Use of epoxidized natural rubber as a toughening agent in plastics

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ABSTRACT: At present, the rubber toughening of plastics has become an attractive field of study in polymer science and technology because brittleness is known to be a drawback in many engineering plastics; it can cause premature failure during application. Among existing rubber materials, epoxidized natural rubber (ENR) has been widely used as an impact modifier or toughening agent in a large number of engineering plastics; in particular, it enhances the impact strength, which deteriorates with the incorporation of other additives, such as fillers and flame retardants. ENR is a modification product from natural rubber produced via an epoxidation reaction. ENR also has good chemical resistance. In this review, we aim to provide a concise current status in the field of ENR toughening agents for plastics with a brief discussion of their associated problems and potential applications. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42270.

INTRODUCTION

Improvement in the toughening of polymer composite materials through the incorporation of a rubber phase has become one of the most important issues in the field of polymer science and technology.[1] Polymer composites are stiff because of the highly rigidity chains of the polymer matrix; this leads to brittleness and poor resistance to crack initiation and propagation.[2,3] Brittleness has been a drawback for many engineering materials and can cause premature failure during application.[4] Among the existing methods of achieving toughened composites,[5,6] the incorporation of a rubber phase has been found to be more favorable in imparting a high toughness to rigid polymer composites.[7] Improvements in the toughness and associated elongation at break are due to the presence of rubber particles, which lead to an increase in the dispersion and distribution of the rigid filler inside the polymer matrix.[8] Meanwhile, the surface characteristics of the rigid filler, the chemical nature of the rubber, and the polymer matrix represent the key parameters in the filler–polymer, rubber–polymer and rubber–filler interactions.[9]

Epoxidized natural rubber (ENR) is a material that possesses high toughness properties relative to original natural rubber (NR) with a nominal reduction in the other mechanical and thermal properties because of the presence of epoxy groups on the backbone chains.[10] ENR has high oil-resistance properties

and gas-barrier properties and a high toughness relative to NR; this results from the existence of epoxy groups distributed randomly along the backbone rubber chains.[11] The introduction of ENR particles in a plastic matrix apparently improves the toughness of the resulting plastics; this makes them suitable for application in automotive, aerospace, thermal, and electrical insulating systems.[12] The major products of ENR/plastic blends are in closed mold forms, such as sponges, curing tubes, carpet underlays, connectors, curing flaps, bumpers, heavy duty pads, seals, gaskets, and wheels.[13] Furthermore, ENR blends are also used as pressure-sensitive adhesives, adhesive tapes, packaging tapes, surgical tapes, and plasters.[14] Currently, ENR has been used as a rubber-toughened material in a number of thermoplastic and thermoset composites. The utilization of ENR as a rubber-toughened material in composite materials began with poly(vinyl chloride) (PVC).[15] Subsequently, other thermoplastics and thermosets, including polyamide 6 (PA6), polypropylene (PP), poly(lactic acid) (PLA), and epoxy resin have also been used.[16–19] The use of ENR as a toughening agent or impact modifier in several polymer blends is schematically depicted in Figure 1.

To obtain high impact properties, a rubbery phase should exist within the composite system, in which rubber particulates are dispersed uniformly throughout the matrix phase.[20] The interaction takes place between the functional groups of the components; this, in turn, transfers the load via shear stress from the

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matrix to the rubber particles.[21] Several factors influence the toughening properties; these include the rubber particle size and diameter, type and concentration of rubber, interfacial adhesion between the rubber particles and the matrix, blending method, and processing conditions.[22] Several authors have concluded that the rubber particle size is one of the main factors controlling toughening; tests on blends containing rubber particles with a range of sizes have shown that toughening preferentially depends on the rubber particles.[23] Voids are more likely to form within rubber particles when the stress conditions are highly triaxial, as they are near crack tips, and toughening will not take place before a certain volume strain is reached.[24]

Early studies of rubber toughening in polymers have highlighted a close relationship between the rubber particles and shear modulus; this is explained by differences in the cavitation stresses throughout the matrix body. However, the stress fields surrounding rubber particles hardly affect the mechanical properties of the elastomer.[25,26] The rubber toughening should be governed by the particle volume strain and a balance between the stored volume energy, void surface energy, and the work required to stretch the rubber surrounding the void biaxially.[27] It is also currently accepted that the effect of the rubber phase itself correlates with the matrix ductility and that the rubber's intrinsic properties play an important role in determining the yield conditions in the matrix.[28] Therefore, toughened plastics have been tailored with suitable concentrations of the rubber phase to prepare materials that can withstand a high load or impact. This review is aimed at providing a concise overview of the current status in the use of the ENR rubber phase as a toughening agent in thermoplastic and thermoset polymer materials.

MANUFACTURING OF ENR

NR is a high-molecular-weight polymer with structure of $cis-1,4$-polyisoprene containing unsaturated double bonds in their long rubbery chain. The unsaturated double bond at every five carbon atoms is the functional group of the rubber molecule; it can be transformed into a new copolymer or branching.[29] It has been recognized that NR can be chemically modified into new materials through various reaction routes. Chlorinated, hydrochlorinated, and cyclized NRs have all been produced commercially, and poly(methyl methacrylate)-grafted and depolymerized NR are still available.[30]

ENR is an NR derivative that contains epoxy groups distributed randomly along the NR backbone chains.[31] ENR was first commercialized by a Malaysian company (Kumpulan Guthrie Berhad, currently known as Sime Darby Berhad) in the late 1980s in a joint venture with Malaysian Rubber Producers' Research Association, Tun Abdul Razak Laboratory (United Kingdom), and Rubber Research Institute of Malaysia. ENR is produced through the controlled chemical modification of the NR molecular structure into an epoxidized form, normally with the use of acetic or formic peroxy acids, which are either preformed or generated *in situ* before coagulation and drying.[32] Figure 2 illustrates the production of ENR by the *in situ* peroxy formic acid route. The molar ratio of formic acid to hydrogen peroxide
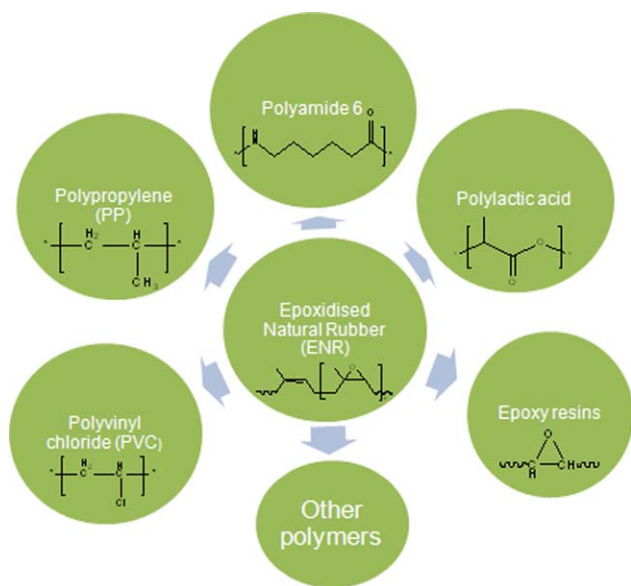
Figure 1. Diagram of ENR with several polymer matrices. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

used is normally around 0.2–0.5, as the former reagent is recycled within the reaction sequence. Epoxidized liquid natural rubber (ELNR) is the liquid form of ENR, which can be produced by epoxidation of LNR with glacial acetic acid and hydrogen peroxide. L-ELNR and H-ELNR, on the other hand, are types of ELNR having low and high molecular weights, respectively. Constant-viscosity standard Malaysian rubber (SMR-CV) is a grade of relatively low and consistent-viscosity rubber offering considerable processing advantages to the consumer. In the production of SMR-CV, viscosity variations due to the transit and storage of the raw NR are repressed chemically so that a much more consistent rubber can be produced.

The level of epoxidation is indicated by the numbers of NR molecules that are transformed into an epoxidized form during the epoxidation process.[31] Commercially produced ENRs that contain 25 and 50 mol % epoxy contents are assigned as ENR-25 and ENR-50, respectively.[33] An increase in the level of epoxidation increases the density, solubility parameter, and glass-transition temperature (T_g) and decreases the refractive index and crystallinity.[34] ENR containing epoxidized-form opened ring structures shows excellent properties, including insolubility, air impermeability, oil and organic solvent resistant, a good wet grip, and high damping characteristics. Its strain crystallization characteristics also lead to superior tensile, fatigue, and impact properties.[35,36] It is noticeable that T_g has a direct relationship with the level of epoxidation of ENR. The increment of 1 mol % epoxy content in NR molecules leads to an increase in T_g of approximately 1°C.[37] It is noticeable that the strain crystallization and the increase in T_g are two factors responsible for the high tensile strength.

ENR AS AN IMPACT MODIFIER IN THERMOPLASTICS

It has been widely accepted that the incorporation of a suitable amount of ENR particulates in polymer blends and composites

is done to gain a higher impact toughness in the resulting materials. Extended chain conformation and rubbery phase morphology produce composite blends with significantly higher load-carrying capabilities.[38] Table I summarizes the effects of the addition of different types of ENR at various contents on the impact toughness properties of several polymer blends.

PVC/ENR Plastic Blends
PVC is one of the earliest polymers to which ENR was added to improve its impact properties. It is recognized that PVC is very brittle at room temperature. Some modifications are thereby required to obtain a modified PVC that can be molded into many products used today; hence, this process enlarges PVC's field of application.[39] The blend of PVC with ENR-50 was reported to produce a miscible blend, which formed a single thermodynamic phase because of the formation of hydrogen bonds between the PVC and ENR molecules. This miscible blend of PVC and ENR-50 was a rare case, and it later received the most attention.[40] The interaction between the epoxy groups of ENR with the chlorine groups of PVC led to miscibility. However, only partial miscibility was observed in a blend of ENR-25 with PVC.[41]

As mentioned earlier, ELNR is the liquid form of ENR that can be produced by the epoxidation of LNR with glacial acetic acid and hydrogen peroxide. Nair et al.[42] studied the effect of the epoxidation level and the molecular masses of ELNR on the impact properties of PVC polymer. The observed results show that the impact strength of L-ELNR/PVC blends was higher than that of H-ELNR/PVC blends at the same level of epoxidation. The PVC blend containing L-ELNR-20 (20 mol % epoxidation) exhibited the highest impact strength, followed by the PVC blends with L-ELNR-10 and L-ELNR-30. At these low levels of epoxidation, liquid rubber provided partial miscibility with PVC because of insufficient intermolecular interaction. The lower impact strengths with L-ELNR-40 and L-ELNR-50 were an indication of excessive intermolecular interactions between the blend components; this led to the miscibility of the component polymers. The longer chains of the H-ELNR restricted the dispersability of the rubber chains in the PVC matrix, and this led to a decreased efficiency of load transfer.[43] The high molecular weight apparently resulted in the formation of an immiscible blend with PVC. However, the increase in the epoxide concentration contributed to the appearance of a homogeneous miscible blend.[44]

In addition to the epoxidation level, suitable mixing conditions are necessary to achieve optimum blend properties. Earlier research has indicated that PVC/ENR-50 blends were miscible at any blend ratio; this suggested diversification in terms of the
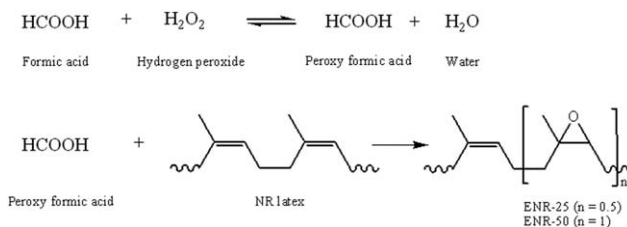
Figure 2. Schematic reaction of the production of ENR via an *in situ* peroxy formic acid route.

Table I. Effects of the ENR Content on the Impact Strength and Tensile Strength of Several Polymer Blends and Polymer Composites

| Number | ENR/polymer blend | Amount of ENR used (wt %) | Impact strength | | Tensile strength | | Reference |
			With ENR	Without ENR	With ENR (MPa)	Without ENR (MPa)	
1.	PVC/L-ENR-20	10	900 J/m	310 J/m	35.60	38.50	[31
2.	PVC/H-ENR-20	10	850 J/m	310 J/m	32.00	38.50	[31
3.	PVC/ENR-50	50	—	—	15.9	38.0	[27
4.	PP/OMMT/ENR-25	20	118 J/m	24 J/m	—	—	[44
5.	PLA/ENR-50	10	7 MPa	4 MPa	59	80	[58
6.	PLA/talc/ENR-50	20	160 J/m	30 J/m	15.3	55	[61
7.	PA6/OMMT/ENR-50	10	5.8 kJ/m^2	2 kJ/m^2	51	84	[53
8.	PA6/HNT/ENR-50	10	7 kJ/m^2	3 kJ/m^2	56.3	85	[50
9.	Epoxy/Glass Fiber/LENR	12	12.5 kJ/m^2	10 kJ/m^2	192	190	[15
10.	Epoxy/ENR-50	3.5	43 kJ/m^2	11 kJ/m^2	65	85	[71
11.	Epoxy/LENR-50	10	45.8 kJ/m^2	11 kJ/m^2	79	85	[71

processing and properties of the PVC/ENR blends.[45] Interestingly, some findings have indicated an enhancement in the mechanical properties of PVC/ENR-50 blends with treatment with electron-beam irradiation. It was reported that PVC and ENR formed self-crosslinkable blends.[46] Mousa et al.[47,48] studied various properties of dynamically vulcanized PVC/ENR blends.

Ratnam and Zaman[49] reported that electron-beam-irradiation-induced stabilization of PVC and ENR-50 blends in the presence of various PVC stabilizers. The observation confirmed that among common PVC stabilizers used, tribasic lead sulfate was efficient in stabilizing PVC/ENR blends and enhancing the blend properties with irradiation.[49] The relatively poor tensile strength of the unstabilized blends was due to the excessive degradation of PVC both during processing and irradiation.[50] However, an increase in the tensile strength with irradiation dose could also be attributed to changes in the blend compatibility coupled with the radiation-induced crosslinking of the rubber phase. In another study, the incorporation of Irganox 1010 inhibited the irradiation-induced crosslinking of PVC/ENR blends, although it simultaneously stabilized the blends against oxidative degradation. The addition of 0.5-phr Irganox 1010 was found to be efficient in improving the aging properties with a minimum loss in the mechanical properties with irradiation.[51]

Ratnam et al.[52] used polyfunctional polymers in irradiated PVC/ENR blend formulations as polyfunctional polymers; they were found to be very effective in decreasing the dose level to achieve optimum properties without deteriorating the base polymer much. It was observed that irradiation-induced crosslinking occurred in PVC/ENR blends. The addition of trimethylol propane triacrylate significantly enhanced irradiation-induced crosslinking in the PVC/ENR blend, and this led to an increase in the mechanical properties.

PP/ENR Blends

It was reported that the toughening properties of PP improved in the presence of a suitable amount of ENR particles. The addition of ENR into PP blends improved the impact strength compared to that of incompatible blends of PP with SMR-CV.[53,54] ENR was miscible with PP with the appearance of a single T_g and a co-crosslinking reaction that took place in the system. Meanwhile, the introduction of SMR-CV into PP blends resulted in the appearance of two T_g's; this indicated incompatibility between both components. Similarly, Huang et al.[55] reported that the blends with an ENR content of 20% showed a homogeneous structure free from any separated domains. The homogeneous morphology confirmed the miscibility of the two polymers. When the ENR content reached 30%, the blend exhibited phase separation. It was obvious that the miscibility of a PP/ENR blend was dependent on its composition. The interfacial structure of the PP/ENR blend was apparently related to the interaction of the two polymers. The interpenetrating structure of the phases implied a strong interfacial adhesion. The strong interfacial adhesion provided toughening materials of high performance. The impact strength of the measured 70:30 PP/ENR was twice that of the untoughened PP polymer.

The increase in the impact strength of PP/organically modified montmorillonite (OMMT) nanocomposites with the addition of various ENR contents was also reported by Balakrishnan et al.[56] The presence of ENR apparently resulted in the formation of a rubber phase morphology and a good distribution of OMMT nanoparticles; thus, this increased in the toughness strength. Li et al.[57] reported that ENR obviously improved the dispersion of coal gangue powder (CGP) particles in the PP matrix and the interfacial adhesion between CGP particles and PP matrix with the well-established interfacial layer. They found that all of the composites fractured in a ductile manner as the ligament yielded completely and the cracks were propagated steadily. The fracture toughness of the composites was significantly improved when the complete interfacial layer formed by ENR on the surface of the CGP particles. With increasing ENR content, the specific plastic work per volume unit of plastic zone of the composites increased considerably, despite the restricted plastic deformation of plastic zones.

In another study,[58] various vulcanization systems were reported to be used to increase the toughness strength of the PP/ENR blend based thermoplastic vulcanizates (TPVs). The mechanical properties of the TPVs with the mixed-cure system were higher than those of the sulfur and peroxide-cured systems. In the peroxide systems, the peroxide degraded the PP molecules particularly by a ß-scission mechanism during shearing at high temperature. It is noticeable that the degradation of PP overshadowed the effect of dynamic crosslinking of the ENR phase.[59] It was also found that the curing systems did not affect the hardness properties and solvent resistance of the TPVs. The dispersed vulcanized rubber particles of the mixed-cured system were marginally larger than those of the peroxide-cured system but smaller than those of the sulfur-cured system. Therefore, it provided the highest mechanical strength and rheological properties.

PA6/ENR Blends

Tanrattanakul et al.[60] reported the effective toughening of ENR particles in PA6 as a result of enhanced adhesion between the interface of PA6 and ENR. The polar groups of ENR were mainly responsible for possible interaction with the functional groups of PA6; this led to enhanced interfacial adhesion and improved mechanical properties. The toughening properties of PA6 at various contents of ENR particles were also extensively studied.[61] The impact strength of PA6 increased remarkably with increasing ENR content. However, the tensile properties were found to decrease consequently because of the formation of agglomerated rubber particles. The addition of a hard rigid filler considerably decreased the impact strength as the filler that was dispersed in the polymer matrix acted as stress concentrator. Sharif et al.[62] reported that the impact strength of the PA6/halloysite nanotube (HNT) nanocomposites blend increased up to 300% with the addition of 20 wt % ENR-50 as compared to that of the PA6/HNT nanocomposites alone. The ENR-50 could delay the crack propagation during notch Izod testing; this indicated that a high impact energy was needed for failure. The presence of the HNTs did not distort or hinder the toughness effect of ENR-50. Ahn and Paul[63] reported an increase in the impact strength up to 500% with the addition of ENR-g-MA in the PA6 nanocomposites.

Balakrishnan et al.[64] and Nouparvar et al.[65] reported the relationship between the epoxidation level and rubber particle size. It was found that a higher epoxy content led to a decrease in the rubber particle size. The reduction in the size of the rubber particles indicated an increase in the toughness of the nanocomposites.[66] The size of the rubber particles in the blend decreased because of the reduction in the particle–particle coalescence rate during the melt mixing. The reductions in the ENR particle size, uniform dispersion, shear yielding, and crazing contributed to the enhancement of the toughened ENR in the polymer matrix, as morphologically depicted in Figure 3.

PLA/ENR Blends

It is widely known that PLA is a synthetic biodegradable thermoplastic polyester alternative to petroleum-based polymers and that it is very brittle.[67] Many methods have been used to
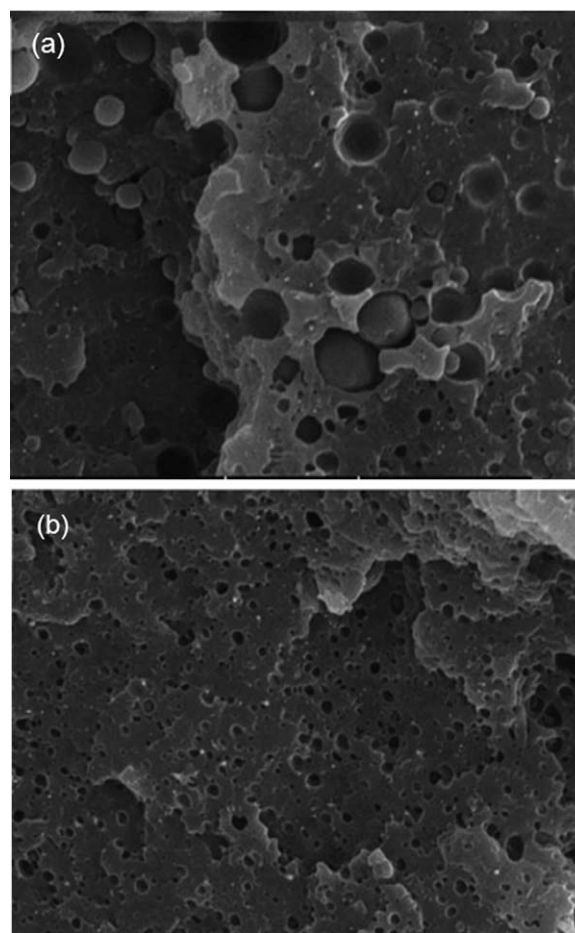
Figure 3. Reduction of the particle size and uniform dispersion of the ENR particle rubber phase in PA6/4 wt % HNT/ENR composites as a function of the ENR content: (a) 10 and (b) 15 wt %.

reduce the brittleness of PLA; these include blending with thermoplastic polymers and rubber materials.[68,69] Zhang et al.[70] reported an improvement in the impact strength of PLA with the incorporation of 20 wt % of ENR-20. ENR-20 was found to impart higher impact strength of PLA matrix as compared with ENR-50. Higher content of epoxy groups in ENR-50 played a major role in improving the viscosity leading to decreased deformability of the blends. Inter chain crosslinking reaction and molecular entanglements were more pronounced in PLA/ENR-50 blends, which in turn increased the tensile strength.

Nghia et al.[71] reported the enhancement of the miscibility of liquid epoxidized natural rubber (LENR) in polylactide blends upon deproteinization. Under controlled reaction conditions, the epoxy group content of deproteinized liquid natural rubber (LEDPNR) increased abruptly in comparison with neat LENR. T_g of LEDPNR in LEDPNR/PLLA blend increased, whereas T_g and the melting temperature of PLLA decreased. This suggested that the compatibility of the LEDPNR/PLLA blend was enhanced by a reaction between the epoxy group of LEDPNR and the ester group of PLLA. The changes in T_g and melting temperature might have been due to the removal of proteins.[71,72]

On other hand, the inclusion of talc filler in PLA/ENR-50 had no significant effect on the toughening of ENR in the PLA blends, as the impact strength considerably improved at various filler contents. It was suggested that ENR enhanced the mobility of the PLA chains and allowed them to deform easily during impact load. An increase in the impact strength of the PLA/talc/ENR composites was due to the existence of the grafted ENR; this generated a higher degree of chain entanglements and a closer match in the solubility of the components and led to an increase in the impact strength. The study showed that the use of ENR as an impact modifier was better for maintaining the stiffness and enhancing the toughness of PLA.[73]

ENR AS AN IMPACT MODIFIER IN THE THERMOSETS

Epoxy Resin/ENR Blends

Engineering toughness using rubber, without a significant loss in the optimal properties of the otherwise unmodified epoxy matrix, focuses on changes in the craze density, deformation, and failure properties. The latter are affected by the dispersed-phase chemistry and microstructure, the dispersed-phase loading and dimensions, and the extent of crosslinking within the epoxy network.[74,75] In respect to the toughening mechanisms of the reactive rubber in the epoxy resin, the formation and development of the dispersed particulate rubber phase in the initially homogeneous epoxy mixture during curing is crucial in enhancing the toughness of the epoxy system.[76] Curing reactions leading to network formation include the ring opening of epoxide and glycidyl groups by the carboxylic termini of the rubber; this generates chemical crosslinking ties between the two phases.[77]

ENR was used to reinforce the epoxy system because of its good reactivity and acceptable compatibility with the epoxy resin.[78] The curing reaction of the epoxy system can be changed by the presence of ENR because of the participation of ENR during curing.[79] Hong and Chan[80] reported that the curing behavior of the ENR modified epoxy/dicyandiamide system was fully affected by the presence of reactive ENR. The dilution of the curing agent content and an increase in the viscosity by the presence of ENR resulted in a stoichiometric imbalance and led to a change in the reaction mechanisms. The flexible ENR had a lower T_g compared to the epoxy matrix; this affected the structure of the cured resin and the conversion near the gel. This also increased the conversion at maximum temperature with ENR content. The formation of a spherical rubber phase appeared in the rubber-modified epoxy system.[81] The polymerization-induced spinodal decomposition resulted from the increase in the molecular weight of the epoxy matrix during curing. This led to the formation of a second rubbery phase.[82]

Cizravi and Subramaniam[83,84] prepared two sets of modified epoxy resin based on diglycidyl ether of bisphenol A formulations with ENR-50 and LENR-50. Upon the introduction of LENR-50 into the epoxy resin, the dispersion dimensions of the spherical rubber phase fell within the range 0.33 ± 0.40 mm. Meanwhile, the mean particle sizes of the ENR-50 dispersions fell within the range 0.48 ± 0.67 mm. The increased impact energies were less steep in the case of LENR-50 compared to ENR-50. The impact energies were higher for formulations containing a marginal 1.01 wt % reactive diluent; this made the backbone flexible at the expense of stiff diglycidyl ether of bisphenol A segments. The tensile toughness and impact toughness of the LENR-50 modified epoxy resin improved remarkably by 250 and 125%, respectively, compared to those of the neat formulation with ENR-50, which had even higher tensile and impact toughnesses.

In other studies, the inclusion of NR and ENR as rubber-toughening materials into epoxy resin brought about significant improvements in the impact toughness, in which the ENR/epoxy resins had a higher strength compared to the NR/epoxy resins.[85] The incorporation of the liquid version of the ENR impact modifier in the epoxy resin resulted in a higher impact strength as compared to that of the NR impact modifier.[86] Kallitsis and Kalfoglou[87] indicated that the compatibility of ENR with aromatic polymers followed the order ENR/novolac > ENR/resole > ENR/phenoxy > ENR/bisphenol A epoxy because of the difference in the acid characteristics of the hydroxyl groups of resins.

OTHER POLYMER/ENR BLENDS

ENR has also been inserted into some other polymer blends for impact modification in the past. Ismail and Ooi[88] prepared high-density polyethylene (HDPE)/soya powder (SP) blends by melt mixing in an internal mixer and investigated effect of ENR-50 as a compatibilizer in HDPE/SP blend systems. The addition of ENR-50 increased the stabilization torque and the mechanical properties of the HDPE/SP blends because of the elastomeric behavior of ENR-50. The vulcanization of the HDPE/ENR blends under various curing systems was reported to impart an increase in the mechanical properties. It was also found that vulcanized HDPE/ENR treated with phenolic resin exhibited superior mechanical properties and the smallest vulcanized rubber domains.[89] The effect of electron-beam irradiation on the properties of linear low-density polyethylene/ENR-50/SP blends indicated that an increase in the oxygenated product led to enhanced compatibilization in the blend; this, in turn, increased the mechanical properties and thermal stability.[90]

Heat-shrinkable material prepared from green thermoplastic elastomers based on polycaprolactone (PCL)/ENR blends were studied by Mishra et al.[91] Heat shrinkability increased substantially when the blend was crosslinked by a small amount of dicumyl peroxide (DCP). The crosslinked point acted as a memory point during shrinkage and improved the heat shrinkability.[92] The crosslinking also enhanced the mechanical properties and crystallinity; this implied that a high-performance PCL/ENR could be prepared by crosslinking with DCP. Surprisingly, the addition of a high content of DCP resulted in crosslinked PCL/ENR with a more pronounced shear thinning effect and a higher elasticity compared to the uncrosslinked blends.[93]

The addition of carbon black filler was observed to have a remarkable effect on the self-crosslinking of PLA and ENR blends. PLA was believed to be chemisorbed on the carbon

black surface, whereas ENR was believed to be adsorbed physically on the filler surface. Crosslinking between PLA and ENR took place during molding through the carbon black particles, and the otherwise inhomogeneous blend became homogeneous.[94,95] On the other hand, the miscibility of polychloroprene and ENR was adversely affected by the presence of carbon black filler, which corresponded to the formation of phase separation.[96] Microheterogeneous characteristics in the blend systems arose because of the furanization of the ENR chain induced by HCl liberated from polychloroprene during high-temperature molding. Carbon black catalyzed HCl liberation from polychloroprene and the consequent furanization of ENR in the blend; this caused phase separation.

CONCLUSIONS AND FUTURE PROSPECTS

The improvement in the plastic toughness by the inclusion of the rubber phase has become a promising method in polymer science and technology for overcoming problems arising from the brittleness of polymers such as PLA, PA, and PVC. However, many more challenges must be addressed to reach its full potential utilization. In this review, an overview of the recent research regarding ENR-toughened plastics and insights into factors that control the properties of rubber-toughened plastics have been reported. It has been noted that the ENR particle size and distribution are the main factors controlling the toughening. The rubbery phase exists within the blend system, in which the rubber particles are dispersed uniformly throughout the matrix phase. The epoxidation of NR increases the polarity of the polymer and T_g, whereas the ability to strain crystallize is retained. The functionality of ENR apparently provides a substantial enhancement in the toughening of filled plastic composites because the presence of ENR may induce the formation of rubbery-bound filler within the matrix phase. The interaction takes place between the functional groups of the components, through which the load is transferred via shear stress from the matrix to the rubbery-bound fillers. In other words, the level of epoxidation strongly influences the effectiveness of formation of ENR rubbery-bound fillers and the load transfer from the matrix to the filler. The presence of ENR in the plastics matrix is expected to improve the dispersion of fillers in the plastics matrix and interfacial adhesion between the fillers and plastics matrix.

ENR is expected to play an important role in the toughening of nanocomposites based on graphene, halloysite, nanotubes, and montmorillonite. The fracture toughness of the composites is expected to be improved with the complete interfacial layer formed by ENR on the surface of the filler particles. Therefore, in addition to the toughening of plastic composites, it is expected that a large number of studies with ENR as a filler-modifying agent for different organic/inorganic fillers will be published in the near future. However, research is still far from the end of the tunnel in terms of understanding the mechanisms of enhancement effect of rubbery-bound filler phenomena in the polymer composites. Fundamental research is necessary to observe these phenomena and enable full exploitation of the potential of ENR in filled plastic composites; this might be useful in automotive and aerospace applications.

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