have been reported as cavitation of the rubbery core followed by plastic void growth, and shear deformation in the polymer matrix [9–11]. In these studies, the CSR particles used were in the micron range. In other work [16,17], cavitation was not observed but there was debonding at the interface between the core and the shell. Both cavitation and debonding relieve the constraint in the epoxy and allow plastic deformation, thus increasing the toughness. It has been suggested the toughening effectiveness decreases when using particles less than 0.2 μm in diameter as they are difficult to cavitate [11]. However, several recent studies

[18–20], have demonstrated that nanoscale CSR particles (i.e. ~100 nm in diameter) can fully cavitate. This is supported by modelling work which shows that more energy is required for the cavitation of small particles, but does not show a size limit below which cavitation will not occur [21].

Recent developments in nanotechnology have seen the utilisation of rigid nanoparticles to toughen epoxies. Nanoparticles such as silica, alumina and titania with a 5–50 nm diameter range [22] have been used widely with epoxy resins. The toughening of polymers using silica nanoparticles has been discussed extensively in the literature [23–29]. The toughening mechanisms have been identified as debonding followed by plastic void growth, and shear deformation in the polymer matrix [27,30]. However, the increases in toughness are generally relatively small compared to those from rubber particles, as only 1 in 7 silica nanoparticles debond to form cavities [31], compared with all of the rubber particles (which either debond or cavitate).

The use of silica nanoparticles in toughening of fibre-reinforced composites (FRCs) has been reported by Kinloch and co-workers under both static [23–25,32] and fatigue [33–35] loading conditions. Among the advantages of using silica nanoparticles are that the particles do not increase the viscosity of the resin significantly, do not exhibit thixotropic properties, have good dispersion and also are free of agglomeration. These properties allow their application in the resin infusion manufacturing method [36]. The suitability of this modified epoxy as a new type of matrix for manufacturing FRCs using injection technology (or liquid composite moulding techniques) has been further discussed by Mahrholz et al. [36]. These studies [23–25,27,32–35] have reported that the silica nanoparticles increase the fracture energy and tensile modulus of the epoxy and have no effect on the thermal properties. An improved fatigue life and reduced fatigue crack growth have been observed [33–35]. In addition to the toughening mechanisms described above, fibre bridging increases the toughness of FRCs. However, the addition of silica nanoparticles may affect the level of fibre to matrix adhesion. Tsai et al. [15] attributed the moderate toughness increase in their NS modified GF composites to the improved interfacial bonding between the matrix and fibre. On the other hand, Wichmann et al. [37] found the fibre/matrix interface of GF composite with a NS-modified matrix was very weak, leading to a nearly entire interfacial failure.

In the present work, the matrix contribution towards the fracture energy for GF composites is discussed, where composites at various CSR and NS concentrations are compared with the unmodified composite (GF-Control). The effect of particle concentration and particle size on the composite toughness is also studied. The toughness transfer from bulk to composite is also discussed. In order to identify the toughening mechanisms responsible, the fracture surfaces of the mode I double cantilever beam (DCB) specimens were examined using scanning electron microscopy.

2. Experimental

2.1. Materials

An anhydride-cured epoxy was used, with a low viscosity and a long pot life which make it suitable for resin transfer moulding and resin infusion [38]. The epoxy resin was a diglycidyl ether of bisphenol A (DGEBA), LY556 from Huntsman Advanced Materials, UK, with an epoxide equivalent weight (EEW) of 186 g/eq. The curing agent was methyl hexahydrophthalic anhydride, Albidur HE 600 from Evonik Hanse, Germany, with an anhydride equivalent weight (AEW) of 170 g/eq. A stoichiometric mixing ratio of 100:91.4 by weight was used.

The glass fibre was a multiaxial ±45° double layer non-crimp fabric (NCF) with an areal weight of 450 g/m², from SP Systems,

UK. The fabric has two layers of unidirectional fibres with a ±45° orientation relative to each other, stitched together for the ease of handling. NCF was chosen because the resulting composites exhibit higher in-plane properties, superior delamination resistance and better damage tolerance compared to conventional woven laminates due to the absence of crimp in the fibre architecture [39].

Two types of core–shell rubber (CSR) particles were used, Kane Ace MX156 and MX960 from Kaneka, Belgium. These were supplied as concentrates comprising 25 wt% of CSR particles dispersed in DGEBA epoxy resin [40]. Note that the use of such a masterbatch can give a better dispersion than conventional CSRs, which are supplied in a powder form. The MX196 and MX960 grades differ in their particle size and core material (see Table 1) where the core material for MX156 has a lower T_g [41,42].

The silica nanoparticles (NS) used were Nanopox F400 from Evonik Hanse, Germany. They were supplied dispersed in DGEBA epoxy resin as a colloidal mixture containing 40 wt% of silica (SiO_2). The particles were supplied surface-modified to prevent agglomeration, and have a narrow particle size distribution with an average particle diameter of 20 nm [43].

The particle-modified epoxy formulations were prepared by stirring the as-received CSR and NS concentrates into the epoxy resin at various concentrations. A Heidolph RZR overhead stirrer was used, fitted with a bladed impeller. The curing agent was added stoichiometrically to these mixtures, and stirred again. The mixtures were degassed prior to infusion to remove any air bubbles resulting from the stirring process.

2.2. Manufacturing of GF composites

The CSR and NS particles were used at concentrations of 2, 5, 10 and 15 wt%. These mixtures were infused into 8 ply glass fibre preforms, arranged as a quasi-isotropic lay-up of [+45/−45/90/0]ₛ to give laminates with a central 0°/0° ply interface. An additional 2 layers of carbon fibre (CF) preforms were added either side of the GF preform stacks prior to infusion. This increased the laminate stiffness to avoid large deflections of the arms during the mode I fracture tests. A layer of non-perforated, 25 μm thick fluorinated ethylene propylene (FEP) release film was inserted into the centre of the lay-up to form a 45–55 mm long starter crack. Resin infusion under flexible tooling (RIFT) was used to prepare the 300 mm × 150 mm plates. The RIFT equipment setup used is similar to that described by Donadon et al. [44,45]. A full vacuum was applied at all times during the process, and was measured to be approximately 0.98 bar below atmospheric. Once infusion was complete, the laminates were cured for 1 h at 90 °C, plus 2 h at 160 °C.

The inclusion of the particles into the resin did not cause significant permeability issues during infusion, and the particles were found to be fully infiltrated into the laminate. Nonetheless, the resin flow speed did decrease with increasing particle concentration and this extended the infusion time. The use of polyethylene spiral tube (supplied by East Coast Fibreglass Supplies, UK), placed around the laminates helped to regulate the resin flow into the dry perform by creating a uniform flow front, thus distributing the resin evenly across the entire laminate.

Table 1
Properties of the core–shell rubber particles [17,41,42,59].

CSR	Material		Nominal diameter		Measured diameter
Type	Core	Shell	Core (nm)	Shell (nm)	Core (nm)
MX156	Polybutadiene	PMMA	100	85–115	58 ± 13
MX960	Siloxane	PMMA	300	250–350	186 ± 100