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Core-shell rubber nanoparticle reinforcement and processing of high toughness fast-curing epoxy composites



A. Keller ^a, H.M. Chong ^{b, c}, A.C. Taylor ^b, C. Dransfeld ^a, K. Masania ^{a, d, *}

^a Institute of Polymer Engineering, FHNW University of Applied Sciences and Arts Northwestern Switzerland, Klosterzelgstrasse 2, 5210 Windisch, Switzerland

^b Department of Mechanical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK ^c Joining Technology Group, Singapore Institute of Manufacturing Technology, 2 Fusionopolis Way, 138634, Singapore

^d Complex Materials Group, Department of Materials, ETH Zürich, 8093 Zürich, Switzerland

Complex Materials Gloup, Department of Materials, ETH Zurich, 8095 Zurich, Switzenana

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ABSTRACT

To simultaneously address the lower toughness and the build-up of internal heat for fast-curing epoxy matrices, the influence of nominal 100 nm and 300 nm core-shell rubber (CSR) particles on the properties and rheo-kinetics were studied. The fracture energy was enhanced by a factor of 14.5, up to 2572 ± 84 J m⁻² with 14.5 wt% of the nominal 300 nm diameter CSR particles, with evidence of cavitation and plastic void growth of the rubber core combined with shear band yielding of the epoxy matrix. These toughening mechanisms were modelled with an approximately linear increase up to 10 wt% for both particle types. At higher concentrations, deviation between the measured and modelled data was observed due to insufficient epoxy to dissipate additional energy. The CSR particles were not filtered out or damaged during the manufacturing of composites and reduced the total heat of reaction with a linear correlation, demonstrating a multi-functionality of simultaneous toughening and reduction of the exothermic peak.

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1. Introduction

The highly cross-linked structure of epoxy polymers results in high modulus, high strength, low creep and good performance at temperatures below the glass transition. However, this molecular structure also leads to a poor resistance to crack initiation and propagation. Hence, epoxy polymers typically have a low fracture energy (or toughness), reducing the durability and damage resistance of composite materials.

The fracture energy can be increased by the addition of a second phase, such as rubber [1-3] or a thermoplastic polymer [4-6]. While the fracture energy can be increased, the rubber or thermoplastic particles may decrease the tensile Young's modulus of the cured epoxy polymer, increase the viscosity of the epoxy resin and, in the case of rubber, further decrease the glass transition temperature. This affects both the processability and application of epoxy polymers as matrices in composite materials.

E-mail address: kunal.masania@mat.ethz.ch (K. Masania).

Adding rigid fillers, such as silica nanoparticles, can increase the stiffness and fracture energy [7–9] of the epoxy without influencing the kinetic properties, e.g. the degree of cure and glass transition temperature [10]. The silica nanoparticles are not filtered out during infusion [11] and have only a small effect on the viscosity up to 20 wt% [12]. However, the increase in fracture energy due to the addition of silica nanoparticles is small compared to that from rubber particles [13].

Traditionally the toughness of epoxies has been increased using reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile (CTBN). These rubbers are initially soluble in the uncured resin, then phase-separate during curing to form rubbery particles. However, it is well known that such phase-separation depends on the curing conditions, e.g. [14], so for fast-curing epoxies there may be considerable differences in the microstructure between the centre and surface of the fibre composite plates. The fast cure times may also mean that the rubber domain formation is insufficient and incomplete when fast curing resin systems are used.

To address these problems, the use of pre-formed core-shell rubber (CSR) particles has been investigated [15]. These particles consist of a soft rubbery core inside a harder polymer shell. For these particles, the particle size can be controlled as they are

^{*} Corresponding author. Institute of Polymer Engineering, FHNW University of Applied Sciences and Arts Northwestern Switzerland, Klosterzelgstrasse 2, 5210 Windisch, Switzerland.

formed by emulsion polymerisation before they are dispersed into the epoxy resin. Advances in the field have allowed the production of CSR particles that remain well dispersed in the epoxy matrix, and increase the fracture toughness without influencing the glass transition temperature of the epoxy [15] while still maintaining low viscosity for composite processing [16].

Only a few works have addressed toughening of fast-curing epoxies, i.e. those with curing times of a few minutes [12,17]. Keller et al. [12] used silica nanoparticles, which reduced the exotherm successfully but only increased the fracture energy slightly. Sprenger et al. [12,17] modified a relatively fast-curing epoxy (15 min at 120 °C) with a reactive liquid rubber and silica nanoparticles, but used a 2 h postcure. Although they did increase the fracture energy by the addition of 10 wt% rubber, no significant increase was measured with the addition of silica nanoparticles.

In the present work, the epoxy has a curing time of 5 min at 100 °C. The strong exothermic reaction during this short cure may lead to a significant overshoot of the resin temperature during cure [12] as is also observed when manufacturing very thick parts with slow-curing resins [18]. Kinetic modelling is vital for optimisation of cure for parts [19] whilst managing the exotherm. The addition of non-reactive particles provides further advantages of reducing the exothermic temperature peak during cure, reducing cure shrinkage and leading to more uniform properties over the thickness of manufactured parts [12,20], without sacrificing the short cycle time.

The aim of this study was to investigate the influence of two types of core-shell rubber particles on the fracture properties and processability of a fast-curing epoxy for fibre composites. The kinetic and rheological properties were measured and carbon fibre reinforced composite plates were manufactured using compression resin transfer moulding (CRTM) [21] to study the effect of possible filtration of the CSR particles during infusion.

2. Materials

A diglycidyl ether of bisphenol A (DGEBA) epoxy resin with an epoxy equivalent weight (EEW) of 181.5 g eq⁻¹, XB 3585 from Huntsman Advanced Materials, Switzerland, was used. The curing agent was a mixture of diethylenetriamine and 4,4'-iso-propylidenediphenol, XB 3458 from Huntsman Advanced Materials, Switzerland, which was used at a stoichiometric ratio of 100:19 by weight of epoxy to hardener.

Two different core-shell rubber (CSR) particles, MX156 and MX960, were supplied by Kaneka, Belgium, pre-dispersed at 25 wt % in a DGEBA resin with an EEW of 243 g eq⁻¹. The particles are distinguished by the core material and size. The MX156 has a polybutadiene core and a nominal particle diameter of 100 nm, while the MX960 has a siloxane core and a nominal particle diameter of 300 nm [15]. The shell was made of poly(methyl methacrylate) (PMMA) for both particles. For the epoxy formulation used, a maximum weight percentage of 21.9 wt% CSR was possible when mixed with the curing agent. Weight fractions of 4.5, 10, 15 and 20 wt% were prepared for the MX156 and 4.5, 9, 15 and 20 wt% for the MX960 modified materials.

Carbon fibre non-crimp triaxial [45/0/-45] preform fabrics (759 g m⁻², Toray T620SC 24k fibres) from Saertex, Germany, were used as a layup of $[(45/0/-45/-45/0/45)_2]_s$ as reinforcement in the manufactured fibre composites.

3. Experimental methods

3.1. Manufacturing

Bulk epoxy plates which were 6 mm thick were cast into 8 mm

thick, preheated and release agent coated aluminium alloy moulds. The plates were cured in an oven at 80 °C for 12 min. This slightly slower cure cycle was used to prevent the strong exothermic reaction and decomposition, which was found to occur for 6 mm thick plates manufactured with the unmodified epoxy at higher temperatures, e.g. 100 °C [12].

CRTM, a through-thickness impregnation process, was used to manufacture the carbon fibre composite plates. The fibre preform was placed into the open tool (preheated to 80 °C to be consistent with the bulk epoxy plates), and the resin was dosed on top of the preform. Fabric compression and simultaneous impregnation took place via the velocity driven (0.5 mm s⁻¹) closing of the tool, followed by a final dwell pressure of 20 bar to produce 4 mm thick plates with a fibre volume fraction of about 60%.

3.2. Microstructural imaging

An atomic force microscope (AFM) was employed to determine the morphology of the bulk epoxy polymers. A MultiMode scanning probe microscope with a NanoScope IV controller and an 'E' scanner from Veeco, USA, was used. A PowerTome XL cryo-microtome from RMC Products, USA, was used to create the smooth surface required by cutting thin slices off the surface of a cured sample. A silicon probe with an 8 nm tip was used to scan the surface at 1 Hz to obtain height and phase images. The images were then postprocessed by flattening the images using a 3rd order polynomial fit to remove vertical offset, tilt and bow. The volume fraction and particle sizes were then measured from the post-processed AFM phase images [22].

3.3. Compression properties

Plane strain compression (PSC) tests were performed to determine the bulk compressive properties as proposed by Williams and Ford [23], and as developed further in [7]. Polished specimens with dimensions of 40 mm \times 40 mm \times 3 mm were compressed between two parallel dies of 12 mm width using an Instron 5585H universal testing machine at a constant displacement rate of 0.1 mm min⁻¹.

Three samples were tested for each formulation, of which one sample was interrupted in the strain-softening region, sectioned to a thickness of 100 μ m and polished. This sample was placed between crossed polarisers and examined using transmission optical microscopy to confirm that shear band yielding could be observed.

3.4. Fracture properties

Single edge notched bending (SENB) tests were performed according to ASTM D5045 [24] to determine the plane strain fracture energy, G_c , of the bulk unmodified and of the CSR-modified epoxies. Samples with dimensions of 60 mm × 12 mm × 6 mm, and a V-notch of 4 mm depth, were cut using a water-jet. A sharp pre-crack was then obtained by tapping a new razor blade, cooled with liquid nitrogen, into the V-notch. A universal testing machine (Walter + Bai, Switzerland) was used to perform the tests at a constant displacement rate of 1 mm min⁻¹. At least 5 valid samples were analysed for each formulation.

3.5. Fractography

A Carl Zeiss Ultra Plus field-emission gun scanning electron microscope (FEGSEM) was used to obtain high-resolution images of the fracture surfaces using the in-lens detector. Samples approximately 3 mm thick were cut from the fracture test samples using a Struers Accutom-5 precision cutter equipped with a saw blade. The samples were then sputter-coated with a 5 nm thick layer of gold/ palladium (Au/Pd) using a Cressington 208HR high resolution sputter coater to prevent charging. The thickness was measured during the sputter coating process with a Cressington MTM-20 high resolution film thickness controller. A typical accelerating voltage of 5 kV and working distance of 6 mm were used for the microscopic observation.

3.6. Kinetic characterisation

The glass transition temperature, T_g , of the cured resin and the total heat of reaction, ΔH_{tot} , were measured with a Mettler DSC 1 using 5 mg of resin in hermetic aluminium pans. A temperature range of 25 °C–150 °C was used to determine the T_g with a heating rate of 10 °C/min. To determine ΔH_{tot} , a temperature range of –50 °C to 220 °C was used. Each formulation was measured at least twice. All measurements were conducted using a nitrogen sample purge flow to reduce oxidation of the resin.

3.7. Rheological study

A PAAR Physica MCR 302 plate-plate rheometer was used to measure viscosity development in the unmodified and the CSR-modified epoxies with a strain of 1% and an angular frequency of 10 s⁻¹. Disposable 25 mm diameter aluminium plates were used with the plate gap set to 1 mm for measurements at 25 °C, 40 °C and 50 °C.

4. Results

4.1. Microstructure studies

The morphology of the CSR-modified epoxy polymers at different concentrations is shown in Fig. 1. For both types of CSR

particles, visual inspection showed that there was no agglomeration of the rubber particles, even at higher concentrations. This was further verified by quantifying the dispersion using the area disorder approach [8], as shown in Fig. 2 (a). The mean value of the area disorder of the Delaunay network, *AD*, represents the dispersion type [8]; it is a dimensionless value between 0 and 1, and is defined as

$$AD = 1 - \left(1 + \frac{2Ns_{\Omega}}{L^2}\right)^{-1} \tag{1}$$

where 2*N* is the number of Delaunay triangles, s_{Ω} is the standard deviation of the Delaunay triangles' areas and L^2 is the total area of the micrograph (*L* is the side length of the square AFM micrographs).

The values of area disorder lie on the line corresponding to a "random-like" dispersion, which can be interpreted as the particles being dispersed in a manner that is indistinguishable from random.

A mean core diameter of 48 ± 6 nm was measured for the MX156 CSR particles, and 110 ± 4 nm was measured for the MX960 CSR particles (see Table 1) from the AFM images, which was significantly lower than the nominal diameters given in the respective manufacturer datasheets (100 nm and 300 nm).

The volume fractions and mean diameters measured from the AFM phase images were typically lower than those expected from the known quantities of particles added. This is because the PMMA shell has a similar value of modulus and hardness to the epoxy matrix, hence it would not be possible to distinguish the shell from the epoxy matrix. This means that the AFM phase images only show the core of the rubber particles, thus reducing the apparent volume fraction and the mean diameter. The PMMA shell wall thickness was determined to be approximately 10–20 nm using transmission electron micrographs from the manufacturer. The discrepancy



Fig. 1. AFM phase images of (a) 4.5 wt% MX156, (b) 20 wt% MX156, (c) 4.5 wt% MX960, and (d) 20 wt% MX960.

Fig. 2. (a) The area disorder and (b) the mean diameter of CSR particles by AFM and voids by FEGSEM measured for the MX156 and MX960 modified epoxy polymers.

 Table 1

 Comparison of prepared and measured particle content, as well as particle and void diameters. (Mean and standard deviation shown).

Material	wt%	vol%	vol%	wt%	Core diameter	Void diameter from	Percentage increase
	Manufact	ured	Measured core	from AFM	from AFM (nm)	FEGSEM (nm)	(Void/Core diameter)
MX156	4.5	4.9	4.9 ± 0.8	4.5 ± 0.7	41.8 ± 4.3	63.4 ± 2.0	52
	10	11	9.9 ± 2.1	9.1 ± 1.9	46.5 ± 3.8	57.1 ± 6.3	23
	15	16.5	13.7 ± 1.0	12.6 ± 0.9	48.9 ± 0.5	54.4 ± 0.1	11
	20	22	19.2 ± 2.6	17.6 ± 2.4	54.9 ± 2.5	49.1 ± 1.2	-11
MX960	4.5	4.9	5.0 ± 1.1	4.6 ± 1.0	107.8 ± 5.5	240.1 ± 9.9	123
	9	9.9	8.9 ± 1.5	8.2 ± 1.4	107.6 ± 9.7	218.2 ± 16.3	103
	15	16.5	12.6 ± 1.6	11.6 ± 1.5	108.5 ± 8.5	184.3 ± 8.7	70
	20	22	15.8 ± 1.5	14.5 ± 1.4	115.3 ± 4.6	163.8 ± 11.1	42

between the measured and expected mean diameter is also due to the microtoming process which cuts through the particle at random locations. Assuming the particle size is monodisperse, the actual diameter can be estimated from the diameter at the planed surface by multiplying by $4/\pi$ [25]. This gives core diameters of 61 nm and 140 nm for the MX156 and MX960 CSR particles, respectively.

The measured volume fractions of CSR particles measured from the bulk plates were found to differ from the calculated values after mixing (see Table 1), especially at higher concentrations, i.e. 10 wt% and above. This deviation may result from the presence of the PMMA shell.

The volume fractions of the CSR particles in the carbon fibre composite plates were analysed at the top, middle and bottom with respect to the composite plate thickness, which corresponds to the impregnation direction for CRTM, as shown in Fig. 3. Samples were taken by fracturing the composite material between plies and studying the interlaminar region. A maximum variation of 1 wt% was measured between the top and bottom of the plates, which indicates that neither the MX156 nor the MX960 particles were readily filtered or damaged during the infusion process when manufacturing the carbon fibre composite plates.

4.2. Compressive properties

The different epoxy formulations exhibit similar behaviours in the compressive true stress vs true strain curves, as shown in Fig. 4 and summarised in Table 2. The compressive modulus decreases linearly with the volume fraction of CSR, as observed in a previous study as well [14], due to the lower modulus of the rubber compared to that of the epoxy. The initial elastic region of the curve remains linear up to the yield point, albeit at different gradients as the addition of the relatively softer CSR particles reduces the modulus. All of the modified epoxy polymers show strain softening after the yield point, where the compressive true stress decreases while the true strain increases further. The presence of this strain softening region suggests that shear band yielding is a major toughening mechanism. A further increase of the true strain leads to an increase of the true stress and a strain hardening region, until the material failure point.

For both types of CSR-modified epoxies, the strain softening region becomes less well defined (i.e. there is a smaller drop in the stress with increasing strain) with increasing particle concentration, as shown in Fig. 4. This provides an indication that the shear band yielding process has changed for higher amounts of CSR particles. To understand these changes, one sample of each formulation was compressed to the strain softening limit (i.e. the minimum stress), then sectioned and polished to a thickness of 100 µm. The samples were placed between crossed polarisers and examined using transmission optical microscopy, as shown in Fig. 5. Note that if no shear bands are seen, then the plane of the polarised light is not rotated and the image would appear black, e.g. [13]. Shear bands are clearly visible for the unmodified epoxy and appear diffuse. The shear band intensity appears to be less but the shear bands become sharper as the loading of MX156 CSR increases, i.e. shear band yielding contributes less to the toughening of the epoxy at higher concentrations.

The MX960 CSR particles are larger (140 nm), and thus the bulk

Fig. 3. SEM images of the fracture surface at the interlaminar regions for the (a) unmodified composite (b) bottom of MX156 (8.7 wt%), (c) top of MX156 (9.6 wt%), (d) bottom of MX960 (22.5 wt%), and (e) top of MX960 (22.8 wt%) modified carbon fibre composite plates.

Fig. 4. Compressive true stress vs compressive true strain curves for (a) the MX156, and (b) the MX960 CSR-modified epoxies.

samples were opaque at higher concentrations of 20 wt%, even when sectioned to smaller thicknesses. Hence, the images in Fig. 5 for the MX960 modified epoxies were not as clear as for the MX156. However, the visible trend for this formulation does not appear to change with CSR concentration, i.e. qualitatively the same amount of shear band yielding was observed for all of the MX960 modified epoxy polymers.

4.3. Fracture properties

The measured values of the fracture energy are summarised in Table 2. A mean fracture energy of $177 \pm 35 \text{ J m}^{-2}$ was measured for the unmodified epoxy. The addition of only 4.5 wt% of MX156 CSR particles significantly increases the fracture energy up to 1126 J m⁻², corresponding to an increase of 540%. This increase in fracture energy for the MX156 is linear up to about 9.1 wt%, where

Table 2

Fracture energy, G_{c_1} and compressive properties: true yield stress, σ_{vc_2} true yield strain, ε_{vc_2} true failure stress, σ_{f_1} and true failure strain, ε_{f_1} (Mean and standard deviation shown).

	wt%	wt% measured	$G_{\rm c} ({\rm J} {\rm m}^{-2})$	$\sigma_{ m yc}$ (MPa)	ε _{yc}	$\sigma_{\rm f}({\rm MPa})$	٤f
Unmodified	0	0	177 ± 35	94 ± 2	0.08 ± 0.00	219 ± 15	0.96 ± 0.01
MX156	4.5	4.5 ± 0.7	1126 ± 67	85 ± 1	0.08 ± 0.00	174 ± 2	0.86 ± 0.02
	10	9.1 ± 1.9	1889 ± 69	70 ± 0	0.08 ± 0.00	159	0.99
	15	12.6 ± 0.9	2054 ± 108	66 ± 0	0.07 ± 0.00	155 ± 8	0.96 ± 0.08
	20	17.6 ± 2.4	2464 ± 78	54 ± 1	0.07 ± 0.00	114	0.87
MX960	4.5	4.6 ± 1.0	1025 ± 58	84 ± 1	0.09 ± 0.01	160	0.85
	9	8.2 ± 1.4	1830 ± 88	76 ± 2	0.09 ± 0.00	125	0.93
	15	11.6 ± 1.5	2410 ± 113	66 ± 0	0.07 ± 0.00	129 ± 5	0.94 ± 0.06
	20	14.5 ± 1.4	2572 ± 84	60 ± 0	0.07 ± 0.00	88 ± 11	0.90 ± 0.04

Unmodified

4.5 wt% MX156

4.5 wt% MX960 10 wt% MX156 9 wt% MX960 20 wt% MX156 20 wt% MX960

Fig. 5. Images taken using cross-polarised light of PSC samples, tested until within the strain softening region.

values of fracture energy up to 1889 J m^{-2} were measured. At CSR contents above 9.1 wt%, the relative increase in fracture energy was less, and the maximum value of G_c was measured to be 2464 J m⁻². The fracture energy values for the MX960 CSR particle modified epoxy are similar at low weight contents, i.e. $1025 \text{ J} \text{ m}^{-2}$ with 4.5 wt % CSR, and increase linearly up to about 11.5 wt% with a value of 2410 J m⁻². The relative increase in fracture energy was again less at higher concentrations with a value of 2572 J m⁻² being measured at 14.5 wt%.

4.4. Fractography

The fracture surfaces of the unmodified epoxy were found to be smooth and glassy, as is typical for brittle homogeneous thermoset polymers, see Fig. 7 (a). With the addition of the CSR particles, the fracture surfaces appear much rougher, as shown in Fig. 7 (b–e). At higher resolutions, the individual rubber particles can be observed to have cavitated, followed by plastic void growth of the epoxy matrix. These voids were clearly visible within the process zone for all of the CSR-modified epoxy formulations. This correlates well with the high measured values of the fracture energy. There was no evidence that the PMMA shell debonds from the epoxy matrix, or

that the rubber debonds from the PMMA because no debonded particles are visible on the fracture surfaces. By swelling with solvent, butadiene rubber was confirmed to be present in the voids. This shows that the epoxy matrix is well bonded to the PMMA shell, which in turn, remains in contact with the butadiene core, and that the rubber cavitates.

1 mm

The plastic void growth process increased the size of the voids, compared to the original rubber core size measured from the AFM micrographs, as shown in Fig. 2 (b). There is a clear trend of decreasing void diameter with increasing rubber content. The larger MX960 CSR particles formed relatively large voids, with a wt % dependent diameter of 140%-220% of the original size, corresponding to a maximum void diameter of 240 ± 10 nm as shown in the tabulated data in Table 1. In comparison, the MX156 CSR particles only show a maximum void size of 150% of the original core size for the 4.5 wt% modified epoxy, which corresponds to a mean diameter of 63 ± 2 nm. A decrease in diameter was measured for the 20 wt% MX156 modified epoxy. However, this is most likely due to standard errors in image processing as the highly toughened resins also have significant height changes which can affect the measurements.

It should also be noted that at the highest concentrations of

Table 3				
Modelling parameters to	o calculate	the f	racture	energy.

Parameter		Value	Reference
Radius of the core-shell particles	$r_{\rm p}$ (nm)	30.5 or 70	This study
Radius of the voids after void growth	r_{pv} (nm)	$(1 + \gamma_{\rm f})r_{\rm p}$	[7]
Plane strain compressive true yield stress	$\sigma_{\rm vc}$ (MPa)	94	This study
Plane strain compressive fracture true strain	٤fu	0.96	This study
Uniaxial tensile yield true stress	$\sigma_{\rm yt}$ (MPa)	83	This study
Pressure-dependent yield stress parameter	$\mu_{\rm m}$	0.2	[29]
Maximum stress concentration for von Mises stresses around a rigid particle	Kp	$0.59v_f + 1.6471$	[30]
Von Mises stress concentration factor for voids	K _v	$0.0918v_{\rm f} + 2.1126$	[30]
Fracture energy of unmodified epoxy	G_{cu} (J m ⁻²)	177	[12]
Fracture toughness of unmodified epoxy	$K_{\rm cu}$ (MPa m ^{0.5})	0.85	[12]

rubber used, the rubber particles/voids can be very close to each other, often with only a thin ligament of epoxy between them, as shown in Fig. 7 (c) and (e).

4.5. Modelling fracture energy

An analytical method to calculate the toughening contribution of micron-sized CTBN particles based on physically-observed mechanisms was first presented by Huang and Kinloch [28]. This approach was later used by Giannakopoulos et al. [15] to successfully predict the increases in toughness due to the addition of coreshell rubber particles in relatively slow-curing epoxies. The fracture energy, *G*_c, can be calculated using the unmodified epoxy properties as:

$$G_c = G_{cu} + \Psi \tag{2}$$

where G_{cu} is the fracture energy of the unmodified epoxy and Ψ is the overall toughening contribution due to the particles. The same analysis can be used for the CSR particles in this work. The two major toughening mechanisms observed experimentally are (i) plastic shear band yielding, ΔG_s , and (ii) cavitation of the CSR particles and subsequent plastic void growth of the epoxy, ΔG_v , where ΔG_v can be seen as the dominant toughening mechanism [27], hence:

$$\Psi = \Delta G_{\rm s} + \Delta G_{\rm v} \tag{3}$$

The toughening contribution due to shear band yielding in the epoxy can be expressed as [28]:

$$\Delta G_{\rm s} = 0.5 \nu_f \sigma_{\rm yc} \varepsilon_{\rm fu} F'(r_{\rm y}) \tag{4}$$

where v_f is the volume fraction of CSR particles, σ_{yc} is the plane strain compressive true yield stress, ε_{fu} is the true fracture strain of the unmodified epoxy and $F(r_y)$ is a term taken from [13] which has the following form:

$$F'(r_y) = r_y \left[\left(\frac{4\pi}{3\nu_f}\right)^{\frac{1}{3}} \left(1 - \frac{r_p}{r_y}\right)^3 - \frac{8}{5} \left(1 - \frac{r_p}{r_y}\right) \left(\frac{r_p}{r_y}\right)^{\frac{5}{2}} - \frac{16}{35} \left(\frac{r_p}{r_y}\right)^{\frac{7}{2}} - 2\left(1 - \frac{r_p}{r_y}\right)^2 + \frac{16}{35} \right]$$

$$(5)$$

where r_y is the increased plastic zone size due to stress concentrations in the epoxy and can be calculated using:

$$r_{y} = K_{p}^{2} \left(1 + \frac{\mu_{m}}{\sqrt{3}} \right)^{2} r_{pzu}$$
(6)

where $\mu_{\rm m}$ is a material constant which allows for the pressuredependency of the yield stress, which was found to be in the range of 0.175–0.225 by Sultan and McGarry [29] and was taken as 0.2. The parameter $K_{\rm p}$ is the maximum stress concentration for the von Mises stresses around a particle. Within the measured range of volume fractions, the value of $K_{\rm p}$ varies from 1.66 to 1.78, as calculated by Guild and Young [30] for glass particles in an epoxy matrix. The Irwin prediction of the plane strain plastic zone radius for the unmodified epoxy at fracture, $r_{\rm pzu}$, from Eq. (6) was calculated according to [31] using:

$$r_{pzu} = \frac{1}{6\pi} \frac{K_{cu}^2}{\sigma_{yt}^2} \tag{7}$$

where K_{cu} is the fracture toughness and σ_{yt} is the tensile true yield strength of the unmodified epoxy.

The toughening contribution of the plastic void growth, ΔG_{v} , was calculated according to [28] using:

$$\Delta G_{\nu} = \left(1 - \frac{\mu_m^2}{3}\right) \left(v_{f\nu} - v_{fp}\right) \sigma_{yc} r_{pzu} K_{\nu}^2 \tag{8}$$

where $\mu_{\rm m}$ is the same constant as in Eq. (6), and $v_{\rm fv}$ and $v_{\rm fp}$ are the volume fraction of voids and CSR particles, respectively. The maximum hoop strain that a shell void could sustain is $(1+_{\rm efu})r_{\rm p}$, and this value was used to calculate $v_{\rm fv}$. The von Mises stress concentration factor for voids, $K_{\rm v}$ was taken from Huang and Kinloch [28] and varied between 2.11 and 2.13 for the studied volume fractions.

The overall toughening contribution, Ψ can then be expressed in the following form by combining Eqs. (3), (4) and (8) to give:

$$\Psi = 0.5 \nu_f \sigma_{yc} \gamma_{fu} F'(r_y) + \left(1 - \frac{\mu_m^2}{3}\right) \left(\nu_{f\nu} - \nu_f\right) \sigma_{yc} r_{pzu} K_{\nu}^2 \tag{9}$$

The values of the parameters used for the modelling are given in Table 3 and the results are summarised in Fig. 6. The fracture surfaces showed that all of the CSR particles cavitated, as can be seen in Fig. 7, hence 100% of the particles were assumed in the modelling to have initiated shear bands and allowed plastic void growth of the epoxy matrix to the maximum extent.

4.6. Kinetic properties

The value of $T_{\rm g}$ for the uncured epoxy, $T_{\rm g0}$, was measured to

Fig. 6. Measured (points) and the modelled (line) fracture energy, using the Huang-Kinloch model. (Mean and standard deviation shown for experimental data.)

be -28.0 ± 1 °C, and for the cured epoxy, $T_{g_{00}}$, to be 117 ± 1 °C with no change for the CSR-modified epoxy. The value of the cured T_g is slightly lower compared to a previous result [12], where a T_g of 121 ± 1 °C was measured with a new batch of materials and considering experimental variation there is no significant difference.

The total heat of reaction, ΔH_{tot} , of the unmodified epoxy,

obtained from dynamic measurements with a heating rate of 10 °C/ min as shown in Fig. 8, was determined to be 513 \pm 3 J g⁻¹, which shows a slight deviation compared to previous measurements (494 \pm 4 J g⁻¹) [12]. The addition of the particles reduces the mass of the epoxy matrix, and as such leads to a linear proportional reduction of ΔH_{tot} with a slope of -5.15 J g⁻¹ wt%, as the exothermic mass was reduced with the addition of non-reacting particles such

Fig. 8. Dynamic DSC measurements with a heating rate of 10 °C/min for the MX156 CSR-modified epoxies.

Fig. 7. SEM images of the fracture surface for the (a) unmodified epoxy, (b) 9.1 wt% MX156, (c) 17.6 wt% MX156, (d) 8.2 wt% MX960, and (e) 14.5 wt% MX960 modified epoxy polymers. Crack propagation is from right to left.

Fig. 9. Initial viscosity values for (a) the MX156, and (b) the MX960 CSR-modified epoxies.

as core-shell rubber. The degree of cure progression of the dynamic measurements remains equal for all wt% of CSR at identical temperatures and respective heating rates.

4.7. Rheological properties

Isothermal measurements from room temperature to 50 °C were conducted to study the influence of the core-shell rubbers on the initial viscosity, i.e. the viscosity at which impregnation would be conducted (see Fig. 9). Roughly 30–60 s of rheometry data were lost between the time when the resin first touched the preheated plates and start of the measurement due to the closing motion of the upper plate.

The initial viscosity increased exponentially with increasing wt% of the core-shell rubbers. A similar increase was measured for both CSRs at low wt%, e.g. with the addition of 4.5 wt% the viscosity increased by a factor of 1.34 ± 0.03 with the MX960 compared to 1.38 ± 0.03 with the addition of MX156 for a temperature range between 25 and 50 °C. A more significant increase was measured for the MX156 in the case of high wt%. Hence, particle size effects seem to be more significant with higher wt% of the CSR particles.

A particle dependent exponential term can be added to the Arrhenius law previously shown in [12] as:

$$\eta_0(T) = A_1 \exp\left(\frac{E_1}{RT}\right) C_1 \exp(D_1 CSR_{wt\%})$$
(10)

where *T* is the temperature in Kelvin, *R* is the universal gas constant, A_1 , E_1 , C_1 and D_1 are constants given in Table 4, and CSR_{wt%} denotes the wt% of the CSR particles. The values of A_1 and E_1 were taken from [12] whilst C_1 and D_1 were determined by fitting to the experiments.

Eq. (10) can be used to calculate the initial viscosity during infusion, and hence can be used to predict the filling time of a composite part when using a liquid composite moulding processes

 Table 4

 Constants to calculate the initial viscosity from the temperature and core-shell rubber wt%.

	<i>A</i> ₁ [12]	<i>E</i> ₁ [12]	<i>C</i> ₁	<i>D</i> ₁
MX156	1.32×10^{-9}	52931	0.954	0.0918
MX960	1.32×10^{-9}	52931	0.987	0.0690

for the whole range of CSR wt%.

5. Discussion

Based on the analytical description of the particle position from microscopy, the CSR particles remained well dispersed in the matrix with a random-like distribution. The T_g remained unaffected with a value of 117 \pm 1 °C and a linear decrease of the total heat of reaction was observed, resulting from the decreased exothermic mass (epoxy and curing agent). No influence on the curing reaction was observed and the particles aid reduction of the exothermic temperature peak during cure.

There were no significant differences in fracture energy between the MX156 and MX960 CSR-modified epoxy polymers up to about 9.1 wt%, with a linear increase in toughness for both particles. Higher concentrations lead to a more gradual increase in the fracture energy. Furthermore, it is known that the bulk polymer fracture energy shows efficient toughness transfer to that of a fibre composite up to a point, e.g. Refs. [11,16]. Hunston et al. [32] argued that full toughness transfer from bulk to fibre composite occurs up to a fracture energy of 1000 J m⁻², and above this value the composite toughness still increases but at a slower rate. Bradley [33] as cited by Siddiqui et al. [34] proposed that the toughness transfer was relatively good up to G_c values of 2000 J m⁻², above which there is little increase in G_c of the fibre composite. Thus, the fibre composite with this polymer as the matrix material should be appropriately toughened provided that the fibre matrix interface is sufficiently strong. The mathematical models provided good agreement to the measured values for both CSRs while the increase in fracture energy was approximately linear with increasing wt%. This indicates that up to 9.1 wt%, shear band yielding and plastic void growth after cavitation of the particles were pertinent to the enhanced toughening.

However, the fracture behaviour at higher wt% loadings was not described accurately by the model, as the increase in the fracture energy became more gradual. This difference is believed to be a result of stress overlaps around particles and the lack of sufficient epoxy to plastically deform, when the particles are close together, resulting in a saturation of the fracture energy enhancement. SEM images confirmed that only a thin ligament of epoxy remains between rubber particles/voids at higher concentrations, as shown in Fig. 7 (b) and (d). The more gradual increase in fracture energy was also reflected in the measured void diameters, where the void diameter continually decreases with the weight percentage of CSR particles. This shows that there is a lower energy contribution from the void growth of each cavitated particle due to the space constraint which means that there is a smaller volume of epoxy which is able to deform around each particle.

Compression tests showed a clear strain-softening region, suggesting that shear band yielding occurs, which is a major toughening mechanism due to the large amounts of plastic deformation that occur. Indeed, shear bands were observed in micrographs taken from polished samples using cross-polarised light. A further toughening mechanism, rubber core cavitation and plastic void growth was observed from SEM images of the fracture surface.

The addition of CSR particles resulted in an exponential increase of the initial viscosity, and the particle size effect on the viscosity was found to be more significant with increasing wt%. At 4.5 wt%, the influence is relatively small with an increase in viscosity by factors of 1.38 and 1.34 for the MX156 and MX960 particles respectively. Interestingly, a larger increase was measured with the addition of MX156 with smaller particle size at higher particle content, i.e. an increase by a factor of 2.3 with 10 wt%, compared to by 1.9 with MX960.

6. Conclusions

A fast-curing epoxy was modified with the addition of two coreshell rubbers (CSR), with measured particle core diameters of 61 nm and 140 nm, to investigate the mechanical and rheo-kinetic properties, size effects and filtration during infusion. Both particles remained well dispersed with no evidence of filtration in the fibre composite, and with a constant T_g , showed no influence on the curing reaction. The total heat of reaction was identical for both particle types with a linear decrease with increasing wt% of CSR. This helps to reduce the strong exothermic reaction exhibited by the fast-curing resin that was studied.

No significant effect of particle size was found for the fracture energy up to 10 wt% CSR. Extremely tough parts were produced corresponding to a maximum increase in fracture energy by a factor of 14.5. Shear band yielding and plastic void growth was observed for both CSR particles, which at higher particle content, plateaued due to insufficient epoxy to dissipate energy.

Experimental measurements showed that very tough epoxy polymers can be fully cured in a few minutes. The measured viscosity values for 4.5 wt% CSR increase by a factor of only of 1.38 and 1.34 for the MX156 and MX960 respectively. Simultaneously, a significant increase in the fracture energy was measured by a factor of 6.36 and 5.79 respectively. In comparison, a similar increase of viscosity was measured with the addition of 10 wt% of silica nanoparticles, but without a significant toughening effect [12].

Eqs. (2) and (10) can be used to find the optimal balance between toughness and infusion time by predicting the fracture energy and initial viscosity of the resin for different wt%.

During manufacture using compression resin transfer moulding, none of the CSR particles were filtered out during infusion in the through-thickness direction when using a pressure of up to 20 bar, indicating that these particles are suitable to be used to manufacture fibre composites. We could demonstrate, that the combination of these nanometre scaled CSR particles with a fast-curing epoxy represents an attractive approach to produce very tough composite parts with cycle times of a few minutes.

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