# FAST VS TOUGH; THE EFFECT OF FASTER CURE CYCLES ON THE FRACTURE PROPERTIES OF TOUGHENED EPOXIES

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## ABSTRACT

Epoxy resin systems are widely used in composite materials. Epoxy resins can exhibit high moduli and strengths for polymers, whilst being easy to process into fiber reinforced composites. They can also be considered brittle, when compared to many other polymers. Enhancing the toughness of epoxy-based matrices can lead to significant improvements in the toughness and, therefore, damage resistance of fiber reinforced composites. These improvements in toughness can be achieved through the incorporation and/or formation of nano-scale particles or structures in the matrix by the addition of core-shell rubber particles or block copolymers, for example. However, the efficacy of these toughening agents in increasing the toughness of these materials is heavily influenced by their ability to produce a coherent microstructure within the epoxy. It was observed that the fracture energy of toughened epoxies, determined via testing on single edge notched beams, decreased with higher cure temperatures. A loss of coherency in the microstructures, as cure temperature increased, was observed via electron microscopy. This was linked to the reduction in toughness enhancements attained as systematically varied resin formulations were cured more rapidly.

## 1. INTRODUCTION

Epoxy polymers are used extensively in aerospace, auto-motive and electronics applications in the form of adhesives, surface coatings and advanced composite materials. The widespread use of epoxy materials in engineering applications is due to the development of toughened epoxy polymers [1,2]. Soft rubber particles have been the most successful method to enhance the toughness of epoxy polymers [3-6].

The manufacturing processes involved in the formation of toughened epoxy polymers can have a great impact on the material properties and thermal processing can alter the effectiveness of the tougheners [7]. The performance of the final product greatly depends on several phenomena which take place during the curing process: thermal expansion, chemical shrinkage and material degradation or relaxation [8].

From a commercial point of view, minimizing the cure time by increasing the cure temperature and hence the cure rates of the epoxy systems will lead to a reduction in cost. However, when the cure cycle is accelerated to reduce manufacturing time and expense, the possibility of a runaway exotherm is increased which could result in the degradation and breakdown of the epoxy polymer.



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The focus of this work has been devoted to the effect of fast cure rates on toughened epoxy polymers which was addressed by systematically varying the cure temperature and hence the cure rate of the studied epoxy systems.

# 2. EXPERIMENTATION

## 2.1 Materials

Two different epoxy systems were investigated during this study. The adhesive matrix used in the first part of this work is a blended epoxy resin developed by FAC Technology with an epoxide equivalent weight of 170 g/eq. The hardener, also developed by FAC Technology is an amine blend tailored to give a glass transition temperature of circa. 80°C and maximum toughenability of the resin. Three different toughening formulations were investigated as additives to the resin:

(1) a symmetric triblock copolymer (BCP) of poly (methyl methacrylate)-b-poly(butylacrylate)-b-poly (methyl methacrylate) obtained in powder form from Arkema, France.

(2) a carboxyl-terminated butadiene acrylonitrile (CTBN) liquid rubber, supplied as 'Albipox 1000' adduct at 40 wt.% (Evonik Hanse, Germany).

(3) a polysiloxane core shell rubber (CSR), 'Albidur EP2240A', supplied pre-dispersed at 40 wt.% in DGEBA.

The toughening effects of these additives on epoxy polymers has been extensively studied previously [9,10]. Epoxy polymers containing 6 wt.% of each of the toughening additives were prepared and cured isothermally at temperatures between 30°C and 105°C.

In order to better understand the relationship between faster rates of curing and toughness, a simplified epoxy system was used. The resin formulation was slightly modified while the hardener formulation remained the same. An amine-based cured diglycidyl ether of bisphenol-A (DGEBA) formed the basis of the second epoxy system used. The epoxy resin was a standard DGEBA with an epoxide equivalent weight (EEW) of 185 g/eq. The resin formulation was altered by replacing 10 wt.% of the DGEBA resin with a reactive diluent. The diluent agent was a hexanediol diglycidylether (HDDGE) with an EEW of 170 g/eq. The reactive diluent helps the ease of manufacturing by lowering the viscosity of the epoxy resin.

The same polysiloxane core shell rubber (CSR) particles mentioned above were added to the mixtures. Formulations containing 3 %, 6 % and 9 % weight percentage of CSR were prepared and cured isothermally at 40°C, 50°C, 60°C and 70°C. All formulations were post cured at 90°C for 2 hours and cooled to room temperature inside an oven at a low rate of ≈ 1°C/min in order to mitigate against the influence of thermal induced residual stresses.

## 2.2 Manufacturing

The DGEBA epoxy resin was first mixed with the reactive diluent. Afterwards, the toughening nanoparticles (BCP, CTBN, CSR) were added and the constituents were properly stirred until a uniform mixture was achieved. The mixture was degassed in a catch pot connected to a vacuum pump for 15 minutes. A stoichiometric amount of the hardener was then added, stirred and a second degassing step of 10 minutes was applied. The formulation was then poured into horizontal silicon molds to give 8 mm thick plates.

Finally, each sample was post cured at 90°C for 2 hours and cooled to room temperature inside an oven at a rate of ≈ 1°C /min in order to alleviate the presence of thermal induced residual stresses. A schematic of the manufacturing process can be seen in Figure 1.

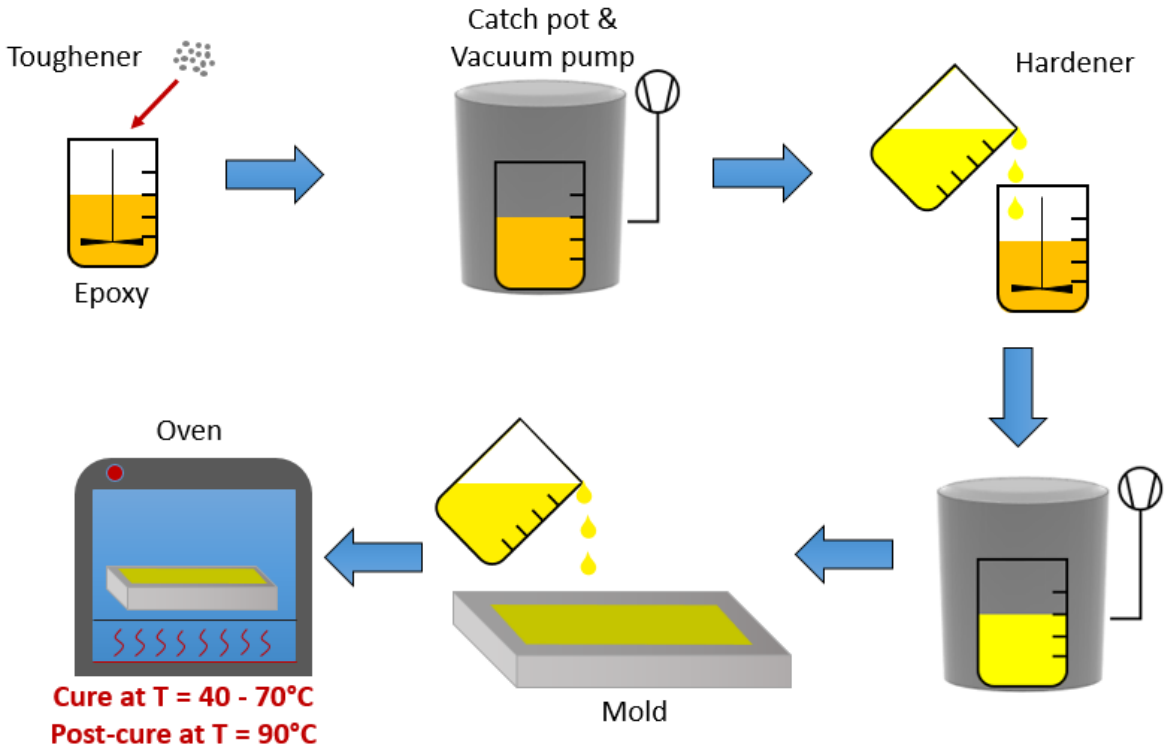



Figure 1: Bulk plate manufacturing illustration.

## 2.3 Mechanical testing

Single-edge notched bending (SENB) tests were performed to obtain the fracture energy, $G_{Ic}$, in the opening mode according to the ASTM standard. The fracture energy was computed using the energy method approach via:

$$G_{Ic} = U/bw\emptyset \quad (1)$$

where $U$ is the energy under the corrected load-displacement curve, $b$ and $w$ are the thickness and width of the specimen, respectively, and $\phi$ is an energy calibration factor. A razor blade cooled to -90°C was tapped into the notch prior to testing to ensure the presence of a sharp crack.

### 2.4 Microscopy

Scanning electron microscopy (SEM) was used to validate the presence of voids and to determine their volume fraction on the fracture surface of SENB samples. Previous studies [11] have shown that if void growth has occurred during fracture, the diameters of the cavitated CSR particles are significantly bigger than the corresponding diameters measured prior to fracture. To investigate further the fracture mechanisms a field-emission gun scanning-electron microscope (FEGSEM) was used to study the morphology of the SENB specimens.

### 2.5 Spectrophotometry

In the case of the epoxy systems where the rubber particles are formed via reaction induced phase separation, i.e. BCP and CTBN, spectrophotometry was used to further understand the point at which phase separation took place. The principle of spectrophotometry is that by firing a beam of light of known wavelength through a sample of material with a defined thickness and measuring the amount of light transmitted, it is possible to work out some optical characteristics of the material. In the phase separating systems, the samples are initially transparent at most wavelengths and most of the light passes throughout. As the phase separation progresses, triggered by the increase in viscosity of the crosslinking epoxy system, particles begin to form and these particles scatter light which leads to an increase in Absorbance, or a corresponding decrease in Transmittance.

## 3. RESULTS

### 3.1 Fracture properties

Figure 2 presents the fracture energy of the epoxy polymers modified with 6 wt.% of the nano-material additives as a function of the isothermal cure temperature. The fracture energy of the unmodified resin was measured as 248 ± 36 J/m$^2$. It can be clearly observed that the addition of the nano-materials results in a substantial increase in the measure fracture energy regardless of the temperature of cure.

A closer inspection of Figure 2 reveals that the temperature of cure has a significant impact on the measured fracture properties. The most striking aspect of the graph is the large fall off in fracture energy of the epoxy polymers modified with BCP, from a value of approximately 3,000 J/m$^2$ at a curing temperature of 40°C or below to approximately 1,350 J/m$^2$ at a curing temperature of 50°C or above. Moreover, the lower values of fracture energy measured appear to be independent of the curing temperature.

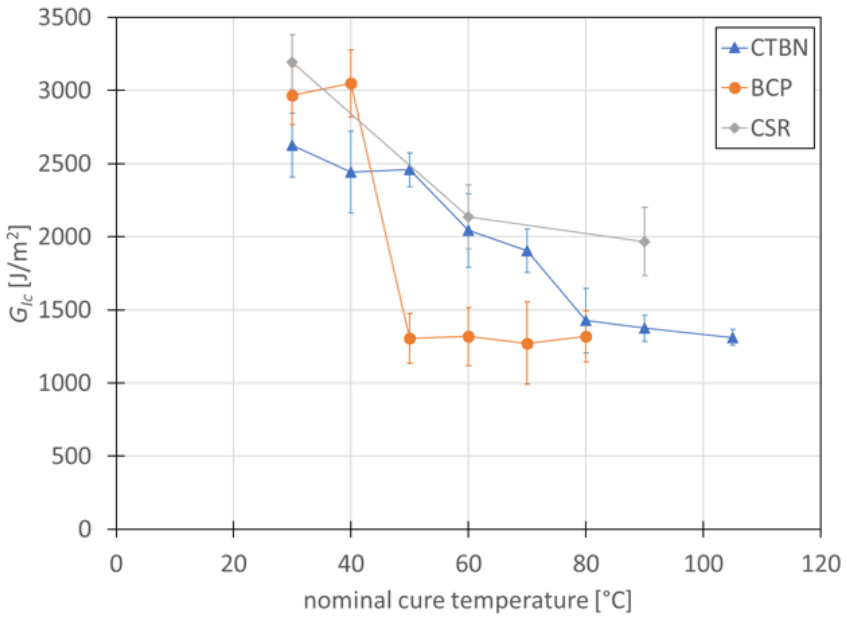
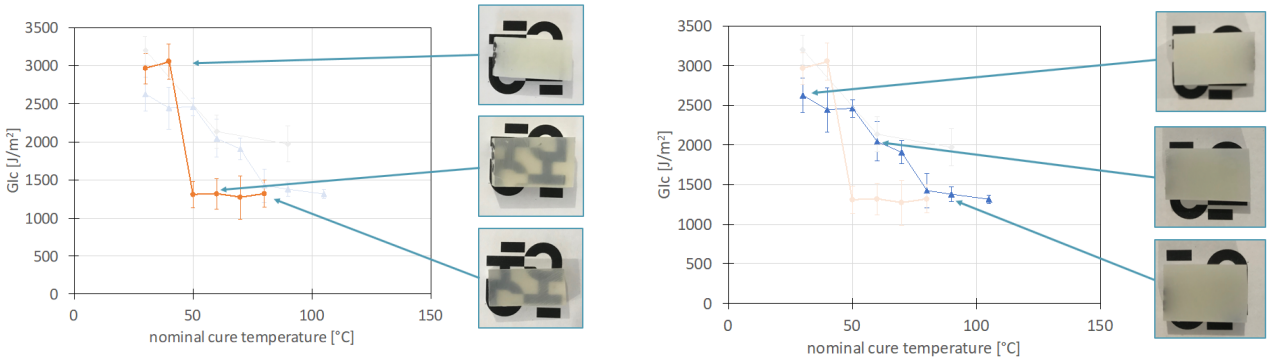



Figure 2: Fracture energy of nano-toughened epoxy polymers as a function of cure temperature.

From Figure 3 (a), it is clear that the samples prepared for fracture toughness and cured at a temperature lower than 40°C were opaque. This indicates that a nanostructure with a length scale of at least that of the wavelength of visible light has formed. At the higher curing temperatures, the samples were transparent and very similar in appearance to the unmodified epoxy polymer. This demonstrates that a coherent nanostructure has not formed. This is due to the reduced time available for the BCP to assemble before gelation and vitrification of the matrix inhibits molecular motion. However, although the toughness has dropped significantly, it is still over five times that of the unmodified epoxy polymer.




(a) (b)

Figure 3: Relationship between transparency and toughness: BCP nanomodified systems (a), CTBN nanomodified systems (b).

The epoxy polymers modified with CTBN, demonstrate a different behavior to that exhibited by the polymers modified with BCP. The measured fracture properties are higher at a lower cure temperature with a lower plateau measured at the highest cure temperatures. However, there is a more gradual decrease in fracture energy in the intermediate. It is important to note that all of the samples tested were opaque indicating that phase separation and formation of a toughening nanostructure occurred as can be seen in Figure 3 (b).

The epoxy polymers modified with CSR particles differ from the other two rubbers investigated in this study, in that the CSR particles are preformed and no reaction induced phase separation takes place during the curing reaction. Nevertheless, a reduction in the measured toughness is noted as the cure temperature (and hence curing rate) increases.

To further investigate this drop, a simplified epoxy system was used. This time, the CSR particulates were added in three different weight percentages (3 %, 6 % and 9 %) and each formulation was cured at 40°C, 50°C, 60°C and 70°C.

A maximum fracture energy, $G_{Ic}$, of 339 ± 77 J/m$^2$ was measured for the unmodified epoxy polymer. The value was obtained at a cure temperature of 40°C. The addition of CSR nano-particles to the polymer system increased this value significantly to 3920 ± 140 J/m$^2$. This represents an increase in fracture energy of approximately 1000 % when the extent of CSR is increased from 0 wt.% to 9 wt.%.

From Figure 4, it is evident that the toughness of the material increases proportionally to the content of CSR nano-particles added to the epoxy matrix.

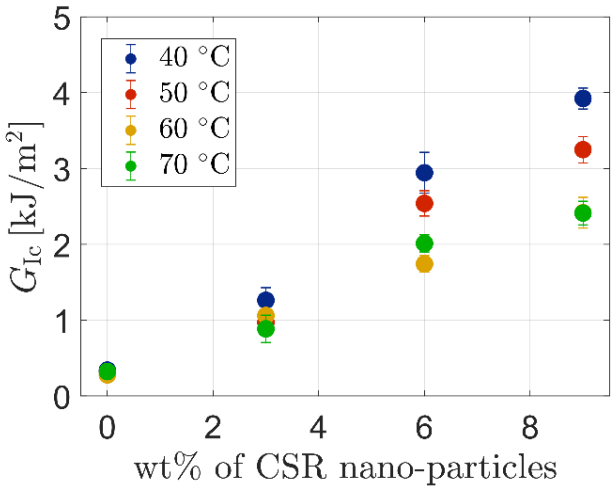



Figure 4: Fracture energy versus weight percentage of CSR nano-particles.

The cure rates and cure temperature do not alter the fracture energy and the fracture toughness for epoxy systems containing only a small amount of CSR (0 wt.% and 3 wt.%). On the contrary from Figure 5, it is clear that when the amount of rubber particles is significant (6 wt.% and 9 wt.%), the temperature at which the sample is cured reduces the fracture properties of the material significantly.

For example, the fracture energy of an epoxy system modified with 9 wt.% of CSR cured at 40°C is 3920 ± 140 J/m$^2$. This value drops to 2411 ± 156 J/m$^2$ when the same formulation is cured at 70°C leading to a loss of toughness which is almost 40 %.

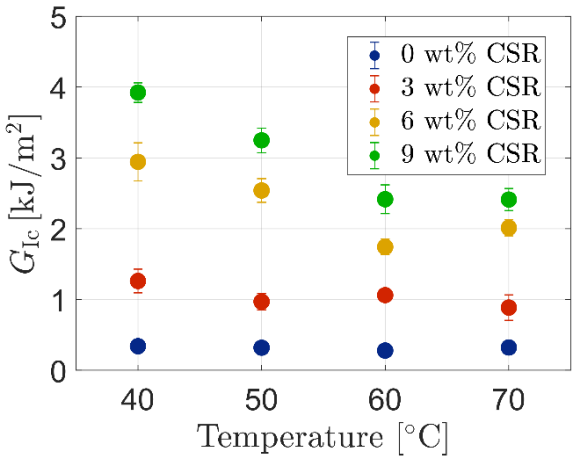



Figure 5: Fracture energy versus curing temperature for CSR nano-modified epoxy systems.

### 3.2 Phase separation and toughness

Figure 6 plots the increase in absorbance for an epoxy polymer modified with CTBN rubber versus reaction time and across a range of wavelengths. It can be clearly seen that there in an increase in Absorbance across all wavelengths.

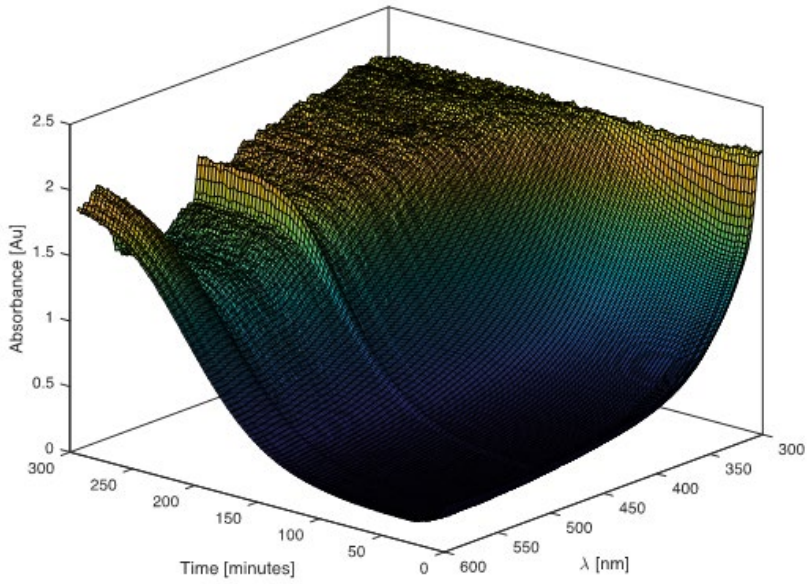



Figure 6: Measured Absorbance of CTBN nanomodified epoxy as function of reaction time and wavelength

A number of observations may be made on inspection of this graph. First, there is a uniformly high Absorbance at $\lambda$ = 300 nm. This is related to the characteristic absorption wavelength of the oxirane ring. Secondly, it appears that there is some functional relationship between the increase in absorbance and the wavelength of light from the Spectrophotometer. This is more clearly illustrated when the time derivative of the change in absorbance is taken as shown in Figure 7.

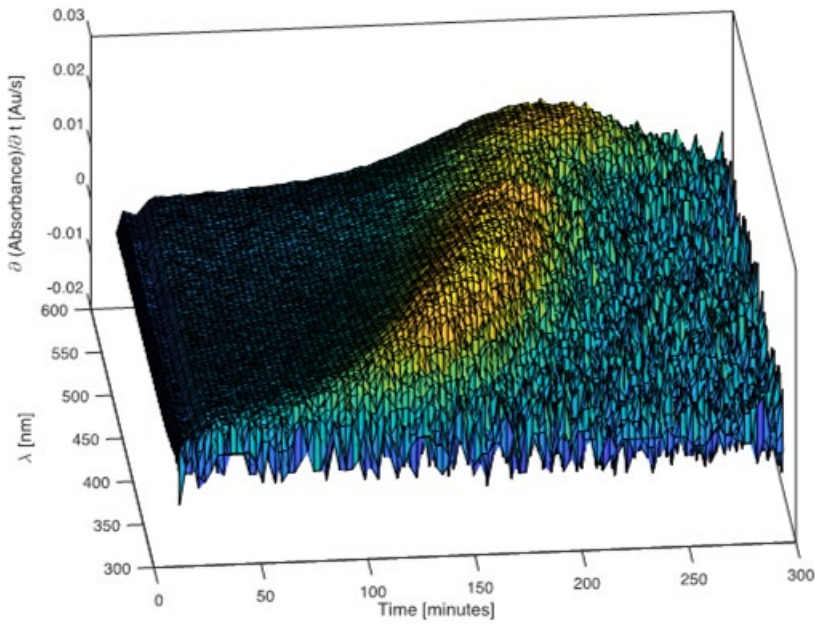



Figure 7: Derivative of measured Absorbance of CTBN nanomodified epoxy as function of reaction time and wavelength

A clear relationship now appears. The derivative at any one wavelength is reminiscent of an Arrhenius type kinetic process. Moreover, the temporal location of the maximum value of the time derivative of Absorbance occurs later in the reaction time as the wavelength of the investigating light beam increases. The wavelength at which light scatters is related to the size of the scattering particles. The growth rate of particles is a phase separating was first formalized by Lifshitz and Slyosov [12] and Wagner [13]. They showed that in a three-dimensional system the average particle size, measured linearly, is directly proportional to the cube root of time. Plotting this data in Figure 8, and using the temporal location of the maximum rate of change of Absorbance, a lineal relationship was indeed found. This potentially means that we can use in-line spectral investigation to monitor reaction induced phase separation during the curing process. Indeed, knowing exactly during the curing process when phase separation takes place will allow the design of optimal cure cycles, as the phase separation reaction is initiated by the increase in viscosity of the crosslinking epoxy and subsequently terminated by the gelation and vitrification of the matrix, which hinders molecular mobility. Thus, control of the curing kinetics will lead directly to control of the formation of phase separated nano-structures which are responsible for toughness and play a vital role in the performance and durability of the composite part.

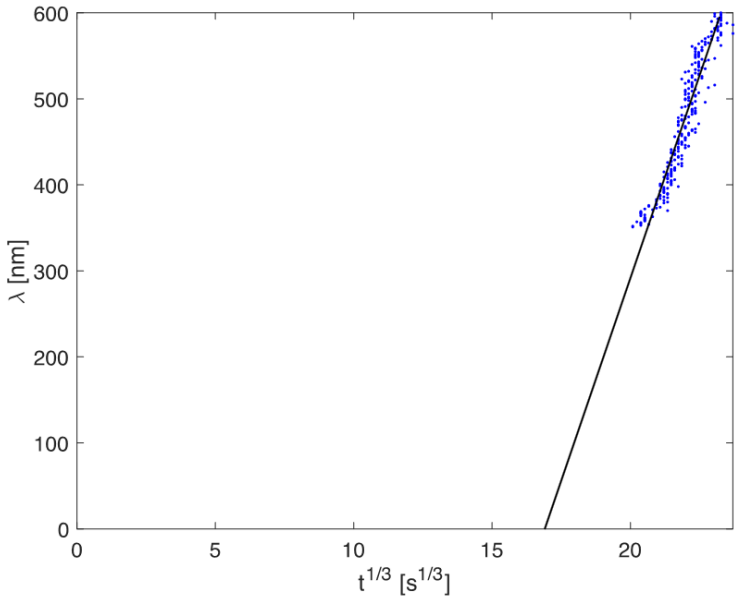


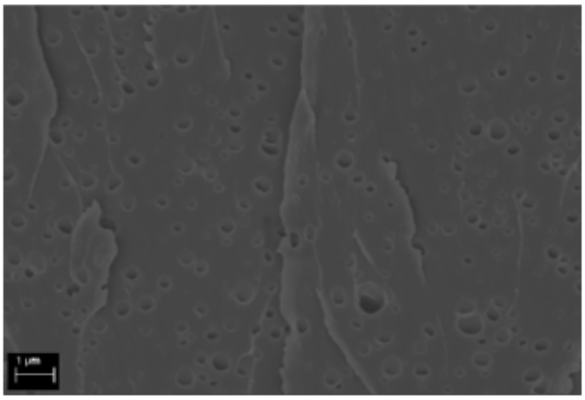

Figure 8: Experimental measurement of particle size during phase separation using spectral wavelength as a direct proxy for lineal particle size.

### 3.3 Curing rate and toughness

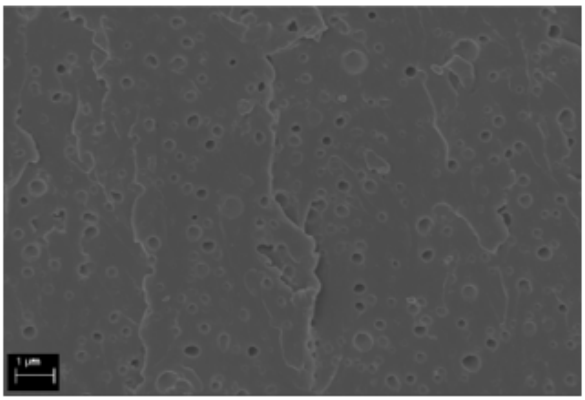
The principal toughening mechanisms associated with CSR nano-modified polymers [14, 15] are (a) localized plastic shear-yielding of the epoxy polymer and (b) plastic void growth of the matrix initiated by cavitation of the toughening particles. Shear-yielding can be defined as a constant volume process that absorbs energy [16]. For epoxy systems modified with CSR, the rubber particles act as stress concentrators where localized shear bands can originate and this facilitates plastic energy dissipation.

Additionally, CSR nano-particles cavitate. The process absorbs little energy in itself, but is paramount to relieve the state of hydrostatic stress ahead of the crack tip by creating a void, which subsequently allows plastic deformation of the epoxy polymer around the void to occur. Plastic void growth can absorb a significant amount of energy and can be observed experimentally using a SEM by comparing the initial size of the included particles with the increased size of the void post fracture.

The fracture surface of nano-modified epoxy systems cured at 40°C can be seen in Figure 9. In each of these micrographs, a well-dispersed microstructure of voids can be clearly observed. As expected, when a higher content of CSR is added to the epoxy mixture, a greater density of voids is visible on the fracture surface. The radius of these cavitated particles is larger than the corresponding radius of the nano-particles prior to failure. This phenomenon demonstrates that void growth has occurred and this is well established as one of the main toughening mechanisms in rubber modified epoxy systems.



(a)



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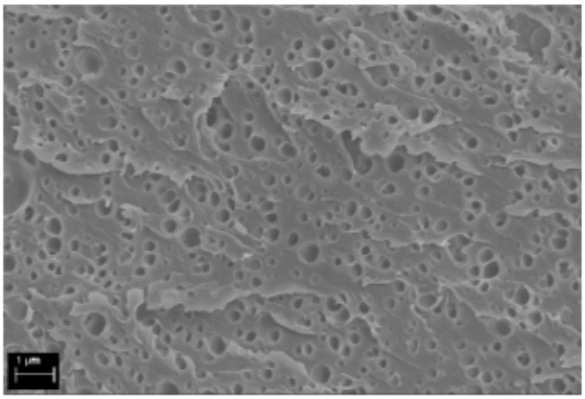
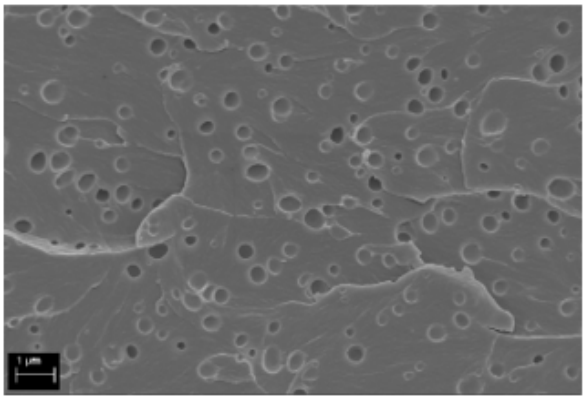
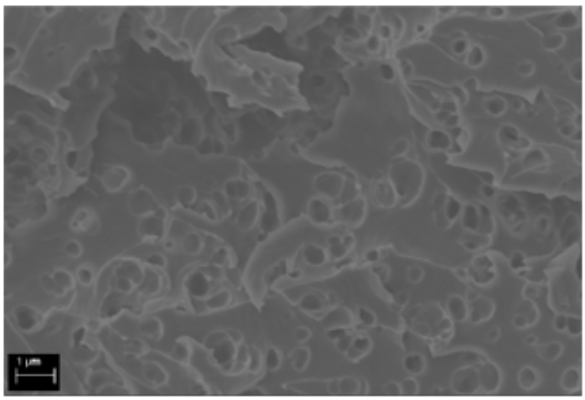


(c)

Figure 9: SEM images of the fracture surface of epoxy systems cured at 40°C containing 3 wt% (a), 6 wt% (b), and 9 wt% (c) of CSR nano-particles.



(a)



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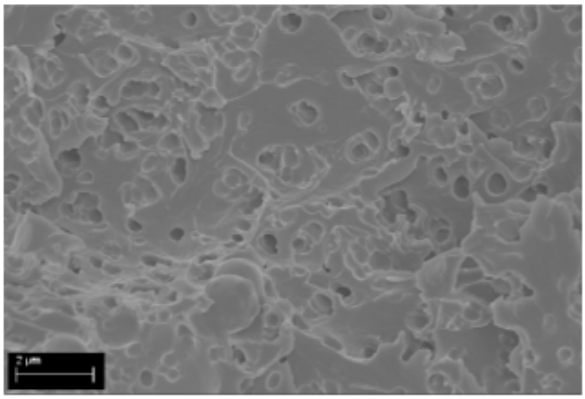

(c)

Figure 10: SEM images of the fracture surface of epoxy systems cured at 70°C containing 3 wt% (a), 6 wt% (b), and 9 wt% (c) of CSR nano-particles.

From Figure 10, it can be seen that curing of this epoxy system at a higher temperature, and hence a faster cure rate, leads to some clustering and agglomeration of the particles. This is clearly evident in Figures 10 (b) and (c) containing 6 wt% and 9 wt% of CSR particles respectively. Only few voids are still identifiable as coherent structures and retain a spherical shape. In those two pictures, it is clear that the fracture surface of epoxy systems with a high content of CSR nano-particles is an incoherent structure where rounded and elongated shapes are

surrounded by irregular features which are similar to fractals. The preformed CSR particles are no longer clearly distinguishable on the fracture surface and bear no relationship to the preformed CSR particles added at the beginning of the manufacturing process. On the contrary, when 3 wt.% of CSR was added to the epoxy mixture, the voids are still reasonably well dispersed and they manifest on the fracture surface as circular objects.

By comparing the different micro-graphs, it is possible to observe that when the rate of cure of the epoxy resin is increased, the dispersion of the CSR particles is affected. In the epoxy polymer with high content of CSR, the toughening additives interact with each-other, coalesce and as a result the voids observed on the fracture surface are not evenly distributed. Hence, the toughening effect of the CSR nano-particles is inhibited since the growth of the voids surrounding these particles is limited by their surrounding space at the micro-structure of the material.

Figure 5 clearly highlights this conclusion since for epoxy systems containing 6 wt.% and 9 wt.% of CSR nano-particles, the fracture energy of the material drops significantly as the cure temperature and rate of cure are increased. For epoxy systems containing either no toughening additives or a comparatively small amount (i.e. 3 wt.%), the aforementioned trend is not readily apparent in the experimental results since the CSR nano-particles have enough surrounding matrix material to fully grow and form voids.

It is important to note that this is a result of the increase in cure rate and not the increase in cure temperature. In the current work, an increased cure temperature has been used as a proxy for increased cure rate. For an anhydride cured system, e.g. that investigated by Carolan et al. [10], the material was cured at 90°C with a post cure at 160°C. Both of these temperatures exceed the maximum cure temperature in the current work, but the rate of cure in the anhydride cure system will be significantly lower than that for the amines investigated in the current work, due to the lower reactivity of the anhydride hardening agent.

## 4. CONCLUSIONS

This study has demonstrated the importance of understanding the epoxy resin system used when incorporating various commercially available nanomaterials to toughen the polymer. The fracture properties of epoxy polymers modified with a symmetric triblock copolymer (BCP), a carboxyl-terminated butadiene acrylonitrile (CTBN) liquid rubber and poly-siloxane core-shell rubber (CSR) nano-particles were studied. The addition of those toughening formulations to the epoxy matrix leads to a significant toughening of the polymer. However, the speed of cure is the decisive factor which determines the effectiveness of the toughening additives.

For nanomaterials which form in-situ, i.e. reaction induced phase separating materials, consideration must be given to the time required to form a nanostructure which can effectively toughen the epoxy polymer. A difference in transparency of the cured material at different cure temperatures was noted. When phase separation occurs, the epoxy system becomes opaque and as a result its toughness increases.

For preformed nanomaterials, the increased rate of cure can cause the agglomeration of the CSR nano-particles which can inhibit the toughenability of a particular epoxy polymer. Moreover, when fast cure cycles are applied, the weight fraction of CSR nano-particles present in the epoxy system is the principal indicator of the extent to which the increase in toughness of the epoxy polymer is inhibited. The higher the content of CSR particles, the greater the drop-in fracture energy observed experimentally.

The realities of the physics governing the behavior of toughened adhesives are often in conflict with the commercial requirement to produce adhesive joints and composite components in a timely fashion. It is therefore, important to fully understand the behavior of your resin, both alone and in combination with the toughening nano-particles.

On these grounds, when designing the cure cycle of toughened epoxy systems in an industrial setting, the detrimental effects on the toughness which arise as a result of both high temperature and faster cure cycles should be properly accounted for.

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