Rubber-Thermoset Blends: Micro and Nano Structured

Jin Kuk Kim and Sanjoy Datta

Abstract Highly cross-linked thermosets which are susceptible to brittle failure can be effectively toughened by blending them with rubbers. However, if the materials are already cross-linked, then blending with rubber as it is done in the conventional way with thermoplastics, is virtually impossible. Thus it asks for an altogether different method to accomplish successful blending. Initially, miscible liquid rubbers in small amounts or preformed rubber particles are incorporated in the matrix of curing agent incorporated precured thermosets resins and then the whole mass is subjected to curing. The phase separation, in case of liquid rubber toughening depends upon the formulation, processing and curing conditions and incomplete phase separation may occur resulting in unwanted lowering of glass transition temperature. The phase separation in case of liquid rubber is based upon nucleation and growth. In case of preformed rubber particles, these difficulties are not encountered and the resulting morphology can be better controlled. However, the problem of proper dispersion of these particles in the themoset resins limits the use of this method. The improvement in fracture resistance occurs in either case due to dissipation of mechanical energy by cavitation of rubber particles followed by shear yielding of the matrix. Rubber particle size plays an important role in improving toughening and very small or very large sizes are undesirable. The toughenability increases with increase in inherent ductility of the matrix.

1 Introduction: Concept of Rubber-Thermoset Blends

Highly crosslinked thermosets like epoxies, phenolics and cyanate esters have come to the fore with many application outlets but one disadvantage in common with these thermosets is that they all have low toughness and are susceptible to

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brittle failure. Thus, for applications asking for higher toughness without substantially sacrificing other desirable properties, it is mandatory to modify them. They may be modified with plastics, oils or fibres.

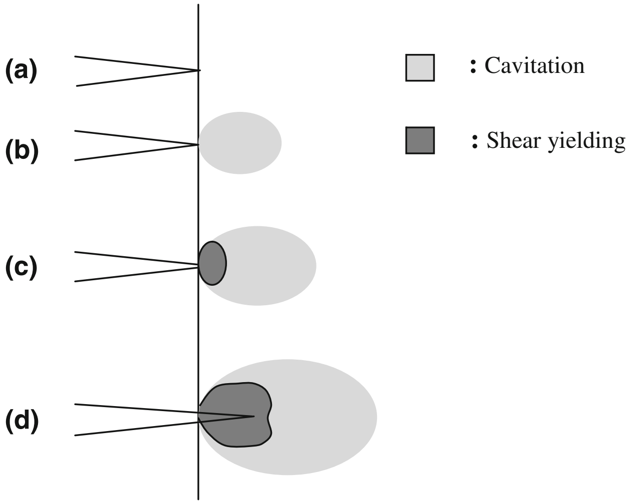
Another route to accomplish the same relatively easily with cheaper initial investment is by blending with rubber, though the processing may sometimes turn out to be somewhat more difficult. Progressive research works have carved routes to do away with the impediments of processing obstacles, and customary to say, rubber modified thermosets are gaining importance. However, it is noteworthy to mention that rubber/thermoplastic blends and thermoplastic vulcanizates (TPVs) are far more established over rubber/thermoset blends. It is the business of the present chapter to focus on the latter. Studies show that rubber toughening in thermosetting epoxy resin is very well established. However, this is not the case for phenolics, especially for the resol type. Some aspects of both rubber toughening of epoxies and phenolics, the two most commonly encountered thermosets will be the main area of discussion of this chapter.

1.1 Morphology of Rubber-Thermoset Blends

Thermosets can be toughened by rubber particles with mainly two different morphologies which are either the use of ‘core–shell rubber particles’ or initially ‘miscible reactive rubbers’. Emulsion polymerization is the route to the preparation of Core–shell rubber particles and exhibit alternating rubbery and glassy layers. These particles have been successfully used to modify thermosets, such as epoxies, cyanates and vinyl ester resins. The constituents of such a particle are a rubbery core and an outer shell of a glassy polymer. The rubbery core is generally based on polybutadiene. The outer glassy shell is required to prevent coalescence of rubbery particles during synthesis, and enhances a good interface with the matrix. The shell is usually based on styrene/acrylonitrile copolymers. However, the core–shell toughening does not bring about good dispersion [1]. This is why the most widely used method for the rubber toughening is the addition of initially miscible rubbers into the thermosetting matrix. The rubber may form a secondary phase during the polymerization (curing) reaction depending upon the type of rubber and thermosetting material used. The degree of this phase separation can control not only the amount of toughening obtained, but also a number of other properties such as modulus of the system along with glass transition temperature [2].

1.2 Toughening Mechanism of Rubber-Thermoset Blends

Usually more than one toughening mechanism takes place before failure occurs in thermoset systems. Therefore, it is important to first consider the most effective



Scheme 1 A sketched sequence of the toughening mechanism of core shell rubber modified epoxy thermoset system (a) initial starter crack; (b) formation of a cavitation zone in front of the crack tip; (c) geometry with the initial yielded plastic zone; (d) shear yielding

toughening mechanism like 'shear yielding' and then mention other effective but minor toughening mechanistic routes.

In the mechanism of 'shear yielding', shear bands or deformation zones are initiated by rubber particles leading to stress concentration at the surrounding matrix. The improvement upon toughness is proportional to the number of such particles, higher number contributing to the creation of more deformation zones before fracture occurs. The general approach to shear yielding is briefly discussed. Small rubber particles to the tune of fractions of a micrometer are quite effective in promoting extended shear yielding of the brittle thermoset matrix. The matrix undergoes plastic deformation. This type of plastic deformation is supported by the fact that the rubber particles at the crack tip elongates to the same extent as the matrix evidenced by microscopic studies compared with undeformed spherical rubber particles. The major toughening mechanism, as it appears to be is cavitation of the rubber particles followed by shear yielding of the matrix. The cavitation of the rubber particles helps relieve the plane strain constraint induced by thick specimen and sharp crack. The shear stress component around the crack tip is greatly raised and causes extended yielding of the matrix. A schematic diagram is shown in Scheme 1 [3] for understanding the phenomenon more clearly. It is, therefore, possible to toughen highly crosslinked thermosets via shear yield mechanism as long as the toughener can effectively alter the crack-tip stress state from one that favours brittle fracture to one that promotes shear yielding. In addition to shear yielding, some other toughening mechanisms such as micro-cracking, crack deflection, crack bifurcation, crack pinning, crack bridging or multilevel fracture path (enlargement of fracture surface area) can also be operative. However, these mechanisms are less effective than the ‘shear yielding’ mechanism and relatively low in energy absorption capacity.

In the scheme, (a) represents the initial starter crack followed by the formation of a cavitation zone in front of the crack tip when the specimen is initially loaded (b). This develops into a geometry shown in (c), when formation of initial shear-yielded plastic zone around the crack tip takes place with the relieving of the hydrostatic tension. This is due to the cavitation of the rubber particles. Once the build up of shear strain energy reaches a critical value, the material begins to undergo shear yielding allowing the crack to propagate and leaving a damage zone around the propagating crack as is shown in (d). Thereafter the crack grows again.

1.2.1 Review of Toughening Concepts

The first serious attempt to explain the question of how an immobile, crosslinked glassy thermoset can be toughened by rubber particles was made by Kunz and Douglass [4]. The model developed by them was based on the principle of energy dissipation during stretching and bridging of the crack surfaces by rubber particles. The particle bridging mechanism is rather a straightforward phenomenon. When the crack advances in the rubber modified epoxy system, it has a tendency to grow preferentially in the more brittle epoxy matrix phase, in effect around the rubber particles in the initial stage of the crack growth. Subsequent to this, when the crack begins to open up, the rubber particles start to span between the two separating crack planes. These rubber particles are extremely ductile and strain-harden rapidly. As a result the fracture energy required to make the crack grow is somewhat increased. In other words the brittle thermoset is toughened. The bridging particle should have the capacity to stretch between the two crack planes and so they must exhibit ductility. The size of the particle has to be much larger than that of the crack tip radius for it to function as an effective bridge. Finally, the interfacial adhesion between the particle and the matrix needs to be stronger the cohesive strength of the particle itself. If all these requirements are satisfied then the particle bridging mechanism will be effective. However, it was proved later that rubber bridging mechanism only plays a secondary role in the toughening of brittle thermosets.

Sultan and McGarry [5] highlighted the role of rubber particle size in the use of rubber toughening in a thermosetting matrix and they chose an epoxy system. In their study, they used carboxyl-terminated acrylonitrile (CTBN) liquid rubber to toughen diglycidyl ether of bisphenol A (DGEBA) epoxy resin. They set off with the concept that toughening depends on the rubber particle size and showed that 40 nm particles were not as efficient as 1 mm particles. Thus nearly five-fold increase in fracture energy values were obtained when large particles (1 mm) were used instead of small ones (40 nm). Further to this, Pearson and Yee [6] tried to investigate the rubber particle size dependence on toughening mechanisms. They prepared an epoxy system (DGEBA) with liquid reactive rubber (CTBN). From their study, they concluded that relatively large particles provided only a modest increase in fracture toughness by a particle bridging/crack deflection mechanism.

In contrast, smaller particles provided a significant increase in toughness by a shear banding mechanism.

Frounchi et al. [7] experimented with solid acrylonitrile-butadiene rubbers (NBR) added to DGEBA type epoxy resin matrix. Their study showed that increasing the acrylonitrile content of the rubber (from 19 to 33 %) caused better compatibility between NBR and epoxy resin. Thus, they obtained effective toughening and 40 % increase in impact resistance. Kaynak et al. [8–12] investigated rubber toughening of DGEBA-type epoxy resin through the incorporation of various modifiers, such as hydroxyl terminated polybutadiene (HTPB) rubber, a silane coupling agent (SCA), recycled scrap tire rubber particles and a liquid elastomer. They used these modifiers separately and with various combinations. They also studied effects of mixing order during specimen preparation, and surface modification of these rubber particles. They indicated that toughness of the brittle epoxy can be improved most effectively when these modifiers were used at certain synergistic combinations with certain surface treatments.

Chen and Jan [13] prepared bimodal distributed liquid rubber particles (CTBN) in epoxy resin (DGEBA) to study the fracture behaviour of the system. They eventually found out that a 171 % increase in fracture energy was obtained by using bimodal rubber particles over the unimodal ones. However, this was not reflected in the work of Pearson and Yee [6]. They tried out the bimodal mixtures of epoxies containing small and large particles, but did not observe any significant improvement in fracture energy.

Geisler and Kelley [14] used a combination of alumina and core–shell rubber particles with epoxy matrix in order to overcome some of the drawbacks produced by rubber toughening (decrease in modulus and high temperature performance). They observed that a cured epoxy system having rubber and alumina particles had fracture toughness values 25 % higher than those of epoxy systems having only rubber or only alumina particles. They also argued that toughness improvement does not lead to any decrease in glass transition temperature (T_g) and modulus. Yee and Pearson [15] also analysed the effect of matrix Tg on rubber toughening. They demonstrated that the low crosslink density epoxies were far more readily toughened than the high crosslink density ones.

From what has been discussed so far, it is customary to say that rubber toughening in thermosetting epoxy resins is very well studied and quite established. However, this is not the case for phenolics, especially for resol type phenolic resins. The reason may be due to the difficulties encountered during curing such specimens by casting. Curing in resol-type phenolic resins should be conducted at temperatures below 100 °C to avoid boiling of water which is a byproduct of the curing reaction. Water evaporation causes bubble formation and densely voided structures. To get rid of such a condition, curing is accomplished at a temperature around 80 °C leading to very long curing times of 2 or 3 days. With further lowering of the curing temperature to a measure of 40 °C bubble formation can almost be eliminated but the curing period becomes very impractical. It was observed that even after a period of 4 days enough rigid crosslinked structure was not obtained.

2 Various Types of Rubber-Thermoset Blends

Though many kinds of thermoset materials can be and have been experimented upon with blends of rubbers purely on research basis, yet here only two such most important blends will be considered; rubber-phenolic and rubber-epoxy.

2.1 Rubber-Phenolic Blends

Phenolic resins (PR) have been widely used as coatings, adhesives, composites, etc. due to their excellent flame resistance, heat resistance, insulativity, dimensional stability and chemical resistance. However, their application has significantly been limited by inherent brittleness. Materials used as toughening agents of PR include elastomers such as natural rubber and nitrile butadiene rubber (NBR) [16], reactive liquid polymers such as liquid nitrile butadiene [17] and carboxyl terminated butadiene acrylonitrile (CTBN) [18], plastics [19, 20] such as polysulfone and polyamide, oils such as cashew nut shell liquid [21], tung oil [22] and linseed oil [23], and fibres such as glass fibres and aramid fibres [24].

The most widely used toughening agents are elastomers due to their high efficiency and low cost. However, the phenolic network is subject to deterioration in heat resistance, strengths and modulus after the incorporation of elastomers and flexible compounds.

Stiff aromatic heterocyclic structures are usually introduced into PR molecules to improve its heat resistance. However, the same stiff structures will also decrease the PR toughness. Obviously, the method for toughening and heat resistance improving is incompatible. Recently, studies on PR modification by addition of nanoparticles, including carbon nanotubes [25] and layered silicates [26, 27], were reported. These nanoparticles are able to greatly improve heat resistance and stiffness of phenolic materials, but can only slightly enhance toughness.

Modification of PR with organic nanoparticles has been reported [28]. A new kind of PR/organic nanoparticle composite, including PR/nitrile butadiene elastomeric nanoparticle (NBENP) composite and PR/carboxylic nitrile butadiene elastomeric nanoparticle (CNBENP) composite have been successfully developed.

Since phenolic blends are less openly published, it is discussed in some details in this chapter with reference to two relevant and promising works.

2.1.1 Rubber Toughening of Phenolic Resin Using Nitrile Rubber and Amino Silane

Kaynak and Cagatay [29] have reported the toughening of phenolic resin using nirtile rubber and aminosilane. For the phenolic resin, a resol-type liquid phenol–formaldehyde was used. Powder rubber particles used for toughening were

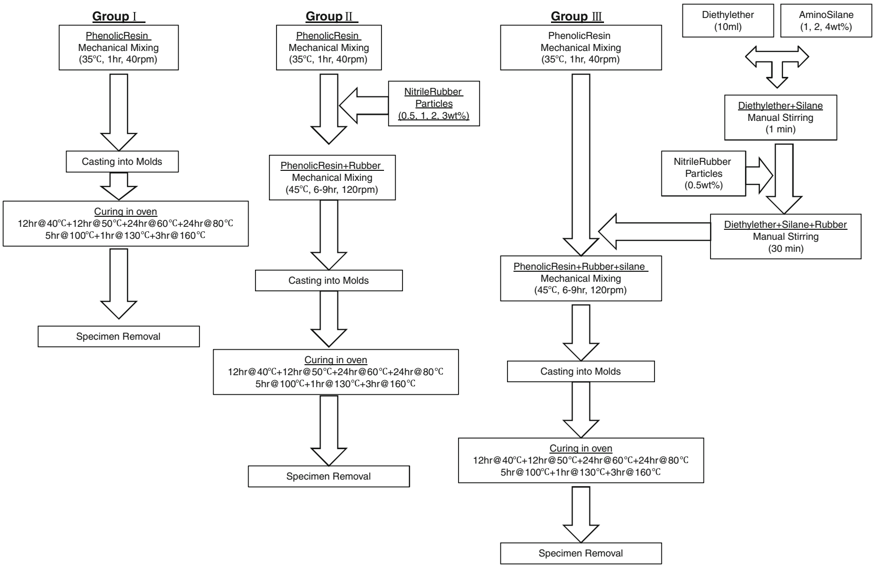


Fig. 1 Production scheme of the three groups of specimens [29]

acrylonitrile–butadiene rubber (NBR). An amino silane (3-aminopropyltriethoxysilane) was also used together with the nitrile rubber particles contemplated to investigate synergistic effect in rubber toughening if any. Specimens were produced in three main groups. In the first group, only neat phenolic resin was used. In the second group, phenolic matrix was modified with nitrile rubber particles. Modification was carried out both with nitrile rubber and amino silane in the third group. The production schemes of these three main groups are given in Fig. 1.

This is of utmost importance because without a proper approach to blending only poor toughening is usually observed.

Group I specimens were prepared by putting the neat phenolic resins from refrigerator onto a hotplate. Then, it was mechanically mixed at 40 rpm at 35 °C for 1 h in order to decrease the viscosity. Finally, the resin was poured into PTFE (polytetrafluoroethylene) moulds and cured in an oven. In the preparation of Group II specimens, the resin was first mechanically mixed at 35 °C for 1 h. Then, rubber particles without further purification were added to the liquid phenolic resin, and this mixture was mixed by a stirrer at 120 rpm and 45 °C to dissolve the rubber particles. In this group, since the matrix resin was modified with four different amounts of rubber at 0.5, 1.0, 2.0, and 3.0 weight percent, therefore, the mixing period was different for varying concentrations of rubber and ranged from 6 to 9 h with the increasing rubber concentration. Finally, the resin–rubber mixture was poured into PTFE molds and oven cured. The preparations of Group III specimens were somewhat more complicated with the further incorporation of the amonosilane. In this group, first of all, liquid amino silane was dissolved in 10 ml diethylether solvent by stirring manually for 1 min. followed by the addition of nitrile rubber particles to the silane–diethylether system. Since specimens having 0.5 wt% rubber content resulted in highest performance in Group II, so this concentration was kept fixed in Group III.

However, to investigate the effects of amino silane addition, three different silane concentrations were used at 1, 2, and 4 wt% with respect to the amount of rubber particles. Solvent–rubber–silane mixture was kept at room temperature for 30 min for evaporation of the solvent. Then, this silane–rubber mixture was added to the mechanically mixed (at 35 °C for 1 h) resin system. Next, this resin–rubber–silane mixture was mechanically mixed (120 rpm, 45 °C, 6–9 h) and, finally, poured into the mould to cure.

As explained previously, phenolic resins should be cured carefully, else the evaporation of the by-product water molecules may lead to void formation in the specimens. This study was devoted to various trials in order to obtain an efficient curing schedule. First, a high curing temperature of 160 °C was used and it was observed that specimens were cured in only 30 min. This led to the unwanted formation of a large amount of bubbles and the entire structure was rendered useless. A gradual decrease in curing temperature can be an alternative solution. However this approach reflected the formation of some voids even at a temperature of 100 °C. When the curing temperature was lowered to a measure of 40 °C then bubble formation was almost eliminated but the curing period was impractical. It was observed that even a period of 4 days was not enough to obtain a rigid crosslinked structure.

The best method is to cure the specimens, starting from low temperatures with successive increases. An optimized curing method which can be applied based on the studies is as follows: 12 h at 40 °C, another 12 h at 50 °C followed by 24 h at 60 °C and finally 24 h at 80 °C. However, this cure scheme did not furnish a concrete route to produce a specimen with sufficient mechanical properties. It was judged best to post cure the specimens at 100 °C for 5 h and then 130 °C for 1 h and finally 160 °C for 3 h. The specimen designation in this case study is shown in Table 1.

Flexural, notched Charpy impact and plane-strain fracture toughness tests were performed in order to characterize the mechanical behaviour, especially toughness, of the specimens. Figure 2 gives the mechanical properties of the resol-type

Table 1 specimen designation used [29]

Designation	Specimen
P	Neat phenolic resin
PR0.5	Phenolic resin with 0.5 wt% nitrile rubber
PR1	Phenolic resin with 1 wt% nitrile rubber
PR2	Phenolic resin with 2 wt% nitrile rubber
PR3	Phenolic resin with 3 wt% nitrile rubber
PRS1	Phenolic resin with 0.5 wt% nitrile rubber and 1 wt% amino silane (with respect to nitrile rubber)
PRS2	Phenolic resin with 0.5 wt% nitrile rubber and 2 wt% amino silane (with respect to nitrile rubber)
PRS4	Phenolic resin with 0.5 wt% nitrile rubber and 4 wt% amino silane (with respect to nitrile rubber)

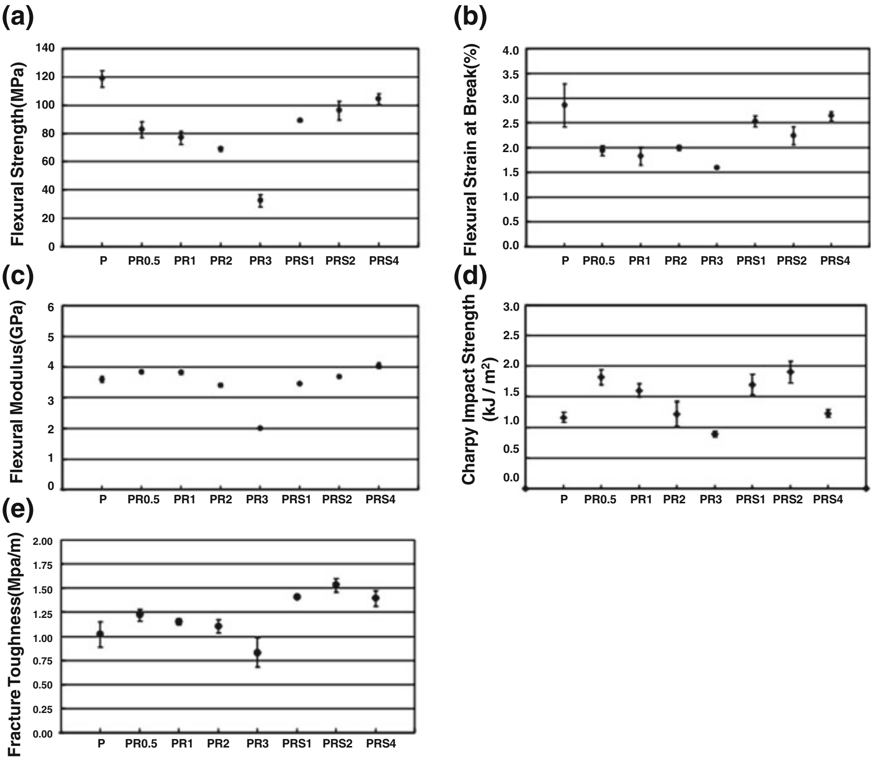


Fig. 2 Results of flexural, impact, and fracture toughness tests: **a** flexural strength, **b** flexural strain at break, **c** flexural modulus, **d** charpy impact strength, and **e** fracture toughness [29]

Table 2 Mechanical properties of the specimens [29]

Specimen designation	Flexural strength (MPa)	Flexural strain at break (%)	Flexural modulus (GPa)	Charpy impact strength (KJ/m^2)	Fracture toughness (Mpa m$^{1/2}$)
P	119 ± 6	2.85 ± 0.44	3.58 ± 0.10	1.17 ± 0.08	1.02 ± 0.13
PR0.5	83 ± 6	1.93 ± 0.10	3.82 ± 0.05	1.82 ± 0.12	1.22 ± 0.06
PR1	77 ± 5	1.82 ± 0.18	3.81 ± 0.07	1.60 ± 0.11	1.15 ± 0.03
PR2	69 ± 1	1.99 ± 0.05	3.39 ± 0.05	1.22 ± 0.20	1.10 ± 0.07
PR3	32 ± 4	1.59 ± 0.02	2.00 ± 0.04	0.89 ± 0.05	0.83 ± 0.15
PRS1	89 ± 1	2.53 ± 0.11	3.43 ± 0.04	1.70 ± 0.17	1.41 ± 0.02
PRS2	96 ± 7	2.24 ± 0.18	3.67 ± 0.03	1.90 ± 0.18	1.53 ± 0.07
PRS4	104 ± 4	2.64 ± 0.09	4.04 ± 0.09	1.24 ± 0.06	1.39 ± 0.08

phenolic resin specimens modified by nitrile rubber particles and an amino silane determined by flexural, impact, and fracture toughness tests. For comparison, the data are also tabulated in Table 2.

Figure 2a shows that use of nitrile rubber particles in phenolic matrix decreased flexural strength. These decreases can be due to two main reasons: first of all, since nitrile rubbers have elastomeric behaviour with low strength, it is a reasonable argument that the flexural strength values will decrease for the phenolic matrix. The second reason may be attributed to the difficulties encountered during specimen production. For instance, formation of voids in the specimens due to the water evaporation during very long curing schedules. Another problem in specimen production was the difficulty in dissolving solid rubber particles in liquid phenolic resin, which increased more with increase in rubber content. Figure 2a also shows that use of amino silane together with nitrile rubber in the phenolic matrix increased the flexural strength.

Specimens having 0.5 % rubber and 2 % silane (PRS2) and 4 % silane (PRS4) have 16 and 25 % higher flexural strength than the specimen having 0.5 % rubber only i.e., (PR0.5). Here ‘synergistic’ effect of amino silane with nitrile rubber particles took place.

As seen in Fig. 2b, flexural strain at break also decreased when nitrile rubber particles were used in the phenolic matrix. Normally, since these particles are elastomeric materials, it is expected that the strain values should increase.

Unfortunately, due to the specimen production problems, this was not observed. Void formation and debonded solid rubber particles led to lower strain values at failure. However, synergistic effect of amino silane with nitrile rubber increased these strain values. It is seen that strain at failure increased by 16 and 37 % in the specimens PRS1 and PRS4, respectively, compared to PR0.5 specimen.

Figure 2c indicates that flexural modulus values did not decrease when phenolic matrix was modified with nitrile rubber particles, except for the specimen PR3 having the highest rubber content, which again can be due to the specimen production problems mentioned above. Use of amino silane with nitrile rubber increased the modulus values slightly, the highest increase being 13 % in the specimen PRS4 compared to neat phenolic specimen (P).

Figure 2d shows that Charpy impact strength value of neat phenolic specimen (P) improved when modified with nitrile rubber particles, for instance the increases being 56 and 37 % in the specimens PR0.5 and PR1, respectively. This is reasonable due to the ‘rubber toughening’ effect of nitrile rubber domains in the phenolic matrix. However, increasing rubber content decreased the improvement so that the specimen having highest rubber content (PR3) had lower impact strength than the neat phenolic specimen (P). This could again be due to the problems encountered during specimen production. As the rubber content increased, the time period required to dissolve these rubber particles in liquid phenolic resin also increased. These longer periods led to some pro-curing in the phenolic structure and made the mixture more viscous. Due to the difficulty in stirring the more viscous mixture, very small air bubbles were introduced into the mixture. Although many of these bubbles might have left the system from the surface, yet, some of them, especially those located at the bottom could not escape. As a result, these tiny voids at the bottom surface made the specimen more brittle by acting as stress raisers or cracks. Figure 2d also shows that the use of amino silane together with nitrile rubber increased Charpy impact strength of the neat phenolic specimen (P) significantly. This synergistic increase in rubber toughening was as much as 46 and 63 % in the specimens PRS1 and PRS2, respectively.

Figure 2e indicates that fracture toughness test results are very well correlated with the Charpy impact test results. When the neat phenolic specimen (P) was modified with nitrile rubber, its fracture toughness increased by 20, 13, and 8 % in the specimens PR0.5, PR1, and PR2, respectively. Again, increasing rubber content decreased the improvement due to the specimen production difficulties discussed earlier. Figure 2e also indicates that rubber toughening is more effective when nitrile rubber was used together with amino silane. In this synergistic case, fracture toughness of the neat phenolic specimen (P) increased by 38, 50 and 36 % in the specimens PRS1, PRS2, and PRS4, respectively.

Toughness improvement via rubber toughening was achieved by the formation of rubber domains and silane domains, which delayed and/or decreased the growth rate of main and secondary cracks propagating in the stiff but brittle phenolic matrix. Thus, phenolic resins were toughened by several energy absorption mechanisms.

Fracture surfaces obtained from flexural and fracture toughness test specimens were examined by scanning electron microscopy (Fig. 3). Fractographic studies were especially useful in determining possible rubber toughening mechanisms and distribution and interaction of rubber domains with the phenolic matrix.

Low magnification fractographs indicate that nitrile rubber domains formed in the phenolic matrix were generally uniformly distributed (Fig. 3a). They also indicate that increasing the rubber content not only increased the number of the rubber domains, but also the amount of deformation lines and the level of fracture surface roughness. Furthermore, higher magnification shows that these nitrile rubber domains have round shapes with a diameter around 10 mm (Fig. 3b), and there is a good interface between the rubber domains and the phenolic matrix with no debonding (Fig. 3c).

Due to the high viscosity and stirring difficulties mentioned before, when the rubber content was high (e.g., PR3 specimen) all the rubber particles were not dissolved in the liquid phenolic matrix. In this case, some rubber particles remained as solid particles in the crosslinked phenolic structure (Fig. 3d). Since rubber particles are not as effective as rubber domains, PR3 specimens had lower mechanical properties.

Figure 3e shows that domains of amino silanes formed in the phenolic matrix are similar to the nitrile rubber domains, but they are more spherical and have a lighter colour. To differentiate amino silane domains from the nitrile rubber domains, EDX analysis was also carried out.

Figure 3f reflects domains of both nitrile rubber and amino silane together, which resulted in synergistic improvement in rubber toughening of the brittle phenolic structure. All the fractographs indicated that the main rubber toughening mechanism was shear yielding observed as deformation lines, especially initiated at the domains of nitrile rubber and amino silane.

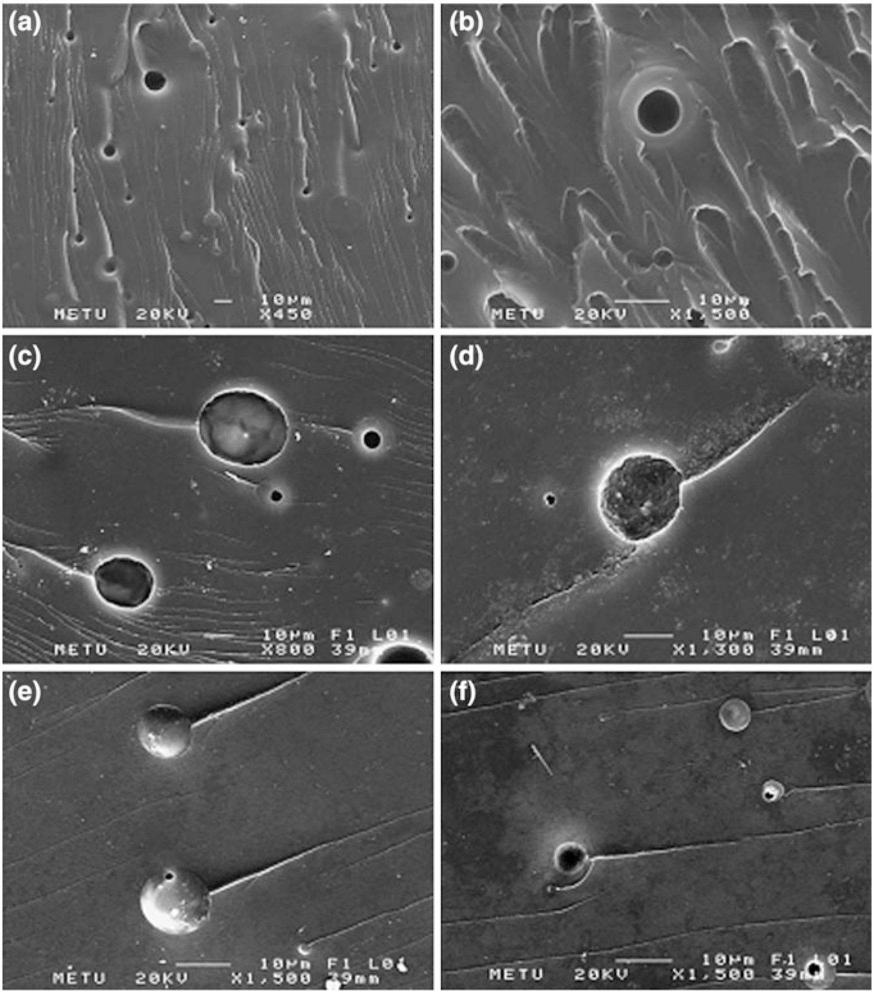


Fig. 3 Sem fractographs of the specimen fracture surfaces: **a** uniform distribution of the nitrile rubber domains, **b** round shaped nitrile rubber domains and deformation lines, **c** proper interface between nitrile rubber domains and phenolic matrix, **d** undissolved nitrile rubber particles left in the matrix, **e** amino silane domains, **f** domains of both nitrile rubber and amino silane [29]

Dynamic mechanical analysis over a temperature range of 25–250 °C was done in order to obtain storage modulus (E_0) and glass transition temperature (T_g), and the results are shown in Fig. 4.

Figure 4b shows that Tg (peaks of tan d curves) of neat phenolic specimen (P) increased slightly when modified by nitrile rubber particles alone or together with amino silane. This might be due to certain interactions between the phenolic matrix and domains of nitrile rubber and amino silane. As shown in Fig. 4c, storage modulus values (at 50 °C) of neat phenolic specimens (P) increasd slightly

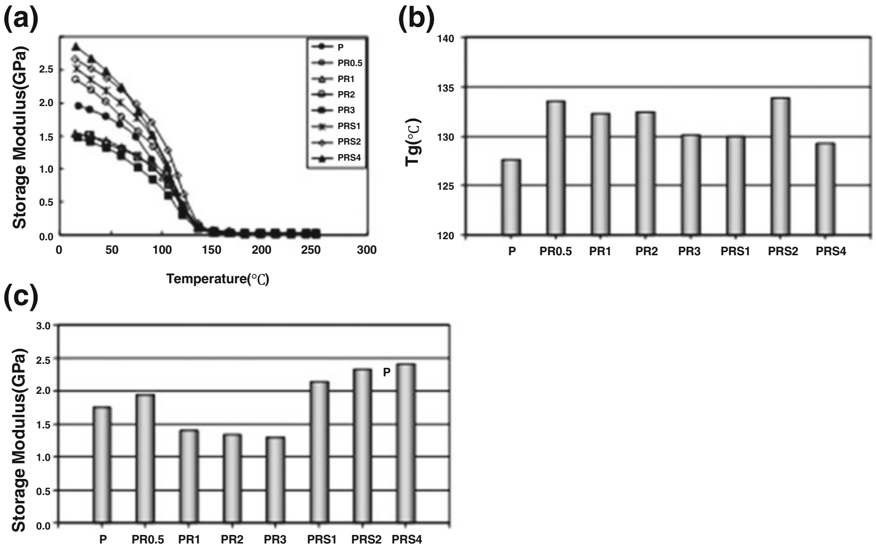


Fig. 4 DMA results of the specimens: **a** storage modulus versus temperature curves, **b** glass transition temperature values (tan d Peaks), **c** storage modulus values (at 50 °C) [29]

when modified with very low amount of nitrile rubber (PR0.5). Higher rubber contents decreasd the modulus value, possibly due to the specimen production difficulties discussed before. However, when the neat phenolic specimen was modified with nitrile rubber and amino silane together, significant increase in the storage modulus values was obtained.

From this elaborate case study it can well be concluded that a seemingly difficult development becomes easy if the underlying scientific principles can be deciphered and explained. Resol-type phenol–formaldehyde resin can be toughened by a judicious choice of nitrile rubber along with the use of an aminosilane.

2.1.2 Effect of Elastomeric Nanoparticles on Properties of Phenolic Resin

Ma et al. [28] reported the use of elastomeric nanoparticles (ENP) to modify the impact strength of phenolic resins (PR) and achieved the simultaneous modification of flexural strength and heat resistance. They used two sets of blends in their studies, namely, PR/nitrile butadiene elastomeric nanoparticle (NBENP) composite and PR/carboxylic nitrile butadiene elastomeric nanoparticle (CNBENP) composite. The elastomeric nanoparticles (ENP) studied were special ultra-fine full vulcanized powdered rubbers, prepared by a special irradiation technique [30, 31].

The ENP were uniformly dispersed in phenolic matrix (Fig. 5) with a diameter of about 100 nm. The size of dispersion phase was much smaller than that of

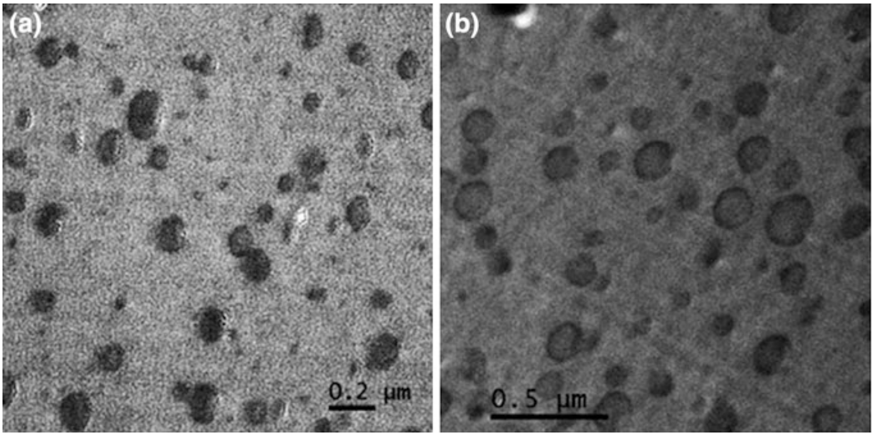


Fig. 5 TEM photographs of (**a**) PRC5 wt% NBENP and (**b**) PRC5 wt% CNBENP blends [28]

conventional rubbers [32]. The positive outcome of such class of composites are their high toughening effect, low addition amount (less than 5 wt%) and simple addition process. ENPs have already found application in PR industry [33].

However, the problem of aggregation was encountered when the rubber concentration mounted above 5 weight percent. The new type of PR composite modified by ENP exhibited large interface because of the large specific surface area of nanoparticles. Furthermore, it was also found that the uniform dispersion of rubbers can be ensured by adequate blending time and appropriate addition amount.

SEM photographs of impact fracture surface of ENP modified PR are shown in Fig. 6.

It was observed that the average distance between microcracks was over 5 mm on the fracture surface of pure phenolic network, as shown in Fig. 6a, b; however, the average distance between microcracks initiated by ENP wasonly about 0.5 mm on the fracture surface of PR/ENP blends, as shown in Fig. 6c, d. Therefore, there were much more microcracks on the fracture surface of PR/ENP blends than that on the fracture surface of pure phenolic network due to smaller distance between microcracks. It is well known that plastic deformation of the matrix is limited in thermoset plastics with high crosslink density and microcrack is a main toughening mechanism [34, 35]. The amount of microcracks, initiated by rubber particles, depends on the particle size of rubber in PR/rubber composite if same amount of rubber is used; therefore, it is explanatory that the ENP toughened PR system, where rubber particles are nanostructured (about 100 nm), has much more microcracks and much higher impact strength than the conventional rubber toughened PR system.

The reaction between PR and ENP was supported through FTIR studies which are shown in Fig. 7.

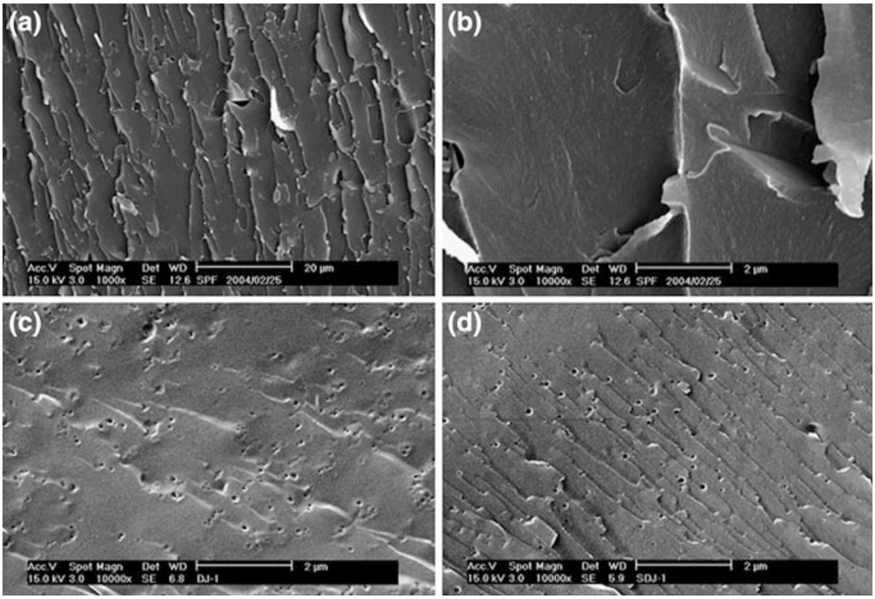


Fig. 6 SEM photographs of fracture surface of toughened phenolic network (**a**) and (**b**) un-toughened; **c** 5 wt% NBENP toughened; **d** 5 wt% CNBENP toughened [28]

The characteristic peaks of phenolic hydroxyl group were changed after melt blending. Before melt blending, the stretching vibration of hydroxyl group showed a broad peak at 3,352 cm^{-1} (hydrogen bond) with a shoulder peak at 3,490 cm^{-1} (free hydroxyl group). After melt blending, only one symmetric peak at

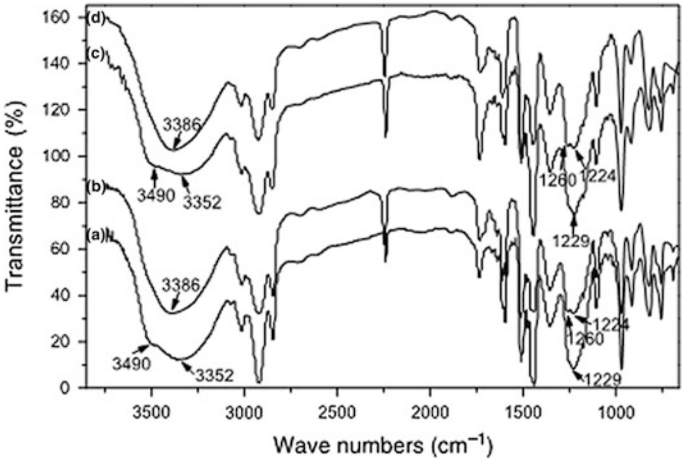


Fig. 7 FTIR spectra of: *a* NBENP/PR and *c* CNBENP/PR before melt blending; *b* NBENP/PR and *d* CNBENP/PR after melt blending [28]

3,394 cm^{-1} was noticeable, which indicated that some hydrogen bonds were broken by ENP. Moreover, the peak at 1,230 cm^{-1}, which is attributed to stretching vibration of phenolic C–OH, splited and shifted to higher wave numbers after melt blending, which shows the influence of ENP on some phenolic hydroxyl groups. Since the hydrogen atoms at ortho or para position of phenolic hydroxyl group are very active, they are subject to substitution by some active functional groups on ENP surface during melt blending. As a result of substituent reaction, crosslinked ENP, acting as a large substituent group, was introduced onto the benzene ring of PR. Therefore, the induction effect of large substituent groups causeed a shift of peak at 1,230 cm^{-1} to higher wave numbers.

Since only active groups on rubber surface can react with PR so other weak changes were not observed in the FTIR spectra.

However, FTIR analysis conclusively indicated chemical reaction between rubbers and PR during melt blending of the components as a result of which enhancement of interfacial adhesion between ENP and PR took place.

2.2 Rubber-Epoxy Blends

One of the most important classes of thermosetting polymers is the epoxy resins as their applications can cover a wide spectrum. They are extensively used in various fields of coating, high performance adhesives and engineering applications. Cured epoxy polymers are characterized by high chemical and corrosion resistance simultaneously having good mechanical and thermal properties. Epoxy resins are reactive monomers, which are commonly cured with amine to form thermosetting polymers. When cured with an aromatic amine of sufficient functionality, it results in a highly cross-linked network with relatively high stiffness, glass transition temperature (Tg) and chemical resistance. However, the inherent toughness of tightly cross-linked polymer networks is relatively low. It is therefore desirable to enhance toughness without adversely affecting the other useful properties of the polymer. Aside from inorganic reinforcement, elastomer modification is one of the most frequently used methods of toughening rigid network polymers [36–39]. The principle mechanism of rubber toughening for network polymers is thought [36, 37, 39] to be the enhancement of shear yielding at the crack tip through a change in stress state in the region around a rubber particle. Stress fields around the particles must overlap to bring about optimal shear banding. For determining the toughness of the blended and processed material the particle diameter and inter-particle spacing are important.

The most common methods of rubber toughening are by the use of liquid rubbers or preformed rubber particles. In the former method, the rubber is initially dissolved into the epoxy resin [40, 41], but during cure the rubber phase separates as a discrete particulate phase. Studies [42–45] show that the phase separation process is a result of the decrease in configurational entropy due to the increase in molecular weight as the epoxy cures. As a consequence the free energy of mixing changes, leading to a decrease in the solubility of the rubber. This is then the driving force for phase separation. Thus the functionality of the matrix monomers, which control the development of the network and the cross-link density of the epoxy matrix, has an effect on the phase precipitation process. The particle size and concentration of the precipitated rubber also depends on the curing process and the interaction between the rubber and the epoxy resin.

With butadiene-based rubbers the solubility may be increased by forming a copolymer with the more polar acrylonitrile monomer. Another way to modify the liquid rubber is to alter their interaction with the matrix by functionalising the chain ends with carboxyl, amine or epoxide groups that may couple with the reacting matrix [39, 43, 46]. The mechanism of reinforcement has been discussed in the introductory part along with some reiteration in this section.

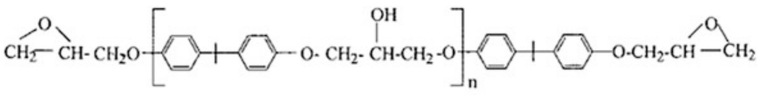
2.2.1 Epoxy Toughening by Liquid Rubber

It is well over 40 years since rubber toughened epoxy was first patented. McGarry and Willner [47] reported the use of low molecular weight carboxyl terminated copolymer of butadiene and acrylonitrile as the liquid rubber in their effort to toughen the epoxide. Various diglycidyl ether of bisphenol A (DGBEA) epoxides were cured with piperidine (PIP) and CTBN as the toughening agent. Since then much efforts have been put by various researchers to decipher the morphology development during curing, morphology and fracture property relationship and the mechanism of toughening. These researches also paved the way to various new types of toughening agents as potential replacements for CTBN.

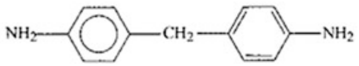
A comprehensive idea of rubber toughened epoxy is somewhat difficult to write in a nutshell because of complications arising out of several factors. Literature study reveals the use of different types of curing agents (amines, anhydrides) and a spectrum within each type. The target of these researches was of course the same, i.e., to improve the resistance to mechanical and thermal shocks. The modified epoxy resins were characterized with respect to their fracture behaviour and adhesive bond strengths. The frequently conducted tests were peel strength, resistance to peel force, resistance to crack propagation, fracture toughness, impact strength and critical strain energy rate. Usually difunctional epoxy resins were used for experimentation. The chemical structures of a typical epoxy resin (DGBEA) and some of the more important amine curing agents are shown in Fig. 8 [48].

2.2.2 Chemistry

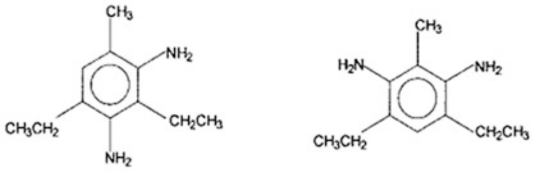
The liquid rubber should have to be chemically bonded to the epoxy matrix to bring about effective toughening [49, 50]. If there is weak bonding then failure of the toughened system may take place through debonding of the particles. Free



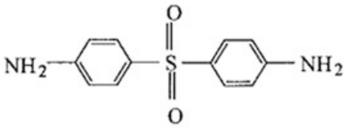
Diglycidyl ether of bis phenol-A (DGEBA)



Diamino diphenyl methane (DDM)



Diethyl toluene diamine (DETDA)



Diamino diphenyl sulfone (DDS)

$NH_2-C_2H_4-NH-C_2H_4-NH-C_2H_4-NH_2$

Fig. 8 Chemical structure of epoxy and amine curing system [48]

liquid rubber is also undesirable because the collection of these molecules at the metal interface will create weak boundary layers, thus decreasing the joint strength [51, 52]. Sibert and Riew [53] proposed the formation an epoxy-CTBN-epoxy adduct which is chain extended and crosslinked with more epoxy resin. The dispersed rubber phase and the resin matrix are chemically bonded through the progression. PIP is a selective catalyst for carboxyl-epoxy reaction. However, most of the curing agents favour epoxy-amine reactions suppressing the epoxy-carboxyl one. The problem has been resolved [54, 55] by precipitating the liquid rubber and the epoxy resin in an alkyl hydroxyl esterification reaction in presence of triphenyl phosphene catalyst. The acid adducts so formed can then be cured with any curing agent as they contain only epoxy groups similar to the epoxy resins. The reaction scheme is furnished in Fig. 9.

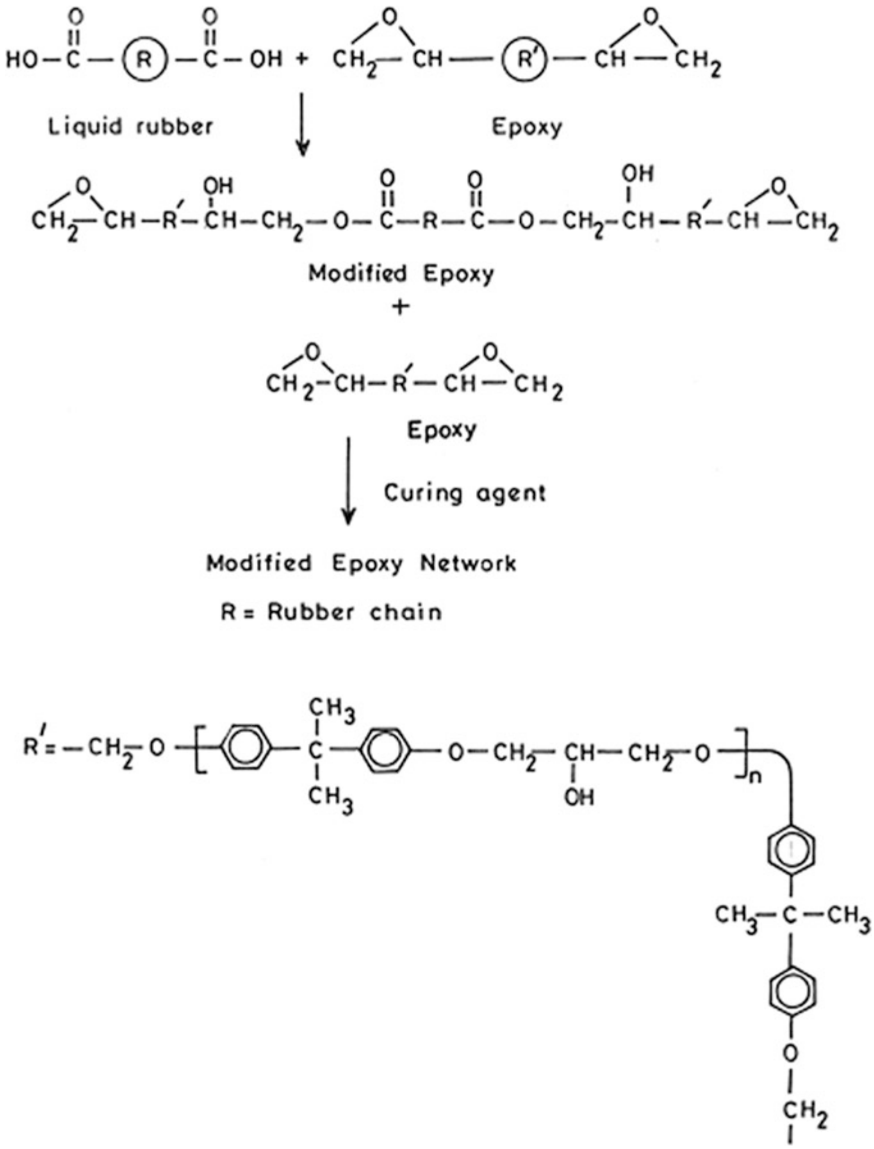


Fig. 9 Prereaction of liquid rubber with epoxy [48]

2.2.3 Thermodynamic Consideration

There should be thermodynamic compatibility between the liquid rubber and the epoxy resin before curing at the curing temperature [56]. Thus, the change in Gibb's free energy should have to be negative [56, 57].

$$(\Delta G_m)_{P,T} < 0 \tag{1}$$

The combined Flory-Huggin's equation and the Hildebrand equation give the expression of the free energy of mixing as follows:

$$(\Delta G_m)/V = \phi_e \phi_r (\delta_e - \delta_r) + RT\left(\frac{\phi_e}{V_e} \cdot \ln \phi_e + \frac{\phi_r}{V_r} \cdot \ln \phi_r\right) \tag{2}$$

where ϕ_e, ϕ_r are the volume fractions, δ_e, δ_r are the solubility parameters and V_e and V_r are the molar volumes of the epoxy resin and the rubber respectively. The second term of the right hand side of the equation is always negative since both ϕ_e and ϕ_r is a fraction.

For a fixed rubber/epoxy weight composition, negative free energy change is favoured if the value of V_r is low and simultaneously the values of δ_e and δ_r are quite close. This means that the rubber should have low molecular weight and the solubility parameter values of the rubber and the epoxy resin should be close. If these two parameters are controlled and ΔG_m is slightly negative the rubber will be compatible with the epoxy matrix. However, as the curing advances on the time scale, both V_e and V_r increase due to increase in molecular weight of rubber as well as the epoxy resin. With this advancement a time comes when the free energy just becomes positive and the rubber starts to phase separate out at the cloud point.

Hence the phase separation process is explained [58–60] and is pictorially shown in Fig. 10.

An initially homogeneous monophasic phase ($p = 0$) passes through a cloud point conversion (p_{cp}) and the final morphology is arrested at gelation (p_{gel}) [61, 62]. Actually due to manifold increase in viscosity of the reacting system, the final morphology is arrested well before gelation. However, there are reports of changes in phase composition even after gelation [58, 63]. For complete phase separation, the phase separation time should necessarily be greater than the time required for the diffusion of rubber particles from the epoxy matrix and here the role of temperature

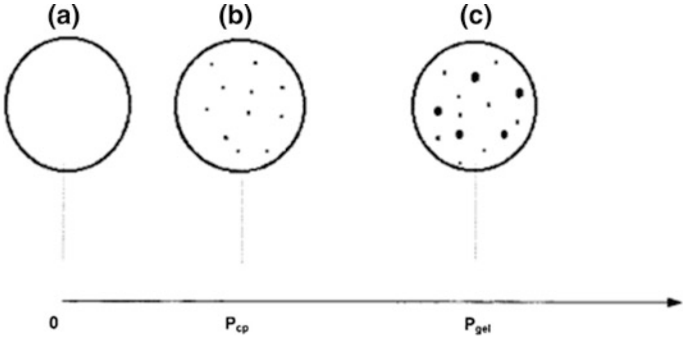


Fig. 10 Phase separation of rubber in a typical epoxy matrix: **a** homogeneous solution at the start of the reaction ($p = 0$), **b** phase separation at cloud point conversion (p_{cp}), **c** morphology at gelation (p_{gel}) [48]

becomes important. The initial cure temperature greatly affects the resulting morphology but post curing temperature does not because phase separation is arrested at gelation.

CTBN with higher acrylonitrile content is shown to have greater compatibility with epoxy matrix and undergoes phase separation at a much advanced curing state [64, 65]. With acrylonitrile content above 30 % no phase separation occurs resulting in a single phase morphology.

The morphology for rubber modified epoxy system is a discrete one as reported by many authors and consists of spherical particles of the rubber dispersed in the epoxy matrix [64–66]. A model was developed by William et al. [67] to calculate the fraction, composition and average particle diameter of the dispersed phase formed during the thermoset polymerisation based on the principle of nucleation, coalescence and growth. The thermodynamic consideration as discussed above was applied in their approach to predict the same. The morphological variation with cure temperature as was observed experimentally was presumably a result of the effect of temperature on the rate of nucleation and subsequent growth of the dispersed rubbery phase [67–70]. Increase in cure temperature also increase rate of epoxy reaction with a decrease in the viscosity of the system. Since the activation energy of curing reaction is higher than that for prepolymer viscosity, the rate of reaction increases more than the rate of diffusion with an increase in the growth of rubber particles. However for a significant increase in temperature the situation may be different [71, 72]. Here, ΔG_m may attain such a high value that no phase separation takes place making the system completely miscible. Another possible explanation may be that the demixed particles cannot attain larger size due to the high system viscosity arising as a result of high levels of conversion. Therefore, the plot of average particle diameter versus temperature goes through a maximum as has been experimentally observed [70].

Some other authors stressed upon a spinodal decomposition as the origin of phase separation assigned to textures exhibiting a cocotinuous structure. Yamanaka et al. [73, 74] and Kims ruled out the possibility of the nucleation-growth mechanism based on the fact that nucleation is supposed to be a very slow process. They argued that the spherical domain structures evolved from an initial cocontinuous structure although they were incapable of producing direct evidence of this model.

2.2.4 Liquid Rubbers Other than CTBN

From the foregoing discussion, it is generalized that it is the presence of rubbery particles that toughens the epoxy matrix and it is not mandatory that the particles be necessarily made up of CTBN. Other kinds of nitrile rubbers having some other end groups like amine, mercaptan and hydroxyl have also been studied [75]. However it is the carboxyl-terminated acrylonitrile (CTBN) gives the best performance [76]. The presence of the carboxyl group in CTBN provides better adhesive strength with the substrate in CTBN modified epoxy.

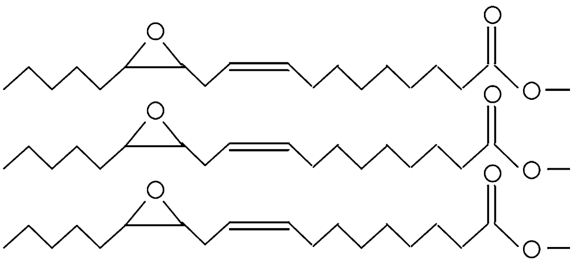


Fig. 11 Chemical structure of vernonia (epoxy group containing triglyceride) oil

Significant enhancement in toughness can be brought about by using poly(methyl methacrylate) (PMMA) grafted natural rubber in place of CTBN as has been reported by Rezaiford et al. [77] Carboxyl terminated polyisobutylene [78] and polysulphide [79] rubbers are also reported as effective toughening agents for DGEBA resin using different types of amine hardener. Mizutani [80] has reported the use of hydroxyl terminated liquid polychloroprene rubber as a toughening agent containing up to a maximum of 10 volume percent of this liquid rubber, completely phase separated. However, due to similar refractive index with the epoxy, the modified networks are transparent.

Epoxy group containing modified triglyceride oils have been tried as modifiers of epoxy resin. Amongst these, the use of vernonia oil, epoxidised soybean oil and castor oil are reported in the literature [81, 82]. Figure 11 shows the structure of vernoria oil which is a plant product. Vernonia oil is extracted from the seeds of Vernonia galamensis (ironweed), a plant native to eastern Africa. The seeds contain about 40–42 % oil of which 73–80 % is vernolic acid. Products that can be made from vernonia oil include epoxies for manufacturing adhesives, varnishes and paints, and industrial coatings. Its low viscosity recommends its use as a nonvolatile solvent and thus it is eco-friendly.

If the epoxidised oil is directly mixed with the resin then it results in a two-phase microstructure with a plasticizing effect. Two-phase microstructure was however also observed when the prepolymer of epoxidised soybean oil (ESO) and amine hardener was used instead of pure ESO. Since the prepolymer has a high molecular weight, so compatibility with the epoxy matrix is reduced resulting in phase separation. The effect of ESO content on impact properties of modified epoxy network was studied by Ratna et al. [83] Both one stage and two stage routes were studied and the impact strengths were reported. It was found that impact strength increased as a function of modifier in both the cases, but it was more significant in the two stage process. This is illustrated in Fig. 12. It is evident from the figure that at 20 phr concentration of the toughener in the two stage process the maximum impact strength was obtained. Above 30 phr, phase inversion occurs [82, 83].

A novel route has been tried by Kim, Moon and Boonkerd to synthesise and couple poly(butadiene) with ESO. Butadiene monomer was reacted in a high pressure glass reactor in a solvent (hexane) and modifier (tetrahydrofuran) purged with nitrogen gas. The temperature was maintained at 30 °C and n-butyllithium initiator was injected into the system. After the temperature was stabilised, ESO

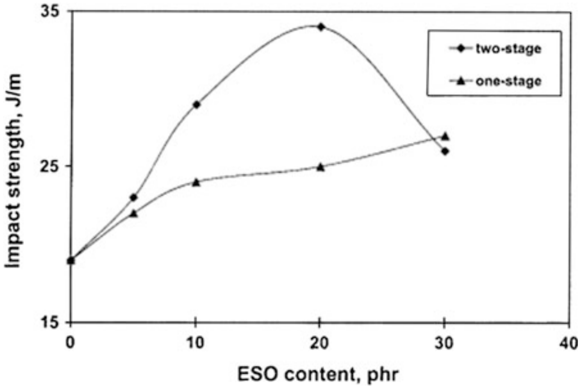


Fig. 12 Effect of ESO content on impact strength of toughened epoxy network [83]

was injected into the reaction system. The reaction was terminated by methanol containing BTH as the antioxidant. Precipitation of the product using excess of methanol followed by removal of unreacted ESO by acetone was done to get the pure product. Finally drying was done using a vacuum oven to remove the excess of acetone. The reaction variables were the temperature and catalyst concentration. Molecular weight distribution was determined using gel permeation chromatography (GPC). This product can be tried as an alternative for CTBN to improve the impact resistance of epoxy thermosets. The reaction scheme is shown in Fig. 13.

2.2.5 Saturated Liquid Rubbers

The outstanding modification in the fracture properties of epoxy resins exhibited with the toughening by liquid rubber like carboxyl terminated copolymer of acrylonitrile butadiene (CTBN) in the field of technology and engineering of adhesives [84] is not altogether an unmixed blessing. Since the butadiene component of the elastomer contains unsaturation, it is a site for premature thermal and/or oxidative stability. Thus, even such modified resins are not suitable for application at high temperature [85]. Excessive crosslinking may take place with time which would detract from otherwise improvements brought about in their structures. Another problem encountered is related to some unreacted acrylonitrile remaining in the system which may be carcinogenic [86]. These are the reasons which asked for an alternative to CTBN and considerable efforts have been made to come up with potential substitutes.

Siloxane rubbers were thought to be attractive in this direction because of some of the more important features like high chain flexibility, very low glass transition temperature ($T_g \sim -100$ °C) low surface tension and surface energy along with hydrophobic nature which are rewarding properties for toughening. However, poly (dimethyl siloxane) oligomer cannot be used as such, because it is extremely

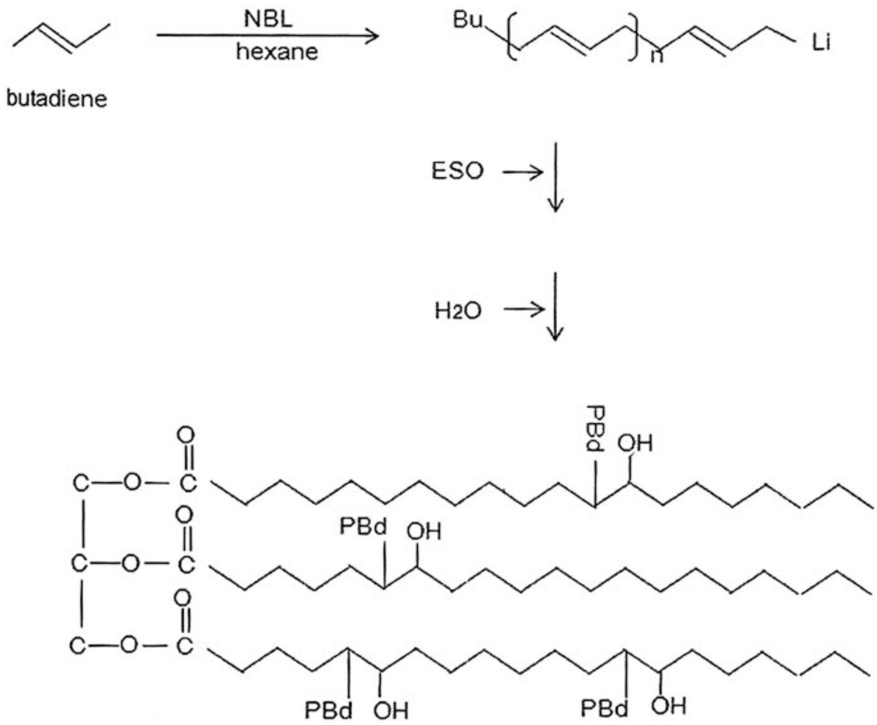


Fig. 13 Coupling reaction of polybutadiene with ESO

incompatible with epoxy. The compatibility is increased by copolymerizing dimethyl siloxane with diphenyl siloxane or dimethyl fluoropropylsiloxane [87]. Such a copolymer having controlled structure can be used as a toughening agent [87–89]. Riffele et al. [90, 91] developed an epoxy-terminated siloxane oligomer and it was successfully used to toughen epoxy resin. The epoxy-terminated oligomer was reacted with piperazine to produce secondary amine group end capped oligomer which has been used as toughening agent. Silicone-epoxy block copolymers have also been reported [92] as toughening agent for epoxy. Laurienzo et al. [93] have modified epoxy resin by hydroxyl terminated block copolymers of poly(dimethylsiloxane) (PDMS) and polyoxyethylene (PDMS-co-POE) elastomer and functionalized saturated polybutene. Oxidative stability of these networks showed improvement but the mechanical properties were inferior to CTBN.

Polyepichlorohydrin (PECH) has been successfully incorporated [94] as toughening agent. The degree of toughening was somewhat proportional to the molecular weight of PECH, It was found that matrix properties like Tg, modulus and hot/wet properties were comparable with CTBN.

Many other polymers were tried and some of the more important ones with their roles are stated in the following discussion. Carboxyl terminated poly(propylene glycol) was developed for an ambient temperature curing of epoxy adhesives [95]. Recently polyurethane (PU) elastomer has been investigated as a modifier by Wang et al. [96]. They developed hydroxyl, amine and anhydride terminated PU prepolymer and found that the hydroxyl terminated oligomers at 20 wt% gave the best result with a fivefold increase in fracture energy over the unmodified epoxy.

Many other modifiers have been used in systems where the curing system is not a diamine one. Laeuger et al. [97] have reported the toughening of anhydride cured DGEBA resin using diol and bis(4-hydroxy benzoate) terminated poly(tetrahydrofuran) liquid rubber. In their work they have supported the morphology development via spinodal decomposition. The bis(4-hydroxy benzoate) terminated poly(tetrahydrofuran) gives better performance over the diol terminated one as far as the mechanical and the fracture properties are concerned. Wang et al. have synthesized polyfunctional poly(n-butyl acrylates) (containing epoxy and carboxyl groups) by photo polymerization, and used it as a modifier to toughen epoxy resin cured with diamino diphenyl methane (DDM). The concept of optimum functionality to get maximum impact resistance epoxy and carboxyl functionalized and epoxy functionalized liquid rubber modified systems was introduced in the work. Similar results were obtained by Lee and coworkers [98] using n-butyl acrylate/acrylic acid copolymers. They reported improvement of adhesion strength in a DGEBA epoxy matrix and showed that an optimum functionality existed to impart the highest interfacial tension.

A new class of reactive dendritic hyperbranched polymers (HBPs) has been used as liquid rubbers as a modifier for epoxy resin [99–105]. HBPs offer much lower prepolymer viscosity owing to their spherical structure. They also provide better internal bonding and stronger adhesion with the matrix due to the presence of highly dense surface functional groups.

2.2.6 Toughening by Preformed Particles

Preformed, insoluble particles are often directly used in place of liquid rubbers as toughening agents for the epoxy matrix. This is to minimize some of the difficulties encountered while using liquid rubbers as such [106–109]. The phase separation, in case of liquid rubber toughening depends upon the formulation, processing and curing conditions. Incomplete phase separation lowers the glass transition temperature (T_g) significantly. Moreover, the difficulty in controlling the rubber phase which separates during curing may result in uneven particle size. The differences in morphology and also the volume of the separated phase affect the mechanical properties of the product. It is very difficult to study the effect of individual parameter such as morphology, particle size and composition as they are independent.

In case of preformed particle, the size, morphology and composition, shell thickness and crosslink density of the rubbery core can be controlled separately by employing emulsion polymerization and so the effects of various parameters on the toughening of the epoxies can be investigated [110–114]. Interfacial architecture can be controlled by changing the following parameters: (1) shell thickness which depends on the ratio of core–shell material and the mechanism of polymerization; (2) chemical bonding and physical interaction between particles and matrix enhanced by the introduction of functional groups on the surface of the shells; (3) grafting between the shell and the core and (4) molecular weight of the shell material. Core shell, occluded and multilayer morphologies of the composite material can be obtained by controlling the emulsion polymerization [115–117]. The incorporation of the preformed rubber particles in epoxy matrix is enhanced through mechanical mixing. Dispersibility can be increased either by introducing crosslinks into the shell or by using comonomer like acrylonitrile or glycidyl metacrylate (GMA) which increase the interfacial adhesion by polar or chemical interactions [118, 119].

2.2.7 Some Miscellaneous Studies with Rubber-Epoxy Blends

Jansen et al. [120] reported the preparation of thermoset rubbery epoxy particles as novel toughening modifiers for glassy epoxy resins. Two types of liquid epoxy resin with an aromatic backbone were used in this work; a diglycidyl ether of bisphenol A (DGEBA) and a diglycidyl ether of bisphenol F (DGEBF). The aliphatic epoxy resin was diglycidyl ether of polypropyleneoxide (DGEPPO). They showed that curing of water dispersed droplets of an aromatic or aliphatic epoxy resin, respectively, produces glassy or rubbery thermosetting epoxy spheres which can be prepared in a relatively easy way. The rubbery epoxy particles can successfully be applied as a toughening agent for glassy epoxy matrices. The advantage of these preformed modifiers is the control over the final morphology as the size and concentration of the dispersed rubber phase can be chosen independently. The improvement in fracture toughness and the morphological features of the fractured surfaces are identical to standard. The use of this new class of rubber modifiers can be used to produce impact modified composites with predetermined particle size and rubber content. The authors claimed this study to be the first attempt to prepare preformed rubbery aliphatic epoxy particles in dispersion and to apply these particles as toughening agents for glassy aromatic epoxy matrices.

Boyonton and Lee [121] in their work used a synergistic combination of a liquid carboxyl-terminated butadiene acrylonitrile rubber and solid rubber particles of different sizes, the latter obtained from recycled automobile tires. They found no significant improvement in the fracture toughness of the composite when used with solid rubber alone. However, when used in combination with the liquid rubber modifier, it was observed that the fracture toughness of these hybrid epoxies was higher than that of those toughened with liquid rubber alone. This synergistic effect is explained in terms of crack deflection and localized shear yielding. Furthermore, they observed a slight improvement in the fracture toughness as the size of the solid rubber particles increased. Although using a combination of both reactive liquid rubber and solid rubber particles as toughening agents had been investigated previously, here, the solid rubber particles used were from recycled rubber tires. Therefore this work demonstrated an application of producing high quality engineering epoxy systems using toughening modifiers that are relatively low in cost and created higher-value products for recycled solid rubber.

A very similar work has been reported by Bagheri et al. [122] The objective of the research was to investigate the feasibility of using surface treated recycled rubber particles for toughening of epoxy polymers. The particles were obtained through grinding of scrap tires followed by oxidizing the surface of the particles in a reactive gas atmosphere. Surface treated recycled rubber particles with a nominal particle size of approximately 75 μm and a commonly used reactive liquid elastomer, CTBN, was incorporated in a DGEBA epoxy resin. Microscopic studies reveals that, when used alone, recycled rubber particles simply act as large stress concentrators and modestly contribute to toughening via crack deflection and microcracking. In the presence of micron size CTBN particles, which cavitate and induce massive shear yielding in the matrix, however, the recycled particles "stretch" the plastic deformation to distances far from the crack tip. This mechanism cause plastic zone branching and provides an unexpectedly high fracture toughness value. This study, therefore, provides a practical approach for manufacturing engineering polymer blends utilizing the surface modified recycled rubber particles.

2.3 Rubber Toughening of Cyanate Esters

Cyanate ester (CE) monomers undergo polycyclotrimerization to form trifunctional triazine rings, which exhibit excellent dielectrical, thermal and adhesive properties [123]. Consequently, CE resins are currently important thermosetting materials for the encapsulation of electronic devices, high-temperature adhesives and structural aerospace materials. However, low toughness is a major drawback with most crosslinked thermosetting materials, including CE resins. Although a cured cyanate resin has a relatively higher toughness than a cured bismaleimide (BMI) or a cured epoxy resin, it still requires suitable modification to improve toughness without reducing the intrinsic physical strength for structural applications [124]. Accordingly, a number of studies were carried out to improve the toughness of cyanate resin, such as the preparation of flexibilised cyanate resins, the incorporation of monocyanates, the utilization of rubber-toughening technologies, the use of organoclay toughening, and the preparation of semi-interpenetrating networks [124]. Among them, using carboxyl-terminated butadiene-acrylonitrile rubber (CTBN) and other similar functionalized liquid nitrile rubber was proven to be one of the most successful techniques [125–132]. For example, Hillermeier et al. [126] used epoxy-terminated butadiene-acrylonitrile rubber (ETBN), and Hayes and Seferis [127] used CTBN and amine-terminated butadiene-acrylonitrile rubber (ATBN). It was found that incorporation of all of these terminal-functionalized liquid butadieneacrylonitrile rubber provided increased toughness over CE resin. Of the various types of functional groups investigated, carboxylic acid end-groups proved to be most effective [133]. CTBN greatly improves the impact strength of CE resins, but reduces the tensile strength and modulus of CE resins due to its rubbery characteristic. In comparison, Liang et al. [134] found that epoxy resin (EP) could improve the toughness of CE without significant sacrifice of tensile strength or modulus.

Feng et al. [135] used, epoxy resin (EP), which could react with both the cyanate group of cyanate ester (CE) and the carboxyl group of carboxyl-terminated butadiene-acrylonitrile rubber (CTBN). This EP was used together with CTBN as a synergistic toughening component. Its effect on the thermostability of the blends was also evaluated. They found that the addition of an appropriate amount of EP to CE/CTBN improved the mechanical properties and thermostability of the resulting blends. This is attributed to the decrease in the mobility and increase in the stability of CTBN caused by the reaction between CTBN and EP via terminal carboxyl (–COOH) and hydroxyl (–OH) groups. However, very high EP concentration decreases the crosslinking density of CE, consequently reducing the mechanical properties and thermostability of the blends.

3 Concluding Remarks

Brittle thermoset materials can be toughened successfully by blending with proper liquid rubbers in small amounts or by incorporating preformed rubber particles directly. Both of the mentioned methods are in vogue and the choice of using one depends on the feasibility of a system of thermoset. The phase separation, in case of liquid rubber toughening depends upon the formulation, processing and curing conditions and incomplete phase separation may occur resulting in unwanted lowering of glass transition temperature. Difficulty in controlling the rubber phase which separates during curing may result in uneven particle size. It is very difficult to study the effect of individual parameter such as morphology, particle size and composition as they are independent. In case of preformed rubber particles, these difficulties are not encountered and the resulting morphology can be better controlled. However, the problem of proper dispersion of these particles in the themoset resin limits the use of this method. The improvement in fracture resistance occurs in either case due to dissipation of mechanical energy by cavitation of rubber particles followed by shear yielding of the matrix. The toughenability increases with increase in inherent ductility of the matrix. Rubber particle size plays an important role in the direction of toughening and very small or very large sizes are undesirable. The phase separation in case of liquid rubber is based upon nucleation and growth. However, some researchers opposed this theory on the fact that nucleation is a very slow process. They stressed upon spinodal decomposition as the origin of phase separation assigned to textures exhibiting a cocotinuous structure although they were incapable of producing direct evidence of this model.

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