Polymer Blends of Epoxy Resin and Epoxidized Natural Rubber

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ABSTRACT: The aim of this research was to investigate the behaviors of epoxy resin blended with epoxidized natural rubber (ENR). ENRs were prepared via *in situ* epoxidation method so that the obtained ENRs contained epoxide groups 25, 40, 50, 60, 70, and 80 mol %. The amounts of ENRs in the blends were 2, 5, 7, and 10 parts per hundred of epoxy resin (phr). From the results, it was found that the impact strength of epoxy resin can be improved by blending with ENRs. Tensile strength and Young's modulus were found to be decreased with an increasing amount of epoxide groups in ENR and also with an increasing amount of ENR in the blends. Meanwhile, percent elongation at break slightly increased when ENR content was not over 5 phr. In addition, flexural strength and flexural modulus of the blends were mostly lower than the epoxy resin. Scanning electron microscope micrograph of fracture surface suggested that the toughening of epoxy resin was induced by the presence of ENR globular nodules attached to the epoxy matrix. TGA and DSC analysis revealed that thermal decomposition temperature and glass transition temperature of the samples were slightly different. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 452–459, 2006

Key words: rubber; blends; resins; mechanical properties; thermal properties

INTRODUCTION

Epoxy resins are nowadays used extensively because of their excellent properties such as high modulus, low creep, and reasonable elevated temperature performance. However, they easily fail under impact because of highly crosslinked structure.[1,2] As pure materials, epoxies are brittle and have low fracture energy, ranging from 80 to 200 J/m^2.[3,4] Materials that have been added to epoxy solids to improve toughness include hard particulate materials such as inorganic glass particles,[4,5] as well as elastomers and thermoplastics[6] such as hydroxyl terminated polybutadiene,[7] carboxyl terminated butadiene acrylonitrile rubbers,[7–9] and PVC plastisols.[10] Numerous investigations have shown that the addition of such materials can, if used correctly, result in substantial toughness improvements without significantly affecting any other important properties. As epoxies are viscous liquids, their handling and conforming is relatively easy. Therefore, the best combination would be the addition of a liquid rubber to the epoxy resin.

Bussi and Ishida studied the mechanical properties of blends of diglycidyl ether of bisphenol-A based epoxy resin and hydroxyl terminated, internally epoxidized polybutadiene rubber. The epoxidized rubber was prereacted with an excess diepoxide to achieve better bonding between the rubber particles and the epoxy matrix phase. They observed that without rubber prereaction, almost no improvement in fracture toughness was achieved. From dynamic mechanical analysis studies, it was also found that the sample containing prereacted rubber exhibited even lower T_g than did the sample containing the unmodified rubber.[11]

Blends of unsaturated polyesters and functional rubbers such as hydroxy terminated polybutadiene, epoxidized natural rubber (ENR), hydroxy terminated natural rubber (NR), and maleated nitrile rubber were studied. It was reported that the elastomers bearing reactive functional groups show better compatibility with the resin and improve the toughness and impact resistance of the cured resin substantially, compared with unmodified elastomers.[12,13]

The aim of this research was to improve toughness of the epoxy matrix resin by blending with ENR. ENRs used in this research were prepared from high ammonia concentrated NR latex via *in situ* epoxidization method with various amounts of hydrogen peroxide, formic acid, and a surfactant, as described by Chuayjuljit et al.[14] The effects of the ENRs on the mechanical and thermal properties were studied by using different rubber concentrations in the blends.

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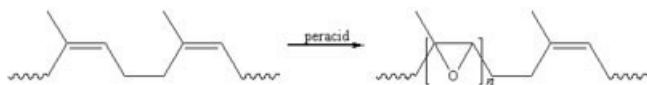
Scheme 1 Expoxidation of natural rubber.

EXPERIMENTAL

High ammonia concentrated NR latex (HA latex), obtained from Thai Rubber Latex (Thailand), was diluted with distilled water to reduce its dry rubber content from 60 to 20%. The diluted latex was reacted with polyalcohol ethylene oxide condensate (Terric 16A-16: Australia) as a stabilizer, 98% formic acid, and hydrogen peroxide. The *in situ* epoxidation reaction was carried on for 4, 6, 8, 10, 14, and 16 h as to obtain ENRs with different amount of epoxide groups. The reaction is shown in Scheme I. The epoxidized products were coagulated with 95% v/v methanol. Sodium carbonate solution and water were used to clean the rubber before drying at 60°C. An infrared spectrophotometer (Perkin–Elmer System 2000 Fourier transform infrared) was used for the determination of epoxide contents.

Bisphenol-type epoxy resin (Epicholrohydrin–bisphenol A: Epiclon 850) supplied by Siam Chemical Industry (Thailand) was mixed with NR and the prepared ENRs at 2, 5, 7, and 10 phr (part per hundred of epoxy resin). Polyamide resin (Luckamide TD-982-E) also supplied by Siam Chemical Industry (Thailand) was used as the curing agent. The composition for the blends is shown in Table I. The mixture was stirred at 50 rpm under room temperature for 20 min. Specimens were prepared by casting the mixture in silicone molds. They were cured at 100°C for 2 h.

Tensile properties of the cured test specimens were determined according to ASTM D638 using Lloyd LR10K Universal Testing Machine equipped with 10 kN loadcell with the test speed of 50 mm/min. Type I specimen size was used and the guage length was set at 50 mm. Lloyd 500 Universal Testing Machine epuipped with 2500N loadcell was employed to investigate flexural strength of specimens with the test speed of 50 mm/min based on ASTM D790. The span

Figure 1 Appearance of (a) epoxy resin, (b) epoxy/NR blend, (c) epoxy/ENR70 blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

length was 50 mm. Charpy impact strength was determined in accordance with ASTM D256 using GO-TECH GT-7045 Charpy Impact Tester. The impact strength was reported in kJ/m^2.

Thermal properties of specimens were analyzed using TGA and DSC techniques. For TGA analysis, specimens were tested with Mettler Toledo TGA/SDTA 851^e at the temperature ranging from 30 to 1000°C with the heating rate of 20°C under nitrogen atmosphere. As for DSC analysis, Mettler Toledo DSC 822^e
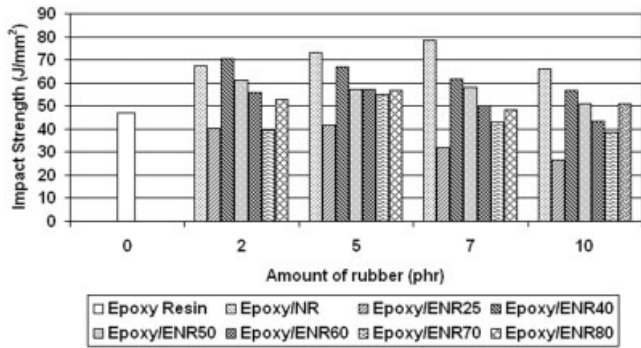
TABLE I
Composition of Blends Used in the Experiment

Epoxy resin/ rubber[a]	Epoxy resin (g)	Rubber (g)	Curing agent (g)
100 : 2	100	2	100
100 : 5	100	5	100
100 : 7	100	7	100
100 : 10	100	10	100

[a] Rubber referred to NR, ENR25, ENR40, ENR50, ENR60, ENR70, and ENR80.

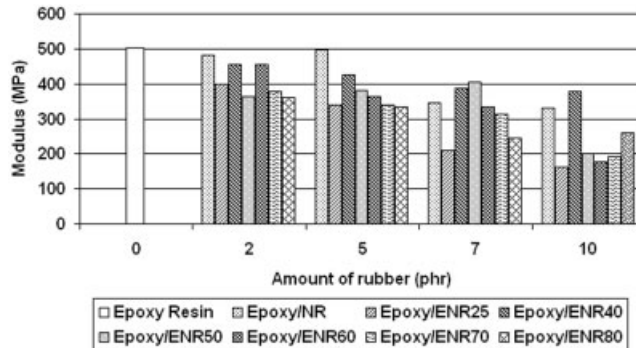**Figure 2** Impact strength of epoxy resin, epoxy/NR blend, and epoxy/ENR blends.

Figure 3 Tensile strength of epoxy resin, epoxy/NR blend, and epoxy/ENR blends.

was used at the temperature ranging from −50 to 150°C with the heating rate of 10°C under nitrogen atmosphere.

Impact fracture surface morphology of the polymer blends were analyzed using scanning electron microscope (SEM) (Jeol JSM-6400).

RESULTS AND DISCUSSION

The amount of epoxide groups in NR after *in situ* epoxidation was calculated using data obtained from

Figure 4 Elongation at break of epoxy resin, epoxy/NR blend, and epoxy/ENR blends.
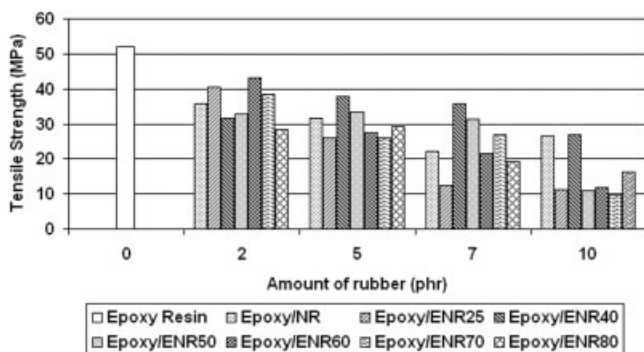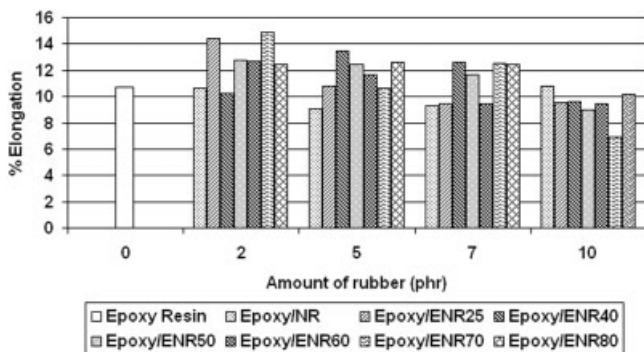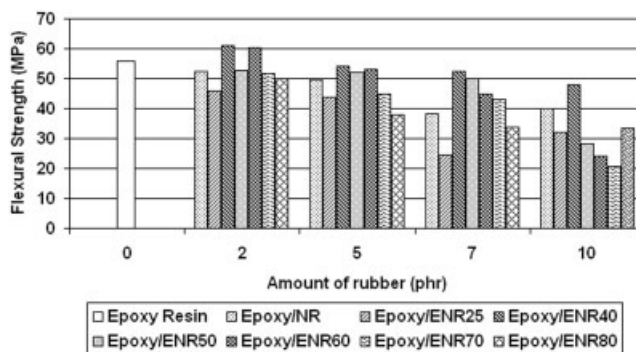

Figure 5 Tensile modulus of epoxy resin, epoxy/NR blend, and epoxy/ENR blends.

Fourier transform infrared spectroscopy analysis. The calculation revealed that the amount of epoxide groups was increased as the reaction time increased. The epoxidized products were denoted ENR25, ENR40, ENR 50, ENR60, ENR70, and ENR80 according to the mole percentage of epoxide groups in ENR. NR and the prepared ENRs were blended with epoxy resin at various ratios.

The blends were successfully cured in silicone casting molds. The cured specimens appeared brownish yellow in color as shown in Figure 1. Blended resin specimens were more opaque than epoxy resin specimens.

Figure 2 shows impact strength of epoxy resin and blended resins. Addition of NR in epoxy resin improved impact strength of epoxy resin markedly. Rubber globular nodules contributed to this toughening effect. Although, when the amount of NR was 10 phr, the impact strength was found to be lowered. This is due to bubbles found in specimens during curing as water was not completely removed from the latex. For epoxy/ENR blends, when the amount of ENRs in the blends was not higher than 10 phr, the impact strength of blend samples was higher than that of epoxy resin as they can distribute more evenly due to improved

Figure 6 Flexural strength of epoxy resin, epoxy/NR blend, and epoxy/ENR blends.

Sample: Epoxy + NR 10 phr (30-1000oC 20 oC/min), 5.9041 mg
Sample: Epoxy + NR 7 phr (30-1000oC 20 oC/min), 5.8241 mg
Sample: Epoxy + NR 5 phr (30-1000oC 20 oC/min), 7.0369 mg
Sample: Epoxy + NR 2 phr (30-1000oC 20oC/min), 5.4881 mg
Sample: Epoxy (30-1000oC 20oC/min), 6.5169 mg

(a)

Sample: Epoxy + ENR70 10 phr (30-1000oC 20oC/min), 4.2979 mg
Sample: Epoxy + ENR70 7 phr (30-1000oC 20oC/min), 4.4300 mg
Sample: Epoxy + ENR70 5 phr (30-1000oC 20oC/min), 5.5349 mg
Sample: Epoxy + ENR70 2 phr (30-1000oC 20oC/min), 4.1379 mg
Sample: Epoxy (30-1000oC 20oC/min), 6.5169 mg

(b)

Figure 7 TGA curves for epoxy resin blended with (a) NR, (b) ENR70. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

epoxy and NR interfacial compatibility. In our previous work, it was proved that with the increasing epoxidation content in NR, the polarity and oil resistance increased and the degree of swelling decreased.[14] This will improve the adhesion of ENR with polar compo-

nent of epoxy. However, for ENR25, the amount of epoxide groups was not enough to improve interfacial compatibility while the rigid characteristics of these epoxide groups increased brittleness in the structure. As the amount of epoxide group increased, impact

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TABLE II
Onset Thermal Decomposition and Glass Transition Temperature

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	Onset thermal decomposition temperature (°C)					Glass transition temperature (°C)		
	0 phr	2 phr	5 phr	7 phr	10 phr	0 phr	5 phr	10 phr
Epoxy resin	353.0					55.8		
Epoxy/NR		353.0	355.0	353.6	354.4		55.3	55.7
Epoxy/ENR25		351.3	353.3	354.3	360.7		52.2	51.1
Epoxy/ENR40		353.9	351.4	352.9	351.5		55.9	51.6
Epoxy/ENR50		350.7	351.4	353.0	363.8		56.9	54.4
Epoxy/ENR60		353.6	352.8	355.4	353.3		57.0	56.8
Epoxy/ENR70		353.2	353.6	359.4	356.2		57.9	56.9
Epoxy/ENR80		352.2	353.8	355.3	355.4		58.1	58.1

strength was decreased. In addition to rigid characteristics of epoxide groups that increased brittleness in the structure, longer reaction time may also shorten rubber molecular chains.

For tensile strength, as shown in Figure 3, as rubber possessed lower tensile strength comparing with epoxy resin, thus the tensile strength of blended resins were less comparing with epoxy resin. It can also be pointed out that as the amount of ENRs in the blends increased, the tensile strength was decreased. The lowering effect was more significant in case of ENR with higher epoxide groups such as ENR60. The in-

crement of double bonds in the structure prohibited strain crystallization during testing. Elongation at break of Epoxy/NR blended resins was superior or similar to that of epoxy resin as shown in Figure 4. It was assumed that rubber component contributed to this elongation. The result for Young's modulus of specimens, as shown in Figure 5, was similar to that for tensile strength.

Flexural strength of epoxy resin and blended resins specimens is shown in Figure 6. As the amount of rubber in the blends increased, the flexural strength tended to decrease. Epoxy blended with ENR40 at 2
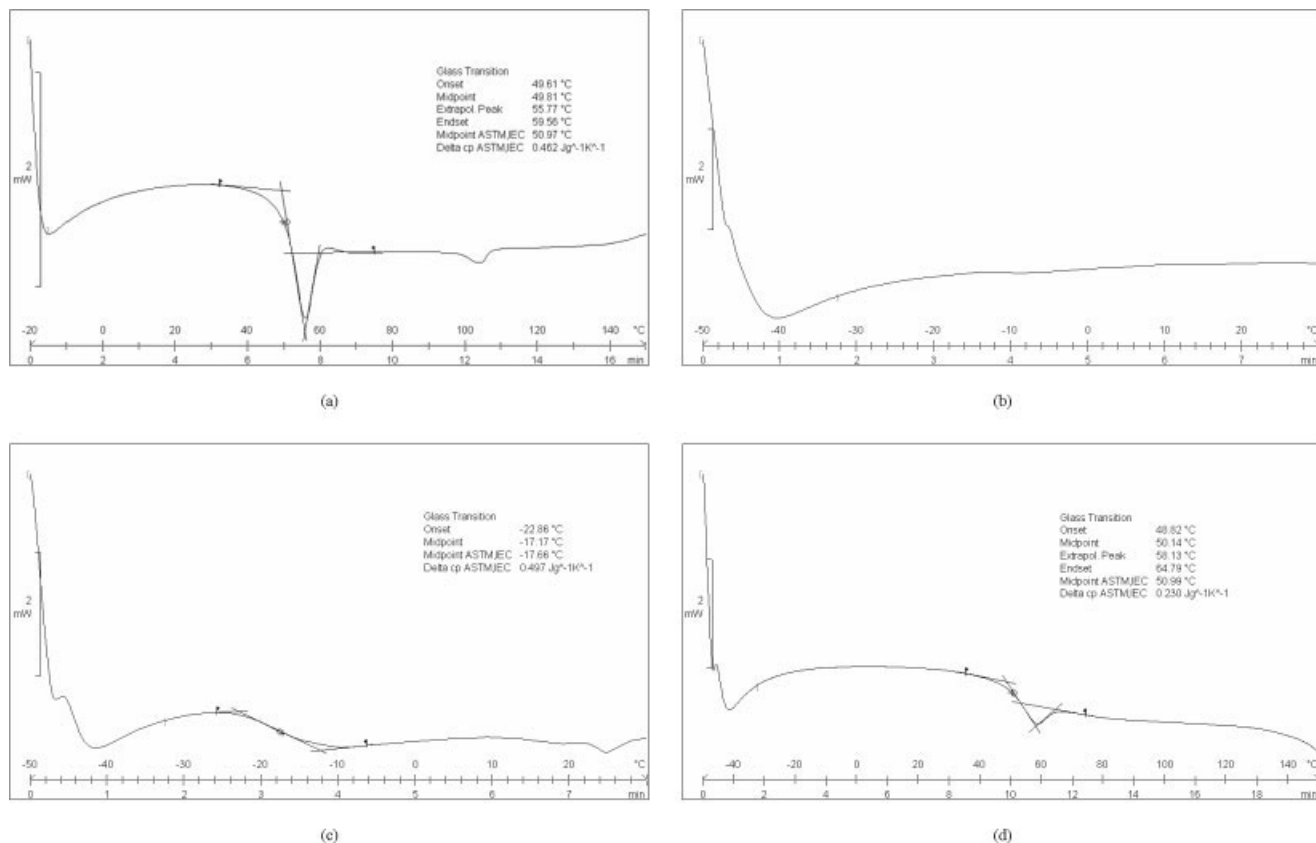

Figure 8 DSC curves for (a) cured epoxy resin, (b) NR, (c) ENR70, (d) Epoxy/ENR70 blended at 10 phr.
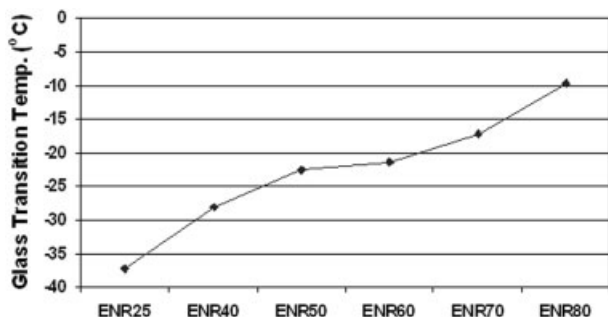
Figure 9 Glass transition temperature of ENRs.

Figure 11 SEM micrograph of fracture surface of epoxy/NR (5 phr) blend at 1500×.

phr possessed higher flexural strength than did epoxy resin. Flexural modulus was found to follow the same trend as the flexural strength.

Figure 7 shows a specimen curve for NR blend and ENR blend. Table II compares the onset thermal decomposition temperature of NR and ENRs. The onset of the decomposition of the blended resins was unchanged compared with that of epoxy resin. Some DSC thermograms are shown in Figure 8. Glass transition temperature of ENRs was increased as the amount of epoxide groups increased as shown in Figure 9. However, the glass transition temperature of blended resin was similar to that of epoxy resin as shown in Table II.

SEM micrographs in Figures 10, 11, and 12 reveal that as the amount of epoxide groups increased, the interfacial adhesion between rubber and epoxy resin was improved. Drastic decrease in microstructure size in the case of epoxy blended with ENR80 was presumably due to higher interfacial bonding between the two as well as shorter rubber molecular chains. Consequently, good distribution of smaller globular nodules was achieved. However, rigidity of epoxide
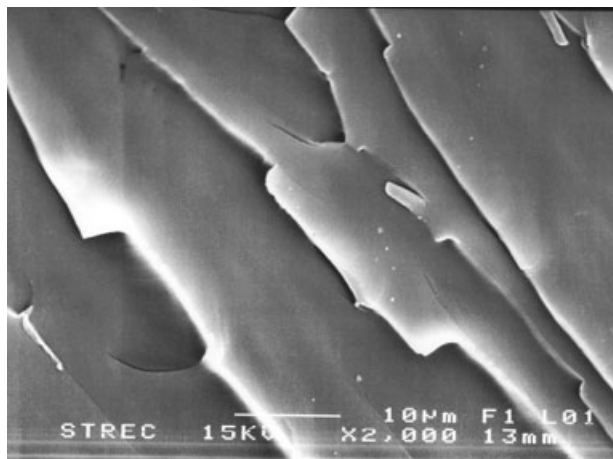
groups and low strain crystallization in ENR80 affected the mechanical properties considerably. The effect was signified as the amount of ENR in the blend increased.

CONCLUSIONS

ENRs were prepared from NR latex using *in situ* epoxidation technique. They were named ENR25, ENR40, ENR 50, ENR60, ENR70, and ENR80 according to the amount of epoxide groups in the structure. These NR and ENRs, at the ratio of 2, 5, 7, and 10 phr, were blended with epoxy resin in the presence of a curing agent.

Mechanical and physical properties as well as fracture surface morphology of the cured resin were investigated. It was found that impact strength increased when the amount of rubber did not exceed 5 phr. At the amount of rubber over 5 phr, the impact strength is decreased. Tensile strength and Young's modulus of the blended resin decreased steadily as the amount of rubber increased. Elongation increased when the amount of rubber was not over 5 phr. Specimens exhibited lower Flexural strength and flexural modulus when the amount of rubber increased.

From SEM micrographs, it can be observed that rubber globular nodules were presented resulting in higher impact strength. The rubber and epoxy resin surface interaction is improved in case of ENRs. TGA and DSC analysis revealed that thermal decomposition temperature and glass transition temperature of the blended resins were similar to epoxy resin, i.e., at the temperature between 351 and 364°C and 51 and 58°C, respectively.

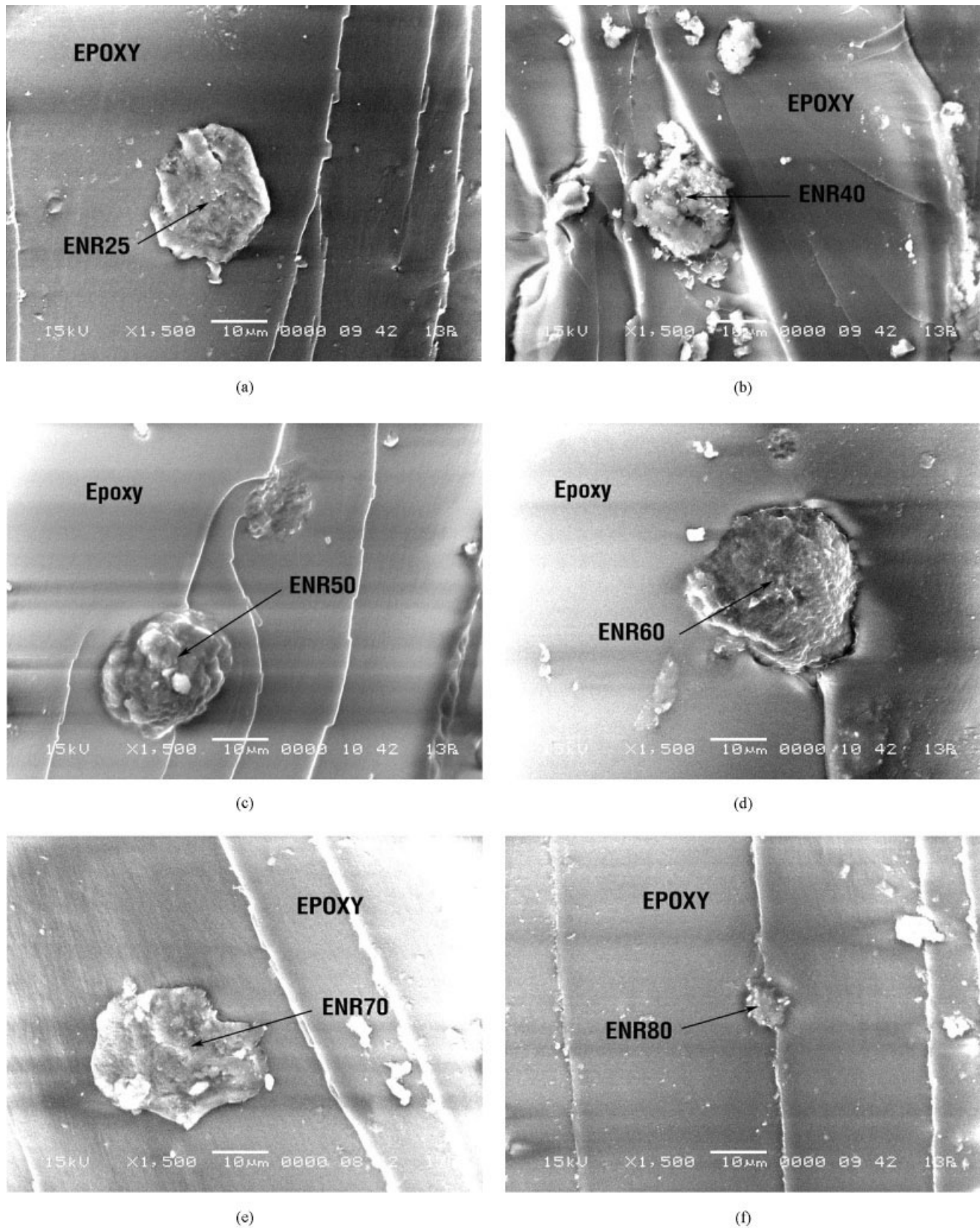**Figure 10** SEM micrograph of fracture surface of epoxy resin at 2000×.

Figure 12   SEM micrograph of fracture surface of epoxy/ENR (5 phr) blends at 1500× (a) ENR25, (b) ENR40, (c) ENR50, (d) ENR60, (e) ENR70, (f) ENR80.

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