

Effect of Network Structure on Thermal and Mechanical Properties of Biphenol-Type Epoxy Resins Cured with Phenols

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SYNOPSIS

In the biphenol-type epoxy resin cured with catechol novolac (CN), a very weak glass transition and, thus, a very high rubbery modulus were observed. On the other hand, the glass transition was clearly observed in the system cured with phenol novolac (PN). This means that the micro-Brownian motion of network chains is highly suppressed in the system cured with CN. The reason for this suppression of the chain motion in the CN-cured system has been pursued from the viewpoint of the conformation of network chains. The disappearance of the glass transition in the biphenol-type resin depends on the formation of the active hydrogens in the curing agents. Thus, it was suggested that the suppression of the micro-Brownian motion is due to the orientation of the biphenyl groups in the network. Moreover, it has been shown that the mechanical and bonding strength at high temperature is considerably improved by the suppression of the network chain motion in the CN-cured biphenol resin system. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recently, many investigations have reported on the synthesis and the optical and mechanical properties of a new type of epoxy resin in which the mesogenic groups were introduced into their backbone structure. We also investigated the thermal and mechanical properties of such a new type of resin which includes the biphenol structure as a mesogenic group.¹⁻³ In our previous report,⁴⁻⁶ the biphenol-type epoxy resin cured with 4,4'-diaminodiphenylmethane (DDM) had no clear glass transition and thus had a very high tensile modulus in the rubbery region. It was clear that the micro-Brownian motion of the network chains is highly suppressed in this system. We also revealed that the DDM-cured system has a very high mechanical strength at high temperatures.

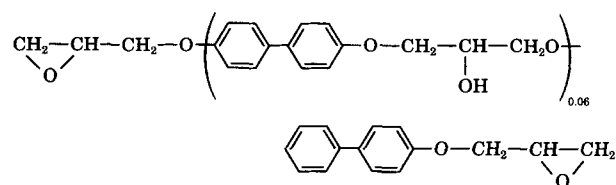
However, it is expected in such an epoxy resin including a mesogenic group that the thermal and

mechanical properties will be considerably affected by the chemical structure of the curing agents. In this report, we investigated the thermal and mechanical properties of the biphenol-type resin cured with phenol novolacs. Moreover, we discuss in detail the relation between these properties and the network structure in the epoxy resin which includes a mesogenic group, such as a biphenol group, in the backbone structure.

EXPERIMENTAL

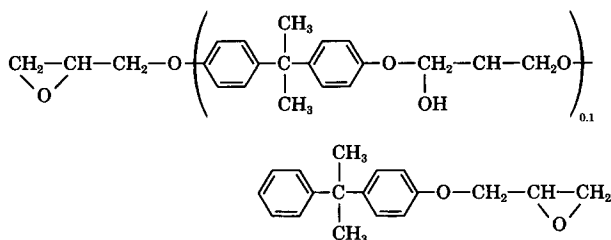
Materials

The epoxy resins used were biphenol diglycidyl ether (BPDGE):

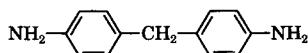


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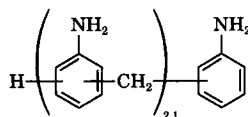
and bisphenol-A diglycidyl ether (BADGE).



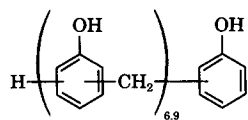
4,4'-Diaminodiphenylmethane (DDM):



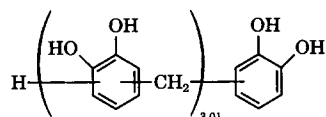
and aniline novolac (AN):



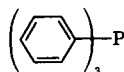
were used as amine curing agents. Phenol novolac (PN):



and catechol novolac (CN):



were used as phenolic curing agents. Triphenylphosphine (TPP):



was used as an accelerator. This curing agent (DDM) and the accelerator were Ep grade materials and were used without further purification.

Sample Preparation

Synthesis of Catechol Novolac

A mixture of 100 g of 37% catechol-formaldehyde solution, 1–2 mL of hydrochloric acid, and 400 mL

of water was refluxed for 6 h. Then, the water and the hydrogen chloride were evaporated at 90°C under reduced pressure (20–40 mmHg). Then, the unreacted catechol was removed by washing it with toluene and evaporating it at 120–160°C under reduced pressure (1–3 mmHg) for a few hours. The molecule weight of the catechol novolac was measured by GPC.

Curing of Epoxy Resin

The biphenol-type epoxy resin was melted at 180°C. Then, stoichiometric amounts (one epoxy group corresponds to one active hydrogen of amine or hydroxy groups) of amine or phenolic curing agents were added at 160°C. The mixture was stirred at 160°C. In the phenol-cured system, 1 phr of TPP was added as an accelerator. After the gelation, the compounds were cured at 180°C for 6 h and at 230°C for 1 h.

The bisphenol-A-type epoxy resin was degassed at 80°C under a reduced pressure (1–3 mmHg). Then, stoichiometric amounts of amine curing agents were added and stirred at 80°C. In the phenol-cured system, 1 phr of TPP was added to the mixtures. The compounds were cured at 80°C for 2 h and at 180°C for 6 h.

Measurement

Dynamic mechanical properties were determined over the temperature range –150 to 350°C by a non-resonance, forced vibration viscoelastometer (DVE-3, Rheology Co. Ltd.). The frequency was adjusted to 10 Hz and the heating rate was 2°C/min.

The thermal expansion coefficient was calculated from the change of the sample length using a thermomechanical analyzer (TMA/SS120C, Seiko Instruments Inc.). The temperature range measured was from –140 to 300°C and the heating rate was 5°C/min.

Tensile properties were measured using an Instron-type tensile machine (Shimazu Autograph, AGS-100) at a crosshead speed of 10 mm/min according to ASTM D 1708-79. The lap shear strength of joints was measured using an Instron-type tensile machine (Shimazu Autograph, AGS-2000E) at a crosshead speed of 50 mm/min according to ASTM D 1002-72.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of Amine-cured Epoxy Resins

The dynamic mechanical properties of biphenol and bisphenol-A-type epoxy resins cured with DDM are

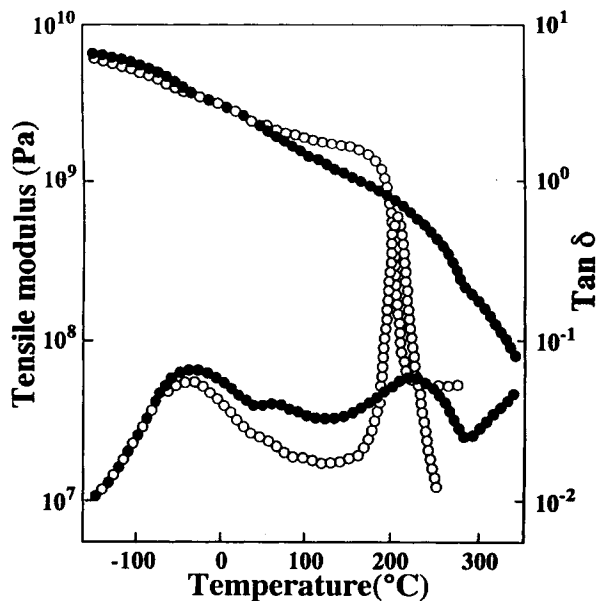


Figure 1 Dynamic mechanical properties of biphenol and bisphenol-A type epoxy resins cured with an amine. Epoxy resins: (●) biphenol DGE; (○) bisphenol-A DGE. Curing agent: DDM. Measuring frequency: 10 Hz.

shown in Figure 1. The bisphenol-A-type resin system revealed a typical viscoelastic chart which is observed in an ordinary thermoset resin. This system showed a clear glass transition near 190°C and, thus, a low modulus in the rubbery region. In contrast to this system, the amine-cured biphenol resin system has no clear glass transition and thus has a very high tensile modulus in the rubbery region, namely, in the transition and rubbery region, the dynamic mechanical behavior of the biphenol-type resin system is completely different from those of the bisphenol-A-type resin system. The values of the epoxy equivalent of both the epoxy resins are almost the same. Thus, the crosslinking density of these two networks seems to be on the same level. In a previous report,⁴ the difference in the viscoelastic properties of these two networks was stated to be due to the stereostructure of the main chain in the epoxy resins. Two phenylene rings in the biphenol-type resin are directly bonded to each other and thus have more a planar formation compared with those in the bisphenol-A-type resin which has a carbon bridge between the two phenylene rings. The biphenol group is one of the typical mesogenic groups.⁷ Thus, the network chains in the cured biphenol-type resin are more easily oriented and more closely packed so that they completely lose their chain mobility in the transition and rubbery regions.

However, the biphenol-type epoxy resin is one of the most important resins in the field of packaging

materials for LSI. In this field, an epoxy resin is used mainly as a phenol-cured system,^{8,9} not as an amine-cured system. Thus, it is interesting to discuss the mechanical and thermal properties of the phenol-cured biphenol resin system compared with those of the amine-cured system.

Dynamic Mechanical Properties of Phenol-cured Epoxy Resins

The dynamic mechanical properties of the biphenol-type epoxy resin cured with PN are shown in Figure 2, compared with those of the amine (DDM)-cured biphenol system. Contrary to our expectation in Figure 1, the biphenol-type epoxy resin cured with PN showed a clear glass transition and a significant decrement of modulus in the transition region, and, thus, the system had a low modulus in the rubbery region. These results show that the dynamic mechanical properties of the phenol-cured biphenol-type resin are different from those of the amine-cured resin. To study the mechanisms for these phenomena, dynamic mechanical properties of the biphenol-type resin cured with various curing agents were investigated.

First, the effects of the introduction of the novolac structure on the dynamic mechanical properties of the biphenol resin systems were studied. Figure 3 shows the dynamic mechanical properties of the bi-

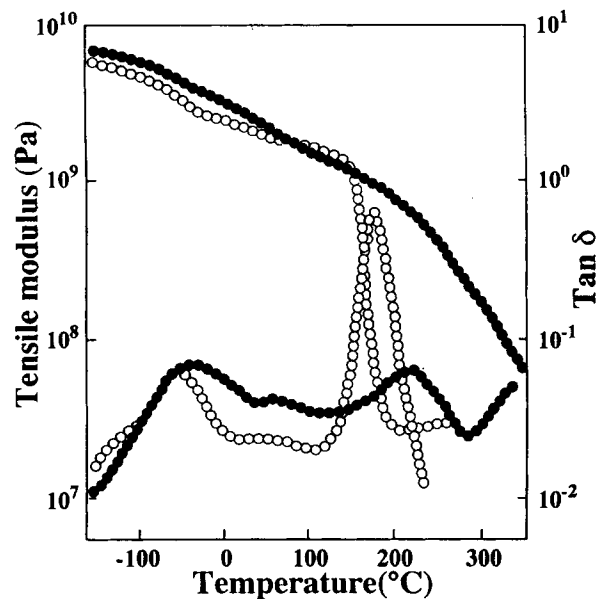


Figure 2 Dynamic mechanical properties of biphenol-type epoxy resin cured with an amine and a phenol. Epoxy resin: biphenol DGE. Curing agents: (●) DDM; (○) PN. Measuring frequency: 10 Hz.

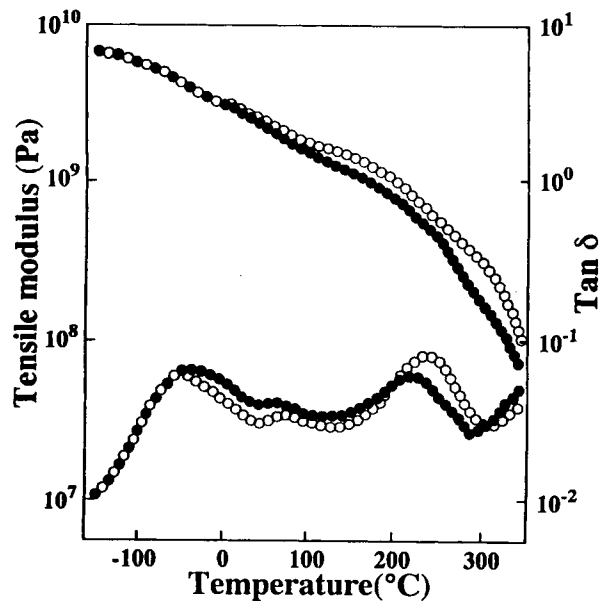


Figure 3 Dynamic mechanical properties of biphenol-type epoxy resin cured with amines. Epoxy resin: biphenol DGE. Curing agents: (●) DDM; (○) AN. Measuring frequency: 10 Hz.

phenol-type resin cured with DDM and AN. The biphenol-type resin cured with AN, which is the novolac of primary amine, showed analogous characteristics with those of the DDM-cured system. This result shows that the dynamic mechanical properties of the biphenol-type resin cured with amines would not be affected by the presence of the novolac structure in the curing agents. Thus, we can conclude that the high chain mobility in the biphenol-type resin cured with PN (Fig. 2) is not due to the introduction of the novolac structure into the networks.

Next, we studied the effects of the stereostructure of active hydrogen in PN. The dynamic mechanical properties of the biphenol-type resin cured with PN and CN are shown in Figure 4. Biphenol-type epoxy resins cured with CN, which has two active hydrogens on the *ortho*-position of the aromatic ring in the novolac structure, showed a very weak glass transition and, thus, a very high rubbery modulus. This result showed that the dynamic mechanical properties of the CN-cured biphenol system are close to those of the DDM-cured system, namely, we consider that the mobility of network chains in the biphenol-type resin system is strongly affected by the formation of active hydrogens found in the curing agents.

However, we must consider the possibility that the very weak glass transition observed in the CN-cured biphenol system is due to the higher cross-

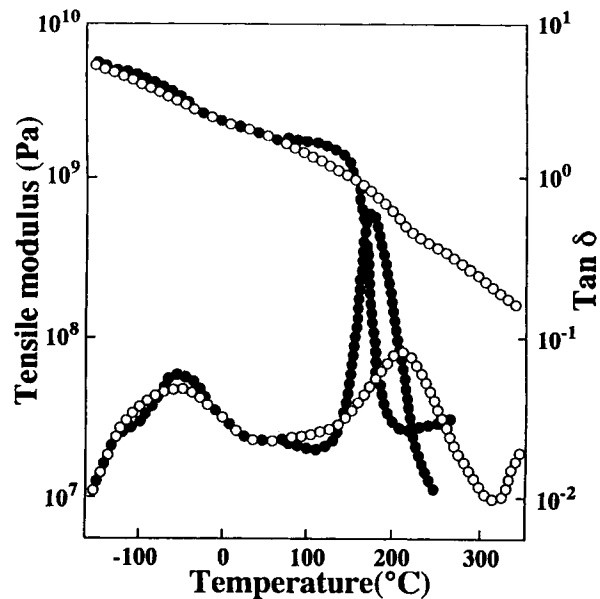


Figure 4 Dynamic mechanical properties of biphenol-type epoxy resin cured with phenols. Epoxy resin: biphenol DGE. Curing agents: (○) CN; (●) PN. Measuring frequency: 10 Hz.

linking density of this system. To discuss this point, dynamic mechanical properties of the bisphenol-A and biphenol-type resins cured with the catechol novolacs are shown in Figure 5. As described in the previous section, the biphenol-type resin cured with

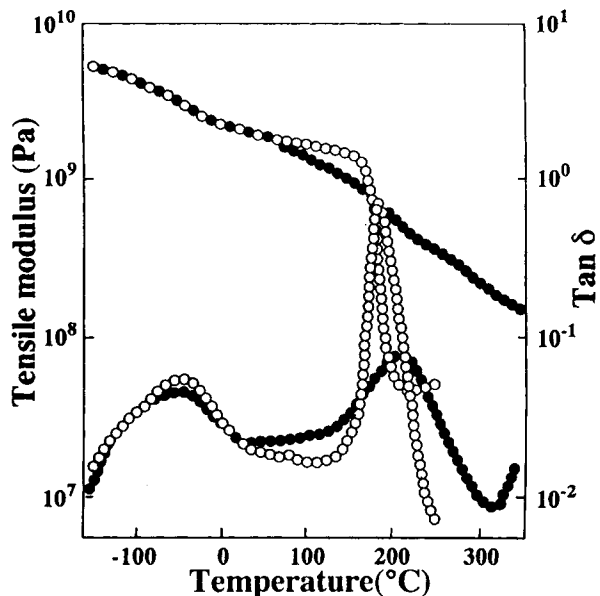


Figure 5 Dynamic mechanical properties of biphenol and bisphenol-A-type epoxy resins. Epoxy resins: (●) biphenol DGE; (○) bisphenol-A DGE. Curing agent: CN. Measuring frequency: 10 Hz.

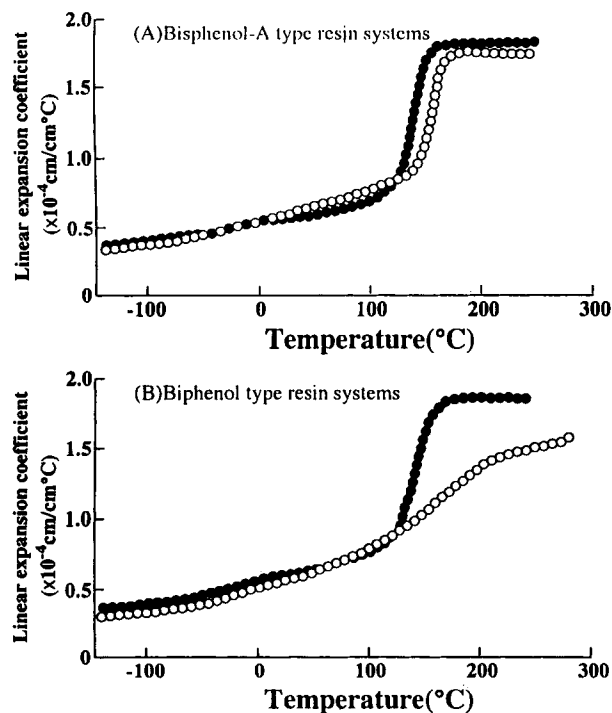


Figure 6 Linear expansion coefficient of biphenol and bisphenol-A-type epoxy resins cured with phenols. Curing agents: (O) CN; (●) PN.

CN has no clear glass transition and has a high rubbery modulus. But the bisphenol-A-type resin has a clear transition even if the resin is cured with the CN which has the neighboring active hydrogens. This result means that the strong suppression for the chain motion in the networks does not depend on the crosslinking density of the cured resins, but depends on the stereostructure of the network chains.

Linear Expansion Coefficient of Phenol-cured Epoxy Resins

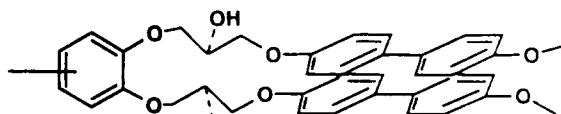
Linear expansion coefficient–temperature curves for epoxy resin cured with PN and CN are shown in Figure 6. The values of the linear expansion coefficient of the bisphenol-A-type resin systems [Fig. 6(A)] cured with PN and CN showed almost the same behavior in this temperature region. This result means that the mobility of network chains in the bisphenol-A-type resin systems does not depend on the formation of active hydrogen in the novolac-type curing agents.

Figure 6(B) shows the linear expansion coefficient of the biphenol-type resin systems. In this figure, the PN-cured system has a clear glass transition and a high expansion coefficient in the rubbery region. On the other hand, the CN-cured system does not have a clear glass transition and its expansion coefficient in the transition and rubbery regions is considerably lower than that of the former system. This shows that the motion of network chains in the CN-cured biphenol-type resin is tightly suppressed in the transition and rubbery regions. From these results, we can conclude that the suppression of the chain mobility occurred only in the system where the biphenol resin is cured with curing agents which have neighboring active hydrogens, such as a CN.

Network Structure Model of Cured Epoxy Resins

Models for network structures of phenol-cured epoxy resins near the crosslinking point are shown in Figure 7. When the biphenol-type resin is cured with the curing agents which have neighboring active hydrogens, such as CN, the biphenol groups in the

(A) Catechol novolac-cured system



(B) Phenol novolac-cured system

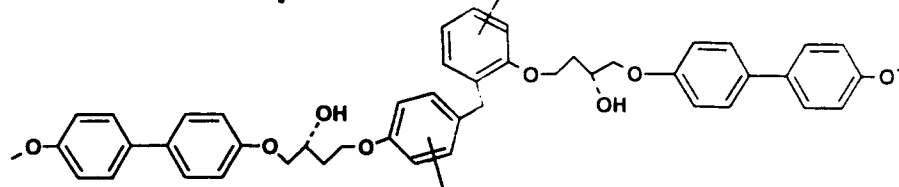


Figure 7 Model structures near crosslinking points in the biphenol-type epoxy resins cured with two different types of phenols.

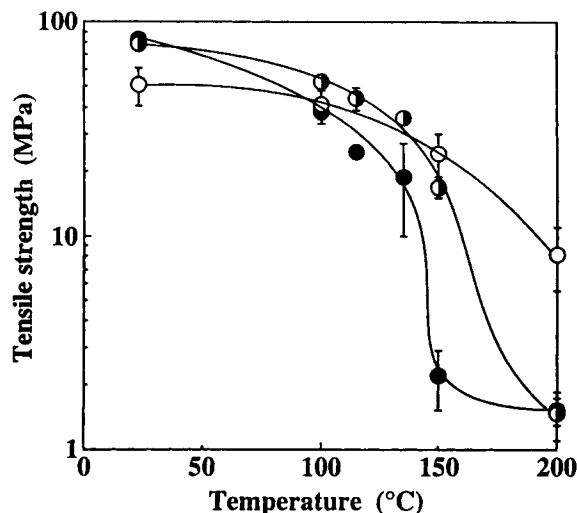


Figure 8 Tensile strength of cured epoxy resins. Epoxy resin/curing agent: (○) BP/CN; (●) BP/PN; (●) BA/CN.

epoxy molecules which will react with the neighboring hydrogens should be close to each other. It is natural to consider that the neighboring biphenol groups should be oriented in this network [Fig. 7(A)], taking into account that the biphenol group is one of the typical mesogenic groups. As a result of this orientation of the network chains, the CN-cured biphenol resin system has a poor glass transition (Figs. 4 and 6), high rubbery modulus (Fig. 5), and low rubbery expansion coefficient (Fig. 6). On the other hand, when the same epoxy resin is cured with the curing agent, such as PN, whose active hydrogens are distributed in a random direction, the biphenol groups in the epoxy molecules could not be oriented in the networks [Fig. 7(B)]. Thus, the motion of network chains in the rubbery region of the latter system could not be suppressed. From this consideration, we suggest that the peculiar phenomena observed in the biphenol-type resin system cured with CN are due to the orientation of biphenol groups in epoxy networks.

Mechanical Properties of Cured Epoxy Resins

The temperature dependence of the tensile strength of biphenol and bisphenol-A epoxy resins cured with phenols is shown in Figure 8. In the bisphenol-A epoxy/catechol novolac (BA/CN) and biphenol epoxy/phenol novolac (BP/PN) systems, the values of their tensile strength decreased remarkably near the glass transition temperature (T_g). On the contrary, such a remarkable decrease in the mechanical strength near the T_g was not observed in the BP/CN system. Thus, the latter system had a consid-

erably higher tensile strength in the rubbery region, compared with those of the former two systems. It is reasonable to consider that the high mechanical strength in the rubbery region of the BP/CN system is caused by the suppression of the micro-Brownian motion discussed in the previous sections.

The temperature dependence of the tensile elongation of cured epoxy resins is shown in Figure 9. The elongation of the BP/PN and BA/CN systems revealed clear maximum values near the T_g . This phenomenon is well known in the field of failure mechanics for polymer materials.¹⁰ The biphenol-type epoxy resin cured with catechol novolac (BP/CN) did not show a maximum peak, because of the lack of the glass transition phenomenon in this system. Moreover, this system showed the lowest value in the elongation of the rubbery region. It is clear that such a low deformability of the BP/CN system in the transition and rubbery regions is due to the high suppression of the chain motion caused by the particular network structure of this system.

The temperature dependence of the lap shear strength of cured epoxy resins is shown in Figure 10. The BP/CN system revealed the highest adhesive bonding strength in the rubbery region. It is very clear that such a phenomenon is caused by the high suppression of the motion of network chains in the rubbery region.

CONCLUSION

The biphenol-type epoxy resin which has a mesogenic group in the main structure was cured with

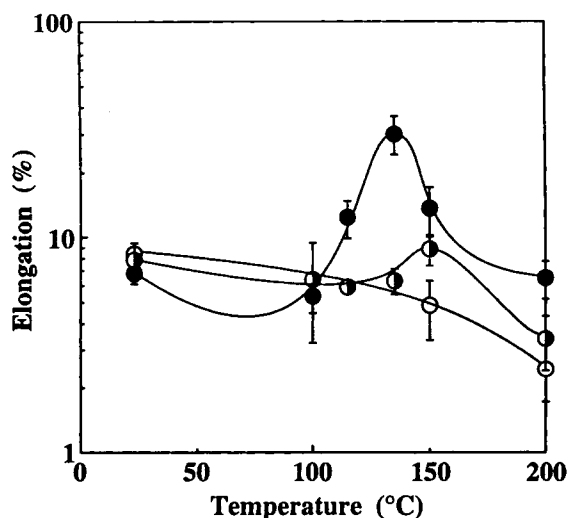


Figure 9 Elongation of cured epoxy resins. Notations as in Figure 8.

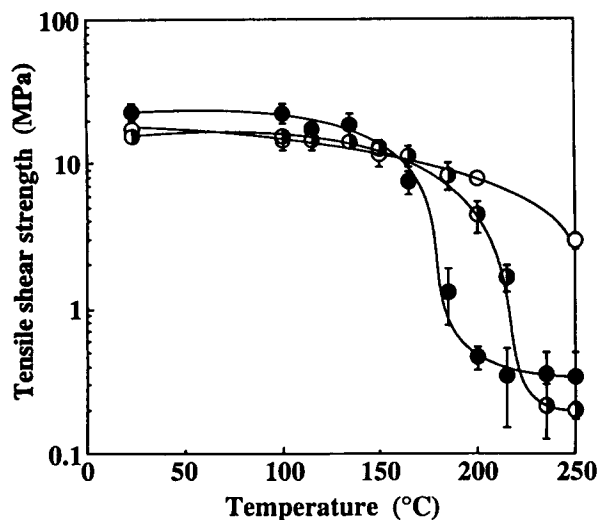


Figure 10 Adhesive joint strength of cured epoxy resins. Notations as in Figure 8. All samples revealed the mixed failure mode of the cohesive and contact failure.

phenol and catechol novolacs. The effect of the formation of the active hydrogens in the novolacs on the mechanical and thermal properties of the cured resins was investigated in detail. The following conclusions were reached:

1. In the biphenol-type epoxy resin cured with catechol novolac which has two active hydrogens on an aromatic ring, the glass transition was not clearly observed and, thus, a high elastic modulus was obtained in the rubbery region. On the other hand, the glass transition of the system cured with phenol novolac which has one active hydrogen on an aromatic ring was clearly observed. Thus, it is clear that the micro-Brownian motion of the network chains is strongly suppressed in the former system.

2. The biphenol-type resin cured with catechol novolac had a very high modulus and mechanical and bonding strength at the high-temperature region of over 200°C, because of the strong suppression of the network chain motion.
3. It was suggested that the suppression of the chain motion in the biphenol resin/catechol novolac system was due to the orientation of a mesogenic group, such as a biphenol group, in the networks.

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Received June 3, 1994

Accepted December 8, 1994