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The influence of clay and elastomer concentration on the morphology and fracture energy of preformed acrylic rubber dispersed clay filled epoxy nanocomposites

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Abstract

The influence of toughener and clay concentration on the morphology and mechanical properties of three-phase, rubber-modified epoxy nanocomposites was studied. Nanocomposite samples were prepared by adding octadecyl ammonium ion exchanged clay to a dispersion of preformed acrylic rubber particles in liquid epoxy, so as to minimize alteration to the rubber morphology in the final cured specimen. The state of clay platelet exfoliation and rubber dispersion in the cured nanocomposites was studied using transmission electron microscopy. The amounts of clay platelet separation and dispersion of clay aggregates in the epoxy matrix were found to be sensitive to clay and toughener concentration, and clay platelets preferentially adsorb to the rubber particles. Tensile modulus and strength increase and ductility decreases with increasing organoclay content, while rubber has the opposite effects on the properties of epoxy resin. When both additives are present in epoxy resin, a favorable combination is produced: ductility is enhanced without compromising modulus and strength. Modulus and strength are improved by nano and micro dispersion of nanoclay in the epoxy matrix, whereas elongation and toughness are improved by clay adsorption to the rubber particle surface, which promotes cavitation. The glass transition temperature of epoxy resin remains relatively unchanged with clay addition. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Preformed acrylic rubber; Epoxy; Nanocomposite

1. Introduction

Epoxy resins are widely employed as structural adhesives, matrices in fiber-reinforced composites, and coatings for metals because of their excellent bulk properties such as high modulus, low creep, and good performance at elevated temperature. However, like other thermoset resins, the crosslinking character of cured epoxies produces a highly undesirable property: they are relatively brittle, having poor resistance to crack initiation and growth. To address this defect, resin formulators have developed technology that permits some thermosets to be toughened by the addition of a second elastomeric phase [1–4], introducing an acceptable sacrifice of desirable properties. By increasing the concentration of elastomer phase, an increase in fracture energy of up to 15–20 times that of the unmodified epoxy has been achieved [5,6].

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It is widely reported that the toughness depends not only on the concentration of the elastomeric phase, but also on the composition of each phase, and their morphology. Many such epoxy systems use carboxy-terminated acrylonitrile butadiene (CTBN) as the elastomeric phase. When this system is cured, the epoxy polymerizes and the CTBN reacts with epoxy to form a copolymer. With increase in molecular weight, the soluble reactive liquid CTBN rubber phase separates from epoxy because of decrease in rubber/epoxy compatability. The elastomeric phase forms small discrete particles, typically in the micrometer range, that are dispersed in and bonded to the thermoset matrix. Although the morphology of rubber in toughened epoxy systems is mostly spherical, the average particle size and distribution can vary greatly depending on the cure reactions, cure cycle and concentration of rubber in the epoxy system [6,7]. Since the morphology of rubber is generated during epoxy cure, it is extremely difficult to control and maintain good phase separation of rubber particles, especially at high rubber concentration.

In response to this limitation of CTBN based epoxy, the approach taken here is to use pre-formed rubber particles dispersed in uncured resin, to retain the rubber particle

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morphology when the epoxy resin is cured. By pre-forming and stabilizing the rubber particles, the undesirable effect of some soluble rubber remaining in the epoxy matrix is reduced and the microstructural integrity of rubber is retained while the epoxy is cured. Because the particles are preformed in the epoxy, another advantage of the system is retention of particulate morphology when the epoxy concentration is varied over a wide range, by dilution with additional epoxy. The system being used here is a material developed by Dow Chemical Co. [8–10]. The starting material is generated by forming a suspension of acrylic rubber particles in a liquid epoxy. In our earlier papers [11-16], we examined the effect of changing the particle concentration at a fixed morphology on the fracture behavior of epoxy system. The acrylic rubber particle concentration is specified as percent mass ratio of rubber to epoxy (phr). The fracture energy reaches a maximum and remains relatively constant for phr between 12.5 and 25. As expected, our study established that the modulus of rubber dispersed epoxy decreases with an increase in acrylic rubber concentration. The results followed a simple logarithmic relationship:

$$\log E = \log E_{\rm e}(1 - V_{\rm r}) + \log E_{\rm r}(V_{\rm r}) \tag{1}$$

where E, E_e , and E_r are the bending moduli of rubber modified epoxy, epoxy, and acrylic rubber, respectively, and V_r is the volume fraction of rubber in the modified epoxy. These observations suggest that strategies to improve the toughness of rubber modified epoxy should also incorporate methods to retain/improve the modulus of resin system.

Recently, there has emerged a new approach for improving the modulus of thermoplastic and thermoset systems by the formation of a nanophase structure in the polymer matrix, where the nanophase consists of small rigid particles, whiskers or tubes (e.g. layered silicates or silica particles or carbon nanotubes) [17–23]. The nanophase has at least one dimension approximately of nanometer length scale. One of the most ubiquitous nanoparticles is a layered silicate, montmorillonite. These particles are naturally available, thermally inert, inexpensive, and render enormous surface area for improving polymer/clay compatibility. Because of such compatibility, properties of composites with a small percent of layered silicate in polymeric resin are vastly better than those of micron-sized filler composites. Although these rigid nanofillers improve the strength and modulus of epoxy resins, the fracture toughness and failure strain is reduced to some extent or remain unaffected [24,25].

This paper discusses the effects of combining the benefits of adding rubber and clay to epoxy so as to develop improved matrix material with the aim of attaining higher fracture energy without compromising the other desired mechanical and thermal properties of the epoxy resin. The objective of this study is to examine the influence of rubber and clay concentration on the morphology and mechanical properties of three-phase nanoclay filled rubber-dispersed epoxy system. The use of preformed 'stabilized' rubber particles to toughen a thermoset resin has been known for many years, but the use of this system to perform fundamental structure-property relationship studies in the area of nanocomposite is relatively new.

2. Experimental

2.1. Materials

The following materials were used in this study: diglycidyl ether of bisphenol A epoxy resin (DER 331, Dow Chemical)¹ which has molar mass of approximately 172 g/mol and piperdine from Aldrich Chemical. Preformed acrylic rubber particles were prepared in a two-step procedure (i) vinylization and (ii) vinyl polymerization using the following chemicals: 2,2'-azobis (2-methyl propionitrile), 2-ethyl hexyl acrylate, and glycidyl methacrylate (Aldrich Chemical Co.); methacrylic acid (Fisher Chemicals), and ethyl phosphonium acetate (Alfa Aesar).

2.2. Surface treatment of montmorillonite

 Na^+ -MMT (Na-montmorillonite) was provided by Southern Clay Products under the trade name of sodium cloisite (Na-cloisite). The interlayer spacing of Na⁺-MMT before surface treatment is 1.2 nm (i.e. containing bound water). By adding an aqueous solution of 0.3 g of octadecyl amine hydrochloride to an aqueous slurry of 1 g of Na⁺-MMT and heating at 80 °C, filtering, washing with a hot water/ ethanol mixture and drying, a solid precipitate organoclay was obtained. The interlayer spacing of this treated dried clay increased to 1.8 nm.

2.3. Synthesis of acrylic rubber dispersion in epoxy resin

The detailed synthetic steps for dispersing acrylic rubber (poly(2-ethylhexyl acrylate-*co*-glycidyl methacrylate)) in epoxy can be found elsewhere [8,9]. Typically, to the preheated liquid epoxy resin (20 g), 0.01 g of ethyl phosphonium acetate and 0.25 g of methacrylic acid are added, and the mixture is stirred while being maintained at 120 °C for 1 h in a blanket of nitrogen atmosphere. Then a slurry of 2,2' azo-bis (2 methyl propionitrile) (0.2 g) in 2-ethyl hexyl acetate (12.4 g) and glycidyl methacrylate (0.79 g) is gradually added to the mixture which is stirred while maintained at 100 °C. The entire mixture is further heated for an additional hour at 120 °C before allowing the mixture to attain room temperature. Finally the volatile remnants remaining in the mixture are stripped by placing it under vacuum.

2.4. Preparation of cured samples

To prepare acrylic rubber modified epoxy samples, the acrylic rubber dispersion is hand mixed with appropriate

¹ Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that these are necessarily the best available for the purpose.

amount of epoxy for 5–10 min. Piperdine curing agent is added to the diluted epoxy sample and the mixture is poured into a dog-bone cavity silicone mold and cured at 120 °C for 16 h using a Lab Line Instrumentation programmable oven. The oven is then turned off and allowed to cool slowly to room temperature. All samples received the same thermal history.

To prepare the rubber-toughened epoxy nanocomposite, organoclay (e.g. 0.275 g), the preformed acrylic rubber dispersion (e.g. 0.75 g), epoxy (e.g. 5 g), and tetrahydrofuran (THF) (e.g. 1 g) were mixed. THF (15% by mass) was used as a swelling agent for rubber and as a solvent to lower the viscosity of resin and promote diffusion of resin in the clay gallery. The clay/rubber epoxy mixture was sonicated with a high powered sonic dismembrator (VWR Branson sonifier 250R) for 30 min. During ultrasonication, the power of sonication was gradually raised while maintaining the temperature of the mixture at 35 °C by placing the reaction vessel in an ice jacket. A considerable amount of froth forms and there is a lowering of viscosity during sonication. After sonication, the vessel was allowed to equilibrate to room temperature and the swelling agent (THF) was stripped by placing the sonicated mixture in a vacuum oven at 60 °C for 4 h. Then the clay/rubber/epoxy mixture was hand mixed with an amount of curative (piperidine) that was 5% of the mass of epoxy. The curative added mixture was poured into a dog-bone cavity silicone mold and subject to the curing and cooling schedule, as described above. For compositional study, nanocomposites samples were prepared where phr (the content of rubber) ranged from 0 to 16, while the content of organoclay ranged from 0 to 5.5% by mass. The samples varied in color from brownish yellow to a creamy yellow, depending on the rubber content, and from opaque to a transparent, depending on the clay content.

For comparison purposes, epoxy resin was mixed with the same amount of curing agent and cured using the same schedule as above and is designated as pristine epoxy. This sample serves as a reference to establish the effectiveness of clay and rubber in altering the mechanical properties of the epoxy matrix.

2.5. Measurement of mechanical properties of cured specimens

The molding process produced dog-bone specimens that are approximately 6 cm (length) by 4 mm (gauge width) by 2 mm (thickness). Tensile experiments were conducted in an Instron tensile tester equipped with 50 kN load cell capability. The experiments were conducted at room temperature using a cross-head speed of 2 mm/min. The stress-strain curves were recorded for seven specimens of each composition. Fig. 1 shows stress-strain curves for filled and unfilled specimens. From these, we compute the tensile modulus, tensile strength, fracture strain and toughness. The tensile strength of the nanocomposite was determined at peak stress. Toughness was described from tensile-test data by integrating area under the curve of engineering stress versus engineering strain. Standard uncertainties reported here associated with these mechanical properties correspond to ± 1 standard deviation, computed from all tests.



Fig. 1. Sample tensile engineering stress–strain curves of each of four material compositions as noted in the legend (clay concentration either 0 or 5.5% by mass and rubber concentration phr either 0 or 16). These curves illustrate the four major tensile properties reported here: modulus, tensile strength, strain at break and toughness.

2.6. Morphological characterization of cured specimens

Transmission electron microscope (TEM) samples were cut from undeformed dog-bone specimens using an ultramicrotome equipped with a diamond knife. The microtomed samples were collected in a trough filled with water and lifted out of water using copper grids. The structure of dispersed clay and rubber in nanocomposites was investigated using TEM (Philips EM 400T) by operating at a voltage of 120 kV. To examine the failure mechanism, tensile fractured samples were mounted on a stub, Au–Pd was deposited on the fractured surface and observed using Philips E3 ESEM scanning electron microscope.

2.7. DSC characterization of cured specimen

Differential scanning calorimeter (DSC) experiments were conducted over a temperature range from 25 to 150 °C. Generally, samples were cooled at 10 °C/min and heated at 20 °C/min. The first scan was ignored while the second scan was used to determine the $T_{\rm g}$ of epoxy and that of rubber in the cured specimen.

3. Results and discussion

3.1. Morphological characterization of rubber dispersed epoxy nanocomposite

Three-phase morphology is evident in the TEM micrographs (Figs. 2 and 3): the clay appears dark, the epoxy gray and the location of rubber particles is white. The rubber particles are dispersed in the matrix and have a size ranging from 0.1 to 1.0 μ m, and an average diameter of approximately 0.5 μ m. The size of these rubber domains is consistent with that obtained previously in TEM and AFM studies [13,16]. At rubber concentration phr equal to 16, there is no evidence of



Fig. 2. Association of clay and rubber particles in nanocomposite with 0.75% by mass organo clay and acrylic rubber phr 16. TEM micrographs at (a) lower and (b) higher magnification.

phase inversion (the particulate morphology is retained). Furthermore, there is no change in the morphology of the rubber particles in epoxy nanocomposite when phr was decreased from 16 phr. All these results point to retention of particle morphology in the clay filled rubber dispersed epoxy specimen for all compositions studied.

The observed morphology of clay platelets in rubber filled nanocomposite can be best described as partially delaminated. TEM images show individual silicate layers of thickness in the order of 1 nm with an aspect ratio in the range of 100–500, when the clay layers are more or less perpendicular to the section. Clay layers that lie in the plane of the section also contribute additional weaker contrast in the matrix. TEM micrographs also reveal $0.5-2 \,\mu$ m aggregates in which the individual clay platelets retain their original face to face stacking. These aggregates are much smaller than the large aggregates observed in poorly mixed systems. It should be mentioned that these specimens were prepared with use of volatile solvent (THF) and ultrasonication to facilitate resin transport in the clay gallery, since mass transport of highly viscous resin into clay galleries is widely considered one of

the limiting steps to clay platelet separation. We recently reported that the relative amounts of clay platelet separation and aggregation in thermoset vinyl ester nanocomposite depend strongly on the details of the mixing technique (e.g. swelling duration of organoclay, solvent used for swelling organoclay, method of mixing) and the surfactant used for modifying clay platelet [26,27]. The size of clay ribbons/ aggregates observed for rubber dispersed epoxy nanocomposite is a reasonable match for the size dimension obtained previously in TEM studies of nanocomposites [27].

In addition to clay in the epoxy matrix, we notice that the clay particles align along the interface of rubber and epoxy matrix (Fig. 2(b)). In other words, the clay particles arrange along the boundaries of rubber particles. This is particularly evident with a relatively small amount of organoclay (e.g. 0.75% by mass) and a large amount of rubber (e.g. phr=16); nearly all the clay particles are associated with the rubber particles (Fig. 2). A systematic morphological examination of 1.5, 3, and 5.5% mass organoclay in epoxy with phr acrylic rubber equal to 8 and 16 confirms the adsorption of clay particles on the surface of the rubber particles (Fig. 3).



Fig. 3. TEM micrographs of nanocomposite with acrylic rubber phr=16 and organoclay content of (a) 1.5% by mass, (b) 3% by mass, and (c) 5.5% by mass.

The rubber particle surfaces are essentially saturated with clay at relatively low concentrations of organoclay. Since the rubber particles provide a limited surface area, as relative organoclay concentration is increased further, a greater fraction of clay is dispersed in the epoxy matrix (Fig. 3). As expected, this also holds true when the concentration of organoclay is held constant, while the acrylic rubber concentration is decreased. These clay particles are thus surface active, a phenomenon long used in 'Pickering' emulsions and of current interest [28]. Adsorption of clay particles to the rubber particles here significantly mediates the effect of nanoclay concentration on modulus and toughness of the composites, as discussed below.

3.2. Evaluation of mechanical properties of nanocomposite

Fig. 4 compares the tensile behavior of cured specimens as a function of composition type (organoclay 0 or 5.5% by mass and acrylic rubber phr 0 or 16; 4 combinations). In comparison to pristine epoxy resin, the addition of nanoclay enhances both the tensile strength and modulus: from 161 ± 3 to 178 ± 5 MPa and 2260 ± 90 to 2780 ± 60 MPa, respectively. While, the addition of acrylic rubber to epoxy resin causes the tensile strength and modulus to drop: 161 ± 3 to 143 ± 1 MPa and from 2260 ± 90 to 1980 ± 110 MPa, respectively. However, the elongation to break of epoxy resin is improved by adding acrylic rubber dispersants (Fig. 4(c)). Compared to an unmodified epoxy resin with no dispersants where the elongation to break is $8.3 \pm 0.7\%$, the elongation to break of rubber modified epoxy resin is 10.0+1.0%. The rubber particles are known to increase the elongation to break of the epoxy resin via interaction of the stress field ahead of the crack tip with the rubber particles. The most commonly accepted mechanism for toughening in such materials indicates that the rubber particles cavitate and thus act to initiate and assist yielding and plastic flow in the epoxy matrix [4,29]. Observations of stress whitening, discussed later, are consistent with this view.

Usually the addition of a rigid particulate filler can reduce the ductility of epoxy matrix. However, this reduction is usually less significant when the particle is nanoscale, thereby initiating many subcritical cracks. Here, the elongation to break is essentially unchanged from $8.3 \pm 0.7\%$ to $8.2 \pm 0.43\%$, with the addition of 5.5% by mass organoclay.

Significantly, with the presence of both organoclay and rubber, the elongation to break achieves its highest value: $11.5 \pm 0.6\%$. It is even higher than that of rubber only toughened epoxy $(10.0 \pm 1.0\%)$, contrary to the expectation that addition of rigid nanoclay should, if anything, lower the strain value of rubber modified epoxy resin. It is not clear why the presence of nanoclay filler should further increase the elongation to break of the rubber dispersed epoxy matrix. Although, it must be noted that a similar increase in toughness of rubber toughened epoxy resin has been observed when nanosilica particles were added to an epoxy-rubber formulation mix [19]. Sue et al. [30,31] noticed no compromise in the ductility of the rubber toughened epoxy resin due to the addition of rigid α -zirconium phosphate layer to the formulation mix. Since the nanoclay coats the surface of the rubber particles, perhaps the nanoclay facilitates the initiation of plastic deformation around the rubber particles. This is again consistent with stresswhitening observations, which are discussed next.

In rubber dispersed epoxy nanocomposite specimen, the stress-strain curve shows a smooth transition from a region where the load increases linearly with displacement to a maximum value followed by yielding which is accompanied by failure of specimen. We also notice a distinct region of stress whitened region over a fraction of the gauge length of the test specimen, an indication of cavitation under stressed condition. It must also be mentioned that the stress whitening region for rubber modified clay nanocomposite was found to be much more and over a wider area of gauge length of test specimen than rubber modified epoxy specimen. Also as the concentration of acrylic rubber in the specimen was increased, there was an increase in the stress whitened region of the fractured specimen. In contrast, clay-only composites exhibited very little, and pristine epoxy showed no stress whitening. Thus, while rubber particles alone produce stress whitening as expected, the presence of both rubber particles and organoclay



Fig. 4. Tensile behavior of cured nanocomposites as a function of composition type. Error bars represent the standard deviation.

is remarkably more effective for cavitation and toughening. This behavior apparently stems from adsorption of clay particles on the rubber particle surface (Figs. 2 and 3).

The area under the stress–strain curve was used to determine the fracture energy. The values of fracture energy for various cured systems are shown in Fig. 4(d). The results are averages from measurements on a minimum of four samples. The standard uncertainties shown in the figure correspond to ± 1 standard deviation. The unmodified epoxy has a comparatively low value of fracture energy, a reflection of the brittle characteristic of this crosslinked system. As expected, the addition of rigid nanoclay platelets did not improve the fracture energy of filled epoxy. However, with the addition of acrylic rubber to epoxy, there is an improvement in fracture energy of the composite system. With the addition of acrylic rubber and clay to epoxy there is a steep increase in fracture toughness of nanocomposite. It is evident that the presence of nanoclay filler and rubber dispersant is able to help facilitate the toughening process.

Another interesting observation is that the addition of nanoclay filler to rubber dispersed epoxy resin has enhanced both the tensile strength and modulus of the rubber dispersed epoxy matrix from 143 ± 1 to 161 ± 5 MPa and 1980 ± 110 to 2350 ± 90 MPa, respectively. In fact, the results show that the addition of 5.5% by mass organoclay to rubber dispersed epoxy can offset the loss in modulus and strength resulting from the addition of rubber dispersants to epoxy. These results show the benefits of adding nanoclay filler and micron sized rubber dispersants to improve the mechanical properties of epoxy

resin. The next section deals with concentration effects of preformed 'stabilized' rubber particles and organoclay on the mechanical properties of three-phase rubber-toughened nanoclay filled epoxy system; these effects are consistent with adsorption of clay to the rubber.

3.3. Influence of organoclay and acrylic rubber concentration on mechanical properties

The strength, modulus and elongation to break of the rubber dispersed nanocomposites for a range of clay concentration are shown in Fig. 5. There is not a significant change in the modulus of clay filled epoxy resin over the rubber dispersed epoxy resin until clay concentration of 5.5% (Fig. 5(a)), where for the first time a significant fraction of the organoclay is also in the epoxy matrix, in addition to coating the rubber particles (Fig. 3). The increase in modulus is about 20% over that of rubber modified epoxy resin. The enhancement in modulus is not surprising given that clay aggregate count increases with increase in clay concentration. Among the compositions studied, the clay aggregation was maximum at the maximum organoclay concentration. It is conceivable that the high clay concentration system makes the nanocomposite behave as micrometer sized filler filled system. [32] Likewise, the effect of organoclay concentration on tensile strength of rubber dispersed epoxy nanocomposite is similar (Fig. 5(b)).

The largest strain to break occurs when the clay concentration is small (Fig. 5(c)). The significant increase in (c) 14



Fig. 5. Tensile strength, modulus, elongation to break, and fracture energy of rubber dispersed nanocomposite (phr=16) with a range of organoclay concentration.

strain to break with the addition of 0.75% by mass organoclay is consistent with the concept that strain to break is augmented by a greater degree of cavitation, which is facilitated by coating of the rubber particles by the organoclay. As expected, the strain to break and modulus results for the nanocomposite system are roughly interdependent. In other words, increasing the nanoclay concentration to 5.5% by mass from 0.75% by mass, does not substantially change the fracture energy of the rubber dispersed nanocomposite (Fig. 5(d)). Similar improvement in fracture energy has been reported when nano-silica particles at a mass concentration of about 1% to 8% were added to rubber toughened epoxy. [19]

The mechanical response of these nanocomposites, therefore, derives from the distribution of nanoclay among three states: exfoliated, aggregated, or adsorbed to the rubber surface. When adsorbed to the rubber, the modulus and strength are hardly affected, but the elongation and toughness are improved, since nanoclay adsorbed to the interface promotes cavitation. When dispersed in the epoxy matrix, either individually or in aggregates, the modulus and strength improve. The observed modest increases in these properties reflect the preponderance of aggregates [32]. A greater degree of exfoliation would likely also decrease the total mass of organoclay adsorbed to the rubber surface, if individual platelets and smaller aggregates saturate the surface. In this case, smaller total amounts of nanoclay would be required to accomplish both functions of reinforcing the epoxy matrix (through micro and nano dispersion of the nanoclay in the matrix) and promoting cavitation (through adsorption of nanoclay to the rubber interface).

3.4. SEM analysis of fractured specimen

In order to understand how the nanoclay filler and rubber particles impact the fracture behavior, SEM examination of fractured acrylic rubber dispersed epoxy and acrylic rubber dispersed epoxy nanocomposite was performed. Fig. 6(a) shows a micrograph of a fractured rubber modified epoxy sample. As is commonly noticed on fractured surfaces of rubber toughened material, a large number of holes where the rubber particles have cavitated are visible. In some of the holes, the rubber particles can be seen suggesting failure at the epoxy matrix-rubber particle interface. Holes in the stress whitened region presumably result from rupture of elastomeric particles. Under tensile stress, the rubber particle should contract laterally more than the matrix but the chemical bonding between the rubber particle and matrix prevents the rubber particle from doing so, inducing a triaxial stress on the rubber particle. The rubber particle tears and relieves this triaxial stress, resulting in removal of rubber particles that appear as depressions on the fractured surface. The cavitation in the rubber particle makes it easy to see the two phase (rubber particles dispersed in epoxy matrix) morphology. The rubber modified epoxy exhibits considerable matrix yielding and plastic deformation as expected for a relatively ductile system.

Fig. 6(b) shows a micrograph of a fracture surface for an epoxy sample with rubber concentration phr 16 and 5.5% mass organoclay. The morphology of the rubber particles is still evident. Surprisingly, the clay does not affect the ability of the epoxy matrix to undergo shear yielding. It is generally thought that the presence of nanofiller can hinder the mobility of the surrounding polymer chains, thus limiting the ability of epoxy to undergo plastic deformation. Contrary to the expectation, we notice that the fractured surface of rubber dispersed epoxy nanocomposite shows considerable yielding and plastic deformation similar to the rubber dispersed epoxy system. Another explanation put forth to explain the enhancement in the plastic deformation of epoxy matrix is that the rigid particles are involved in crack deflection and crack twisting around the rigid particles [19,33,34]. It must be noted that these mechanisms have been primarily discussed for explaining toughening for micrometer sized filler based composite and not nanometer sized filler based system. We also notice the roughness of the sample to increase in rubber dispersed nanocomposite compared to rubber toughened epoxy resin. This observation is consistent with a behavior reported for intercalated clay nanocomposite and clay nanocomposites from unsaturated polyesters [34,35]. We infer that a number of mechanisms, specifically, stress transferring capability of individual clay platelet, crack diversion by clay platelet, rubber particle cavitation, plastic flow and yielding of the matrix initiated by the rubber particle, contributed in improving the failure strain and fracture energy of rubber dispersed clay nanocomposite. Additional work is needed to test and validate the above inference.



Fig. 6. Scanning electron micrograph of the fracture surface of nanocomposites with acrylic rubber concentration phr equal to 16 and organoclay concentration of (a) 0% by mass and (b) 5.5% by mass.

3.5. DSC analysis of cured specimen

The DSC experiments for all cured specimens showed a transition temperature at and around 90 °C. This temperature corresponds to the glass transition temperature for the epoxy when cured with piperidine for 16 h at 120 °C. The rubber modified epoxies showed the transition temperature at $94\pm$ 2 °C while clay filled epoxy and pure epoxy showed the transition temperature at 88 ± 2 °C. In a number of rubber toughened epoxy systems, the glass transition temperature of epoxy falls when rubber concentration is high. Generally the drop in T_{σ} is discussed in light of incomplete phase separation of rubber particles from the epoxy phase. If the cure state in all specimens is assumed to be the same for all samples, the results are consistent with the exception of rubber modified epoxies. We did not expect the small increase in $T_{\rm g}$ of rubber dispersed epoxy if there was complete phase separation of acrylic rubber. However, there may be residual levels of soluble rubber and stabilizer that remain miscible in the matrix resin, which may contribute to the higher observed T_g of resin. Finally, the glass transition temperature of the epoxy remains relatively unchanged in the three phase nanocomposite system.

4. Conclusions

The influence of toughener and clay concentration on the morphology of three-phase, rubber dispersed epoxy nanocomposite was studied. Through TEM observation, an interesting observation of clay particle alignment along the rubber particle/epoxy interface was identified. Apparently, these particles facilitate the cavitation of the rubber particles, and are, therefore, effective for additional toughening. Additional clay in the epoxy matrix leads to an improvement in the modulus of the composite. The clay particle distribution in the epoxy matrix of three phase nanocomposite was found to be sensitive to the composition of the formulation mix. Ductility of epoxy resin is enhanced without considerable reduction in the modulus and strength when organoclay and rubber dispersants are added to epoxy resin. By examining the fracture behavior of rubber dispersed epoxy and clay filled rubber dispersed epoxy, it has been inferred that a combination of mechanisms including rubber particle cavitation, yielding and plastic deformation of matrix initiated by rubber particles, crack diversion by clay platelets, and energy dissipation to create additional roughened area, may contribute to the improvement in the ductility of the three phase nanocomposite system. The glass transition temperature of the epoxy remains relatively unchanged over the concentration range for rubber and clay studied.

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