Experimental studies of the deformation mechanisms of core-shell rubber-modified diglycidyl ether of bisphenol-A epoxy at cryogenic temperatures
Hayley R Brown, Judy A Schneider and Taylor L Murphy

Journal of Composite Materials published online 3 May 2013
DOI: 10.1177/0021998313485262

The online version of this article can be found at:
http://jcm.sagepub.com/content/early/2013/05/01/0021998313485262
Experimental studies of the deformation mechanisms of core-shell rubber-modified diglycidyl ether of bisphenol-A epoxy at cryogenic temperatures

Hayley R Brown, Judy A Schneider and Taylor L Murphy

Abstract
Epoxy polymers, although often used in fiber-reinforced polymeric composites, have an inherent low toughness that further decreases with decreasing temperatures. Second-phase additives have been effective in increasing the toughness of epoxies at room temperature; however, the mechanisms at low temperatures are still not understood. In this study, the deformation mechanisms of a diglycidyl ether of bisphenol-A epoxy modified with MX960 core-shell rubber particles were investigated under quasi-static tensile and impact loads at room temperature and liquid nitrogen temperature. Overall, the core-shell rubber had little effect on the tensile properties at room temperature and liquid nitrogen temperature. The impact strength decreased from neat to 1 wt% and 3 wt% but increased from neat to 5 wt% at room temperature and liquid nitrogen temperature, with a higher impact strength at room temperature at all core-shell rubber loadings. While a large toughening effect was not seen in this study, the mechanisms analyzed herein will likely be of use for further material investigations at cryogenic temperatures.

Keywords
Core-shell rubber, epoxy, toughening, cryogenic, rubber, impact, tension, composite

Introduction
To meet an industrial need for higher performance components, the use of high strength-to-weight ratio materials is increasing. Although polymeric composite materials provided higher strength-to-weight ratios than metals, the knowledge of the mechanisms that govern their behavior is still in its infancy. For designers to increase their use of polymeric composite materials in the transportation industries, there is a need to further understand the behavior and response to different loading conditions and environments.

Many high performance composites are fabricated using fiber-reinforced epoxy resins. However, epoxy resins have an inherent low toughness that further decreases with decreasing temperature. Thus, the incorporation of different types of tougheners is being explored to provide better properties over a range of temperatures. In this study, neat and core-shell rubber (CSR)-modified EPON 828 diglycidyl ether of bisphenol-A (DGEBA) epoxy resin was investigated using dynamic mechanical analysis (DMA), quasi-static tension testing, and Charpy impact testing at room temperature (RT) and liquid nitrogen (LN2) temperature. Transmission electron microscopy (TEM) was used to record the initial microstructure and scanning electron microscopy (SEM) was used to record the post-test fracture surfaces. The goal of this study is to develop the structure–property relationships for CSR-modified epoxies at cryogenic temperatures in order to better understand the governing mechanisms and provide material selection guidelines for industry.

Department of Mechanical Engineering, Mississippi State University, USA

Corresponding author:
Hayley R Brown, Department of Mechanical Engineering, Mississippi State University, 210 Carpenter Hall, Mississippi State, MS 39762, USA.
Email: brown_hayley_r@cat.com
Background information

Materials

Epoxy polymers are thermosets, which have been polymerized to form chains, which cross-link during cure. Neat epoxies typically have a RT tensile strength of ~100 MPa, elongation to failure of ~3%, elastic modulus of 3.5 GPa, \(^{1}\) and fracture toughness of ~1.0 MPa-m\(^{1/2} \). \(^{2}\) A common epoxy used extensively as matrix material for reinforced composites is DGEBA; this epoxy was chosen as the focus of this study because the strain-to-failure of DGEBA at LN\(_2\) temperature is comparable to the strain-to-failure of a typical carbon fiber at LN\(_2\) temperature.\(^{3,4}\)

Due to the highly cross-linked polymer chains that provide good strength and stiffness, thermosets are generally considered brittle materials with low toughness.\(^{1}\) However, varying the cure cycle or curing agent greatly affects the tensile stress–strain response. Le et al.\(^{5}\) investigated the tensile properties of a DGEBA epoxy cured with Jeffamine D230 and 4,4'-diaminodiphenyl sulfone (DDS) and found that the curing agent greatly affected the tensile response of the cured epoxy. The epoxy cured with Jeffamine D230 has a stress–strain response with the characteristic stress softening generally seen in thermoplastics, while the epoxy cured with DDS has a stress–strain response generally associated with brittle thermosets. By changing the curing cycle or curing agent, the amount of cross-linking in the epoxy is altered.\(^{6}\) Many authors have investigated the effect of cross-link density on the mechanical properties of epoxies,\(^{6,10}\) all agreeing that the fracture toughness decreases with an increase in cross-link density. The work of these authors has shown that a decrease in cross-link density generally corresponds to a decrease in strength and an increase in ductility of the epoxy. However, this increase in ductility has been proposed to be correlated with an increase in the capacity of the epoxy to be toughened by elastomeric modification.\(^{6,7,10}\)

Preformed CSR particles are an additive often used to toughen epoxies.\(^{11–16}\) The particles are easily manufactured into different sizes and the volume fraction may be easily varied.\(^{17}\) The shells are formulated for better bonding to epoxies in an effort to eliminate the particle–epoxy interface problems seen with other modifiers. The particles distribute throughout the matrix well, so agglomeration is not an issue. The handling, curing, and processing are simple and the CSR particles have been reported to increase the impact resistance of epoxies with a minimal effect on quasi-static properties. Because of these attributes of CSR particles, they have been selected for this study.

Toughening mechanisms

Many authors have investigated and postulated on the RT toughening mechanisms of second-phase modified epoxies, as well as proposed analytical models of such mechanisms.\(^{16,18–20}\) However, few authors have considered these mechanisms at cryogenic temperatures.\(^{21,62}\) Three of the main mechanisms in the CSR-modified epoxy literature are introduced (shear banding, plastic void growth, and rubber bridging), as well as two mechanisms originally introduced for ceramics (crack deflection and crack pinning).

Particle cavitation is an important precursor to several toughening mechanisms described below. It is generally agreed that the role of particle cavitation in rubber-toughened epoxies is to relieve the plane strain constraint from the matrix ahead of the crack, allowing plastic deformation of the matrix.\(^{21,11,12,23–26}\) Because the rubber cavitation relieves the triaxial stress in front of the crack tip, extensive yielding can occur in the surrounding matrix.\(^{27}\) Since cavitation has been established as a precursor to plastic deformation ahead of the crack tip and provides voids that allow more plastic deformation than that of a neat epoxy, it has been considered important to select modifiers that will cavitate. Becu-Longuet et al.\(^{28}\) indicated that there is a critical size below which particles will not cavitate while Dompas et al.\(^{29}\) indicated that, along with size, cavitation is dependent on the elastic and molecular properties of the rubber particles. Cavitation is reported to be difficult with particles less than 200 nm in diameter\(^{29–32}\) for many materials; thus, 200 nm has been identified as the critical size. However, cavitation was seen with 120 nm particles in tension\(^{25}\) and 150 nm particles during Izod impact.\(^{29}\)

The internal cavitation ability of a rubber particle is highly dependent on its modulus and Poisson’s ratio. Huang and Kinloch\(^{33}\) stated that a particle with a high Poisson’s ratio is more likely to undergo internal cavitation than a particle with a low Poisson’s ratio; also, an increase in Young’s modulus is likely to suppress internal cavitation of a rubber particle. Huang and Kinloch\(^{33}\) showed that for a CTBN-modified epoxy, the Poisson’s ratio of the rubber had to be above 0.497 for internal rubber cavitation to occur before any other toughening mechanisms. For several RT vulcanizing silicone rubbers, O’Hara\(^{34}\) found that the Poisson’s ratio peaked at 0.49 even under high pressures. Therefore, cavitation of a particle made of a similar rubber to that in the study of O’Hara\(^{34}\) is not likely.

Although cavitation has received more attention in the literature than particle debonding, some authors have suggested that the method of void nucleation, whether cavitation or debonding, is not important as long as void nucleation occurs.\(^{29,35}\) Dompas et al.\(^{29}\) found that in polyvinyl chloride (PVC) modified with
methyl methacrylate-butadiene-styrene, both internal cavitation and debonding at the matrix/particle interface promoted toughening of the PVC matrix, regardless of the void initiation mechanism. Le et al.\(^5\) attributed the presence of voids in a DGEBA epoxy toughened by CSR particles to debonding of the MX120 CSR nanoparticles. Huang et al.\(^35\) stated that although the cavitation or debonding of particles may provide a small amount of toughening, it is insignificant compared to the energy consumed by the plastic deformation made possible by void nucleation.

Kinloch et al.\(^36\) postulated that the occurrence of localized shear yielding due to the triaxial stress state ahead of a crack tip is an important mechanism in the toughening of epoxies. Yee and Pearson\(^26\) found that an epoxy’s toughness is most affected by the ability of the matrix to deform in shear. The CSR particles essentially act as void nucleators, which promote shear deformation of the matrix. Due to the difficulty of nucleating voids in a homogeneous matrix, the neat epoxy is not highly capable of shear deformation, which contributes to the inherently low toughness. Thus, the main function of the CSR particles is to enlarge the volume in which energy dissipation via plastic deformation of the epoxy can occur.\(^37\) CSR particles must cavitate or debond to allow widespread local plastic dilatation in the matrix because the rubber is rigid under triaxial stresses due to its high Poisson’s ratio (almost an infinite bulk modulus).\(^38\)

The rubber particles, or the voids created by cavitated or debonded particles, act as stress concentrators, with the maximum stress being at the equator of the particle. These regions of localized plastic deformation can form into defined shear bands between neighboring particles.\(^39\) The shear band forms at the equator of a particle and travels until it reaches another particle. As many as four shear bands can form off each particle, typically at a 45° angle to the loading direction.\(^39,40\)

Bascom et al.\(^37\) introduced the concept of plastic growth of internal voids as a toughening mechanism in epoxies. The void growth mechanism hinges on the idea presented above that the triaxial stress state in front of the crack causes the rubber particles to cavitate or debond at the particle-matrix interface, forming voids within the matrix.\(^37\) Plastic growth of these voids can cause energy dissipation, thus toughening the material.\(^38\) Plastic void growth is encouraged by the stress softening that often occurs after yield in many plastics. However, if the matrix is still bonded to the rubber by the time the epoxy begins to strain harden, the plastic void growth mechanism will be suppressed. This also implies that void growth will not be as likely for plastics that do not undergo a stress-softening region.

As a crack propagates through the matrix, particles in the path of the crack can alter the crack trajectory. Rather than continuing to travel across an even front, the crack will bow out between the particles but remain stuck, or pinned, at the particles, thus increasing the total crack surface area.\(^41\) As the pinned areas of the crack break away from the particles, the crack front creates steps, which are visible on the fracture surface. Lange\(^42\) proposed that an increase in energy is required to lengthen the crack front, which has been pinned by particles. This increases the energy necessary to grow the crack, thus toughening the material. Lange also goes on to say that the stress fields associated with the crack front begin to interact between and around the particles, which makes particle size and interparticle distance important features in this mechanism. According to this premise, larger particles are more effective at pinning cracks and increasing the fracture energy of the material than smaller particles. Bagheri and Pearson\(^43\) captured this mechanism in SEM micrographs of fracture surfaces of rubber-toughened epoxies. Bagheri and Pearson\(^43\) stated that crack pinning due to particles showed a decrease in the crack driving force in the vicinity of the particles.

Kunz-Douglass et al.\(^44\) proposed that as a crack advances through an elastomer-modified epoxy, rubber particles behind the crack bridge the gap, acting as ligaments or springs inhibiting the crack from opening further. As the crack continues to advance, the rubber particles will keep stretching until the tearing energy of the rubber is reached and the particles fracture. Therefore, this mechanism is based on the tearing energy of the rubber particles and the strength of the interfacial bond between the particles and the matrix. Because the contribution is reported to be negligible at RT,\(^2,19\) the crack bridging mechanism has been omitted from many RT models for CSR-toughened epoxy with good agreement with experimental data.\(^16\)

Evans and Faber\(^45\) proposed that cracks twist and tilt when they encounter an inhomogeneity in a matrix. Since there are local stress concentrations at the twisted and tilted regions of a crack front, the energy required to advance the crack is increased. Although not popular in rubber-modified epoxy literature, crack path deflection has been cited to produce a toughening effect in thermoplastic-modified epoxies. The rigid particles cause a crack to deviate from its path, resulting in an increased surface area, and therefore an increase in energy required to propagate the crack.\(^2\) While this mechanism has not been included in published modeling studies of CSR-toughened epoxy, it is included in the current experimental study because the stiffness of CSR particles will greatly increase at LN\(_2\) temperature due to the rubber being below its \(T_g\).
Materials and experimental methods

Materials and specimen preparation

The basic epoxy resin used in this study was DGEBA, commercially available as EPON 828 (Hexion Specialty Chemicals, Inc.) EPIKURE W was used as a curing agent with a 24:100 ratio of W to EPON 828. Kane Ace MX960 CSR nanoparticles (Kaneka Texas, Inc.) were supplied with a concentration of 25 wt% in an unmodified liquid DGEBA epoxy resin. The MX960 CSR particles had a reported overall average diameter of 250 nm with a siloxane core functionalized with a poly(methyl methacrylate) (PMMA) shell.16 The material system designations throughout this article are shown in Table 1.

The epoxy resin chosen for this study was selected after performing uniaxial tension tests on many different resins at RT and in a LN2 bath.46 EPON 828 was chosen due to the similarity of the strain-to-failure to that of various carbon fibers, which is around 2.2% at LN2 temperature (77 K). 3,4 Specimens in this study were fabricated with 0 to 5 wt% MX960 loading. The bulk samples were hand-mixed using varying amounts of MX960 with the liquid DGEBA epoxy resin and hardener for approximately 5–10 min, as mixing time increased with increasing weight fractions. This mixture was then preheated at 338 K for 20 min followed by degassing in a vacuum chamber for 20 min. The bulk mixture was poured into a preheated mold and cured at 397 K for 8 h. After curing, the mold was air cooled to RT.

Specimens for DMA and impact testing were machined from nominal 10 mm-thick cast sheets and the specimens for tension testing were machined from nominal 2 mm-thick cast sheets.

Dynamic mechanical analysis

DMA was performed on a Q800 dynamic mechanical analyzer using a single cantilever configuration on rectangular specimens measuring 35.7 mm × 23.7 mm × 3 mm. Both neat and 10 wt% MX960 loading were tested to differentiate between the transitions in the resin and the transitions in the CSR. The specimens were strained to 0.30% at a frequency of 1 Hz with a minimum load of 0.01 N to maintain a positive displacement and ensure accurate displacement measurement.47 The specimens underwent cooling and heating cycles using a constant 2°C/min ramp rate. For the low-temperature cycle, specimens were cooled to 133 K (the minimum temperature possible), allowed to soak for 1 min, and ramped to 298 K. For the elevated temperature cycle, specimens were ramped from 298 to 473 K. Only the neat resin was tested at elevated temperature, as the incorporation of CSR particles has not been reported to affect the glass transition temperature ($T_g$) of the resin.11

Quasi-static tensile testing

Tensile tests were conducted on an INSTRON 5869 load frame equipped with a 50 kN load cell. Tensile specimens were machined from the cast sheets into a modified type IV dog-bone sample,46 the geometry of which is shown in Figure 1. The machined edges and mold faces were sanded using 150- and 300-grit sand paper to ensure good surface conditions prior to testing. For RT tests, the specimens were loaded in wedge action grips and instrumented with an INSTRON Model 2630-115 extensometer. Although not developed for LN2 tests, the conditions listed in ASTM D638 were used as a baseline.48 All tests were conducted in displacement control at a constant cross-head speed of 0.127 cm/min.

Bolt-loaded grips with 40-grit emery paper grip faces were used for the LN2 temperature tests. The grips and specimens were submerged in LN2 prior to tightening the bolts to a torque of 5.08 Nm. The gage length of the specimen was taken as the distance between the inside edges of the grips at LN2 temperature. A cryogenically rated MTS model 634.11E-21 extensometer was attached to the specimen using rubber bands. Once installed in the load frame, the specimen, extensometer, and grips were soaked in LN2 for 10 min (average time taken to reach thermal equilibrium) while the load frame was in load control to prevent thermal contraction of the fixtures from loading the specimen. Once thermal equilibrium was reached, a 222 N preload was applied to the specimen at a displacement rate of

---

Table 1. Designations for various CSR loadings.

<table>
<thead>
<tr>
<th>Epoxy Resin/Hardener</th>
<th>Wt% CSR</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPON 828/W</td>
<td>0</td>
<td>828-0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>828-1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>828-3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>828-5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>828-10</td>
</tr>
</tbody>
</table>

CSR: core-shell rubber.
0.0051 cm/min before the test was started. The effects of thermal contraction were factored into the cross-sectional area for calculation of stress (a 2.4% reduction). The 77 K strain-to-failure data was corrected for cryostat and fixture compliance by removing the data prior to the point where the load steadily increased after the slack was taken out of the system. An example of the correction is provided in the results section.

Impact testing
Impact testing was performed using an INSTRON Dynatup 9250 HV instrumented drop tower. The drop energy was kept constant at 45 J by using a drop height of 0.662 m and drop mass of 6.94 kg. Impulse software was used to continuously record force and deflection throughout the duration of the test. Specimens were machined from cast sheets into unnotched 10 x 10 x 127 mm rectangular bars. Five specimens were tested for each CSR loading at RT and LN₂ temperature to obtain average impact strength. The effects of thermal contraction were factored into the cross-sectional area (a 2.4% reduction) for calculation of cryogenic impact strength. For the cryogenic tests, the specimens were immersed in a LN₂ bath for 10 min and tested within 30 s after removal from the LN₂ bath. The time to establish thermal equilibrium was separately verified with a type E thermocouple embedded in the center of a specimen. The temperature reached an equilibrium temperature of 77 K after 4 min and warmed to 100 K after being removed for 1 min. Thus, the test temperature was considered to be 100 K. The impact strength, $R_s$, was calculated using equation (1), where $W$ is the energy at maximum load, $t$ is the width of the specimen, and $h$ is the height of the specimen.

$$ R_s = \frac{W}{t \times h} $$

Microscopy
TEM bright field images were obtained using a JEOL JEM-100CX TEM, operated at an excitation voltage of 80 KV. Representative samples of 828-1, 828-3, and 828-5 specimens were prepared using an ultracut microtome. The specimens were approximately 90 nm thick and mounted on a formvar-coated copper grid for support. To enhance the phase contrast between the CSR nanoparticles and the epoxy resin, the TEM specimens were stained for 30 min in a 4 wt% aqueous solution of osmium tetroxide (OsO₄). In order to determine the diameter of the particles without any influence from the method of sectioning, the CSR particles were extracted from the carrier epoxy resin and imaged using TEM, as well. All TEM images were captured on film, which was digitized with a resolution of 2.5 nm/pixel. SEM was used to record the fracture morphology of tensile and impact specimens. The fracture surfaces were sputter-coated with a 10 nm layer of either Au/Pd or Pt and viewed in a Jeol 6500F field emission SEM operated between 5 and 20 keV.

Results and discussion
Dynamic mechanical analysis
DMA of 828-0 and 828-10 showed three peaks of interest in the tan $\delta$ versus temperature curve, shown in Figure 2. These peaks show that for the EPON 828, the $T_g$ was 431 K and the $T_{c1}$ was 213 K. The peak at 150 K is believed to be the $T_g$ of the MX960, which corresponds to the known $T_g$ for silicone rubber. In agreement with the literature, the current results show several molecular relaxations occurring at different temperatures in this material system. The primary relaxation is the $T_g$ and denotes a change from a rubber to glassy response of the epoxy. The secondary relaxation temperature, $T_{c1}$, is said to be related to the toughness and is associated with the movement of polymer side groups.

Quasi-static tensile testing
The stress versus strain response of representative specimens at each CSR loading tested at RT and 77 K are
shown in Figure 3(a) and (b), respectively. The RT tests showed more ductility than the 77 K tests; the RT tests yielded, whereas the 77 K specimens did not. Figure 3(c) shows the removal of cryostat compliance from the test data for a typical 77 K tension test of 828-0.

The effect of the amount of CSR loading on the elastic modulus and the 0.2% offset yield strength is shown in Figure 4(a) and (b), respectively, as well as the effect of cryogenic temperature on the modulus (Figure 4(a)). Because the specimens did not yield at 77 K, only the RT 0.2% offset yield strength is shown. The modulus at 77 K was higher than at RT for all CSR loadings tested, which was expected due to the reduction of molecular mobility in the epoxy with the reduction of temperature.62 As seen from the DMA results, the CSR dropped below its $T_g$ at 77 K (making the rubber stiffer) and the epoxy resin dropped below its $T_C$. The addition of CSR had little effect on the modulus at both RT and 77 K. The RT modulus decreased slightly in a somewhat linear trend from 828-0 to 828-5, which was expected since the modulus of the CSR particles is lower than the modulus of the epoxy. The 77 K modulus followed the same trend up to 828-3 but then increased at 828-5.

![Figure 3](image.png)

Figure 3. Tensile stress versus strain response of 828-0, 828-1, 828-3, and 828-5 at: (a) RT and (b) 77 K. (c) Removal of cryostat compliance from 77 K data of a typical test of 828-0. RT: room temperature.
However, when considering the scatter in the data and the fact that the modulus of 828-5 was only 1.5% higher than 828-0, the difference is negligible. The yield strength at RT remained constant from neat to 828-1 but decreased from 828-1 to 828-3. The difference in yield strength between 828-3 and 828-5 was negligible. This is a little different from other trends in literature, which have showed a linear decrease in yield strength with increased loading of second phase particulate modifiers.23

Impact testing

The impact strength as a function of CSR loading calculated from the Charpy impact testing at RT and 100 K is shown in Figure 5. Although there is a significant amount of scatter in the data, possibly due to manufacturing or machining defects, there are clear trends associated with CSR loading and temperature. The RT impact strength decreased by 20% from 828-0 to 828-1 and by 36% from 828-0 to 828-3. However, the impact strength increased by 7.6% from 828-0 to 828-5. The 100 K impact strength followed the same trend as the RT, with a 26% and 37% decrease from 828-0 to 828-1 and 828-3, respectively. The 100 K impact strength increased by 17% from 828/W to 828-5. The impact strength was higher at RT than at 100 K for all CSR loadings. Roulin-Moloney et al.22 attributed the lower impact strength at low temperatures to a reduced molecular mobility with reduced temperatures, which made material deformation more difficult, thus reducing the impact strength.

The load versus deflection responses of typical specimens of each CSR loading at RT and 100 K are shown in Figure 6(a) and (b), respectively. The deflection and load axes are the same in Figure 6(a) and Figure 6(b), highlighting the different response between RT and 100 K testing. Oscillations appeared in the load-deflection data and are due to the vibration of the specimen after impact of the tup.52 However, for the current study, these oscillations will not be considered since the data is being used for comparison among various materials under the same manner of loading. The specimens tested at 100 K had a stiffer
response than those at RT, regardless of CSR loading. The specimens tested at RT showed an increasing deviation from linearity in the load–displacement curve as the CSR loading increased, unlike those tested at 100 K, which remained linear until failure. There was a notable decrease in linearity in the 828-5 at RT, which coincides with the CSR loading where the CSR ceased to be detrimental and caused some amount of toughening.

The trends in impact strength with CSR loading shown in Figure 5 show that the current material system at the loadings examined does not perform as well as similar material systems in the literature. Therefore, the major mechanisms attributed with toughening in the literature are not expected to be seen in substantial amounts in this material system. However, the effect of the CSR particles on the deformation mechanisms with respect to impact strength are investigated in the following sections so as to expand the current knowledge of these material systems at cryogenic temperatures.

Initial microstructure

TEM images showed a uniform spatial distribution of CSR particles in the matrix over a range of loading (1–5 wt%), as seen by a representative slice of 828-5 in Figure 7(a). Since only the cores were susceptible to the OsO₄ staining, only the cores appear dark in the micrographs. Some of the particles, the voids of which are shown by the bright spots in the TEM images, debonded and were ejected during microtoming of the sample. The TEM images showed an average core diameter of 131 ± 82 nm; however, due to the presence of the so-called tomato salad effect when imaging thin slices of material, this diameter is expected to be smaller than the actual diameter. The tomato salad effect describes why the measured diameter in thin slices of material is smaller than the actual particle diameter. Whereas the maximum diameter is considered to be the actual diameter, if a particle is sliced such that the cutting plane does not pass through the centroid of a CSR particle, the measured diameter is smaller than the actual diameter. The total particle diameter (core + shell) has been reported as 250 ± 96 nm and the core diameter as 186 ± 100 nm, both determined during atomic force microscopy. Figure 7(b) shows MX960 particles that were extracted from the carrier epoxy resin using acetone. The average diameter measured from the extracted particles was 186 ± 50 nm, which is the same diameter reported for the cores by Giannakopoulos et al. Therefore, the acetone dissolved the carrier epoxy resin as well as the PMMA shell.
Figure 8(a) shows an impact fracture surface of a typical 828-3 specimen tested at RT at 15 ×. The impact occurred on the left side of the image, putting that side of the specimen in compression and the right side in tension. The region of crack initiation is apparent on the upper right hand corner of the specimen, showing that the crack initiated on the tension side, as expected. No clear defect was seen in the initiation region in the majority of the specimens imaged. The compressive side of the specimen shows a region that appears to be brittle fracture. This agrees with the findings of Lu et al.,54 as the region of brittle fracture appears smoother under SEM observation. The three major regions discussed in the literature were apparent on every fracture surface: mirror, mist, and hackle.22,55,56 Figure 8(b) and (c) provide magnified images at 500 × and 10,000 ×, respectively, of the mist region (Figure 8(a)) showing voids left by debonded MX960 particles that were ejected during fracture. The mirror region is smooth with very few features such as voids left by debonded particles. The mist region has a greater surface roughness than the mirror region, with parabolic features caused by the formation of secondary cracks.55 The hackle region has the greatest surface roughness and contains hackles, which are similar to rivermarks in metals, pointing back to the site of crack initiation.36

Figure 9 shows representative fracture surfaces from 828-5 tested at RT (Figure 9(a)–(c)) and 100 K (Figure 9(d)–(f)) in the mirror (Figure 9(a) and (d)), mist (Figure 9(b) and (e)), and hackle (Figure 9(c) and (f)) regions. As seen from Figure 9(a), (b), (d), and (f), the mist region appeared to have more local plastic deformation than the mirror region at both RT and 100 K. From visual inspection of Figure 9(b), (c), (e), and (f), the hackle regions seemed to have somewhat more local plastic deformation than the mist regions at both RT and 100 K. Comparing Figure 9(b) and (e), the secondary cracks, which formed off the primary cracks, tended to grow in the same direction as the primary cracks on the RT fracture surfaces, whereas the secondary cracks on the 100 K fracture surfaces did not stay confined to the direction of the primary crack. Also comparing Figure 9(b) and (e) it appears that more plastic shear deformation occurred in the RT specimens than on the 100 K specimens, which was expected after viewing the force-displacement curves in Figure 6(a) and (b). From a mechanistic standpoint, Figure 9(b) is quite similar to images in the literature57 that show local shear yielding around inclusions. This increase in local shear yielding likely correlates with the increase in impact strength of 828-5 tested at RT. As a comment on Figure 9(a) and (d) and the presence or absence of voids in the mirror region, there was no clear trend with respect to CSR loading or testing temperature regarding void presence. It is unknown why there were voids in some mirror regions but no voids in others. This could be due to a manufacturing defect, such as poor dispersion, but it is unlikely as there were no obvious regions absent of voids throughout the rest of the fracture surfaces.

As shown in the plots in Figure 10, the impact strength decreased as the areas of the mirror (Figure 10(a)) and mist (Figure 10(b)) regions increased. This was true for all CSR loadings, including...
the neat material. There was more scatter in the areas of the mist region, but that is likely due to the fact that the mist regions were not as easily defined as the mirror regions on the fracture surfaces. The plots in Figure 10 imply that the larger the hackle region is, the larger the impact strength is. This partly explains why the 828-3 did so poorly; the 828-3 had larger mirror and mist regions and a smaller hackle region, thus reducing the amount of large-scale shear deformation experienced prior to failure.

This trend of decreasing hackle size also correlates, though with a fair amount of scatter, to the volume fraction of CSR particles in the material, as shown in Figure 11. As a comment on the scatter in Figures 10 and 11, the sizes of the various regions were determined from SEM images of the fracture surfaces manually using image analysis software, therefore increasing the opportunity for measurement error. It is likely that a large portion of the scatter present in these plots is a function of the human judgment used to determine where one region ended and the next began. The scatter not induced by the measurement technique is likely associated with the scatter present in the impact strength as seen in Figure 5. Figure 11(a) and (b)
show the mirror area versus impact strength for RT and 100 K, respectively, while Figure 11(c) and (d) show the mist area versus impact strength for RT and 100 K, respectively, with the various CSR loadings denoted by different symbols. The 828-3 specimens generally provided more scatter in the data due to the 828-3 specimen tested at RT that had an impact strength of 72 kJ/m², which was somewhat of an outlier with respect to the CSR loading. However, except for this data point, the trend of decreasing hackle region (and therefore shear deformation) with increasing CSR content holds. It is interesting to note that although the 828-3 RT data point is an outlier within the confines of CSR loading, it is within the trend associating an increase in hackle area with an increase in impact strength. The general trend of decrease in shear deformation with increase in CSR loading up to 3 wt% is likely responsible for the decrease in impact strength from 828-0 to 828-3. Some of the increase in impact strength between 828-3 and 828-5 appears to be due to the increase in shear deformation (hackle area) from 828-3 to 828-5.

An interesting note on the behavior of the neat epoxy at RT and 100 K is that, while many authors have stated that the fracture surfaces of neat epoxies were smooth and featureless with limited or no stress whitening, there were a substantial amount of macroscale features on the neat fracture surfaces in this study. Figure 12 shows the transition from mirror to mist at the site of crack initiation in neat impact specimens tested at RT (Figure 12(a)) and 100 K (Figure 12(b)). Note what appears to be a decrease in the distance a crack was able to travel before a secondary crack formed due to the limited ductility at 100 K (Figure 12(b)) when compared to RT (Figure 12(a)). At the microscale there was some evidence of crack arrest.
at both RT and 100 K, shown in Figure 13 for 100 K, but there was no indication of microvoiding or crazing on any fracture surface at any CSR-loading tested at RT or 100 K.

**Particle debonding**

Remnants of MX960 particles were seen in the bottom of the voids on the tensile fracture surfaces but were absent from the vast majority of voids on the impact fracture surfaces. These particle remnants on the tensile fracture surfaces are likely due to particle debonding and then tearing. While the CSR particles debonded and ejected in such a way that there were no remnants of rubber cores at the bottom of the voids in the mirror, mist, and hackle regions, there were some remnants of rubber in the voids in the brittle fracture region, as marked in Figure 8. To further verify that there were no remnants of the rubber cores left in the seemingly empty voids and that the voids were not lined with rubber due to cavitation, OsO$_4$, along with an SEM electron backscatter detector were used to image the fracture surfaces. Several representative fracture surfaces were stained with OsO$_4$, which, due to bonding, is absorbed by the rubber core but not the epoxy matrix or the PMMA shell. Under backscatter observation, any areas that absorbed OsO$_4$ would appear lighter than unaffected areas. From this technique, all voids that appeared not to contain rubber using the secondary electron detector were verified as containing no rubber. Although cavitation of the rubber particles did not occur, the debonding of the rubber induced voids in the matrix, which can promote plastic deformation.

**Void growth**

As stated earlier, void size has been reported to be indicative of plastic deformation, i.e. voids larger than the initial particle size indicate that the matrix has plastically deformed, and is a prevalent toughening mechanism. In Figure 14, the average area of the voids present on the impact fracture surfaces for 828-1, 828-3, and 828-5 at RT and 100 K are given. Also provided are the initial core cross-sectional area (this study and the study of Giannakopoulos et al. and core + shell cross-sectional area). When compared with the initial core measurement, the RT void areas show that the core likely debonded from the PMMA shell, as seen with a similar material system in the study of Giannakopoulos et al. Because the 828-3 average void area lines up almost exactly with the initial core area, it would appear as if no void growth occurred. Although average void area at 828-1 is higher that the initial core area, the scatter in the data prevents an accurate determination of void growth.
determination of the presence of the void growth mechanism. Therefore, if present at 828-1, the void growth mechanism is likely negligible. The 828-5 showed a significantly larger void area on the RT fracture surface. This implies that the void growth mechanism was activated at the 5 wt% MX960 loading. It is believed that this void growth contributed to the change from a decreasing impact strength trend to an increasing impact strength trend and accounts for the increase from 828-0 to 828-5 that was not accounted for with the increase in shear deformation.

From Figure 14, it is believed that at 100 K the core debonded from the shell at 828-1 and 828-3, but the shell debonded from the matrix at 828-5. First, consider the 828-1 and 828-3 100 K void areas. Although they are larger than the RT voids, it is believed that preferential crack path is responsible rather than void growth. For the RT voids, there is likely a plastic zone at the equator of the void that tends to cause a crack to move around it through unyielded material at a smaller part of the void, causing a small measured area, as shown in Figure 15(a). Because of the limited amount of ductility at 100 K, the cracks may travel through the largest diameter of the void where a stress concentration, but no plastic zone, exists, as shown in Figure 15(b). For the 828-5 fracture surfaces tested at 100 K, it appears as though the shell debonded from the epoxy matrix rather than the core from the shell because the void area aligns with the initial overall CSR particle diameter from the study of Giannakopoulos et al. This change in debonding location is possibly due to a restraint placed on the epoxy during cooling by interaction of neighboring stress fields induced by the CTE mismatch between rubber and epoxy.

The presence of void growth at only 828-5 tested at RT also agrees with the material’s capability for plastic deformation, as shown by the tensile stress–strain response of each material. The void growth mechanism is often suppressed in materials with particles that do not undergo cavitation or debonding prior to strain hardening (so that the void growth may occur during the period of stress softening). Recalling the RT stress–strain response in Figure 3(a), 828-5 tested at RT had the lowest yield point and the slope of the stress–strain curve at the yield point was nearly horizontal, whereas the slope of the stress–strain curves of the other CSR loadings, including neat, were still positive at RT. Recalling Figure 3(b), the 100 K specimens did not yield, much less stress soften. Therefore, of all the materials tested, the 828-5 tested at RT was the most likely of all materials tested to experience void growth.

**Local shear deformation**

Figure 16 shows SEM fractographs taken in the mist region of 828-1 tested at (a) RT and (b) 100 K, 828-3 tested at (c) RT and (d) 100 K, and 828-5 tested at (e) RT and (f) 100 K. From the micrographs in Figure 16 it appears that there is an increase in local shear yielding at 828-5, both at RT and 100 K, as evidenced by the flanges of material rising from the fracture surfaces. It can also be seen that the amount of secondary cracking increases with decreasing temperature within each CSR loading and from 1 to 5 wt% CSR loading at 100 K. This increase in local shear yielding and secondary cracking at 828-5 likely has a toughening effect that is additive with the void growth in 828-5 at RT and shell-matrix debonding in 828-5 at 100 K.
effects are minor because the amount of toughening from 828-0 to 828-5 was minimal.

As evidenced by the lack of toughening effect of the CSR and the fact that the 828-0 does not undergo stress softening post-yield, the shear banding mechanism was not present in this material system, nor was it expected. As stated earlier, it is thought that a plastic zone did form at the equator of the voids at RT. However, these plastic zones did not grow such that they created ligaments of shear-yielded material connecting voids at 45° angles due to the limited ductility of the epoxy matrix.

**Crack growth and interactions**

Secondary cracks often form off primary cracks in both neat and modified epoxies. This secondary cracking dissipates more energy than just one large crack traveling through a material. Roulin-Moloney et al.\(^2^2\) showed that these secondary cracks are evidenced by either parabolic or elliptical regions on the fracture surfaces. If the primary crack has a higher growth rate than that of the secondary crack, the secondary crack becomes enclosed and forms an ellipse on the fracture surface. However, if the primary crack growth is the same as that of the secondary crack, a parabola is formed on the fracture surface.\(^2^2,5^5\)

As a secondary crack moves toward a void at RT, it approaches a plastic zone at the equator of the void caused by the stress concentration associated with a spherical void within a matrix in tension,\(^3^9\) as well as a region of residual stresses from cooling after cure due to the CTE mismatch between rubber and epoxy.\(^6^2,3^6\) This plastic zone can cause the crack to tilt or twist out of its original growth plane as it moves into and past the void.\(^5^8,5^9\) The same is believed to be true at 100 K, though the plastic zone will be understandably smaller or nonexistent but the residual stresses due to the CTE mismatch will be greater due to cooling in the LN\(_2\) bath. Other influencing factors could be neighboring secondary cracks, residual stress fields from neighboring particles, as well as the primary crack growth. After the crack (which is essentially acting as two different cracks on either side of the void) grows all the way around the void, the two sides of the crack rejoin if there is nothing behind the void to prevent interaction. This rejoining forms a step tail behind the void.\(^5^9\) However, if another void is present behind the original void, it can influence the secondary crack and prevent it from snapping back, causing it to continue moving outwards away from the void. It is also possible that the sides of the crack separated at a void will snap together between the voids, forming a channel-like feature between the two voids. Secondary cracks can interact with each other as well; when two cracks get close enough to each other, they can snap together to form a larger step. Several of these cracking events are labeled in Figure 17. They are labeled as follows:

1. Parabola formed by the back side of a secondary crack off the primary crack growing through the material from right to left.
2. The secondary crack initiated at 1 tilted at the void between 1 and 2. The two sides of the crack rejoined and formed a snap tail at 2.

**Figure 16.** SEM images taken in the mist region of 828-1 tested at: (a) RT (6000x) and (b) 100 K (9000x), 828-3 tested at (c) RT (9500x) and (d) 100 K (6000x), and 828-5 tested at (e) RT (4300x) and (f) 100 K (5500x).

RT: room temperature; SEM: scanning electron microscopy.
3. A secondary crack front interrupted by a void.
4. The void at 4 prevented the secondary crack from growing or snapping together behind the void at 3.
5. The secondary crack grew around the void with relatively little influence from the surrounding environment. The crack snapped closed behind the void, forming a step tail.

The same microstructural features associated with secondary crack interactions with voids that were present on the RT fracture surfaces were also present on the 100 K fracture surfaces. The 100 K fracture surfaces had a higher frequency of steps formed by secondary cracks than for the specimens tested at RT, as shown in Figure 18(a) and (b). This was expected as epoxy is more brittle at lower temperatures, allowing cracking at smaller strains. It is likely that the increase in secondary cracking at 828-5 tested at 100 K shown in Figures 16(f) and 18 accounted for some amount of the increase in impact strength (in conjunction with the change in debonding location) from 828-0 to 828-5 at 100 K due to the increase in the number of voids available to tilt and twist the increased number of secondary cracks.

Critical nearest neighbor distance
Many authors have pointed to a critical distance or ligament width between particles that must be reached before toughening will occur. Van Der Sanden et al. suggested that the critical distance was between 0.2 and 0.3 μm, depending on the nature of the epoxy and second-phase modifiers. However, Bagheri and Pearson pointed out that the critical distance shifts upwards two orders of magnitude for particles on the order of 15–40 μm.

The major effect of nearest neighbor distance (NND), or volume fraction, is likely the overlapping of residual stresses caused from the CTE mismatch between the rubber and the epoxy, as well as any plastic zones created at the equator of the voids due to stress concentrations. From observing the NND (centroid-to-centroid) for each initial CSR loading in the TEM slices, the critical NND for the current material system appears to be between 0.3 μm (5 wt% CSR) and 0.41 μm (3 wt% CSR). It is thought that at this NND, the stress fields of neighboring particles begin to overlap and have a cumulative effect. Therefore, it is suspected that the toughening of the current system might be increased as the loading of MX960 is increased above 5 wt%. Naturally there will be a maximum CSR loading possible due to the increase in viscosity with the increase in loading that will begin to affect the manufacturing process. However, an increase up the maximum is likely to increase the toughening capability of the MX960 particles. However, even at high MX960 loading, the formation of shear bands or

Figure 17. Fracture surface of a typical 828-1 specimen at 6000x tested at RT showing secondary crack interactions with voids created by debonded CSR particles. RT: room temperature.

Figure 18. (a) 1200x and (b) 9000x magnification of a fracture surface of a typical 828-1 specimen tested at 100 K showing the high frequency of secondary cracking, as well as the interactions between secondary cracks and voids.
a significantly larger amount of void growth is still not likely as this material system does not undergo post-yield stress softening.

Summary and conclusions

In this study, the deformation mechanisms of a DGEBA epoxy modified with MX960 CSR particles were investigated under quasi-static tensile and impact loads at RT and LN2 temperature. Overall, the CSR had little effect on the tensile properties at RT and 77 K. The impact strength decreased from 828-0 to 828-3 but increased from 828-0 to 828-5 at RT and 100 K, with a higher impact strength at RT at all CSR loadings.

The CSR particles debonded at the core-shell interface ahead of the crack tip at RT impact testing of 828-1, 828-3, and 828-5 and 100 K impact testing of 828-1 and 828-3. The 828-5 tested at 100 K debonded between the shell and epoxy, possibly due to the restrictions placed on the matrix due to overlapping stress fields caused by the CTE mismatch between the rubber core, PMMA shell, and epoxy matrix during cooling to LN2 temperature. The absence of cavitation is not thought to be responsible for the lack of toughening; the role of cavitation or debonding is simply to relieve the constraints on the epoxy matrix ahead of the crack tip to allow the possibility of massive shear yielding and void growth. There was evidence of plastic shear deformation on the fracture surfaces; however, the shear deformation was not massive enough to cause a substantial increase in the energy required to propagate a crack through the material. There was evidence of plastic void growth only on the 828-5 tested at RT. Also, localized shear bands were not formed between neighboring voids at any CSR loading tested at RT or 100 K. Secondary cracks formed off the primary cracks and interacted with the voids at both testing temperatures but there was more secondary crack formation at 100 K. While the increase in shear deformation and void growth likely accounted for the higher impact strength of 828-5 tested at RT, it is believed that the change in debonding location (to the shell–epoxy interface) and increase in secondary cracking is responsible for the higher impact strength of 828-5 tested at 100 K. A summary of the mechanisms present for the various CSR loading and testing temperatures is provided in Table 2.

Ultimately, the inability to stress-soften due to the high cross-link density of the epoxy prevented the major toughening mechanisms (local shear banding and substantial void growth) from being activated in the material systems tested. However, the lower energy mechanisms caused by and affected by the CSR particles were investigated in detail. It is likely that the low cross-link density epoxies that are susceptible to the toughening mechanisms activated by CSR at RT will have these mechanisms suppressed at cryogenic temperatures. Therefore, there is merit in considering these lower energy mechanisms in non-toughening epoxies in order to further understand the limitations encountered at cryogenic temperatures. The increase in secondary cracking and the interaction between neighboring residual stress fields at 828-5 tested at LN2 temperature caused a similar toughening increment as the increase in shear deformation and void growth of 828-5 at RT. Therefore, the increase in secondary cracking and the interaction between neighboring residual stress fields are the two main mechanisms capable of toughening an epoxy at cryogenic temperatures. Further testing and complimentary modeling efforts will be useful in determining the appropriate volume fraction and interparticle spacing of the CSR, as well as the effect of the presence of carbon fibers.

As demonstrated in this study and in other studies, ductility governs the higher energy toughening mechanisms activated by CSR. In response to the ultimate goal of using CSR to provide tougher epoxies

<table>
<thead>
<tr>
<th>Wt% CSR</th>
<th>Location of debonding</th>
<th>Mechanisms present</th>
<th>Reference figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Core-shell</td>
<td>Secondary crack growth interactions</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>Core-shell</td>
<td>Secondary crack growth interactions</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>Core-shell</td>
<td>Secondary crack growth interactions, plastic void growth, increased shear deformation</td>
<td>17, 14, 16</td>
</tr>
<tr>
<td>100 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Core-shell</td>
<td>Secondary crack growth interactions</td>
<td>16, 18</td>
</tr>
<tr>
<td>3</td>
<td>Core-shell</td>
<td>Secondary crack growth interactions</td>
<td>16, 18</td>
</tr>
<tr>
<td>5</td>
<td>Matrix-shell</td>
<td>Secondary crack growth interactions, interaction between cooling-induced residual stresses</td>
<td>16, 18</td>
</tr>
</tbody>
</table>

CSR: core-shell rubber.
for use in COPVs, the requirements for an epoxy to be susceptible to the toughening mechanisms initiated by rubber modifiers are not in line with the need to use an epoxy with a similar strain-to-failure as that of carbon fiber – both elastic and plastic regions need to be present.

Acknowledgements

The authors would like to thank Tom Delay, NASA MSFC, Team Lead, Non-Metallics Manufacturing Group, for technical discussions and Doug Sober, Kaneka Texas, for supplying the MX960 CSR.

Conflict of interest

None declared.

Funding

This work was supported by the Mississippi Space Grant Consortium (11-02-045).

References


46. Jackson JR. Fracture toughness of polymer resins at cryogenic temperatures. MS Thesis, Mississippi State University, Mississippi State, MS, 2005.


