

Toughening of Cycloaliphatic Epoxy Resin Improved by Reactive Copolymers with Flexible Alkyl Side Chains

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ABSTRACT: Reactive copolymers with flexible alkyl side chains were used as modifiers to improve the toughness of a cycloaliphatic epoxy resin. In this study, we used three types of copolymers with different alkyl chain length (C₄H₉, C₆H₁₃, and C₁₀H₂₁). As a result, the system with an added copolymer having the longest alkyl chain length (C₁₀H₂₁) formed a phase separation structure. The addition of this copolymer (C₁₀H₂₁) led to a 50% increase in the fracture toughness (K_{IC}) of the cured resin at the slight

expense of its glass transition temperature. Scanning electron microscope observations in the vicinity of a crack tip after a compact tension test showed that cavitation of the dispersed phase occurred. The crack growth was inhibited and thus the toughness was improved due to the plastic deformation of the epoxy matrix followed by cavitation. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4572–4578, 2012

Key words: epoxy; polymer blend; toughening

INTRODUCTION

Cycloaliphatic epoxy resin has good electrical insulating properties, high glass transition temperatures and excellent formability.¹ For these reasons, this resin has been utilized in a variety of industrial applications such as paints, coatings, inks, reactive diluents, encapsulation of electronic circuit elements, and printed circuit-board coatings.² However, this resin is brittle because of its highly cross-linked structure. In addition, cycloaliphatic epoxy resin is usually cured with anhydrides because of their low reactivity with amine- and amide-type curing agents.¹ Anhydride curing systems are generally brittle compared to amine-cured systems. Thus toughening of the cycloaliphatic epoxy resin is required for various industrial uses.

The toughness of epoxy resins has been increased by the modification with reactive elastomers or thermoplastic polymers. In this field, it is well-known that epoxy resins modified with carboxy-terminated butadiene acrylonitrile (CTBN) copolymer^{3–6} or carboxy-randomized butadiene acrylonitrile (CRBN) rubber⁷ have a considerably improved toughness. However, these methods drastically decrease the glass transition temperature of the cured resins

because a part of CTBN dissolves in epoxy resin. In addition, toughening of epoxy resin by forming co-continuous structure was investigated.^{8–11} The high-molecular weight is necessary for toughening of the cured resin. As a result, the resin has an extremely high viscosity and becomes difficult to mold.

Tomoi and coworkers¹² prepared new reactive copolymers that have flexible side chains and pendant epoxy groups. The modification of the diglycidyl ether of bisphenol-A epoxy resin with the reactive copolymer was carried out in order to increase the toughness of the cured epoxy resin. They reported that the addition of the copolymer resulted in an increase in the fracture toughness (K_{IC}) of the cured resin at the minimal expense of strength and modulus of the resin.¹³

We focused on novel copolymers, 3, 4-epoxycyclohexane-1-aryl carboxylic acid / α -olefin (1 : 2.5) copolymer (CEA/ α -olefin copolymer) with flexible alkyl side chains and cycloaliphatic epoxy groups as the functional groups. The novel copolymers have flexible alkyl chains not in the main chain but in the side chain. We assumed that the addition of these copolymers can improve the fracture toughness (K_{IC}) of the cured resin at a slight expense of its glass transition temperature compared to systems with an alkyl chain in the main chain.

In this study, CEA/ α -olefin copolymers were added to a typical cycloaliphatic epoxy resin, (3', 4'-epoxycyclohexane) methyl 3, 4-epoxycyclohexyl-carboxylate. These resin and copolymers have a cycloaliphatic epoxy functional group to be cured by the same curing agent. We used three kinds of copolymers in which the length of the alkyl side

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TABLE 1
Compositions of Unmodified and Modified Epoxy Systems

Sample code	Amount of monomers (g)				MeHHPA ^b	DBU ^c	Modifier additive amount (wt %) ^d
	CER ^a	CEA/1-hexene copolymer	CEA/1-octene copolymer	CEA/1-dodecene copolymer			
1	50.0	–	–	–	66.6	1.5	0
2	38.5	11.5	–	–	57.1	1.5	23
3	20.0	30.0	–	–	42.0	1.5	60
4	38.5	–	11.5	–	56.3	1.5	23
5	20.0	–	30.0	–	39.8	1.5	60
6	38.5	–	–	11.5	55.1	1.5	23
7	30.0	–	–	20.0	46.6	1.5	40
8	20.0	–	–	30.0	36.5	1.5	60
9	10.0	–	–	40.0	26.5	1.5	80

^a Cycloaliphatic epoxy resin.

^b Methyl-cis-hexahydrophthalic anhydride.

^c 1, 8-Diazabicyclo[5.4.0]-7-undecene.

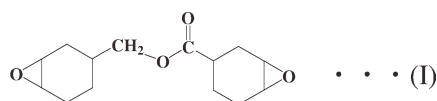
^d Modifier added (wt %) was calculated from the total of epoxy resin and modifiers.

chain was different. We also investigated the effect of the content and the side chain length of the added modifier on the thermal and mechanical properties of the cured resins.

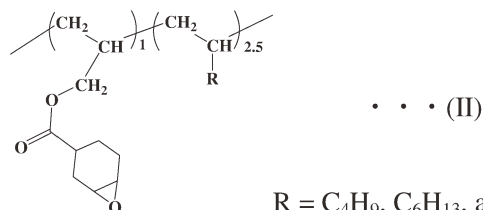
EXPERIMENTAL

Materials

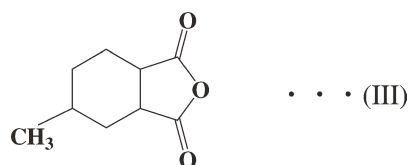
The cycloaliphatic epoxy resin used was (3', 4'-epoxycyclohexane) methyl 3, 4-epoxycyclohexyl-carboxylate (CER, $M_w = 252.3$, Daicel Chemical Industries).



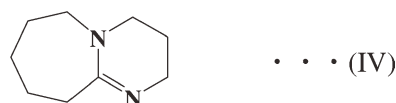
The reactive copolymers used were 3, 4-epoxycyclohexane-1-aryl carboxylic acid / α -olefin (1 : 2.5) copolymer (CEA/ α -olefin copolymer, Showa Denko K. K.). In this study, three types of copolymers in which the length of the alkyl side chain was different were used: CEA/1-hexene copolymer ($R = C_4H_9$, epoxy equivalent: 383 g/mEq.), CEA/1-octene copolymer ($R = C_6H_{13}$, epoxy equivalent: 329 g/mEq.) and CEA/1-dodecene copolymer ($R = C_{10}H_{21}$, epoxy equivalent: 509 g/mEq.).



The curing agent used was methyl-cis-hexahydrophthalic anhydride (MeHHPA, $M_w = 168$, Tokyo Chemical Industry).



The accelerator used was 1, 8-diazabicyclo[5.4.0]-7-undecene (DBU, $M_w = 152.2$, Tokyo Chemical Industry).



Curing of epoxy resin

The cycloaliphatic epoxy resin^(I) was mixed with different amounts of the copolymers^(II). An accelerator^(IV) was added 3 phr for the total amounts of the epoxy resin and copolymers. Stoichiometric amounts (one epoxy group corresponds to one anhydride group) of the acid anhydride^(III) were then added and stirred. The compositions of the cycloaliphatic epoxy resin systems modified with the CEA/ α -olefin copolymers are summarized in Table I. The concentration of the epoxy group decreases with an increase in the content of the copolymer. The mixtures were poured into a mould and put into a vacuum oven for 60 min at 60°C to remove air bubbles. They were then cured for 60 min at 100°C, then for 90 min at 150°C, and then for 90 min at 180°C in the atmospheric condition.

Measurements

Confirmation of the epoxy curing was carried out by FTIR (SPECTRUM 100R, Perkin Elmer) measurements. Resolution of the IR spectrum was 4 cm^{-1} . The intensity of the absorption peak at about

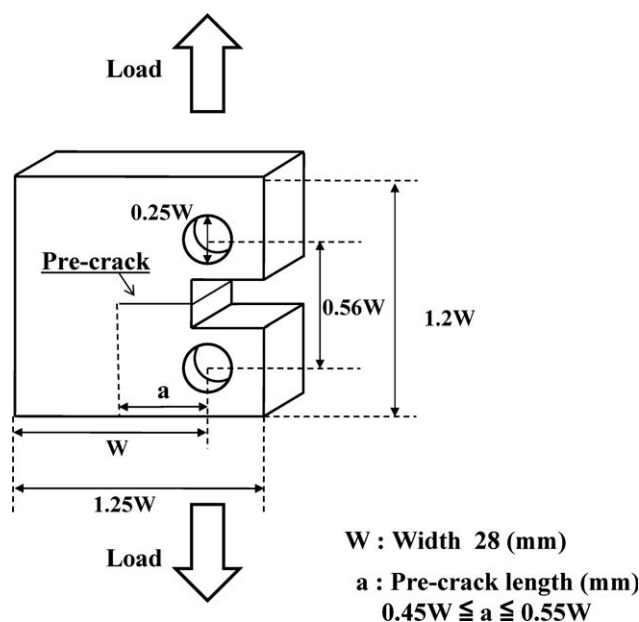


Figure 1 Shape and geometry of the specimen for a compact tension test.

2750–3100 cm^{-1} , which is the characteristic peak on the C—H stretching vibration of cyclohexane, methylene, and methyl group, was used as the internal standard absorption peak.

Both the surfaces of the cured resins cut with a razor blade in liquid nitrogen and the fracture surfaces of the specimen after the compact tension test were observed using a scanning electron microscope (SEM: JSM-6500, JEOL) at an accelerating voltage of 5 kV. Prior to the examination, the surfaces were coated with a thin layer of platinum to improve the conductivity and prevent charging. The average diameter D of the dispersed phase was estimated by applying the pin drop test¹⁴ to the scanning electron microphotographs, assuming that the dispersed phase is spherical in shape and is homogeneously dispersed in the matrix resin. In this test, the average diameter D is calculated from the following equation:

$$D = 3Lh/2P \quad (1)$$

where P and h are the total number of intersections and the hit number between the dispersed phases and the test pins, respectively, and L is the length of the test pin.

The dynamic mechanical properties of the cured systems were determined using a non-resonance forced vibration viscoelastometer (DVE-V4, UBM). The dimensions of the samples were 30 mm × 4 mm × 0.4 mm. The frequency was adjusted to 10 Hz, and the heating rate was 2°C/min from –150 to 300°C.

The fracture behavior of the epoxy materials was examined using a fracture mechanics approach, and the stress intensity factor, K_{IC} , for the initiation of

crack growth was determined from a compact tension specimen shown in Figure 1 according to ASTM E 399-81. The thickness of the specimens was adjusted to 4.0 mm. A sharp crack was formed at the base of the slot by carefully tapping the specimen with a fresh razor blade.¹⁵ The specimen was mounted in an Instron type tensile machine (AGS-J, Shimadzu) and loaded at a constant cross-head speed (0.5 mm/min). The experiments were conducted at room temperature. The value of the stress intensity factor, K_{IC} , was calculated from

$$K_{IC} = \frac{P}{BW^{1/2}}f(\alpha) \quad (2)$$

where

$$f(\alpha) = \frac{(2 + \alpha)(0.886 + 4.64\alpha - 13.32\alpha^2 + 14.72\alpha^3 - 5.6\alpha^4)}{(1 - \alpha)^{3/2}}, \quad \left(\alpha = \frac{a_0}{W}\right) \quad (3)$$

and where P and a_0 are the load and the crack length at crack initiation, B and W are the thickness and the width of the specimen, respectively, and $f(\alpha)$ is a geometric factor.

RESULTS AND DISCUSSION

FTIR measurements in curing process

Figure 2 shows the FTIR spectra in the curing process of the cycloaliphatic epoxy system with an added 23wt % of CEA/1-dodecene copolymer (sample code 6 in Table I). The absorption near 1865 and 1790 cm^{-1} (anhydride C=O stretching) and 860 cm^{-1} (epoxide C—O—C ring deformation) decreased with the progress of the curing reaction. On the

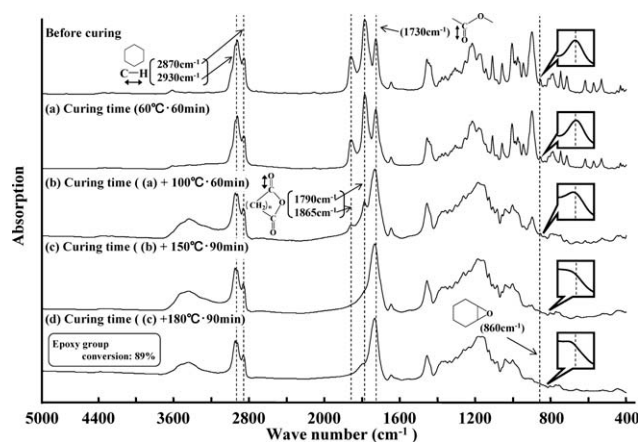


Figure 2 FTIR spectra of cycloaliphatic epoxy resin (CER) modified with CEA/1-dodecene copolymer with the progress of curing. Modifier added: 23 wt %.

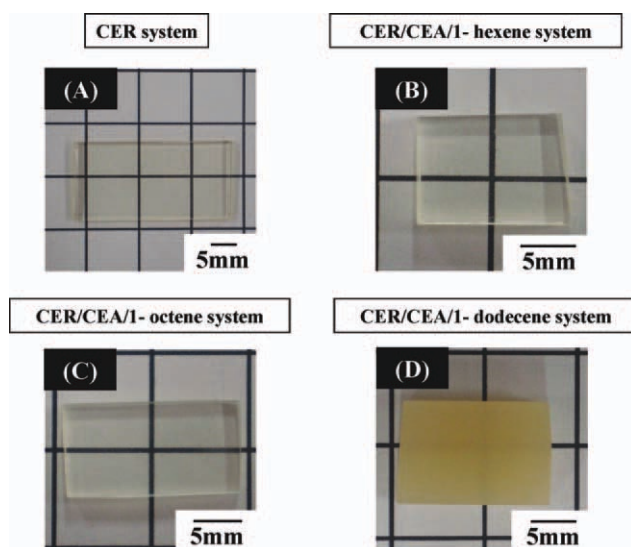


Figure 3 Optical photographs of cycloaliphatic epoxy resin (CER) unmodified and modified with CEA/ α -olefin copolymer. Modifier added: 23 wt %. Curing time: (60°C · 60 min) + (100°C · 60 min) + (150°C · 90 min) + (180°C · 90 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

other hand, the absorption near 1730 cm^{-1} (ester C=O stretching) increased. These are clear signs of ester formation during the epoxy-anhydride curing. The conversion of the epoxy group was calculated from the area of the absorption peak (where the C—H stretching band at about 2750–3100 cm^{-1} was used as a reference band and the C—O stretching band at 860 cm^{-1} was used for the epoxy groups¹⁶). The results indicate that the conversion of the epoxy group reached about 89%. We measured FTIR spectra those systems. In addition, I was confirmed in all systems studied in the work that the conversion of the epoxy group occurred to a similar extent.

Morphology of the cured unmodified and modified systems

Figure 3 shows the optical photographs of the neat cycloaliphatic epoxy resin and the resin system modified with three types of copolymer (copolymer content: 23 wt %). The cured neat resin [Fig. 3(A)] and the resin system [Fig. 3(B,C)] modified with a copolymer with a short alkyl side chain showed excellent transparency. On the other hand, the cured resin system modified with a copolymer with a long alkyl side chain [Fig. 3(D)] was opaque in appearance. This means that a phase separation structure was formed in the CEA/1-dodecene copolymer-added system. To confirm the morphology, observation by a scanning electron microscope (SEM) was carried out as shown in Figure 4. The results of the SEM observation showed that the neat cycloaliphatic epoxy resin [Fig. 4(A)] and the resin modified with

CEA/1-hexene copolymer or CEA/1-octene copolymer systems [Fig. 4(B,C)] were a homogeneous phase structure. On the other hand, the cycloaliphatic epoxy resin modified with CEA/1-dodecene copolymer system [Fig. 4(D)] showed a heterogeneous structure with a domain of micro meter order. Because all the copolymers have the epoxy groups as a functional group, they can react with the curing agent and thus are incorporated into the cycloaliphatic epoxy resin network. Thus, we infer that the dispersed phase in the cured resin is composed of the alkyl side chain of the copolymer. It is thought that an opaque cured resin by visual confirmation was obtained by the phase separation of the long alkyl side chain.

Thermal properties of the cured unmodified and modified systems

To investigate the thermal properties, a dynamic mechanical analysis was carried out. Figure 5 shows the storage modulus, E' , and $\tan \delta$ curves for the unmodified and CEA/1-hexene copolymer modified systems. The storage modulus clearly decreased between the glassy region and the rubbery region, and the peak of $\tan \delta$ was observed in the glass-transition (T_g) region of the cured resin. An increase in the CEA/1-hexene copolymer content led to a shift in the glass-transition peak in the $\tan \delta$ curves towards a lower temperature. This result is attributed to the increase in the mobility of the network by the plasticizing effect of the alkyl chains. However, a decrement in T_g was less than 40°C even for the system to which CEA/1-hexane copolymer was added at 60 wt %. This result means that the

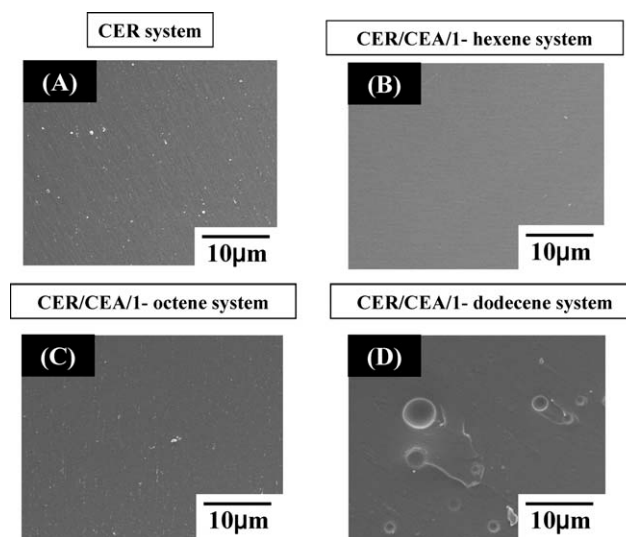


Figure 4 Scanning electron micrographs of fracture surfaces of cycloaliphatic epoxy resin (CER) unmodified and modified with CEA/ α -olefin copolymer. Modifier added: 23 wt %.

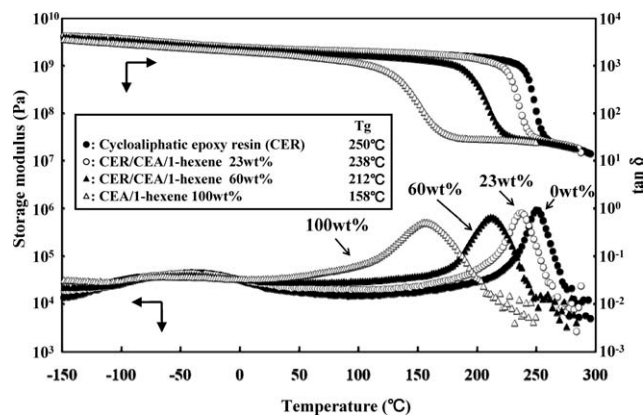


Figure 5 Dynamic mechanical properties of cycloaliphatic epoxy resin (CER) unmodified and modified with CEA/1-hexene copolymer.

decrease in cross-linking density of the matrix was inhibited because the flexible alkyl chains were introduced into the side chain. Moreover, the increase in the CEA/1-hexene copolymer content led to an increase in peak width of the glass-transition in the $\tan \delta$ curves. This result is due to the broad molecular weight distribution of the added copolymer (PDIs of CEA/1-hexene copolymer: 1.49, CEA/1-octene copolymer: 1.42, CEA/1-dodecene copolymer: 1.70) in the cured resin.

Figure 6 shows the dynamic mechanical properties of the neat cycloaliphatic epoxy resin and the resins modified with the three types of the copolymers (copolymer content: 60 wt %). Though CEA/1-octene copolymer and CEA/1-dodecene copolymer have longer alkyl chains compared to the CEA/1-hexene copolymer, a large decrease in T_g was not observed. This means that the decrease in T_g was suppressed by the introduction of the flexible alkyl chains as side chains. Moreover, the CEA/1-dodecene copolymer-modified system with the longest alkyl chain showed a higher T_g than that of the CEA/1-octene

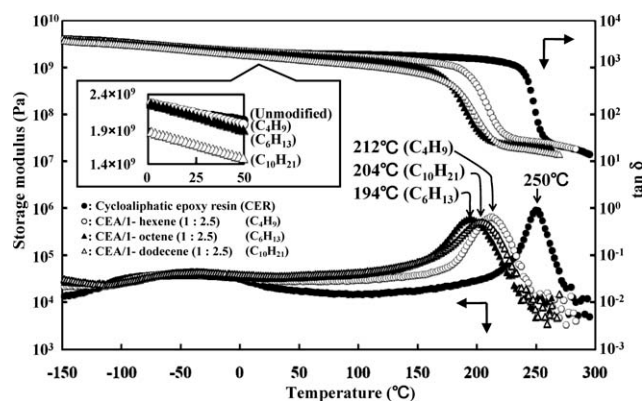


Figure 6 Dynamic mechanical properties of cycloaliphatic epoxy resin (CER) unmodified and modified with CEA/ α -olefin copolymer. Modifier added: 60 wt %.

copolymer-modified system. As previously mentioned, phase separation occurred in the CEA/1-dodecene copolymer-modified system. Therefore, it is clear that the decrease in the cross-linking density of the matrix was inhibited in this cured resin.

The storage modulus values near room temperature of the CEA/1-hexene and CEA/1-octene copolymer-modified systems with homogeneous structure are at the same level. On the other hand, the storage modulus in the CEA/1-dodecene copolymer-modified system with a heterogeneous structure showed a lower value compared to the two modified systems. In general, the storage modulus decreases by two steps as the temperature increases in the phase separation system. The CEA/1-dodecene copolymer-modified system which has the phase separation structure might have the T_g based on the dispersed phase (alkyl side chain segments) below -150°C . As a result, the storage modulus of this system near room temperature is lower than these of the other systems.

Figure 7 shows the T_g of unmodified and copolymer-modified systems containing different amounts of copolymer. T_g decreased with an increase in the added amounts of copolymer in all the modified systems. This result is attributed to the plasticizing effect of the flexible alkyl chains. However, a large decrease in T_g was not observed in the region with a small added amount of the copolymer. This result means that the cross-linking density of the cured resin remains at about the same level in this region. In addition, the decreased T_g in the CEA/1-dodecene copolymer-modified (copolymer content: ~ 60 wt %) system is smaller than that of the other systems, because the phase separation structure was formed in this system. On the other hand, when the content of the copolymer is over 80 wt %, SEM observation confirms that the homogeneous structure is formed. The cycloaliphatic epoxy resin dissolves to the modifier when a lot of modifier additive

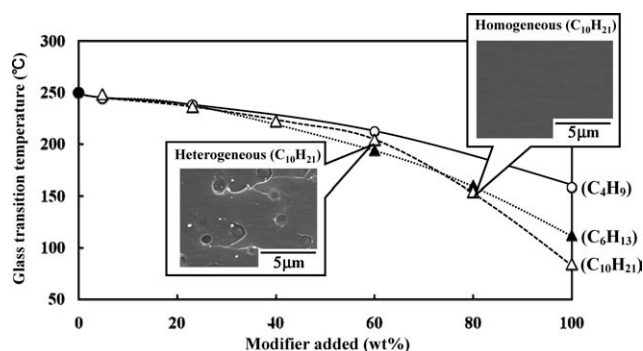


Figure 7 Glass transition temperature of cycloaliphatic epoxy resin (CER) unmodified and modified with CEA/ α -olefin copolymer. (●) Cycloaliphatic epoxy resin. Modifier: (○) CEA/1-hexene copolymer (C_4H_9), (▲) CEA/1-octene copolymer (C_6H_{13}), (△) CEA/1-dodecene copolymer ($\text{C}_{10}\text{H}_{21}$).

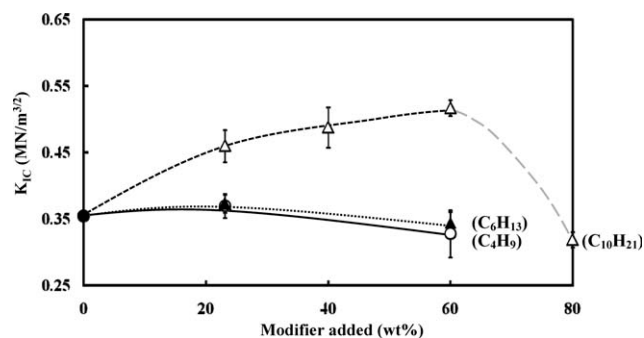


Figure 8 Fracture toughness (K_{IC}) of cycloaliphatic epoxy resin (CER) unmodified and modified with CEA/ α -olefin copolymer. (\bullet) Cycloaliphatic epoxy resin. Modifier: (\circ) CEA/1-hexene copolymer (C_4H_9), (\blacktriangle) CEA/1-octene copolymer (C_6H_{13}), (\triangle) CEA/1-dodecene copolymer ($C_{10}H_{21}$).

amount. Thus, in this region, the mobility of the network was increased by the plasticizing effect of the alkyl chains, and the T_g decreased dramatically.

Mechanical properties of the cured unmodified and modified systems

Figure 8 shows the fracture toughness (K_{IC}) of unmodified and copolymer-modified systems containing different amounts of modifier. The changes in K_{IC} in CEA/1-hexene copolymer or CEA/1-octene copolymer-modified systems were hardly observed compared with the unmodified system. On the other hand, the values of K_{IC} increased with an increase in the content of the CEA/1-dodecene copolymer, and a 50% increase in K_{IC} was attained at 60 wt % of the copoly-

mer content. However, in the system where the content of the copolymer is more than 80 wt %, the K_{IC} decreased rapidly. This means that a large toughening effect is attained only in the phase separated systems.

SEM observations of the fracture surfaces in the vicinity of the crack tip of unmodified and copolymer-modified systems are shown in Figure 9. A smooth fracture surface was observed in unmodified and CEA/1-hexene copolymer-modified systems [Fig. 9(A,B)], and thus, a plastic deformation region was hardly observed in these systems. On the other hand, in the fracture surface [Fig. 9(C)] of the CEA/1-dodecene copolymer-modified system, a plastic deformation area was clearly observed. These results indicate that the plastic deformation of the cured resin in the crack tip region easily occurs in the system modified with CEA/1-dodecene copolymer, that is, the heterogeneous phase structure was formed.

The crack tip region in the CEA/1-dodecene copolymer-modified system was enlarged to observe the fracture morphology in detail. Figure 10 shows SEM photographs of the fracture surface fractured at liquid nitrogen temperature and the fracture surface after the compact tension test. The result indicates that the diameter of the domain in the fracture surface after the compact tension test increased 1.1 times that of the fracture surface at liquid nitrogen temperature, and in the latter fracture surface, part of domain formed a cavity. This means that cavitation of the dispersed phase occurred in the fracture process. Namely, the plastic deformation of the matrix near the crack tip causes the cavitation of the dispersed soft phases, and thus the fracture energy

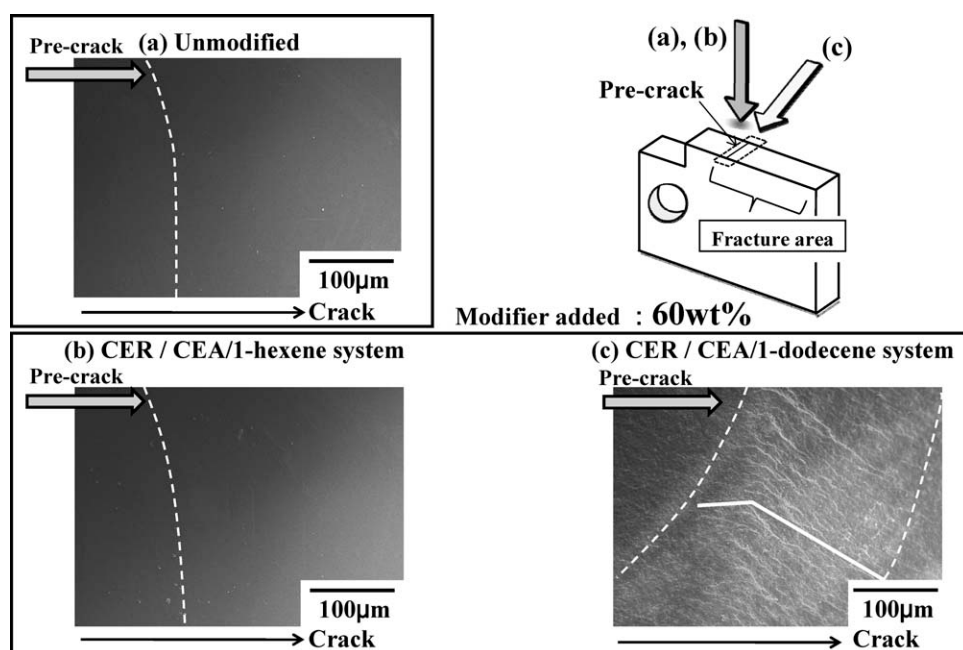


Figure 9 Scanning electron micrographs of the fracture surface of cycloaliphatic epoxy resin (CER) unmodified and modified with CEA/ α -olefin copolymer after the compact tension test.

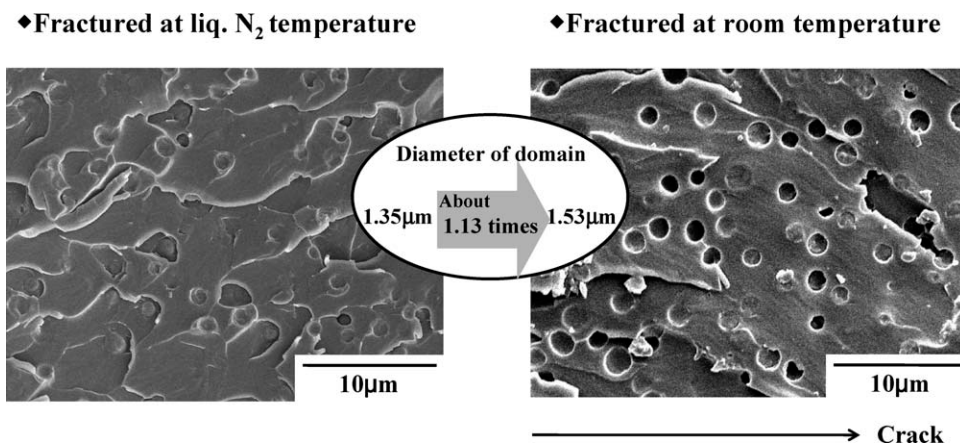


Figure 10 Scanning electron micrographs of the fracture surface of cycloaliphatic epoxy resin (CER) modified with CEA/1-dodecene copolymer. Modifier added: 60 wt %, Accelerating voltage: 5 KV.

seems to be consumed by the plastic deformation of the matrix.

Ochi et al.⁵ have already reported a similar toughening mechanism for Aramid-CTBN block copolymer-modified system. The main mechanisms for toughening of Aramid-CTBN block copolymer-modified system in the cavitation of rubber particles and the shear deformation of epoxy matrix near the crack tip. This statement is supported by the results of our work.

CONCLUSION

Reactive copolymers with flexible alkyl side chains were used as modifiers to improve the toughness of a cycloaliphatic epoxy resin. A large decrease in T_g was not observed in the system with a small added amount of the copolymers. This indicates that a decrease in the cross-linking density of matrix was inhibited because the flexible alkyl chains were introduced in the side chain. Changes in K_{IC} in CEA/1-hexene copolymer-modified or CEA/1-octene copolymer-modified systems were hardly observed, compared with that of the unmodified system. On the other hand, the addition of CEA/1-dodecene copolymer led to a 50% increase in the fracture toughness (K_{IC}) of the cured resin. The improvement in the toughness of this modified system is due to the energy absorption by the plastic deformation of the epoxy matrix and the cavitation of the dispersed phase.

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