EFFECT OF DIFFERENT TYPES OF LIQUID NATURAL RUBBERS ON THE MODIFICATION OF DGEBA-BASED EPOXY RESIN

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ABSTRACT

Diglycidyl ether of bisphenol A (DGEBA)-based epoxy and varying content of hydroxyl terminated liquid natural rubber (HTNR) or carboxyl-terminated liquid natural rubber (CTNR) were cured using an aromatic amine hardener. The ultimate aim of the study was to modify the brittle epoxy matrix by liquid rubber to improve the toughness characteristics. Tensile, flexural, and fracture toughness behaviors of neat as well as modified networks have been studied to observe the effect of different types of liquid natural rubber modification. The morphological evolution of the toughened networks was examined by scanning electron microscope (SEM), and the observations were used effectively to explain the impact properties of the network having varying content of liquid natural rubbers. The results showed that the impact resistance of both HTNR-modified DGEBA and CTNR-modified DGEBA was superior to that of the pure epoxy resin, among which the impact resistance of CTNR-modified DGEBA was better than that of HTNR-modified DGEBA. For all the composites with HTNR or CTNR, the impact resistance increased with elastomer concentration up to 15.0 parts per hundred parts of resin (phr). Higher concentration of the elastomers resulted in larger particles and gave lower impact values. These results allow the conclusion that 15 phr is the maximum content of HTPB or CTNR that might be added in DGEBA composites for a positive effect upon the impact strength.

*Abbreviations***:** liquid natural rubber: LNR; hydroxyl-terminated liquid narural rubber: HTNR; natural rubber (NR); bisphenol-A diglycidyl eter-based epoxy: DGEBA; epoxy resin: ER.

1. INTRODUCTION

Epoxy resins (ER) are one type of thermoset resins combining many attractive properties, such as high mechanical properties, and excellent dimensional, thermal and environmental stabilities, toughness, rigidity, high temperature performance, chemical resistance, adhesive

properties, formulation latitude, and reactivity with a wide variety of chemical curing agents, high mechanical properties, and excellent dimensional, thermal and environmental stabilities. Up to now, ERs are widely applied as matrix of coatings, adhesives and composites. However, a practical disadvantage of highly crosslinked materials is, their poor resistance to crack propagation. These materials are brittle and cannot be used for damage tolerant applications due to the high cross-linking and inherent low toughness of ER. So, it is desirable to enhance their toughness without adverse influence on others useful properties, i.e., high thermal stabilities and low cure shrinkage [1 – 3].

To overcome the above-said disadvantages, many types of modifiers were employed to improve the mechanical and thermal properties of ER, such as reactive liquid rubbers [4, 5] amine-terminated poly(arylene ether ketone)s [6], triblock copolymers [7], thermoplastics [8], carbon nanotubes [9] and silicate-based nanofillers [10]. Modification with reactive liquid rubbers is one of the most effective strategies to toughen ER. In this strategy, the liquid rubbers are initially dissolved into ER, and then the rubber separates as discrete particulate phase due to the decreased solubility of rubber in matrix that is caused by the increase of molecular weight of the cross-linked ER [2]. Many reactive liquid rubbers, such as acrylate rubber [1], carboxyl-terminated polybutadiene (CTPB) [11], carboxyl-terminated butadiene and acrylonitrile copolymer (CTBN) [12] and hydroxyl terminated polybutadiene (HTPB) [13], have been employed as effective toughening modifiers for ER. Other high performance polymers have also been used to modify ER, include polysulfone (PSF), poly(etherimide)(PEI), polyimide(PI) [14], poly(ether ether ketone) [15], polyetesulfone (PES) [16], amino-terminatd poly(arylene ether ketone) [6]. Up to now, there have been no publications that concern the use of liquid natural rubbers (LNR), in general, and HTNR, in particular, to modify ER.

The main objective of the present work was to investigate the effects of two types of LNR, i.e., hydroxyl-terminated liquid natural rubber (HTNR) and carboxyl-terminated liquid natural rubber (CTNR) on the modification of bisphenol-A diglycidyl ether-based epoxy resin (DGEBA).

2. EXPERIMENTAL

2.1. Materials

DGEBA-based ER used in all experiments was DER 331, supplied by Dow Chemical Company Co. (USA), with a number-average molecular weight (Mn) of 380 g mol L^{-1} and an epoxide equivalent of 192 g equiv^{-1} as determined by acid titration. Diethyl toluene diamine (DETD) (ETHACURE-100), which existed as a mixture of the two DETD isomers (74 – 80 % 2,4-isomer and 18 – 24 % 2,6-isomer, amine equivalent weight = 44.3), was purchased from Albemarle Corporation, USA. HTNR having Mn of 3200 and a hydroxyl number of 0.8 g mequiv^{-1} was prepared by the procedure described in detail in [17]. Maleic anhydride (Merck) was distilled under vacuum before use. Triphenylphosphine (Merck) was used as received. All polymers were dried under vacuum for 24 h at room temperature before use. Table 1 summarises the experimental conditions used to fabricate NR-modified DGEBA epoxy systems.

2.2. Preparation of carboxyl-terminated liquid natural rubber (CTNR)

CTNR was prepared by the procedure described in detail in[18] with some modifications as follows (Scheme 1): HTNR having Mn of 3200 and a hydroxyl number of 0.8 g mequiv^{-1}, was

converted into the corresponding CTNR by the reaction of HTNR with an excess amount of maleic anhydride (MA). The reaction was performed in bulk at 80ºC for 48 h with magnetic stirring, under nitrogen atmosphere. The carboxyl content of CTNR was determined by titration with a NaOH methanolic solution of 0.10 mol L^{-1}, using phenolphthalein as an indicator. The excess of MA was removed by precipitation of toluene solution into large amount of methanol. The obtained CTNR was dried under vacuum at 50 ^{0}C to constant weight.

Table 1. Composition in parts per hundred parts of resin (phr) for each component in the final materials.

Sample Code	ER-HTNR-DETD	ER-CTNR-DETD
P0	100:0:20	
P1	100:5:20	
P2	100:10:20	
P3	100:15:20	
P4	100:20:20	
P5		100:5:20
P6		100:10:20
P7		100:15:20
P8		100:20:20
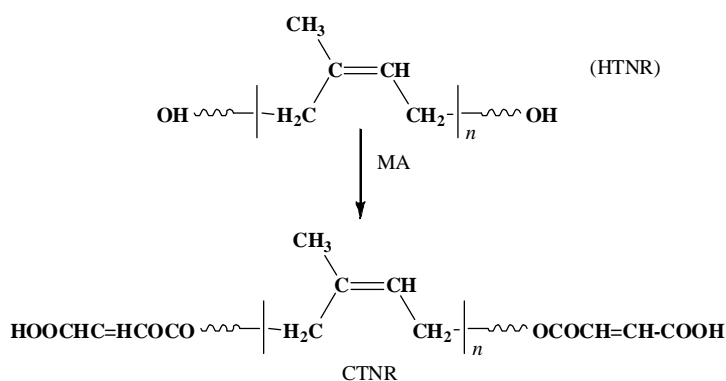
Scheme 1. Preparation of CTNR.

2.3. Preparation of natural rubber-modified DGEBA materials

The DGEBA was modified with different amounts of HTNR or CTNR without the presence of solvent. All network polymers were prepared from mixtures of the DGEBA and the hardener, DETD (see Table 1 for the formulations). In the case of preparing DGEBA/CTNR samples, 0.2 % m/m of triphenylphosphine was used as catalyst.

DGEBA /HTNR samples were prepared as follows: a proper amount of DER 331 was first degassed for 60 min in a vacuum oven at 80 ºC. Different amount of HTNR was also degassed separately under the same conditions. Both components were mixed and the hardener was added. The mixtures were gently stirred for about 10 min to ensure proper dispersion of the hardener DETD, degassed for 10 min. The bubble-free mixtures were then poured into the preheated steel

mold in an oven. The inner geometry of the steel mold is following the recommendation of ASTM D638-96 for making tensile specimens. The dimensions of tensile specimens are 4 mm × 6 mm in the working section. The inner dimensions of the steel mold for making impact specimens are 4 mm × 10 mm × 80 mm. The modified epoxy resins were cured at 60 ^{0}C for 48 h, then 100 ^{0}C for 2 h at normal pressure. This cure condition was chosen from DSC studies performed in the static mode at 100 ℃, which revealed that almost all curing processes happened before 60 min.

DGEBA/CTNR samples were prepared by the same procedure as described above. All the DGEBA/CTNR samples were obtained by reacting DGEBA-based ER with different amount of CTPB and 0.2 % m/m of triphenylphosphine as a catalyst.

2.4. Characterization

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 equipment. The cure conditions were determined in a static mode at 100 ℃ and in dynamic mode at 10 ℃ min^{-1} under nitrogen. The static mode has been employed to verify the necessary time to complete the curing process and the dynamic mode was employed to calculate the enthalpy related to the curing process.

The gel point was determined according to ASTM 2471, by putting about 100 mg of the sample in several tubes, which were placed into an oil bath at 100 ℃. The tubes were withdrawn from the bath at different times and chilled in an ice bath to quench the reaction. The polymeric material was dissolved with tetrahydrofuran (THF). The gelation point was determined from the presence of insoluble fraction.

Scanning electron microscopy (SEM) was performed using a JEOL JSM-5610LV SEM with an electron voltage of 25 – 30 kV and secondary electron detector. The epoxy networks were handling fractured and the surface was first treated with chloroform to extract the rubber phase, then dried under vacuum and coated with thin layer of gold before analyzing. The SEM micrographs of the composites were taken from the surface after the impact test, which were also coated with a thin layer of gold before analyzing.

The size and size distribution of the dispersed particle were determined by means of semiautomatic image analysis. The SEM micrographs of the fractured samples were first scanned and converted into digitized images, which were analyzed using an (AnalySIS 3.0 program) to obtain the average diameter values of the dispersed particles, d_n, and the particle size distribution.

Mechanical testing

Flexural tests of ER networks and the corresponding composites were performed using an Instron 4204 testing machine fitted with a three-point bending fixture at a crosshead speed of 1 mm min^{-1}, according to ASTM D-790. The dimensions of the specimens were 75 × 25 × 2 mm and the span-to-thickness ratio was set at L/D = 32 to 1 in all cases. The values were taken from an average of at least five specimens.

The tensile tests of the cured epoxy system were performed using an Instron 4204 testing machine at a crosshead speed of 1 mm min^{-1}, according to ASTM D-638.

The impact strength of the notched specimens was determined by using a Charpy Monsanto Tensiometer, using rectangular specimens of 50 × 10 × 5 mm, according to ASTM D-256. The tests were carried out at room temperature and the values were taken from an average of at least

ten specimens. ER networks were tested with the help of a 0.22 kg hammer was employed.

3. RESULTS AND DISCUSSION

3.1. Evaluation of the cure parameters

The effects of HTNR or CTNR on cure parameters of the cured epoxy networks (T_{cure} = 100 ^{0}C) are furnished in Table 2.

Table 2. Curing parameters of pure DGEBA and those natural rubber-modified epoxy systems.

Sample	ΔH(*) (J/g)	Gel time (min)	Cure time [a] (min)
P0	210.8	16.1	35
P1	208.4	18.6	37
P2	207.7	21.5	38
P3	207.9	24.9	41
P4	208.1	26.6	45
P5	201.2	14.1	33
P6	194.1	13.4	31
P7	191.3	12.7	30
P8	186.7	11.5	29

(*) Obtained from DSC measurements taken in the dynamic mode

[a] Obtained from DSC isothermal mode

The heat content, ΔH values related to the cure reaction, was measured in an isothermal mode. The values estimated from the area of the exothermic peak at a particular temperature did not change significantly upon the addition of HTNR indicating that the presence of the rubber has not influenced the mechanism of cross-linking reaction. Gel times which represent the necessary time to produce the minimum amount of insoluble fraction was found to be greater for modified ER with the addition of rubber and are tabulated in Table 2. This may be attributed to the dilution effect caused by the inclusion of HTNR, i.e., this delay might be due to lower reactivity of the modified ER produced as a result of chain extension and increase in viscosity of the medium due to the addition of rubber. As dilution increases with the addition of rubber, the concentration of reacting species gets reduced that impair reactivity. In addition to that, the natural rubber (NR) particles can occupy positions in between the reaction centers of the DGEBA and the hardener, thereby separating the crosslinking points. Thus, the addition of HTNR reduces the crosslinking density of the formed network.

The cure time also increases with the inclusion of the elastomer. This may, again, be due to the effect of dilution. As dilution increases with the addition of HTNR, there will be decrease in the density of the reaction groups of the DGEBA and the hardener.

Concerning the effect of CTNR on cure parameters of the cured epoxy network, it can be seen from Table 2 that when modifying DGEBA-based ER with CTNR, both gel time and cure time decreased. Such behaviour can be explained by the fact that during the reaction of CTNR

with the ER, some of the exothermic energy released during epoxy crosslinking might have been consumed by CTNR resulting in a decrease in gel and cure time (more rapid reaction) as well as a decrease in the exotherm peak. It is obvious to say that the use of CTNR in modifying DGEBA is attractive because of the high reactivity of the end groups with the epoxide ring which result in shorter gel times.

3.2. Mechanical properties

The impact strength, flexural and tensile properties of the cured DGEBA samples containing different amount of NR agent are summarized in Table 3.
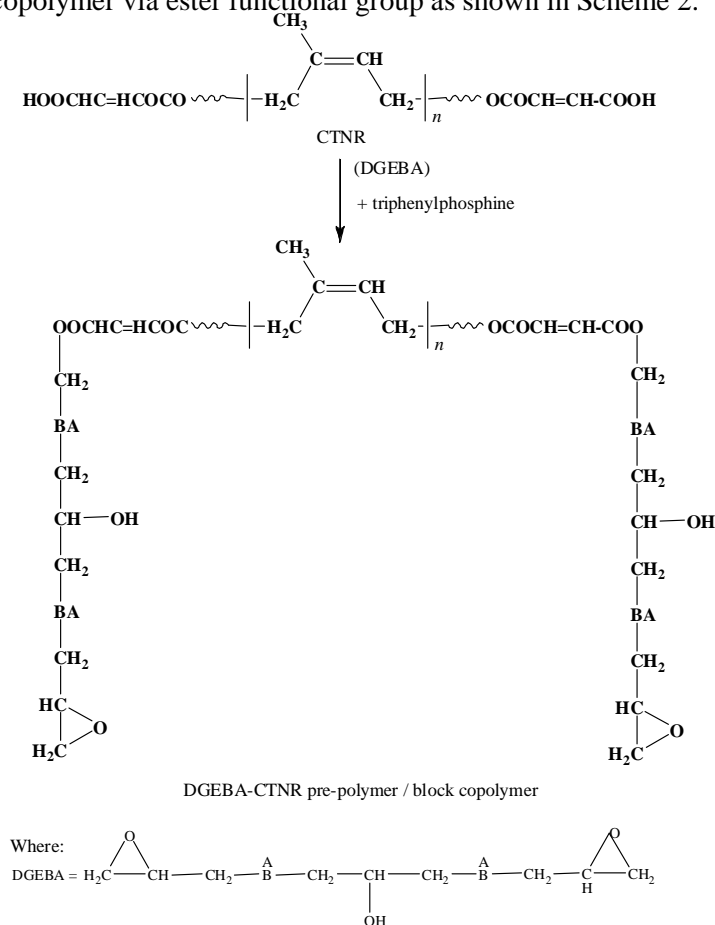
Table 3. Tensile properties of unmodified and modified of DGEBA-based ER with different amount of HTNR or CTNR.

Sample code	impact strength (J m^{-2})	flexural yield stress (MPa)	flexural modulus (MPa)	tensile yield stress (MPa)
P0	9.1 ± 0.7	81.7 ± 0.5	2436	55.7 ± 4.6
P1	10.6± 0.6	76.4 ± 0.3	2227	51.5 ± 3.7
P2	12.3± 0.5	71.2 ± 0.4	2019	50.2 ± 4.6
P3	14.1± 0.4	67.1 ± 0.5	1934	48.6 ± 2.6
P4	11.8± 0.5	65.6 ± 0.2	1919	46.7 ± 3.0
P5	11.0± 0.5	89.6 ± 0.5	2347	86.7 ± 4.1
P6	13.5± 0.3	84.6 ± 0.4	2250	83.3 ± 3.5
P7	17.1± 0.4	77.1 ± 0.2	2278	84.6 ± 2.6
P8	14.7± 0.4	74.1 ± 0.2	2198	79.8 ± 3.2

It can be seen that the modification of DGEBA with both HTNR and CTNR resulted in an improvement of the impact resistance. In general, the impact strength increases with increasing the flexible NR content for both HTNR and CTNR at 5 - 15 %. The increased impact strength can be attributed to the reduction of internal stress due to the stress relaxation by flexible molecular chains of NR, when the samples were subjected to impact. It is verified that the increasing of HTNR or CTBN contents determines an improvement of the impact strength. The impact strength of these materials increased with HTPB or CTNR concentrations, up to 15 phr, but decreased as more elastomers was incorporated. It might be attributed to the agglomeration of NR particles with the increase of the rubber concentration. The presence of agglomerates acts as defects and initiates catastrophic failure. These results allow the conclusion that 15 phr is the maximum content of HTPB or CTNR that might be added in DGEBA composites for a positive effect upon the impact strength.

It is interesting to see from Table 3 that the impact resistance of CTNR-modified DGEBA is better than that of HTNR-modified DGEBA. The reason for this might be due to the reactivity and selectivity of HTNR or CTNR. It is well known that the reactivity and selectivity of the elastomers play an important role in the epoxy curing process. Functional groups must be present in the chain of the rubber in order to promote the formation of chemical bonds with the epoxy matrix, which are necessary for an efficient stress transfer between the rubber particles and the matrix. In the case of HTNR used as an impact modifier for DGEBA system, the elastomer can not react with the epoxy resin because of the low reactivity of the hydroxyls of the HTNR toward the epoxy groups. Whereas, in the case of the CTNR-modified DGEBA system, carboxyl group of the CTNR can readily react with the epoxy groups, especially in the presence

of triphenylphosphine as a catalyst, leading to the formation of DGEBA-CTNR pre-polymer/block copolymer via ester functional group as shown in Scheme 2.

$$\text{HOOCHC=HCOCO} \sim\!\!\sim \left| -H_2C \underset{\underset{\displaystyle CH_2}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C=CH}}}}{} CH_2- \right|_n \sim\!\!\sim \text{OCOCH=CH-COOH}$$

CTNR

(DGEBA)

+ triphenylphosphine

$$\text{OOCHC=HCOC} \sim\!\!\sim \left| -H_2C \underset{}{\overset{CH_3}{\overset{|}{C=CH}}} CH_2- \right|_n \sim\!\!\sim \text{OCOCH=CH-COO}$$

CH₂		CH₂
BA		BA
CH₂		CH₂
CH—OH		CH—OH
CH₂		CH₂
BA		BA
CH₂		CH₂
HC, O		HC, O
H₂C		H₂C

DGEBA-CTNR pre-polymer / block copolymer

Where:

DGEBA = H₂C——CH——CH₂——B̲A̲——CH₂——CH——CH₂——B̲A̲——CH₂——C——CH₂ (with OH and epoxide groups)

Scheme 2. Curic reaction of CTNR with DGEBA.

The carboxyl functionality of CTNR can also react with the secondary hydroxyl groups of the DGEBA-based ER to form diester as depicted in Scheme 3. Therefore, it could be said that the addition of CTNR to the epoxy formulation resulted in a faster curing reaction due to the crosslinking network between ER and CTNR. This might further be attributed that the addition of CTNR in DGEBA/CTBN matrix might accelerate the rate of curing reactions. This could probably because of higher reactivity of epoxy and CTNR. This is the reason why the systems containing CTNR crosslink faster than those consisted of pure DGEBA or HTNR-modified DGEBA as mentioned and discussed above, and also why the impact resistance of CTNR-modified DGEBA is better than that of HTNR-modified DGEBA.

The impact behaviour of the cured epoxy could be explained based on the two-phase nature of the system. According to Buck-nall [19] the rubber particles were considered to bridge the crack as it propagates through the material. Thus, the rubber particles were able to prevent the crack growing to a catastrophic size. The increase in toughness was due to the amount of elastic energy stored in the rubber particles during stretching. Thus, the deformation of the rubber particles in the matrix seemed to be responsible for the enhanced stress transfer and hence impact resistance. Shear yielding of the matrix was another reasonable mechanism that might be operating.

The flexural properties of both DGEBA/HTNR and DGEBA/CTNR systems seem not to be affected by the addition of 5 – 20 % of HTNR or CTNR, when compared to the neat epoxy network.

With regard to tensile strength, it is well known that the addition of soft matters like rubber and polyurethane to ER usually results in reductions of the tensile strength of the modified systems. In the case of DGEBA/HTNR composite, we also observed the reductions of the tensile strength. It is very interesting, however, to see that the best tensile strength has been achieved with DGEBA/CTNR system where CTNR was used as an epoxy modifier. The reason may be the same as discussed above for impact strength. It can be seen from Table 3 that the tensile strength is greatly improved by the addition of CTNR in the range from 5 - 15 phr but decreased as more elastomers was incorporated. It might be attributed to the fact that as the flexible NR content increases, the cross-linking density decreases, leading to the reduction of the tensile strength of the samples.
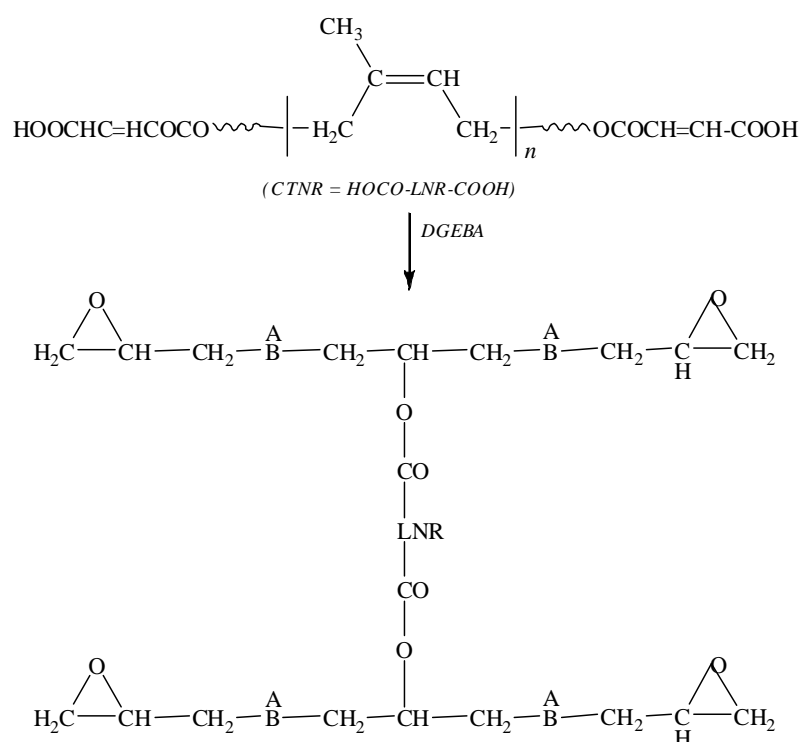
Scheme 3. Curic reaction of CTNR with the secondary hydroxyl groups of DGEBA.

3.3. Morphology

Figure 1 (a,b,c) shows the SEM micrographs of the fractured surface of the unmodified and modified DGEBA with HTNR or CTNR. The pattern of morphology observed for the neat DGEBA (Fig. 5a) were the characteristics of brittle systems having smooth, glassy, and rivery fractured surfaces with ripples in different planes. The relative smoothness of the fractured surface, irrespective of the presence of some shear deformation lines, indicates that no significant plastic deformation had occurred. The morphological development during cure can be correlated with the impact behavior. The ripples are due to the brittle fracture of the network,

which accounts for its poor impact strength, as there is no energy dissipation mechanism operating here.

The micrographs of DGEBA modified with HTNR displayed distinct separated particles of rubber, indicating a heterogeneous two-phase system. The holes observed in the micrograph are related to the rubber particles that were withdrawn from the surface after the treatment with toluene for 12 h, indicating no chemical bond between the blend components. The size and size distribution of the dispersed particle were determined by means of semiautomatic image analysis. The SEM micrographs of the fractured samples were first scanned and converted into digitized images, which were analyzed using an (AnalySIS 3.0 program) to obtain the average diameter values of the dispersed particles, d_n, and the particle size distribution. The results show that the particle size distribution was large, in the range of 0.2 – 12 µm, most of them situated in the range of 5 - 8 µm (Figure 2a).

DGEBA matrix modified with CTNR also presented two-phase morphology in SEM micrograph (Figure 1c), but the size of the domain was considerably smaller than that observed for epoxy-HTNR system and the rubber particle size distribution was more uniform, with particle size diameters in the range between 0.6 to 4 µm (Figure 2b), that might be due to the crosslinking network between epoxy and CTNR occurred as discussed above. In addition, one can observe the presence of several rubber particles that were not extracted with toluene for 12 h, i.e., no holes observed in the micrograph, indicating strong interfacial adhesion and the interaction between the particles. This morphological situation is believed to be responsible for the highest impact performance.
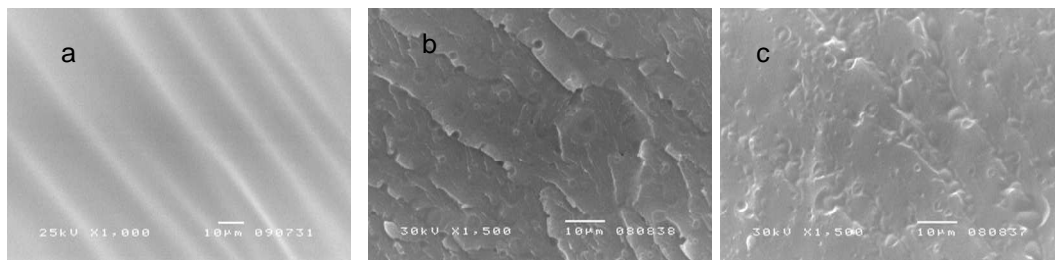

Figure 1. SEMs of the fracture surfaces of the neat DGEBA (a), DGEBA modified with 15 phr of HTNR(b), and DGEBA modified with 15 phr of CTNR(c).
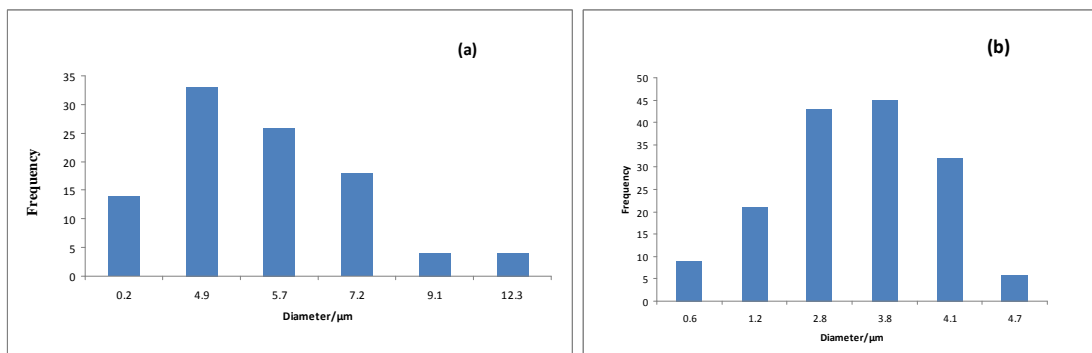

Figure 2. Particle size distribution forDGEBA-based epoxy resin networks toughened with 15 % of (a) HTNR and (b) CTNR.

The SEM micrograph of the DGEBA/ CTNR system containing 20 phr CTNR is shown in Figure 3. It can be seen that with rubber levels higher than the optimum, the second rubbery phase got more and more aggregated. This situation led to flexibilization of the matrix resulting in the reduction of mechanical properties, impact strength and toughness. The fractured surfaces of most of the rubber-toughened epoxy systems have a rigid continuous epoxy matrix with a dispersed rubbery phase as isolated particles. Different mechanisms like crazing, shear bonding and elastic deformation of the rubber particles have been proposed and these mechanisms were thought to act alone or in combination, to produce the toughening effect in rubber-modified epoxies [20].
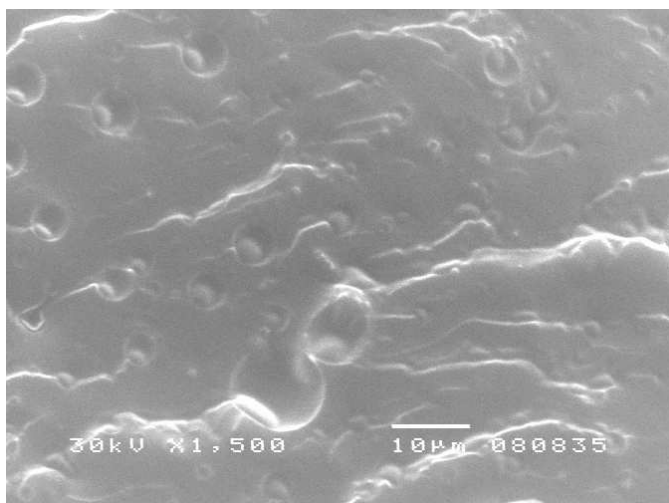

Figure 3. SEM of the fracture surfaces of DGEBA modified with 20 % of CTNR.

4. CONCLUSION

Hydroxyl-terminated liquid natural rubber (HTNR) and carboxyl-terminated liquid natural rubber (CTNR) were used to modify DGEBA-based epoxy resin in order to improve its impact resistance and mechanical performance in terms of flexural and tensile properties. The mechanical properties of the composites were evaluated and compared. The results showed that the impact resistance of both HTNR-modified DGEBA and CTNR-modified DGEBA was superior to that of the pure epoxy resin, among which the impact resistance of CTNR-modified DGEBA was better than that of HTNR-modified DGEBA. For all the composites with HTNR or CTNR, the impact resistance increased with elastomer concentration up to 15 phr. Higher concentration of the elastomers resulted in larger particles and gave lower impact values. These results allow the conclusion that 15 phr is the maximum content of HTNR or CTNR that might be added in DGEBA composites for a positive effect upon the impact strength. The microstructure studies, employing scanning electronic microscopy (SEM), have clearly identified the two-phase nature of the natural rubber-modified DGEBA based epoxy, consisting of rubbery particles embedded in an epoxy matrix and, also, showed excellent dispersion of the elastomeric particles in the epoxy matrix. Both HTNR and CTNR have a potential as a toughening agent for ER, but the use of CTNR in modifying DGEBA is more attractive because of the higher reactivity of the end groups with the epoxide ring which result in shorter gel times.

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TÓM TẮT

HIỆU ỨNG CỦA CÁC LOẠI CAO SU THIÊN NHIÊN LỎNG ĐỐI VỚI SỰ BIẾN TÍNH NHỰA EPOXY TRÊN CƠ SỞ DGEBA

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Hỗn hợp nhựa epoxy trên cơ sở DGEBA và cao su thiên nhiên lỏng có các nhóm hydroxyl (OH) cuối mạch (HTNR) hoặc cao su thiên nhiên lỏng có các nhóm carboxyl CTNR) đã được đóng rắn bằng một loại chất đóng rắn gốc amin. Mục đích của nghiên cứu này là nâng cao các tính năng cơ lí của nhựa epoxy giòn bằng cách biến tính với cao su lỏng. Thông qua sự biến đổi của các tính chất cơ lí như độ bền kéo đứt, độ dãn dài… có thể xác định được hiệu ứng của các loại cao su thiên nhiên lỏng dùng để biến tính. Hình thái học của các mẫu nghiên cứu được xác định bằng SEM và các kết quả được sử dụng để giải thích sự thay đổi của các tính chất chịu va đập. Các kết quả nghiên cứu cho thấy độ bền va đập của cả hai hệ nhựa biến tính là HTNR/ DGEBA và CTNR/DGEBA đều tốt hơn hẳn nhựa epoxy không biến tính, trong đó độ bền va đập của CTNR/DGEBA tốt hơn hệ nhựa biến tính HTNR/ DGEBA. Đối với tất các các loại vật liệu compozit với HTNR hoặc CTNR, độ bền va đập tăng khi nồng độ của các loại cao su thiên nhiên lỏng đến 15 %. Nếu vượt quá nồng độ này các hạt cao su biến tính có kích thước lớn hơn và làm giảm độ bền va đập. Vì vậy 15 % là nồng độ tối ưu của HTPB / CTNR để biến tính nhựa epoxy DGEBA với hiệu ứng biến tính tốt nhất.

Từ khóa: cao su tự nhiên, cao su thiên nhiên lỏng, chịu va đập, tính chất cơ học, FT - IR, nhựa epoxy