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Characterization in the Toughening Process of CTBN Modified Epoxy Resins Induced by Electron Beam Radiation

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ABSTRACT

Epoxy resins are widely utilized as high performance thermosetting resins for many industrial applications but characterized by a relatively low toughness. Electron beam (EB) curing of polymer resins has a number of advantages over conventional thermal curing, such as shorter curing time, low energy consumption, low cure temperature, dimensional stability, reduced manufacturing cost. In the present work liquid carboxyl-terminated butadiene acrylonitrile (CTBN) copolymers containing 8% acrylonitrile is added at different contents to improve the toughness of diglycidyl ether of bisphenol A (DGEBA) epoxy resins using triarylsulfonium hexafluoroanimonate as a photointiator. The EB irradiation was conducted 5 kGy to 250 kGy in nitrogen. The physics properties of CTBN modified epoxy resins were examined by determine gel content, DMA (dynamic mechanical analysis), UTM (Instron model 4443), SEM (scanning electron microscopy).

Key Words: Epoxy resin; CTBN; Electron beam curing; Flexural properties.

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INTRODUCTION

The application of the cured epoxy resins have been expanded in various field such as coatings, adhesives, and other engineering applications. However, a major drawback of epoxy resins is their inherent brittleness due to theirs highly cross-linked structure, which has led to extensive research efforts to improve their low toughness.[1] It is desirable to enhance toughness without adversely affecting the other useful properties of the polymer. Therefore, epoxy resins are usually toughened by modifying with a liquid rubber.[2–8] When epoxy resins together with liquid rubber is cured, the domains of rubber are separated from the epoxy matrix due to the incompatibility between epoxy resin and liquid rubber and liquid rubber modified epoxy resins were improved the toughness by absorbing the impact energy.[7] The morphology of the final modified epoxy resins can significantly affect the toughening mechanism and consequently its fracture toughness.[9,10] Electron beam (EB) curing processes some special features compared with conventional thermal curing such as better controlled process. For example, shorter curing time, low energy consumption, low cure temperature, dimensional stability, reduced manufacturing cost.[11–14] This study investigated that CTBN/DGEBA epoxy resins were irradiated with different radiation dose. To enhance the toughness of the cured epoxy resins, DGEBA epoxy resins were contained with different content of CTBN. The aim of this study can be mechanical properties and gelation effects of CTBN modified epoxy reins induced by electron beam radiation and effectively toughened by the addition of optimum content of CTBN, and large improvements in fracture toughness have been recorded without adversely affecting the other useful properties.

EXPERIMENTAL

Materials

The epoxy monomer used was diglycidyl ether of bisphenol-A (DGEBA) (YD128, supplied by: Viscosity 11500 ~ 13500 cps, Density 1.16 ~ 1.18 g/cm^3, EEW 184 ~ 190 g/eq). The end-functionalized liquid rubber consisted of carboxyl terminated butadiene-acrylonitrile copolymers (CTBN) (Hycar 1300 × 8, supplied by B.F. Goodrich), Hycar CTBN 1300 × 8 with 18% acrylonitrile content and with nominal molecular weights of 3550 g/mol. Triphenylphosphyne (TPP) was used as the catalyst. The photoinitiator used was triarylsulfonium hexafluoroantimonite (TASHFA).

Curing of Epoxy Resin

The CTBN with the DGEBA (60 g CTBN per 100 g DGEBA) was vigorously mixed at 80°C for 2 h. In this reaction, TPP was used as the catalyst. The CTBN modified epoxy resin (5 phr, 10 phr, 15 phr and 20 phr) was added to DGEBA. The unit "phr" is the abbreviation of "part per one hundred base resin" and the base resin, in here, is DGEBA.[7] All samples were radiated using ELV-4 electron beam accelerator with a current 2.5 mA under nitrogen.

Test and Analysis

The gelation of samples was determined by measuring the insoluble content using soxhlet extractor method. The samples were extracted with boiling acetone for 24 h, and dried at 70°C for 24 h in vacuum oven and at 120°C for 24 h in dry oven to a constant weight. The dynamic-mechanical properties were investigated on the dynamic-mechanical analyzer (DMA, DMA 2980, TA instrument Co). The samples were measured from −150°C to 200°C at 1 Hz with a heating rate of 5°C/min. The T_g was identified as the maximum of the tan δ curves. In order to get a deeper understanding on the effect of morphology on the fracture mechanical response the surface of cured epoxy resins was inspected in a scanning electron microscopy (SEM) (XL Series30S, Philips Co). Specimen fractured surfaces were coated with a thin layer of gold palladium alloy by sputtering to provide a conductive surface. The flexural strength was measured with 3-point bending method (ASTM D 790) by an Instron 4443 universal test machine at room temperature. The cross head speed of Instron was 0.8 mm/min (1.33×10^{-5} m/sec). The size of the specimens were 50 × 25 mm, the thickness was about 0.6 mm.

RESULTS AND DISCUSSION

Gelation Effect of CTBN Modified Epoxy Resin

The gelation of CTBN modified epoxy resins radiated with different dose were measured by using soxhlet extractor method, as shown in Fig. 1. It can be seen that cross-linking reactions proceeded continuously and gelation in the resins increased with

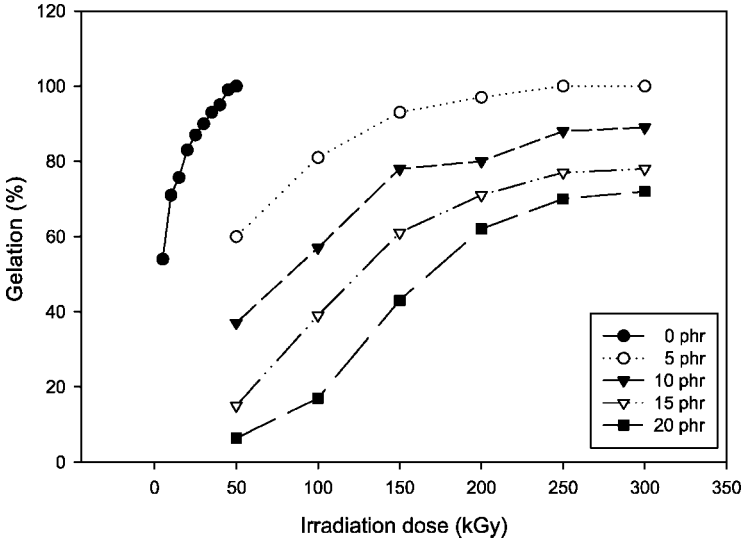

Figure 1. Gelation of CTBN modified epoxy resins with increasing content of CTBN (content of TASHFA is 5 wt%).

increasing of radiation dose. The gelation of epoxy resin without CTBN reached 100% at 50 kGy radiation dose. However, the gelation of CTBN modified epoxy resins decreased with increasing content of CTBN. When radiation dose is 250 kGy, the gelation of 5 phr CTBN modified epoxy resin is 91% and 20 phr CTBN modified epoxy resin is 70%. When polymers are subjected to ionizing radiation crosslinking and main chain scission are usually observed. The processes ultimately cause formation of insoluble gel if crosslinking predominates over scission. Charlesby–Pinner first obtained a simple expression[1] relating sol fraction, S, to absorbed dose D:

$$S + S^{1/2} = po/qo + 2/(qo\,u\,D) \tag{1}$$

where po is degradation density, average number of main chain scissions per monomer unit and per unit dose. qo is crosslinking density, proportion of monomer units crosslinked per unit dose, u is initial weight average degree of polymerization. A plot of $S+S^{1/2}$ gives an idea of the ratio of chain scission to crosslinking. A sol-gel analysis has been performed to quantitate the fraction of radiation-induced insoluble epoxy resins. The soluble fraction (S) of epoxy discerned from this analysis is presented as a function of 1/D in Fig. 2. Figure 2 shows the dependence of $S+S^{1/2}$ of CTBN modified epoxy resins with increasing content of CTBN. The high value of ratio for CTBN modified epoxy resin with decrease CTBN content compared with that for CTBN modified epoxy resin with increase CTBN content. The T_g was identified as the maximum of the tan δ curves. Figure 3 depicts the T_g and gelation of 10 phr CTBN modified epoxy with increasing radiation dose. The gelation of 10 phr CTBN modified epoxy resin increased according to increasing radiation dose and T_g are shifted to higher temperature with increasing radiation dose. Figure 4 shows the gelation and T_g of 10 phr CTBN modified epoxy resin irradiated at 250 kGy with increasing content of TASHFA. The gelation of 10 phr CTBN modified epoxy resin containing 5 wt% TASHFA is 88% and that of containing 3 wt% TASHFA is 74%. The T_g

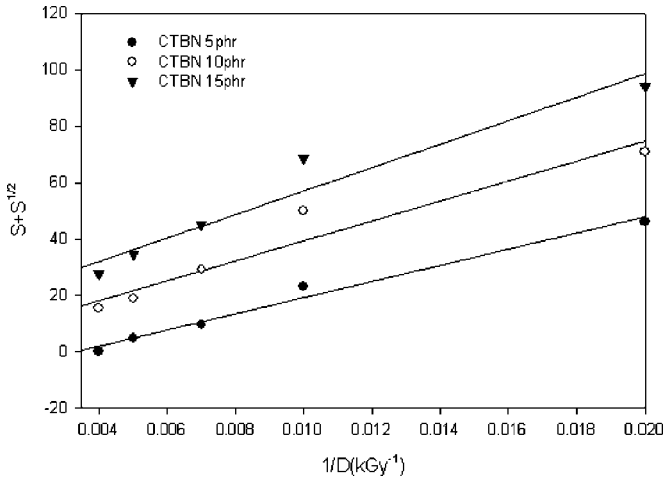

Figure 2. The dependence of $S+S^{1/2}$ of CTBN modified epoxy resins with increasing content of CTBN (content of TASHFA is 5 wt%).

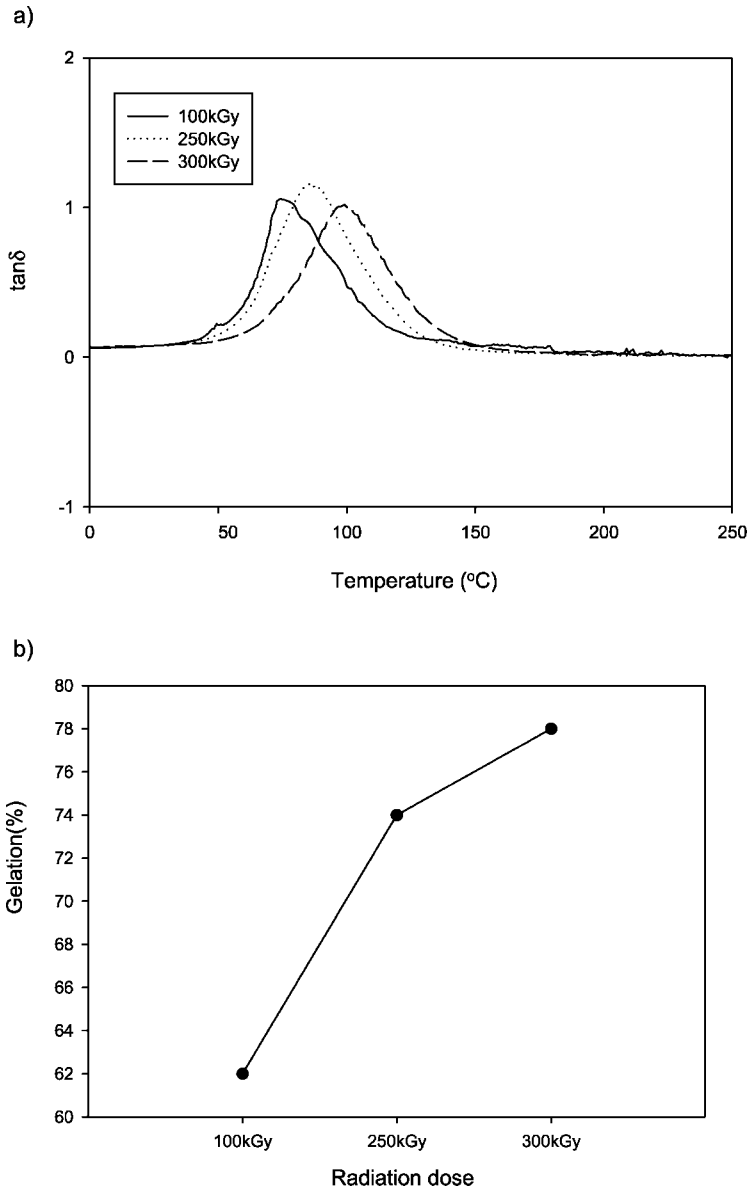

Figure 3. The comparison a)DMA curves and b)gelation of 10 phr CTBN modified epoxy resin with increasing radiation dose (content of TASHFA is 3 wt%).

of 10 phr CTBN modified epoxy resins are shifted to higher temperature with increasing contents of TASHFA. It is directly associated with increasing gelation because molecular mobility decreased to the cross-linking of the materials due to the radiation dose and initiator. This proves that high dose of irradiation and increase of initiator induces further

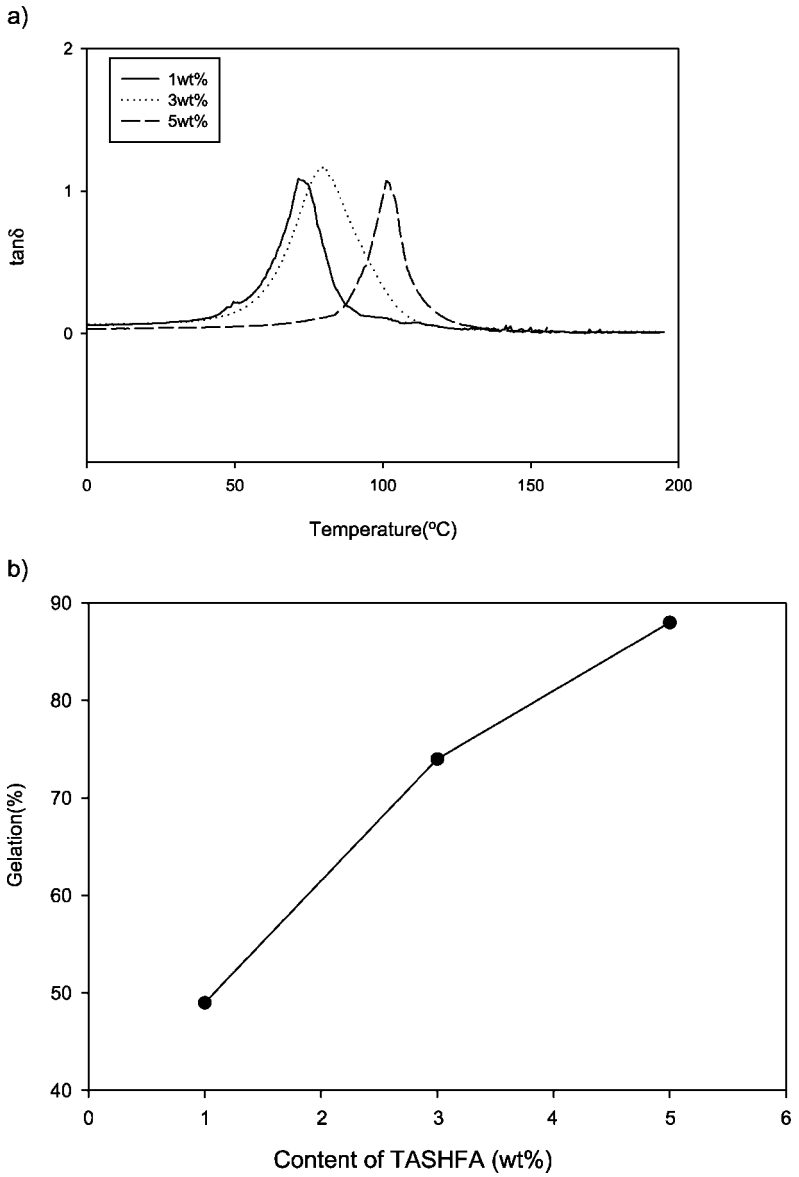

Figure 4. The comparison a)DMA curves and b)gel fraction with increasing content of TASHFA (content of CTBN is 10 phr and radiation dose is 250 kGy).

cross-linking of the materials (Figs. 1–4). This result can be seen from Fig. 5. Figure 5 shows the T_g of CTBN modified epoxy resin with increasing content of CTBN. The gelation of CTBN modified epoxy resin decreased with increasing content of CTBN (Fig. 1). The T_g of CTBN modified epoxy resin are shifted to lower temperature according to increasing content of CTBN and decreasing gelation.

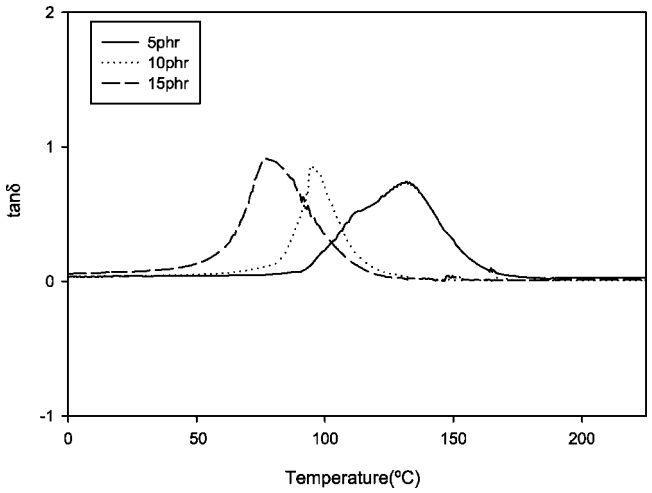

Figure 5. The DMA curves of CTBN modified epoxy resins with increasing content of CTBN (content of TASHFA is 5 wt% and radiation dose is 250 kGy).

Fractography of CTBN Modified Epoxy Resin

The morphology of CTBN modified epoxy resins can significantly affect the toughening mechanism and consequently, its fracture toughness. Figure 6 represents SEM micrograph of notched impact fractured epoxy resin without CTBN. The gelation of the sample is 100% (Fig. 1). The smooth surface indicates that this specimen fractured in a brittle manner. It was no special feature and no significant plastic deformation had occurred. Figure 7 shows fractured surfaces of CTBN modified epoxy resin with increasing content of CTBN. The domains of rubbers were uniformly distributed through the matrix. Small amount of deformation lines and the smooth surfaces are observed. The bright interfacial layer around the rubber domains may indicate rubber particles. Higher CTBN concentrations produced many bright interfacial layers. This feature of CTBN modified epoxy resins correlation with morphology generated by phase separation induced by curing.[9] When the fracture surfaces in these micrographs are compared with Fig. 6, it was observed that epoxy resin without CTBN has no interfacial layers. Therefore, these brighter domains may be attributed to weak interaction between rubber particles and epoxy matrix.[10] This proves that gelation of modified CTBN epoxy resins decreases with increasing contents of CTBN (Fig. 1).

Flexural Properties of CTBN Modified Epoxy Resins

Figure 8 shows strain at yield of CTBN modified epoxy resins according to increasing content of CTBN. It can be seen that strain at yield of CTBN modified epoxy resins drastically increased with increasing content of CTBN. Figure 9 shows the stress at yield of CTBN modified epoxy resin. It was observed that the stress at yield decreased according to

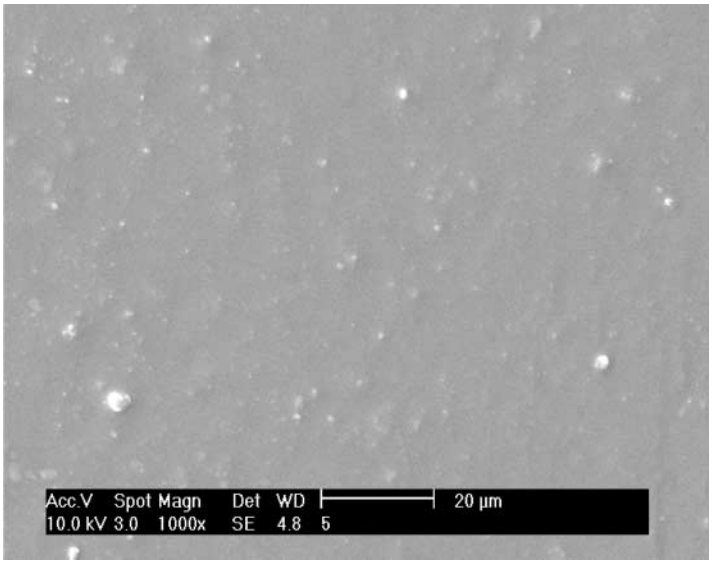

Figure 6. SEM micrographs of fracture surfaces of epoxy resin without CTBN (content of TASHFA is 5 wt%, and the radiation dose is 50 kGy).

increase content of CTBN. Specially, the stress at yield of 15 phr CTBN modified epoxy resin drastically decreased. But the stress at yield of 5 phr and 10 phr CTBN modified epoxy resin had almost the same value as that of epoxy resin without CTBN. Figure 10 depicts Young's modulus CTBN modified epoxy resins with increasing content of CTBN. Also, Young's modulus of CTBN modified epoxy resins had the same result as Fig. 9 and that of 15 phr CTBN modified epoxy resin drastically decreased. Figure 11 represents the stress vs. strain curves of CTBN modified epoxy resins. Brittle fracture is evidenced for epoxy resin without CTBN absence of yield point. However, the 15 phr and 20 phr CTBN modified epoxy resin exhibit a ductile deformation with appearance of an upper yield point. When the epoxy resins were contained CTBN above 15 phr, stress at yield was too small and characteristics of epoxy resin lost. Specifically, a characteristic of rubbers is too strong. However, stress at yield of 10 phr CTBN modified epoxy resin had almost the same value and strain at yield increased in case of more than that of epoxy resin without CTBN. This result can be seen from Fig. 12. Figure 12 shows the toughness at yield of CTBN modified epoxy resin. The stress at yield of CTBN modified epoxy resins improved with increasing content of CTBN. Generally, 10 phr of CTBN modified epoxy resin had the highest toughness at yield. However, gel fraction and toughness of epoxy/CTBN system decreased significantly with the further addition of CTBN because of separation of CTBN from epoxy resin. It is well known that in order to toughen an epoxy resin with a liquid rubber, first, the liquid rubber should form a rubbery second phase which is dispersed throughout the matrix and second, the rubbery second phase should be bonded to the matrix through the functional groups of the liquid rubber.[2] The magnitude of this optimum value is expected to depend on compatibility between epoxy resin and rubber. 10 phr CTBN modified epoxy resin is expected to have the highest compatibility between epoxy resin and CTBN.

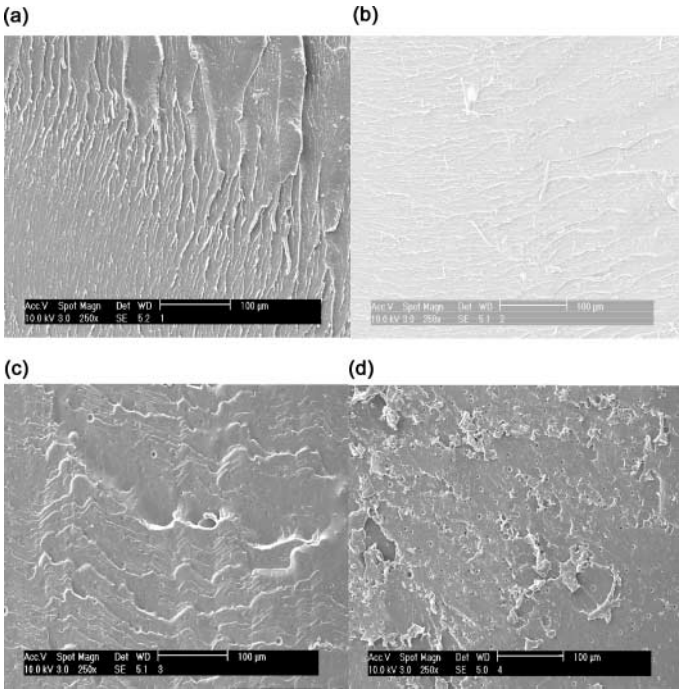

Figure 7. SEM micrographs of fracture surfaces of materials of irradiated at 250 kGy with CTBN a) content of CTBN is 5 phr b) content of CTBN is 10 phr c) content of CTBN is 15 phr d) content of CTBN is 20 phr.

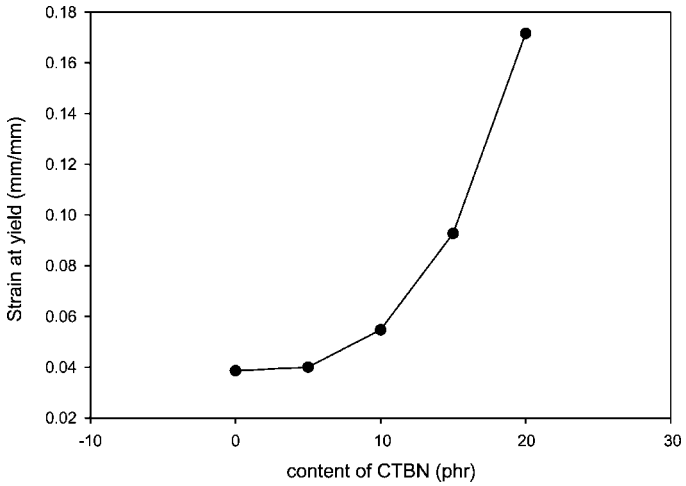

Figure 8. Strain at yield of BPA/CTBN resins with increasing content of CTBN. (content of TASHFA is 5 wt% and radiation dose is 250 kGy).

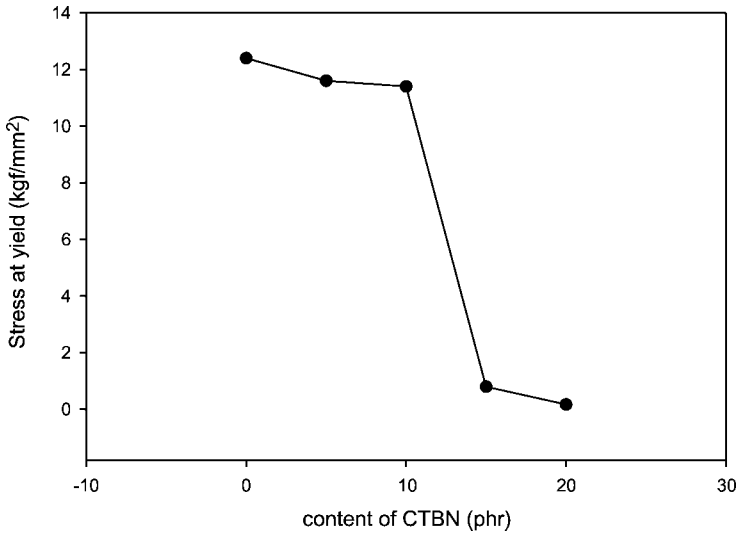

Figure 9. Stress at yield of BPA/CTBN resins with increasing content of CTBN. (content of TASHFA is 5 wt% and radiation dose is 250 kGy).

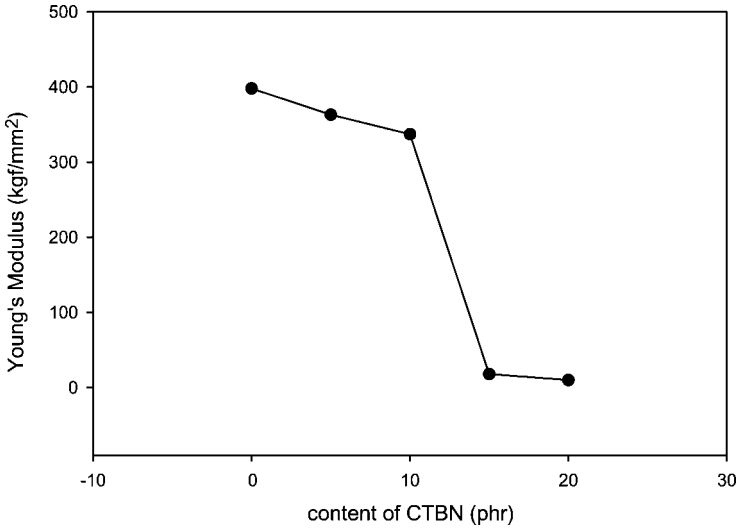

Figure 10. Young's modulus of CTBN modified epoxy resins with increasing content of CTBN. (content of TASHFA is 5 wt% and radiation dose is 250 kGy).

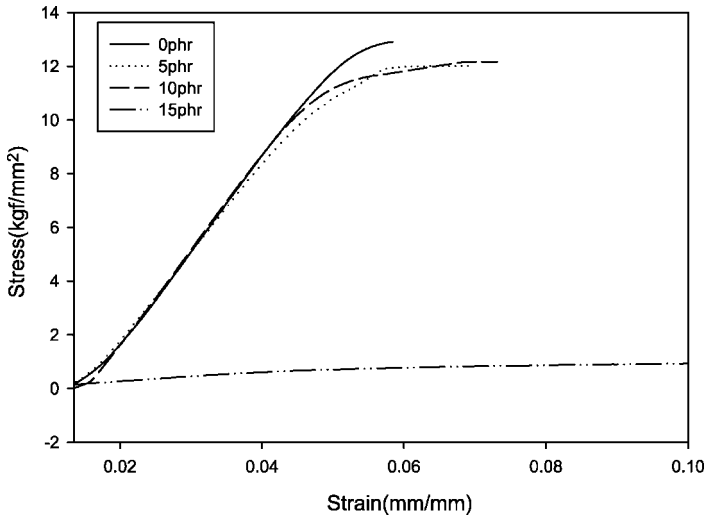

Figure 11. Stress–Strain curve of BPA epoxy resins with increasing content of CTBN (the sample of CTBN 0 phr is irradiated 50 kGy and the others are irradiated 250 kGy and content of TASHFA is 5 wt%).

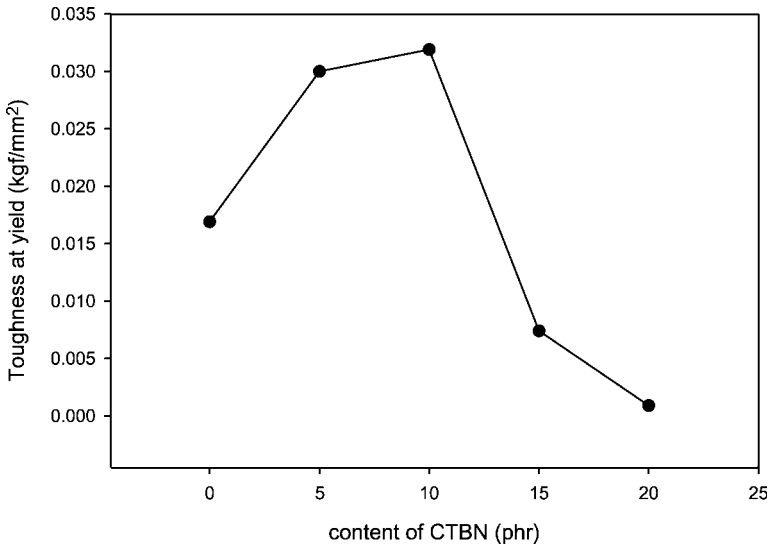

Figure 12. Toughness at yield of CTBN modified epoxy resins with increasing content of CTBN (content of TASHFA is 5 wt% and radiation dose is 250 kGy).

CONCLUSIONS

The effects of irradiation, gelation, content of CTBN and morphology on the characteristics of CTBN modified epoxy resin were investigated. The gelation of CTBN modified epoxy resins increased with increasing radiation dose, but decreased with increasing content of CTBN. Also, tan δ peaks are shifted to higher temperature with according to gelation. It is directly associated with increasing gelation because molecular mobility decreased to the cross-linking of the materials. The morphology of CTBN modified epoxy resins can significantly affect the toughening mechanism and consequently its fracture toughness. The bright interfacial layer around the rubber domains may indicate rubber particles. Higher CTBN concentrations produced many bright interfacial layers. This feature of CTBN modified epoxy resins correlation with morphology generated by phase separation induced by curing. The displacement at yield and strain at yield of CTBN modified epoxy resins drastically increased with increasing content of CTBN. The stress at yield and Young's modulus of CTBN modified epoxy resins improved with increasing content of CTBN. Specially, those of 15 phr CTBN modified epoxy resin drastically decreased. Brittle fracture is evidenced for epoxy resin without CTBN absence of yield point in the stress versus strain curves of CTBN modified epoxy resins. However, the 15 phr and 20 phr CTBN modified epoxy resin exhibit a ductile deformation with appearance of an upper yield point. When the epoxy resins were contained CTBN above 15 phr, stress at yield was too small and characteristics of epoxy resin lost. Specially, a characteristic of rubbers is too strong. 10 phr CTBN modified epoxy resin had the highest toughness at yield. However, toughness at yield of CTBN modified epoxy resin containing above 15 phr drastically decreased. The magnitude of this optimum value is expected to depend on compatibility between epoxy resin and rubber.

ACKNOWLEDGMENTS

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REFERENCES

1. Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw-Hill: New York, 1967.
2. Chikhi, N.; Fellahi, S.; Bakar, M. Modification of epoxy resin using reactive liquid (ATBN) rubber. Eur. Polym. J. **2002**, *38*, 251–264.
3. Mitsukazu, O.; Takahide, M.; Shinobu, K.; Miyuki, H. Network chain orientation in the toughening process of the elastomer modified mesogenic epoxy resin. Polymer **2001**, *42*, 9687–9695.
4. Wise, C.W.; Cook, W.D.; Goodwin, A.A. CTBN rubber phase precipitation in model epoxy resins. Polymer **2000**, *41*, 4625–4633.
5. Pearce, P.J.; Morris, C.E.M.; Ennis, B.C. Rubber toughening of practical tetraglycidyl methylenedianiline–piperidine adduct systems. Polymer **1996**, *37*, 1137–1150.

6. Morancho, J.M.; Salla, J.M. Relaxation in partially cured samples of an epoxy resin and of the same resin modified with a carboxy-terminated rubber. Polymer **1999**, *40*, 2821–2828.
7. Lee, J.Y.; Shim, M.J.; Kim, S.W. Effect of modified rubber compound on the cure kinetics of DGEBA/MDA system by Kissinger and isoconversional methods. Thermochim. Acta **2001**, *371*, 45–51.
8. Gryshchuk, O.; Jost, N.; Karger-Kocsis, J. Toughening of vinylester-urethane hybrid resins by functional liquid nitrile rubbers and hyperbranched polymers. Polymer **2002**, *43*, 4763–4768.
9. Auad, M.L.; Frontini, P.M.; Borrajo, J.; Aranguren, M.I. Liquid rubber modified vinyl ester resins: fracture and mechanical behavior. Polymer **2001**, *42*, 3723–3730.
10. Ozturk, A.; Kaynak, C.; Tincer, T. Effects of liquid rubber modification on the behavior of epoxy resin. Eur. Polym. J. **2001**, *37*, 2353–2363.
11. Glauser, T.; Johansson, A.; Hult, A. Electron-beam curing of thick thermoset composite matrices. Polymer **1999**, *40*, 5297–5302.
12. Mohamad, A.S.; William, L.M. On the mechanisms of radiation-induced curing of epoxy-fiber composites. Radiat. Phys. Chem. **1996**, *48*, 201–206.
13. Lopata, V.J.; Saunders, C.B.; Singh, A.; Janke, C.J.; Wrenn, G.E.; Havens, S.J. Electron-beam curable epoxy resins for the manufacture of high-performance composites. Radiat. Phys. Chem. **1999**, *56*, 405–415.
14. Korenev, S. Electron beam curing of composites. Vaccum **2001**, *62*, 233–236.
15. Charlesby *Atomic Radiation on Polymers*; Pergamon Press: Oxford, 1960.

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