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Novel Self-Assembling Block Copolymers Versus Traditional Telechelic Oligomers

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Toughening of Epoxies: Novel Self-Assembling Block Copolymers Versus Traditional Telechelic Oligomers

by

Lauren N. Bacigalupo

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ABSTRACT

Epoxy resins are commonly utilized because of their adhesive capacity and high strength. However, epoxies are inherently brittle; much research has been dedicated to improving their fracture toughness. This study compares a traditional telechelic oligomer, CTBN, and a novel self-assembling block copolymer, SBM, as it relates to improving the fracture toughness of a lightly crosslinked epoxy system.

After characterizing the modified systems for fracture toughness, mechanical and thermal properties, namely yield stress and the glass transition, will be determined in order to discern the impact these modifiers have on the overall properties of the blend. TEM, SEM and TOM techniques will be utilized for characterizing morphology, fractography and subsurface damage, respectively.

Once this was accomplished, it was deduced that the toughening mechanisms of CTBN and SBM-modified epoxies are very similar. The main difference between the two is that the inherent structure of SBM allows the SBM-modified epoxy to retain its compressive yield strength. This, consequently, makes SBM ideal for thin bondline applications in the industrial adhesive and/or electronics industry.
I. Introduction

I.1. Motivation

Epoxies are often used as underfill resins in microelectronic packaging to reduce the shear stress of the solder joints between the chip and the substrate that result due to the mismatch in the CTEs [1]. Since epoxy-based resins react with an array of curing agents that can yield a wide range of properties, these resins can be tailored for each desired application [2]. However, while epoxies have good creep and adhesive properties as well as high strength, they are inherently very brittle. Hence, it is advantageous to toughen these brittle epoxy resins with rubber-toughing agents in order to increase the fatigue lifetime of the flip chip electronics package for which it was designed [3]. As illustrated in Figure 1, the role of the epoxy as underfill is important to the success of the flip chip package. Toughening the epoxy is lucrative to the electronic packaging industry because it promotes a longer fatigue lifetime, and subsequently, more reliable electronics.

Figure 1. Schematic of flip chip packaging.
More recent studies have explored the use of rubber-toughened epoxy to improve the drop test reliability of portable electronics [4]. The results in Figure 2 show that implementing toughened underfill yields improved impact resistance of traditional lead-base solder as well as lead-free solder. In order to meet current industrial standards, lead-free solder must be used in place of traditional lead-base solder to reduce its environmental impact. However, although it is more environmentally conscious, lead-free solder is also inherently more brittle than traditional lead-base solder, so the use of modified epoxy becomes crucial. Consequently, many researchers are interested in toughening epoxy in order to improve the reliability of lead-free solder.

Figure 2. Drop-test results for lead-free solder when underfill (UF) is varied [4].

1.2. Fracture Mechanics

Fracture mechanics allows engineers to predict the tolerance of a material as it relates to an existing imperfection. In many cases, this is taken to be a crack or a void in the material that may affect mechanical properties such as modulus and yield strength.
The first quantitative attempt to understand fracture was by A.A. Griffith who determined that, in the presence of a crack in a plate of elastic material, there must be a correlation between the decrease in potential energy via external loads and the increase in surface energy resulting from crack formation [5]. In the classic example of a through-thickness crack in a large plate, as seen in Figure 3, the change in potential energy, $U$, in the presence of a crack is represented by the equation:

$$U - U_0 = - \frac{\pi \sigma^2 a^2 t}{E} + 4a t \gamma_s \quad (1)$$

or,

$$U = 4a t \gamma_s - \frac{\pi \sigma^2 a^2 t}{E} + U_0 \quad (2)$$

where,

$U$ is the potential energy of body with crack, $U_0$ is the potential energy of body without crack, $\sigma$ is the applied stress, $a$ is one-half crack length, $t$ is the thickness, $E$ is modulus of elasticity and $\gamma_s$ is the specific surface energy.

By differentiating equation 2 by the crack length and setting it to zero, the following equation represents the equilibrium condition:

$$2\gamma_s = \frac{\pi \sigma^2 a^2}{E} \quad (3)$$

However, the second derivative of this is negative, so equation 3 is not always valid. As a result, Griffith rewrote equation 3 as:

$$\sigma = \sqrt{\frac{2E \gamma_s}{\pi a}} \quad (4)$$
This relation was derived for an elastic material and is therefore not accurate for materials that are capable of plastic deformation. As a result, Irwin amended Griffith’s theory to include an energy source term and to therefore define $\frac{d\gamma}{da}$ as $G$ rather than set $\frac{d\gamma}{da}$ to zero. Irwin then proved that

$$\sigma = \sqrt{\frac{EG}{\pi a}} \quad (5)$$

In order to better define the magnitude of stress at the crack tip, a parameter called the stress-intensity factor, $K$, was instituted. Irwin defined $K$ as

$$K = f(\sigma, a) \quad (6)$$

where $K$ is taken to be a function of the configuration of the crack as well as the loads applied [5]. It has become common practice to define this function as $Y (a/W)$, where there are solutions for common configurations and test sample geometries [6]. Stress intensity factors become an important parameter when deciding what material will be used for a specific application. Often, the following equation is used in order to account for potential flaws and design a component that will resist failure:
In addition to fracture toughness, this research investigated the crack-tip plastic-zone size, which developed where the stresses that the material experienced was higher than the yield strength. As a result, it can be deduced from Figure 4 that the elastic stress \( \sigma_y = \frac{K}{\sqrt{2\pi r}} \) will be greater than the yield strength, \( \sigma_{ys} \), some distance, \( r \), from the crack tip.

Therefore, the yield stress at the start of the plastic-zone is

\[
\sigma_{ys} = \frac{K}{\sqrt{2\pi r}} \quad (8)
\]

In the plane stress case, the radius of the plastic zone is taken to be:

\[
r_y \approx \frac{1}{2\pi} \frac{K^2}{\sigma_{ys}^2} \quad (9)
\]
For the plane strain case, where the triaxial stress field suppresses the plastic zone, a smaller plastic-zone radius is estimated to be

\[ r_y \approx \frac{1}{6\pi} \frac{K^2}{\sigma_{ys}} \]  \hspace{2cm} (10)

\[ \sigma_y = \frac{K}{\sqrt{2\pi r}} \]

Figure 4. Onset of plastic deformation at the crack tip, taken from Deformation and Fracture Mechanics of Engineering Materials by R. W. Hertzberg.

In this study, a single-edge-notch three-point-bend (SEN-3PB) sample was utilized in accordance with ASTM D5045 and, using the function \( Y(a/W) \), an empirical solution for equation 6. Plane-strain fracture-toughness, \( K_{IC} \), was measured based on this principal. Essentially, \( K_{IC} \) is a material property that illustrates a material’s capacity to arrest a crack already present in the material. However, this crack must be properly constrained according to Brown and Strawley [7], namely,

\[ \text{thickness}(t) \text{and } a \geq 2.5 \left( \frac{K_{IC}}{\sigma_{ys}} \right)^2 \]  \hspace{2cm} (11)

7
Provided the cracks in this study were properly constrained, the relationship between the fracture toughness and the plastic zone size will be observed. A better understanding of the toughening mechanisms present in the materials studied can be obtained through this relationship as well as subsequent microscopy studies.

I.3. Rubber Particle Size and Matrix Toughenability

Aside from the composition of rubber modifier, modifier particle size is also believed to have an effect on the capacity to toughen a brittle matrix. In one study, it was deduced that with rubber particles less than 100 nm, cavitation can only take place if the volume of the rubber domain allows enough energy to be released; even if the stress state would allow for the initiation of cavitation [8]. Kim et al. have also experimentally determined that in order to toughen effectively, the rubber particle diameter should be larger than 0.2 µm since cavitation is difficult otherwise [9]. The concern raised in both studies was that the particle itself would lack the capacity to internally shear, or cavitate, even if the surrounding stress state imparted by the matrix was conducive to cavitation. Figure 5 shows the fracture toughness limit with particle size, where the toughening limit is highlighted by a dashed arrow.

As discussed in the work of Pearson and Yee, another variable to consider regarding fracture toughness is the cross-link density [10]. While the modifier chosen does influence the capacity to toughen, it should be noted that if the epoxy matrix is not toughenable, or is highly crosslinked, then the fracture toughness will not be improved even with the addition of modifier. Toughening modifiers are designed to enhance the
ductility of the matrix, but if the structure of the matrix is heavily crosslinked, then there is not enough mainchain mobility to allow toughening mechanisms to become active [10]. In this study, a lightly cross-link system will be utilized in order to best observe the toughening mechanisms active in CTBN and SBM-modified epoxy.

Figure 5. Particle size vs. fracture toughness in core-shell rubber-toughened epoxy system [9].
I.4 Model Epoxy System: DGEBA/PIP Toughened With CTBN

1.4.1 Phase Formation

For the last several decades, epoxy resins have been toughened using butadiene-based copolymers such as carboxyl terminated butadiene acrylonitrile copolymers (CTBN) [11]. CTBN is a random copolymer that consists of butadiene and acrylonitrile. The acrylonitrile content dictates the miscibility of CTBN in the epoxy resin as well as the resulting size of the CTBN particles [12]. Figure 6 shows a morphology map from the work of L. T. Manzione et al. that illustrates the size of particles as a result of time and temperature of gelation. The general trend is that for a faster cure, the CTBN particles will be smaller.

During cure, CTBN will phase separate out of the epoxy matrix due to a decrease in the solubility. However, more than just solubility will dictate the extent of phase separation exhibited by the CTBN particles. A study by Moschiar et al. found that an increase in the initial rubber content in an ETBN (epoxy terminated instead of carboxyl terminate butadiene acrylonitrile) system will yield and increase in: the volume fraction of dispersed phase, average diameter and rubber concentration after cure [13]. Williams et al. specifically investigated the relationship between the point where phase separation begins with respect to gel conversion [14]. It was concluded that the more time between
phase separation with respect to gel conversion would result in the following properties: an increase in the concentration of dispersed particles and volume fraction of the dispersed phase, and a decrease in the amount of residual rubber in the matrix [14]. Increasing the cure temperature was also found, by Pascault et al., to affect CTBN by increasing the average size of dispersed domains [16]. It was also noted in this study that this trend is observed when the morphology is controlled by phase separation as opposed to polymerization rate.
I.5. Block Copolymer Toughened Epoxies

I.5.1 Phase Formation

Block copolymers possess a structure such that one block is immiscible in the epoxy precursors and another block is initially miscible. Such block copolymers self-assemble into nano-scale phases during network formation [17].

F. S. Bates has done extensive research in the field of nanostructured block copolymer modified epoxies [18, 19]. In these studies, poly (ethylene oxide)-poly (ethylene-\textit{alt}-propylene) (PEO-PEP) and poly (methyl methacrylate-\textit{ran}-glycidyl methacrylate)-poly (2-ethylhexyl methacrylate) (P (MMA-\textit{ran}-GMA)-PEHMA) were the diblock copolymers used. Figure 7 illustrates the morphology results of the toughened epoxy resins: spherical micelle, wormlike micelle and vesicle [18].

![Figure 7](image_url)
Another study by Bates et al. focused on the micellular structure and mechanical properties of epoxies modified with block copolymers [19]. This research used PEO-PEP diblock copolymer with PEO volume fractions of 0.5-0.26 and yielded spherical micelle and vesicle morphologies. Most importantly, the modulus decreased only by 0.6 GPa, but the fracture toughness was improved by .89 MPam^{0.5} when compared to the average [19]. Consequently, the advantages of block copolymers become readily apparent when improvements in toughness are observed without a proportional decrease in mechanical properties. Controlling the morphology via the block lengths continues to be an area of active research.

Similar studies of PEO-PEP done by Lipic et al. have also shown the nanostructured morphologies possible by triblock copolymers [20]. Analogous to the triblock copolymer morphologies observed in the studies done by Lipic are those of the polystyrene-block-polybutadiene-block-poly (methyl methacrylate) (SBM) triblock copolymers studied by J.P. Pascault et al. [21, 22]. Since there are three components in the SBM triblock copolymers, there are two variables (based on SBM chemical structure alone) that will dictate the morphology of the resulting nanocomposite: the volume fraction of S and B and the immiscibility of M in the epoxy. Figure 8 shows a schematic of the organization of such ABC triblock copolymers.
Figure 8. Schematic representation of an SBM thermoset before and after curing [21].

In order to better understand the structure formation of SBM particles, a schematic has been provided in Figure 9 illuminating the formation of the SBM micelles [23]. As illustrated in the figure, the SBM forms a rigid styrene core, surrounded by a polybutadiene shell, which is also encompassed by methyl methacrylate ligands. It has been deduced that this particular structure is characteristic of an SBM type where the immiscible middle block is in the minority and has been called the spheres on spheres type morphology [24]. This structure not only allows for more particles with less rubber, but also dictates the space between particles via the ligands of methyl methacrylate. In addition, this morphology is uniform throughout the matrix and does not form large domains of rubber, substantially different from the morphology of CTBN in terms of structure.
Figure 9. Schematic of nano-structured self-assembly of SBM in a DGEBA epoxy matrix [23].

Subsequent studies conducted by Pascault et al. have found that the SBM in a DGEBA-based epoxy, cured with Jeffamine, increases the $K_{IC}$ of the epoxy matrix by 2.2 MPAm$^{0.5}$ [25]. Interestingly, it was found in this study that the SB impurities present in the overall polybutadiene (PB) portion of the blend increased the fracture toughness. This would imply that the overall weight percent of PB has a direct impact on the capacity for the SBM triblock copolymer to toughen epoxy.

In a study by Pearson and Hydro, two different SBM triblock copolymers were observed. It was concluded that the smaller amount of PB in the one modifier was at
fault for the lack of toughenability of the epoxy matrix. Surprisingly, the fracture
toughness is increased without significant hindrance of the yield stress. This result is
thought to be due to the small domain size of the PB [22]. Though some physical
properties of SBM-modified epoxy were discussed briefly in order to relate the
morphology with the subsequent mechanical properties, it is also important to note what
is happening at the structural level to these modified epoxy composites. Therefore, the
next section is dedicated to the factors that alter the physical properties of rubber-
modified epoxy.

I.6. Physical Property Changes Due to Rubber Modification

Although traditional toughening modifiers such as CTBN are effective in
toughening the epoxy matrix, studies have shown that an increase in toughness typically
correlates to a hindrance in mechanical properties. Pearson and Yee found that adding
CTBN improved fracture while decreasing the yield stress, $\sigma_y$, Young’s modulus, $E$, and
glass transition temperature, $T_g$ [26, 27]. Additionally, it was noted that the larger plastic
zone size was observed, corresponding to an increase in the shear yielding of the matrix
and, subsequently, higher fracture toughness. The major factors that contribute to the
effects on physical properties are: inter-particle distance, morphology and retention of
polybutadiene in the epoxy matrix. It is vital to understand how these parameters affect
the physical properties of a modified-epoxy in order to deduce what happens at the
structural level.
Bagheri and Pearson studied the role of particle cavitation in rubber-toughened epoxies as it relates to inter-particle distance [28]. It was concluded that the fracture toughness in toughened blends goes through a ductile-to-brittle transition with increasing inter-particle distance. The reasoning behind this result is the change in stress state created by the voided particles. In this particular study, it was shown that the modified epoxy goes through a brittle-to-tough transition with decreasing inter-particle distance. As a result, it can be thought that the role of particle cavitation is to relieve the plane strain constraint from the surrounding matrix, allowing for plastic deformation in the ligament [28]. It is important to note that a modifier with smaller particle size, SBM, will have a smaller inter-particle distance than one of a larger particle size, CTBN, therefore for the same volume fraction of particles the inter-particle distance for the SBM will be smaller. This argument goes along with the previously mentioned notion that if the crosslink density makes the epoxy very rigid, then the matrix becomes untoughenable. The SBM and CTBN-modified systems in this study are both of uniform distribution, so this theory on the effect of inter-particle distance is satisfactory. However, it should be noted that co-continuous microstructures have also been found with SBM and this will also affect the resulting fracture toughness [25].

Diamine curing agents are frequently used in the literature and yield relatively brittle structures and induce gelation faster than less reactive curing agents such as piperidine. DDS (4, 4’-diaminodiphenylsulfone) was used as hardener in a study by Pascault et al. which induced the phase separation of the PMMA blocks during the early stages of polymerization [21]. This resulted in flocculated, micrometer size elongated
nanoparticles. However, in the same study, MCDEA (4, 4’-methylenebis [3-chloro 2, 6 diethylanilene] was used and domain sizes were not affected throughout network formation. Instead of a flocculated morphology, MCDEA yields a spheres on spheres morphology (previously mentioned in section I.5.1). In this instance, the PMMA remained fixed in the epoxy network. A companion paper to this work illustrated the influence of copolymer concentration on the morphology [29]. When the block copolymer concentration was significantly increased, the morphology yielded was either a spheres on spheres structure or a core-shell structure as opposed to the micelles achieved at lower concentration. This addition was found to increase the fracture toughness from 0.65 to 2 MPam$^{0.5}$ [29]. Instead of phase-inversion, as seen with high weight percent of CTBN, different morphologies were generated by the SBM. Although this is not completely understood, it is worth noting that this will have an effect on the overall physical properties of the epoxy blend.

Depending on the cure schedule and processing conditions, the rubbery phase of the toughening modifiers could potentially be present in the epoxy matrix [30]. A study by Saleh et al. has shown that mechanical properties such as tensile strength and Young’s modulus decrease in the presence of low modulus rubber particles in the epoxy matrix. This is a result of a chemical effect or a softening effect. In the case of a chemical effect, there will be some rubber that remains in the epoxy phase which not only lowers Tg, but strength as well. The softening effect results from the rubber particles present in the epoxy matrix that are much softer than the matrix itself. In a study by Pearson and Yee, the Tg of a CTBN-modified epoxy system containing 10 phr of modifier was only altered
by 2°C. This result indicates that very little rubber is present in the epoxy matrix, so it follows that the decrease in the tensile modulus would be minimal, 0.8 GPa in this case [31].

There are many physical properties that are affected by characteristics of the rubber-based toughening agent such as compatibility with the epoxy matrix, particle size and shape, morphology, and the degree of phase separation of the rubbery phase [32]. The factors to be mindful of are those that affect the ability of the matrix to ductility deform. It is also worth noting that with the advent of block copolymers, morphology will play an integral role in the ability to improve physical properties. Particle-particle interactions is also an important parameter in block copolymer-modified blends because more than with traditional micron-size modifiers, the nano-size modifiers will inevitably have more of a dependency on neighboring particles since there exists more particles in block copolymer blends than traditional telechelic blends given the same amount of monomer by weight. All of these factors will contribute to the overall effect that toughening modifiers have on the epoxy matrix, so it is important to take them into consideration when predicting, modeling and explaining toughness as well as toughening mechanisms.

I.7. Predicting Fracture Toughness

The work of Pearson, Hertzberg and Yee [33, 26, 27] focuses on the fracture toughness performance of CTBN in a diglycidyl ether of bisphenol A (DGEBA) system cured with piperidine. Toughening mechanisms that are recognized in the literature are
summarized in the work of Azimi, Pearson and Hertzberg, where it is noted that the three main toughening mechanisms are: 1. localized shear yielding, 2. plastic void growth and 3. particle bridging [33]. The work of Huang and Kinloch [34, 35] recognizes that a model predicting fracture toughness needs to account for these various energy-dissipating mechanisms present in a toughened system and their individual contributions to the total toughness. However, a better understanding of the overall toughness is gained when the reader knows how each toughening mechanism is defined. Localized shear yielding refers to the shear banding within the epoxy matrix that manifests between the rubber particles since the epoxy matrix is now ductile enough to support plastic deformation. Depending on the system being studied, void growth is initiated by cavitation or debonding of the rubber particles. This originates from the fact that the triaxial stress state at the crack tip gives the rubber particles no choice but to cavitate since the Poisson’s ratio of rubber is about a half. Finally, rubber particle bridging occurs behind the crack tip and is when the particles themselves act to arrest the crack. A schematic in Figure 10 illustrates these accepted toughening mechanisms. In the CTBN system, cavitation is the dominant toughening mechanism observed.

A quantitative means of modeling the toughening mechanisms in rubber-modified epoxy polymers was derived by Huang and Kinloch [34, 35]. In this work, the fracture energy of a rubber-toughened polymer is described by

$$G_{IC} = G_{ICu} + \Psi \quad (12)$$
where $G_{IC}$ is the fracture energy, $G_{Icu}$ is the fracture energy of the neat epoxy and $\Psi$ represents the overall toughening effect of the toughening modifier. $\Psi$ can be broken down to include the contributions from the three toughening mechanisms described previously. Therefore, $\Psi$ is described as

$$\Psi = \Delta G_s + \Delta G_v + \Delta G_r \quad (13)$$

, where $\Delta G_s$ is the fracture energy due to shear banding, $\Delta G_v$ is the fracture energy due to plastic void growth and $\Delta G_r$ is the fracture energy due to rubber particle bridging. The equation

$$\Delta G_s \text{ or } \Delta G_v = 2 \int_0^r U_s(r) dr \quad (14)$$
where $U_s(r)$ is the strain energy density that is generated from the shear banding mechanism and $r$ is the distance from the crack tip. Equation 14 was integrated from 0 to $r_y$, which represents the radius of the plastic zone ahead of the crack tip. This yields a fracture energy equation that represents the shearing of the rubber particle system given by

$$\Delta G_{rps} = 0.5 V_f \sigma_{yc} \gamma_f F(r_y) \quad (15)$$

, where $V_f$ is the volume fraction of particles, $\sigma_{yc}$ is the compressive yield stress of the neat resin and $\gamma_f$ is the yield strain of the neat resin. $F(r_y)$ is represented by the equation

$$F(r_y) = \left[ \left( \frac{4\pi}{3V_f} \right)^{1/3} - \frac{54}{35} \right] \quad (16)$$

In order to describe the increase in the plastic zone size, a relation had to be determined. By relating $K_{vm}$, the maximum stress concentration factor of the von Mises stress in the plastic matrix, $\mu_m$, a material constant, and $r_{yu}$, the plastic zone size for the neat resin, the following relation has been derived:

$$r_y = K_{vm}^2 \left( 1 + \frac{\mu_m}{3\gamma_f} \right)^2 r_{yu} \quad (17)$$

Based on equations 15 through 17, the rubber particle shear component of the overall fracture energy can be written as

$$\Delta G_{rps} = 0.5 \left( 1 + \frac{\mu_m}{3\gamma_f} \right)^2 \left[ \left( \frac{4\pi}{3V_f} \right)^{1/3} - \frac{54}{35} \right] V_f \sigma_{yc} \gamma_f r_{yu} K_{vm}^2 \quad (17)$$
The contribution to the overall toughness via plastic void growth is $\Delta G_{rpv}$ in the case of a matrix toughened by rubber particles. An expression for void growth begins with equation 14 since both components are related to the size of the plastic zone. It is also important to consider the strain-energy density, $U_v$, for a void to grow. This is given by the equation

$$U_v(r) = \int_{V_0}^{V_1} p d\theta \quad (18)$$

where the strain-energy density is determined over a volume $V_0$ to $V_1$ by integrating $p$, the local hydrostatic stress in relation to the volumetric strain, $d\theta$. The volumetric strain is given by the relationship $d\theta = V_t dV/V$, where $V_t$ and $V$ are the volume fraction and average volume of voids, respectively. The hydrostatic stress in this case assumes linear elastic fracture mechanics (LEFM) and so it can be deduced that $p$ is approximately $0.5\sigma_{yt}$, where $\sigma_{yt}$ is the tensile stress of the material. It has also been determined that $V_1$ and $V_0$ are related to the volume fraction of rubber, $V_{fr}$, and volume fraction of voids, $V_{fv}$, by the following equation

$$\frac{V_1}{V_0} = \frac{V_{fv}}{V_{fr}} \quad (19)$$

By substituting equation 19 into equation 18 as well as taking into account the assumptions made, the equation for the strain-energy density becomes

$$U_v(r) = 0.5\sigma_{yt}(V_{fv} - V_{fr}) \quad (20)$$

The contribution to the increase in fracture energy from the plastic void mechanism can then be given by
The contribution of rubber particle bridging on the fracture toughness has been proposed by Kunz-Douglass et al. It was found that the fracture energy due to particle bridging, \( \Delta G_r \), is given by

\[
\Delta G_r = 4\Gamma_f(T)V_{fr} \quad (22)
\]

, where \( \Gamma_f(T) \) represents the tearing energy of the rubber particles. In the study performed by Kunz-Douglass et al., measurements of the tear energy were taken at different temperatures and essentially measured the energy dissipated during the stretching of these rubber particles. This was then related to the toughening contribution by the volume fraction of rubber particles. Although this toughening mechanism is effective in some systems, the CTBN and SBM-modified systems in this study do not appear to obtain a significant amount of toughening via rubber particle bridging.

Although values of \( K_{IC} \) were experimentally measured in this research, assuming LEFM, \( G_{IC} \) can be calculated using the relation

\[
G_{IC} = \frac{k^2 IC}{E} (1 - v^2) \quad (23)
\]

, where \( E \) is Young’s modulus and \( v \) is the Poisson’s ratio of the epoxy. By combining the results of mechanical tests and microscopy studies, it was deduced whether CTBN and SBM-modified epoxy fit the Huang and Kinloch toughening model.
I.8. Objectives

The first objective of this research was to characterize SBM with regard to its capacity to increase the fracture toughness of a model epoxy. A more specific goal was to compare SBM to a more traditional modifier, in this case CTBN, to determine if the toughening mechanisms differ between the two systems. Another area of interest was to determine if fracture toughness can be improved while decreasing the impact on other mechanical properties such as yield strength. Finally, it was of particular interest to elucidate if the current toughening models would be able to predict the fracture toughness obtained by SBM-modified epoxy given the assumptions made to derive the model itself.

II. Experimental Procedures

II.1. Materials and Processing

The epoxy system used in this study consisted of a diglycidyl ether of bisphenol A (DGEBA) cured with piperidine (Sigma-Aldrich). Dow Chemical Co. provided the DGEBA resin, which is given the designation D.E.R. 331. D.E.R. 331 has an epoxy equivalent weight of 187 g/eq.. Piperidine was added in a ratio of 5 parts-per-hundred parts resin (phr) and cures the DGEBA-based epoxy via a catalytic mechanism.

Two toughening modifiers, a styrene-butadiene-methyl methacrylate triblock copolymer, SBM, and a carboxyl acid terminated copolymer of butadiene-acrylonitrile (CTBN). The SBM was provided by Arkema Inc. and was given the designation of
Nanostrength E20 SBM and the CTBN was provided by Hycar Chemical Co. and given the designation Hycar CTBN 1300X8.

Master batches of the SBM were diluted in order to obtain the desired concentrations of rubber modifier. The CTBN was processed as received. The modifiers and epoxy were mixed at 80°C via mechanical mixing for four hours. For the first two hours, mixing was conducted at 80°C without a vacuum, followed by two hours under vacuum at 80°C and 140°C for the CTBN and SBM, respectively. The samples were then brought to 80°C and injected with 5 phr of the curing agent, piperidine, and mixed for ten minutes. Afterwards, the mixture was poured into a preheated aluminum mold and cured for six hours at 160°C.

II.2. Mechanical Testing

II.2.1. Fracture Toughness

Fracture toughness, $K_Q$, was determined via a single-edge-notched, three-point-bend (SEN-3PB) test conducted according to ASTM D5045 guidelines. 3PB samples were machined from 250 mm x 250 mm x 6.4 mm cast plaques into dimensions of 75.6 mm x 12.7 mm x 6.0 mm. Machined 3PB specimens were notched with a jewelers saw, and then a nitrogen-dipped razor blade was inserted and tapped with a rubber mallet to induce a sharp precrack. Fracture toughness tests were performed with a screw-driven universal testing machine, Instron model 5567, at a crosshead speed of one mm/min in compression mode with a constant span of 50.8 mm. Fracture toughness was then calculated using the following equations found in the ASTM D5045 standard:
\[ K_Q = \frac{P_Q}{BW^2} f\left(\frac{a}{W}\right), \text{ where } f(x) = 6x^{1/2} \frac{\left[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)\right]}{91 + 2x(1-x)^{3/2}} \]

At least five SEN-3PB specimens were tested for each composition to obtain an average fracture toughness value. Load versus displacement curves were evaluated using Bluehill software on the Instron 5567 mechanical testing machine using a 500 N load cell.

II.2.2. Compressive Yield Stress

The screw-driven universal testing machine, Instron model 5567, was also used to perform compressive yield strength, \(\sigma_y\), measurements according to ASTM D790. Uniaxial compression behavior of the rubber-toughened epoxies was determined with 6mm x 6mm x 12mm samples where the square cross-sectional area was exposed to a crosshead speed of one mm/min in compressive mode with a 500 N load cell. A total of five samples were tested to report an average of each concentration.

II.3. Thermal Testing

II.3.1. \(T_g\) Measurements

The glass transition temperature, \(T_g\), was determined with a TA Instruments 2910 differential scanning calorimeter (DSC) using aluminum hermetically sealed pans. Samples size ranged between ten and twenty milligrams. Each sample was equilibrated at room temperature and ramped 10°C/min to 200°C. A second scan was used to erase any thermal history. The midpoint method was used to determine the \(T_g\) via the TA Universal Analysis software.
II.4. Microscopy

II.4.1. Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) was utilized in order to observe the morphology present in the CTBN and SBM modified epoxy. Specimens were sent to the University of Massachusetts at Lowell for osmium tetroxide (OsO₄) staining and cryo-microtoming. The OsO₄ stains the butadiene segments of the CTBN and SBM so that the overall morphology of the blends can be observed. Samples made with the cryo-microtome ranged from 70 to 110 nm in thickness.

II.4.2. Scanning Electron Microscopy (SEM)

In order to examine the fracture surfaces of the SEN-3PB samples, a Hitachi 4300 low vacuum Scanning Electron Microscopy (SEM) was used with an accelerating voltage of 5kV. Fracture surfaces were coated with a thin layer of Iridium for 30 seconds to minimize charge build-up. SEM images were taken to illuminate the toughening mechanisms present in each type of rubber-toughened epoxy. The amount of plasticity and void growth was of particular interest.

II.4.3. Transmission Optical Microscopy (TOM)

In order to investigate subsurface damage, Transmission Optical Microscopy (TOM) was used. TOM samples were made from cross-sections of SEN-3PB specimens by first mounting them into clear mounting epoxy preparing them via standard metallographic preparation. Afterwards, the sample is then glued onto a petrographic
slide and then thinned down to about 120 microns for TOM viewing. Two modes are used on an Olympus BH-2 Optical Microscope: bright field and crossed polars. Bright field mode allows rubber particle cavitation to be observed since they scatter light while crossed polars allows shear banding to be observed since oriented polars are birefringent.

III. Results and Discussion

III.1. Morphology (TEM)

Transmission electron microscopy (TEM) was used to elucidate the morphology of both the CTBN and SBM toughened epoxies. Figure 11 depicts the CTBN as well as the SBM- modified epoxy morphology; the rubbery phase (which contains polybutadiene) appears dark once stained with OsO4. Note that the CTBN particles are spherical and uniform in composition with sizes ranging from 1-5 µm in diameter. However, the of SBM morphology consists of spheroidal, structured particles with only one third rubber by weight. The SBM particle structure consists of a rigid styrene core, a middle layer of polybutadiene and outer-PMMA layer. The average particle size of the SBM particles was nominally 40 nm.
III.2. Glass Transition Temperature

In order to determine what affect both the CTBN and the SBM-modified epoxy had on the glass transition temperature, $T_g$, neat resin as well as two concentrations of each modifier were studied. By conducting two runs on each sample, thermal history was erased so that the $T_g$ was unaffected by processing conditions. The results are given in Table 1, which shows that only at higher concentrations of CTBN does the $T_g$ begin to decrease by a statistically significant amount. Although this is slightly surprising, since CTBN has approximately three times the rubber content, a possible explanation for this is that both modifiers almost completely phase separate upon cure in this epoxy system, so the crosslinked matrix predominately determines the $T_g$. If this were the case, it would also explain why SBM-modified epoxy retains the $T_g$ better than the CTBN-modified epoxy at higher concentrations, but only by 2°C. A study conducted by Pearson and
Hydro also found a slight decrease in the glass transition, $T_g$, was observed between the SBM-modified epoxy and the neat resin [22].

**Table 1. $T_g$ results for SBM and CTBN, respectively.**

*Glass Transition Temperature Results*

<table>
<thead>
<tr>
<th>Modifier content, phr</th>
<th>SBM</th>
<th>CTBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>76°C</td>
<td>76°C</td>
</tr>
<tr>
<td>10/11</td>
<td>75°C</td>
<td>76°C</td>
</tr>
<tr>
<td>20/22</td>
<td>73°C</td>
<td>71°C</td>
</tr>
</tbody>
</table>

**III.3. Compressive Yield Stress**

Although the $T_g$ study did not infer that there would be a drastic change in mechanical properties, the yield stress data exhibits a significant drop with the addition of CTBN. As seen in Figure 12, there is a decrease in the yield stress compared to the neat resin, which is at 98.8 MPa, in both the CTBN and the SBM-modified epoxy. Although this decline starts off gradually, the difference between SBM and CTBN-modified epoxy being within 10 MPa, this changes substantially when more than 15 parts-per-hundred resin (phr) is added. Additionally, the most the yield stress decreases with the addition of SBM is 24 MPa, while CTBN-modified epoxy exhibits a decrease in yield stress of approximately 43 MPa. This is also numerically shown in Table 2 for further clarification.

This difference in yield strength can be attributed, in part, to the overall amount of rubber contained in both types of toughened epoxies. Fortunately, the $T_g$ was retained
reasonably well for both modifiers so matrix mobility was the same for both types of toughened epoxies. It is hypothesized that the rigid styrene core of the SBM contributes to some of the retention of mechanical properties. Since the polystyrene is able to impart structural rigidity upon the polybutadiene layer, it is probably that this is what allows SBM to maintain the yield stress of the SBM-modified epoxy.

Figure 12. Yield Stress versus Modifier Content of SBM and CTBN-based rubber particles.
Table 2. Yield Stress results for SBM and CTBN, respectively.

<table>
<thead>
<tr>
<th>Modifier content, phr</th>
<th>SBM</th>
<th>CTBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>98.8 MPa</td>
<td>98.8 MPa</td>
</tr>
<tr>
<td>5</td>
<td>86.7 MPa</td>
<td>75.3 MPa</td>
</tr>
<tr>
<td>10/11</td>
<td>80.8 MPa</td>
<td>68.8 MPa</td>
</tr>
<tr>
<td>15/16</td>
<td>77.6 MPa</td>
<td>62.6 MPa</td>
</tr>
<tr>
<td>20/22</td>
<td>74.9 MPa</td>
<td>55.6 MPa</td>
</tr>
</tbody>
</table>

III.4. Fracture Toughness

As illustrated in Figure 13, the fracture toughness of the SBM-modified epoxy exceeds the CTBN-modified epoxy, even at low concentrations. However, the SBM-modified epoxy continues to increase in toughness past 10 phr, while the CTBN-modified epoxy plateaus at about 13 phr and decreases at higher concentrations. What is surprising about the SBM-modified epoxy is that it continues to increase even up to 25 phr and yields a $K_{IC}$ of $4.74 \text{ MPa m}^{0.5}$, a value that is seldom reached in the literature. SEM and TOM will be discussed in later sections to explain this large increase in fracture toughness.
Figure 13. Effect of Rubber Particle Types on Fracture Toughness, a comparison between SBM and CTBN.

It is also worth observing the trend between rubber content and $K_{IC}$ with CTBN and SBM-modified epoxy. As shown in Figure 14, SBM-modified epoxy manages to increase the toughness more than CTBN-modified epoxy with a more effective use of the polybutadiene in the inherent structure. Since only one third the rubber content is present in the SBM compared to that of the CTBN, it is interesting to note that there must be a structure and/or volume fraction of particle effect present in order to yield such a significant increase in $K_{IC}$.
III.5. Fractography (SEM)

In order to observe the toughening mechanisms exhibited by the SBM and CTBN-modified epoxy systems, fractography was conducted via SEM. SEM revealed that the CTBN-modified epoxy in this study displayed the typical uniform morphology with evidence of rubber particle cavitation as well as matrix deformation [22]. As can be seen in Figure 15, and is especially worth noting, the sizes of the dilated cavities are not significantly larger than the CTBN particles prior to the SEN-3PB test.

Figure 14. Effect of Rubber Content on Fracture Toughness, a comparison between SBM and CTBN.
Figure 15. Low and high magnification SEM micrographs of CTBN at two concentrations.

Since the addition of SBM had such a markedly large increase in fracture toughness, it was thought that possibly there were other toughening mechanisms active than those currently mentioned in the literature. SEM, however, demonstrated that the SBM-modified epoxy displayed the same rubber particle cavitation and subsequent matrix void growth as seen in CTBN-modified epoxy (see Figures 16 and 17) [22].

Although the SBM-modified epoxy fracture surface is on the nano-scale, as opposed to the micro-scale, the toughening mechanisms do not appear to differ. There are, however, two important observations to assess. First, the fracture surface of the
SBM-modified epoxy does exhibit ductile tearing of the matrix that is not apparent in the CTBN-modified epoxy. This is observed at low magnification in Figure 16 and is the lighter portions of the micrographs where the topography of the surface is the roughest. The second point worth noting is that the dilation of the cavities formed on the fracture surface are considerably larger than the particles were initially. As will be discussed in the next

![Figure 16. Low magnification images of SBM in four concentrations.](image)
Figure 17. High magnification images of SBM in four concentrations.

section, most models of toughening mechanism in rubber-modified epoxies assume that
the shear bands produced as a result of matrix plasticity are not larger than the initial
particle size [34].
III.6 Subsurface Damage (TOM)

In order to observe the subsurface damage, cross sections of the fractured SEN-3PB specimens were prepared via petrographic polishing to a preferred thickness. Once prepared, the samples were viewed under bright field and cross-polar optical microscope conditions. Bright field mode is when unfiltered light is passed through the sample and contrast comes from light being scattered by the sample. This mode allows cavitation to be seen, as is the case for Figure 18. Cross-polar mode is when polarized light is passed through a sample and birefringence is seen as a result of the directional dependence of the material. Shear plasticity is observed under cross-polars, as seen in Figure 19. When directly comparing the subsurface damage zones of the SBM-modified and CTBN-modified epoxies, it becomes obvious that the damage zones for the CTBN-modified epoxy are substantially larger than the damage zones observed in SBM-modified epoxy. In addition, the damage zones in CTBN-modified epoxy are diffuse in both bright field and cross-polars except right at the fracture surface. However, the damage zones in SBM-modified epoxy are concentrated and do not exhibit the diffuse nature of the CTBN-modified epoxy in neither bright field nor cross-polars. Table 3 summarizes the measured plastic zone depth taken from the bright field images.
Figure 18. Subsurface damage zones of CTBN and SBM viewed via bright field illumination.

Figure 19. Subsurface damage zones of CTBN and SBM viewed via cross-polar illumination.
Table 3. Plastic zone measurements for SBM and CTBN, respectively.

*Plastic Zone Depth Results*

<table>
<thead>
<tr>
<th>Modifier content, phr</th>
<th>SBM</th>
<th>CTBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/11</td>
<td>62.8 µm</td>
<td>208.3 µm</td>
</tr>
<tr>
<td>15/16</td>
<td>139.3 µm</td>
<td>284.4 µm</td>
</tr>
<tr>
<td>25/22</td>
<td>144 µm</td>
<td>542.6 µm</td>
</tr>
</tbody>
</table>

III.7. Predicting Plastic Zone Size

A popular relation in the literature for predicting plastic zone size is the Irwin Plastic Zone Model [12]. This model relates $K_{IC}$ and $\sigma_y$ to the plastic zone size, $r_p$, as is stated in *equation 10*. As seen in Figure 20, CTBN-modified epoxies correlate well to this model, with a proportional increase in $K_{IC}$ in relation to the $r_p$. However, SBM-modified epoxies exhibit a completely different trend. This is thought to be because of the high increase in the $K_{IC}$ with only a slight decrease in the $\sigma_y$, so the expected plastic zone size is calculated to be much smaller than that of CTBN-modified epoxy. It should be noted, however, that this is only the case for concentrations above 10 phr. Until that point, the trends in Figure 17 for both the CTBN and SBM-modified epoxy are similar. Again, this is due to the retention of the yield stress, which will make the predicted $r_p$ value much lower than expected. From experimental data, it is also seen that the measured $r_p$ values are even lower than predicted. This result was surprising and it still not completely understood. Although it is known that the birefringent area is not diffuse,
and that the fracture surface exhibits a large amount of ductility, from TOM and SEM techniques, respectively, there still needs to be more research done to figure out exactly why the plastic zone size for the SBM-modified epoxy is so much smaller than anticipated.

Figure 20. Measured versus Predicted Plastic Zone Depth of CTBN and SBM-modified epoxy.

Figure 21 further illustrates the unusually high fracture toughness exhibited by the SBM-modified epoxy in relation to the measured plastic zone depth. Although the first two data points of the SBM-modified epoxy and the first data point of the CTBN-modified epoxy are relatively close together, the SBM-modified epoxy deviates from the trend after this juncture. The main advantage of using SBM would, therefore, be that at
high concentrations and fracture toughness, the damage zone size of SBM-modified epoxy remains comparatively small, making it ideal for thin bondline applications.

![Fracture Toughness Versus Plastic Zone Depth](image)

**Figure 21. Fracture Toughness versus Plastic Zone Depth of CTBN and SBM-modified epoxy.**

### III.8 Parameters for Predicting Fracture Energy, $G_{IC}$

The two most important parameters for predicting the Fracture energy, $G_{IC}$, are the volume fraction of voids, $V_{fv}$, and the volume fraction of rubber, $V_{fr}$. It was found by Pearson that the volume fraction of rubber in CTBN-modified epoxy is equal to the volume fraction [36]. However, to calculate the volume fraction of SBM in the epoxy, the density was tabulated taking into consideration that the three blocks are composed of one mer unit each. The average density for the three blocks was then taken and the weight was determined for each phr since the amount of epoxy used in each composition
was known. From there, the volume fraction was determined. **Table 4** shows the results for the volume fraction of rubber. Note that the volume fraction of particles calculations assumed that both the CTBN and SBM all phase separated upon cure. This is a fair assumption due to the $T_g$ measurements which were nearly the same as for the neat resin. Also note that the SBM was calculated for volume fraction of SBM particles but only one third of the particle is rubber.

**Table 4. Volume fraction of rubber present in SBM an CTBN.**

$V_f$ *Calculations*

<table>
<thead>
<tr>
<th>Modifier content, phr</th>
<th>SBM</th>
<th>CTBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>.018</td>
<td>.05</td>
</tr>
<tr>
<td>10</td>
<td>.034</td>
<td>.10</td>
</tr>
<tr>
<td>15/13</td>
<td>.050</td>
<td>.13</td>
</tr>
</tbody>
</table>

To determine the volume fraction of voids in the two materials, SEM micrographs were taken of the stress whitened region and the void diameter was measured manually. The volume fraction of voids was then tabulated, as seen in **Table 5**.

**Table 5. Volume fraction of SBM an CTBN voids.**

$V_f$ *Calculations*

<table>
<thead>
<tr>
<th>Modifier content, phr</th>
<th>SBM</th>
<th>CTBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>.215</td>
<td>N/A</td>
</tr>
<tr>
<td>10</td>
<td>.109</td>
<td>N/A</td>
</tr>
<tr>
<td>15/13</td>
<td>.174</td>
<td>.278</td>
</tr>
</tbody>
</table>
Interestingly, it was observed that at 5 phr SBM there was clustering of the particles, which led to more void dilation. This is worth noting because most models, including the Huang and Kinloch model, assume that the particles do not interact with one another. However, the micrograph in Figure 17 suggests that particle interaction does occur or the difference in the volume fraction of voids when clustering occurs would not be as significant. Additionally, taking the SBM initial diameter to be 40 nanometers, it was found that the average void size was about 67 nanometers at 10 phr. This is almost a 67% increase in diameter compared with the 2.5% calculated for CTBN-modified epoxy at nearly the same composition (15 phr SBM and 13 phr CTBN, respectively). Consequently, the plastic void growth contribution to the total toughness for the SBM should be greater than that of CTBN.

As seen in equations 17 and 21, the values of \( V_{fr} \) and \( V_{fv} \) are the only parameters that change when calculating the toughening contributions of shear and plastic void growth. These measurements were based on one SEM micrograph to gain some insight on the particle fraction and void fraction, more quantitative analysis must be conducted on different regions of the fracture surface in order to accurately apply these values to the Huang and Kinloch model.

IV. Conclusions

1. The toughening mechanisms for CTBN and SBM-modified epoxy are similar, but at high SBM contents, there is ductile tearing of the matrix present.
2. Yield strength decreases with increasing modifier content, but loss of strength is reduced when SBM is employed.

3. SBM-modified epoxy exhibits a smaller than expected plastic zone size according to the Irwin theory based on linear elastic fracture mechanics.

4. Since the plastic zone size of the SBM-modified epoxy is small, it is ideal for use in thin bondline applications.

V. Future Work

In order to better understand the toughening mechanisms that make SBM-modified epoxy different than CTBN-modified epoxy, there are several experiments that should be conducted. The first is a quantitative TEM analysis to determine more accurate values for the volume fraction of rubber and particles in order to deduce if this effect lead to more efficient toughening. Secondly, an SEM study to quantify the amount of void growth in the fast fracture and stress whitened portion of the SBM fracture surface would give a more accurate representation of the total matrix dilation. Lastly, once these studies are conducted, an attempt should be made to apply the Huang and Kinloch rubber toughening model to determine the contribution of shear banding and void growth to the fracture toughness measured.
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Vita

Lauren Nicole Bacigalupo was born in Rahway, NJ on April 25, 1986. She was raised in Linden, NJ until she came to college. In 2004, Lauren came to Lehigh University and obtained a B.S. in Materials Science and Engineering in May 2008. Since she enjoyed research as an undergraduate, she continued on to graduate school at Lehigh University where she will receive her M.S. in Materials Science and Engineering in September 2011. Recently, she has been accepted into the Polymer Science and Engineering program at Lehigh University and is expected to receive her Ph.D. in May 2013.