Influence of Network Chain Orientation on the Mechanical Property of Epoxy Resin Filled with Silica Particles

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ABSTRACT: When tensile stress was applied to epoxy resin filled with silica particles, we expected that the stress concentration would occur in the epoxy matrix near the interface between the matrix and the silica particles. We investigated the plastic deformation of the network chains near the interface, which was quantitatively evaluated using a polarized microscope FTIR technique. A biphenol-type epoxy resin, which has a mesogenic group in the backbone moiety, was used as the matrix resin. As a result, reorientation of the network chains along the direction of the tensile stress near the interface with the silica particles was observed. Especially when the silica/matrix interface has good bonding properties, the reorientation of the network chains was observed at a larger area around the silica particles. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 787–794, 2003

Key words: silica; surface treatment; network chain orientation

INTRODUCTION

Biphenol and tetramethylbiphenol-type epoxy resins have excellent electric and mechanical properties. It has been reported that these biphenol-type epoxy resins have high rigidity in the high-temperature region and low shrinkage during curing.[1,2] Moreover, it has been also reported that biphenol-type resins have very low viscosity and good bonding properties with metal.[3] Because of these excellent properties, this type of epoxy resin is used as a material for the packaging of semiconductor devices. However, the packaging materials must have thermal expansion coefficients that are close to those of the semiconductor devices for decreasing internal stress. Therefore, the epoxy resin is usually loaded with silica particles as a filler. Many investigators have already studied the influence of the filler shape, size, and content[4–9] on the mechanical properties of a silica-filled epoxy resin. Moreover, the influence of the bonding in the silica/matrix interface on the mechanical properties has been also reported.[9–12] In this study, we investigated the effects of bonding properties of the silica/matrix interface on the toughness of a silica-filled biphenol-type epoxy resin and the toughening mechanisms in a filled biphenol-type epoxy resin based on the network chain orientation of the matrix near the silica particles.

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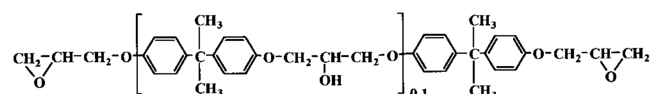
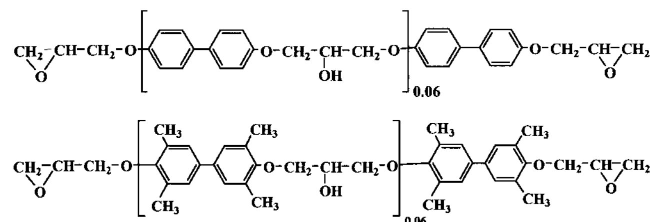
EXPERIMENTAL

Materials

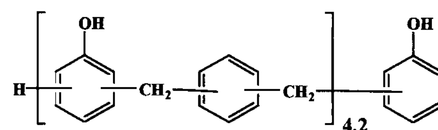
The epoxy resins used were a commercial grade of the diglycidyl ether of bisphenol A (Epikote 828, Yuka-shell Epoxy Co., Ltd.):



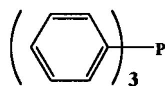
and a biphenol-type epoxy resin (YL6121, Yuka-shell Epoxy Co., Ltd.), which is a mixture of the following two epoxy resins:



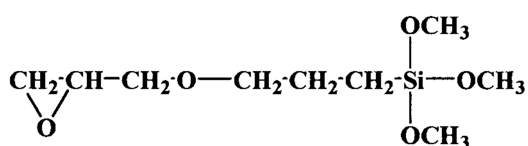
The curing agent used was phenol-*p*-xylendiolnovolac (XL-225-3L, Mitsui-kagaku Co., Ltd.):



and triphenylphosphine (TPP, Kanto-Chemical Co., Ltd.) was used as an accelarator for the curing of the epoxy resin:



Spherical silica (FB-35, Denki Kagaku Kougyou Co., Ltd., Japan) was used as the filler. The mean size of the silica particles was 10 μm. A commercial-grade silane decoupling agent, hexamethyldisilazane, (HMDS, Tokyo-Kasei Co., Ltd., Japan), $[(CH_3)_3Si]_2NH$, and a silane coupling agent, γ-glycidoxypropyltrimethoxysilane (GPS, Kanto-Chemical Co., Ltd., Japan) were used as surfactants for the silica filler:



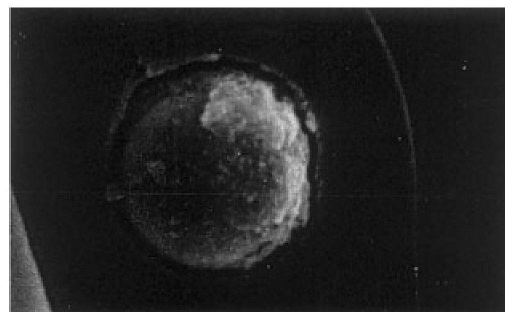
Surface treatment

The bonding properties of the filler/matrix interface were controlled by treating the filler surface with two types of surfactants, GPS or HMDS. For good bonding, the silica filler was treated with GPS by the wet-treatment method[9] as follows: The silica particles were mixed with 2 phf (parts per hundred filler) of GPS in methanol for 4 h at room temperature. Then, the particles were dried at room temperature for 1 day and heated at 110°C for 2 h. On the other hand, for poor bonding, the silica particles were treated with HMDS by the dry-treatment method as follows: HMDS, 30 phf, was added to the particles and mixed for 3 h at room temperature. Then, the particles were placed at room temperature for 3 days and heated at 110°C for 20 min.

The fracture surfaces of the epoxy resins filled with the treated silica particles were observed using a scanning electron microscope (SEM). The SEM photographs are shown in Figure 1. In the HMDS-treated system, the delamination of the silica/matrix interface occurred because of its poor bonding. However, in the GPS-treated system, delamination of the interface did not occur and the crack propagated through the matrix around the silica particles because of the good bonding of the interface. It was confirmed from these results that the surface treatment of the silica particles was completed and two types of silica particles that have good or poor bonding interfaces could be prepared.

Curing of epoxy resins

The bisphenol A- and biphenol-type epoxy resins were heated and melted at 130 and 150°C, respectively. Stoichiometric amounts (one epoxy group corresponds to one active hydroxy group) of the curing agent were added to the epoxy resins at the temperature at which each resin has low viscosity. The silica particles treated with GPS or HMDS were dispersed in the mixture. The content of the silica particles in the mixture was 30 wt %. Then, 1 phr of TPP was added as an accelerator. The bisphenol A-type epoxy resin preparation was cured at 130°C for 2 h, 180°C for 3 h, and 230°C for 1.5 h. The biphenol-type epoxy resin preparation was cured at 180°C for 5 h and 230°C for 4.5 h.



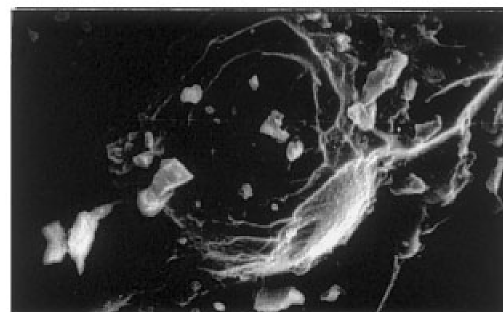


Figure 1 SEM photographs of fracture surfaces of the cured epoxy resin filled with silica particles which have a poor or good bonding interface.

Measurement

The fracture surface of the epoxy resin filled with silica was observed using an SEM (JSM-6500, JEOL Co., Ltd.). Prior to the examination, surfaces were coated with a thin layer of gold to improve conductivity and prevent charging.

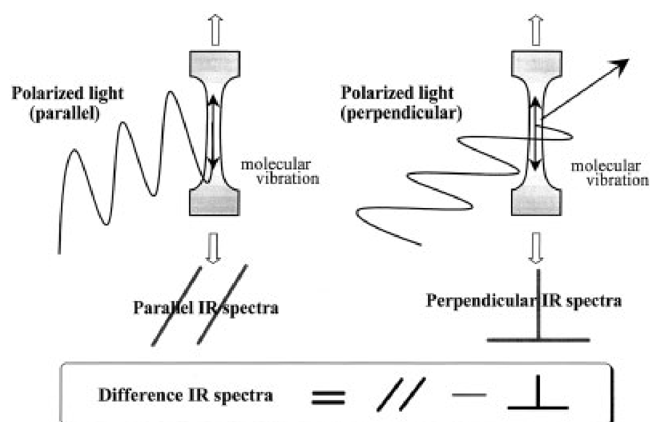


Figure 2 Principle of the polarized IR measurement.

The compliance of the cured epoxy resins was calculated based on the creep test. The dimensions of the sample were approximately 3.0 × 8.0 × 0.15 mm. The specimen was mounted in a thermomechanical analyzer (TMA/SS, Seiko Instrument Inc.). A tensile stress of 5 MPa was loaded for the specimen.

The tensile strength of the cured epoxy resins was measured according to JIS K7113 (half-size type).[13] The thickness of the specimen was 2 mm. The specimen was mounted in an Instron-type tensile machine and loaded at a constant test speed (1 mm/min). The fracture energy of the cured epoxy resin in the tensile test was determined from the area under the stress–strain curve.

The polarized IR spectrum of the cured epoxy resin was measured using a polarized FTIR spectrometer (Spectrum One, PerkinElmer Japan Co., Ltd.) equipped with a microscope (Auto Image, PerkinElmer Japan Co., Ltd.). The resolution of the IR spectrum was 8 cm^{-1}. The spectra were collected after 64 scans. The sample (thickness: 25 μm) for the IR measurement was cut from the loaded tensile specimen until just before fracture in the tensile test. The principle of the polarized IR measurement is shown in Figure 2. The polarized IR light is irradiated onto the sample. When the vibration plane of the polarized IR light is parallel with that of the chemical bonds, the polarized light is absorbed by the vibration of the chemical bonds. However, the polarized IR light, which is perpendicular to the vibration of the objective chemical bond, is not absorbed. Thus, the difference spectra obtained by subtracting the perpendicular spectra ($A_\perp$) from the parallel spectra ($A_\parallel$) should give information about the degree and direction of the orientation of the chemical bonds.

In this article, the direction of the tensile stress is defined as the parallel direction of the polarized IR light. If a chemical bond of the epoxy network more strongly absorbs the parallel polarized IR light, the chemical bond should be oriented along the direction of the tensile stress.

RESULTS AND DISCUSSION

Deformability of cured epoxy resins

The creep compliance *J* of the bisphenol A- and biphenol-type epoxy resins is shown in Figure 3. The values of the creep compliance of both epoxy resins increased with the length of time. Moreover, the value of the biphenol-type epoxy resin was always higher than that of the bisphenol A-type epoxy resin. This result shows that the biphenol-type epoxy resin can deform more than can the bisphenol A-type resin.

We consider that the difference of the deformation ability in bisphenol A- and biphenyl-type epoxy resins is dependent on the backbone structure, taking into account that both resin systems have about the same crosslinking density (ν_{biphenol}: 2.28 × 10^{-3}, $\nu_{\text{bisphenol A}}$: 2.18 × 10^{-3} mol/cm^3) and almost the same T_g ($T_{g\text{biphenol}}$: 140°C, $T_{g\text{bisphenol A}}$: 125°C). The 3D images of each epoxy resin are shown in Figure 4. In the bisphenol A-type epoxy resin, it is clear that the backbone moiety has a bulky and folded structure containing two aromatic rings and two methyl branches. On the other hand, in the biphenol-type epoxy resin, the backbone moiety, which is one of the typical mesogenic groups, has a compact and planar structure. Thus, we consider that the above structural difference of the backbone moieties in both the epoxy resins should cause the difference in the mobility of the network chains, namely, the deformability of the matrix resin was increased due to the introduction of the compact and planer backbone moiety. This means that the matrix composed of the biphenol-type (mesogenic) epoxy resin is more easily deformed compared with that of the bisphenol A-type resin. Ober et al.[14] also showed that the epoxy network chains containing mesogenic groups could easily deform under an external stress field.

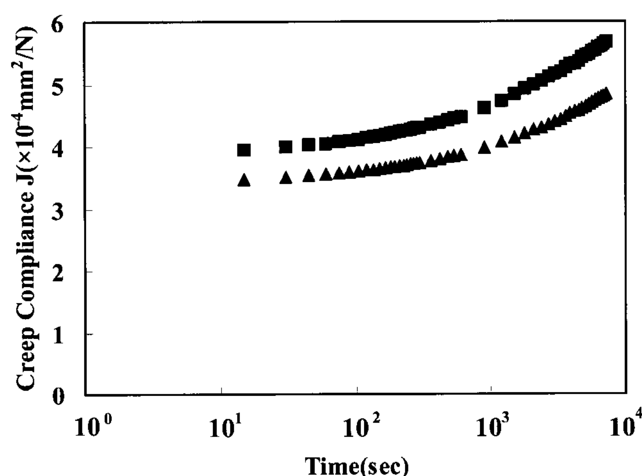
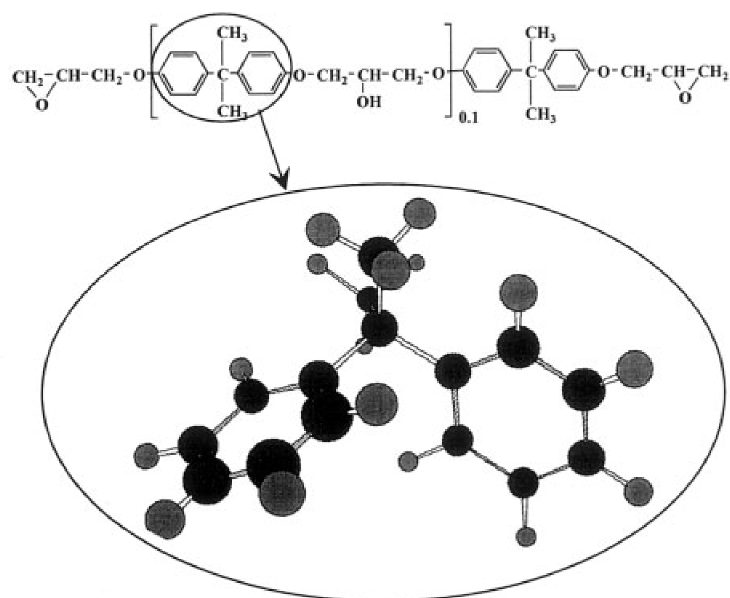


Figure 3 Creep compliance of cured epoxy resins: (▲) bisphenol-A type; (■) biphenol type.

(A)Bisphenol A DGE



(B)Biphenol DGE

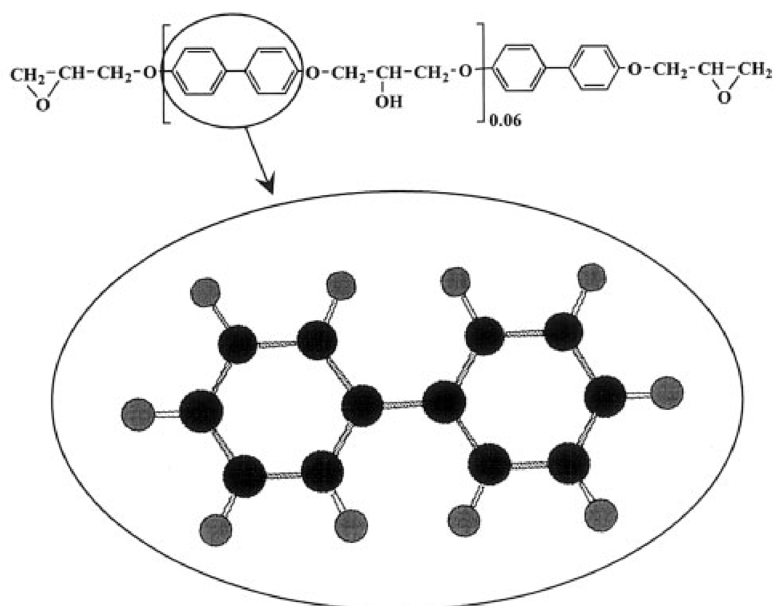


Figure 4 3D models of the backbone moieties of epoxy resins.

Tensile strength of cured epoxy resins filled with silica particles

The stress–strain curves of the bisphenol A-type and biphenol-type epoxy resins filled with silica particles, treated with the two types of surface-treatment agents, are shown in Figure 5. In the silica-filled bisphenol A-type resin systems, which have a good or poor bonding interface, the stress–strain curves showed the same behavior regardless of the bonding properties of the silica/matrix interface. This shows that the difference of the bonding property at the silica/matrix interface scarcely has any influence on the stress–strain curves of the biphenol-A resin systems. The ultimate strain of the bisphenol A-type resin systems was considerably lower than that of the biphenol-type resin systems. This means that the bisphenol A-type epoxy resin is a more brittle matrix resin, compared with the biphenol-type resin system.

In the biphenol-type resin systems, the values of the tensile strength and ultimate strain were affected con-

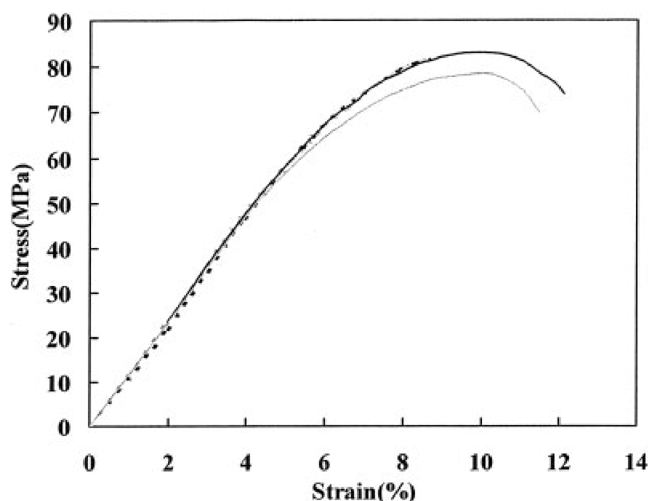


Figure 5 Stress–strain curves of cured epoxy resins filled with silica particles. Biphenol A type resin system: (—) good bonding: (---) poor bonding. Bisphenol-A-type resin system: (—) good bonding; (···) poor bonding.

siderably by the bonding properties of the silica/matrix interface. Particularly, although the tensile moduli are similar to each other, the values of both the ultimate strain and strength of the silica-filled system with a good bonding interface are higher than those of the filled system with a poor bonding interface. In the system which has a poor bonding interface, it is easy to cause debonding at the silica/matrix interface; thus, the crack propagates immediately from the debonded silica/matrix interface by the stress concentration. Therefore, it is reasonable that this system has low ultimate strain. On the other hand, in the system that has a good adhesion interface, the interface between silica and the epoxy matrix does not break down by the external stress. Thus, the magnitude of the stress concentration around the silica particles should be at a lower level compared with that of the former system, and, therefore, the biphenol-type resin filled with silica particles, which has a good bonding interface, shows better mechanical properties.

Yamaguchi and Nakamura[15] reported that an epoxy system filled with alumina particles, which have a poor bonding interface, showed better mechanical properties than those of the filled system with a good bonding interface. They reported that, in their system, cavitation occurred at the alumina/matrix interface; thus, the improvement of mechanical properties is achieved by energy consumption with the deformation of the matrix. However, in our system, the mechanical properties of the good bonding system show better performance than those of the poor bonding system. We suppose that this result is due to the large deformation ability of the biphenol-type epoxy resin used as the matrix. Subsequently described, the biphenol-type resin, which has a good bonding interface, is plastically deformed in a larger area with the rearrangementof network chains under the stress field. We expect that the reorientation process of the network chains should cause the large energy consumption.

The temperature dependence of the tensile strength and ultimate strain over a wide temperature range is shown in Figure 6. The tensile strength of both systems, which have a good or poor bonding interface, decreases with an increasing ambient temperature and finally reaches the same constant value. This is natural, taking into account that the molecular motion of the network chains is activated with an increase in the ambient temperature. The difference of the bonding properties of the silica/matrix interface would not affect the tensile strength of the silica-filled resins. The ultimate strain of both systems showed peaks in the glass transition region. It is well known that the ultimate strain of polymer materials has a maximum value at the glass transition region[16] because of the good balance in the cohesive force and mobility of polymer chains in this temperature region. The strain of the system, which has a good bonding interface, showed higher values than those of the poor bonding interface system. This is due to the debonding of the interface which occurred more easily in the latter system.

The fracture energy of the good and poor interface systems was about 66 and 142 kJ/m^2 at 100°C, respectively. The fracture energy of the good interface system was considerably higher than that of the poor interface system. This means that the toughness of the silica-filled biphenol-type resin system could be improved with an increase in the bonding strength of the silica/epoxy interface. It is clear that the high toughness of the good interface system is due to the high ultimate strength and strain of this system. This reveals that the matrix resin of the good interface system

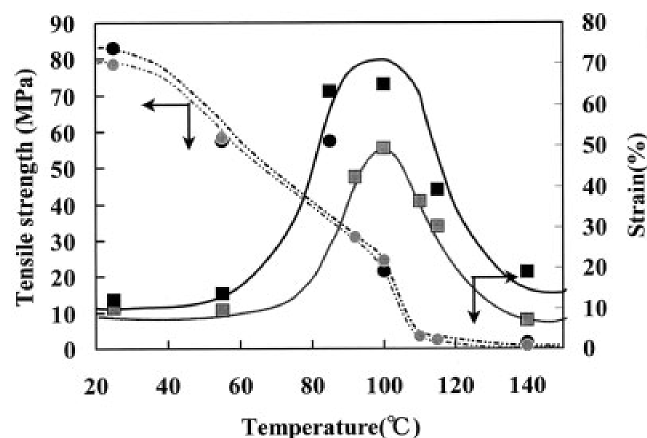


Figure 6 (Dot–dash lines) tensile strength and (solid lines) ultimate strain of cured biphenol-type epoxy resin filled with silica particles: (—) good bonding interface; (—) poor bonding interface.

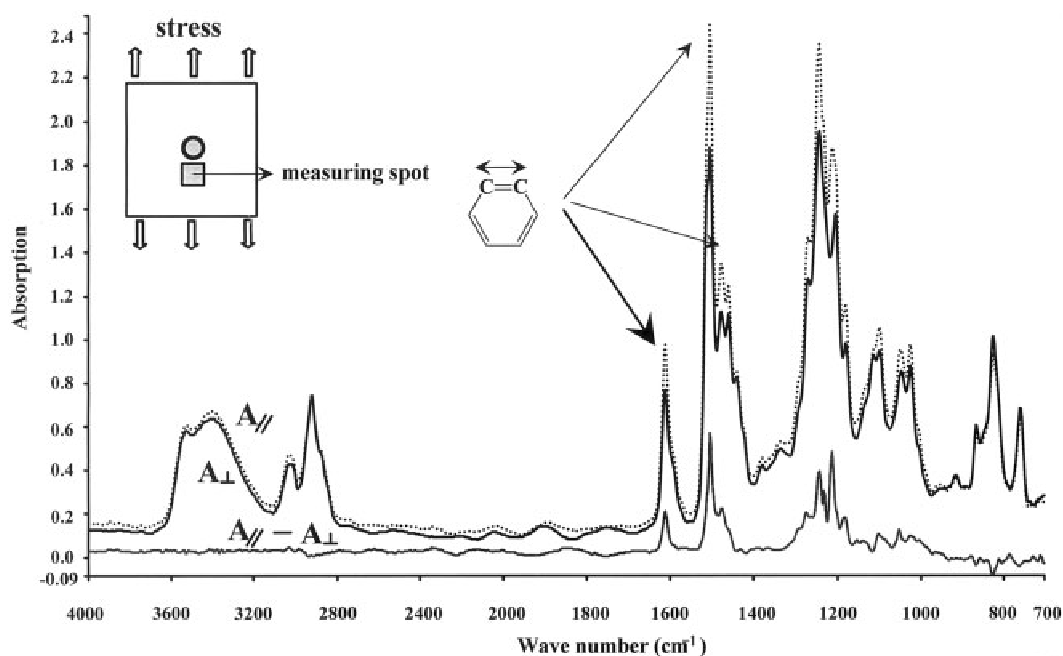


Figure 7 Polarized IR spectra of cured biphenol type epoxy resin filled with silica particles which have a good bonding interface: (···) $A_{\parallel}$; (—) $A_{\perp}$.

could deform more as compared with the deformation of the poor interface system. These phenomena are most peculiar in the sample fractured at the glass transition region. Thus, the plastic deformation of the matrix resin fractured at this temperature region was evaluated near the silica/matrix interface using polarized IR techniques as described in the next section.

Polarized IR measurement of cured epoxy resins

The polarized IR spectra of the biphenol-type epoxy resins are shown in Figure 7. The sample was cut from the tensile test specimen, which was loaded about 90% of the ultimate stress. The spectra were measured on the matrix around a silica particle. The peaks at 1600, 1500, and 1450 cm^{-1} are assigned as the stretching vibration of the aromatic C═C bond and the peaks at 1000–1200 cm^{-1} originate from the in-plane deformation vibration of the hydrogen atom on an aromatic ring. In these peaks, the intensity of the parallel IR spectrum peaks has higher values than those of the perpendicular IR spectrum peaks. Thus, it is clear that the oriented direction of these vibrations coincide with the direction of the applied stress. On the other hand, for the peak at 800 cm^{-1} which originates from the out-of-plane deformation vibration of the aromatic hydrogen atom, the intensity of the parallel IR spectrum peak has a lower value than that of the perpendicular IR spectrum peak.

It is natural to consider that the vibration direction of this molecular motion is across in reaction to the applied stress. As the difference IR spectra are defined as $A_{\parallel} - A_{\perp}$, these results show that the network chains containing the aromatic rings are reoriented along the parallel direction of the applied stress. Thus, it is clear that the network chains of the cured biphenol epoxy resin should have a large-scale molecular motion and, thus, the matrix is plastically deformed during the tensile process, even though the matrix resin is composed of a densely crosslinked network structure. In this study, the stretching vibration of the aromatic C═C bond is used as an indicator to determine the rearrangement of the network chains under the stress field. Because the two aromatic rings in the biphenol-type resin are on a line, the vector sum of the stretching vibration of the aromatic C═C bond is, thus, parallel with the line of the network chains.

Kim et al.[17] also reported that the orientation of the network chains could be investigated by observing the direction of the molecular vibration of the network chains using an IR technique. They studied the orientation of soft and hard segments in a polyether–urethane–urea copolymer under stress by using the NH— stretching vibration (hard segment) and the CH— stretching vibration (soft segment) as indicators. Nair et al.[18,19] suggested a relation between an applied strain and orientation behavior of the mesogenic groups in side-chain liquid crystalline polyurethane by observing the direction of the CN— stretching and phenyl—O stretching vibration in the mesogenic group and the NH— stretching vibration and H-bonded urethane and amide in the hard segments.

To investigate the rearrangement of the network chains in detail, the intensity of the IR absorption was

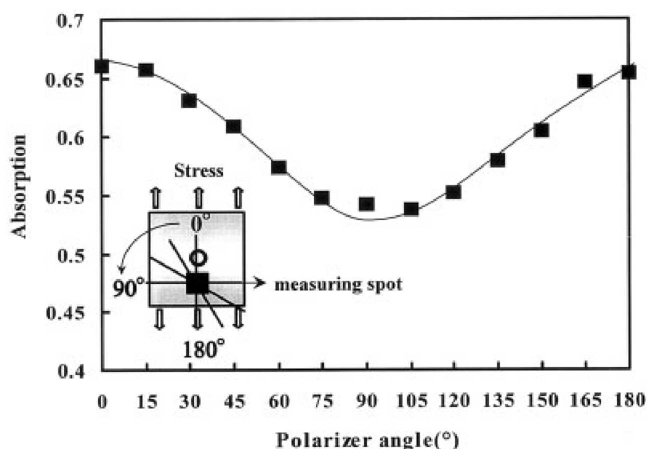


Figure 8 Effect of polarizer angle on the intensity of IR absorption at 1610 cm^{-1} in the biphenol-type resin.

measured in the same area by changing the angle of the polarizer in narrow intervals. The intensity of the IR absorption measured is shown in Figure 8. When the polarizer's angle was 0°, that is, parallel to the direction of the applied stress, the intensity of the peak at 1600 cm^{-1} (the stretching vibration of the aromatic C=C bond) was largest and then decreased with an increase in the polarizer angle. When the polarizer's angle was 90°, that is, perpendicular to the direction of the applied stress, the peak intensity had the lowest value. These results also show that the orientation direction of the network chains was parallel to the direction of the applied stress.

To observe the reorientation of the network chains in the whole area around the silica particles, a map of the network chain orientation was drawn from the polarized IR spectrum. The method of the IR mapping is shown in Figure 9. Forty-nine small areas (7 × 7) were set up around a silica particle. Parallel and perpendicular polarized IR spectra were measured in each setting area. The dichroic ratio R in each area was estimated from each IR absorbance. The dichroic ratio was calculated by $R = (A_{\parallel} - A_{\perp})/(A_{\parallel} + A_{\perp})$, where $A_{\parallel}$ and $A_{\perp}$ are the intensity of the parallel and perpendicular polarized IR absorbance, respectively. The value of this dichroic ratio is defined from −1 to 1. Note that the sample thickness of each measurement area may have a subtle difference. However, by using this ratio, there is no need to consider the influence of the sample thickness. When the network chain of the matrix orients along the direction of the applied stress, the dichroic ratio has a positive value because the value of $A_{\parallel}$ is larger than that of $A_{\perp}$. On the other hand, when the network chain of the matrix orients along the perpendicular direction, the dichroic ratio has a negative value.

A map of the distribution of the dichroic ratio near the silica particle is shown in Figure 10 for the systems which have good or poor bonding silica/matrix interfaces. In the poor bonding interface system, the debonding of the silica/matrix interface was observed around the silica particle at the beginning of the fracture process and high values of the dichroic ratio appeared in some specific locations. These results show that the reorientation of network chains in this system is not uniform in the field of the external stress.

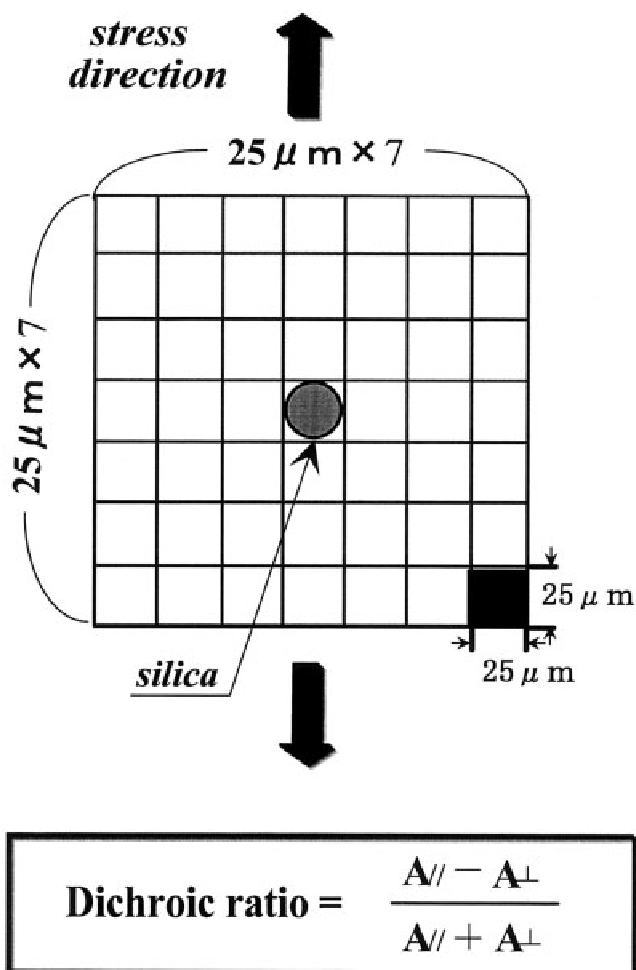


Figure 9 Mapping method of the polarized IR measurement.

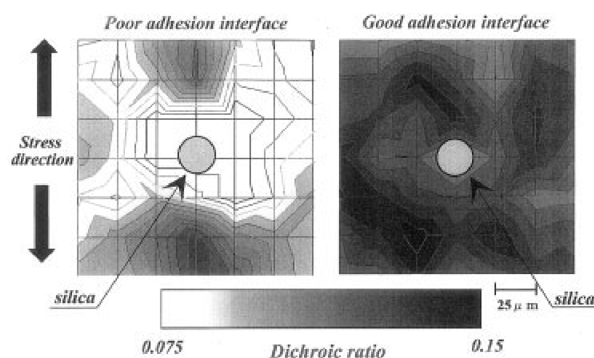


Figure 10 Dichroic ratio map at 1610 cm^{-1} of the biphenol-type system.

We suppose that the crack should initiate from the debonding of the silica/matrix interface before enough reorientation of network chains occurs. On the other hand, in the good bonding interface system, we observed that a higher dichroic ratio compared with that of the poor bonding system distributes over an entire area around the silica particles. This means that the reorientation of the network chains in this system more often occurred in a larger area compared with that in the former system. In the good bonding system, the debonding of the silica/matrix interface was not observed. Thus, we consider that the degree of the stress concentration is lower and thus the external stress is more uniformly distributed in a matrix around the silica particle. Accordingly, we suppose that the plastic deformation of the matrix resin occurs in preference to the crack propagation observed in the poor bonding system, namely, we consider that the high fracture energy in the good bonding interface is due to the reorientation of the network chains containing a mesogenic (biphenol) group in a larger area around the silica particles.

CONCLUSIONS

Two types (bisphenol A and biphenol types) of epoxy resins were filled with silica particles that were treated by coupling or decoupling agents. Toughness and toughening mechanisms were studied of the silica-filled epoxy resins. The following conclusions were obtained:

The fracture energy of the biphenol-type resin in a tensile test was considerably higher than that of the bisphenol A-type resin. The mechanism was studied based on the rearrangement of the network chains under tensile stress, which was characterized using a polarized FTIR technique. Thus, we clarified that the network chains of the biphenol-type epoxy resin containing the mesogenic groups are more easily rearranged under the stress field than those of the bisphenol A-type epoxy resin. The distribution of the network chain orientation around the silica particle depended clearly on the adhesion of the silica/matrix interface. When the silica/matrix interface has good bonding strength, the rearrangement of the network chains occurred uniformly in a large area near the silica/matrix interface. From these results, we concluded that the high toughness of the silica-filled biphenol-type resin with a good bonding interface is due to the large plastic deformation of the matrix around the silica particle.

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