

# Bonding properties of epoxy resin containing mesogenic group

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## Abstract

A liquid crystalline epoxy resin with a mesogenic group was synthesized and its adhesive bonding properties are compared to that of the bisphenol-A type epoxy resin. The bonding strength of the former resin system was higher than that of the latter. This suggested that the high bonding strength of the liquid crystalline epoxy system was due to the large deformation of this system along the stress direction. Bonding strength of all the cured systems had a maximum peak during curing, due to the increase in the internal stress which occurred during the curing shrinkage of the epoxy resins. To decrease the internal stress, we cured the epoxy resin with an excess amount of curing agents. Bonding strength of the system with the added excess amount of curing agent showed a higher value than that for the system with an equivalent amount of curing agent. It was considered that the high bonding strength of the former system was due to the low internal stress in this system. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Epoxy resin; Mesogenic group; Bonding properties

## 1. Introduction

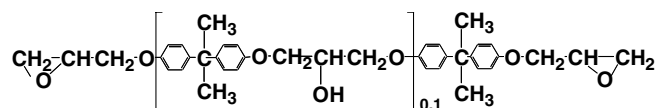
Epoxy resins are widely used as adhesives and as matrix resins of composites because of their many desirable properties, such as bonding properties, excellent chemical and thermal stabilities and electrical properties [1]. Recently, liquid crystalline epoxy resins which contain mesogenic groups in their backbone, such as the biphenol-type [2–5], azine-type [6], stilbene-type [7], and hydroxybenzoic acid-type resins [8,9] have been noted. Possible application of these materials includes waveguides and mechanically switched optical devices etc. [9]. Many investigations have reported the synthesis and the optical and mechanical properties of the liquid crystalline epoxy resins [2–11]. We have also reported the thermal and mechanical properties of a liquid crystalline epoxy resin containing a mesogenic group [2,3,5]. In the report [2], we discussed that the liquid crystalline epoxy resin containing a mesogenic group cured with a curing agent, which have neighboring active hydrogens, had a very weak glass transition and thus a very high rubbery modulus. On the other hand, Economy et al. [12–14] have reported that the use of a liquid crystalline polymer as an adhesive for bonding metal gave a good adhesion to metal substrates. In this case, the failure of the adhesive joints always occurred within the polymer adhesive layer [12–14].

In this work, we synthesized a novel liquid crystalline epoxy resin containing a mesogenic group. Its adhesive bonding property was compared with that of the bisphenol-A type epoxy resin.

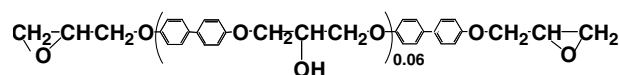
## 2. Experimental

### 2.1. Materials

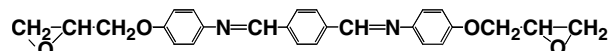
The epoxy resins used were the diglycidyl ether of bisphenol-A (DGEBA; MW = 380, Yuka Shell Epoxy Co.),



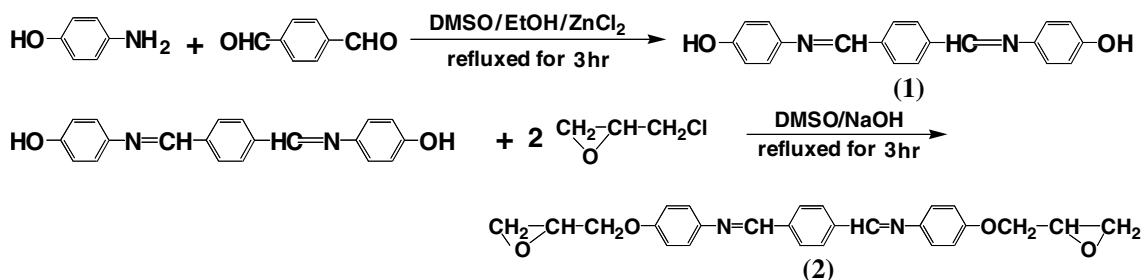
the diglycidyl ether of biphenol (DGEBP; MW = 330, Yuka Shell Epoxy Co.)



and the diglycidyl ether of terephthalylidene-bis-(*p*-aminophenol) (DGETA; MW = 428).

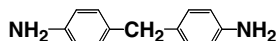


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Scheme 1.

4,4'-Diaminodiphenylmethane (DDM; MW = 198, Kanto Chemical Co.)



was used as the amine curing agent.

## 2.2. Synthesis of the diglycidyl ether of terephthalylidene-bis(*p*-aminophenol)

The synthesis pathway of the diglycidyl ether of terephthalylidene-bis(*p*-aminophenol) is shown in Scheme 1. Terephthalylidene-bis(*p*-aminophenol) (1) was synthesized from terephthalaldehyde 20 g (0.15 mol) and *p*-aminophenol 30 g (0.3 mol) in a solvent mixture of dimethyl sulfoxide (300 ml) and ethanol (600 ml) using zinc chloride (0.6 g) as the catalyst. The diglycidyl ether of terephthalylidene-bis(*p*-aminophenol) (2) was synthesized from terephthalylidene-bis(*p*-aminophenol) (17.56 g, 0.056 mol) and 1-chloro-2,3-epoxypropane (102.69 g, 1.11 mol) in dimethyl sulfoxide (50 ml) using tetra-*n*-butylammonium chloride (5 g, 0.016 mol) as the catalyst. The structure of the synthesized compounds was confirmed by <sup>1</sup>H NMR and FTIR spectroscopy.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.77–2.93 ppm (m, 4H, epoxy CH<sub>2</sub>);

3.37 ppm (m, 2H, CH); 3.97–4.27 ppm (m, 4H, CH<sub>2</sub>OPh); 6.96–6.97 ppm (d, 4H, aromatic); 7.25–7.27 ppm (d, 4H, aromatic); 7.98 ppm (s, 4H, aromatic); 8.53 ppm (s, 2H, CH=N).

IR (KBr): 2900–2930 cm<sup>-1</sup> (CH<sub>2</sub>), 1616 cm<sup>-1</sup> (CH=N), 1029 cm<sup>-1</sup> (ether), 914 cm<sup>-1</sup> (epoxy group).

## 2.3. Curing of epoxy resin

The terephthalylidene-type and biphenol-type epoxy resins were melted at 190°C. Stoichiometric amounts of the amine curing agent were then added. The terephthalylidene-type and biphenol-type cured systems were cured for 1 h at 190°C and for 3 h at 190°C, respectively.

The bisphenol-A type epoxy resin was degassed at 80°C under reduced pressure. Stoichiometric amounts of the amine curing agent was then added and stirred at 80°C. The compounds were cured at 80°C for 2 h and at 180°C for 4 h.

## 2.4. Measurements

Optical anisotropy of the cured epoxy resin was observed using an optical microscope (BH-2, Olympus Co., Ltd.) under crossed polarized light. The observation under the polarized microscope was carried out during the process of curing on a hot stage.

The morphology of the fracture surface after the lap shear test was observed using a scanning electron microscope (SEM: JSM-6500, JEOL Co., Ltd.) at an accelerating voltage of 15 kV. Prior to the examination, the surface was coated with a thin layer of gold to improve the conductivity and prevent charging.

The lap shear strength of the joints was measured using an Instron-type tensile machine (Shimadzu Autograph, AGS-2000E) at a cross-head speed of 50 mm/min according to ASTM D 1002-72. A steel plate was used as the substrate. The steel plate was degreased with acetone vapor, abraded with sandpaper, and then washed again with acetone vapor.

The internal stress of the cured epoxy resins was measured using the apparatus shown in Fig. 1. A phosphor bronze plate (90 × 30 × 0.2 mm<sup>3</sup>) was coated with the epoxy resin. As the coated resin was cured, the specimen was bent due to the difference between the linear thermal expansion coefficient of the phosphor bronze plate and the

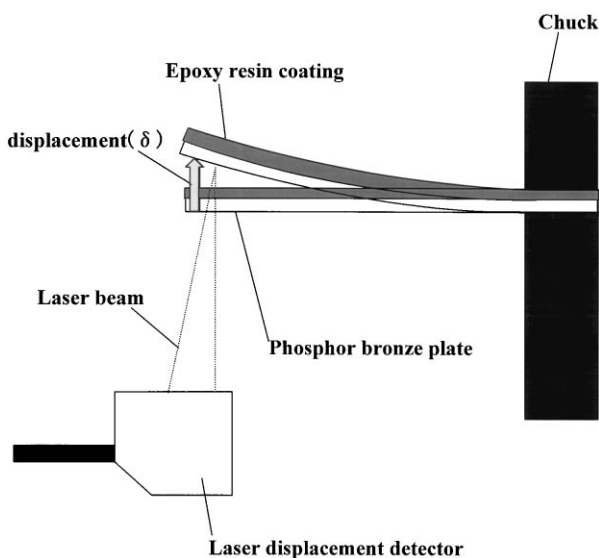


Fig. 1. Apparatus for measuring the internal stress of epoxy resin coatings.

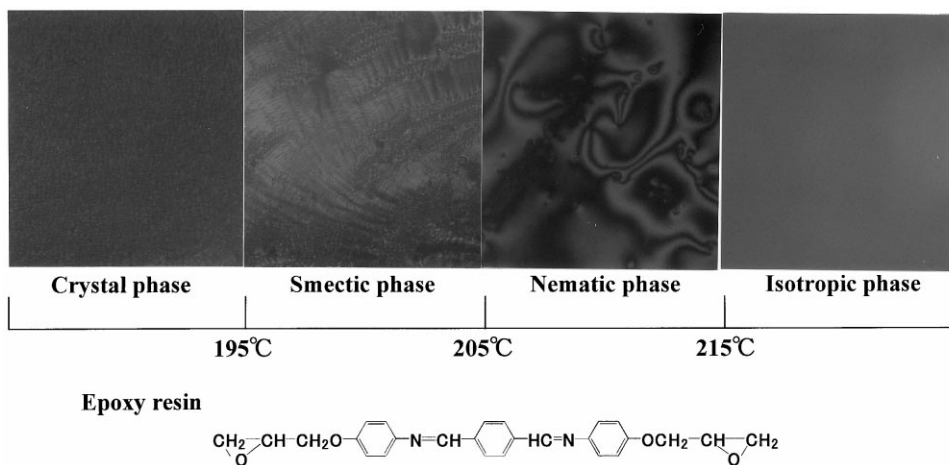


Fig. 2. Polarized micrographs of terephthalylidene-bis-(*p*-aminophenyl)DGE (DGETA). Magnification: 100 ×.

cured epoxy resin. The amount of the displacement,  $\delta$  was measured using a laser displacement detector (LB-01, Keyence Co., Ltd., Japan). The internal stress,  $\sigma$ , was calculated by the following equations: where  $E_1$  is Young's modulus of the phosphor bronze plate ( $1.22 \times 10^6$  kg/cm<sup>2</sup>),  $l/2$  is the distance from a fulcrum to the measuring point,  $h_1$  and  $h_2$  are the thicknesses of the metal plate and the coatings, respectively,  $H$  is the total thickness ( $h_1 + h_2$ ),  $\delta$  is the displacement,  $\rho$  is the radius of curvature and  $\sigma$  is the internal stress.

### 3. Results and discussion

#### 3.1. Optical properties of terephthalylidene-type epoxy resin

The polarized micrographs of the terephthalylidene-type epoxy resin (DGETA) are shown in Fig. 2. A well-defined colored pattern due to the orientation of the epoxy molecules was observed in the temperature range lower than 215°C. The crystal phase was observed up to 195°C. The

colored patterns which are similar to a baton-net and a Schlieren texture, were clearly observed at 195–205°C and 205–215°C, respectively. This means that the epoxy resin containing the mesogenic group is in the smectic and nematic liquid crystalline states in the corresponding temperature regions. These colored patterns disappeared over 215°C. The results show that the terephthalylidene-type epoxy resin containing the mesogenic group should have some ordered structures at 195–215°C. It has been reported that many types of mesogenic epoxy resins, e.g. the azine-type [6], stilbene-type [7], and hydroxybenzoic acid-type [8,9], etc. have some molecular order similar to a nematic liquid crystal in a particular temperature range. However, most of the liquid crystalline epoxy resins have not shown the smectic liquid crystalline state. This means that the terephthalylidene-type mesogenic group has a higher orientation ability, because of its large aspect ratio and anisotropy of polarity.

To confirm that the terephthalylidene-type epoxy resin has a liquid crystal structure even in the cured network structure, the DGETA/DDM system was observed under a polarization microscope. The polarized micrograph is

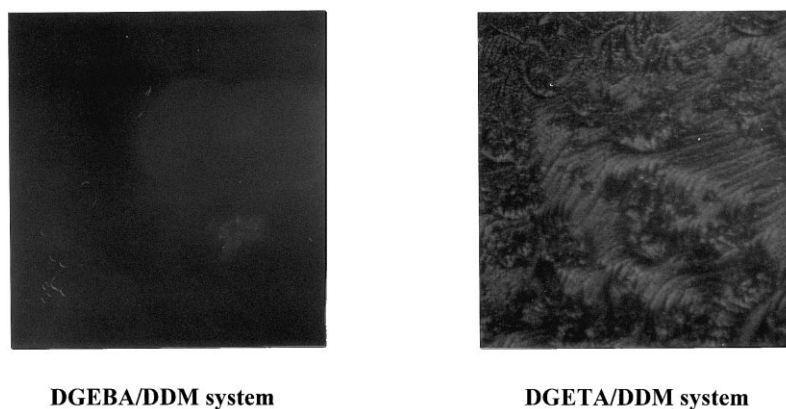


Fig. 3. Polarized micrographs of bisphenol-A and mesogenic epoxy resins cured with aromatic amine. Magnification: 100 ×.

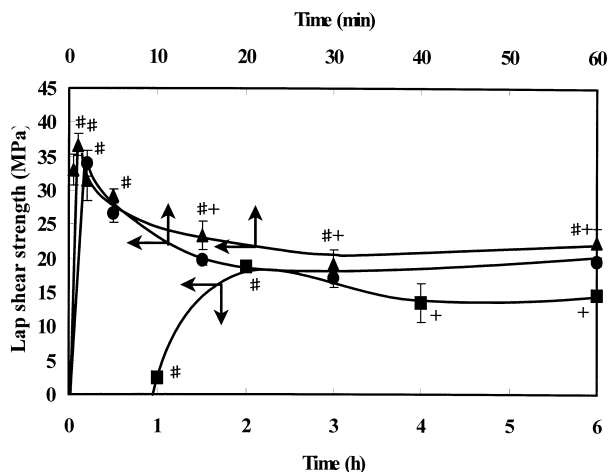
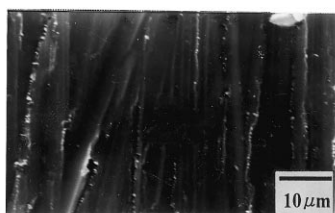
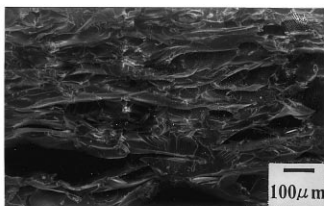


Fig. 4. Lap shear strength of bisphenol-A and mesogenic epoxy resins during curing. (+) contact failure; (#) cohesive failure. Epoxy resins: (■) DGEBA; (●) DGEBP; (▲) DGETA. Curing agent: DDM.

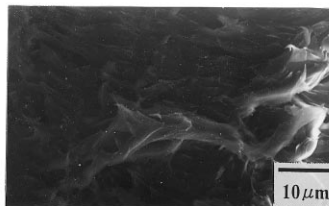
shown in Fig. 3, and compared with that of the DGEBA/DDM system. Nothing could be seen under the crossed polarized light in the DGEBA/DDM system. This means that the DGEBA/DDM system is an isotropic material and thus has no ordered structure. On the other hand, a well-defined colored pattern, which is similar to a smectic liquid crystal, was observed under the crossed polarized light in the DGETA/DDM system. This means that the network



a) Bisphenol A DGE/DDM system



b) Biphenol DGE/DDM system



c) Terephthalylidene-bis-(p-aminophenol)DGE/DDM system

Fig. 5. SEM of fractured surfaces of epoxy resin adhesive joints.

Table 1  
Work of adhesion and surface free energy of cured epoxy resin systems

	Bisphenol A type	Biphenol type	Terphthalylidene type
Surface free energy (dyn/cm)	57.4	63.7	63.4
Work of adhesion (erg/cm <sup>2</sup> )	110.2	114.9	114.9

chains of the DGETA/DDM system containing the mesogenic group should have an ordered structure which is analogous to that of a smectic liquid crystalline and thus the cured resin is optically anisotropic.

### 3.2. Bonding properties and bonding mechanism of epoxy resin containing mesogenic group

The lap shear strengths during the curing process of liquid crystalline epoxy resins are shown in Fig. 4, compared with that of the bisphenol-A type epoxy resin. Bonding strength of all the cured resin systems had a maximum value during the initial stage of curing. In this stage, a cohesive failure was observed for all the cured systems. After that, the bonding strength decreased and then reached some constant value during the final stage of the curing. In the final stage, the bisphenol-A type resin system showed contact failure, and the liquid crystalline epoxy system showed a mixed fracture mode of contact and cohesive failure. These results mean that though the bonding strength should increase with curing, the internal stress occurred with an increase in the curing shrinkage of the epoxy resin so that the bonding strength decrease after the vitrification of the cured resin. However, the bonding strength of the liquid crystalline epoxy resin was considerably higher than that of the bisphenol-A type epoxy resin. This shows that the introduction of a mesogen group into the epoxy resin backbone structure could effectively improve the bonding strength of the epoxy resins.

To investigate the reason why the liquid crystalline epoxy resins containing mesogenic groups have high bonding strengths, the morphology of the fracture surfaces after the lap shear test was observed using a scanning electron microscope. The SEM results are shown in Fig. 5. The fracture surface of the bisphenol-A type epoxy resin system in the final stage of curing showed a contact failure while the adhesive layer showed no deformation. This shows that the fracture of the adhesive joint occurred at the interface between the epoxy resin and the substrate. On the other hand, the fracture surfaces of the liquid crystalline epoxy resin systems during the final stage of curing showed the mixed mode fracture of cohesive and contact failures. Fig. 5b and c shows the morphology of the cohesive failure region in these systems. In the cohesive failure region of these systems, the adhesive layer was largely lengthened and then broke down. Generally speaking, the cohesive

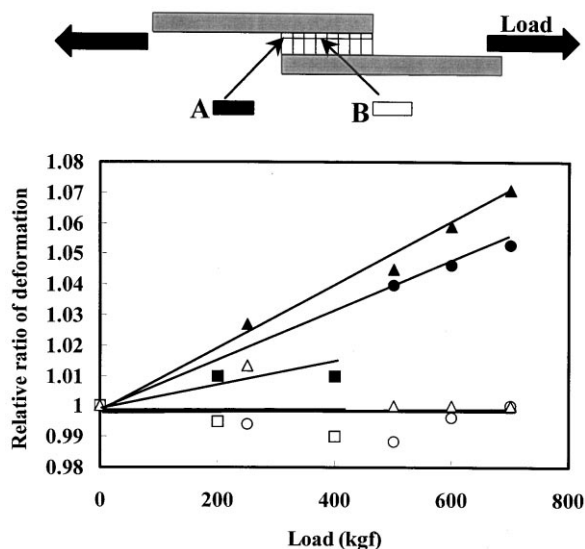


Fig. 6. Deformation in adhesive layer with loading during lap shear test. At point A: (■) DGEBA; (●) DGEBP; (▲) DGETA. At point B: (□) DGEBA; (○) DGEBP; (△) DGETA. Curing agent: DDM.

failure of the adhesive joints is observed when the deformation of the adhesive layer more easily occurs than the fracture of the interface. Thus, the following two hypotheses are proposed: first, the bonding energy of the interface in the liquid crystalline epoxy resin system is considerably higher than that of the bisphenol-A epoxy resin system, and secondly, the deformability of the former epoxy resin is higher than that of the latter epoxy resin. Thus, in these epoxy systems, the work of adhesion was calculated from the surface free energy of the adhesives and the substrate. The values of the work of adhesion and surface free energy are shown in Table 1. The values for the work of adhesion in the cured epoxy resins were about 115 and 110 erg/cm<sup>2</sup> in the liquid crystalline epoxy resins and in the bisphenol-A type resin, respectively. The work of adhesion of both the

liquid crystalline epoxy resin and the bisphenol-A type epoxy resin were nearly the same. This shows that the adhesion at the interface of the epoxy resins was same as that of the bisphenol-A type resin. Therefore, it is concluded that the difference in the fracture mode shown in Fig. 5 is not due to the difference in the adhesion at the interface.

To confirm the deformation of the adhesive layer during the lap shear test, the relative strain of the center and edge parts of the adhesive layer was observed using a reading-microscope. These results are shown in Fig. 6. The deformation of the center part of the adhesive layer with loading was very small for all the cured resin systems, because most of the load should be borne by the edge part of the adhesive joints. On the other hand, the deformation of the edge part of the adhesive layer significantly increased with increasing load on the adhesive joints. Furthermore, the deformation of the edge part of the liquid crystalline epoxy resin systems was larger than that of bisphenol-A type epoxy resin system. This result shows that the load on the adhesive joint is dispersed on the larger area of the bonding interface in the former epoxy adhesive joint systems. Thus, it is concluded that the high bonding strength of the liquid crystalline epoxy resin system was due to the large deformation of the adhesive resin.

### 3.3. Internal stress of cured resin systems

The internal stress generated during curing of the epoxy resin systems is shown in Fig. 7. The internal stress of all the cured resin systems rapidly increased during the initial stage of the curing. In addition, the internal stress is generated at the about same time when the maximum value of the lap shear strength was observed (Fig. 3) and then the bonding strength decreased with an increase in the internal stress during the curing process. Thus, it is natural to consider that the decrease in the lap shear strength with curing is due to the occurrence of the internal stress in the adhesive joints.

Internal stress of the liquid crystalline epoxy resin system was considerably higher than that of the bisphenol-A type epoxy resin system. This should be due to the high glass transition temperature of the liquid crystalline epoxy resin containing a mesogenic group. Therefore, it is easily supposed that if it is possible to reduce the internal stress that occurs in the curing process, the bonding strength of the cured liquid crystalline resin system could be significantly improved.

Thus, in order to decrease the internal stress, we cured the epoxy resin with an excess amount of curing agent. The comparison between the internal stress in the epoxy resins cured with excess and equivalent amounts of curing agent is shown in Fig. 8. The Internal stresses of all the cured resin systems increased with curing time and then a constant value is reached during the final stage of curing. Furthermore, the internal stress of the liquid crystalline epoxy resin cured with an excess amount of curing agent is about

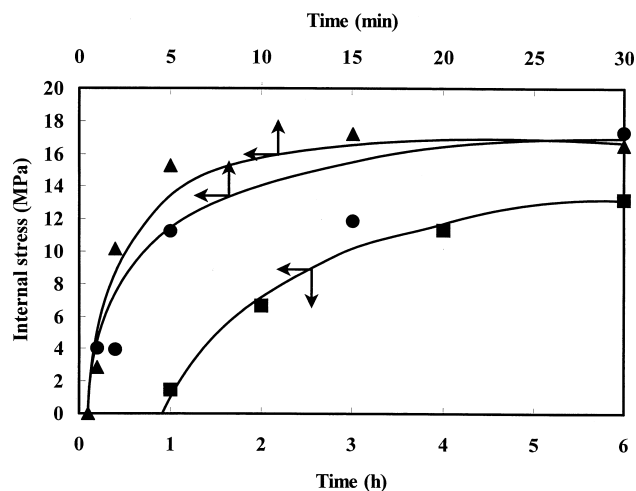


Fig. 7. Internal stress of bisphenol-A and mesogenic epoxy resins during curing. Symbols are the same as in Fig. 4.

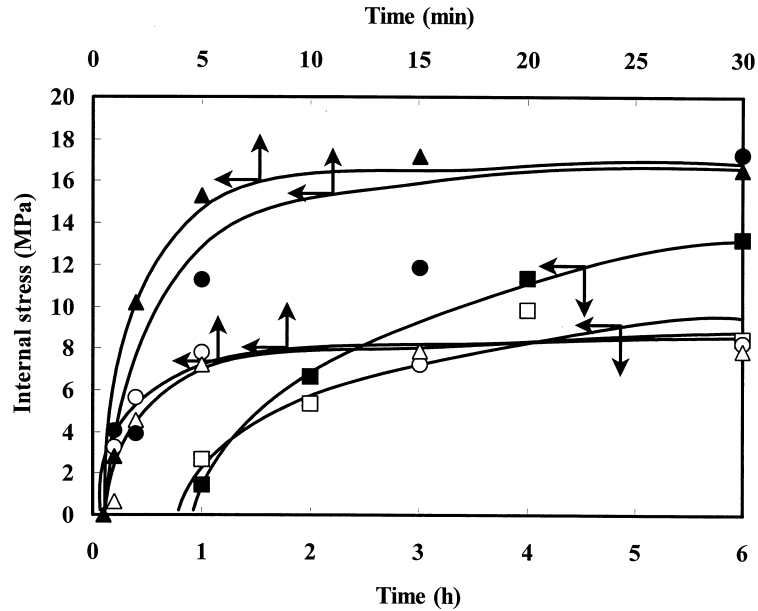


Fig. 8. Internal stress of bisphenol-A and mesogenic epoxy resins during curing. (■) DGEBA/DDM; (●) DGEBP/DDM; (▲) DGETA/DDM; (□) DGEBA/DDM (1.5 eq); (○) DGEBP/DDM (1.5 eq); (△) DGETA/DDM (2.0 eq).

10 MPa lower compared with that of the system cured with the equivalent amount of curing agent. The decrease in the internal stress is attributed to the decrease in the glass transition temperature of the epoxy resin cured with an excess amount of curing agent.

The dynamic mechanical properties of all the cured resin systems are shown in Fig. 9. In the cured epoxy resins with an excess amount of curing agent, the elastic modulus showed a lower value in the rubbery region. This result shows that the mobility of epoxy network increased due to the decrease in the cross-linked density due to the excess amount of curing agent. The elastic modulus in the rubbery region of the liquid crystalline epoxy resin systems significantly decreased compared with that of the bisphenol-A

type epoxy resin system. We previously reported [5] that the thermal motion of the network chains in the cured mesogenic epoxy resin was highly suppressed by orientation of the mesogenic group. Therefore, it is concluded that the precipitous decrease of the elastic modulus in the glass transition region of the liquid crystalline epoxy resin systems was due to an improvement the network mobility due to the excess amount of curing agent. Also,  $\tan \delta$  peaks of the cured systems shifted to a lower temperature in the systems cured with an excess amount of curing agent. As mentioned above, the decrease in the glass transition temperature could cause the decrease in the internal stress of the cured resins.

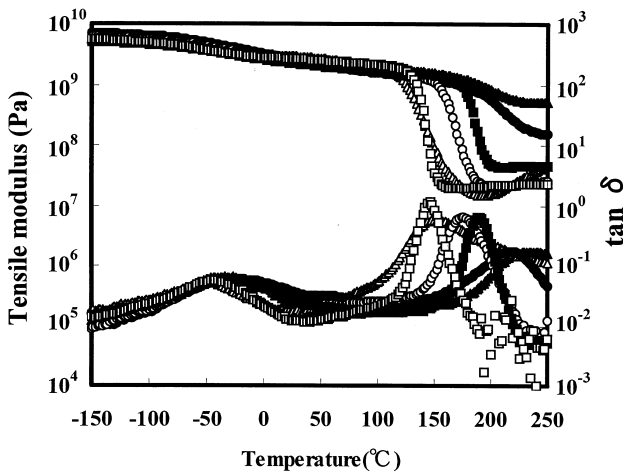


Fig. 9. Dynamic mechanical properties of cured epoxy resins. Symbols are the same as in Fig. 8.

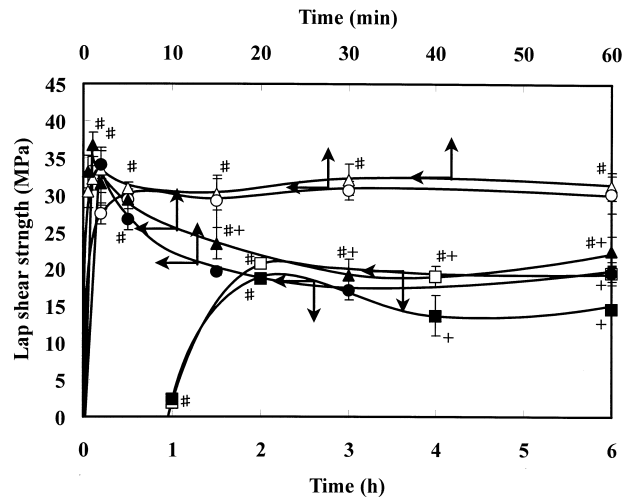


Fig. 10. Lap shear strength of bisphenol-A and mesogenic epoxy resins during curing: (+) contact failure; (#) cohesive failure. Symbols are the same as in Fig. 8.

The lap shear strength in the epoxy resin cured with an excess amount of curing agent is shown in Fig. 10, and compared with the equivalent amount of curing agent. Bonding strength of the systems with the excess amount of curing agent is higher than that of the systems with the equivalent amount of curing agent. In addition, the decrease in the bonding strength during the initial curing stage with the generation of internal stress was not observed. Therefore, we concluded that the bonding strength of the mesogenic epoxy systems are significantly improved by decreasing the internal stress of this resin system. In addition, the fracture surface of the liquid crystalline epoxy resin cured with an excess amount of curing agent showed cohesive failure even during the final stage of curing, though the systems cured with the equivalent amount of curing agent showed the mixed fracture mode during this curing stage. This result also shows that the bonding strength of the epoxy adhesive joints is improved due to a decrease in the internal stress of the epoxy adhesive layer cured with the excess amount.

#### 4. Conclusions

Liquid crystalline epoxy resins containing mesogenic groups were synthesized and their adhesive bonding strength was measured. Thus, we reached the following conclusions.

Liquid crystalline epoxy resin systems had a higher bonding strength than the commercial bisphenol-A type epoxy

resin. The high bonding strength of the liquid crystalline epoxy resin system was due to the large deformation of the resin along the stress direction. In addition, the lap shear strength of this resin system could be improved by reducing the internal stress which occurred during the curing.

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