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Toughening of epoxy resins using nano rubber particles: Effects of particle size, surface functionality, and morphology on impact fracture properties

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ABSTRACT

A novel method to synthesis reactive nano-rubber particles is described. Considered as a frontier engineering material, reactive nano-rubber particles will find the way in almost all applications, specifically, in toughening of brittle materials. The process involves two steps: natural rubber sample (*cis*-1,4-polyisoprene) is emulsified using *soap-in-situ* method to sub-micro (nano) size particles, followed by a crosslinking reaction in the bulk of the particle. Some remaining double bonds on the surface were then used for further functionalization (epoxidation). Then, these epoxidized nano-rubber particles have been introduced before curing reaction to epoxy resins which is considered as a novel method for providing toughness with excellent adhesion in brittle epoxies. The combination of Scanning Electron Microscope (SEM) and Transmitting Electron Microscope (TEM) results indicates the effectiveness of the grafting reaction and consequently the interfacial adhesion between the dispersed rubber particles and the continuous domain of the investigated epoxy resins. Incorporation of 15 w% of nano-rubber particles enhances the flexibility of the modified epoxy sample to the required value. © 2010 Trade Science Inc. - INDIA

KEYWORDS

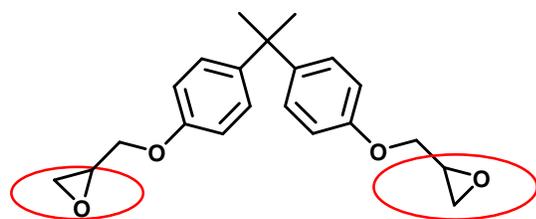
Nano rubber particles;
Toughening;
Epoxy resins.

INTRODUCTION

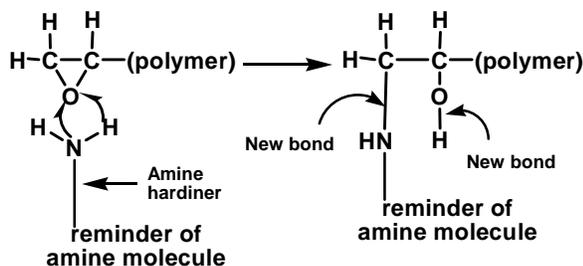
Generally, the mechanical properties of rigid (brittle) materials are enhanced by the introduction of a dispersed rubbery phase. This “toughening” procedure^[1] is commonly applied to increase material resistance to cracking/fatigue at low temperatures and to boost stability with minimum creep at higher temperatures in almost every high performance structure materials, in-

cluding thermoplastic and thermoset polymers^[2], asphalt^[3], and composite products^[4]. The most convenient process is by blending elastomer with rigid material in melt or solution with or without an interfacial agent to control morphology and interfacial adhesion. Core-shell morphology^[5], having a cross-linked rubber core and a grafted shell connecting the rubber particle with the rigid matrix, is an ideal structure for achieving toughness. Many examples, including HIPS (high impact poly-

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(a) Typical Epoxy diglycidyl ether of bisphenol A

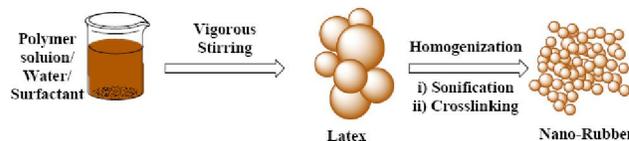


(b) Epoxy Reaction

Figure 1 : (a) Typical epoxy and (b) epoxy reaction^[15]

styrene), ABS (acrylonitrile-butadiene-styrene) engineering plastic^[6], and rubber-toughened epoxy resins, exhibit both high impact strength and good rigidity and make them the materials of choice for many applications.

The first rubber-toughened epoxy resins were developed during the late 1960s and early 1970s, and use the phase separation route with reactive liquid rubbers as the toughening agents^[7]. These materials are prepared by dissolving the rubber in the epoxy resin monomer, which is then polymerized. As the molar mass of the epoxy resin increases, its miscibility with the liquid rubber diminishes and eventually the rubber phase separates from the epoxy resin matrix to form rubber particles, which are covalently bonded to the matrix because of reaction between the epoxy resin and reactive end-groups of the rubber molecules. The most important liquid rubbers are carboxy-terminated copolymers of butadiene and acrylonitrile (known as CTBNs), the use of which has been thoroughly documented^[8]. However, the usual problems associated with phase separation routes^[9] are evident, with the size and morphology of the final rubber particles being influenced by the chemical structures and the molar masses of the epoxy resin and the rubber, the concentration of the curing agent and the conditions of cure, the rate of rubber particle nucleation and domain growth, and the



quenching of rubber particle development by gelation^[10]. Independent control of matrix properties and rubber particle size and morphology is difficult and, additionally, incomplete phase separation leads to reductions in the glass transition temperature of the matrix. It is for these reasons that use of the pre-formed particle route for toughening epoxy resins has been explored in recent years^[11].

Epoxy resins are generally formed by the three member epoxy group rings. The most common type of epoxy used is known as the diglycidyl ether of bisphenol A (DGEBA) (Figure 1). Epoxy groups could be located in different locations other than the ends. At least two epoxy groups have to be on the polymer molecule for crosslinking. Epoxies usually have high viscosities at room temperature; therefore diluents that also contain epoxy groups are used to lower the viscosity. Hardeners are used to crosslink epoxies. Amine hardeners are the most common; hardener should be added in amounts such that the number of epoxy groups is equivalent to the number of crosslinking sites provided by the hardener^[12]. If the hardener is added in the right amounts, a well crosslinked structure with the maximum properties will result. Some epoxies are formulated to crosslink at room temperature, but most epoxies used in composite applications require an increased temperature to initiate the crosslinking^[13]. Physical and mechanical properties are also improved by increasing the molecular weight when curing. As for polyester resins, no condensation by-products are formed during epoxy curing reactions.

The toughness of epoxies depends on the length of the polymer chain between epoxy groups. Longer chains (higher molecular weight) will result in tougher polymers. One disadvantage of long chains is that there are less crosslinks per unit length (lower crosslink density), which results in less stiff and less strong materials, with lower modulus and heat resistance. Rubber polymers are added to epoxy resins to increase toughness. Epoxies are usually more expensive than unsaturated polyesters, but have important advantages where epoxies are stronger, stiffer, tougher, more durable, more sol-

vent resistant and have a higher maximum operating temperature than polyester thermosets^[14].

The current paper is the first in a series from a systematic study of the effects of particle surface functionality, size and morphology on the pre-formed particle route to rubber-toughened epoxy resins. The paper concentrates on the effects these variables have on impact fracture behavior. Future papers will give full details of the preparation of the particles, data from tensile testing and low-rate fracture testing, and results from studies aimed at elucidating the mechanism(s) of deformation taking place during fracture.

Here we show a new class of pre-formed functional polyolefin rubber particles with well-defined particle sizes; specifically in the nano-scale which exhibits good processibility, good chemical and physical stability, and an *in situ* forming core-shell rubber particle structure with epoxy resins.

EXPERIMENTAL

Chemicals

Divinylbenzene and isoprene as crosslinkers (Aldrich) were dried and vacuum distilled over calcium hydride. Sodium dodecyl benzene sulfonate (SDBS, Fluka, technical grade, 80 %), polyisoprene (NR; Narobien), benzoyl peroxide (BPO, Fluka, 75 %), methylene bis acryl amide (MBA), potassium hydroxide KOH, sodium hydroxide NaOH, palmitic acid (surfactant), hexane, toluene, were used as received.

Synthesis of natural rubber (NR) nano-particles by emulsion

5.0 g NR (natural rubber), was dissolved in 50 mL toluene containing (5-7)wt% divinylbenzene or isoprene as a crosslinker and 5 % (wt) of palmitic acid (emulsifier) and about 1.0wt% of benzoyl peroxide as a free radical initiator was added. In a second step, the whole organic phase was slowly added to a vigorously stirred solution of KOH in 100 mL de-ionized H₂O such that the final emulsion has a pH slightly alkaline. After strong stirring for 30 min, the emulsion was homogenized by sonification for another 30 min in an ultrasonic processor homogenizer operating at 300 bars under nitrogen.

The flask was purged with N₂ for 30 min before rising the temperature to 90°C. Processing times ranged

from 2 to 6 h, depending on the viscosity of the samples and consequently on the molecular weight of the used rubber. The product was coagulated by HCl/methanol, re-dispersed in chloroform and precipitated with methanol to remove the surfactant before an overnight drying under vacuum.

Epoxidation^[16]

NR rubber particles (5.0 g) were dispersed in 80 mL toluene in a flask with 1.8 g of *m*-chloroperbenzoic acid. The reaction was performed at 70°C for 4 hrs with stirring under N₂ atmosphere, then the product was obtained by precipitating with methanol, washed and vacuum dried.

Epoxy resin modification (toughening) with the epoxidized nano-rubber particles

A sample of the epoxidized nano-rubber particles was premixed with the base material of the epoxy resin containing the required thinner amount. Consequently, the hardener component was added and followed by well stirring. Then the sample was applied using an airless sprayer on the stainless steel panel (10×15 cm). Another sample was poured into a Petri-dish to form a film for the required morphological studies. This process has been repeated using different amounts of the epoxidized nano-rubber particles (3, 5, 10 and 15% by weight). All samples were left for full curing (7 days at room temperature according to the material data sheet) before characterizations.

Characterization

During the emulsification process; colloidal samples were isolated by syringing in time intervals for the determination of the particle size distribution and volume-average diameters of the particles by Light-Scattering analyzer.

All ¹H-NMR spectra were recorded at room temperature on a Bruker AM-300 spectrometer with the DISNMR software. The NMR samples were prepared in *d*-chloroform that is a good solvent for all samples.

Bulk morphology in the polymer films was examined by Scanning Electron Microscope (SEM), using a Topcon International Scientific Instruments ISI-SX-40 with secondary electron imaging. SEM samples were prepared from films cryo-fractured in liquid N₂. Samples were mounted on an aluminum stub and gold coated to

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form a conductive coating. Transmission Electron Microscopy (TEM) was performed at 120 kv using model JEOL JEM 1200 EXII equipped with a video camera, a Gatan Bioscan 792 camera and a high resolution Tietz F224 camera and a PGT Prism light element detector. Samples were prepared by dipping the grid in a dilute epoxy resin solution (before curing) followed by evaporating the solvent which affords a very thin film for TEM analysis.

Mandrel bending test^[17]

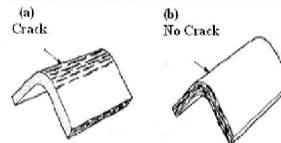
Mandrel test, performed under ASTM D522, is used to evaluate the flexibility of coated strip metal that is to be formed during a fabrication process. ASTM D522 contains two test methods which are used to determine the flexibility and resistance to cracking of organic coatings on substrates of sheet metal.

The coating material; epoxy/rubber particles nanocomposite was applied at a uniform thickness to panels of sheet metal. After curing, the coated panels were bent over a mandrel and the resistance to cracking of the coating was determined.

Coatings attached to substrates are elongated when the substrates are bent during the manufacture of articles or when the articles are abused in service. Conical mandrel bend tester is applicable to determine extensibility of epoxy coatings on metal panels which are clamped in position and formed round the conical mandrel by rotating the roller frame. The panels are examined to evaluate crack resistance detachment from the metal substrate of coated surface which is coated with epoxy under standard condition.

RESULTS AND DISCUSSION

This class of reactive rubber particles is represented by formula (I), in which the rubber particle is a cross-linked polyolefin elastomer with a low glass transition temperature ($T_g < -60^\circ\text{C}$)^[18] and a sub-micro (nano) particle size. Some reactive groups (X), can be introduced via the remaining double bonds located on or near the surface, include a broad choice of desirable functional groups, such as OH, COOH, NH_2 , epoxide, anhydride, styrene, borane, silane, and mixtures, which can engage in chemical reactions with various rigid materials during the reactive blending, extrusion, and po-



lymerization processes.

Epoxidizing these nano-particles produces the rubber core that have been mixed with the base material of the epoxy resin before adding the hardener. Consequently, the resulting core-shell rubber particles are homogeneously embedded in the matrix with excellent interfacial interactions.

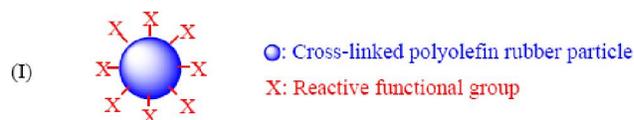
The process involves in the first step, emulsification of the rubber sample using *soap-in-situ* method followed by crosslinking. The remaining double bonds on the surface are successfully epoxidized and consequently imbedded into the epoxy resins during the curing reaction. SEM and TEM measurements show the introduction of strong interfacial adhesion between the rubber particles and the matrix domains of the investigated polymer.

Morphological studies

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) were used to characterize the morphology of reactive blending and to compare with their physical blends^[19]. SEM shows the liquid N_2 -fracture surface, representing the undistorted polymer bulk. On the other hand, TEM picture provides a 3-D view of the nano-rubber particles in the epoxy matrix.

Scanning electron microscopy (SEM) results

Two samples were examined by SEM, and their micrographs are shown in figure 2. These samples were prepared by fracturing the polymer films under liquid nitrogen conditions, and SEM micrographs were taken on the fractured surfaces. For comparison, the epoxy



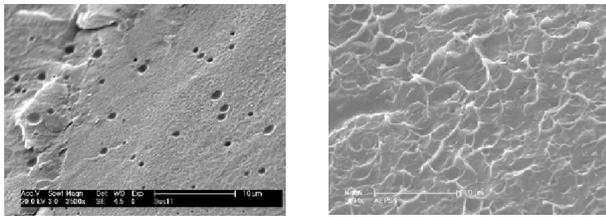


Figure 2 : SEM micrographs of (left) a simple blend between unfunctionalized nano-rubber particles and epoxy resin and (right) the reactive blend between epoxidized particles and epoxy resin

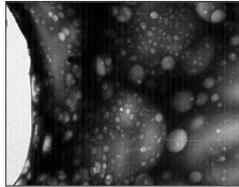
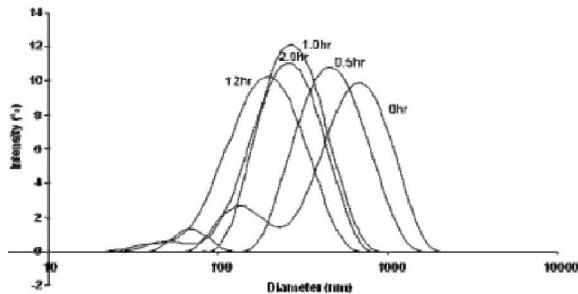
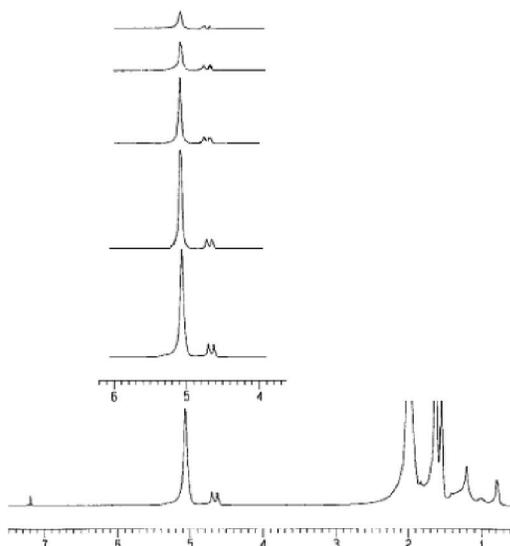


Figure 3 : TEM Micrograph of the reactive blend between epoxidized particles and epoxy resin



(a)



(b)

Figure 4 : (a) Particle size distribution measured by light scattering and (b) vinyl proton chemical shift patterns monitored by ^1H NMR spectra during crosslinking of polyisoprene/DVB

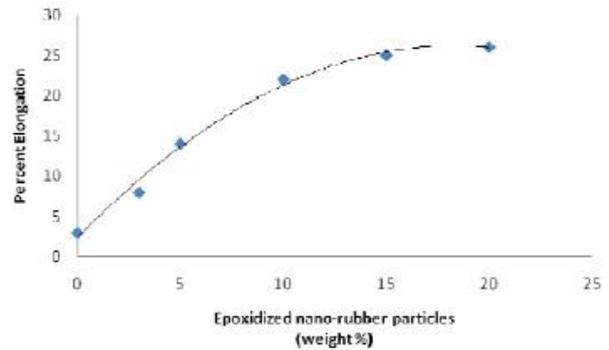


Figure 5 : The resistance to cracking (flexibility) of epoxy/rubber particles nanocomposite

modified sample is side-by-side compared with the corresponding simple polymer blend (physical mixing of unfunctionalized particles and epoxy resin). In each case, a lot of convex particles and concave holes exist on the fracture surfaces of the simple polymer blends. The existence of these particles or holes is a clear indication of poor interface adhesion that results in clean separation or pullout of the rubber particles from the continuous polymer matrix during fracturing the blended sample. On the other hand, the micrograph of the other sample prepared by mixing the epoxidized particles with the epoxy resin shows no convex particles or concave holes on their fracture surfaces. The uniform fracture surface implies the cohesive failure in the continuous epoxy matrix, not at the rubber particle-epoxy matrix interfaces.

Transmission electron microscopy (TEM) result

Transmission electron microscope (TEM) was also used to examine polymer morphology. Sample preparation was done as explained in the experimental part, where several epoxy solutions with different concentrations were prepared for grid dipping. After evaporating the solvent, the suitable semi-transparent thin film with proper thickness on the grid was selected by optical microscopy before taking TEM micrograph. Figure 3 shows the TEM micrograph of an epoxidized nano-rubber particles/epoxy resin sample. It is clear that the rubber particles are well-dispersed in the epoxy matrix, strongly indicating the required structure for toughening.

Particle size and ^1H NMR spectra of the nano-rubber particles

In emulsion, it was easy to sample out samples at

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different time intervals during the course of the reaction for examining the degree of crosslinking and the rubber particle size. Figure 4 (top) shows the change in particle size by light scattering with the reaction time and Figure 4 (bottom) shows the ^1H NMR of the double bond pattern. The ^1H NMR spectra of poly (isoprene) showed the expected signals for both the aliphatic and olefinic protons of the isoprene backbone^[20]. As shown in figure 4 (bottom); the two chemical shifts—one major at 5.1 ppm and one minor at 4.8 ppm—correspond to the 1,4-isoprene structure. The double bonds consumed during the crosslinking and consequently, the particle diameter. It is clear that, as the reaction running, more double bonds are consumed during the cross-linking reaction and the particle shrinks more. Therefore, the particle size diameter reduced with the reaction time.

Flexibility of epoxy/rubber particles nanocomposite

Figure 5 shows the relationship between the percent elongation and the weight percent amount of nano-rubber particles added to the epoxy. It is clear that the percent elongation increases exponentially with the added amount of the nano-rubber particles. From the curve and based on ASTM D522; it is obvious that 15 w% enhances the flexibility of the modified epoxy sample to the required value.

CONCLUSION

A novel method for synthesizing reactive rubber particles has been developed. The process involves two steps; the first step requires emulsification of cis-1,4-polyisoprene using *soap-in-situ* method to form sub-micro nano size particles followed by crosslinking. The particles contain several double bonds on or near the surface, which are very versatile for many applications. Therefore; and as the second step, these double bonds were used for further functionalization reactions (epoxidation) to provide the important interface adhesion with the brittle epoxy polymers. By following up the crosslinking time with particle size measurement and ^1H NMR; the double bonds consumed during the crosslinking and consequently, the particle diameter.

In addition, the combination of SEM and TEM results indicates the effectiveness of the functionalization

reaction of the prepared nano-rubber particles and consequently the interfacial adhesion with the continuous epoxy resin domain. Mandrel test clearly showed that incorporating 15 w% of nano-rubber particles enhances the flexibility of the modified epoxy sample to the required value.

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