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Effect of Electron Beam and γ-Ray Irradiation on the Curing of Epoxy Resin

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Abstract: The effect of an electron beam and γ-ray irradiation on the curing of epoxy resins was investigated. Diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether of bisphenol F (DGEBF) as epoxy resin were used. The epoxy resins containing 1.0-3.0 wt% of triarylsulphonium hexafluoroantimonate(TASHFA) and triarylsulphonium hexafluorophosphate(TASHFP) as initiator were irradiated under nitrogen at room temperature with different dosage of EB and γ-rays from a Co^{60} source. The chemical and mechanical characteristics of irradiated epoxy resins were compared after curing of EB and γ-ray irradiation. The thermal properties of cured epoxy were investigated using dynamic mechanical thermal analysis. The chemical structures of cured epoxy were characterized using near infrared spectroscopy. Mechanical properties such as flexural strength, modulus were measured. The gel fraction of DGEBA with γ-ray was higher than that of the epoxy with EB at the same dose. Young's modulus of the sample irradiated by γ-ray is higher than that of sample cured by EB. From the result of strain at yield, it was found that the epoxy cured by γ-ray had a higher stiff property compared with the irradiated by EB.

Keywords: epoxy resins, electron beam, γ-ray irradiation, curing, initiator.

Introduction

Epoxy resins are the most important thermosetting polymers widely used as matrices in reinforced composites, adhesives in the aerospace industry, surface coatings, etc.[1-3] The use of electron beam (EB) to initiate polymerization reactions is one area on which much interest has focused.[4] There has been a considerable development about the EB curing advanced composites for the use of aerospace and other industries. The EB curing of composites offers many advantages compared with conventional thermal curing, such as a reduced cure time, ambient temperature cure, greater design flexibility, and an unlimited material shelf life.[5-9] Crivello *et al.* studied the cationic curing of epoxy reins using onium salts as initiator.[10,11] Most varieties of epoxy resin have been confirmed to possess radiation reactivity and have already become chief resin matrix used in EB curable composites.[12-14] But not many works about fundamental investigation of EB and γ-irradiation on physical properties of cured epoxy resins have been reported. The majority of studies focus on the polymerization of epoxy resins by irradiation. It is important to understand differences between EB and γ-irradiation on curing of epoxy. Therefore in this study, the radiation process of epoxy was investigated to elucidate clearly EB and γ-irradiation effect on curing of epoxy. In the present work, irradiation was carried out up to 50 kGy with EB and γ-rays. The chemical and mechanical characteristics of irradiated epoxy resins were compared after curing of electron beam and γ-ray irradiation. The thermal properties of cured epoxy were investigated using dynamic mechanical thermal analysis. The chemical structures of cured epoxy were characterized using near infrared spectroscopy. Mechanical properties such as flexural strength, modulus were measured.

Experimental

Materials. Diglycidyl ether of bisphenol A (DGEBA) (YD128, viscosity: 11,500-13,500 cps) and diglycidyl ether of bisphenol F (DGEBF)(YDF170, viscosity: 2,000-5,000 cps) supplied by the Kukdo Chemical Co., Ltd. Korea were used as base epoxy resins. Triarylsulphonium hexafluoroantimonate (TASHFA) and triarylsulphonium hexafluorophosphate (TASHFP) as cationic initiator were supplied by Aldrich Chemical Co. USA.

Manufacturing and Procedure of Radiation. The initiator was mixed with epoxy resins uniformly at 70 °C. The epoxy-initiator mixture was poured into an aluminum molding with 150× 150× 2 mm which was treated with a release

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agent and then cured by electron beam and γ-ray. Irradiation was carried out at a dose rate of 10 kGy/h with γ-rays from a Co^{60} source, while electron beams were irradiated at a dose rate 7500 kGy/h using ELV-4 accelerator (energy: 1 MeV, current: 2.5 mA) of EB Tech Co., Ltd. Korea in nitrogen atmosphere, respectively. The EB and γ-ray irradiation were performed up to 50 kGy.

Curing Measurement. The gel fraction of irradiated epoxy was determined by the extraction method. Samples were extracted with boiling acetone for 24 h, then it was dried in vacuum at 80 °C.

FT-NIR Analysis. To estimate epoxy conversion after radiation curing, the transmission NIR spectra of the samples cured by irradiation were recorded with an Vector 22/N NIR spectrometer (Bruker Optik GmbH, Germany) in the range 4000-7000 cm^{-1}.

Flexural Test. The mechanical properties of the cured epoxy resin were evaluated by a flexural test. The flexural strength was measured with 3-point bending method (ASTM D 790) by an Instron 4443 universal test machine at room temperature. The size of the specimens was 50× 25 mm, the thickness was about 0.6 mm, and the cross head speed was 0.8 mm/min.

DMA Test. The dynamic mechanical properties were investigated on the dynamic mechanical analyzer (DMA, DMA 2980, TA instrument Co. USA). The samples were measured from -150 to 250 °C. The storage modulus(E'), the loss modulus (E''), and tanδ were measured as a function of temperature by DMA with a double cantilever geometry at a constant frequency of 1 Hz and a heating rate of 5 °C/min. The T_g was identified as the maximum of the tanδ curves.

Temperature Evolution from the Curing Reaction. The temperature of the epoxy during curing was measured with a thread thermocouple and recorded by a Fluke-2000 equipment.

SEM Measurement. SEM (XL30S, Philips Co., Netherlands) was used to observe the cross-section of cured epoxy resin. The fracture surfaces were gold coated.

Results and Discussion

Influence of Irradiation on the Curing of Epoxy. To ascertain the effect of irradiation dose on the curing of epoxy resin, the gel fraction of irradiated epoxy was determined by the extraction method. Figure 1 shows the effect of absorbed dose on the gel fraction of DGEBA and DGEBF with TASHFA by EB under N_2 atmosphere. It can be seen that, the gel fraction of two epoxy resin increases markedly with the increase of dose, and that the values of gel fraction of DGEBF samples are higher than that of DGEBA. It is directly associated with the structure of epoxy resin such as molecular weight and viscosity. DGEBF has a lower molecular weight and viscosity relating the mobility of the epoxy than DGEBA. According to Anseth,[15] a significant amount of unreacted active groups are present in radiated systems due to fact that the mobility of the monomers is reduced.

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[16] first obtained a simple expression(1) relating sol fraction, S, to absorbed dose D:

$$S + S^{1/2} = p_o / q_o + 2/(q_o\, u\, D) \quad (1)$$

where p_o is degradation density, average number of main chain scissions per monomer unit and per unit dose. q_o 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. Therefore we used it to analyze the radiation crosslinking of DGEBA and DGEBF. 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 Figure 2. Figure 2 presents the result of sol-gel analysis referring to the radiation crosslinking of DGEBA and DGEBF with initiator TASHFA. The much lower value of the ratio for DGEBF(0.24) compared with that for DGEBA(0.58) supports the increased crosslinking DGEBF system at the lower radiation doses used.

The gel fraction was measured for the DGEBA γ-irradiated and EB at room temperature in N_2 atmosphere. The result is shown in Figure 3. It can be seen that crosslinking reactions proceeded continuously and the gel fraction of DGEBA increased up to 100% by irradiation to 50 kGy regardless of irradiation type. When the DGEBA was irradiated by γ-ray to a dose above 20 kGy, the gel fraction is over 90%. The gel fraction of DGEBA with a γ-ray was higher

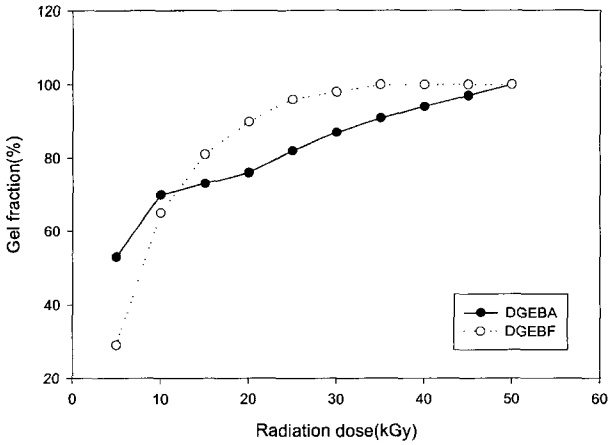

Figure 1. Gel fraction of DGEBA and DGEBF containing TASHFA irradiated by EB in N_2.

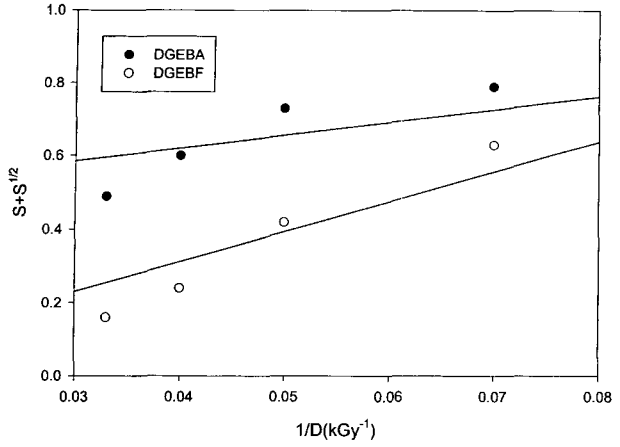

Figure 2. The dependence of $S + S^{1/2}$ of DGEBA and DGEBF on $1/D(\text{kGy}^{-1})$.

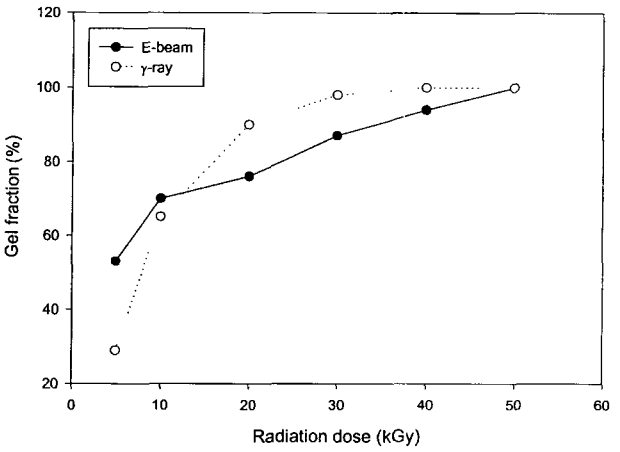

Figure 3. Gel fraction of DGEBA containing TASHFA (2.0 wt%) irradiated by EB and γ-ray in N_2.

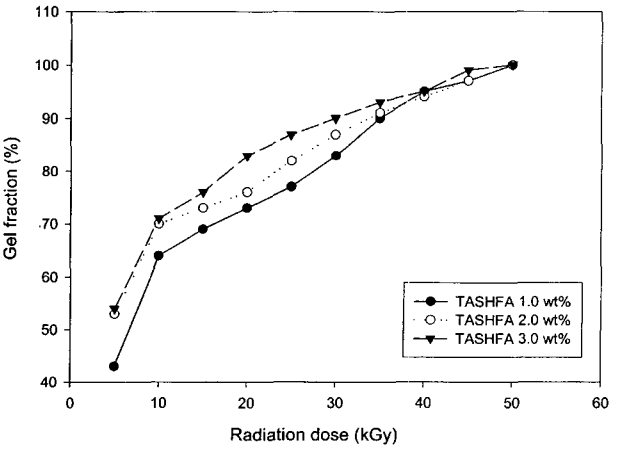

Figure 4. Gel fraction of DGEBA containing TASHFA irradiated by EB N_2.

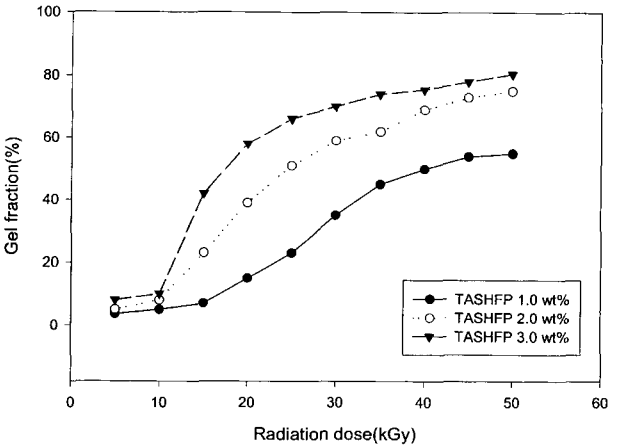

Figure 5. Gel fraction of DGEBA containing TASHFP by EB in N_2.

than that of the epoxy with EB at the same dosage. The difference between electron beam and γ-ray irradiation is different distribution of radicals in the irradiated materials.[17] γ-ray irradiation produces radicals almost homogeneously throughout the cross-section of the irradiated specimen, while irradiation with electron beams yields radicals mostly localized at the subsurface region at much higher densities than γ-ray irradiation. As consequence, the radical disappearance due to radical recombination will be much faster for the polymer irradiated with electron beams because of the higher radical density.

Influence of Initiator on Curing of Epoxy. Figures 4 and 5 show the effect of irradiation dose on the gel fraction for DGEBA containing TASHFA and TASHFP as initiator. As mentioned above, in this work, initiators used for radiation curing of epoxy were TASHFA and TASHFP. The concentrations of the initiator were 1.0, 2.0, and 3.0 wt%. As shown in Figure 4, the more the absorbed radiation dose and content of initiator were, the higher the gel fractions of the sample were. Figure 5 shows a gel fraction of the sample containing TASHFP. It was found that the use of TASHFA gave a positive effect on gel fraction compared with that of TASHFP. Janke *et al.*[5] reported the effectiveness of the initiator on radiation curing of epoxy. They described that the effectiveness of catalyst is immensely related to the nucleophilicity of the counteranion. The catalysts incorporating weaker nucleophilicty anion are generally more efficient, because they generate the stronger acid. The effect of the counteranion has been described in the literature: SbF_6^- > AsF_6^- > PF_6^- > BF_6^-.

Figures 6 and 7 show the effect of irradiation dose on the gel fraction for DGEBF containing TASHFA and TASHFP as initiator. The gel content of the sample increased with irradiation does regardless of initiator. The gel fraction increased drastically up to 30 kGy, and increased steadily as the absorbed dose increased to 50 kGy. The sample contain-

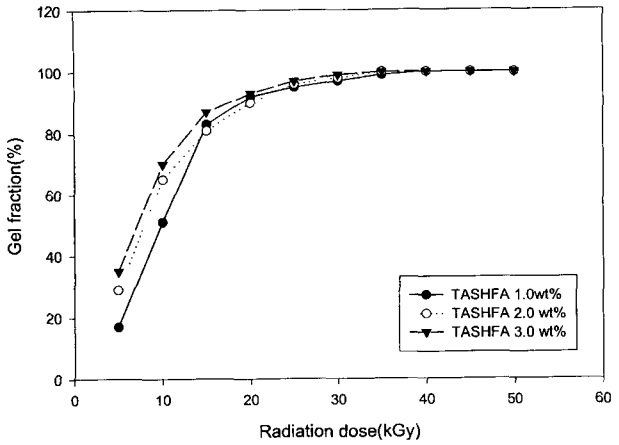

Figure 6. Gel fraction of DGEBF containing TASHFA irradiated by EB in N_2.

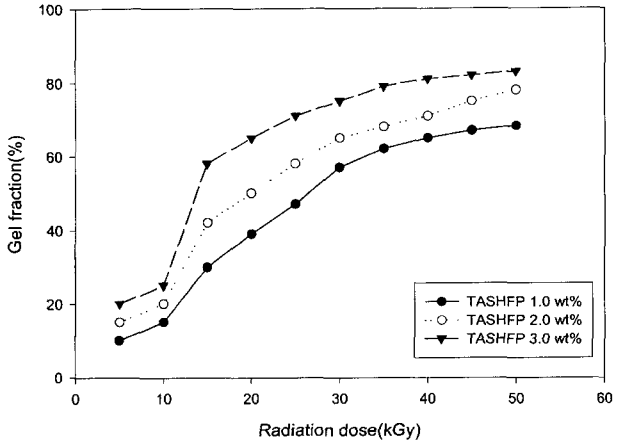

Figure 7. Gel fraction of DGEBF containing TASHFP irradiated by EB in N_2.

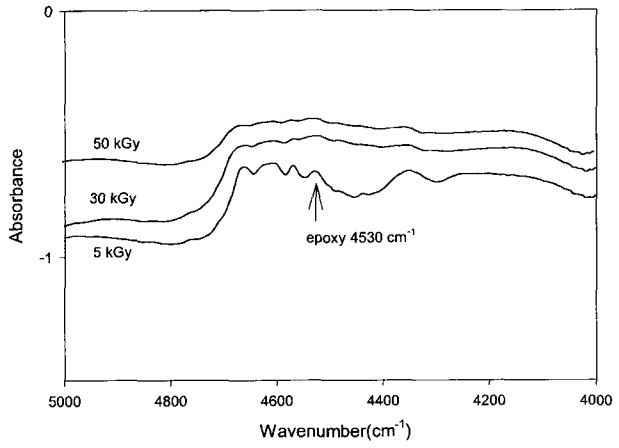

Figure 8. NIR spectra of DGEBF containing TASHFA irradiated by EB in N_2.

ing TASHFP had a lower gel fraction value compared with TASHFA. These results agree well with previous observations, showing the effect of the counteranion ($SbF_6^- > AsF_6^- > PF_6^- > BF_6^-$). The more the content of initiator in resin systems, the higher the concentration of reactive species under the same doses of radiation and the faster curing reaction rate.

Figures 8 and 9 show the NIR spectra of DGEBF containing TASHFA irradiated by EB and γ-ray. Min *et al.*[18] found epoxy absorption peaks at 4530 cm^{-1} in the DGEBA/DDS system. The reactions that occur during the curing process change the final epoxy network based on curing condition such as irradiation dose. The peak of epoxy group at 4530 cm^{-1} disappeared with increasing radiation dose as shown in Figures 8 and 9.

Influence of Radiation on Physical Properties of Epoxy. Figure 10 shows T_g of DGEBF/TASHFA and

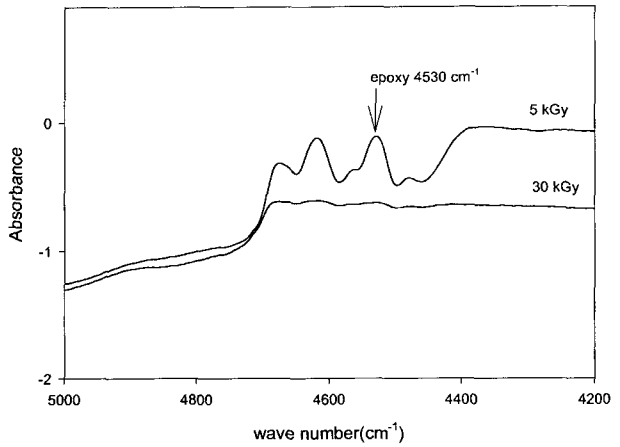

Figure 9. NIR spectra of DGEBF containing TASHFA irradiated by γ-ray in N_2.

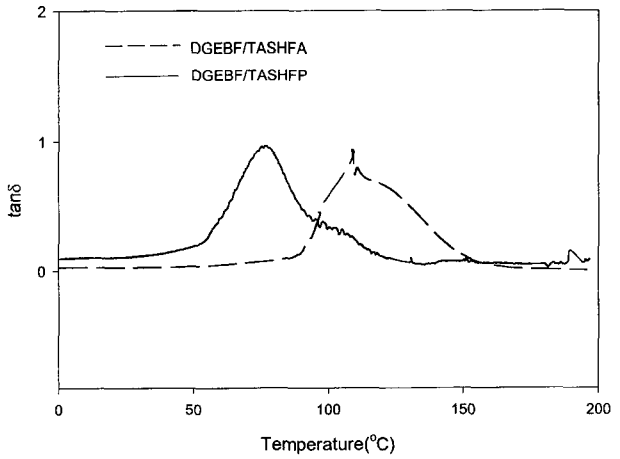

Figure 10. The tanδ as finction of temperature for DGEBF/TASHFA and DGEBF/TASHFP irradiated by EB in N_2, content of initiator: 2.0 wt%, and the irradiation dose: 50 kGy.

DGEBF/TASHFP. The gel fraction of DGEBF/TASHFA is higher than that of DGEBF/TASHFP as shown in Figures 6 and 7. T_g of these radiated epoxy resins increased with increasing gel fraction. It was found that the degree of curing is an important factor which can affect T_g of epoxy resin. Figure 11 shows change of exothermic temperature of the epoxy during curing by EB at 50 kGy. The heat formation during the curing of epoxy by radiation is mainly governed by the enthalpy of polymerization and the heat dissipation to the environment or the mold. The exotherm due to the polymerization occurs mainly during the first sweep of the radiation.[19] Comparing the polymerization of DGEBF/TASHFA with DGEBA/TASHFA, it was shown that both heat of polymerization and propagation rate of DGEBF was substantially larger than those of DGEBA. This means that DGEBF resin may produce more heat and polymerize more rapidly.

Figure 12 shows Young's modulus of DGEBF containing TASHFA irradiated by γ-ray and EB in N_2 as a function of radiation dose. The Young's modulus of the cured sample increases continuously with the radiation dose. It can be seen that Young's modulus of the sample irradiated by γ-ray is higher than that of sample cured by EB. Figure 13 shows the strain at yield of cured epoxy resin. The strain at yield of epoxy resin irradiated by EB drastically decreases with increasing irradiation dose. From the result of the strain at yield, it was found that the epoxy cured by γ-ray had a higher stiff property compared with the irradiated by EB. The strain at yield decreased owing to the increase in crosslinking structure of the epoxy resin as irradiation dose increased. As shown in Figures 14 and 15, the stress at yield of DGEBF and DGEBA increases with increasing irradiation dose. The stress at yield of DGEBF with 100% of gel fraction by irradiation at 40 kGy is higher than that of irradiated DGEBA with 100% of gel fraction by irradiation at 50 kGy.

The SEM was used to observe the cross-section of cured

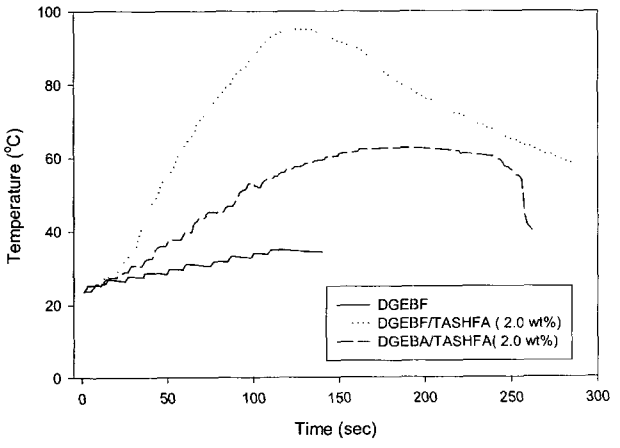

Figure 11. Thermogram of DGEBA and DGEBF irradiated at 50 kGy by EB in N_2.

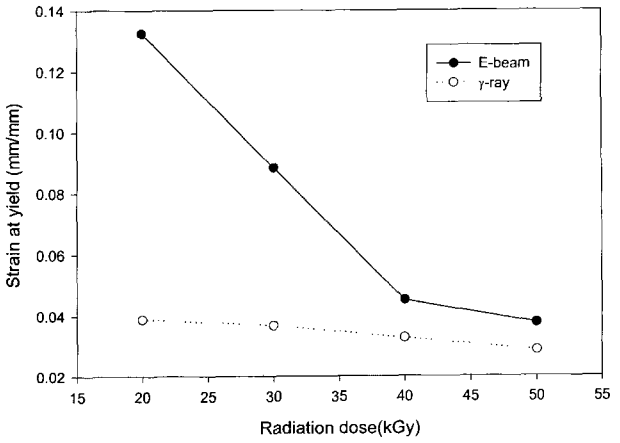

Figure 13. Strain at yield DGEBF/TASHFA irradiated by γ-ray and EB in N_2.

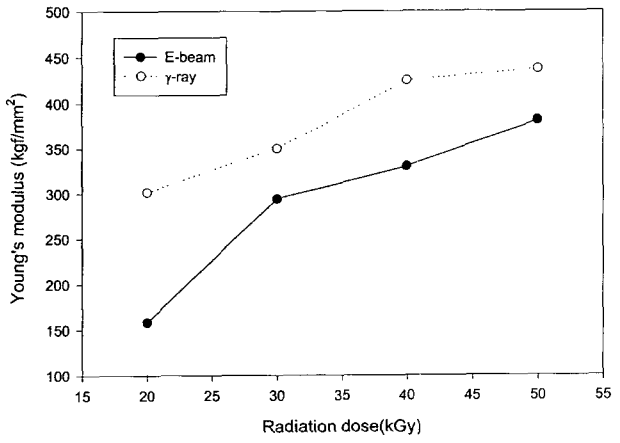

Figure 12. Young's modulus of DGEBF/TASHFA irradiated by γ-ray and EB in N_2.

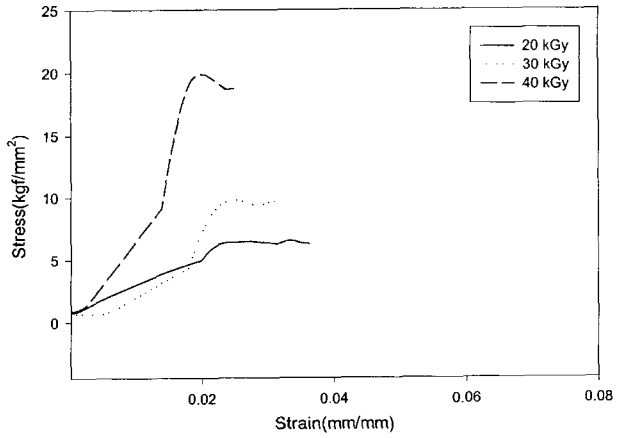

Figure 14. Stress-strain curves of DGEBF/TASHFA irradiated by EB in N_2.

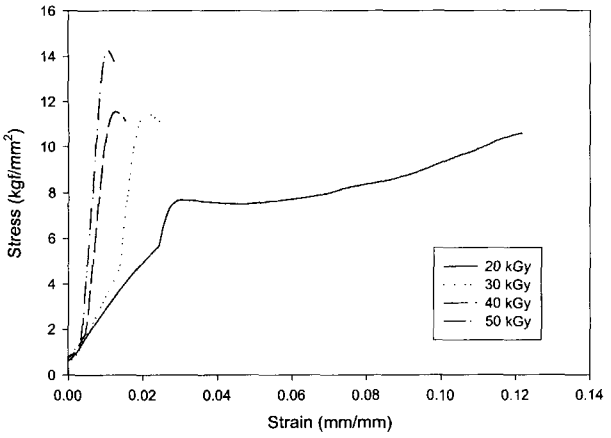

Figure 15. Stress-strain curves of DGEBA/TASHFA irradiated by EB in N_2.

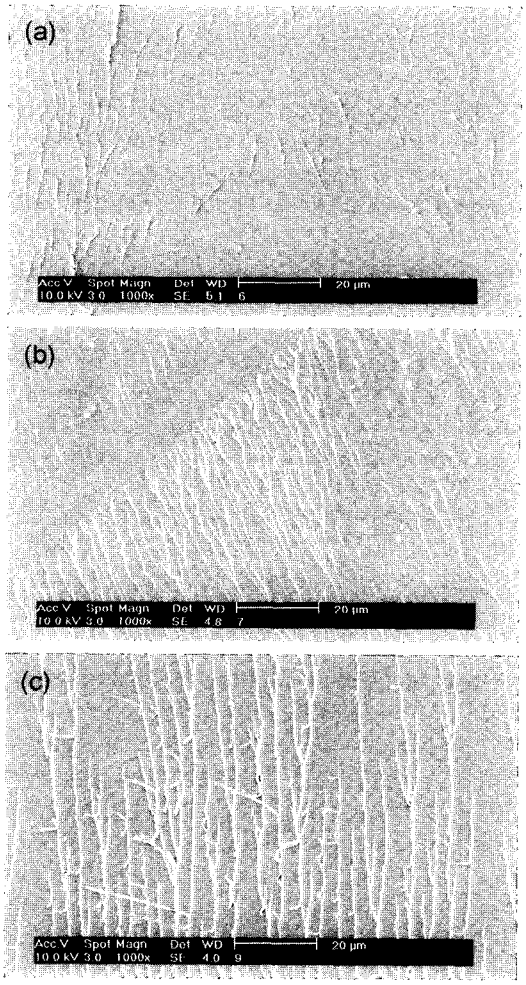

Figure 16. SEM micrographs of the cross-sectional of EB irradiated epoxy (a) DGEBF/TASHFA irradiated at 10 kGy, (b) DGEBF/TASHFA irradiated at 30 kGy, and (c) DGEBF/TASHFA irradiated at 50 kGy.

epoxy by irradiation, and the results were shown in Figure 16. As shown in Figure 16 whole cured section consists many lamellar structures. In case of (a), (b) and (c), the lamellar structure of cured epoxy can be seen evidently with increasing irradiation dose.

Conclusions

Two kinds of epoxy resin, DGEBA and DGEBF, were cured with different irradiation condition and initiator for the fundamental investigation of EB and γ-irradiation on physical properties of cured epoxy resins. Epoxy was irradiated with γ-ray and EB to a dosage of 10-50 kGy in N_2 atmosphere. The more the absorbed radiation dose and content of initiator were, the higher the gel fractions of the sample were. It was found that the use of TASHFA gave a positive effect on gel fraction compared with that of TASHFP. The gel fraction of DGEBA with γ-ray was higher than that of the epoxy with EB at the same dose. The stress at yield of all epoxy resins increases with increasing irradiation dose. The stress at yield of irradiated DGEBF with 100% of gel fraction is higher than that of irradiated DGEBA with 100% of gel fraction. Youngs modulus of the sample irradiated by γ-ray is higher than that of sample cured by EB. From the result of strain at yield, it was found that the epoxy cured by γ-ray had a higher stiff property compared with the irradiated by EB.

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