DYNAMIC MECHANICAL PROPERTIES AND FRACTURE SURFACE MORPHOLOGIES OF CORE-SHELL RUBBER (CSR) TOUGHENED EPOXY AT LIQUID NITROGEN (LN_2) TEMPERATURES

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ABSTRACT

The dynamic mechanical properties and fracture surface morphologies were evaluated for a commercial epoxy resin toughened with two types of core-shell rubber (CSR) toughening agents (Kane Ace® MX130 and MX960). The impact resistance (R) was evaluated by the resulting breaking energy measured in Charpy impact tests conducted on an instrumented drop tower. The resulting fracture surface morphologies were examined using Scanning Electron Microscopy (SEM). Fractographic observations of the CSR toughened epoxy tested at ambient temperature, showed a fracture as characterized by slender dendrite textures with large voids. The increasing number of dendrites and decreasing size of scale-like texture with more CSR particles corresponded with increased R. As the temperature decreased to Liquid Nitrogen (LN_2), the fracture surfaces showed a fracture characterized by a rough, torn texture containing many river markings and deep furrows.

1. INTRODUCTION

Due to their high stiffness and strength to weight ratio, continuous fiber reinforced polymeric composites are being considered for high pressure, cryogenic fuel storage of liquid hydrogen (LH_2) at 20K, liquid oxygen (LOX) at 90K, liquefied natural gas at 113K, and liquid nitrogen (LN_2) at 77K [1-3]. Previous studies [4-5] have show that fracture toughness of epoxy resins can be increased by adding Kaneka MX series of core-shell rubber (CSR) nanoparticles. At ambient temperature, the deformation of the toughened epoxy resin has been extensively studied in the literature [6-16]. Reported toughening mechanisms in rubber modified epoxy resins include; crack-pinning [7-8], rubber tear-energy [9], micro cracking [10-11], particle bridging [12-13], crack–path deflection [14], massive shear banding [15], localized shear yielding mechanisms [12-13,16]. At ambient temperature , a localized shear yielding mechanism is considered to be the major energy absorption mechanism as proposed by Kinloch and Pearson [12-13]. This includes the dilatational deformation of the matrix and cavitation of the toughening particles in response to the tri-axial stresses near the crack tip, combined with the shear yielding between the holes formed by the cavitated rubber particles [6]. Thus as the material is impacted, the deformation of the plastic matrix blunts the crack tip and reduces the local stress concentration, allowing the material to carry a higher load before failure occurs [6, 12-13]. This study investigates the dynamic impact response of these toughened materials at LN_2 temperatures. In this study, varying amounts of two different toughening agents, MX130 and MX960, are added to a neat epoxy resin. Instrumented Charpy impact test measurements were made using unnotched specimens. The fracture surface morphologies of CSR toughened epoxy resin are

investigated using SEM. A difference in fracture behavior was observed as the temperature was decreased from ambient temperature to LN_2 temperatures.

2. EXPERIMENTATION

2.1 Specimen Fabrication

The basic resin used in this study was diglycidyl ether of bisphenol-F (DGEBF) epoxy resin, commercially available as EPON 862 [17]. Epikure W [17] was used as a curing agent with a 26:100 weight ratio. Kane Ace® toughening agents, added to the carry resin contained a 25% concentration of CSR toughening agent in an unmodified liquid epoxy resin. The carrier resin for the Kane Ace® tougheners were based on EPON 862 Bisphenol-F and for the MX 130 [18] and Bisphenol-A for the MX 960 [18]. The CSR cores were butadiene styrene core with the diameter of 85-115 nm in the MX 130 system and siloxane core with the diameter of 280-320nm for the MX 960 system [18]. Kane Ace® MX130 and Kane Ace® MX960 are formulated to prevent the CSR particles from agglomerating when mixed with epoxy resins under normal handing, formulating and curing conditions.

The formulations of the specimens used in this study are summarized in Table I. The bulk epoxy specimens were hand-mixed using varying amounts of Kane Ace® MX130 toughening agent with the EPON 862 for approximately 5-10 minutes. This mixture was preheated at approximately 65°C for 15-30 mins, followed by degassing in a vacuum chamber until the frothing stopped. The mixture was air cooled to 25°C prior to adding the curing agent Epikure W. The bulk mixture was then poured into a preheated mould and cured at 124°C for 8 hrs. After curing, the mould was air cooled in the furnace to 25°C. Specimens for tensile testing were cast into 3mm thick sheets and those for Charpy impact testing were cast into 10mm sheets. Fabrication of the Kane Ace® MX960 epoxy resins used the same method with a change of toughening agent to MX 960.

2.2 Dynamic Charpy Impact Test

Dynamic impact tests were conducted using a Charpy fixture in an INSTRON Dynatup 9250HV Instrumented Drop Tower as shown in Figure 1. This apparatus is capable of impacting samples at energies of up to 826 J. For this study, all samples were impacted with a 6.9-kg drop weight. The samples were impacted with a 12.7-mm diameter tup, constructed with high-strength steel. Continuous data collection of the loads captured the impact event and allowed calculation of the absorbed energy. Unnotched specimens were machined from the cast 10mm thick sheets into 10mm×10mm×127mm specimen bars. Three to eight specimens were tested for the neat resin and for each CSR concentration to obtain the average R at ambient and LN_2 temperatures (77K). For the cryogenic temperature tests, the specimens were immersed in a LN_2 bath for 10 min to ensure a uniform temperature distribution. The tests were performed at a penetrator impact speed of 216 m/min, and a corresponding energy of 58 N-m. The R values were obtained from maximum absorbed energy divided by the fracture area according to ASTM standard D6110 [19].

2.3 Fracture Surface Characterization

A JOEL 6500F field emission (FE) SEM was used to examine the fracture surface of the Charpy impact test specimens. Specimens for SEM examinations of fracture surface were saw-cut from

fractured test specimens, about 5 mm below the fracture surface, mounted on aluminum stubs (12 mm dia.) after cleaning, and then sputter coated with Au-Pd in a JEOL Vacuum Evaporator.

Table 1. Epoxy nanocomposites specimen formulations.

Epoxy Resin	**Amount of CSR (phr)***	**Designation**
EPON 862/W neat resin	0	862/W
EPON 862/W MX130 CSR	1	MX130-1
	3	MX130-3
	4.6	MX130-4.6
	5	MX130-5
	7	MX130-7
	9.2	MX130-9.2
	10	MX130-10
	13.8	MX130-13.8
EPON 862/W MX960 CSR	1	MX960-1
	3	MX960-3
	5	MX960-5
	7	MX960-7
	9	MX960-9

*phr: parts per hundred resin by weight.

Figure 1. Overview of Instron Dynatup 9250HV Instrumented Drop Tower.

3. RESULTS AND DISCUSSION

3.1 Dynamic Mechanical Properties

Figure 2 provides a comparison of the R values of EPON 862/Epikure W resin with varying amounts of CSR additives at ambient and LN_2 temperatures. Because the Charpy impact specimens tested were unnotched, a variation in fracture surface area was observed. Thus, there is more data scatter than would be expected with notched specimens. The specimens were unnotched to avoid stress concentrations in the epoxy resin especially as temperatures were decreased to LN_2.

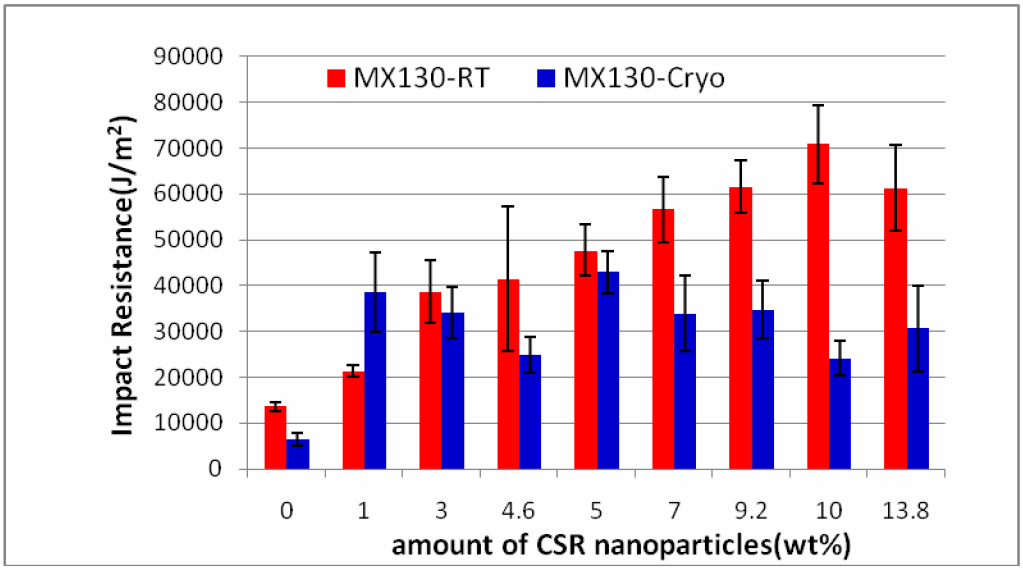
A 7-fold increase in R was achieved after toughening with MX 130 and MX 960 at ambient temperature whereas a 3-fold increase was observed at LN_2 temperature. Figure 2a shows an increase in the R value of MX 130 CSR toughened epoxy at both ambient temperature and LN_2. R values increased steadily at ambient temperature with varying weight loading of MX130 additives up to 10%, While at LN_2 temperatures, additives over 1 wt% loading showed no substantial change to R within the experimental uncertainty.

A similar increase in R is observed in Figure 2b with various weight loadings of MX 960 tougheners. Although the maximum increase in R at ambient temperature is observed with a lower 3 wt% loading. A similar trend is observed at LN_2 temperatures with maximum increase in R observed with 1 wt% loading of tougheners. Figure 2 shows that at LN_2 temperature, specimens with 1 wt% loading of either MX130 or MX960, have similar increases in the R value. Increasing the amount of either toughener doesn't effectively change the R value. This suggests that the R value is independent of the species of toughening agents at LN_2 temperature.

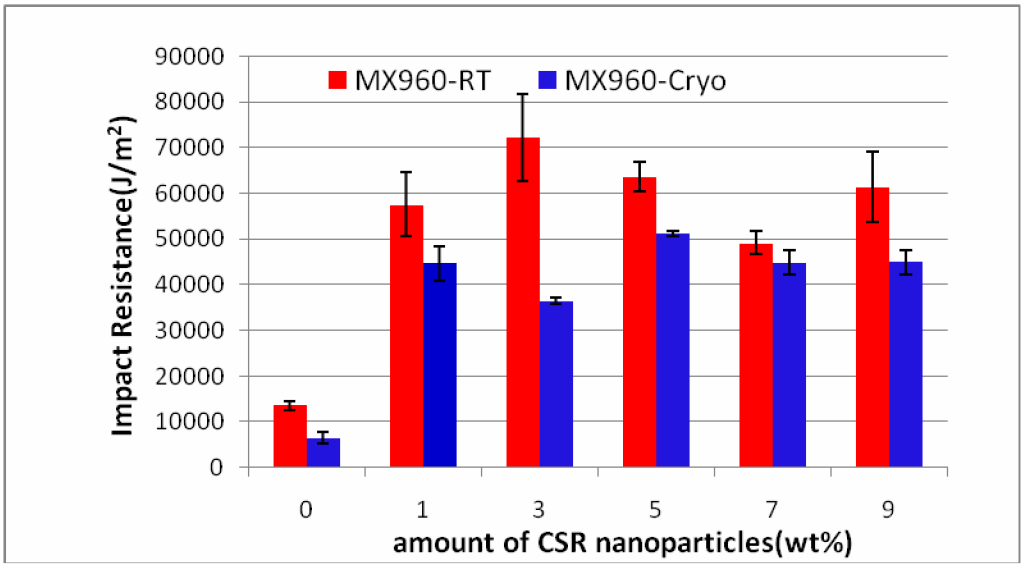
3.2 Fracture Surface Morphologies

Figure 3a and b summarize the SEM images of the fracture surfaces of neat and MX 130 modified epoxy resin specimens tested at LN_2 temperature. All images were taken at the center of the fracture surface. The neat resin shown in Figure 3a is essentially a one-phase material and shows wave-like fracture steps that are featureless up to magnifications of 10,000X. The absence of significant topographical features correlates well with the low toughness shown for the neat resin in Figure 2a. With the addition of CSR toughening particles, the fracture lines observed in Figure 3b become jagged and scale-like indicating a greater resistance to the dynamic load. It is speculated that the CSR nanoparticles act as barriers to crack propagation. The jagged and scale-liked edges may correspond to CSR nanoparticles location as the linear serration rate of the edge increases as the weight loading percent of CSR nanoparticles increases [21].

In order to understand the relationships between microstructure and fracture behavior of MX series modified epoxy resin. Figure 4a and b present low magnification SEM images of the fracture surface morphologies of MX 960 with 1 wt% loading at ambient temperature and LN_2 temperatures, respectively. Three areas–smooth, rough, and a transition region are observed in each image [22]. At ambient temperature, the rough area dominates the fracture surface, indicating that large plastic deformation occurred. Figure 4a shows the rough, torn surface containing many river markings and deep furrows. Associated with these features is evidence of extensive shear failure connecting the adjacent crack fronts of different planes [21-22]. While in Figure 4b, a much smoother area with small amount of plastic deformation is observed.



a. MX130 additives.

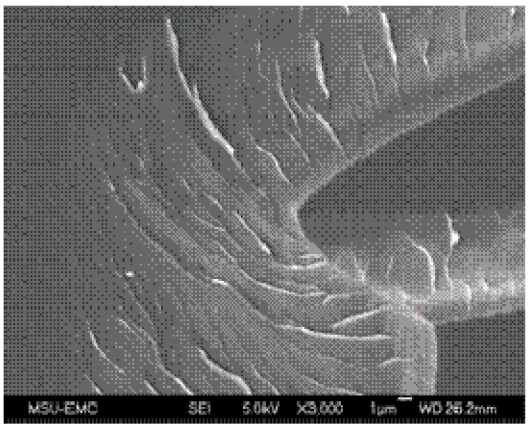


b. MX960 additives.

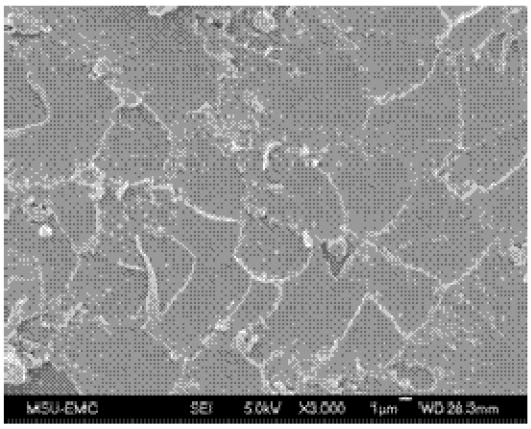
Figure 2. Comparison of average breaking energy of EPON 862/W with increasing loading of CSR particles at ambient and LN_2 temperatures.

In order to investigate the detailed information of the smooth and rough areas, Figure 5 shows the high magnification SEM images of the areas labeled in Figure 4. The main fracture surface of the modified epoxy resin exhibits voids which are the locations of the rubber particles at both temperatures [22]. An increased-number of larger voids was present in specimens tested at ambient temperature than at LN_2 temperature. Extensive voids and cavitation of CSR particles

were noted at ambient temperatures. Voids might indicate the cavitation of the CSR particles and dilatational deformation of matrix which resulted in stresses near the crack tip and then shear yielding between the holes formed by the cavitated rubber particles [6]. Cavitation and shear yielding may cause large plastic deformation which results in the ability of the material to absorb a larger amount of energy before fracturing, corresponding to a higher R value.

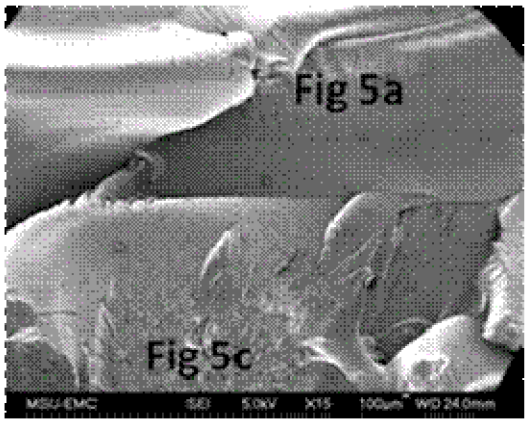


a. SEM image of EPON 862 neat resin.

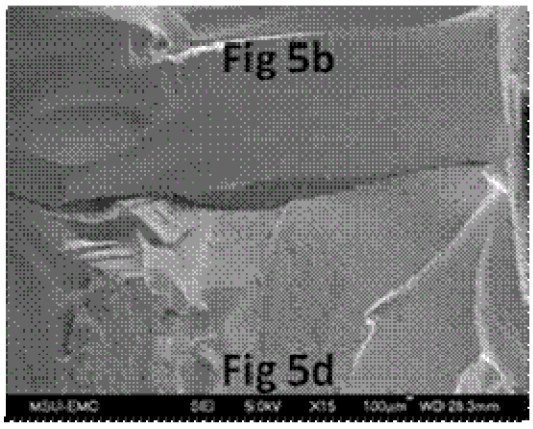


b. SEM image of 5 wt% loading of MX 130 in EPON 862 epoxy resins.

Figure 3. SEM images of fracture surface following Charpy impact test at LN_2 temperature.



a. SEM image of 1 wt% loading of MX 960 at RT.



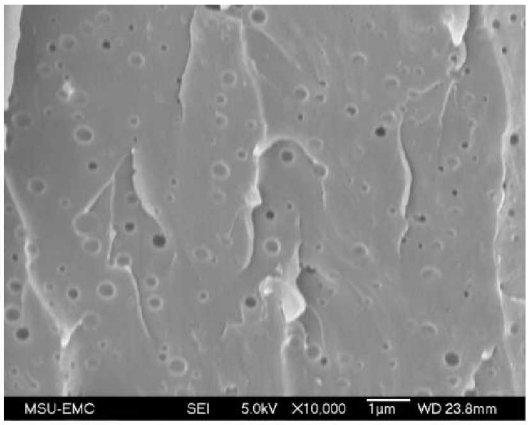
b. SEM image of 1 wt% loading of MX 960 at LN_2.

Figure 4. Low magnification SEM images of fracture surface following Charpy impact test of MX 960 toughened epoxy resin.

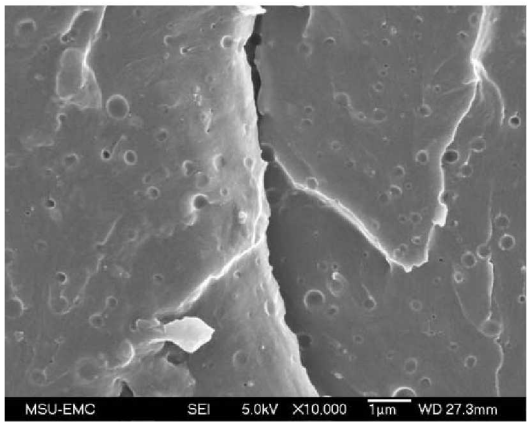
4. SUMMARY

Dynamic Charpy impact tests were conducted on CSR toughened EPON 862 epoxy resins at ambient and LN_2 temperatures. Neat resin performance was compared with different wt% loading of CSR epoxy resin. R was evaluated by the measured breaking energy of Charpy impact

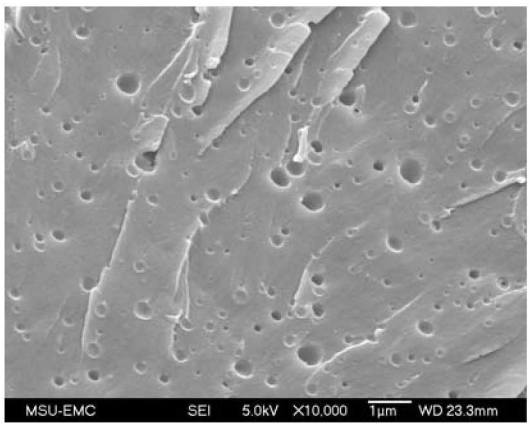
test. A maximum R value at ambient temperature was obtained with 10 wt% loading of MX 130 versus 3 wt% loading of the MX 960. At LN_2 temperatures, R reached a similar maximum value at 1 wt% CSR concentration for both the MX 130 and MX 960 toughened epoxy resins. Further examination of the fracture surface with 1 wt% loading of the MX 960 showed three distinct areas. High magnification SEM images of different areas show that extensive voids and cavitation of CSR particles are observed at ambient temperature while at LN_2 temperatures the limited number and size of those CSR particles are obtained correspond with the differences in the R value.



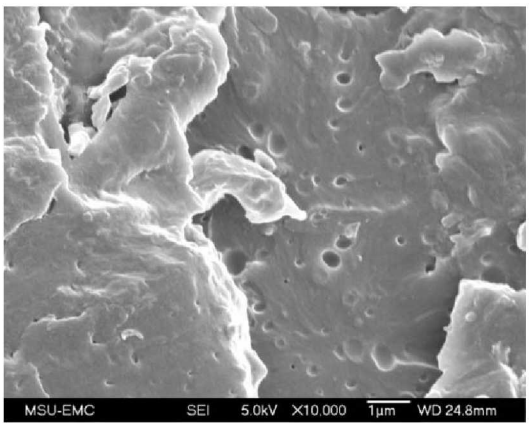
a. MX 960-1 smooth area at RT.



b. MX 960-1 smooth area at LN_2.



c. MX 960-1 rough area at RT.



d. MX 960-1 rough area at LN_2.

Figure 5. High magnification SEM images of fracture surface following Charpy impact test of MX 960 toughened epoxy resin.

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