Investigation of the Role of Rubber Particle Cavitation Resistance on the Toughening Mechanisms of Epoxy Resins

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Abstract: The occurrence of rubber particle cavitation in rubber modified epoxy resins has generated some controversy in the literature and role of cavitation resistance in toughening mechanisms has remained an enigma. In this study, hydroxyl terminated polybutadiene (HTPB) and synthesized epoxy terminated polybutadiene (ETPB) have been used to toughen an epoxy resin. FTIR and titration techniques were used to monitor the ETPB synthesis. Mean fracture toughness, K_{IC}, of 0.65 MPa.m$^{0.5}$ was measured for unmodified epoxy polymer. The measured toughness was increased by the addition of HTPB to 1.23 MPa.m$^{0.5}$ and ETPB to 1.80 MPa.m$^{0.5}$. The cavitation zone of the HTPB modified sample was bigger than that of ETPB modified sample which showed the higher cavitation resistance of ETPB particles. SEM studies showed volumetric expansion of rubbery phase in slow crack growth region of both samples which proved the plastic void growth. The results showed that the elevated cavitation resistance of ETPB did not suppress plastic void growth. The optical microscopy of crack tips showed shear banding which was more significant in ETPB modified sample. SEM micrographs of fracture surface of HTPB modified samples showed no tail formation while pinning tails were present in ETPB modified samples. The results showed that higher cavitation resistance activated crack pinning process and induced larger shear banding zone in ETPB modified samples. Deflection and forking of the main crack into secondary cracks was also observed in ETPB modified samples while these phenomena were not present in HTPB modified samples.

Keywords: Cavitation, epoxy, toughening, fracture.

1. INTRODUCTION

Rubber toughening of epoxy resin is one of the popular methods for improving the toughness of epoxy resin and has been extensively studied by many researchers and several toughening mechanisms have been proposed [1-3]. Rubber cavitation and concomitant shear deformation in the form of dilatational void growth and shear banding between the particles are now generally accepted as the primary toughening mechanism of rubber modified epoxies [1]. Several secondary toughening mechanisms such as plastic void growth [4-7] rubber particle bridging [8-10], crack deflection [1, 11], crack bifurcation [1, 11] and crack pinning [11] may also contribute to the elevated toughness of modified epoxies.

In most of rubber modified epoxies the cavitation of rubber particles was observed [1]. Two main reasons exist for cavitation of rubber particles. First triaxial thermal shrinkage stress which develops in the dispersed domain phase on cooling [12] and second triaxial stress field ahead of crack tip combined with high bulk modulus rubbery phase [1, 13]. Bucknall *et al.* [14] showed that cavitation itself could not be regarded as an important energy absorbing process and it could happen from comparatively small energy interchanges taking place within the rubber particles [14]. Johnsen *et al*. [7] also claimed that debonding process is generally considered to absorb little energy. So the energy of rubber cavitation or debonding cannot be regarded as the reason of the fracture toughness differences observed in rubber modified samples. But, cavitation of rubber particles can influence the toughening mechanisms and there still are controversial discussions about the role of rubber particle cavitation on toughening of epoxy resins [15, 16]. Two hypotheses exist in regard of cavitation [17]. The first hypothesis claims that cavitation phenomena is independent of shear banding and only contributes to onset of plastic dilatation which might occur either before or after shear yielding [17]. But the second hypothesis claims that cavitation resistance influences the size of process zone [17].

Bagheri and Pearson [17] showed that voids at zero cavitation resistance can induce massive shear yielding in low cross-linked matrix. They concluded that cavitation resistance of rubbery phase did not play any role in toughening mechanism of epoxy resin. However, later Mafi and Ebrahimi [15] showed higher

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cavitation resistance of core-shell rubber particles with 120nm size, enhanced the fracture toughness of epoxy resin. They supported the hypothesis that greater cavitation resistance of core-shell rubber particles leads into greater build up of elastic strain energy before cavitation, so the cavitation of rubber particles enables the formation of shear band to proceed faster and results in bigger process zone. Cavitation may also influence the plastic void growth mechanism [13]. Two important mechanisms have been identified for two phase rubber toughened thermosets. The first is localized shear yielding and the second is internal cavitation or interfacial debonding of rubbery particles and consequent plastic void growth [1]. The above mechanisms are triggered by different types of stress concentrations. The shear yielding mechanism is largely governed by von Mises (deviatoric) stress whilst cavitation is mainly controlled by hydrostatic (dilatational) tensile stresses which are acting [18].

The triaxial stress-state part of the crack tip exerts dilatational force to rubbery particles. This dilatational force causes failure and void formation either internally in the rubbery particles (cavitation) or at the particle-matrix interface (debonding). Once the void is formed, it grows and dissipates energy [13]. As the Poisson ratio of rubber is close to 0.5, its bulk modulus tends to infinity. This demonstrates that a rubber particle like a very rigid body resist against volumetric deformation and dilatation when subjected to triaxial stresses. As rigid rubbery phase prohibit large scale plastic dilatation in the matrix, the void formation in rubber modified epoxy is an essential prerequisite for plastic void growth. Epoxy polymers strain soften after yielding which facilitates plastic void growth but they strain harder again [19]. So if the cavitation or debonding occurs after strain hardening the plastic void growth will be suppressed [13]. Thus the necessary criterion for plastic void growth is that rubbery particles cavitates or debonds and do so before strain hardening. This criterion suggests that lower cavitation resistance might facilitate plastic void growth.

In this study, hydroxyl terminated polybutadiene (HTPB) and synthesized epoxy terminated polybutadiene (ETPB) have been used to toughen an epoxy resin. The aim is to generate two blends with almost similar morphology but different particle cavitation resistance to examine the role of cavitation resistance on mentioned mechanisms. Linear elastic fracture mechanics approach and different microscopy techniques are utilized to elucidate the role of cavitation resistance of the rubbery phase in an epoxy polymer.

2. EXPERIMENTAL

2.1. Materials

The materials used in this investigation consisted of a diglycidyl ether of bisphenol-A (DGEBA) based epoxy pre-polymer. The epoxide equivalent weight (EEW) of the epoxy resin was 190g/equiv and it was supplied by Khouzestan Petrochemical Co. (Epiran 6). A cycloaliphatic amine curing agent (Epikure F-205 from Huntsman) with a number of amine groups corresponding to 104g/equiv, was used as the hardener. Hydroxyl terminated polybutadiene (HTPB) with the number average molecular weight of 3400 g/mol was purchased from Zibo Qilong Chemical Industry Co. Ltd. The lab grade of maleic-anhydride (MA) and triphenylphosphine (TPP) were purchased from Merck Chemicals. All materials were used as received.

2.2. Synthesis of Epoxy Terminated Polybutadiene (ETPB)

Synthesis of epoxy terminated polybutadiene was carried out in two steps. In the first step, carboxyl terminated polybutadiene (CTPB) was synthesized by reacting HTPB with maleic anhydride through a ring opening addition reaction at 80°C. This reaction was performed in the presence of epoxy resin to control the viscosity build up during the reaction. The reaction was carried out in a three necked 250 milliliter glass reactor which was equipped with a mechanical stirrer and was blanketed with nitrogen. The reaction time was about 24 hours to ensure complete reaction of reagents. In the next step, ETPB was synthesized by reacting the resulted CTPB with an excess of epoxy resin (i.e. 7.5 wt%) in the presence of 0.2 wt% of triphenylphosphine as catalyst. The reaction was performed at 80°C and under vacuum (12 mmHg) for 24 hours.

2.3. Characterization of Synthesized Resins

The HTPB, CTPB and ETPB were characterized qualitatively by FT-IR spectroscopic technique. The FT-IR spectra of samples were taken on a Bomem FT-IR spectrometer (MB series; ABB Bomem, Inc., Quebec, Canada) at a 4cm^{-1} resolution averaged over 20 scans. In addition, the acid value of synthesized CTPB and ETPB were determined according to ASTM D1639. The epoxy equivalent weight (EEW) of ETPB was also determined according to ASTM D1652.

2.3.1. Sample Preparation

Two sets of samples containing 10phr of HTPB or ETPB were prepared as described below. For preparing the test specimens, the epoxy resin was first degassed for 1 hour at 5mbar in a vacuum oven. After that, 10phr of HTPB (considering total weight of epoxy and hardener) was added to the epoxy resin and was mixed under vacuum for 30min. at 1300rpm. As ETPB samples contained some epoxy resin, the required amount of epoxy resin was added to the synthesized ETPB samples and was mixed for 30min. at 1300rpm.

The stoichiometric amount of hardener was then added to the mixture and was mixed under vacuum. The mixture was poured into a pre-heated Teflon coated steel mold. The mold was placed in an air circulating oven at 80°C for 3 hours followed by 1 hour of post curing at 120°C. In the next step, the mold was removed from the oven and allowed to cool gradually to room temperature. The mold contained cavities with three and four point bending test specimen shapes (according to ASTM D5045) so no further machining of the specimens was required. By using this method, the risk of damage forming of the samples during machining was eliminated.

2.4. Test Methods

The fracture toughness was measured according to ASTM D5045-96 protocol. Fracture toughness, K_{IC}, was determined using a single edge notched type specimen ($6.5*12*80mm^3$) in a three point bending (SEN3PB) geometry with a span of 50mm. Critical strain energy release rate, G_{IC}, was calculated using the integrated area of load- displacement curve obtained in the SEN3PB test. The samples were notched and then pre-cracked by striking a razor blade, previously chilled in liquid nitrogen with rubber hammer. The ratio of the final crack length to the specimen width was held in a range of 0.4 to 0.6. The tests were performed using an Instron 5566 universal frame at the crosshead speed of 1mm/min. A minimum of 6 specimens were tested, for each sample, to ensure accuracy.

Tensile behaviour was measured according to ASTM D638 guideline. Type I dog bone specimens were tested using a screw driven Instron 5566 universal frame at a crosshead speed of 5mm/min. Average of at least 5 measurements was reported for each data point.

Dynamic mechanical data were obtained using a Triton DMTA equipped with a bending fixture. Shear moduli were measured in oscillating bending, at a frequency of 1Hz and strain amplitude of 1%. The samples were heated from -150°C to 160°C using 5°C/min ramp rate.

Double edge notch four point bending (DEN4PB) samples were used to investigate the crack tip damage zone. The bars with dimensions of $125*12*6.5mm^3$ were notched with a milling tool. The distance between notches was 10mm and the spans were 30mm and 90mm. Razor blade was inserted into the notches and two identical cracks were introduced to the samples. The samples were broken in DEN4PB geometry with crosshead speed of 1mm/min. The damage zone around the survived DEN4PB crack was cut along the thickness direction into two halves. The plane-strain core region was prepared for transmission optical microscopy (TOM). For TOM investigations, thin sections of rubber modified samples were obtained by polishing the samples roughly to less than 100 microns. The thin sections were then examined, using a Leica DMR optical microscope.

The fracture surface of the broken specimens was studied using scanning electron microscopy (SEM). The SEM examinations were carried out using a Philips scanning electron microscope at an accelerating voltage of 30kV. In order to the particle size analysis the samples were broken in liquid nitrogen and coated with a thin layer of gold to reduce any charge build up on the surface.

2.5. Results and Discussion

2.5.1. Characterization of Synthesized Components

The amount of carboxyl groups of the resulting CTPB and also ETPB were determined by titration method. It was found that the acid value of the CTPB was about 10mg KOH/g. In comparison to the acid value of the CTPB, the acid value of the ETPB is almost zero mg KOH/g. It shows that all of the carboxyl functionalities of CTPB have reacted with epoxide groups of the epoxy resin.

Also, the epoxy equivalent weight (EEW) of the resulting ETPB was determined to be 268g/eq which was in good agreement with the theoretically calculated EEW. i.e. 255g/eq.

Figure **1** shows the FTIR spectra of HTPB, CTPB and ETPB. The spectrum of HTPB displays a characteristic absorption peak at $3406cm^{-1}$ (peak a) due to hydroxyl stretching vibrations. Observation of an absorption band at 1733cm^{-1} (peak b), which can be ascribed to the carboxyl group of CTPB, confirmed the formation of carbonyl groups by reaction of maleic anhydride with hydroxyl groups of HTPB. As can be seen, the spectrum of the ETPB sample is similar to that of the neat epoxy resin due to the high concentration of epoxy resin in the ETPB sample. Appearance of the absorption bands at 913 and 839cm^{-1}, in the spectrum of ETPB indicates oxirane group in the epoxy resin.

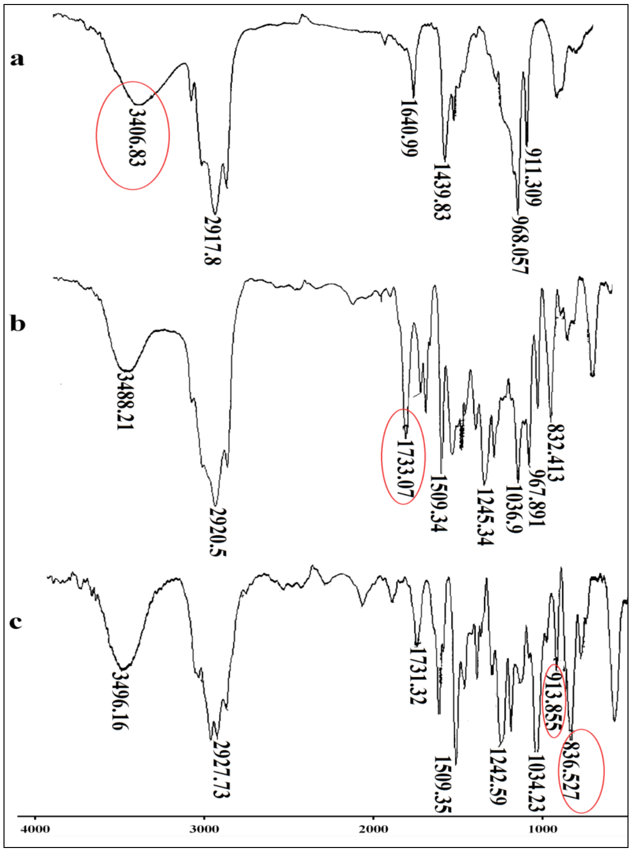

Figure 1: FTIR spectra of: (**a**) HTPB, (**b**) CTPB and (**c**) ETPB.

The dispersion morphology of rubber phase in epoxy matrix was characterized by SEM. Figures **2** and **3** show the SEM micrographs of HTPB and ETPB modified samples, respectively. The rubber volume fraction of modified samples were measured to be 15.4±10% and 14.7±10% vol% for HTPB and ETPB modified samples respectively through image analysis method. As seen, the average particle size in the two blends were in the same order, however the uniform dispersion of the particles seen in figure **2** is not occurring in the blend containing epoxy terminated rubber (Figure **3**). Meanwhile, the latter contains many non-spherical particles. Therefore, one may expect different phase separation behaviours in the two blends. Despite the differences observed in Figures **2** and **3**, the results of this study do not support the claim of Fabio *et al*. [20] who reported structure refinement by epoxy end capping of the rubber molecules.

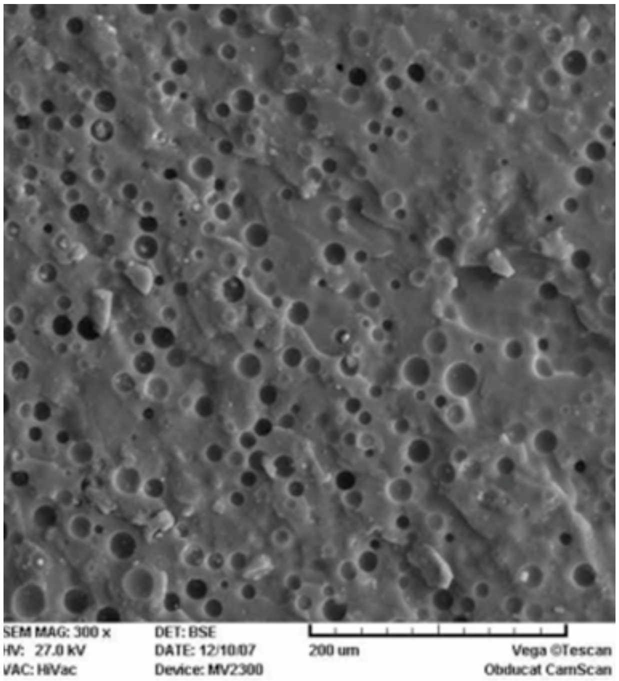

Figure 2: SEM micrograph of HTPB modified sample.

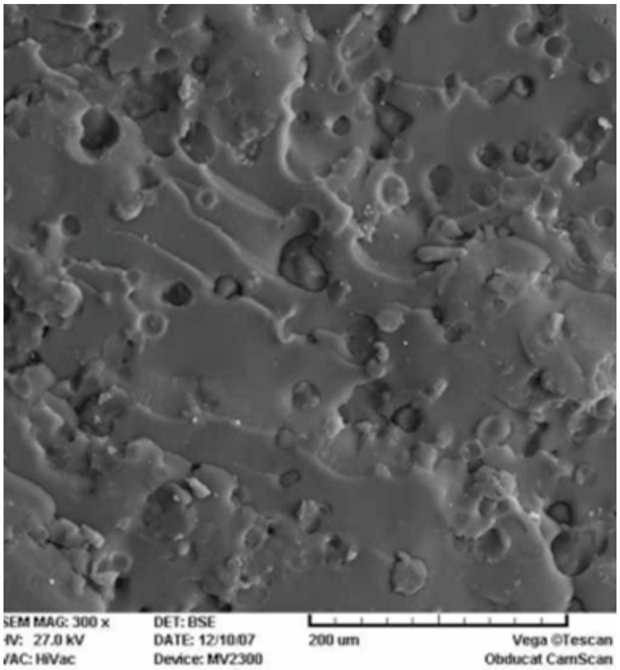

Figure 3: SEM micrograph of ETPB modified sample.

2.6. Mechanical and Fracture Behaviour

The results of fracture toughness and tensile tests are summarized in Table **1**. As expected the mechanical

Table 1: The Results of Fracture Toughness and Yielding Behavior

	K_{IC} (MPa.m$^{1/2}$)	G_{IC} (J/m^2)	Strain at break (%)	Tensile modulus (GPa)	Yield stress (MPa)	Mc (gmol^{-1})
Neat Epoxy	0.65 ± 7%	84 ± 3	2.2 ± 0.05	2.97 ± 0.1	91	377
HTPB Modified Epoxy	1.23 ± 10%	342 ± 27	4.1 ± 0.15	2.37 ± 0.1	78	406
ETPB Modified Epoxy	1.80 ± 10%	793 ± 54	4.3 ± 0.1	2.31 ± 0.1	74	465

properties of the modified resins are affected by rubber modification. The modulus and yield stress of modified epoxies decreased while the strain at break increased which is a typical behaviour of rubber modified epoxies (Table **1** and Figure **4**) [1]. Mean fracture toughness, K_{IC}, of 0.65 MPa.m$^{1/2}$ was measured for the unmodified epoxy. The measured fracture toughness was increased by incorporation of HTPB to 1.23MPa.m$^{1/2}$ and ETPB to 1.80MPa.m$^{1/2}$. Mean fracture energy, G_{IC}, of 84J/m^2 was measured for the unmodified epoxy. The measured fracture energy was increased by incorporation of HTPB to 342J/m^2 and ETPB to 793J/m^2.

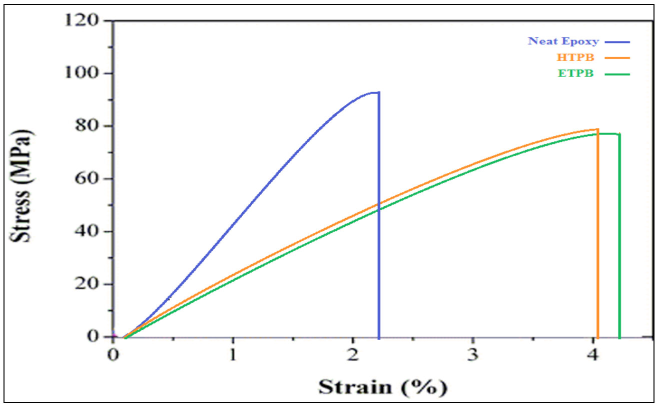

Figure 4: Stress-strain diagram of the samples in tensile experiment.

One might attribute the variation in fracture energy of HTPB and ETPB samples to their degree of adhesion to the matrix but it has been shown experimentally that when the second phase consists of micron size rubber particles, the interfacial bonding has only a modest effect on the fracture properties of material [16, 21].

The fracture surface of unmodified epoxy polymer in slow crack-growth region has been shown in Figure **5**. As can be seen, the fracture surface is smooth and featureless and shows no sign of plastic deformation which is typical of a brittle thermoset polymer [6, 7]. This observation agrees well with the low measured toughness of the material.

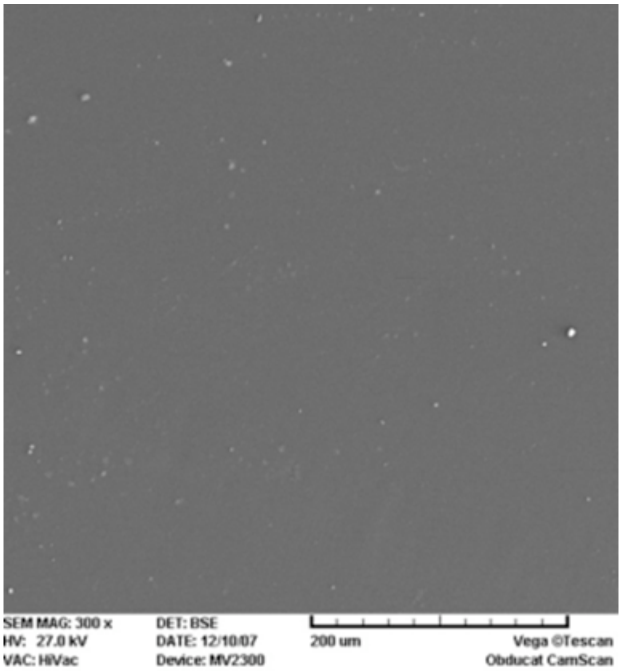

Figure 5: The fracture surface of unmodified epoxy polymer in slow crack-growth region.

The fracture surface of HTPB and ETPB modified samples in slow crack growth region have been shown in Figures **6** and **7**, respectively. Figure **6** clearly shows internal cavitation and tearing of the HTPB particles. No debonding or protrusion of rubber particles was observed in HTPB modified samples, while in ETPB modified specimen a combination of cavitation, debonding and rubber particle pull out is observed (Figure **7**). Observation of torn but not fully cavitated particles in ETPB modified blend (Figure **7**) suggests the possibility of higher cavitation resistance of these particles compared to that of HTPB particles. However, this hypothesis needs to be further explored by means of TOM. Figure **8** illustrates the results of TOM study of the crack tip damage zone in rubber modified blends. As can be clearly seen, the cavitation zone of the HTPB modified sample is bigger than that of ETPB modified sample which supports the hypothesis claimed on the higher cavitation resistance of ETPB specimen. The higher cavitation resistance of ETPB particles can be rationalized considering the existence

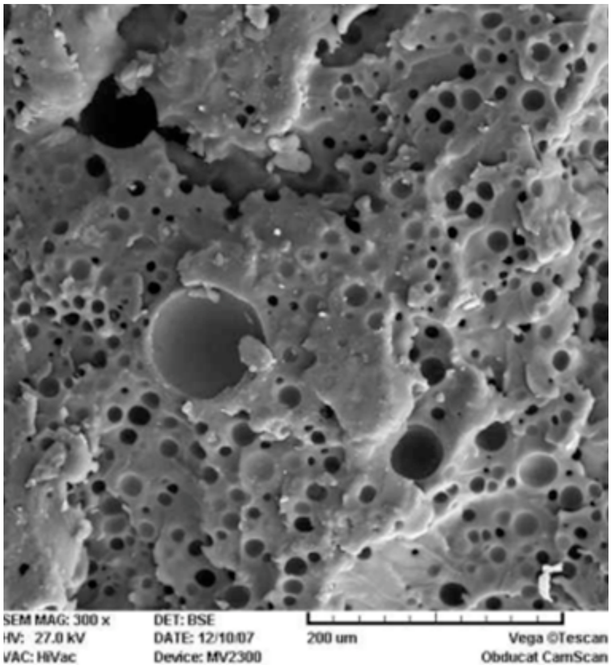

Figure 6: Fracture surface HTPB modified sample in slow crack growth region.

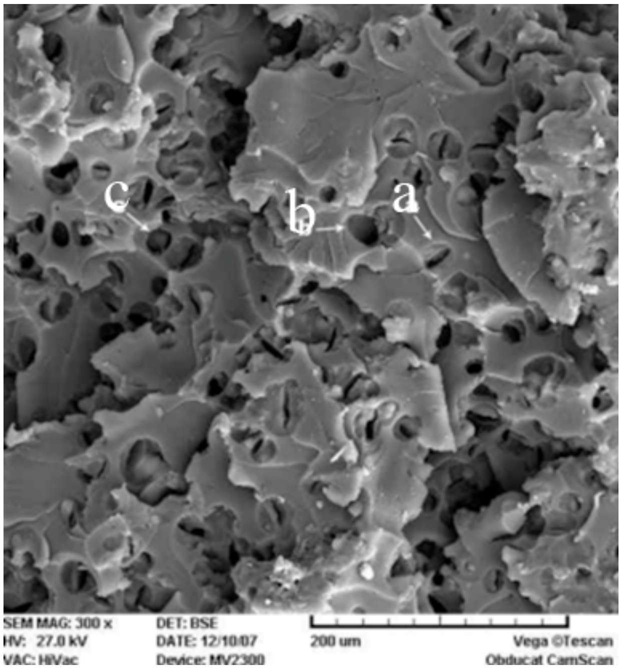

Figure 7: Fracture surface of ETPB modified sample in slow crack growth region showing cavitation (**a**), particle pull out (**b**) and debonding (**c**).

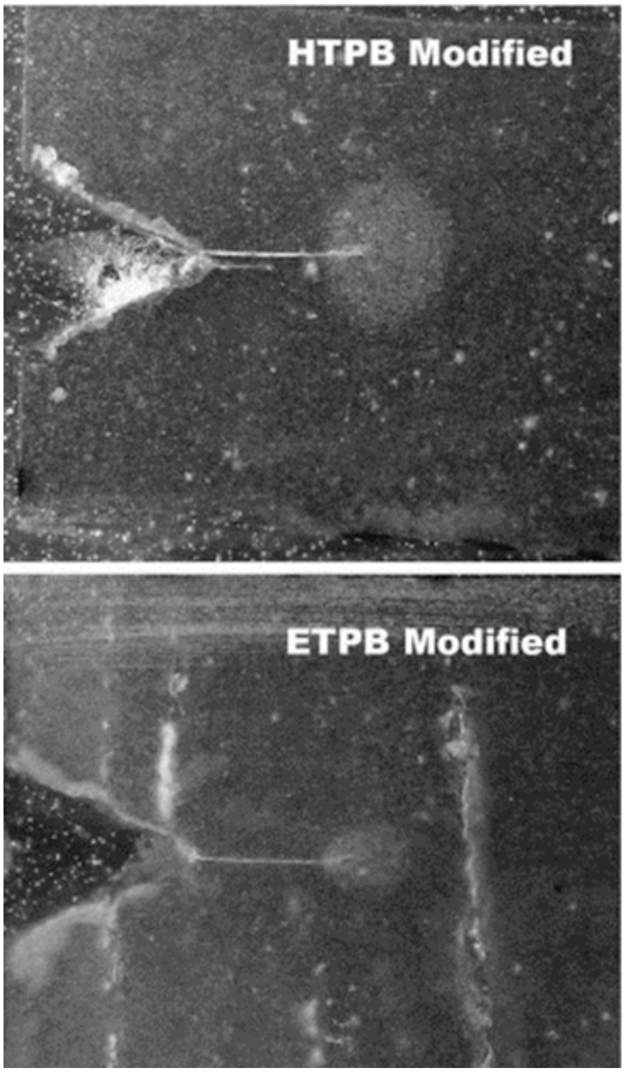

Figure 8: Cavitation zone of HTPB and ETPB modified samples.

of oxirane groups in its molecule that can react with the amine groups in the hardener resulting in the cross linking of the hardener.

DMTA was utilized to investigate this hypothesis. The tan δ and storage moduli of neat and rubber modified samples have been established against temperature in Figures **9** and **10**, respectively. The neat epoxy resin system showed a β peak at around -60˚C. Addition of HTPB and ETPB did not result in a second low temperature peak (associated with the α transition of the rubbery phase) but essentially enhanced the magnitude of the β peak. However even if we could differentiate the peaks, it was not easy to judge the variations in rubber crosslink density according to their glass transition temperatures due to thermal shrinkage stresses. Triaxial thermal shrinkage stress develops in the dispersed domain phase on cooling since the coefficient of thermal expansion of the rubbery phase is larger than that of glassy phase. The domains are constrained by glassy epoxy matrix. The glass transition of the rubber changes [12]. Cross-link density was assessed employing theory of rubber elasticity [22] using the plateau modulus in the DMTA curves (Table **1**). The rubbery region plateau of the specimens shows the decreased crosslink density of ETPB modified samples. This result suggests that a part of hardener was reacted with rubbery phase so a smaller amount of hardener reacted with the epoxy resin and therefore the crosslink density of the ETPB modified sample was decreased.

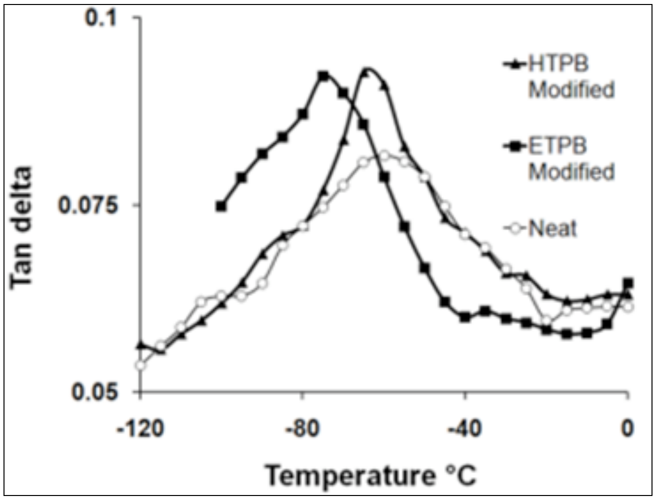

Figure 9: Tan delta of neat and modified epoxies near beta transition temperature.

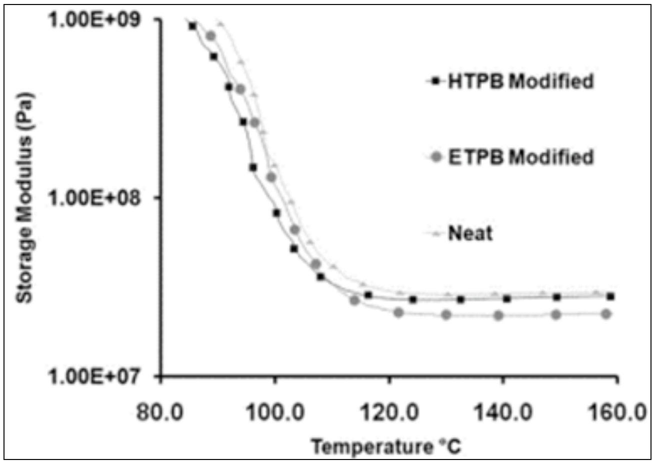

Figure 10: Storage modulus of neat and modified samples in rubbery region.

2.7. Toughening Mechanisms

Figures **11** and **12** compare the fast and slow crack growth regions of HTPB and ETPB modified specimens. Both figures show volumetric expansion of rubbery phase in slow crack growth region which proves the plastic void growth. As mentioned earlier, if the cavitation or debonding occurs after strain hardening the plastic void growth will be suppressed [13]. The results show, that both cases meet the necessary criterion for plastic void growth which is the rubber cavitation or debonding before strain hardening. For this specific case, elevated cavitation resistance of ETPB does not suppress plastic void growth. It is of great importance to quantify the extent of plastic void growth to be able to interpret the difference in fracture energy of ETPB and HTPB modified samples. Volumetric strain measurements can be very misleading since void growth process tends to occur in a small region of the crack tip [13]. Therefore, in present study image analysis method has been used.

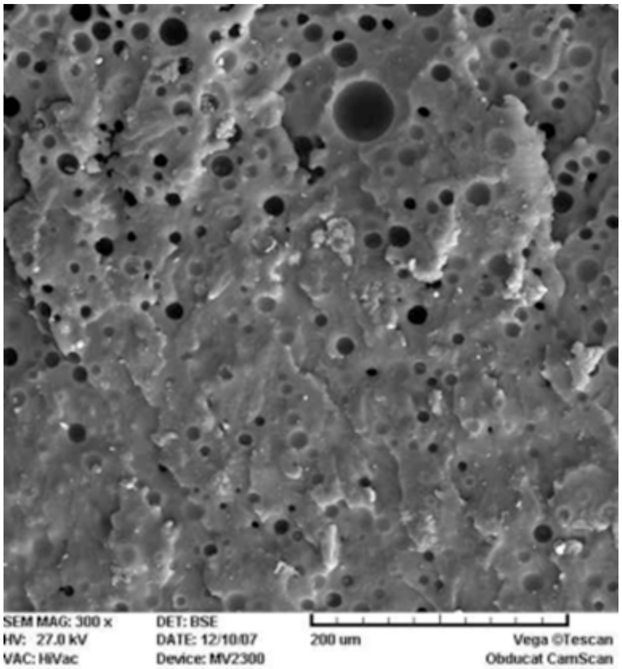

Figure 11: Fast and slow crack growth regions of HTPB modified specimen.

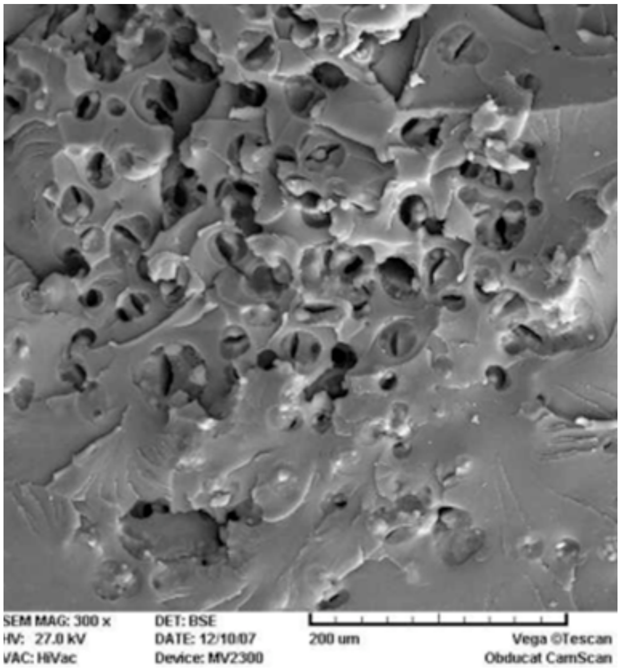

Figure 12: Fast and slow crack growth regions of ETPB modified specimen.

For HTPB and ETPB modified samples 41±15% and 38±15 of increase in volume fraction was measured respectively. Considering the scatter associated with the measured values, the difference in the extent volume fraction increase can be regarded as insignificant.

The other major toughening mechanism which is cavitation and concomitant shear banding mechanism was also investigated in the samples. In this mechanism, the rubber particles cavitate because of triaxial tension ahead of the crack tip. This cavitation reveals the plane-strain constraint ahead of the crack tip and allows the stress concentration associated with cavitated particle to activate shear yielding in the matrix [1]. The role of rubber particle cavitation resistance on shear yielding of the matrix is discussed in our previous paper [15]. It was shown that core shell rubber particles with higher cavitation resistance can enhance the shear yielding of matrix. The TOM micrographs of crack tips of HTPB and ETPB modified samples are shown in Figures **13** and **14**, respectively. Both figures show a shear banding zone at the crack tip, however the size of shear banding zone in ETPB modified sample is slightly bigger. This observation can support aforementioned hypothesis that claims cavitation resistance influences the size of process zone.

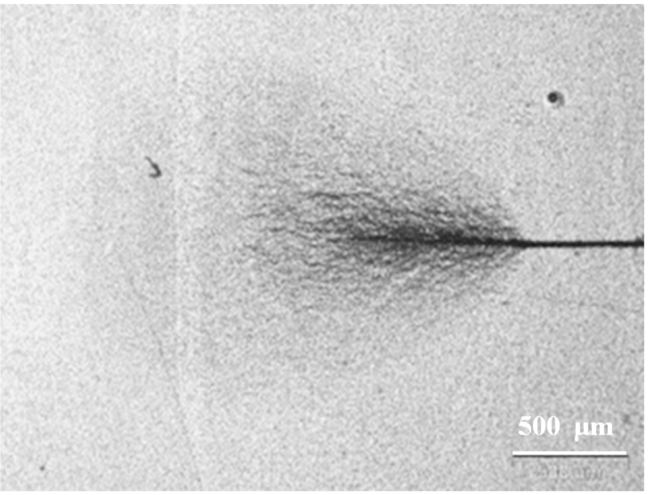

Figure 13: TOM micrograph of HTPB modified sample crack tip.

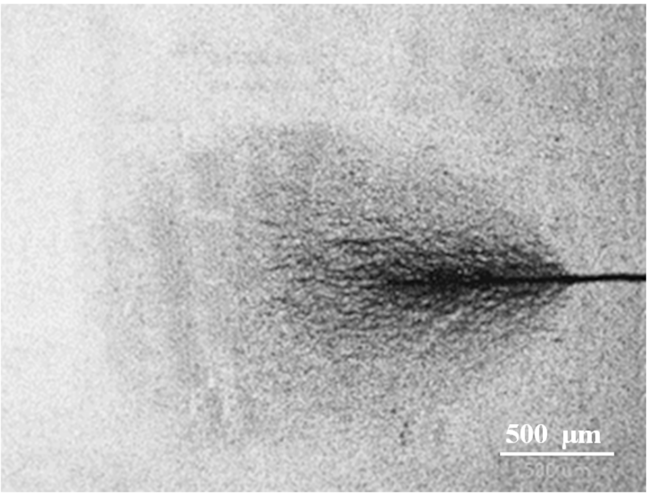

Figure 14: TOM micrograph of ETPB modified sample crack tip.

As can be seen in Figures **13** and **14**, the radius of the plastic zone in ETPB sample is larger than that of HTPB modified sample. Irwin proposed that the fracture toughness is directly proportional to the square root of the radius of the plastic zone [1]. Therefore, one may attribute the difference in fracture toughness of ETPB and HTPB samples to their difference in ability to undergo plastic deformation. However, a more precise look to Figures **13** and **14** indicate that the observed difference in the radius of the process zone does not justify this extent of difference in the fracture toughness. As seen in Figures **13** and **14**, the radius of plastic zone (the zone with different color) of HTPB (Figure **13**) and ETPB (Figure **14**) samples are about 200 and 280 microns, respectively. While the fracture toughness values of these materials are 1.80 and 1.23MPa.m$^{1/2}$, respectively (Table **1**). Therefore, it is necessary to search for other possible toughening mechanism(s) responsible for the difference in fracture toughness values of HTPB and ETPB modified samples.

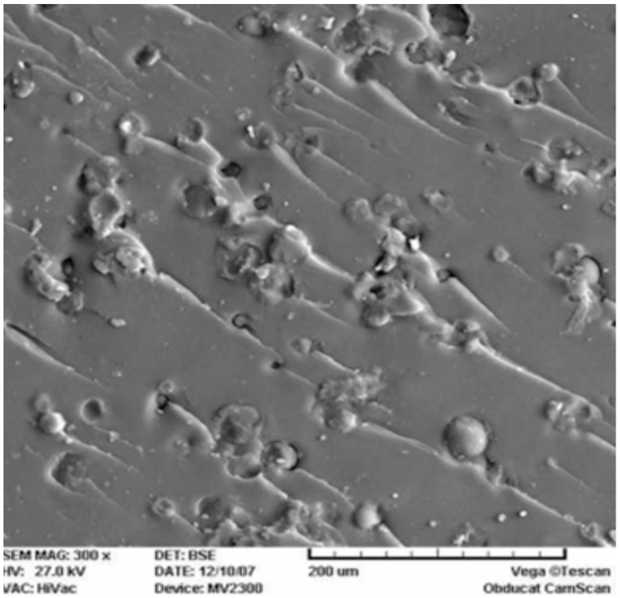

Figure 15: Crack pinning toughening mechanism in ETPB modified sample.

To do so, further microscopic examinations were launched. Figure **15** shows the SEM micrographs of

ETPB modified sample in fast crack-growth region. This figure illustrates the possibility of crack pinning in ETPB modified samples. In this mechanism, the crack begins to propagate within the material, the crack front bows out between the second phase dispersion whilst still remaining pinned at all positions where it has encountered the second phase particles [23]. Crack pinning arises from interactions between the moving crack front and the second phase dispersion. The typical crack pinning feature is the formation of tails behind the rubber particles which is due to the meeting of crack faces in different planes after bowing [11]. Pinning tails can clearly be seen in fast crack growth region of ETPB modified sample (Figure **14**).

Figures **6** and **11** show the SEM micrographs of fracture surface of HTPB modified sample. No tail can be observed in HTPB modified sample. Therefore, it might be concluded that crack pinning is not active in HTPB modified samples.

In order to rationalize the difference in HTPB and ETPB particles in activating pinning mechanisms, one needs to consider their different cavitation behavior. Since the cavitation resistance of HTPB particles is low, the crack front can propagate through the HTPB particles with no bowing. However, in the case of ETPB particles, the high cohesive strength of the particles caused by cross linking and their strong adhesion to the matrix provided by the covalent bonds suppress crack growth in the vicinity of the particles, i.e. crack pinning.

Figures **16** and **17** show the TOM micrographs taken from the crack tip of ETPB modified sample. Figure **16** shows the crack deflection mechanism of ETPB modified specimen. Crack bifurcation is also evident in Figure **17**. In these mechanisms, rubber particles cause the main crack to deviate from the principal plane of propagation (deflection) or fork into many secondary cracks (bifurcation).

Both mechanisms induce a mixed I, opening, and II, in-plane shear, modes of crack propagation. As the consumed energy in mode II of fracture is higher than mode I [24], this mixed mode of crack propagation enhances toughness. These observations can be attributed to the strong interface and high cavitation resistance of ETPB particles which suppress particle tearing when the crack touches rubber particles and thus, activates crack deflection and crack bifurcation mechanisms.

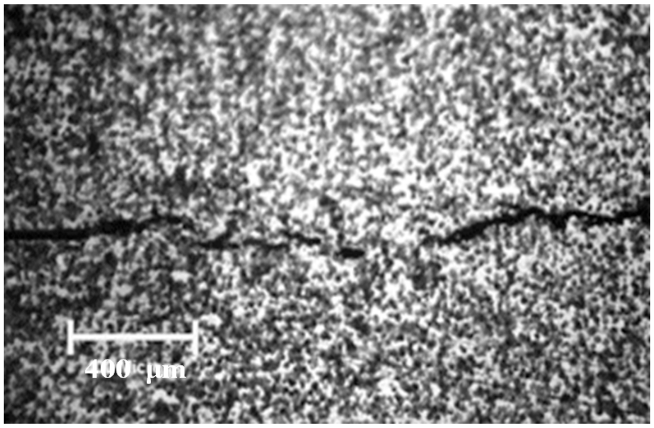

Figure 16: Crack deflection toughening mechanism in ETPB modified sample.

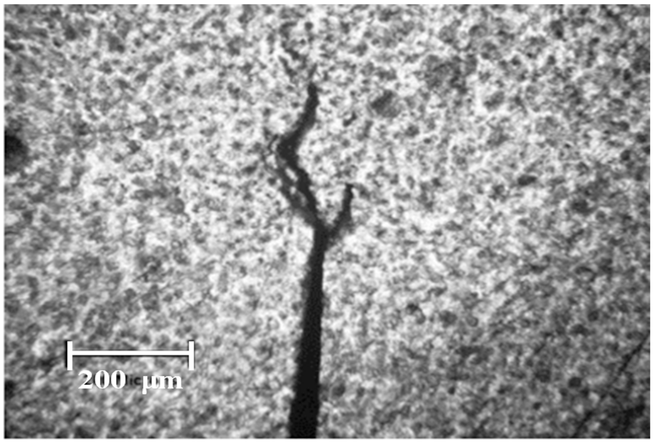

Figure 17: Crack bifurcation toughening mechanism in ETPB modified sample.

In conclusion, ETPB rubber incorporated in this study not only cavitates and induces shear deformation in the epoxy matrix similar to conventional rubber modifiers, but improves the fracture toughness *via* additional mechanisms of crack pinning, crack deflection and bifurcation. This additional positive effect has been brought to ETPB *via* its higher cavitation resistance and reactivity with the matrix. This is while HTPB rubber studied only improves fracture toughness of epoxy *via* cavitation and concomitant shear banding mechanism.

CONCLUSIONS

Epoxy matrix was toughened by incorporation of HTPB and ETPB. ETPB rubber particles appeared to possess higher cavitation resistance than HTPB particles. Both sets of samples showed volumetric expansion of rubbery phase in slow crack growth region which proved the plastic void growth mechanism. The results showed that for this specific case, elevated cavitation resistance did not suppress plastic void growth. Shear banding was observed in both sets of samples which was more significant in ETPB modified sample. The results supported the hypothesis that cavitation resistance of rubber particles influences the onset of cavitation and also the size of process zone.

As the cavitation resistance of HTPB particles was low, the crack could propagate through the HTPB particles and no crack pinning happened. However, in ETPB particles due to the strong interface, the crack front bowed when reached to rubber particles. Higher cavitation resistance activated crack pinning process modified samples. Crack deflection and crack bifurcation processes were also observed in ETPB modified samples due to same reason. Higher cavitation resistance enhanced the toughness of ETPB modified samples by forming a larger process zone ahead of the crack tip and by inducing crack pinning, crack deflection and crack bifurcation processes.

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