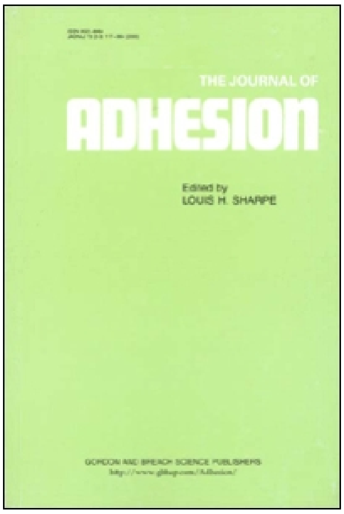

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Bonding Properties of Liquid Crystalline Epoxy Resins Having Different Phase Structures

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Bonding Properties of Liquid Crystalline Epoxy Resins Having Different Phase Structures

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Liquid-crystalline epoxy resin systems, which have different phase structures (isotropic and nematic polydomain), were prepared. The bonding properties of their systems were investigated and related to their phase structure. As a result, the lap shear strength of the nematic system was lower than that of the isotropic system, although the nematic adhesive layer showed larger deformability than the isotropic one. The interfacial bonding properties of both the isotropic and nematic systems were investigated, and, thus, it was clarified that the low bonding strength of the nematic system was due to the low concentration of hydroxyl groups at the adhesive interface. The decrease in the concentration of hydroxyl groups was due to the restriction of the molecular motion derived from the ordered structure of the nematic system.

Keywords: Cross-linking, Orientation, Bonding property

INTRODUCTION

Epoxy resins are widely used as an adhesive, a coating material, and the matrix resin of composites. In these fields, higher toughness and bonding strength are usually required. Recently, liquid-crystalline epoxy resins, which consist of a rigid backbone structure, have become attractive for their properties. Many research studies have already been reported on the synthesis methods [1–3] and mechanical and thermal properties [4–6].

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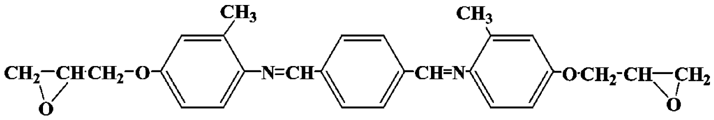
In a previous article, we reported that a terephthalylidene-type liquid-crystalline epoxy resin has considerably high fracture toughness, particularly in the system that consists of a nematic phase rather than an isotropic phase [7]. Taking into account their high toughness, excellent bonding strength of these systems can be expected when they are used as an adhesive layer. Therefore, the bonding property of some liquid-crystalline epoxy systems has already been investigated [8–11]. However, no discussions have occurred on the influence originating from the difference in the phase structure.

In this study, we investigated the bonding properties of a terephthalylidene-type epoxy resin that has different phase structures (isotropic and nematic). Moreover, the interfacial properties in both phase systems were investigated and related to their bonding properties.

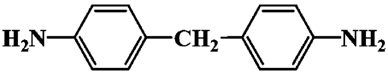
EXPERIMENTAL

Materials

The epoxy resin used was the diglycidyl ether of terephthalylidene-bis-(4-amino-3-methylphenol) (**DGETAM**, Mw = 456).



The curing agent was 4, 4′-diaminodiphenylmethane (DDM, Mw = 198, Kanto Chemical Co., Ltd., Tokyo, Japan).



Synthesis of the Diglycidyl Ether of Terephthalylidene-bis-(4-amino-3-methylphenol) (DGETAM)

The synthetic procedure was carried out using terephthalaldehyde, 4-amino-3-methylphenol, and 1-chloro-2, 3-epoxypropane as previously reported [4]. The structure of the synthesized compounds was confirmed by ^{1}H-NMR and FT-IR spectroscopy. The transition temperature of this synthesized epoxy resin was measured using a differential scanning calorimeter (DSC220C, Seiko Instruments Inc., Chiba, Japan) at a heating rate of 5°C/min. As a result, this liquid-crystalline epoxy resin exhibited a nematic phase between 169 and 212°C: C 169 N 212 I.

Curing of the Epoxy Resin

A mixture of a stoichiometric amount of the epoxy resin and curing agent was heated at two different curing temperatures. Namely, one was cured at 165°C for 10 min and 200°C for 20 min, and the other was cured at 190°C for 30 min.

The sample for the measurement of the contact angle and XPS was cured on Wood's alloy (mp 70°C, Kishida-Chemical Co., Ltd., Osaka, Japan) as a substrate. The Wood's alloy contacted with the epoxy adhesive layer was then heated and removed at 80°C.

Measurement

The liquid-crystalline texture was observed under crossed polarized light using a polarized optical microscope (Olympus Co. Tokyo, Japan, BHS-751P) equipped with a hot stage (Sinku-Riko Co. Kyoto, Japan, TPC-1000).

Wide-angle X-ray diffraction (WAXD, JDX-3530, JEOL Co., Ltd., Tokyo, Japan) was measured to evaluate the microscopic anisotropy of the network chains.

Lap shear strength was measured using an Instron-type tensile machine (Autograph AG-2000E, Shimazu Co., Kyoto, Japan) according to the ASTM D 1002-72. The crosshead speed was 50 mm/min, and a steel plate was used as a substrate (plate thickness: 3.2 mm). The steel plate was degreased with acetone and ground with sandpaper. The ground plate was washed again with acetone. The displacement of the adhesive layer with loading was measured using a calibrating microscope.

The fracture surfaces of the DGETAM/DDM systems were observed using a scanning electron microscope (SEM, JSM-6500, JEOL Co., Ltd., Tokyo, Japan). Prior to the examination, the surfaces were coated with a thin layer of gold to improve conductivity and prevent charging.

The surface free energy was calculated by measurement of the contact angle (FACE CA-V, Kyowa Interface Science Co., Ltd., Saitama, Japan) at room temperature for distilled water and diiodomethane. The work of adhesion was calculated by the expanded Fowkes's equations:

$$\mathrm{Wa}_{(\mathrm{w\text{-}substrate})} = \gamma_{L\mathrm{w}}(1+\cos\theta_{(\mathrm{w\text{-}substrate})}) = 2(\gamma_{\mathrm{s}}^{\mathrm{d}} \cdot \gamma_{L\mathrm{w}}^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{s}}^{\mathrm{p}} \cdot \gamma_{I\mathrm{w}}^{\mathrm{p}})^{1/2}$$

$$\mathrm{Wa}_{(\mathrm{i\text{-}substrate})} = \gamma_{L\mathrm{i}}(1+\cos\theta_{(\mathrm{i\text{-}substrate})}) = 2(\gamma_{\mathrm{s}}^{\mathrm{d}} \cdot \gamma_{L\mathrm{i}}^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{s}}^{\mathrm{p}} \cdot \gamma_{L\mathrm{i}}^{\mathrm{p}})^{1/2}$$

where Wa: work of adhesion; θ contact angle; w: water; i: diiodomethane, γ_L^{d},γ_L^{p}: dispersion and polar force components of the surface free energy of the liquid drop, and γ_s^d, γ_s^p: dispersion and polar force components of the surface free energy of the adhesive layer.

The surface chemical property was evaluated using an X-ray photoelectron spectroscope (XPS, JPS9000MX, JEOL, Co., Ltd., Tokyo, Japan). The spectra were collected after 64 scans. The resolution of the spectrum was 0.1 eV.

RESULTS AND DISCUSSION

Phase Structure of Terephthalylidene-Type Epoxy Resin System

The phase structures of the DGETAM/DDM system with the progress of curing are shown in Figure 1. When the mixture of the epoxy monomer and curing agent are heated at 190°C, the system is in an isotropic state initially. The system then retains the isotropic state until the final stage of curing. Based on this observation, it is considered that the system cured at 190°C has an isotropic phase structure.

On the other hand, the system cured at 165°C was in an isotropic state initially. However, with the progress of curing, it gradually exhibited a birefringence pattern based on the formation of a

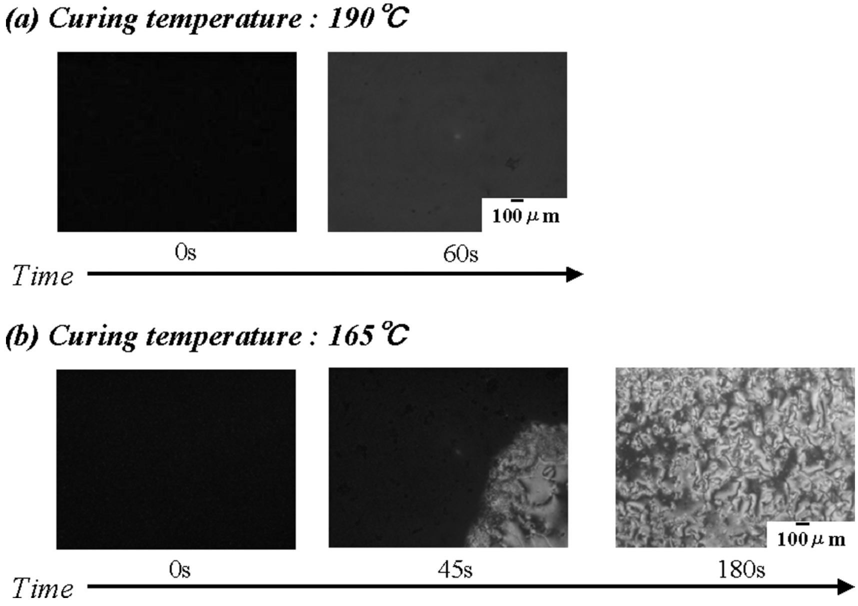


FIGURE 1 Polarized optical micrographs of the DGETAM/DDM systems in the curing process. (See COLOR PLATE I)

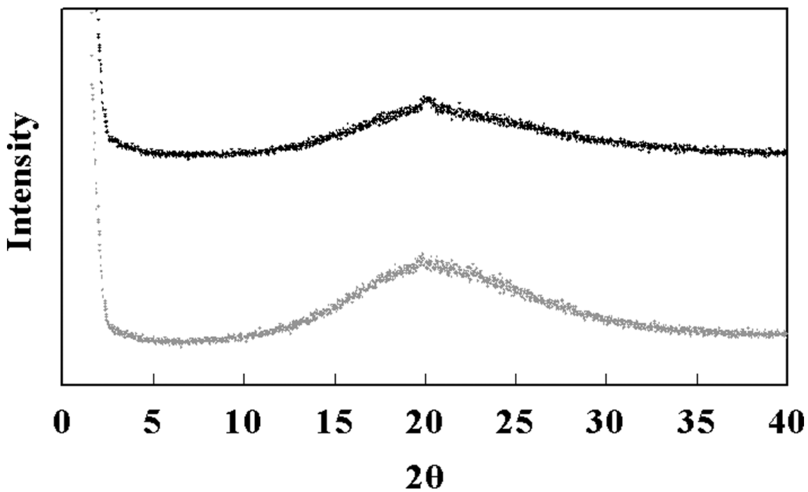


FIGURE 2 Wide angle X-ray diffraction of the DGETAM/DDM systems. (●) isotropic, (○) nematic system.

liquid-crystalline phase. It is considered that this cured system constitutes a liquid-crystalline phase at this curing temperature because it shows a schlieren texture as a locked structure.

To investigate the domain structure of the systems cured at this temperature (165°C), the wide-angle X-ray diffraction pattern was then measured. The relationship between the intensity and diffraction angle is shown is shown in Figure 2. In the system cured at 190°C and 165°C, each peak was observed at around 20° over the broad range of 2θ and, on the other hand, no peaks at a low value of 2θ derived from the smectic liquid-crystalline phase were observed. Moreover, taking into account that only the system cured at 165°C showed a birefringence pattern in the observation by the polarized optical microscope and WAXD picture (Debye–Scherrer ring), it is considered that the system cured at 165°C has a polydomain structure (each domain is constituted from a nematic phase), and the system cured at 190°C has an isotropic phase structure.

Lap Shear Strength of Each Terephthalylidene-Type Epoxy Resin System

The lap shear strength of the DGETAM/DDM system with the progress of curing is shown in Figure 3. In the initial stage of curing, the lap shear strength of both the isotropic and nematic systems showed

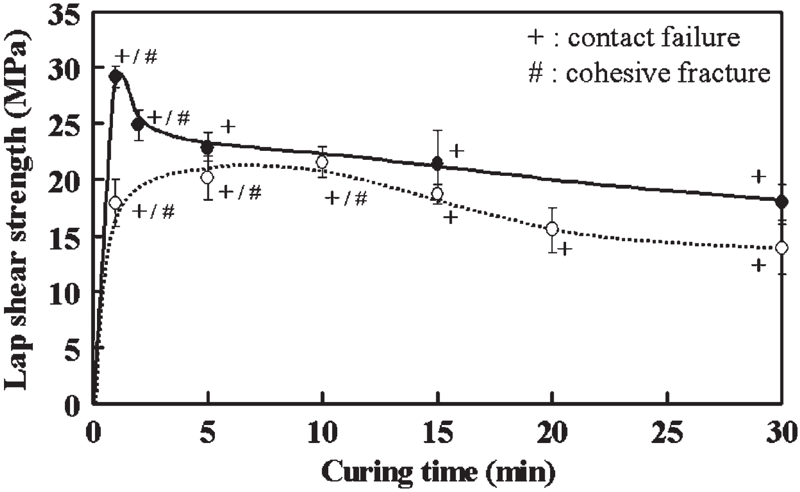


FIGURE 3 Lap.shear strength of the DGETAM/DDM system. (●) isotropic, (○) nematic system.

maximum values. With increasing curing time, the values of the lap shear strength gradually decreased in both systems. It is proposed that these decreases in the lap shear strength during the curing process are derived from the internal stress that is occurring at the interface between the adhesive layer and the substrate [3]. Moreover, the bonding strength of the isotropic system showed a higher value than that of the nematic system throughout the whole curing process. This means that the bonding property of the isotropic system is superior to that of the nematic system. Namely, a difference is observed in their bonding strength, although the resin and curing agent are the same.

Concerning the fracture mode, on the other hand, a mixed fracture of contact and cohesive failures was observed for both the cured systems in the initial curing stage. However, in the final stage of curing, both systems showed contact failure. Although both systems showed contact failure in the final stage of curing, the lap shear strength of the isotropic system was higher than that of the nematic system. For a discussion of these results, one must consider the deformability of the adhesive layer and/or the interfacial bonding property of these systems. First of all, the deformability of the adhesive layer in these systems was investigated.

The deformation of the center and edge parts of the adhesive layer during the lap shear test was then measured using a calibrating microscope. The relationship between the load and the relative strain

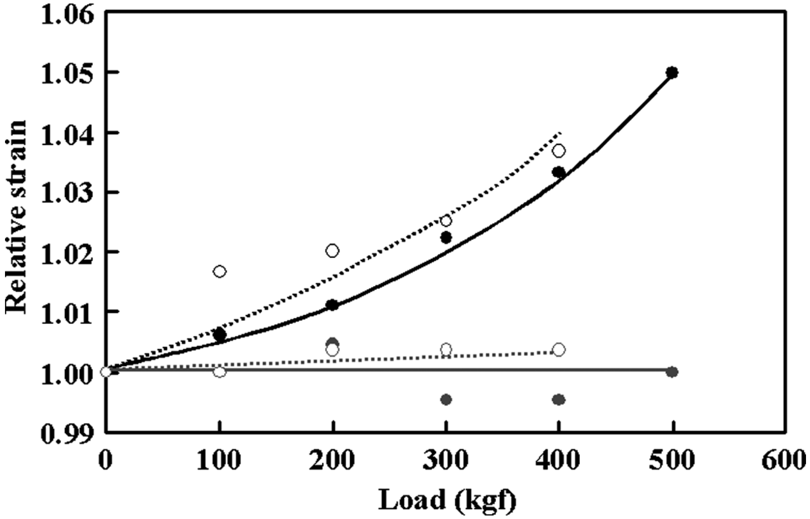


FIGURE 4 Deformation of the DGETAM/DDM adhesive layers. Edge part: (●) isotropic, (○) nematic system. Center part: (●) isotropic, (○) nematic system.

of the adhesive layer is shown in Figure 4. For both cured systems, the relative strain at the center part of the adhesive layer with loading was very small. On the other hand, the relative strain at the edge part significantly increased with an increase in the load. This means that most of the loads originate in the edge part of the adhesive joints. Furthermore, the relative strain at the edge part of the nematic system was larger than that in the isotropic system. This result means that the adhesive layer in the nematic system has considerably larger deformability than that in the isotropic system. This result is in good agreement with the fracture toughness data reported in our previous paper [7]. However, fracture of the adhesive layer in the nematic system was observed at relatively small loads, regardless of the higher deformation ability of the adhesive layer in the nematic system. To investigate other factors affecting their bonding strength, the interfacial bonding properties of these systems were then investigated.

Interfacial Bonding Property of the Terephthalylidene-Type Epoxy Resin System

The surface free energy of the adhesive interface and substrate calculated from the contact angle is shown in Table 1. The value of the

TABLE 1 Surface Free Energy of the DGETAM/DDM System

	γ_s^d (mJ/m^2)	γ_s^p(mJ/m^2)	γ_{total} (mJ/m^2)	W_a (mJ/m^2)
Substrate	33.3	23.9	57.2	—
Isotropic system	34.5	8.6	43.1	96.5
Nematic system	41.8	1.8	43.6	87.7

dispersion force component, γ_s^d, in the isotropic system compared with that in the nematic system was closer to that of the substrate. In the same way, the polar force component, γ_s^p, in the isotropic system compared with that in the nematic system was also closer to that of the substrate. Particularly, the difference in the surface free energy between the isotropic and nematic system was remarkably observed in the polar force component, γ_s^p. It is proposed that the polar groups at the adhesive interface mainly affect the interfacial bonding property. Consequently, the work of adhesion, Wa, calculated from those values showed a high value in the isotropic system. This result means that the isotropic system has a superior interfacial bonding strength compared with that of the nematic system. Therefore, it is considered that the higher lap shear strength of the isotropic system is due to the good interfacial bonding property.

As mentioned above, although the same resin and curing agent were used, the interfacial bonding properties of their systems were different. To consider these phenomena, the chemical property at the adhesive interface was investigated. The chemical composition at the adhesive interface was then measured using the XPS method. The peaks based on a carbon atom bonded with another atom are shown in Figure 5. In this figure, the measurement spectrum and the separated spectrum based on their binding energies are shown. In the separated peaks based on the C–C and C–N bonds, their peak intensity showed almost the same value in both the isotropic and nematic systems. On the other hand, in the peaks of the C–O bond, the intensity in the isotropic system is stronger than that in the nematic system. This result means that the C–O bonds in the isotropic system are more concentrated at the adhesive interface than those in the nematic system. However, it cannot be confirmed from only these data whether this C–O peak is due to an ether group or a hydroxyl group. The peaks based on an oxygen atom bonded with another atom are shown in Figure 6. The peaks based on ether groups in the isotropic system decreased, compared with those in the nematic system. On the other hand, the peak based on hydroxyl groups in this system increased compared with those in the nematic

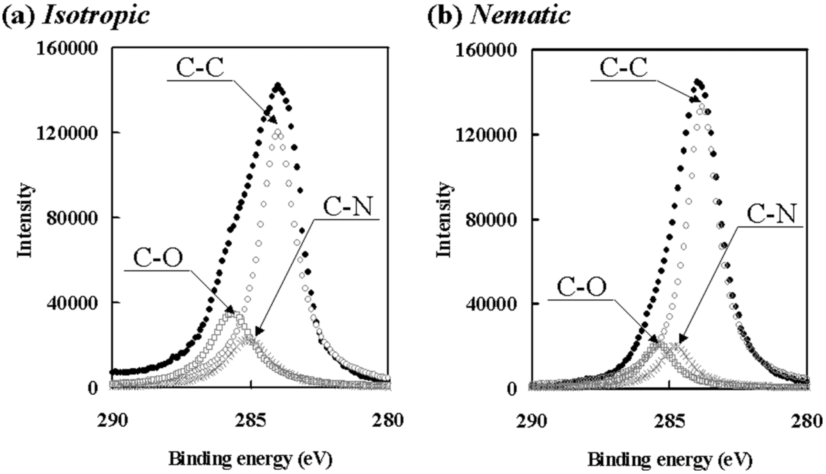


FIGURE 5 Carbon 1s spectra of the (a) isotropic and (b) nematic DGE-TAM/DDM systems. (●) measurement spectrum, (○) C–C spectrum, (□) C–O spectrum, (×) C–N spectrum.

system. This result means that more hydroxyl groups are concentrated at the adhesive interface in the isotropic system. Namely, different phenomena should be occurring at the interface of the isotropic and the nematic systems.

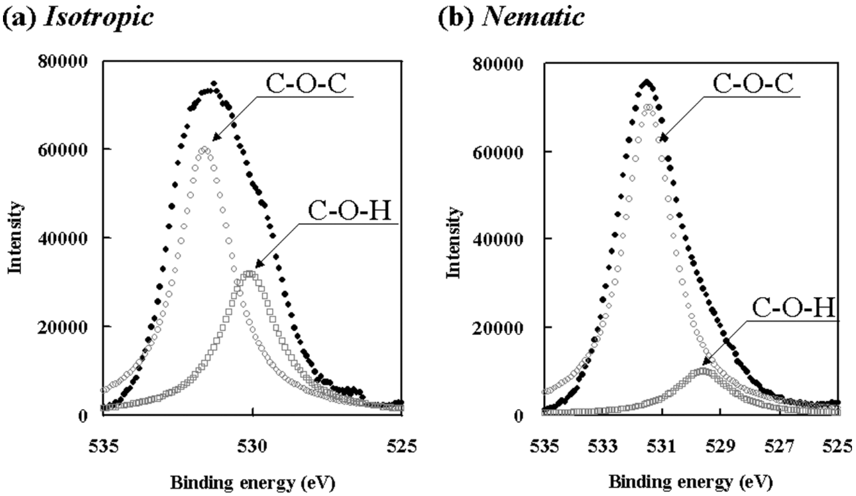


FIGURE 6 Oxyten 1s spectra of the (a) isotropic and (b) nematic DGE-TAM/DDM systems. (●) measurement spectrum, (○) C–O–C spectrum, (□) C–O–H spectrum.

In the curing reaction, it is well known that hydroxyl groups are formed from the ring-opening reaction of the epoxy groups. It is naturally assumed that the formed hydroxyl groups have a strong interaction with the substrate because of their high polarity. Therefore, it is considered that the high interfacial bonding property is due to the localization of the hydroxyl groups formed at the adhesive interface.

As the conversion of the epoxy group increases with the progress of curing, the amount of the formed hydroxyl groups should also increase. To compare the amount of the hydroxyl groups in each curing process, the relative ratio of the hydroxyl group peak intensity at the adhesive interface in each epoxy conversion was calculated. The relative ratio of the hydroxyl group peak intensity means that the value is obtained by dividing the peak areas based on the hydroxyl groups by the peak areas based on the C—C bond as an internal standard, assuming that the peak area of the C—C bond is not affected by the localization of hydroxyl groups.

The relationship between the conversion of the epoxy group and the relative ratio of hydroxyl groups at the adhesive interface is shown in Figure 7. With increasing conversion of the epoxy groups, it was observed that the relative ratio of hydroxyl groups in both systems

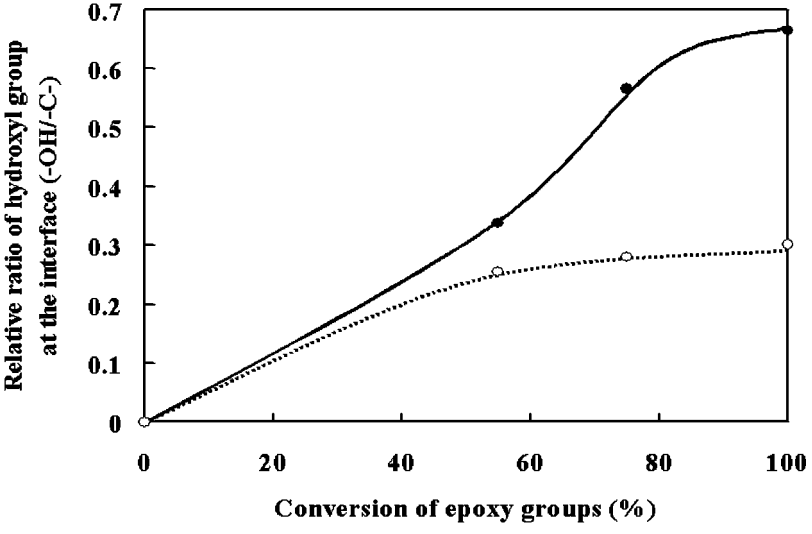


FIGURE 7 Relative ratio of hydroxyl peak intensity in the DGETAM/DDM system. (●) isotropic, (○) nematic system.

increased up to around 50% epoxy conversion. This increase in the relative ratio of hydroxyl groups is due to the ring-opening reaction of the epoxy group. However, at more than 50% epoxy conversion, the hydroxyl group ratio remained at some constant value only in the nematic system. This result means that the amount of hydroxyl groups at the interface decreased in the nematic system. Namely, it is considered that the diffusion of the hydroxyl groups to the adhesive interface was prevented in this system. We consider that this phenomenon is due to the formation of the liquid-crystalline phase, because the liquid-crystalline phase was gradually formed at around 50% epoxy conversion. It is proposed that the molecular motion in the liquid-crystalline network was highly restrictive for the formation of an ordered domain.

Thus, it is considered that the low bonding strength in the nematic system, in spite of the large deformation ability of the adhesive layer, is due to the poor interfacial bonding property. This poor interfacial bonding property is based on the lower localization of hydroxyl groups formed by the epoxy ring-opening reaction at the adhesive interface, because a localization of the hydroxyl groups at the interface is prevented by the ordered structure in the formation of the liquid-crystalline phase.

CONCLUSION

The isotropic system showed a higher bonding strength than the nematic system, although the nematic adhesive layer showed larger deformability than that of the isotropic system. It was clarified that the high bonding strength of the isotropic system was based on a good interfacial bonding property. Moreover, it was considered that this high interfacial bonding property is due to the localization of hydroxyl groups that were formed by the epoxy ring-opening reaction. On the other hand, the hydroxyl group concentrations at the adhesive interface in the nematic system are less than that in the isotropic system. This phenomenon is considered to be due to the restriction of the molecular motion originating in the formation of the liquid-crystalline phase as an ordered structure.

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