Toughening of epoxy-based hybrid nanocomposites

D. Carolan^{a,b}, A.J. Kinloch^a, A. Ivankovic^b, S. Sprenger^c, A.C. Taylor^a

^aDepartment of Mechanical Engineering, Imperial College London, London, SW7 2AZ, UK

^bSchool of Mechanical and Materials Engineering, University College Dublin, Belfield, Dublin 4, Ireland

^cEvonik Hanse GmbH, Charlottenburger Strasse 9, 21502 Geesthacht, Germany

Abstract

The microstructure and fracture performance of an epoxy resin cured with an anhydride hardener containing silica nanoparticles and/or polysiloxane core-shell rubber nanoparticles (CSR) were investigated in the current work. The effect of adding a reactive diluent, i.e. hexanediol diglycidylether, to the epoxy resin was also investigated. The fracture energy of the neat (i.e. unmodified) epoxy polymer increased slightly from 125 J/m² to 172 J/m² due to the addition of 25 wt% of the reactive diluent to the epoxy. The fracture energy of the unmodified epoxy polymer increased to 889 J/m² when 20 wt% of the CSR nanoparticles were added to the epoxy without any reactive diluent being present. However, the results show that the increase in fracture energy due to the addition of the CSR nanoparticles particles was much more marked in the case when 25 wt% of the reactive diluent was present, e.g. an increase to 1,237 J/m² with the addition of 16 wt% of CSR nanoparticles. Furthermore, while the subsequent addition of silica nanoparticles, to give hybrid epoxy polymer nanocomposites, i.e. which contained both silica and CSR nanoparticles, produced only modest increases in the fracture energy in the case of the epoxy with the reactive diluent additive present, some synergistic effects on the toughening were noted. No significant improvements in toughness were found for the hybrid epoxy polymer nanocomposites without reactive diluent. The measured toughness of the hybrid materials can be related to the degree of dispersion of both nanoparticle phases in the epoxy polymer matrix. The toughening mechanisms were identified and the experimentally measured values of toughness were in good agreement with modelling studies.

Keywords: Epoxy polymers, Core-shell particles, silica nanoparticles, Toughening mechanisms

1. Introduction

Epoxy polymers are highly cross-linked thermosets and find use in high-performance applications such as the matrix phase of a fibre reinforced polymer or as adhesives replacing conventional joining technologies in the automotive and aerospace industries. The cross-linked nature of the epoxy dictates that they are inherently brittle. This may greatly limit their utility as a structural material due to their poor resistance to crack initiation and growth. The toughness of epoxy polymers has typically been improved by the addition of either soft rubber particles [1–5] or rigid inorganic particles [6–8], although recently toughening of epoxy polymers via a range of other materials, which can confer added functionality, such as block copolymers [9–11], graphene [12], carbon nanotubes [13, 14] and nano-clay [15] has emerged.

The addition of soft rubber particles to an epoxy resin effectively toughens the composite by a combination of matrix shear banding, particle cavitation and matrix void growth [1–3]. The rubber can be introduced to the epoxy system either by the use of reactive liquid rubbers [2, 16], that phase separate during curing of the epoxy to form small rubber particles in the polymer matrix, or via core-shell rubber (CSR) particles [5, 17–19]. However, the increases in toughness due to the addition of rubber comes at the expense of a reduction in both tensile modulus and yield strength.

For this reason, rigid inorganic fillers have also been investigated as resin toughening agents. The toughening of epoxy resins using rigid particles can increase the fracture toughness without any consequent loss in strength or stiffness. A number of toughening mechanisms have been reported in the literature including crack pinning [20] and crack-path deflection [21–23] in the case of micron-sized glass-beads. The toughening mechanisms in silica-nanoparticle modified epoxies are similar to the mechanisms observed in rubber toughened epoxies, since such materials exhibit shear banding as well as particle debonding and limited matrix void growth [24, 25]. Liang and Pearson [24]

have demonstrated that the particle size is not a critical factor for increasing the toughness when silica nanoparticles are present in epoxy polymers.

An epoxy polymer containing both inorganic rigid particles and a soft rubber phase can be developed to produce materials with increased toughness without the loss of other desirable mechanical properties. In some cases, the toughening effect can be synergistic, with the toughness of the hybrid material, which contains both inorganic rigid particles and a soft rubber phase, being greater than the additive sum of the toughness increases from each individual modifier. Sprenger [26] has recently provided a comprehensive review of the work in this field and the reader is directed to a number of references therein, e.g. [27, 28]. The exact mechanisms of the synergistic effect are not well understood but examination of the fracture surfaces reveal that the fundamental toughening mechanisms appear to be the same as in the non-hybrid materials.

2. Materials and Methods

2.1. Materials

An anhydride-cured epoxy system formed the basis of all the materials investigated in the current work. The resin was a standard diglycidyl ether of bisphenol-A (DGEBA) with an epoxide equivalent weight of 185 g/eq, (Araldite LY556) supplied by Huntsman, UK. This was cured with a stoichiometric amount of an accelerated methylhexahydrophthalic acid anhydride (Albidur HE600) from Evonik Hanse, Germany. In order to examine the role of a reactive diluent on the mechanical properties of the composite a number of formulations were examined using a 3:1 ratio of the DGEBA resin and a reactive diluent, namely hexanediol diglycidylether (HDDGE, DER 734) from Dow Chemicals, Germany. The reactive diluent lowers the viscosity of the epoxy resin which improves the ease of processing in various applications. The silica, SiO_2 , nanoparticles were obtained at 40 wt% in DGEBA, (Nanopox F400, Evonik Hanse), while the CSR particles were also obtained at 40 wt% in DGEBA (Albidur EP2240A, Evonik Hanse). The CSR particles consisted of a polysiloxane core with a glass transition temperature, T_g , of approximately -100°C . The density of the silica nanoparticles was calculated as $1,800 \text{ kg/m}^3$ while that of the CSR nanoparticles was 990 kg/m^3 . Twenty five different formulations in all were prepared with different weight percentages of silica and CSR nanoparticles. Of these

formulations, ten were fabricated without any reactive diluent, while the remainder were manufactured using the 3:1 ratio of DGEBA to reactive diluent. Bulk plates were cast by pouring the resin mixture into heated steel moulds to give either 3 mm or 6 mm thick plates. All formulations were cured at 90°C for one hour with a post cure at 160°C for an additional two hours.

2.2. Dynamic-mechanical thermal analysis

The glass transition temperature, T_g of each polymer nanocomposite was measured using dynamic mechanical thermal analysis. A Q800 DMA from TA instruments was used in a double cantilever mode at a frequency of 1 Hz. A sample size of 60 mm $\times$ 10 mm $\times$ 3 mm was used, taking special care to ensure that all sides were parallel. The temperature range employed was between -100°C and 200°C and the heating rate was 2°C/min. The value of T_g was determined as the location of the peak of the $\tan(\delta)$ curve. The number average molecular weight between crosslinks was calculated from the equilibrium modulus, E_r , in the rubbery region using [29]:

$$M_{nc} = \frac{q\rho RT}{E_r} \quad (1)$$

where T is the temperature in Kelvin at which the value of E_r was taken, ρ is the density of the polymer at temperature T , R is the universal gas constant and q is the front factor (taken as 0.725 from previous work [19]). The densities of the epoxy polymers without and with HDDGE were calculated as 1,127 kg/m³ and 936 kg/m³ respectively at room temperature.

2.3. Microscopy

Microscopically smooth surfaces of each polymer were prepared using an ultramicrotome (RMC Products, USA). These surfaces were then examined using an atomic force microscope to determine the morphology of the material. The surface was scanned using a silicon probe at a scan rate of 1 Hz. Both height and phase images were obtained, which clearly defined the morphology of the nanostructures.

A field-emission gun scanning-electron microscope (FEGSEM) was used to investigate the fracture surfaces. Fracture surfaces were sputter-coated with a 5 nm Au-Pd coating to prevent the build-up of electrical charge in the material.

2.4. Mechanical properties

Tensile tests were conducted on the unmodified epoxy polymers and the nanocomposite formulations to determine the uniaxial tensile stress versus strain curves in accordance with ISO 527 [30]. Dumbbell specimens with a gauge length of 30 mm were machined directly from 3 mm cast plates. The tests were carried out at a constant crosshead displacement rate of 1mm/min. A clip-gauge extensometer was utilised to directly measure the strain in the test specimen. At least five replicates tests for each formulation were carried out to study the repeatability of the results.

Plane-strain compression (PSC) tests were carried out as described by Williams and Ford [31] on polished test specimens of size 40 mm $\times$ 40 mm $\times$ 3 mm. From this test the compressive yield stress, σ_{yc} , and failure strain, γ_f , can be ascertained. The test specimens were loaded in compression between two parallel dies at a constant crosshead displacement rate of 0.1 mm/min. Care was taken to ensure that the effect of load-loop compliance was corrected for.

2.5. Fracture toughness

Single-edge notched bending (SENB) tests in three-point bend configuration were conducted to determine the plane-strain fracture toughness, K_{Ic} , and fracture energy, G_{Ic} , in accordance with ISO-13586 [32]. Test specimens of dimensions 60 mm $\times$ 12 mm $\times$ 6 mm were machined from the cast plates. These specimens were pre-notched to a depth of 4 mm before subsequent tapping of the notch to produce a sharp crack to a depth of $\approx$ 6 mm using a liquid nitrogen chilled razor blade. Testing was conducted using a screw-driven universal testing machine at a constant crosshead displacement rate of 1 mm/min. The fracture toughness was calculated via:

$$K_{Ic} = \frac{P}{bw^{3/2}} f(\alpha) \quad (2)$$

Where P is the load at failure, b and w are the sample thickness and width, respectively, and $f(a)$ is a geometric constant. The fracture energy, G_{Ic} was calculated using the relationship between G_{Ic} , K_{Ic} , the tensile modulus, E_t , and the Poisson's ratio, ν :

$$G_{Ic} = \frac{K_{Ic}^2}{E_t} (1 - \nu^2) \quad (3)$$

where the value of ν was taken to be 0.35. At least eight replicate specimens were tested for each formulation.

3. Results and discussion

3.1. Morphology

Figure 1 shows typical AFM micrographs of the polymer nanocomposites investigated in the current work. It can be clearly seen that, in the absence of HDDGE, (i.e. Figure 1 (a) and (b)) significant clustering of both the silica and CSR nanoparticles occurs in the hybrid-modified DGEBA epoxy polymer matrix. Hsieh et al. [25] have also noted agglomeration of silica nanoparticles in the presence of carboxyl-terminated butadiene-acrylonitrile (CTBN) and amine-terminated butadiene-acrylonitrile (ATBN) rubber particles. They noted that the silica nanoparticles clustered in loose necklace-like agglomerates, whereas in the current study the agglomerations appear to form clusters around the CSR particles, and some clustering of the CSR particles themselves occurs. The CTBN and ATBN used in the previous studies were reactive liquid rubbers that phase separate upon curing, whereas in the current study the preformed CSR particles are already present in the epoxy formulation. This may explain the differences in clustering behaviour between the current study and the previous work.

It is notable that the addition of 25 wt% of HDDGE (see Figure 1 (d)) completely prevented the clustering of the silica and CSR nanoparticles, and a mutually well dispersed system was observed. The dispersion of the CSR particles in the hybrid system with HDDGE (Figure 1 (d)) can be easily compared to the dispersion of CSR particles without silica nanoparticles by comparison with Figure 1 (c). The CSR particles appear similarly dispersed in both cases. Finally, it can be seen that a wide range of CSR particle diameters can be observed on the typical AFM images. Indeed, a careful

examination of the AFM images yielded a size distribution of CSR particles that is best described by a lognormal distribution with a mean particle diameter of 0.16 μm and with a standard deviation of $\pm 0.08 \mu\text{m}$. The silica nanoparticles used in the current work have a mean diameter of 20 nm [25].

3.2. Thermal properties

It can be seen in Figure 2 that the addition of the 25wt% of HDDGE to the epoxy resin significantly reduces the glass transition temperature, T_g , from 157°C to 127°C. The addition of silica nanoparticles was found to have no further significant effect on T_g . This is to be expected as the addition of the HDDGE reduces the crosslink density of the epoxy polymer and is in agreement with similar results reported by other authors [24, 25, 33, 34]. Indeed, the average molecular weight, M_{nc} , between crosslinks for the epoxy polymers without and with diluent were calculated from Equation (1) as 314 g/mol and 370 g/mol, respectively. Furthermore, the addition of CSR particles were also found not to affect T_g . This demonstrates that the CSR remains phase-separated throughout the curing process and agrees with the findings of Chen et al. [19].

3.3. Tensile properties

3.3.1. Two-phase nanocomposites

An elastic modulus of 3.12 ± 0.06 GPa was measured for the unmodified epoxy polymer at room temperature. The addition of HDDGE reduced the modulus of the epoxy to 2.93 ± 0.12 GPa, again as would be expected. The addition of rubber particles caused the modulus to decrease for both base formulations, while the addition of the high-modulus silica nanoparticles led to an increase in the measured elastic modulus. Thus, a maximum elastic modulus of 4.03 ± 0.10 GPa was measured for the DGEBA system containing 20 wt% silica nanoparticles, while a minimum value of Young's modulus of 1.92 ± 0.04 GPa was measured when 16 wt% of CSR nanoparticles were added to the DGEBA:HDDGE system. As might be expected, the effect of adding both silica and rubber particles to the epoxy on the composite elastic modulus was found to depend on the relative quantities of each nano-reinforcement added.

The experimentally measured elastic moduli of these nanocomposites can be compared to predictions from existing theoretical models. A large number of models exist that can be

applied to predict the elastic modulus of a particulate-filled composite. These can be divided into empirically-based models, such as the Halpin-Tsai [35] and Lewis-Nielsen [36] model, and micro-mechanically derived models, such as the Mori-Tanaka [37] and Lielens et al. [38] models. In the current work, only the Halpin-Tsai and Mori-Tanaka models were used, as these are the most widely used models in the literature.

The Halpin-Tsai model is a semi-empirical model that allows the calculation of the Young's modulus of a composite, given the properties of the constituent phases [36]. The composite tensile elastic modulus, E_t , of a reinforced polymer can be calculated as a function of the modulus of the matrix, E_m , the modulus of the reinforcing phase, E_f , and the volume fraction of the reinforcing phase, V_f , such that:

$$E_t = \frac{1 + \zeta \eta V_f}{1 - \eta V_f} E_m \quad (4)$$

where ζ is a shape factor that describes the effect of the particulate geometry on the composite, and where:

$$\eta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \zeta} \quad (5)$$

The shape factor, ζ has no direct physical significance, which is one of the major criticisms of this model. However, Halpin and Kardos [39] recommend a shape factor of $\zeta = 2$ for spherical particles, which is used for all the present predictions of the moduli of the nanocomposites.

The Mori-Tanaka approach is a micromechanics-based approach that uses the Eshelby tensor to determine the Young's modulus of a composite [37, 40, 41]. Using this approach, the ratio of the bulk modulus, K , and shear modulus, G , of a composite to that of the matrix moduli, K_m and G_m can be expressed as:

$$\frac{K}{K_m} = \frac{1}{1 + V_f p} \quad \frac{G}{G_m} = \frac{1}{1 + V_f q} \quad (6)$$

where p and q are parameters derived from the Eshelby tensor and defined by Tandon and Weng [41]. The tensile elastic modulus can then be easily calculated using the standard relationships of linear elasticity.

Figure 3 plots a comparison of the theoretical predictions using both the Halpin-Tsai and Mori-Tanaka models together with the experimental results. For the purposes of modelling predictions, the Young's modulus of the silica nanoparticles was assumed to be 70 GPa with a Poisson's ratio of 0.25 [42]. The Poisson's ratio of the CSR nanoparticles was taken as 0.499 with a Young's modulus of 0.01 GPa [42]. It can be clearly seen that the Mori-Tanaka prediction is significantly better than the Halpin-Tsai prediction when the addition of silica nanoparticles is considered. However, both the Mori-Tanaka and Halpin-Tsai models accurately predict the measured reduction in elastic modulus upon the addition of CSR nanoparticles.

3.3.2. Three-phase (i.e. hybrid) nanocomposites

In order to predict the elastic moduli of the hybrid formulations containing both silica and CSR nanoparticles, a two-stage homogenisation procedure must be employed. One such approach is considered in the current work and consists of the 'cascaded application of a standard two-phase homogenisation procedure'. This approach is a simplification of the method described by Pierard et al. [43] who also considered the effects of the aspect ratio and the orientation of the inclusions in their analysis. For the purposes of this work, it is sufficient to consider a system of unit volume, containing a matrix with a volume fraction, v_m , and two types of spherical inclusions, with volume fractions, v_1 and v_2 respectively. The first homogenisation step decomposes the system in an arbitrary set of regions, A and B , such that each region contains only one inclusion type and matrix with volume fractions of $(1 - v_m)$ and v_m respectively. Each region can then be homogenised using any of the two-phase approaches described above. By the conservation of volume, the problem is now reduced to that of a composite of the two regions, A and B , in the composite with volume fractions of $v_A = v_1/(1 - v_m)$ and $v_B = v_2/(1 - v_m)$ respectively. The predicted moduli for the hybrid formulation investigated in the current work are summarised in Table 1. There is very good agreement between the experimentally measured moduli, E_{exp} , and the predicted moduli, E_{pred} , using this approach.

3.4. Compressive properties

Typical true stress versus true strain relationships calculated from the plane-strain compression tests are given in Figure 4. In general, the plane-strain compression tests indicated a definite yield stress followed by a strain-softening region. Finally, a strain - hardening region was noted up to final failure at a failure strain, γ_f . The failure strain of the neat epoxy polymer without HDDGE was measured as 0.74 with an increase to 0.89 noted with the addition of HDDGE. The addition of rubber particles reduced the compressive yield stress, σ_{yc} , for each polymer. Furthermore, the addition of rubber nanoparticles suppressed the amount of post-yield strain-softening, as measured by the maximum reduction in the stress after the initial yield point. It is of interest to note in Figure 4 that the addition of silica nanoparticles increased the compressive yield stress for the unmodified epoxy polymer without HDDGE present. A compressive yield stress of 104 MPa was measured for the unmodified DGEBA polymer, rising to 111 MPa when 20 wt% silica nanoparticles were added. However, for the DGEBA:HDDGE polymer both the yield stress and subsequent strain softening behaviour were unaffected by the addition of silica nanoparticles, with a value of $\sigma_{yc} = 94$ MPa measured for all the polymers modified with silica nanoparticles. Similar behaviour of the compressive yield stress of an epoxy polymer containing silica nanoparticles has been previously reported by Liang and Pearson [24] and also by Zhang et al. [44]. Hsieh et al. examined the formation of shear bands for similar systems and found evidence of shear banding for all the formulations which strain-softened [25].

3.5 Fracture properties

The fracture energy, G_{Ic} , for both DGEBA and DGEBA:HDDGE polymers modified with either silica or CSR nanoparticles is given in Figure 5, while the fracture energies for the hybrid polymers is given in Figure 6. A mean fracture energy of 125 ± 36 J/m² was measured for the unmodified DGEBA epoxy polymer which compares well to previous work on this polymer [19, 45]. The addition of HDDGE to the polymer system increased this value slightly to 173 ± 33 J/m².

A moderate increase in the fracture energy is observed upon the addition of silica nanoparticles, although the addition of HDDGE to the DGEBA system tends to mitigate the toughening effect, see Figure 5 (a). A substantial linear increase in toughness is noted for the addition of CSR nanoparticles, see Figure 5 (b); with an enhanced toughening effect noted for the DGEBA:HDDGE polymer (i.e. an increase in G_{Ic} of $\approx 67 \text{ J/m}^2$ per wt % of CSR added) compared to the DGEBA polymer (i.e. only an increase of $\approx 39 \text{ J/m}^2$ per wt% of CSR added). Now, both Liang and Pearson [24] and Kinloch et al. [46] have noted that the ‘toughenability’ of epoxy polymers is enhanced with a reduction in the crosslink density and the addition of either silica nanoparticles or rubber particles. Also, Pearson and Yee [47] have reported that the fracture energy of the unmodified epoxy was largely independent of crosslink density but that the fracture energies of the modified polymers were highly dependent on the crosslink density. In the present work the addition of HDDGE to the simple epoxy-resin formulation somewhat reduces the crosslink density of the resin, as shown in Section 3.2. Thus, the enhanced toughening effect, which is seen in the case of CSR particles upon the addition of HDDGE may therefore be attributed to the reduction in crosslink density of the matrix resin. Since, the reduction in crosslink density manifests as a higher strain to failure in the neat (i.e. unmodified) resin. However, in the case of the polymers modified with silica nanoparticles, the addition of the HDDGE reactive diluent does not enhance the ‘toughenability’ of the nanocomposites. These observations are discussed in further detail below.

For the hybrid formulations, it can be observed from Figure 6 that the toughening effect when CSR nanoparticles are added to the epoxy polymer with no HDDGE present is somewhat lost with the subsequent addition of a small loading of silica nanoparticles, to form a hybrid nanocomposite. Indeed, a drop in toughness is noted when 5 wt% silica nanoparticles are added to a CSR-epoxy polymer system. As the loading of silica nanoparticles is increased, some recovery of the toughness to the CSR-only values is observed, but the toughening of the hybrid polymers is still significantly less than the additive effect of both nanoparticles. In contrast, the toughening effect of the hybrid formulations based on the epoxy polymers with 25 wt% of HDDGE present is markedly different. At 2 wt% CSR the toughness of the hybrid nanocomposite polymers mirrors

that of the CSR systems and no synergistic effect is observed. Above 2 wt% of CSR added particles however some synergy (up to 200 J/m²) is noted for the hybrid nanocomposite polymers, especially at higher silica nanoparticle loadings. The toughest hybrid system investigated in the current work was a DGEBA:HDDGE polymer containing 8 wt% silica nanoparticles and 8 wt% CSR nanoparticles and this nanocomposite had an experimentally determined toughness of 1,217±63 J/m². This represents an almost 900% increase over the unmodified epoxy. This value compares reasonably well with that of the toughest non-hybrid system measured in the current work, namely the DGEBA:HDDGE polymer with 16 wt% CSR nanoparticles which possessed a toughness of 1,237±118 J/m². The measured and expected fracture energies based on a purely additive effect are summarised in Table 2. (The purely additive effect is calculated by considering the toughening due to silica nanoparticles alone and the toughening effect due to CSR nanoparticles alone in the epoxy matrix and summing these two individual contributions.)

3.5.1. Fractography

The fracture surfaces of the silica nanoparticle modified epoxy polymer with no HDDGE present is shown in Figure 7. It can be seen that there are regions where the silica nanoparticle has debonded from the matrix and a void has formed, but also that not all the silica nanoparticles have debonded. A quantitative examination of the fracture surfaces using high resolution scanning electron microscopy revealed that approximately 15% of the silica nanoparticles (i.e. the bright spots in Figure 7) have debonded to form voids (i.e. the dark spots in Figure 7). The question of whether a particle has debonded or not to form a cavity on an image of a fracture surface is often subjective. However the results of the current work are in good agreement with the experimental findings of Hsieh et al. [25] who conducted an extensive ‘blind study’ amongst the authors of that work to verify the debond percentage against the subjectivity of the individual scientists and found that 15±5% of silica nanoparticles debonded from this epoxy polymer, and that this value was independent of the wt% of added silica nanoparticles. It is noteworthy that no debonding of the silica nanoparticles was detected for any of the DGEBA:HDDGE nanocomposite polymers.

The fracture surfaces of the CSR modified polymers, both with and without the addition of 25wt% of HDDGE, show significant crack branching and feathering and appear significantly rougher than the fracture surfaces of either the neat (i.e. unmodified) epoxy polymers or the silica nanoparticle modified polymers, see Figure 8 (a) and Figure 9 (a). The voids on the fracture surface appear to be well dispersed. The diameters of the cavitated particles are significantly larger than the corresponding diameters measured from the AFM images in Section 3.1. This indicates that void growth has taken place during the fracture event and this is well established as one of the main toughening mechanisms in rubber-toughened epoxy polymers.

A closer investigation of the fracture surfaces of the hybrid polymers yields significant differences between the DGEBA and DGEBA:HDDGE polymers. A typical fracture surface for a DGEBA hybrid polymer is given in Figure 8 (b). Unlike the non-hybrid polymer systems, the microstructure of the fracture surface is characterised by clustered islands of voids from the CSR particles and still bonded silica nanoparticles surrounded by a ‘sea’ of epoxy matrix polymer. The lack of a well dispersed microstructure accounts for the relatively low fracture energies observed for the hybrid polymers without the addition of HDDGE, see Figure 6. A major reason for this is that there is insufficient polymer matrix between particles within the agglomerates to allow any dissipative toughening mechanisms to take place.

It should be noted that Bagheri and Pearson [48] have demonstrated the possibility of obtaining improved toughnesses via agglomeration of nanoparticles. However, it must be noted that in their case a connected morphology of particle-rich regions was required to improve the nanocomposite toughness. In the current work, there is no indication that such a connected morphology was present. It is also likely that, in the present nanocomposites, the very high density of silica nanoparticles clustering around the CSR particles embrittles the matrix, thus reducing the effectiveness of typical rubber-toughening mechanisms. Conversely, the addition of HDDGE to the DGEBA formulation appears to alleviate the clustering issue for the hybrid polymers, since in Figure 9 (b) both the silica and CSR nanoparticles are very well dispersed throughout the epoxy nanocomposite, although no debonding of the silica particles was observed.

3.5.2. The Huang-Kinloch model

Huang and Kinloch have proposed a model stating that the fracture energy of a nanocomposite, G_C , can be expressed as a sum of the fracture energy of the unmodified resin, G_{CU} plus the toughening contributions from the nanoparticles, ψ [49, 50], such that:

$$G_C = G_{CU} + \psi \quad (7)$$

The term ψ contains the toughening contributions from all of the different toughening mechanisms. Previous work [24, 18] has identified localised plastic shear banding and plastic void growth as the main toughening mechanisms. Thus, ψ can be separated as:

$$\psi = \Delta G_s + \Delta G_v \quad (8)$$

where ΔG_s and ΔG_v represent the contributions from localised shear banding and plastic void growth, respectively. The energy contribution for shear-band yielding, ΔG_s initiated by the particles is given by:

$$\Delta G_s = 0.5V_p\sigma_{yc}\gamma_f F'(r_y) \quad (9)$$

where V_p is the volume fraction of particles, σ_{yc} is the compressive yield stress of the matrix measured from the plane strain compression test, γ_f is the true fracture strain of the polymer without particle addition also measured from the plane-strain compression test and $F'(r_y)$ is a polynomial function depending on the particle radius, r_p , as well as V_p and r_y [24, 51]. The value of r_y can be calculated from:

$$r_y = K_{vm}^2 \left(1 + \frac{\mu_m}{\sqrt{3}} \right)^2 r_{yu} \quad (10)$$

where K_{vm} is the maximum stress concentration factor in the polymer as calculated by the Huang-Kinloch model [49], μ_m is the pressure sensitivity coefficient of the epoxy ($\mu_m = 0.240$ and 0.225 for the DGEBA and DGEBA:HDDGE polymers respectively) [52]. Finally, r_{yu} is the classical Irwin prediction of the radius of the damage zone under plane-strain conditions [53].

$$r_{yu} = \frac{1}{6\pi} \frac{EG_c}{(1-\nu^2)\sigma_y^2} \quad (11)$$

where σ_y is the tensile yield stress of the polymer. The contribution of plastic void growth to the toughening, ΔG_v , is given as:

$$\Delta G_v = \left(1 - \frac{\mu_m^2}{3}\right) (V_v - V_p) \sigma_y r_y K_{vm}^2 \quad (12)$$

where V_v is the volume fraction of voids and the other terms have all been previously described. Liang and Pearson [24] have shown that $(V_v - V_p)$ is correctly given as:

$$(V_v - V_p) = \left(\frac{v_v}{v_v + v_m} - \frac{v_p}{v_p + v_m} \right) \quad (13)$$

where v_v is the volume of a single void, v_p is the volume of a single particle and v_m is the volume of the matrix, which remains constant throughout the fracture process and is calculated as: $v_m = v_p / (V_p - V_p)$. This analysis assumes that all of the particles create voids via either debonding or cavitation. In the case where not all of the particles contribute to void growth, then the actual toughness contribution from void growth will be $f\Delta G_v$, where f is the number fraction of particles which have undergone void growth during the fracture event.

3.5.3. Toughening with silica nanoparticles

Due to the inherent uncertainty in accurately measuring the diameter of a void caused by the debonding of an extremely small particle, even at very high magnification, a predictive approach was adopted, whereby the void was assumed to grow until the failure strain of the epoxy, was reached. The radius of the void, r_v , can then be expressed in terms of the particle radius, r_p and the matrix failure strain, γ_f , as:

$$r_v = r_p (1 + \gamma_f) \quad (14)$$

Figure 10 compares the predicted G_{Ic} values to the experimentally determined values. It may be recalled that the fraction of voided silica particles, f , was approximately 15 % for the DGEBA polymers, while for the DGEBA:HDDGE polymers, no particle debonding was observed and thus $\Delta G_v = 0$ for this case. There is very good agreement between the

predicted and experimental values for the DGEBA polymers. However, the agreement for the DGEBA:HDDGE polymers is not as good, in that a significant over-prediction is observed for intermediate particle loadings.

3.5.4. Role of diluent on morphology and debonding of silica nanoparticles

A central question that arises from the present work is why the addition of HDDGE to the hybrid completely negates the agglomeration of the CSR and silica nanoparticles, which is observed when the reactive diluent, HDDGE, is not present in the epoxy formulation. The agglomeration of both the silica and CSR nanoparticles in the case of the epoxy polymer with no HDDGE indicates that there is a chemical affinity between these particles. Now, the silica nanoparticles used are partially grafted with silanes [54] and the CSR particles consist of a silicone rubber core with a relatively thin skin, rather than a shell [55]. It is therefore not unreasonable to suppose an interaction between the chemically-similar surfaces of the silica nanoparticles and the methyl-siloxane molecules in the two types of nanoparticles. This would explain the nanoparticle clustering that is observed in the absence of HDDGE.

The HDDGE molecule is small and flexible with a similar structure to the silanes grafted to the silica particles. Hence, addition of this reactive diluent to the hybrid systems might well replace the interactions between the CSR and silica nanoparticles by forming an interphase around the silica nanoparticles. This would then lead to a good dispersion of both types of nanoparticles in the hybrid epoxy polymers containing HDDGE, as shown in Figure 1. Furthermore, this interphase would be expected to have a relatively high content of the reactive diluent, HDDGE, compared to the DGEBA epoxy. Hence, the presence of the interphase around the silica nanoparticles would lead to a local decrease in the stiffness around each silica nanoparticle, i.e. the interphase is softer than the epoxy matrix as HDDGE is a much more flexible molecule than the crosslinked DGEBA molecules.

Now, Zhang et al. [44] have suggested that the formation of an interphase with a thickness in the range of the radius of the silica nanoparticle would greatly influence the behaviour of the overall nanocomposite. Zappolorto et al. [56] have demonstrated analytically that, once the interphase region becomes significantly softer than the matrix,

both the interfacial stress at the particle surface and the stress within the particle itself is reduced.

Now, the resulting reduction in the local dilatational stress around the particle due to the presence of the soft interphase would inhibit the process of particle debonding, since debonding of the silica nanoparticles is governed by the dilatational stress. This lack of debonding is exactly what is observed for the silica nanoparticles in the epoxy polymer containing the HDDGE reactive diluent. Whilst, on the other hand, about 15% do debond during the fracture process when they are present in the epoxy polymer with no HDDGE present, i.e. when no interphase is to be expected formed around the silica nanoparticles.

3.5.5. Statistical treatment of CSR void growth

The CSR particles and voids have a lognormal distribution as measured from both the AFM and SEM images. A conventional approach to measure void growth is to measure a large number of particles from a set of suitable AFM or SEM images and subsequently measure a large number of voids on the SEM fracture surfaces. The mean value of these measurements is then taken as the average particle and void diameters, respectively. However this approach does not take account of any differences in the underlying distribution of particle and void diameters. A direct comparison of two complex size distributions cannot be adequately described by simply comparing a single descriptive parameter. Consequently, an underestimation of the predicted toughening effect due to void growth can occur. The second approach, which renders the Huang-Kinloch model truly predictive, assumes that the voids can grow until the failure strain is reached, Equation (14). To overcome the limitation of simply taking the mean value of both particle and void size and also to check the validity of the predictive approach, it is necessary to consider the entire distribution of measured particle and void sizes.

Lognormal distributions are often found to closely approximate the particle size distribution of many nano-modifiers [57, 58]. A lognormal distribution has multiplicative reproductive properties. The product or quotient of two lognormal distributions is also a lognormal distribution with easily calculated scale and shape parameters. More specifically, if D_v and D_p are two lognormally distributed variables, representing the void and particle diameters and defined by the scale and shape parameters (μ_v, σ_v^2) and $(\mu_p,$

σ_p^2), then the distribution of the quotient, $Z = D_v/D_p$, is also lognormally distributed with scale and shape parameters [59]:

$$\begin{aligned}\mu_Z &= \mu_v - \mu_p \\ \sigma_Z^2 &= \sigma_v^2 + \sigma_p^2 - 2\rho\mu_v\mu_p\end{aligned}\tag{15}$$

Where ρ is the correlation coefficient between the variables D_v and D_p . A value of $\rho = 1$ implies that there is a perfect positive correlation between the two variables, while $\rho = 0$ dictates that no correlation exists between the two variables. A negative value of correlation coefficient implies that there is an inverse linear relationship between the two variables. The mean value of the quotient, Z_{mean} , can then be calculated via:

$$Z_{mean} = \frac{D_v}{D_p} = \frac{r_v}{r_p} = \exp\left(\mu_Z + \frac{\sigma_Z^2}{2}\right)\tag{16}$$

Physically, a negative linear dependency between the measured particle and void diameters would not be expected. Intuitively, any void in a fracture surface should always be larger than the corresponding particle before fracture. Therefore, it seems reasonable to suggest that limits of $0 < \rho < 1$ would provide some bounds on the accurate measurement of void growth during a fracture process.

Figure 11 plots the toughness of the epoxy formulations as a function of the wt% of CSR nanoparticles. It can be seen that the widely used mean value approach to calculating the extant of void growth can indeed underestimate the toughening effect of adding CSR nanoparticles to the epoxy polymer containing silica nanoparticles. This is the case for the epoxy polymers with and without HDDGE present. Furthermore, the predictions of the mean value approach lie close to the lower-bound, i.e. $\rho = 1$, predictions when a direct correlation between the distribution measured particle and void diameters is assumed. Figure 12 plots the cumulative distributions of the experimentally measured particle and void diameters for a typical formulation. It can be seen that there is not a significant linear dependency of the measured void diameters on the measured particle diameters. For a perfect linear correlation, i.e. $\rho = 1$, the experimentally measured void distribution should be parallel to the measured particle distribution. The change in slope between both

distributions implies that there is a variation in the extent of void growth on the fracture surface.

The use of the strain to failure, γ_f , to calculate void growth in the Huang-Kinloch model calculated from the plane-strain compression test appears to accurately predict the toughening effect. These experimental values are also found to lie close to the $\rho = 0$ upper-bound indicating that, experimentally, there is a low linear-dependency between the measured void diameters and the measured particle diameters. In addition, the correlation coefficient, ρ , for each of the epoxy polymer nanocomposites examined was directly calculated using the measured data and was found in all case to be very close to zero. The experimental results presented in the preceding section appear to provide a justification for the use of γ_f as the input parameter to a predictive Huang-Kinloch model, rather than having resorting to tedious post-mortem calculations of the void growth from images of the fracture surface. At the very least, a statistical approach to measuring void growth gives some upper- and lower-bounds of toughening predictions using the Huang-Kinloch model.

4. Conclusions

The mechanical and fracture properties of epoxy polymer nanocomposites containing silica nanoparticles and/or polysiloxane core-shell rubber (CSR) nanoparticles have been studied. The effect on these properties of adding a reactive diluent, i.e. hexanediol diglycidylether (HDDGE), to the epoxy (DGEBA) resin was also investigated. A number of conclusions can be drawn from the current work.

The Young's modulus of the epoxy polymer nanocomposites was found to increase with increasing volume fraction of silica nanoparticles and decrease with increasing volume fraction of CSR nanoparticles. The elastic properties of the nanocomposites were accurately predicted using classic homogenisation models from the literature and a three-phase predictive model was found to accurately predict the Young's moduli of the hybrid nanocomposites, which contained both the silica and the CSR nanoparticles. From measurements of the equilibrium modulus, E_r , in the rubbery region the values of the average molecular weight between crosslinks were calculated for the epoxy polymers without and with HDDGE diluent as 314 g/mol and 370 g/mol, respectively. The somewhat lower crosslink density value for the DGEBA:HDDGE epoxy polymer was

reflected in an increased ductility for this material being observed, compared to the DGEBA material. The consequence of this effect of adding the HDDGE is discussed below.

Considering the relationships between the microstructure and toughness of the various epoxy polymer nanocomposites studied, the morphology of the hybrid system, i.e. containing both silica and CSR nanoparticles, was found to depend critically on the presence of HDDGE in the matrix formulation. In the case of the epoxy polymer without HDDGE present, the CSR and silica nanoparticles were found to agglomerate together forming ‘islands’ of particle-rich regions within the microstructure. On the other hand, the silica and CSR nanoparticles were found to both be very well dispersed in the epoxy polymer containing the HDDGE reactive diluent. The differences in morphology between the hybrid formulations for the epoxy polymer without, and with, the reactive diluent present cannot be solely attributed to the reduction in viscosity prior to curing caused by the addition of the HDDGE, since all of the highly loaded non-hybrid epoxy nanocomposites were found to be well dispersed. The improvement in dispersion of the nanoparticles with the addition of HDDGE is ascribed to changes in the affinity between the two different types of nanoparticles due to the absence or presence of the reactive diluent HDDGE. This significant difference in morphology, depending upon whether HDDGE was present, had a major effect on the toughness of the hybrid epoxy nanocomposites, as discussed below.

Plastic void growth and plastic shear banding of the matrix were identified as the main toughening mechanisms in the fracture tests. The addition of HDDGE to the epoxy polymer affected the ability of the nanoparticles to effectively toughen the epoxy polymer in a relatively complex manner. Firstly, the presence of the HDDGE in the matrix of the epoxy polymer nanocomposite diminished the toughening effect of the silica nanoparticles, when compared to the toughness of the unmodified epoxy polymer. This was due to a lack of particle debonding during the fracture process. The formation of a soft interphase around the silica particles has been suggested as being responsible for this. Secondly, the HDDGE enhanced the toughening effect in the case of the CSR nanoparticles. This is attributed to an increase in the level of void growth due to the increased ductility of the epoxy polymer matrix when the HDDGE was present, as

reflected by the higher strain to failure that was measured for the DEGBA:HDDGE epoxy polymer. Thirdly, for the hybrid formulations, in the case of the epoxy polymer without HDDGE present, the CSR and silica nanoparticles were found to agglomerate together forming ‘islands’ of particle-rich regions within the microstructure. This reduced the toughening effect of these particles in these DGEBA epoxy nanocomposites. On the other hand, the silica and CSR nanoparticles were both found to be very well dispersed in the epoxy polymer containing the HDDGE reactive diluent, and a consequent increase in toughness was indeed found.

Finally, the experimental results demonstrate that the use of the true failure strain, γ_f , as measured from a plane-strain compression test, to predict the extent of void growth during the fracture process using the Huang-Kinloch model appears to be justifiable. This confirms the use of the Huang-Kinloch model to be of use as a fully predictive model, rather than simply a post-mortem analysis tool.

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Figure 1 (a): 0% HDDGE, 10 wt% SiO₂, 10 wt% CSR.

Figure 1 (b): 0% HDDGE, 5 wt% SiO₂, 10wt% CSR.

Figure 1 (c): 25% HDDGE, 0 wt% SiO₂, 8 wt% CSR.

Figure 1 (d): 25% HDDGE, 8 wt% SiO₂, 8 wt% CSR.

Figure 1: AFM images of the microstructure of epoxy polymers modified with silica and CSR nanoparticles. The silica nanoparticles are indicated as the small yellow spots while the CSR nanoparticles can be observed as much larger darkened circles. Significantly improved dispersion of the silica in the presence of CSR can be observed in (d) as opposed to either (a) or (b) where the lack of HDDGE causes particle agglomeration. The dispersion of CSR particles without the presence of silica nanoparticles is given in Figure 1(c).

Figure 2: Storage modulus E' and loss factor $\tan(\delta)$ for the DGEBA and DGEBA:HDDGE unmodified epoxy polymers.

Figure 3 (a): NanoSiO₂ particle modified epoxy polymers.

Figure 3 (b): CSR nanoparticle modified epoxy polymers.

Figure 3: Young's modulus versus content of SiO₂ and CSR nanoparticles for both the DGEBA and DGEBA:HDDGE epoxy polymer nanocomposites. The points are experimental data and the lines are the theoretical predictions.

Figure 4 (a) DGEBA epoxy polymers.

Figure 4 (b) DGEBA:HDDGE epoxy polymers.

Figure 4: Typical true stress true strain relationships for the epoxy polymer nanocomposites containing either silica or CSR nanoparticles (final strain-hardening region not shown).

Figure 5 (a): Silica nanoparticle modified epoxy polymers.

Figure 5 (b): CSR nanoparticle modified epoxy polymer.

Figure 5: Fracture energy versus weight percentage (a) silica nanoparticles and (b) CSR nanoparticles for the epoxy polymer nanocomposites with and without HDDGE (non-hybrid formulations).

Figure 6: Fracture energy versus weight percentage of silica and CSR nanoparticles for the epoxy polymer nanocomposites with and without HDDGE present.

Figure 7: FEG-SEM image of the fracture surface of the DGEBA epoxy polymer with 5 wt% of silica nanoparticles.

Figure 8 (a): 5 wt% CSR nanoparticles.

Figure 8 (b): Hybrid nanocomposite with 5 wt%SiO₂ and 5 wt% CSR.

Figure 8: FEG-SEM images of the fracture surface of DGEBA polymer with (a) 5wt% CSR nanoparticles and (b) hybrid nanocomposite with 5wt% SiO₂ and 5wt% CSR nanoparticles.

Figure 9 (a): 8 wt% CSR nanoparticles.

Figure 9 (b): Hybrid nanocomposite with 8 wt%SiO₂ and 8 wt%CSR.

Figure 9: FEG-SEM image of the fracture surface of DGEBA:HDDGE polymer nanocomposites with (a) 8 wt% CSR nanoparticles and (b) hybrid nanocomposite with 8 wt% SiO₂ and 8 wt% CSR nanoparticles.

Figure 10: Huang-Kinloch model toughness predictions for the silica nanoparticle toughened epoxy polymer nanocomposites. The toughening predictions are calculated using $\psi = \Delta G_S + f\Delta G_V$ with $f = 0.15$ and $f = 0$ for 0% HDDGE and 25% HDDGE present, respectively.

Figure 11 (a): Epoxy polymer nanocomposites with 25% HDDGE present and with 0 wt% of SiO₂ nanoparticles.

Figure 11 (b): Epoxy polymer nanocomposites with 25% HDDGE present and with 4 wt% of SiO₂ nanoparticles.

Figure 11 (c): Epoxy polymer nanocomposites with 25% HDDGE present and with 8 wt% of SiO₂ nanoparticles.

Figure 11 (d): Epoxy polymer nanocomposites with 0% HDDGE present and with 0 wt% of SiO₂ nanoparticles.

Figure 11: Predictions of the fracture energy from the Huang-Kinloch model for the CSR toughened epoxy polymer nanocomposites, using a number of approaches for calculating the extent of the void growth toughening mechanism. A representative range of different formulations are shown.

Figure 12: A cumulative distribution plot of the measured particle and void diameters for an epoxy polymer nanocomposite containing 25 wt% HDDGE, 0 wt% SiO_2 nanoparticles and 8 wt% CSR nanoparticles.

wt% SiO ₂	wt% CSR	HDDGE	E _{exp} [GPa]	E _{pred} [GPa]	% error
0	0	N	3.12±0.06	—	—
5	5	N	2.98±0.07	2.95	-1.0
5	10	N	2.81±0.08	2.74	-2.5
10	5	N	3.05±0.12	3.12	+2.3
10	10	N	2.81±0.11	2.79	-0.7
0	0	Y	2.93±0.12	-	-
4	2	Y	2.85±0.16	2.92	+2.4
4	4	Y	2.72±0.06	2.79	+2.6
4	6	Y	2.67±0.10	2.60	-2.7
4	8	Y	2.61±0.04	2.58	-1.1
8	2	Y	2.97±0.07	3.04	+2.3
8	4	Y	2.98±0.03	2.93	-1.7
8	6	Y	2.71±0.15	2.79	+2.9
8	8	Y	2.64±0.14	2.69	+1.9

Table 1: Elastic modulus predictions for the hybrid epoxy polymer nanocomposites.

wt% SiO ₂	wt% CSR	HDDGE	G_{exp} [J/m ²]	$G_{additive}$ [J/m ²]	Difference [J/m ²]
0	0	N	125±36	-	-
5	5	N	174±25	347	-174
5	10	N	255±53	580	-325
10	5	N	218±25	383	-165
10	10	N	597±99	616	-19
0	0	Y	173±33	-	-
4	2	Y	347±38	356	-9
4	4	Y	628±77	523	+105
4	6	Y	779±76	735	+43
4	8	Y	1056±87	947	+108
8	2	Y	368±29	368	+0
8	4	Y	724±109	535	+189
8	6	Y	1073±76	747	+325
8	8	Y	1217±63	929	+288

Table 2: Measured fracture energies of the hybrid epoxy polymer nanocomposites investigated in the current work as a function of the additive used. It can be seen that there is a small synergistic effect for the epoxy nanocomposites containing the HDDGE reactive diluent and for high particle loadings; while a sub-additive effect is noted for the hybrid epoxy polymer nanocomposites without the HDDGE present.