THE FRACTURE PERFORMANCE AND PARTICLE DISPERSION OF RUBBER- AND NANOSILICA PARTICLE-MODIFIED EPOXIES

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Abstract

The microstructure and fracture performance of an anhydride cured epoxy polymer modified by different combinations of preformed core-shell rubber (CSR) particles and 20 nm diameter nanosilica particles are investigated. Two types of CSR particles, with diameters of 100 nm and 300 nm, are used. A quantitative study of the dispersion of CSR particles and nanosilica particles was performed using the area disorder method, and random dispersions of the CSR particles were observed for the CSR modified epoxies. No significant influence was observed on the dispersion of CSR particles with the addition of nanosilica particles in the hybrid CSR-nanosilica modified epoxies. Nanosilica particles were also found to be randomly dispersed in the hybrid modified epoxy matrix. The fracture energy increased from 78 J/m^2 for the unmodified epoxy to 530 J/m^2 with an addition of 9 wt% of 100 nm diameter CSR particles and to 403 J/m^2 with an addition of 300 nm diameter CSR particles; this was further enhanced to 592 J/m^2 by the addition of 9 wt% of nanosilica.

1. Introduction

Epoxies are thermosetting polymers widely used as structural adhesives, coatings and matrices for fibre-reinforced composites in many engineering applications. They possess relatively high Young's modulus and strength, creep resistance, chemical resistance and high-temperature resistance. However, cured epoxies have highly cross-linked polymer networks, which make them inherently brittle. This brittleness can be overcome by the addition of a second micro-phase (e.g. soft or rigid particles), which can significantly increase the toughness of epoxies.

Phase-separating carboxyl-terminated butadiene-acrylonitrile (CTBN) particles are the most commonly used rubber particles to toughen epoxy matrices [1, 2]. More recently, toughness modification by preformed core-shell rubber (CSR) particles has also been investigated [3]. CSR particles have a soft rubber core surrounded by a hard polymer shell. The core imparts impact resistance, and polybutadiene, styrene-butadiene, siloxane and acrylic are the materials most frequently used as the core [3]. Polymethyl methacrylate (PMMA) shells are most commonly used and are compatible with the epoxy matrix.

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When compared to CSR particles, CTBN particles provide a larger toughening effect but reduce the glass transition temperature of the epoxy, while CSR particles increase the toughness of epoxy without affecting the glass transition temperature [3]. Moreover, the size of CTBN particles is dependent on the curing conditions, and therefore it is difficult to control the particle size, whereas the size of CSR particles is pre-determined and independent of the curing conditions [3]. A disadvantage of both CTBN and CSR particles is that they decrease the Young's modulus of epoxy matrices [3].

Rigid-particle toughening incorporates micron sized silica, alumina, and (more recently) nanosilica particles in epoxies [4, 5]; this has a positive effect on the toughness as well as on the Young's modulus of epoxy. Hybrid particles, i.e. combining more than one type of particle, have also been used to modify the toughness of epoxies, and detailed work has been reported for hybrid-modified epoxy with nanosilica and CTBN [5, 6]. However, little work has been reported for hybrid-modified epoxies with CSR particles and nanosilica [3], although this combination can increase the toughness of the material without reducing its Young's modulus.

The dispersion quality of nanoparticles has an influence on the properties of particle-modified materials [7]. Hence, it is important to study the dispersion of nanoparticles quantitatively and find a structure-property correlation.

The objective of the present work is to investigate experimentally the microstructure and fracture performance of an anhydride cured epoxy polymer modified by different combinations of preformed core-shell rubber particles and nanosilica particles.

2. Experimental Methods

2.1. Materials

A diglycidyl ether of bis-phenol A (DGEBA), LY556 (Huntsman, UK), epoxy resin was used. This was crosslinked using an accelerated methylhexahydrophthalic acid anhydride, Albidur HE 600 (Evonik, Germany) [8]. The epoxy equivalent weight (EEW) of the DGEBA resin was 185 g/eq. The CSR particles used in this study were MX156 with a 100 nm diameter poly-butadiene core and an 85-115 nm diameter PMMA shell, and MX960 with a 300 nm siloxane core and 250-350 nm PMMA shell (Kaneka, Belgium) [9]. The particles were supplied dispersed at 25 wt% in a DGEBA with an epoxy equivalent weight of 243 g/eq. The nanosilica particles used were Nanopox F400 (Evonik Germany); they were supplied dispersed at 40 wt% in a DGEBA resin with an epoxy equivalent weight of 295 g/eq and the mean particle diameter was 20 nm [8].

The epoxy formulations manufactured were: unmodified epoxy, epoxies modified with varying weight percentages of CSR particles, and hybrid-modified epoxies containing varying weight percentages of CSR particles and nanosilica particles, see Table 1.

The weight percentages of the tougheners were varied and the epoxy equivalent weight of the mixture was calculated. The mixture was then mechanically stirred for 15 min and degassed at 50 °C and -1 atm in a vacuum oven. A stoichiometric amount of the hardener was mixed in, stirred together for 15 min at 60 °C and degassed. The resin mixture was then poured into pre-heated steel gravity moulds and cured at 90 °C for 1 hour, then post-cured at 160 °C for 2 hours (with a ramp rate of 1 °C/min).

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Table 1. Epoxy formulations (CSR = core-shell rubber, NS = nanosilica).

		Nanosilica content, wt%				
		0	3	6	9	12
CSR content, wt%	0	unmodified	×	×	×	×
	3	3CSR	3CSR3NS	3CSR6NS	3CSR9NS	3CSR12NS
	6	6CSR	6CSR3NS	6CSR6NS	6CSR9NS	6CSR12NS
	9	9CSR	×	×	9CSR9NS	×

2.2 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) was performed to obtain the microstructures of the unmodified and modified epoxies using a MultiMode scanning probe microscope (SPM) controlled with a NanoScope IV controller and an ‘E’ scanner from Veeco, USA. A very smooth surface of cured epoxy was first prepared using a PowerTome XL cryo-microtome from RMC Products, USA. Phase images were taken to study the microstructures of the unmodified and particle modified epoxies.

2.3 Nanoparticle dispersion

Both qualitative and quantitative studies of the dispersion of nanoparticles in the epoxy matrix were performed. The quantitative study of nanoparticle dispersion was performed using the area disorder method of Bray et al. [7]. In this method, the value of a dimensionless number called the area disorder, AD (which varies between 0 and 1), determines the quality of dispersion (see Figure 1).

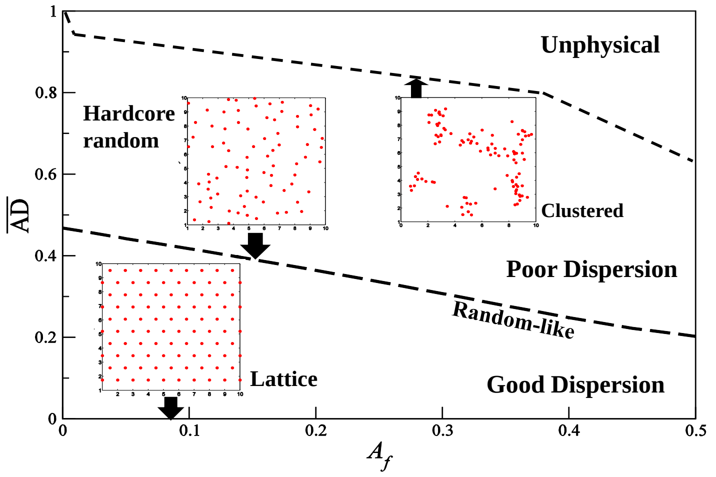

Figure 1. Classification diagram for quantifying the nanoparticle dispersion [7].

2.4. Single-edge-notch bending (SENB) test

The fracture energy, G_c, and fracture toughness, K_c, at the initiation of crack growth were determined using the single-edge-notch bending (SENB) test. The tests were conducted according to the ISO 13586 standard [10] at a displacement rate of 1 mm/min. Twelve samples, each with a size of 60 mm × 12 mm × 6 mm, were machined from 6 mm thick epoxy plates of each formulation, and a sharp pre-

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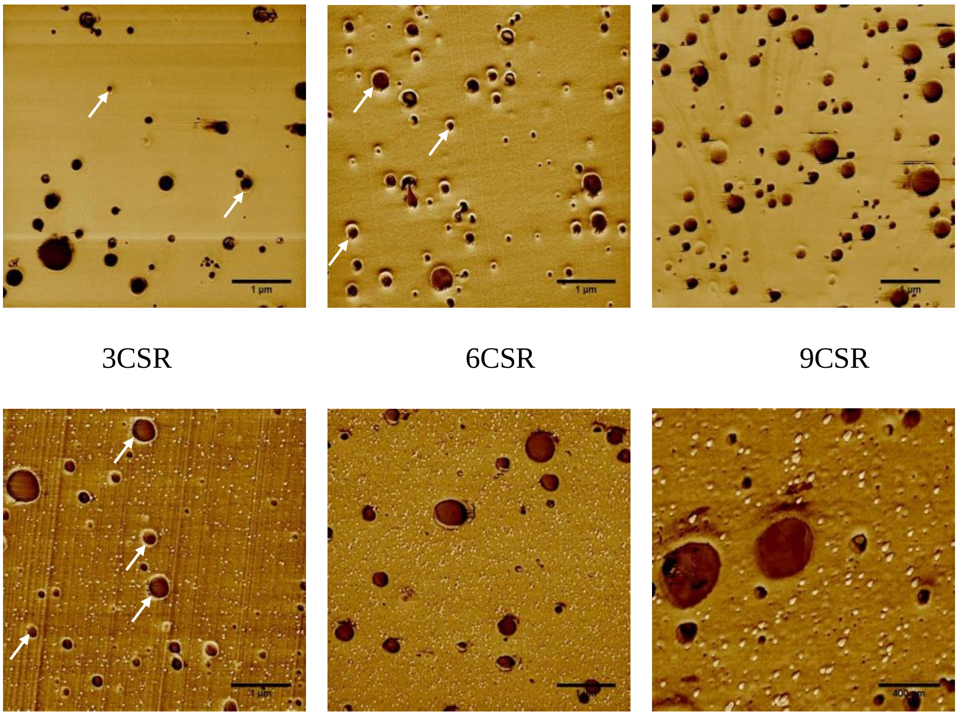
crack was introduced by tapping a liquid nitrogen cooled razor blade into the v-notch. The ratio of crack length to specimen depth was within 0.45 to 0.55.

3. Experimental results

3.1. Microstructure

The morphology of the MX960 CSR particle modified and hybrid MX960 CSR-nanosilica modified epoxies are shown in Figure 2 and those of MX156 CSR particle and hybrid MX156 CSR-nanosilica modified epoxies are shown in Figure 3.



3CSR 6CSR 9CSR

3CSR6NS 3CSR12NS 6CSR6NS

Figure 2. AFM phase images of MX960 CSR particle modified and hybrid MX960 CSR-nanosilica modified epoxies. The white arrows indicate PMMA shell of some CSR particles.

The CSR particles are softer than the epoxy matrix and appear as dark circular features in the phase images. However, the nanosilica particles are harder than the epoxy and appear as brighter dots. The harder shells of the CSR particles are visible as bright rings for some of the particles (shown with white arrows). The phase images show well dispersed CSR particles in the CSR-modified epoxies. Well dispersed CSR particles and nanosilica particles were observed for the hybrid modified epoxy matrix, though few very small regions with clustered nanosilica were found for hybrid modified epoxies (see, for instance, Figure 2 with the 6CSR6NS and Figure 3 with the 3CSR9NS and 3CSR12NS configurations).

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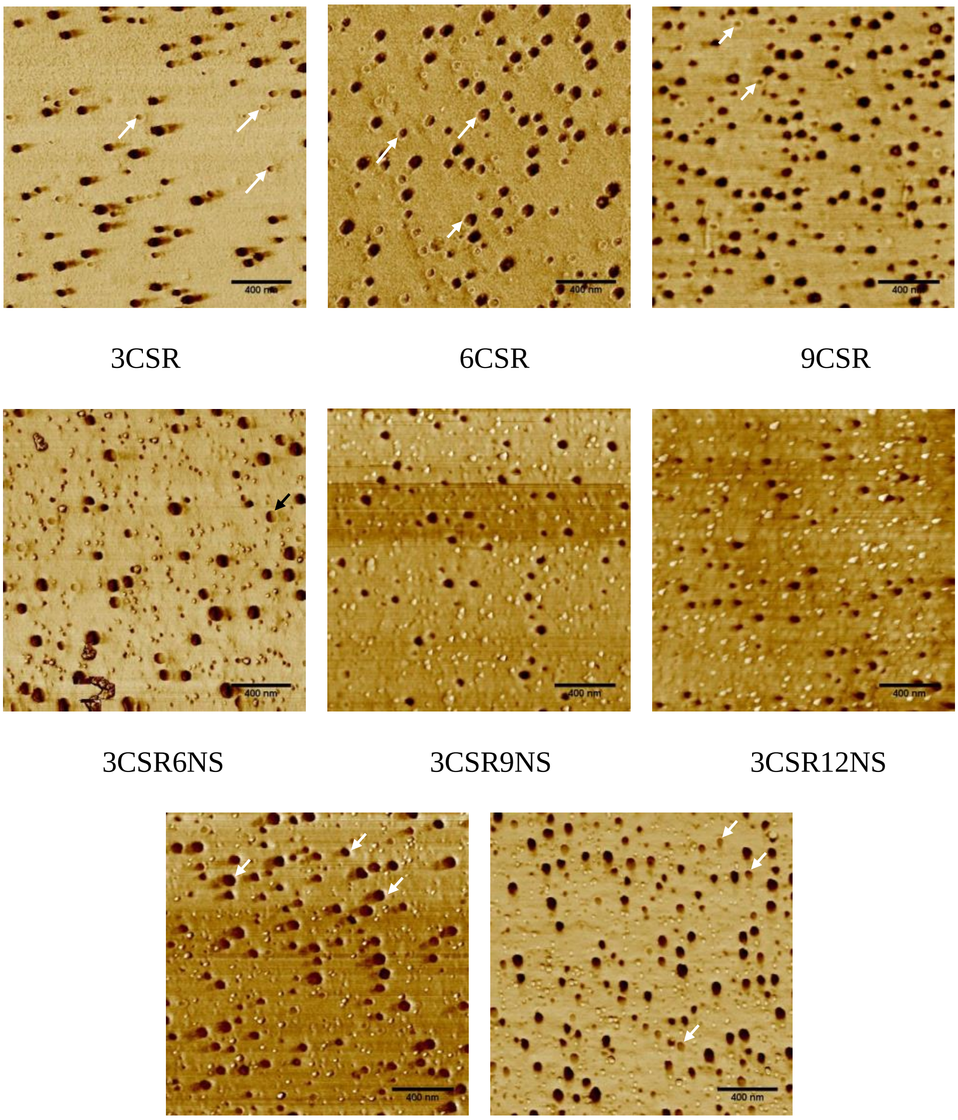

3CSR 6CSR 9CSR

3CSR6NS 3CSR9NS 3CSR12NS

6CSR6NS 9CSR9NS

Figure 3. AFM phase images of MX156 CSR particle modified and hybrid MX156 CSR-nanosilica modified epoxies. The white arrows indicate PMMA shell of some CSR particles.

The area disorder (AD) was calculated for the CSR and nanosilica particles for all the epoxies to quantify the particle dispersion. The AD is plotted as shown in Figures 4 and 5**.**

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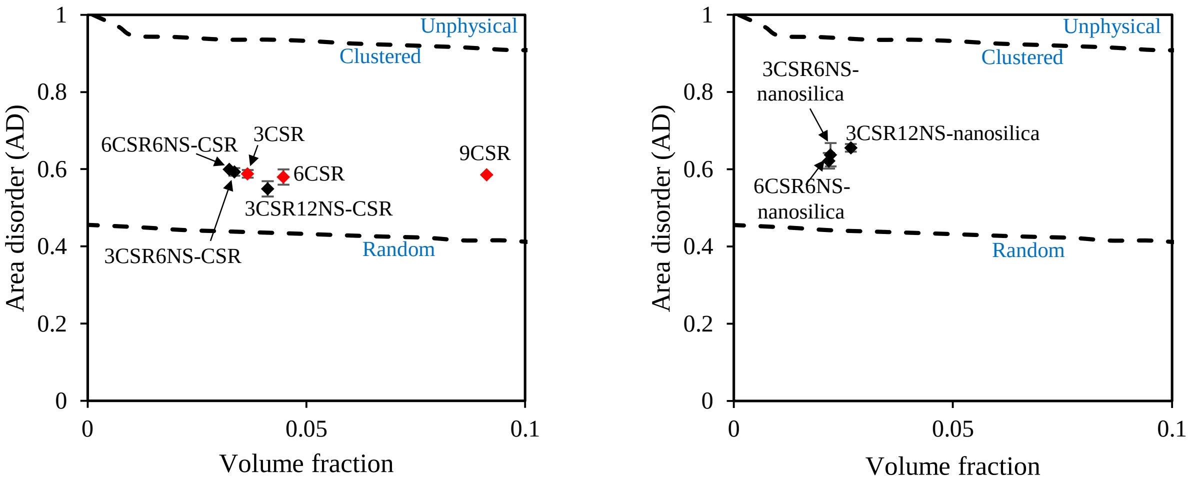
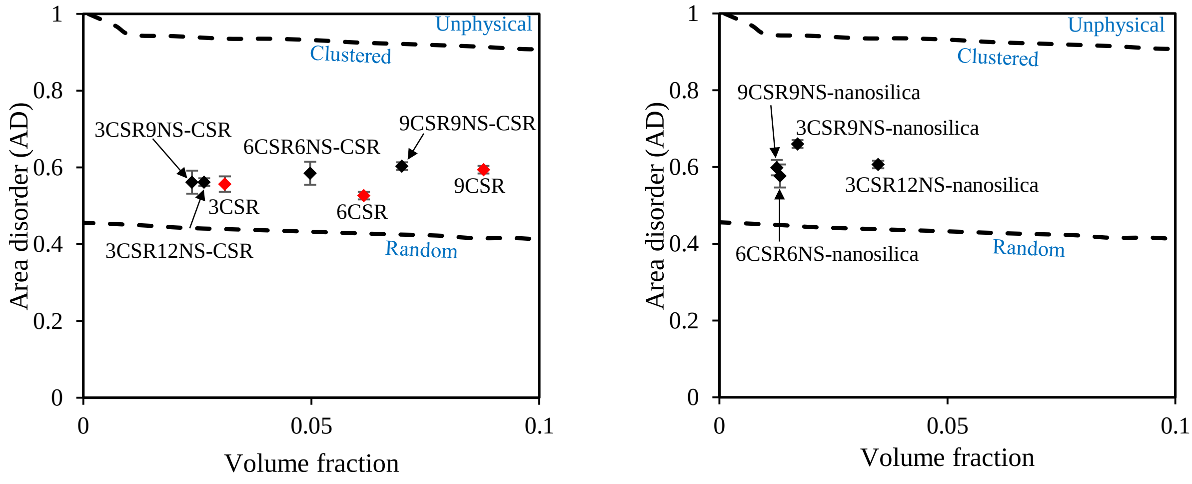


(a) (b)

Figure 4. Area disorder vs. volume fraction plot for MX960 CSR modified and hybrid MX960 CSR-nanosilica modified epoxies – (a) AD plot of CSR particle (b) AD plot of nanosilica particle.



(a) (b)

Figure 5. Area disorder vs. volume fraction plot for MX156 CSR modified and hybrid MX156 CSR-nanosilica modified epoxies – (a) AD plot of CSR particle (b) AD plot of nanosilica particle.

The AD plots indicate that the CSR particles and nanosilica particles are randomly distributed for both types of CSR (MX960 and MX156) particles and hybrid CSR-nanosilica modified epoxies. In both cases, nanosilica particles have slightly higher AD values than the CSR particles. This agrees well with the micrographs, as a few regions with slightly clustered nanosilica particles were found.

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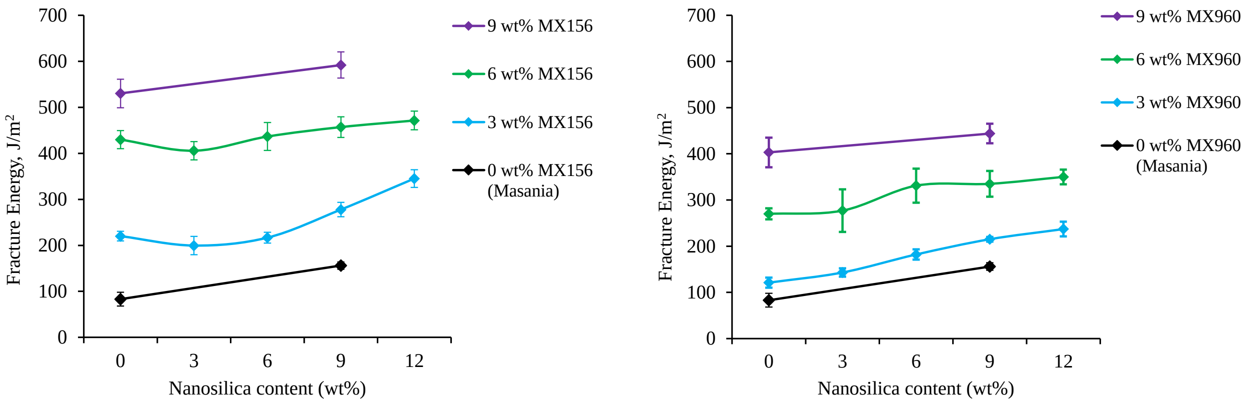
Increasing the weight percentage of the CSR particles has no significant influence on the AD values of the CSR particles for the epoxies modified with CSR particles alone. Also the weight percentage increase of nanosilica did not significantly change the AD values of CSR particles for the CSR-nanosilica hybrid modified epoxies, which is also true for the nanosilica particles with the percentage change of the CSR partciles. Hence, the dispersions of the CSR particle and nanosilica particle in the hybrid modified epoxies are independent of each other. However, the nanosilica particles were found to be clustered with the percentage increase of the CTBN particles in the hybrid CTBN-nanosilica modified epoxies [11].

3.2 Fracture energy

The fracture energy and fracture toughness measured for the unmodified epoxy are 78 J/m^2 and 0.49 MPa m$^{1/2}$ respectively, in good agreement with the 77 J/m^2 and 0.51 MPa m$^{1/2}$ reported by Giannakopoulos et al. for the same epoxy [3].

The fracture energy increases significantly with the increase of both types of CSR particle content, as shown in Figure 6. It was found that MX156 particles have slightly larger toughening effect than MX960 particles. The reasons behind this are currently being investigated.

The addition of nanosilica particles to the CSR modified epoxies further increased the fracture energy (Figure 6), meaning that the toughening effect was additive. However, no synergistic toughening effect was observed. However, for hybrid CTBN-NS modified epoxies synergistic toughening effect was observed [6], meaning that the increase in the toughness achieved with the hybrid particle was smaller than the sum of the individual toughness contribution from each particle type. For hybrid CTBN-nanosilica modified epoxies, a synergistic toughening effect was observed, i.e. the hybrid toughness exceeded the sum of the individual toughness contributions of the particles. The difference in the toughening effect obtained between the hybrid CSR-nanosilica and hybrid CTBN-nanosilica modified epoxies may be due to the difference in the microstructures, as discussed in the previous section.



(a) (b)

Figure 6. Fracture energy versus nanosilica content for (a) 3 wt%, 6 wt% and 9 wt% MX156 CSR particle-modified epoxies (b) 3 wt%, 6 wt% and 9 wt% MX960 CSR particle-modified epoxies. The fracture data for the nanosilica modified-epoxy has been obtained from Masania [6].

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4. Conclusions

An anhydride cured DGEBA epoxy has been modified using hybrid combinations of (i) 100 nm or 300 nm diameter core-shell rubber (CSR) particles and (ii) 20 nm diameter nanosilica particles, with varying weight percentages. The microstructure and fracture performance have been determined for the unmodified and modified epoxies. A quantitative study of the particle dispersion has been performed and randomly dispersed CSR particles were observed, even with the addition of up to 12 wt% of nanosilica.

The hybrid toughening effect has been investigated. The fracture toughness of the unmodified epoxy can be increased from 78 J/m^2 to 592 J/m^2 by the combination of 9 wt% of MX156 CSR particles and 9 wt% of nanosilica. Further studies will be performed to investigate the influence of dispersion quality of nanoparticles on the fracture performance of the particle modified epoxies.

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