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Network chain orientation in the toughening process of the elastomer modified mesogenic epoxy resin

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Abstract

A biphenol-type epoxy resin, which has a mesogenic group in the backbone moiety, was modified with a reactive elastomer (CTBN). Toughness of the epoxy resin was significantly increased with the addition of the CTBN elastomer compared with that of the bisphenol-A type epoxy resin. It was clearly observed by SEM that a large plastic deformation occurred near the crack-tip in the biphenol-type epoxy resin modified with CTBN. The arrangement of the network chains in the plastic deformation region was quantitatively studied by polarized microscopic FT-IR technique, which was related to the toughening mechanism of the elastomer modified epoxy resin. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Elastomer modification; Mesogenic epoxy resin; Toughening

1. Introduction

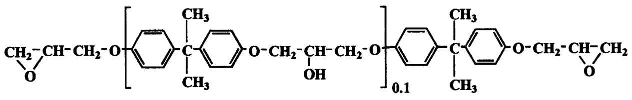
Epoxy resin has excellent electrical and mechanical properties. However, this resin is hard and rather brittle due to its highly cross-linked structure. Thus, epoxy resin is usually toughened by modifying with a liquid elastomer [1–5] and core-shell particle [6–8]. In these modifications, toughening of epoxy resin is achieved by the cavitation of the elastomer phase followed by the shear deformation of the matrix which occurred by stress concentration around the cavitated particle [9–11]. In the modified epoxy system, the stress near the crack-tip is relaxed by an energy consumption with deformation of the matrix. If the matrix then has a higher deformability, the mechanical energy stored near the crack-tip is highly consumed. It is expected that the toughness of the elastomer modified epoxy systems be more significantly improved with an increase in the deformability of the epoxy matrix.

In this study, the biphenol-type epoxy resin in which the backbone moiety is composed of a rigid and plain mesogenic group was used as a matrix resin, because we expected that the deformability of the matrix is increased due to the introduction of the planar backbone structure [12]. We investigated the toughening of the mesogenic-type epoxy resin with the addition of a reactive elastomer. In addition, the toughening mechanism was studied by evaluating the network chain orientation of the matrix near the crack-tip with a polarized microscopic FT-IR technique [13].

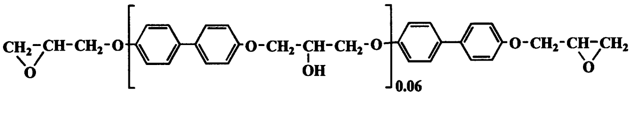
2. Experimental

2.1. Materials

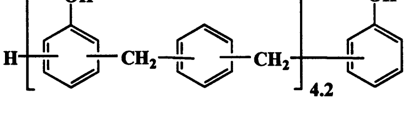
The epoxy resins used were the commercial grade of the diglycidyl ether of bisphenol-A (Epikote 828, $M_w = 380$, Yuka-shell Epoxy Co., Ltd)



and diglycidyl ether of the biphenol ($M_w = 334$, Yuka-shell Epoxy Co., Ltd)



The curing agent used was phenol-*p*-xylendiolnovolac (Mitsui-tohatu-kagaku, $M_w = 926$, XL-225-3L)



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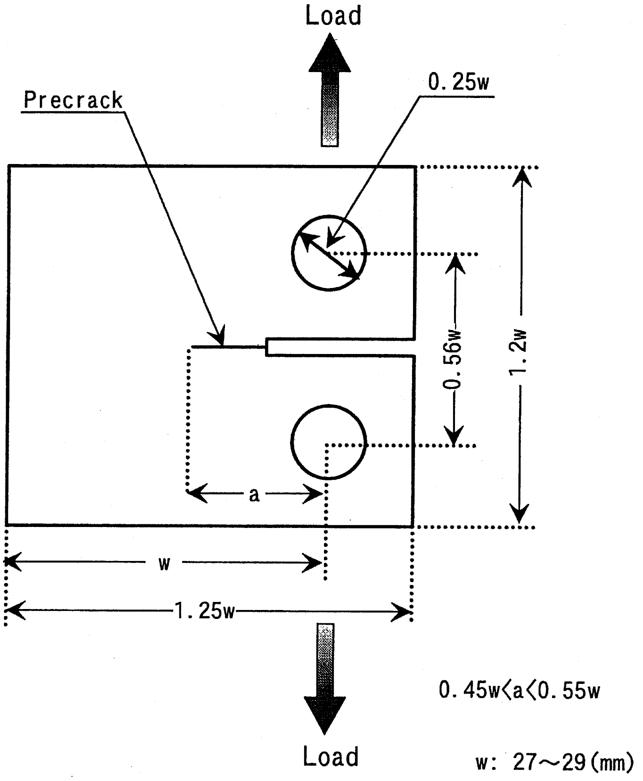
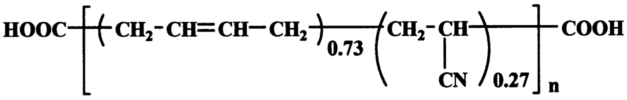


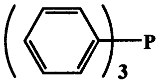
Fig. 1. Compact-tension specimen used for measuring the plastic–elastic fracture toughness.

and the reactive elastomer used was the carboxy-terminated butadiene acrylonitrile copolymer (Ube-kosan Co., Ltd, CTBN).



$$HOOC\left[\left(CH_2-CH=CH-CH_2\right)_{0.73}\left(CH_2-\underset{CN}{CH}\right)_{0.27}\right]_n COOH$$

Triphenylphosphyne (TPP) was used as the accelerator.



2.2. Curing of epoxy resin

2.2.1. Biphenol-type epoxy resin

The biphenol-type epoxy resin was purified by recrystallization using the mixture (1:3) of methyl-ethyl ketone and methyl-*iso*-butyl ketone as the solvent. CTBN was pre-reacted with an excess amount of the epoxy resin (80 g CTBN per 100 g epoxy resin) at 75°C for 30 h. In this reaction, *N*,*N*′-dimethylformamide (DMF) and tetramethylammoniumbromide were used as the solvent and catalyst, respectively. After completing the reaction, the CTBN-modified epoxy resin was precipitated with excess amount of distilled water. The pre-reacted epoxy resin was filtrated and then dried under reduced pressure (<3 mmHg) at 40°C for 10 h. The purified epoxy resin was added to the pre-reacted epoxy resin to prepare the elastomer modified epoxy resins containing the prescribed amount of CTBN. The stoichiometric amount of curing agent (phenol-*p*-xylendiolnovolac) was added to the modified epoxy resin at 180°C. TPP was then added as a catalyst. The compounds were cured at 180°C for 4 h and 230°C for 0.5 h. It was confirmed by FT-IR measurements that the final conversion of the epoxy groups in the cured resin was over 95%.

2.2.2. Bisphenol-A type epoxy resin

CTBN was pre-reacted with an excess amount of epoxy resin (120 g CTBN per 100 g epoxy resin) at 130°C for 70 min. In this reaction, tetrahydrofuran (THF) and tetramethylammoniumbromide were used as the solvent and catalyst, respectively. THF used as a solvent was then removed by evaporation under reduced pressure (<3 mmHg) at 130°C for 2 h. Commercial grade epoxy resin was added to the pre-reacted epoxy resin to prepare the modified epoxy resins containing the prescribed amount of CTBN. The stoichiometric amount of curing agent (phenol-*p*-xylendiolnovolac) was added to the modified epoxy resin at 130°C. TPP was added as a catalyst. The compounds were cured at 130°C for 2 h, 180°C for 3 h and 230°C for 0.5 h. It was confirmed that the final conversion of the epoxy group in the cured resin was over 95%.

2.3. Measurement

The fracture toughness of the cured epoxy resins was evaluated based on the critical value, J_c, of the plastic–elastic fracture toughness factor for the initiation of crack growth, which was determined from the area under the load-opening displacement curve and the dimensions (Fig. 1) of the CT specimen according to JSME S 0001 [14]. The thickness of the specimens was adjusted to be between 3.6 and 4.0 mm. A sharp pre-crack was formed by carefully tapping with a fresh razor blade. The specimen was mounted in an Instron-type tensile machine and loaded at a constant cross-head speed (0.5 mm min^{-1}).

$$J_c = \frac{A}{Bb_0} f(a_0/w)\ [\mathrm{N/m}]$$

$$f(a_0/w) = 2\frac{1+\beta}{1+\beta^2}$$

$$\beta = \left[\left(\frac{2a_0}{b_0}\right)^2 + 2\left(\frac{2a_0}{b_0}\right) + 2\right]^{1/2} - \left(\frac{2a_0}{b_0} + 1\right)$$

where A is the area under the load-opening displacement curve, B is thickness of CT specimen, a_0 is the pre-crack length, w is the width and b_0 is the values of $w - a_0$.

Optical properties of cured epoxy resins were measured using an optical microscope (OM:BH-2, Olympus Co., Ltd) under crossed polarized light.

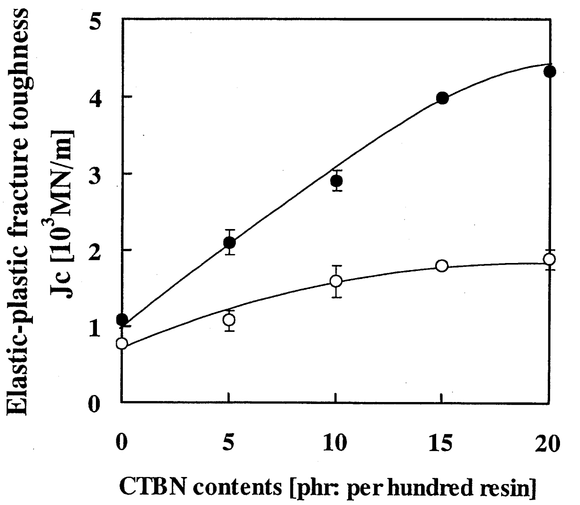


Fig. 2. Elastic–plastic fracture toughness J_c of cured epoxy resins modified with CTBN. Epoxy resins: (○) Bisphenol-A DGE, (●) Biphenol DGE.

The polarized IR spectrum of the cured epoxy resin was measured using a polarized FT-IR spectrometer (SPECTRUM 2000) equipped with a i-Series FT-IR microscope. Resolution of the IR spectrum was 4 cm^{-1}.

3. Results and discussion

3.1. Toughness of cured epoxy resins modified with CTBN

The changes in the elastic–plastic fracture toughness, J_c, of the biphenol and bisphenol-A-type epoxy resins with the addition of the CTBN elastomer are shown in Fig. 2. The values of J_c of both epoxy systems increased with an increase in the CTBN content. Especially, the values of J_c of the biphenol type epoxy resin, which has a mesogenic group in the backbone moiety, was more highly improved than that of the bisphenol-A-type epoxy resin. In the 20 phr CTBN added system, the toughness of the biphenol-type epoxy resin is about 4.4 times higher than that of the unmodified system. On the other hand, the toughness of the bisphenol-A-type epoxy resin is about 2.3 times higher than that of the unmodified system. These results show that the toughness of the biphenol-type epoxy resin is more effectively improved by the modification with CTBN. Yee et al. [1] reported that the toughening of the epoxy resin in the elastomer-modified system is achieved by the shear deformation of the matrix resin, following the cavitation of the elastomer dispersed phase. According to this toughening mechanism, the matrix composed of the biphenol type resin should be more easily deformed compared with the bisphenol-A type resin matrix. Generally speaking, the deformability of the cured epoxy resins could increase with the decreasing cross-linking density of the cured resins. However, the biphenol and bisphenol-A-type resins cured with phenol-*p*-xylendiolnovolac have about the same concentration of network chains (ν_{biphenol}: 2.28, $\nu_{\mathrm{bisphenol\text{-}A}}$: 2.18×10^{-3} mol cm^{-3}). Thus it is expected that the high toughness of the biphenol type resin modified with CTBN is attributed to the introduction of planar and rigid mesogenic group.

3.2. Phase structure of cured epoxy resins modified with CTBN

The fracture surface of the compact tension specimens observed at low magnification using a scanning electron microscope (SEM) are shown in Fig. 3. The plastic deformation region was observed near the crack-tip in both the bisphenol-A and biphenol-type resin systems. In this region, the matrix composed of the biphenol type resin was more largely elongated in the stress direction, compared with the bisphenol-A type resin matrix. Thus, it is considered that the former resin system could dissipate a larger amount of the fracture energy by the plastic deformation of the matrix and thus keep the higher toughness compared to the latter resin system.

The morphology of the fracture surface observed at a higher magnification using the SEM is shown in Fig. 4. In both epoxy systems, the diameter of the CTBN phases is about the same in the fast fracture region. This means that the CTBN dispersed phase originally has about the same size in both resin systems. On the other hand, the diameter of the CTBN phases in the plastic deformation region clearly increased compared with that in the fast fracture region. This means that the cavitation of the dispersed

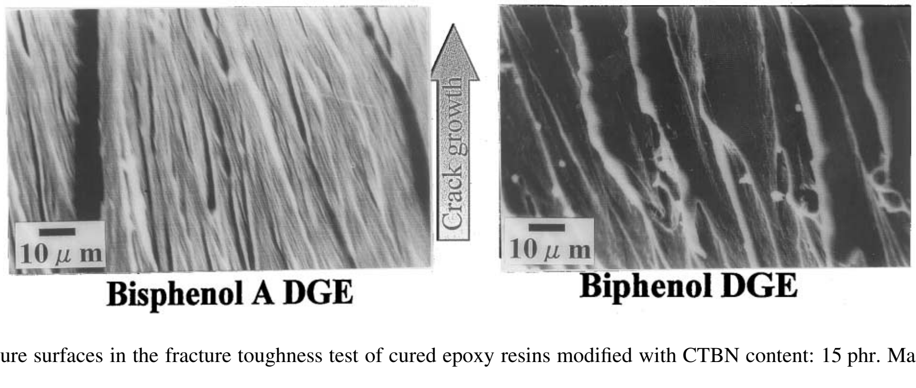


Fig. 3. SEM of fracture surfaces in the fracture toughness test of cured epoxy resins modified with CTBN content: 15 phr. Magnification: × 1000.

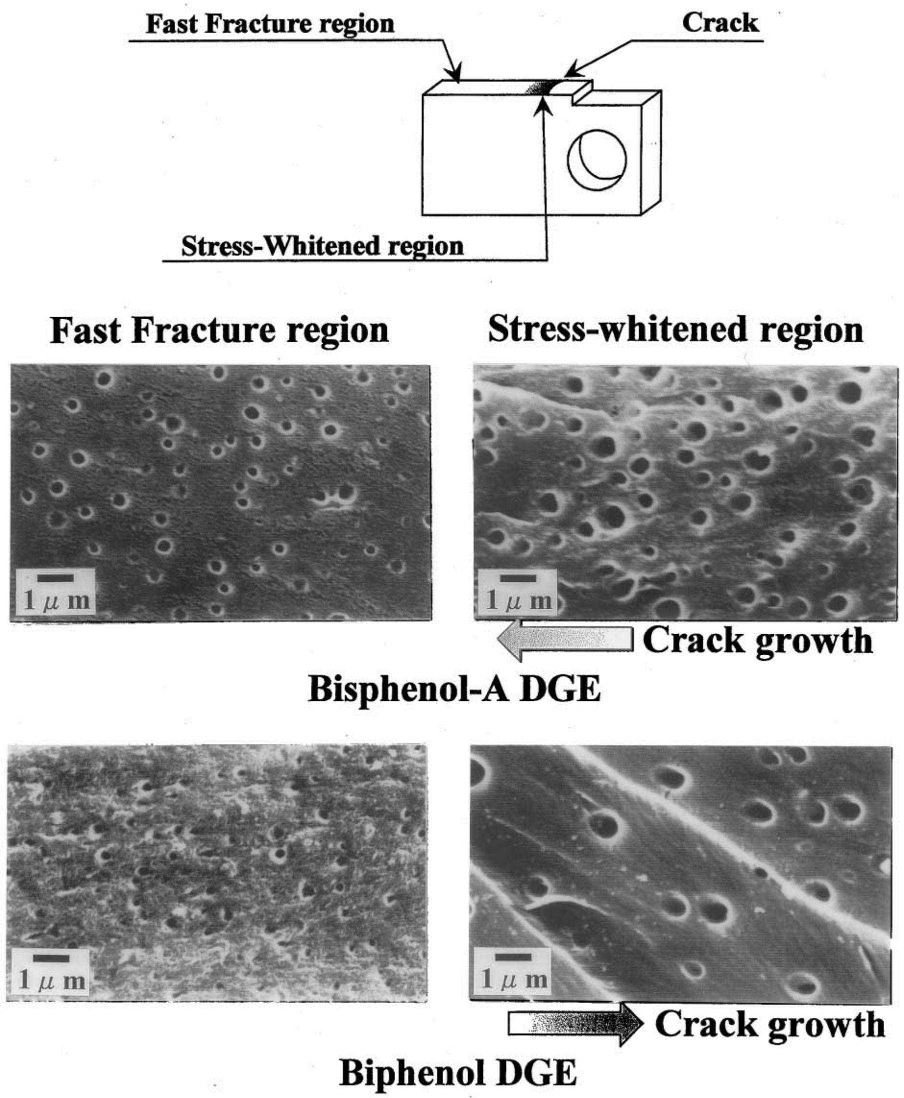


Fig. 4. SEM of the fracture surfaces in the fast fracture and stress-whitened regions of cured epoxy resins modified with CTBN. CTBN content: 15 phr. Magnification: ×1000.

phase occurred in the plastic deformation region. Moreover, in the stress-whitened (plastic deformation) region, the CTBN dispersed phase is clearly deformed into an ellipsoidal shape in the direction of the applied stress. This shows that the deformation of the matrix occurred near the crack-tip in both epoxy resin systems. In addition, the deformation of the dispersed phase into an ellipsoidal is more clearly observed in the biphenol-type epoxy resin system. If the resin has small deformability, it is considered that the crack will propagate before enough deformation of matrix. This means that the matrix composed of the mesogenic epoxy resin is more easily deformed compared with the bisphenol-A resin system. Thus, it is concluded that the high toughening effects (Fig. 2) observed in the CTBN-modified mesogenic epoxy resin is due to the large deformation of the matrix resin in the plastic deformation region of this resin system.

3.3. Optical properties of cured epoxy resins

The polarized micrographs of the biphenol and bisphenol-A type epoxy resin systems are shown in Fig. 5. Each cured epoxy resin systems showed isotropism. The sample (thickness: 350 μm) was cut from the compact tension specimen loaded at 90% of maximum stress before starting the crack propagation in the fracture toughness test. In the bright field, the dark area near the crack-tip in both systems shows that the rubber particles were cavitated. The dark area in the biphenol type resin system is larger than in bisphenol-A type resin system. Moreover, in the crossed polarized field, the network chain orientation of the matrix in the bisphenol-A type epoxy resin system is hardly observed in the area near the crack-tip. On the other hand, in the biphenol type epoxy resin system, the birefringence pattern based on the network chain orientation is clearly observed in

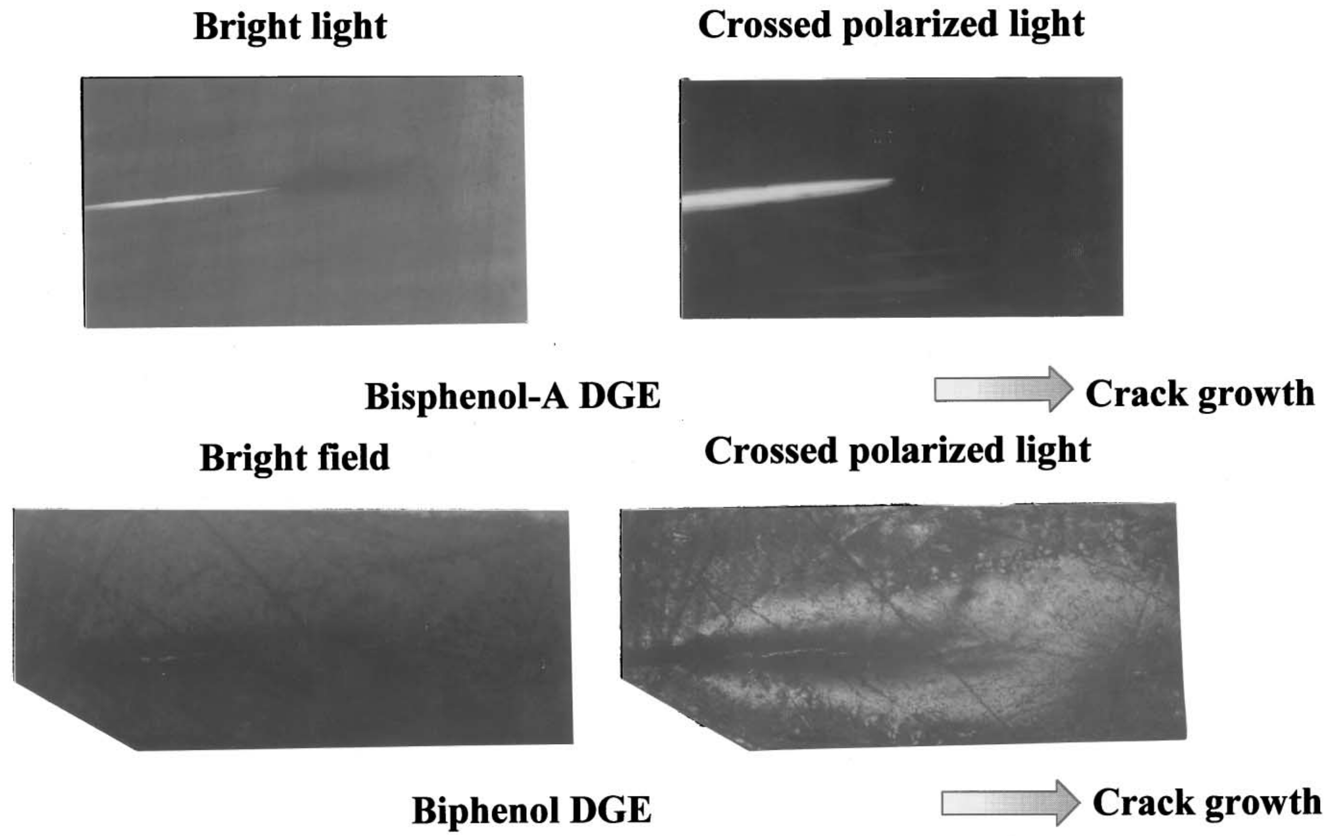


Fig. 5. Polarized optical micrographs of cured epoxy resins modified with CTBN. CTBN content: 20 phr.

the larger area that is close to the crack. This result shows that the network chain orientation with the deformation of the epoxy matrix in biphenol type epoxy resin was easily caused than in bisphenol-A type epoxy resin. As described in the Section 3.2, both epoxy resin systems have about the same cross-linking density. Nevertheless, the deformability of the network chains is entirely different in each epoxy resin system. The difference in the deformability should be caused by the structure of the backbone moiety of the epoxy resins, taking into account that both resin systems have about the same T_g, conversion of epoxy groups and cross-linking density. The 3D images of each epoxy resin are shown in Fig. 6. The mesogenic group of the biphenol-type epoxy resin has a compact and planar structure, but the backbone moiety of the bisphenol-A-type epoxy resin has a bulky and folded structure containing two aromatic rings and two methyl branches. It is expected from the 3D images of the backbone structure that the biphenol groups in the network chains could more easily slip past each other under the external stress field and become arranged along the direction of the applied stress. The arrangement of the mesogenic moiety in the cross-linked networks must be caused by the large-scale motion of the network chains. Thus, it is concluded that the large plastic deformation of the matrix more easily occurred near the crack-tip in the biphenol type epoxy resin system, because of the compact and planar backbone structure of this resin system.

3.4. *Polarized IR measurement of biphenol-type epoxy resin*

The polarized IR spectra of the biphenol-type epoxy resin modified with CTBN are shown in Fig. 7. The sample (thickness: 50 μm) for the IR measurement was also cut from the compact tension specimen loaded at 90% of maximum stress before starting the crack propagation in the fracture toughness test. In this paper, the direction of the crack propagation is defined as the parallel direction of the polarized IR. If a chemical bond in some molecule vibrates in the parallel direction, the parallel polarized IR was more strongly absorbed than the perpendicular polarized IR, and thus the spectrum of the parallel polarized IR has a larger peak than that of the perpendicular polarized IR. When the network chains of the matrix resin are arranged along the stress direction in the fracture process, the degree and the direction of the molecular orientation can be observed in the difference spectrum which is made by subtracting the spectrum of the perpendicular polarized IR from that of the parallel polarized IR. The positive peak in the difference spectrum shows that the network chains should arrange in the parallel direction, that is, the direction of the crack propagation. Kim et al. [15] also reported that the orientation of the network chains could be investigated by observing the direction of molecular vibration included in the network chains by using the polarized IR technique. They studied the orientation of soft and hard segments

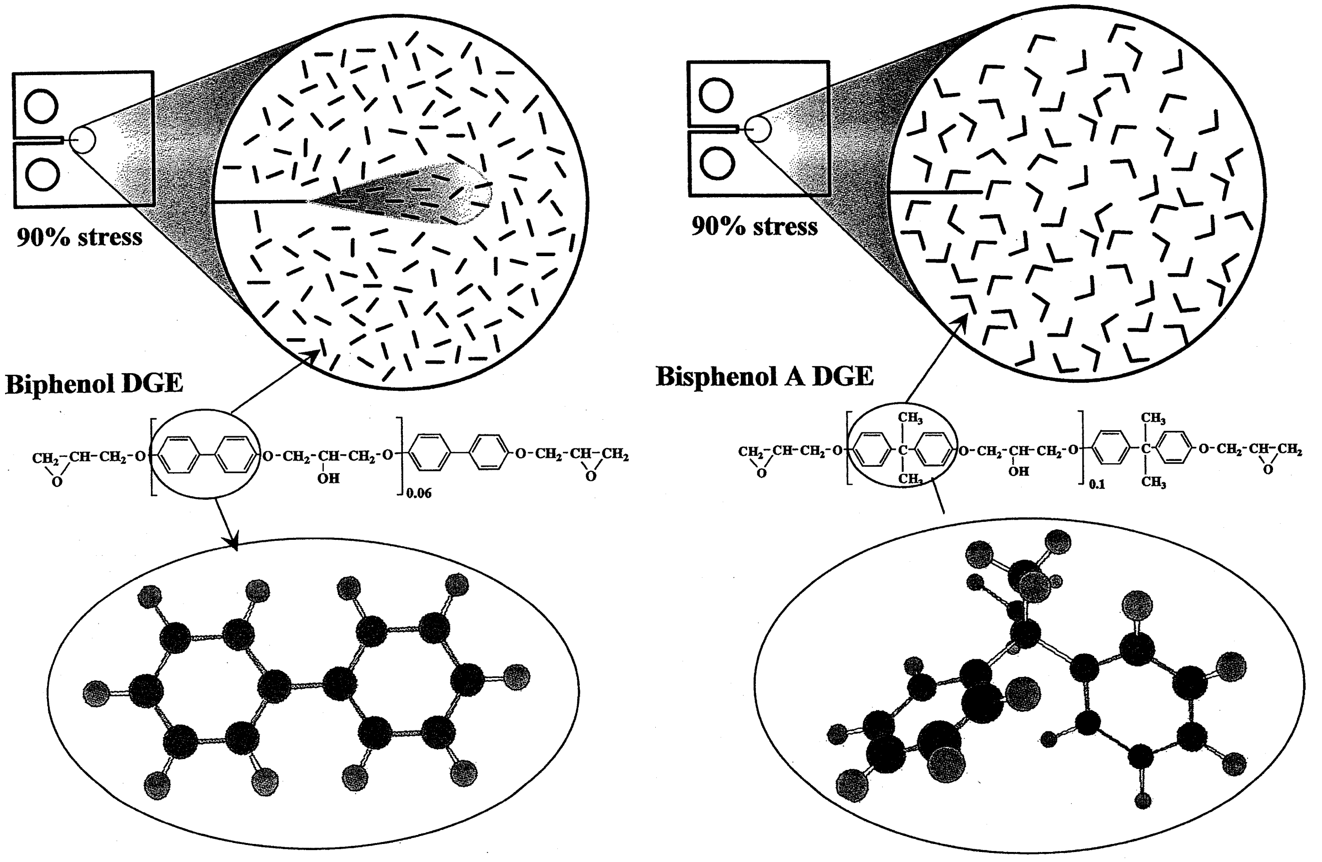


Fig. 6. Model of network orientation near crack-tip in cured epoxy resin modified with CTBN loaded the 90% of maximum stress.

in a polyether–urethane–urea copolymer using the NH–stretching vibration (hard segment) and CH– stretching vibration (soft segment) as indicators, respectively. In this study, the stretching vibration of the aromatic C=C bond was used as an indicator to determine the arrangement of the network chains, because the two aromatic rings in the biphenol type resin are on a line, and thus the vector sum of the stretching vibration of the aromatic C=C bond is parallel with the line of network chains. In the difference spectra shown in Fig. 7, the stretching vibration of the aromatic C=C bond at 1600, 1500 and 1450 cm^{-1} and aromatic ether C–O bond at 1240 cm^{-1} along with the in-plane deformation vibration of the aromatic hydrogen atom at 1000–1200 cm^{-1} showed the positive peaks. These results show that the network chains containing the aromatic ring in the cured mesogenic epoxy resin are arranged in a parallel direction in the damage zone near the crack-tip before starting the crack propagation. Thus, it is clear that the network chains containing the mesogenic group should have a large-scale molecular motion and thus the matrix is plastically deformed during the damaging process, even though the matrix resin has a densely cross-linked network structure.

The difference spectra near the crack-tip of the biphenol type epoxy resin modified with CTBN (20 phr, 10 phr, unmodified) are shown in Fig. 8. In the difference spectra of these systems, the height of the positive peaks in the stretching vibration of the aromatic C=C bond at 1600, 1500 and 1450 cm^{-1} increased with an increase in the CTBN contents. Namely, the degree of the arrangement of the network chains increased with an increase in the CTBN content. This means that the large-scale motion of the network chains more easily occurred in the mesogenic epoxy resin modified with a larger amount of CTBN. Wu et al. [16,17] suggested that the toughening effect observed in the rubber-modified system depends on the thickness of the matrix between the dispersed rubber phases. We also suggested that the toughness of the silicone modified epoxy system increased with a decrease in the diameter of the silicone phase (that is, a decrease in the thickness of the matrix), due to the increase in the area of the damage zone [18]. In this study, it is natural to consider that the thickness of the matrix between the dispersed CTBN phases decreases with an increase in the CTBN content. Thus, we consider that the increase in the arrangement of the network chains with the rubber modification is due to the increase in the deformability of the matrix resin caused by the decrease in the thickness of the matrix between the dispersed phases.

The dichroic ratio values estimated from the polarized IR spectrum in the damage zone of the CTBN modified

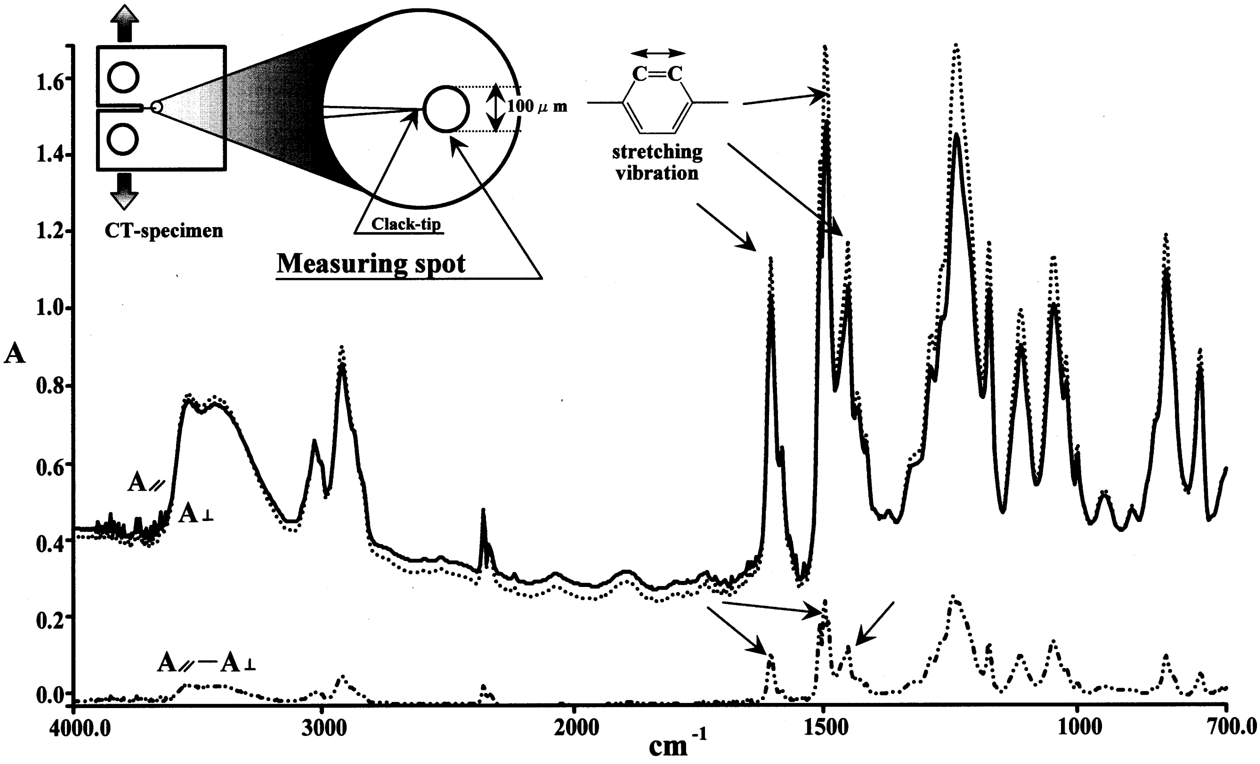


Fig. 7. Polarized IR and difference IR spectra of Biphenol type epoxy resin modified with CTBN. Load: 90% of maximum stress. CTBN content: 20 phr Diameter of measuring spot: 100 μm. (···): parallel IR spectrum ($A_{\|}$), (—): perpendicular IR spectrum ($A_{\perp}$), (–··–): difference IR spectrum ($A_{\|} - A_{\perp}$).

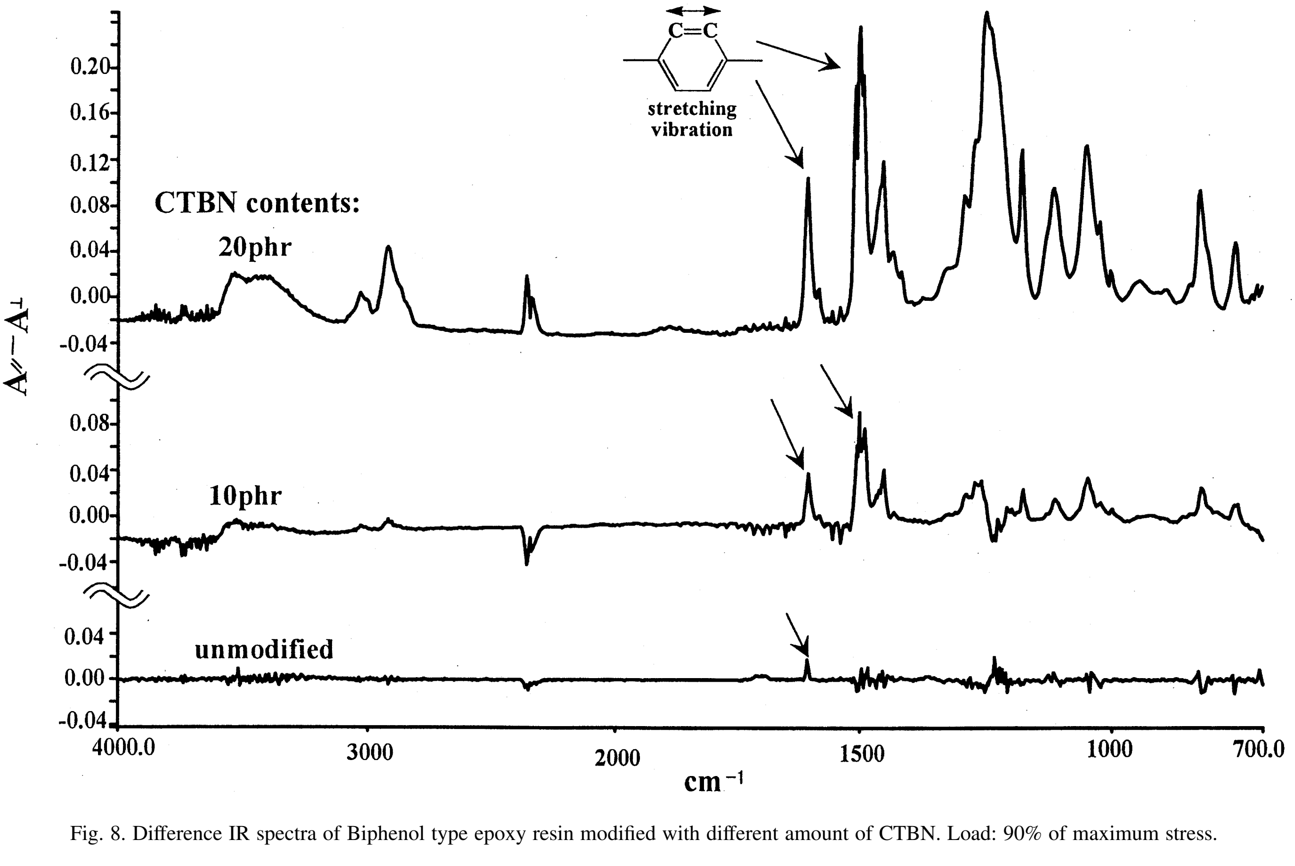


Fig. 8. Difference IR spectra of Biphenol type epoxy resin modified with different amount of CTBN. Load: 90% of maximum stress.

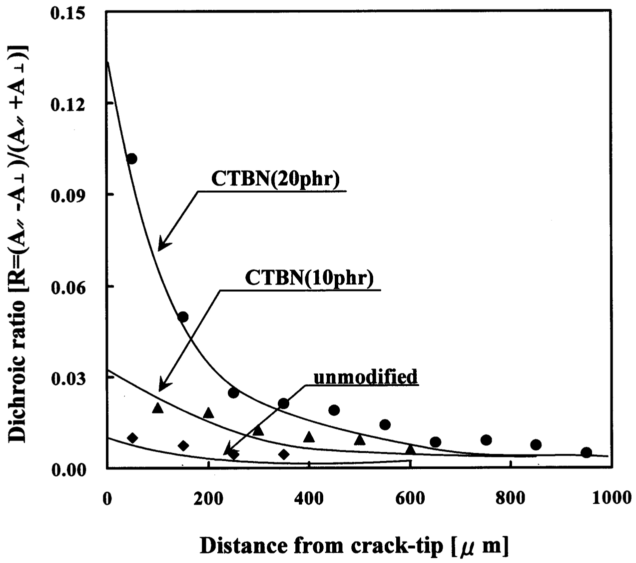


Fig. 9. Dichroic ratio of Biphenol type epoxy resin modified with CTBN. CTBN content (wt%): (◆) 0, (▲) 10, (●) 20. Peak position in IR spectrum: 1605 cm^{-1} (C=C stretching in aromatic ring). Load: 90% of maximum stress.

biphenol type epoxy resin system are shown in Fig. 9. Here, the dichroic ratio R was calculated by $R = (A_{\|} - A_{\perp})/(A_{\|} + A_{\perp})$, where $A_{\|}$ and $A_{\perp}$ are the absorbance of the parallel and perpendicular polarized IR, respectively. When the network chains of the matrix are oriented along the direction of the crack propagation, the dichroic ratio has a positive value. In the unmodified system, the dichroic ratio values are very small. This means that the arrangement of network chains is very small in this system, while the dichroic ratio of the modified systems increased with an increase in the CTBN content. This means that the degree and area of the arrangement of the network chains, that is, the plastic deformation of the matrix in the damage zone increased with the rubber modification. Thus, it is reasonable to consider that one of the important toughening mechanisms in the mesogenic epoxy resin is the energy consumption caused by the arrangement of the network chains containing the mesogenic group.

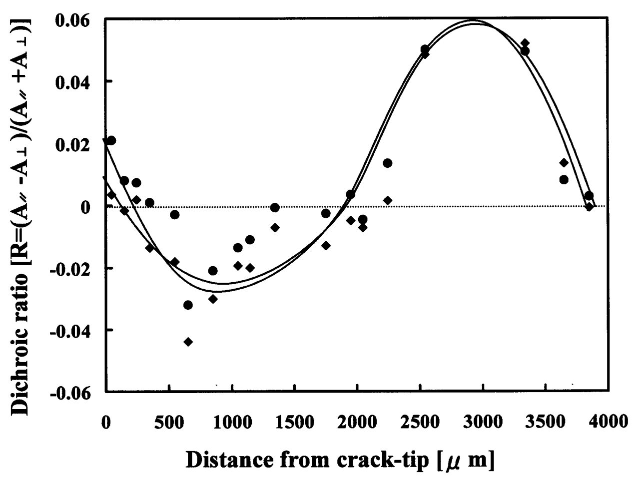


Fig. 10. Dichroic ratio of Biphenol type epoxy resin modified with CTBN after measuring fracture toughness. CTBN content: 20 phr. Peak position in IR spectrum: (●) 1605 cm^{-1} (C=C stretching), (◆) 1240 cm^{-1} (C–O stretching).

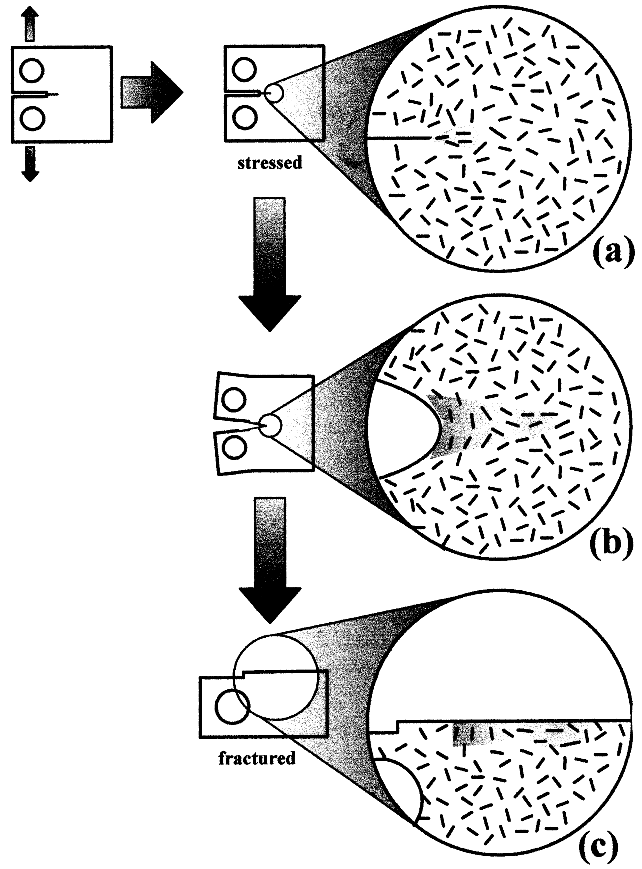


Fig. 11. Model of network orientation near crack-tip in fracture process of mesogenic epoxy resin modified with CTBN: (a) 90% load of maximum stress, (b) large-scale yielding, (c) fracture.

The dichroic ratio, R, of the CTBN-modified biphenol-type epoxy resin fractured in the compact tension CT test is shown in Fig. 10. In the fractured sample of the biphenol-type epoxy resin, the values of the dichroic ratio were negative near the crack-tip but changed to positive as it moved away from the crack-tip. The negative value of the dichroic ratio shows that the network chains containing the mesogenic group are rearranged in the perpendicular direction during the fracture process, though the network chains were arranged in the parallel direction in the damage zone before starting the crack propagation. Namely, the network chains in the vicinity of the crack-tip are elongated in the perpendicular direction during the fracture process. In the region away from the crack tip, the values of the dichroic ratio were positive. This reveals that the network chains in this region are oriented along the direction of the crack propagation. Namely, network chains near the fracture surface are rearranged in the parallel direction with the progress of the crack propagation.

The rearrangement of the network chains in the fracture process before and after starting the crack propagation are shown in Fig. 11. In the CTBN-modified mesogenic epoxy resin loaded at 90% of the maximum stress, the network chains containing the mesogenic groups are arranged in the parallel direction near the crack-tip before starting the crack propagation (Fig. 11(a)). When the maximum stress is loaded on the mesogenic epoxy resin, a large deformation occurred in the vicinity of the crack-tip and thus the network chains near the crack-tip are rearranged in a direction perpendicular to the crack propagation. According to the rearrangement of the network chains, the shape of the crack-tip becomes round (Fig. 11(b)). In the fractured specimen, a large plastic deformation (Fig. 4) of the matrix resin and orientation of the network chains containing the mesogenic group in the perpendicular direction are observed near the crack-tip (Fig. 11(c)). These results show that the network chains of the mesogenic epoxy resin modified with CTBN are significantly rearranged in the fracture process, even though the epoxy matrix has a highly cross-linked network structure. The high toughening effect in the mesogenic epoxy resin systems is due to the large deformation of the matrix caused by the rearrangement of the network chains containing the mesogenic group.

4. Conclusions

The mesogenic epoxy resin was modified with CTBN to improve the toughness of the cured resin. The toughening effects of the mesogenic resin system were compared with that of the bisphenol-A-type resin system. The toughening mechanisms were studied based on the arrangement of the network chains in the fracture process measured by the polarized microscope and polarized FT-IR technique. Thus, the following conclusions were obtained:

1. The toughness of the mesogenic epoxy resin is more effectively improved by the modification with CTBN, compared with that of the commercial grade bisphenol-A type epoxy resin. In the fracture surface of the former resin system, a large plastic deformation of the matrix was observed near the crack-tip. The high toughening effects observed in the mesogenic epoxy resin system are due to the large deformation of the matrix during the fracture process.
2. The arrangement of the network chains in the fracture process of the CTBN-modified epoxy resins was pursed using a polarized FT-IR technique. Thus, it was clarified that the network chains containing the mesogenic group are more easily arranged near the crack-tip. The large plastic deformation observed in the mesogenic epoxy resin is caused by the arrangement of the network chain under the stressed condition.

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