



21st European Conference on Fracture, ECF21, 20-24 June 2016, Catania, Italy

# Mechanical and fracture performance of carbon fibre reinforced composites with nanoparticle modified matrices

Declan Carolan<sup>a,b</sup>, A.J. Kinloch<sup>a\*</sup>, A. Ivankovic<sup>b</sup>, S. Sprenger<sup>c</sup>, A.C. Taylor<sup>a</sup>

<sup>a</sup>Department of Mechanical Engineering, Imperial College London, London, SW7 2AZ, UK

<sup>b</sup>School of Mechanical and Materials Engineering, University College Dublin, Belfield, Dublin 4, Ireland

<sup>c</sup>Evonik Hanse GmbH, Charlottenburger Strasse 9, 21502 Geestacht, Germany

## Abstract

The microstructure and fracture performance of carbon-fibre reinforced polymer (CFRP) composites with an epoxy resin cured with an anhydride hardener containing silica nanoparticles and/or polysiloxane core-shell rubber (CSR) particles were investigated in the current work. Double cantilever beam tests were performed in order to evaluate the fracture energy of the CFRP composites, while the single edge notched bend (SENB) specimen was employed to evaluate the fracture energy of the bulk polymers. Tests were conducted at room temperature and at -80°C. The transferability of the toughness from the bulk polymers to the fibre-composite systems is discussed, with an emphasis on the toughening mechanisms.

© 2016, PROSTR (Procedia Structural Integrity) Hosting by Elsevier Ltd. All rights reserved.  
Peer-review under responsibility of the Scientific Committee of ECF21.

*Keywords:* Composites; Epoxies; Nanoparticles; Toughness

## 1. Introduction

Epoxy polymers find use primarily as adhesives and as the polymer matrices of composite materials. They are amorphous and highly-crosslinked thermoset polymers. This means they are inherently brittle materials, although they possess many desirable engineering properties, such as a relatively high modulus and good high temperature creep resistance. This greatly limits their use as a structural material. The toughness of epoxy polymers has typically been improved by the addition of either soft rubbery particles (Rowe et al. 1970, Kinloch et al. 1983, Yee and

\* Corresponding author. Tel.: +44-207-594-7081.  
E-mail address: [a.kinloch@imperial.ac.uk](mailto:a.kinloch@imperial.ac.uk)

Pearson 1986, Bagheri et al. 2009) or rigid inorganic particles (Kawaguchi and Pearson 2007, Park et al. 2005, Johnsen et al. 2007). Recently toughening of epoxy polymers has been reported on a range of other materials including block copolymers (Fine and Pascault 2006, Hydro and Pearson 2007, Chong and Taylor 2013), graphene (Chandrasekeran et al. 2014) and carbon nanotubes (Gojny et al. 2004, Hsieh et al. 2011). These new materials can confer added functionality to the epoxy polymer such as improved electrical and thermal properties.

The concept of hybrid toughening refers to the use of two or more toughening agents to try to achieve some synergistic effect in the toughness of the overall nanocomposites. Kinloch and co-workers (Kinloch et al. 1985, Young et al. 1986) produced some of the early work on hybrid toughening of an epoxy modified with CTBN rubber and glass microspheres. Since this early work there have been several other groups reporting on these systems, notably the group of Pearson (Liang and Pearson 2010, Marouf et al. 2009) and later work by the group of Kinloch and Taylor (Hsieh et al. 2010, Chong and Taylor 2013, Carolan et al. 2016).

The present work investigates the effect of incorporating silica nanoparticles and/or CSR nanoparticles on the mechanical and fracture properties of an anhydride-cured epoxy polymer. The mechanical and fracture properties are measured both for the bulk polymer and also when used as the matrix for carbon-fibre reinforced polymer (CFRP) composites. The properties at room temperature and low temperatures are measured and the transferability of toughness from the bulk polymers to the fibre-composite materials is discussed with an emphasis on elucidating the toughening mechanisms.

## 2. Experimental

### 2.1 Materials

A standard diglycidylether of bis-phenol A (DGEBA) epoxy resin was used in the current work as the base resin for all of the polymer systems studied. The DGEBA resin, 'LY556' was obtained from Huntsman UK and had an epoxide equivalent weight (EEW) of 185 g/eq. To aid in the infusion of the carbon fibre mats, the base resin formulation was further altered by the addition of a reactive diluent, (1,6-hexanediol diglycidylether, DER 734, EEW = 160 g/eq) from Olin Epoxy, Germany. The addition of the reactive diluent lowers the viscosity of the resin allowing for much easier processing of the material. This resin was cured stoichiometrically with an anhydride curing agent, accelerated methylhexahydrophthalic acid, (Albidur HE600, EEW = 169 g/eq) from Evonik Hanse, Germany. The silica nanoparticles were obtained predispersed in DGEBA at 40 wt%, (Nanopox F400, Evonik Hanse, Germany). The CSR nanoparticles were also obtained predispersed in DGEBA resin at 40 wt%, (Albidur EP2240A, Evonik Hanse, Germany). To manufacture the bulk epoxy polymers the DGEBA epoxy resin was mixed with the resin containing the silica nanoparticles and/or the resin containing the CSR nanoparticles and the reactive diluent in a ratio to achieve the desired nanoparticle concentrations. The reactive diluent was added at a concentration of 25 phr of epoxy resin. This mixture was then thoroughly mixed mechanically at 60°C for 15 minutes followed by degassing in a vacuum oven at 60°C for a further 15 minutes. Following this, a stoichiometric amount of the curing agent was added and mixed and degassed following the procedure already described. The resin mixture was then poured into a pre-heated steel mould coated with a PTFE based release agent (Frekote 700-NC, Henkel, UK). The bulk polymer plates were cured at 90°C for one hour followed by a post cure for a further two hours at 120°C. Bulk specimens were then machined from these plates as required. To manufacture the composite laminates 10 layers of a biaxial textile fabric (Toray T700Sc 50C) provided by Saertex GmbH, Germany were laid up in  $\pm 45^\circ$  configuration on a flat heated vacuum assisted resin infusion tool. The carbon fibre mat was then infused over a period of 8 minutes and subsequently cured under vacuum for 7 hours at 110°C with a post cure ex-vacuum for 13 hours at 120°C and 2 hours at 160°C.

### 2.2 Mechanical testing

Tensile tests were conducted on both the unmodified and nano-modified epoxy polymers to determine the tensile modulus in accordance with ISO 527-2 (1996). Dumbbell specimens with a gauge length of 30 mm were machined directly from 3 mm thick cast plates. A displacement rate of 1 mm/min was used and the tests were carried out both at room temperature (nominally 20°C) and -80°C. The strain was measured directly on the test specimen using a clip

gauge extensometer. At least five repeats were conducted for each specimen and the elastic modulus was calculated.

Plane strain compression (PSC) tests were performed on bulk samples at both room temperature and  $-80^{\circ}\text{C}$ . The PSC test allows determination of the yield stress,  $\sigma_{yc}$ , and the high-strain behaviour, i.e. the failure strain,  $\gamma_f$ . The test was conducted as described by Williams and Ford (1964) on polished test specimens of size  $40 \times 40 \times 3 \text{ mm}^3$ . The test specimens were loaded in compression between two parallel dies at a constant crosshead displacement rate of  $0.1 \text{ mm/min}$ . A minimum of two specimens were tested for each formulation and temperature. Care was taken to ensure that the effect of load-loop compliance was corrected for. At room temperature, two repeat tests were conducted for each test, while at  $-80^{\circ}\text{C}$  only one test was conducted due to the difficulties associated with testing at such a low temperature. The ultimate failure of the samples at low temperature was not recorded as the required load to achieve failure exceeded the capacity of the available load cells.

### 2.3 Fracture energy – Single-edge notch bend (SENB) test

Single-edge notched bending (SENB) tests in three point bend configuration were conducted to determine the plane strain fracture toughness,  $K_{Ic}$ , and fracture energy,  $G_{Ic}$ , in accordance with ISO-13586 (2000). Test specimens of dimensions  $60 \times 12 \times 6 \text{ mm}$  were machined from the cast plates. These specimens were pre-notched to a depth of  $4 \text{ mm}$  before subsequent tapping of a sharp precrack to a depth of  $\approx 6 \text{ mm}$  using a liquid nitrogen chilled razor blade. The length of this precrack was determined post-mortem using a stereo optical microscope. Testing was conducted in a screw-driven universal testing machine at a constant crosshead displacement rate of  $1 \text{ mm/min}$ .

### 2.4 Mode-I interlaminar fracture energy – Double Cantilever Beam Test

Fracture toughness tests of the CFRP composites were conducted using double cantilever beam specimens in accordance with BS-ISO 15024 (2001). Test specimens of  $150 \times 20 \times 3 \text{ mm}^3$  were machined from composite panels. A  $12 \mu\text{m}$  thick PTFE crack starter film of length  $50 \text{ mm}$  was used to ensure an appropriate starter crack. The corrected beam theory (CBT) was employed to calculate the Mode I fracture energy,  $G_{Ic}$ , of the composites in accordance with BS-ISO 15024 (2001). The tests were conducted at a constant crosshead displacement rate of  $5 \text{ mm/min}$  using a tensile testing machine. The loads and displacements were recorded and the crack lengths monitored using a travelling microscope. At least five replicate specimens were tested at each test temperature and for each nanoparticle modified formulation combination.

## 3. Results and discussion

### 3.1 Tensile properties

The tensile properties of the epoxy polymer modified with either silica nanoparticles or CSR nanoparticles tested at both room temperature ('RT') and  $-80^{\circ}\text{C}$  ('LT') are given in Fig. 1. The measured modulus does not differ significantly between the two test temperatures for either material. A tensile modulus of  $2.93 \pm 0.12 \text{ GPa}$  was measured for the epoxy resin at room temperature while at  $-80^{\circ}\text{C}$ , the tensile modulus was noted to increase slightly to  $3.04 \pm 0.04 \text{ GPa}$ , although these differences are not statistically significant. The addition of CSR particles resulted in an approximately linear decrease in modulus with increasing CSR content, while an approximately linear increase in modulus was observed with increasing silica nanoparticle content.

### 3.2 Compressive properties

The mean room temperature value of the true compressive yield stress,  $\sigma_{yc}$ , was measured as  $94 \text{ MPa}$  for the neat epoxy, i.e. without any nanoparticles. The addition of CSR particles further reduced the compressive yield stress. This is expected due to the softness of the polysiloxane rubber. The compressive yield stress was unaffected by the subsequent addition of silica nanoparticles. The addition of CSR particles to the epoxy polymers tended to suppress the amount of strain-softening post yield, while the addition of silica nanoparticles was not observed to significantly affect the post yield strain-softening behaviour. Huang and Kinloch (1992) have explained that the presence of the

CSR particles suppress the formation of macroscopic shear bands by promoting localised shear banding between the particles. These then merge to give a diffuse deformation zone.

At the lower test temperature of  $-80^{\circ}\text{C}$  the epoxy polymers become much more difficult to deform. The compressive yield stress increases markedly for the epoxy polymers at the lower test temperature. At this lower test temperature, there is no longer a well-defined upper yield point or any observable post-yield strain-softening zone post. It should be noted that the room temperature tests were conducted until ultimate failure of the materials while the lower temperature tests were conducted up to the load limit of the test machine. At the lower test temperature there is no longer any strain-softening region and the stress-strain curves monotonically increases, as shown in Figure 2.

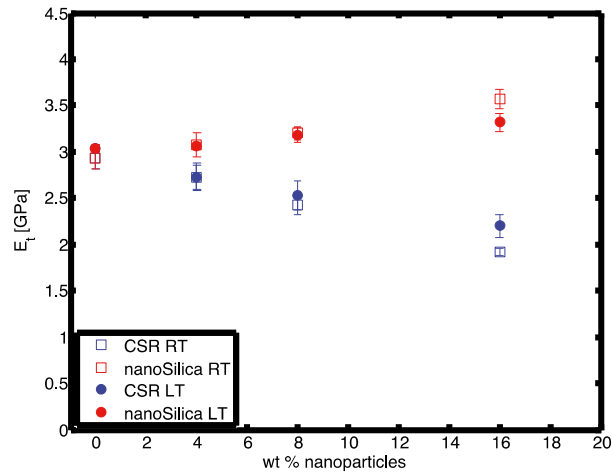


Fig. 1. Experimentally measured tensile modulus at room temperature and  $-80^{\circ}\text{C}$ .

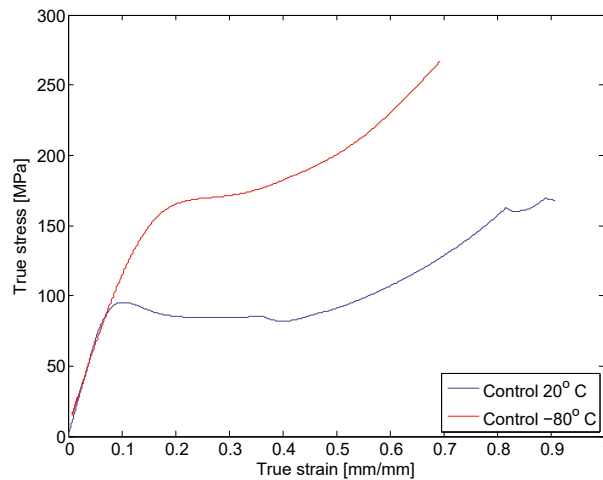


Fig. 2. Experimentally measured true stress versus true strain curves from the plane strain compression test. The room temperature test was conducted until ultimate failure of the material, while the low temperature test was conducted up to the load limit of the test machine.

### 3.3 Fracture properties

The measured fracture energies are detailed in Table 1 and Fig. 3 for the bulk epoxy polymers and the

corresponding CFRP laminates. These data show several interesting effects.

Table 1. Measured fracture properties of bulk polymers and carbon-fibre reinforced polymer composites.

Nanosilica (wt%)	CSR (wt%)	20°C		-80°C	
		$G_{Ic,bulk}$ (J/m <sup>2</sup> )	$G_{Ic,comp}$ (J/m <sup>2</sup> )	$G_{Ic,bulk}$ (J/m <sup>2</sup> )	$G_{Ic,comp}$ (J/m <sup>2</sup> )
0	0	173±33	1246±81	149±33	867±68
0	4	507±101	1538±100	329±53	1192±117
0	8	931±53	1680±129	447±87	1095±172
4	0	188±24	1170±97	246±26	1182±132
8	0	200±20	1311±118	259±24	1072±111
4	4	628±77	1624±139	377±32	1188±214
8	8	1217±63	1761±110	563±57	1352±114
8	4	724±109	1523±101	404±23	1091±106
4	8	1056±87	1851±78	546±57	1184±78

Firstly, at room temperature, solely the addition of silica nanoparticles to the unmodified epoxy bulk polymer or to the matrix of the CFRP laminates has no dramatic effect on the toughness of either material. However, a relatively small, but significant, effect is seen at -80°C for the addition of 4 wt% of silica nanoparticles to either the bulk epoxy polymer or the matrix of the CFRP laminates, but no further increase in toughness is observed if 8 wt% of silica nanoparticles are added.

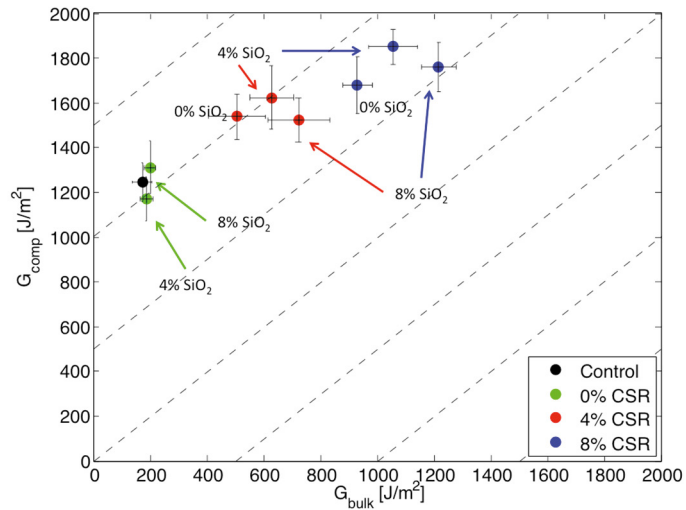
Secondly, the addition of solely 4 wt% of the CSR nanoparticles to the unmodified epoxy bulk polymer significantly increases the value of  $G_{Ic,bulk}$ . This effect is observed for tests conducted both at room temperature and at -80°C. A similar behaviour is observed for the corresponding CFRP composite laminates. However, as would be expected the absolute levels of toughness that are measured are significantly greater at room temperature, compared to -80°C. The reduced toughness at low test temperature for CSR modified epoxy polymers is primarily due to the observed increase in yield stress of the epoxy coupled with an increase in the cavitation resistance of the CSR particles (Pearson and Yee 1991). Now, an increase in the content of the CSR nanoparticles to 8 wt% only further significantly increases the toughness of the bulk epoxy polymer, and then only when the tests are conducted at room temperature.

Thirdly, considering the hybrid formulations, which contain both silica nanoparticles and the CSR nanoparticles, then when tested at room temperature the presence of both types of nanoparticles produced only modest increases in the fracture energy of the bulk epoxy polymer compared to the addition of solely the CSR nanoparticles. Nevertheless, some synergistic effects on the toughening may be noted (Carolan et al. 2016). However, in the case of the CFRP composite laminates, there are no significant increases in toughness due to the use of a hybrid formulation for the epoxy matrix. At -80°C there are no significant increases in toughness in either the bulk epoxy polymer or in the CFRP composite laminates due to the use of a hybrid toughening system for the bulk epoxy polymer or the matrix for the CFRP composite laminates compared to the addition of only the CSR nanoparticles.

Fourthly, it can be clearly observed that any increased toughness of the epoxy polymer due to the addition of silica and/or CSR nanoparticles is transferred to the composite to give an increase in the measured interlaminar fracture energy,  $G_{Ic,comp}$ . However, the steady-state propagation fracture energies of the CFRP composite laminates are far greater than the toughness of the corresponding modified bulk polymer. This is due to the additional toughening mechanisms of fibre-debonding, fibre-bridging and pull-out present in the composites (Ye and Friedrich 1992). The fibre toughening mechanisms dominate the fracture behaviour of the CFRP composite laminate and the experimental scatter in these results masks some of the differences in toughnesses between the various matrix formulations.

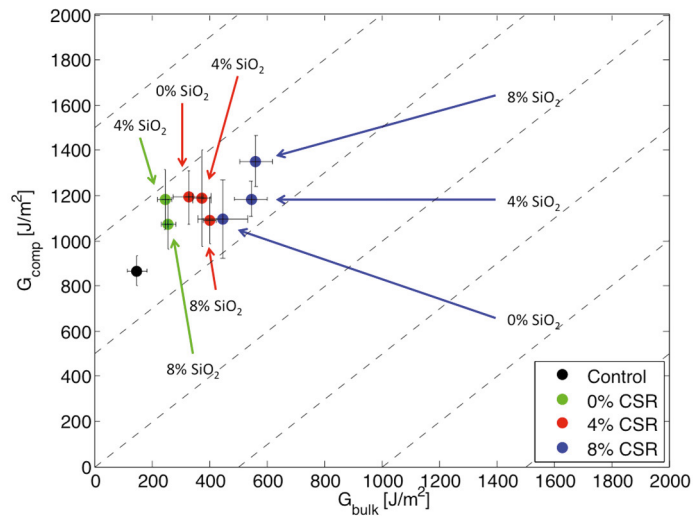
Fig. 4 presents scanning-electron microscopy images of typical fracture surfaces for the CFRP composite laminates modified with the CSR nanoparticles or the silica nanoparticles and tested at room temperature. Both the silica nanoparticles and the CSR nanoparticles appear to be well dispersed within the CFRP composites. In both cases, debonding of the carbon fibre from the surrounding matrix can be clearly identified. Indeed, the surfaces of

the carbon fibres are very clean, indicating that the level of adhesion between the carbon fibres and the matrix is quite poor. The debonding and matrix void-growth mechanism around the CSR nanoparticles can be readily observed in the CFRP composite containing CSR nanoparticles.



(a) Room temperature comparison of composite and bulk fracture energies.

(b)



(b) Low temperature comparison of composite and bulk fracture energies.

Fig. 3. Comparison of interlaminar fracture energy as measured by the DCB tests and bulk fracture energy, from SENB tests at (a) room temperature and (b) -80°C. (The dashed lines on the graph have a slope of 1:1 to aid in interpretation of the data.)

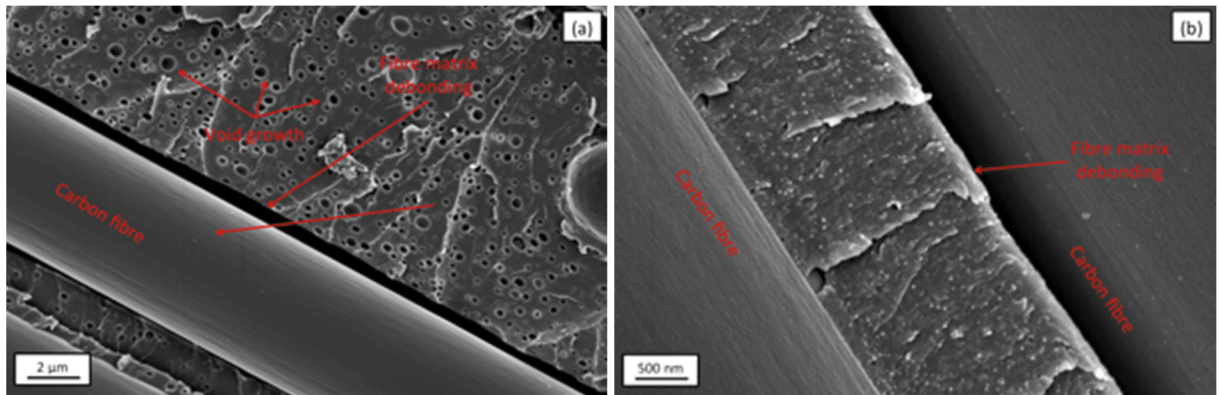


Fig. 4. Typical room temperature fracture surfaces of (a) the CFRP laminate with the epoxy matrix modified with 8 wt% CSR nanoparticles and 0 wt% silica nanoparticles and (b) CFRP laminate with the epoxy matrix modified with 8 wt% silica nanoparticles and 0 wt% CSR nanoparticles.

#### 4. Conclusions

A number of conclusions can be drawn from the current work.

- Toughness increases achieved in the bulk epoxy polymer by the addition of a combination of silica nanoparticles and/or CSR nanoparticles are readily transferable to a toughness increase being seen in the interlaminar fracture energy of the corresponding composite CFRP composite laminates.
- The toughness of an epoxy polymer or CFRP laminate modified with silica nanoparticles and/or CSR nanoparticles typically decreased at the lower test temperature of  $-80^{\circ}\text{C}$  when compared to the measured toughness at room temperature. However significant toughness improvements were still measured compared to the values of the unmodified epoxy polymer, i.e. without any toughening particles present.
- The values of toughness of the CFRP laminates, compared to the bulk epoxy polymer, were further enhanced by additional fibre-based toughening mechanisms, i.e. fibre bridging, fibre debonding and fibre pull-out.

#### Acknowledgements

The authors would like to acknowledge the financial support of the *Irish Research Council* and *Marie Curie Actions* under the *ELEVATE* fellowship scheme for Dr. D. Carolan. Some of the equipment used was provided by Dr. A.C. Taylor's *Royal Society Mercer Junior Award for Innovation*.

#### References

- Bagheri, R., Marouf, B.T., Pearson, R.A., 2009. Rubber toughened epoxies: A critical review. *Polymer Reviews* 49, 4529–4538.
- BS-ISO-15024, 2001, Fibre-reinforced polymer composites – determination of Mode I interlaminar fracture toughness,  $G_{Ic}$ , for unidirectionally reinforced materials, International Standards Organisation: Geneva, Switzerland.
- Carolan, D., Kinloch, A.J., Ivankovic, A., Sprenger, S., Taylor, A.C., 2016. Toughening of epoxy-based hybrid nanocomposites. *Polymer* Accepted March 2016.
- Chandrasekaran, S., Sato, N., Tolle, F., Müllhaupt, R., Fiedler, B., Schulte, K., 2014. Effects of graphene nanoplatelets and graphene nanosheets on fracture toughness of epoxy nanocomposites. *Composites Science and Technology* 97, 90–99.
- Chong, H.M., Taylor, A.C., 2013. The microstructure and fracture performance of styrene-butadiene-methylmethacrylate block copolymer-modified epoxy polymers. *Journal of Materials Science* 48, 6762–6777.
- Fine, T., Pascault, J.-P., 2006. Structured thermoplastic/thermoset blends using block copolymers. *Macromolecular Symposia* 245–246, 375–385.
- Gojny, F.H., Wichmann, M.H.G., Kopke, U., Fiedler, B., Schulte, K., 2004. Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. *Composites Science and Technology* 64, 2363–2371.
- Hsieh, T.H., Kinloch, A.J., Masania, K., Sohn Lee, J., Taylor, A.C., Sprenger, S., 2010. The toughness of epoxy polymers and fibre composites modified with rubber microparticles and silica nanoparticles. *Journal of Materials Science* 45, 1193–1210.

- Hsieh, T.H., Kinloch, A.J., Taylor, A.C., Kinloch, I.A., 2011. The effect of carbon nanotubes on the fracture toughness and fatigue performance of a thermosetting epoxy polymer. *Journal of Materials Science* 46, 7525-7535.
- Huang, Y., Kinloch, A.J., 1992. Modelling of the toughening mechanisms in modified epoxy polymers Part II: A quantitative description of the microstructure-fracture property relationships. *Journal of Materials Science* 27, 2763-2769.
- Hydro, R.M., Pearson, R.A., 2007. Epoxies toughened with triblock copolymers. *Journal of Polymer Science Part B: Polymer Physics* 45, 1470-1481.
- ISO-13586, 2000. Plastics – Determination of fracture toughness (GIC and KIC) – linear elastic fracture mechanics (LEFM) approach, International Standards Organisation: Geneva, Switzerland.
- ISO-527-2, 1996. Plastics - Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics, International Standards Organisation: Geneva, Switzerland.
- Johnsen, B.B., Kinloch, A.J., Mohammed, R.D., Taylor, A.C., Sprenger, S., 2007. Toughening mechanisms of nanoparticle-modified epoxy polymers. *Polymer* 48, 530-541.
- Kawaguchi, T., Pearson, R.A., 2007. The effect of particle-matrix adhesion on the mechanical behaviour of glass filled epoxies: Part 1: A study on yield behaviour and cohesive strength. *Polymer* 48, 4229-4238.
- Kinloch, A.J., Shaw, S.J., Tod, D.A., Hunston, D.L., 1983. Deformation and fracture behaviour of a rubber toughened epoxy: 1. Microstructure and fracture studies. *Polymer* 24, 1341-1354.
- Kinloch, A.J., Maxwell, D.L., Young, R.J., 1985. Micromechanisms of crack propagation in a hybrid particulate composite. *Journal of Materials Science Letters* 20, 1276-1279.
- Liang, Y.L., Pearson, R.A., 2010. The toughening mechanism in hybrid epoxy-silica-rubber nanocomposites (HESRNs). *Polymer* 51, 4880-4890.
- Marouf, B.T., Pearson, R.A., Bagheri, R., 2009. Anomalous fracture behaviour in an epoxy based hybrid composite. *Materials Science and Engineering: A* 515, 49-58.
- Park, S.-J., Jin, F.-L., Lee, C., 2005. Preparation and physical properties of hollow glass microspheres-reinforced epoxy matrix resins. *Materials Science and Engineering: A* 402, 335-340.
- Pearson, R.A., Yee, A.F., 1991. Influence of particle size and particle size distribution on toughening mechanisms in rubber-modified epoxies. *Journal of Materials Science* 26, 3828-3844.
- Rowe, E.H., Siebert, A.R., Drake, R.S., 1970. Toughening thermosets with liquid butadiene/acrylonitrile polymers. *Modern Plastics* 47, 110-117.
- Williams, J.G., Ford, H., 1964. Stress-strain relationships for some unreinforced plastics. *Journal of Mechanical Engineering Science* 6, 405-417.
- Ye, L., Friedrich, K., 1992. Fibre bridging in double cantilever beam specimens and its effect on mode I interlaminar fracture toughness. *Materials Science Letters* 11, 1537-1539.
- Yee, A.F., Pearson, R.A., 1986. Toughening mechanisms in elastomer-modified epoxies. Part 1: Mechanical studies. *Journal of Materials Science* 21, 2462-2474.
- Young, R.J., Maxwell, D.L., Kinloch, A.J., 1986. The deformation of hybrid-particulate composites. *Journal of Materials Science* 21, 380-388.