CORE-SHELL RUBBER NANOPARTICLE TOUGHENED CARBON FIBRE/EPOXY COMPOSITES

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Abstract: A commercially available core-shell rubber nanoparticle dispersion (CSR) was introduced into a carbon fibre/epoxy composite with the primary aim of enhancing the composite's fracture toughness. The dispersion and permeation of the CSR particles through the thickness of the laminate was examined by scanning electron microscopy (SEM). The flexural and compression after impact (CAI) properties of the CSR toughened laminates were investigated. The residual compressive strength values increased between 6-26% with the incorporation of 1 to 3 weight% of CSR. The glass transition temperature of the composite, obtained from dynamic mechanical analysis (DMA), remained unchanged up to 3% loading of CSR. The transverse flexural strength of the composites showed a drop between 6-14% with the addition of 1-5 weight% of CSR. The results indicated that addition of a small amount of CSR (between 1-3 weight%) in the resin formulation might be beneficial to enhance the fracture toughness of carbon fibre/epoxy composites without any concomitant adverse effects on other important properties.

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1. Introduction

Fibre reinforced composites are high specific strength and stiffness materials which are finding wide acceptance for use in large structural parts in the automotive and aeronautical industries, as components of buildings and wind energy. Typically, structural composites comprise fibres, in the form of continuous filaments or woven fabrics, embedded in a polymeric matrix. Such composites may exhibit considerable strength and stiffness, and offer significant weight savings which makes them attractive for use in primary structural applications as a metal replacement. However, acceptance for many structural applications has been limited by the fact that they are brittle in nature and consequently have relatively low impact resistance and damage tolerance. The modification of the resin matrix with liquid rubber and thermoplastic polymers [1-3], incorporation of interleaving materials in the interlaminar regions [4-6] are some common techniques employed to enhance the fracture toughness of composites. However, the use of liquid rubber results in a significant drop in mechanical properties of the composites while increasing the overall toughness value [1]. A useful alternative to liquid rubber is 'core shell rubber nanoparticles' which have been used

mostly to toughen various polymers, but less so for composites [7, 8]. It would therefore be of significant interest to study their role in a fibre reinforced thermoset composite where the resin deformation is highly restricted by the presence of the surrounding stiff fibres.

Scobbie et al. [7] evaluated model systems to compare state of the art nanotoughening technologies using soft and hard nanofillers solely or in combinations. The resin systems investigated in their study were mainly based on multifunctional resins (e.g. trifunctional, Araldite® MY 0510 and/or tetrafunctional, Araldite® MY 721), both from Huntsman Advanced Materials. They formulated toughened resins which showed significant improvement relative to the base unmodified resin. They used a tri-block copolymer of styrene-butadiene-methylmethacrylate (SBM) and core shell rubber nanoparticles (CSR) as soft nanofillers in two systems. In two other systems, they added two hardfillers like multi-walled carbon nanotubes (MWCNT) and nanosilica (NSi) in combination with CSR and SBM respectively. SBM resulted in a resin system with a threefold increase in viscosity compared to that with the CSR. Although the CSR modified system exhibited the lowest viscosity, the addition of MWCNT doubled the viscosity of the system. MWCNT were seen to form aggregates amongst the uniformly distributed CSR nanoparticles. The baseline resin system exhibited a G_{1C} value of 168 J/m^2. Compared to this value, increases of 148, 132, 160 and 85% were observed in systems with SBM, SBM and NSi combinations, CSR, CSR and MWCNT combinations respectively. Compression after impact (CAI) testing was carried out on composite laminates manufactured by resin transfer moulding (RTM) with these four toughened resin systems. The system containing MWCNT resulted in a composite with the lowest compressive residual strength even compared to the baseline untoughened laminate. SBM, CSR and NSi toughened systems showed enhanced performance for impact energies above 40J. A signification observation of this study was that the substantial increase in fracture energy of the nanotoughened resins was not translated into a corresponding increase of the damage tolerance of the composites. The CAI strength was not significantly improved compared to the reference laminates.

Wang et al. [8] evaluated the impact strength, and the subsequent fracture surfaces, of a commercial epoxy resin toughened with two types of core-shell rubber (CSR) toughening agents at ambient temperature and at lower temperatures (ca. 77K) using liquid Nitrogen (LN$_2$). High magnification SEM images of different areas showed that cavitation of CSR particles, void formation and dilatational deformation of the matrix occurred at ambient temperature which absorbed a larger amount of energy before fracturing increasing the impact strength. While at the lower temperatures, restricted matrix deformation reduced the effect of the CSR particles lowering the impact strength.

The aim of the present study was to evaluate the role of core shell rubber nanoparticles as a a toughening agent in carbon fibre reinforced epoxy composites. CSR toughened carbon fibre/epoxy composite panels were manufactured by vacuum infusion moulding (VIM). Flexural properties and compression after impact were investigated. The permeation of the CSR particles through the thickness of the laminate was examined with scanning electron microscopy.

2. Experimental

2.1 Materials

The resin used in this work was a one part epoxy resin Cycom 890 from Cytec Industries. Kaneka MX 156, which is a 25% concentrate of core-shell rubber (CSR) nanoparticles dispersed in an unmodified Bisphenol A base epoxy resin, was used as the toughening agent. The core-shell rubber nanoparticles consisted of an acrylic shell with a polybutadiene core. Diamino diphenyl sulfone (DDS) from Sigma Aldrich was used as the curing agent for the epoxy base of Kaneka 156. Unidirectional non-crimp fabric, or NCF, (Saertex) was used as the reinforcement in the manufacture of the laminates. The NCF consisted of carbon fibres (Tenax, IMS60 E13 24k, 274g/m2 areal weight) and E-glass at ±60° for the purposes of stabilising the carbon-fibres (for handling and pre-forming).

2.2 Resin Preparation

Cycom 890 was heated to 80°C and mixed with MX 156 in three different formulations to have 1, 3 and 5 phr (per hundred parts of resin) of CSR. Cycom 890 is a single component resin. Hence, measured amounts of DDS were added to the resin/CSR blends with respect to the weight of the MX-carrier epoxy resin. The resin blends were initially degassed at 80°C under vacuum prior to any infusion

2.3 Composite Fabrication

Unmodified Cycom 890 resin and 1, 3 and 5 phr CSR modified Cycom 890 were used to manufacture composite panels designated as M0, M1, M3 and M5 respectively. A standard resin infusion technique was employed to manufacture the laminates. Curing was carried out at 180°C for 2 hours.

2.4 Characterisation

Dynamic mechanical properties of the composites were investigated with a DMA Q800 (TA Instruments) with reference to ASTM D5023 in the temperature range between 30°C to 250°C at a heating rate of 5°C/min. Testing was done at a fixed frequency of 1 Hz with an amplitude of 10 micrometres. Samples were extracted from the panels manufactured for the CAI test series (see below). Three repeats were performed for each resin formulation.

Flat $[0°]_{12}$ laminates, of nominal 3 mm thickness, were manufactured and test samples were extracted to measure the transverse flexural strength of the composites. Three point bend (3PB) tests were carried out in accordance with ASTM D7264 on a Tinius Olsen Benchtop Tester (Model H25K-S UTM). A coupon span-to-thickness ratio of 16:1 was used with a support span length of 48 mm. Five repeats were performed for each resin formulation.

Compression After Impact (CAI) tests were carried out to examine the damage tolerance of the laminates. A series of tests were conducted in accordance with test methods ASTM D7136-07 (drop-weight impact event) & ASTM D7137-07 (compressive residual strength properties of damaged polymer matrix composite plates). Panels were manufactured with the

following lay-up: $[(45/0/-45/90)_2]_S$. Each panel consisted of 16 plies with a final thickness of approximately 4.3mm. Coupons were extracted from the panels measuring 100 mm x 150 mm. Based on the results from the antecedent quasi-static indentation (QSI) tests, ASTM D 6264–07, 35 J was chosen as the energy for the impact events on all the specimens. Compression testing was carried out in a 300kN servo-hydraulic testing machine (Zwick, UK). Full-field strain measurments during these tests were captured using a three dimensional digital image correlation (3D DIC) system comprising: two Imager E-lite 2M cameras fitted with 50mm lenses; two gated white light sources; and a computer complete with Davis Strainmaster[®] software (LaVision, GmbH). Four repeats were performed for each resin formulation.

The fracture surfaces obtained from the flexure tests were examined using a Hitachi SU-70 Scanning Electron Microscope (SEM). Prior to analysis, the samples were coated with a thin layer of gold, using an EMITech sputter coater for 30s. An acceleration voltage of 10kV was used.

3. Results and Discussion

DMA revealed that the storage modulus was slightly higher in 1 phr CSR loaded composite (M1) while there was drop in M3 and M5. The glass transition temperature Tg (obtained from onset storage modulus) was found to be nearly 188°C for M0 and M1, while it dropped to 183°C and 167°C in M3 and M5 respectively.


(a)   (b)
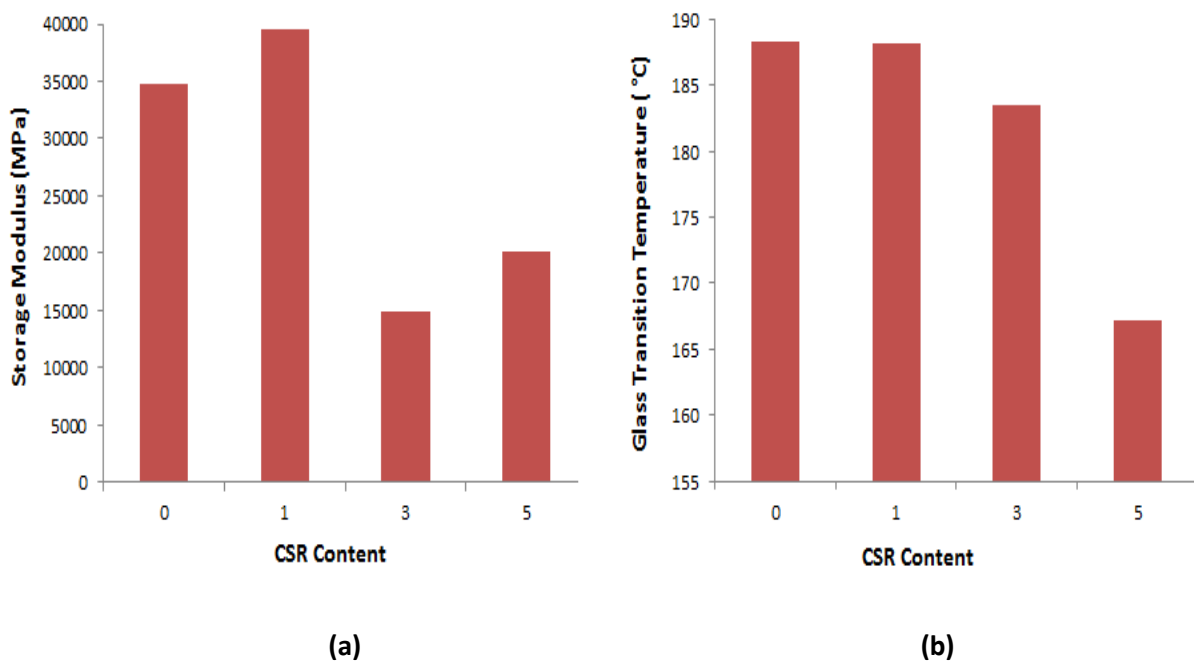
Figure 1: a) Storage modulus, and b) Glass transition temperature of the composites as a function of CSR content

These results indicated that there was a reduction in the resin stiffness when the CSR loading was raised above 3 phr.

143　　The transverse flexural strength, which is predominantly determined by the matrix rather than

144　　the fibres, were measured for M0, M1, M3 and M5, and shown in Figure 2.
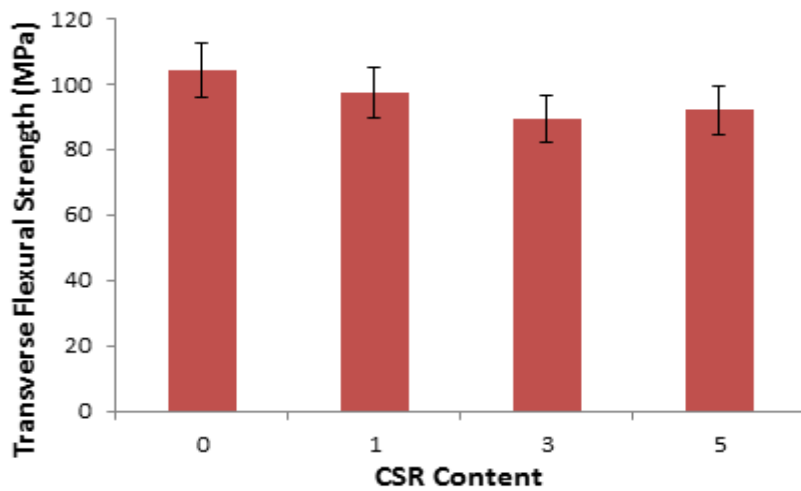
145

146　　**Figure 2: Transverse flexural strength of the composites as a function of CSR content**

147　　The transverse flexural strength dropped by 6% for M1, while for M3 and M5, the drop was

148　　14% to 11%, respectively, compared to that of M0. This decrease indicates a drop in matrix

149　　strength which might be due to the dilution of the high performance Cycom 890 base resin

150　　with the MX-carrier resin (general grade Bisphenol A epoxy resin) which has much lower

151　　mechanical properties than Cycom 890. The drop was more significant above 3% CSR level

152　　where the dilution effect was higher. Unlike liquid rubber, the core of the CSR particle is

153　　highly cross-linked and that minimises any significant drop in resin modulus. However, the

154　　combined effect of CSR nanoparticles and dilution of high performance epoxy resin might be

155　　responsible for the observed drop in transverse flexural strength.
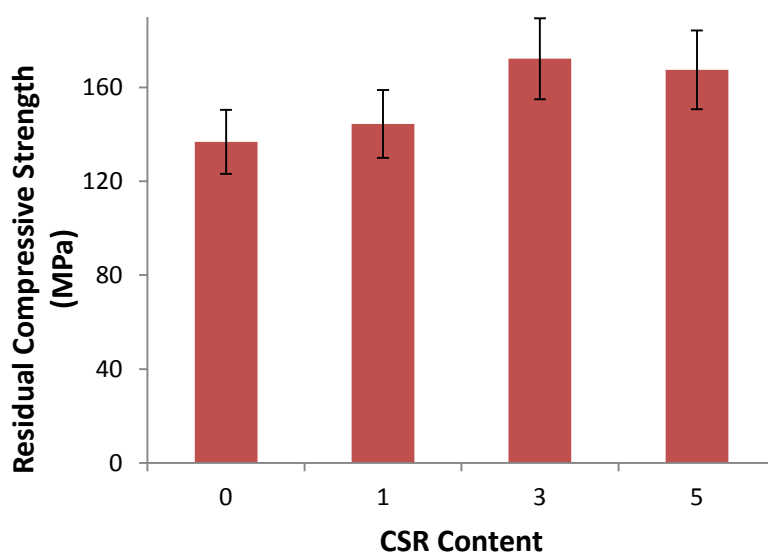
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157　　**Figure 3: Residual compressive strength of the composites as a function of CSR content**

158 The residual compressive strength of the CSR toughened composites is shown in Figure 3.
159 The residual compressive strength increased by 6%, 26% and 22% in M1, M3 and M5
160 respectively compared to that of M0. The strain fields obtained from the 3D DIC during CAI
161 tests are presented in Figure 4. The contour plot for each type of panel was obtained for a
162 load of 50kN to allow for direct comparisons.

163 The surface strain fields in the direction of the compressive load (ε_{yy}) obtained from the 3D
164 DIC during CAI tests are presented in Figure 4. The contour plot for each type of panel was
165 obtained for a load of 50kN to allow for direct comparisons. The same contour legend is used
166 for all images.
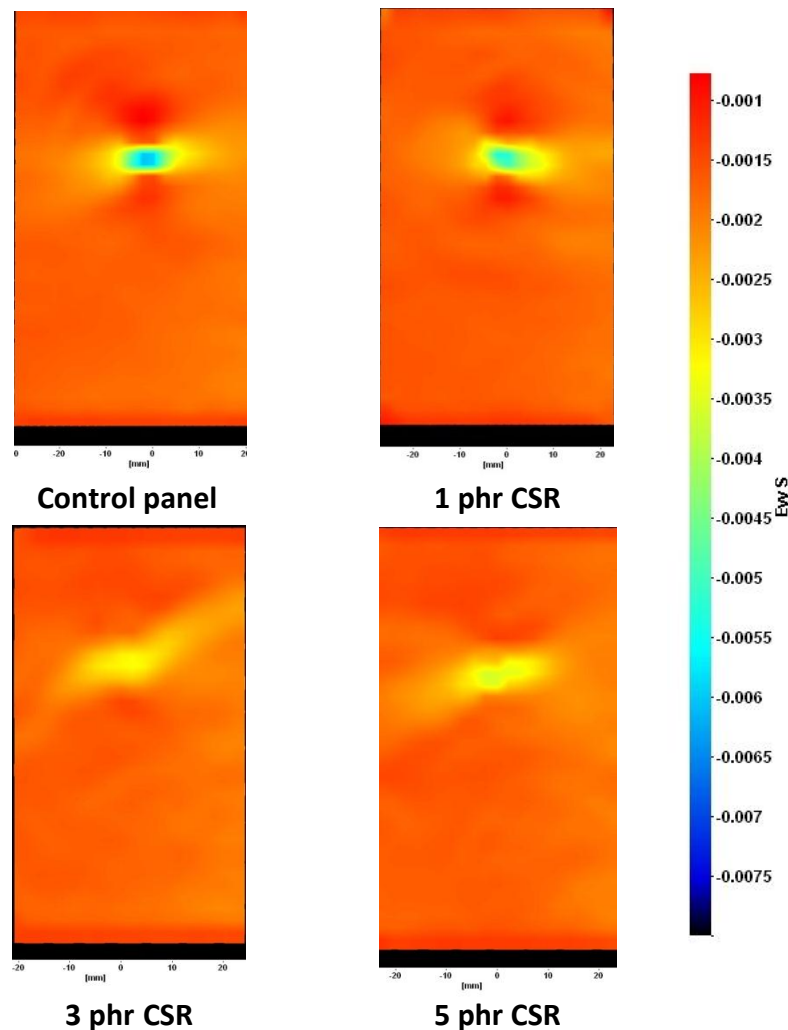

Figure 4: Full-field strain contours obtained from DIC during CAI testing of composite coupons

187 Examination of the DIC images in Figure 4 would suggest that with increasing content of
188 CSR up to 3%: the extent of damage was ameliorated during the impact event; and the
189 composite was rendered more damage tolerant by reducing the maximum compressive strains

induced locally around the area of impact damage. This trend reversed somewhat when the content increased further still to 5%.

The flexure fracture surface of M5 was examined under SEM to investigate the permeation of CSR through the reinforcement fabrics, and shown in Figure 5.
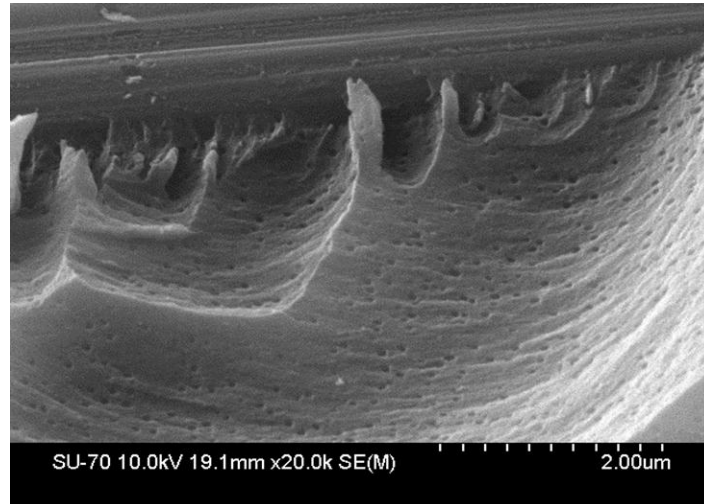
Figure 5: Dispersion of CSR nanoparticles in epoxy matrix in the composites

The distribution of CSR particles appears uniform without any agglomeration. This shows that CSR nanoparticles maintained their uniform dispersion after mixing with the base resin and was not filtered out by the reinforcement fabrics.

Conclusions:

- Core shell rubber nanoparticles (CSR) can be used effectively as a toughness modifier in carbon fibre-epoxy composites.
- A pre-dispersed CSR in a carrier resin is easy to mix during the resin infusion process as an additive by a simple hand mixing technique.
- A suitable carrier resin needs to be selected for making the CSR dispersion which matches the mechanical properties of the base resin of the composite. In this study, the mechanical properties of the carrier resin (Bisphenol A based epoxy) could not match the properties of the high performance aerospace grade epoxy resin and this could be the reason for drop in matrix properties as observed from transverse modulus values.
- Use of the same base resin as a carrier for CSR dispersion is preferred for future work to avoid any deterioration in resin properties.
- The permeation of CSR particles appeared uniform throughout the laminate without any agglomeration.
- Overall, the residual compressive strengths of the CSR toughened panels exhibited an increasing trend with increase in the CSR level up to 3%. However, further in-depth

studies are required to assess the role of CSR in controlling the delamination area during impact and on subsequent resistance of the laminate during CAI testing.

Acknowledgements

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