Effect of network structure on thermal and mechanical properties of cured epoxide resins

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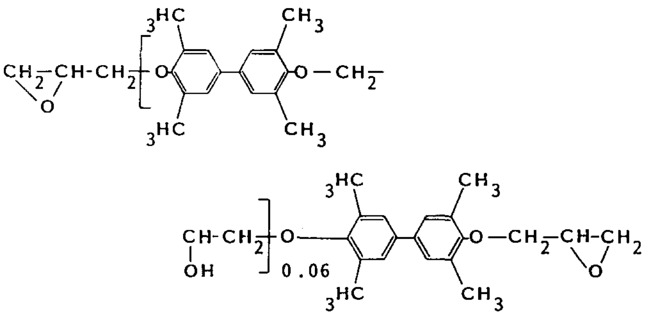
Dynamic mechanical properties and internal stress were investigated using several different kinds of epoxide resins with different chemical structures. Resin containing a tetramethyl biphenol structure showed a very high rubbery modulus, a low glassy modulus and a low internal stress, in addition to exhibiting a high glass transition temperature. Furthermore, the effect of the introduction of methyl branches into the biphenol skeleton on viscoelastic properties of cured epoxide resin was investigated by comparing with that of bisphenol-A type resin in detail. In the case of bisphenol-A type resin, the introduction of methyl branches slightly affected the modulus in the rubbery and the glassy regions and the glass transition temperature. These results show that the introduction of methyl branches into the resin does not significantly affect the mobility of network chains or the free volume of cured resins. In contrast, the introduction of methyl branches into biphenol type resin resulted in a decrease in modulus in the rubbery region and an increase in the peak height of tan δ. These results show that the introduction of methyl branches into biphenol type resin increases the mobility of network chains in the rubbery region. On the other hand, the modulus in the glassy region increased according to the introduction of methyl branches. This is due to the decrease in free volume in the glassy region with an increase in the mobility of network chains in the rubbery region.

(Keywords: bisphenol-A type resin; biphenol type resin; methyl branch; free volume; mobility; modulus; equilibrium state)

INTRODUCTION

Many investigations have been carried out on the structure–property relationships of crosslinked epoxide resins[1,2]. It is desirable to correlate microscopic characteristics, which include crosslinking density, free volume and chain mobility for epoxy systems, with macroscopic properties such as Young's modulus, internal stress, fracture toughness and moisture absorption behaviour. These properties and their relationships may then serve as the basis for a quantitative understanding.

We previously reported[3] that an epoxide resin containing the tetramethyl biphenol structure cured with diaminodiphenylmethane showed a very high rubbery modulus and a low glassy modulus and a broad glass transition. This phenomenon seemed peculiar to this skeleton.

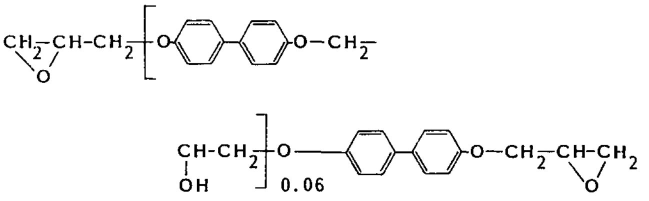


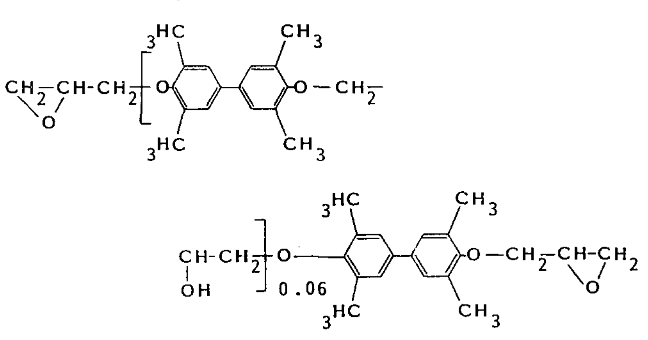
In this paper, the effect of the introduction of methyl branches into epoxide resins having biphenol and bisphenol-A type skeleton structures on the thermal and mechanical properties is systematically examined and discussed from the viewpoint of free volume and the mobility of network chains.

EXPERIMENTAL

Materials

As biphenol type resin, biphenol diglycidyl ether (BPDGE) and tetramethyl biphenol diglycidyl ether (TMBPDGE) were used solely or mixed.





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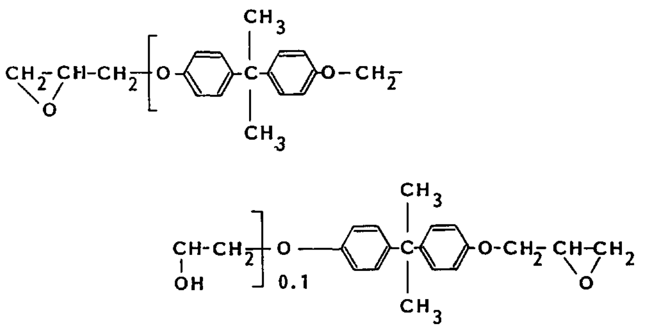
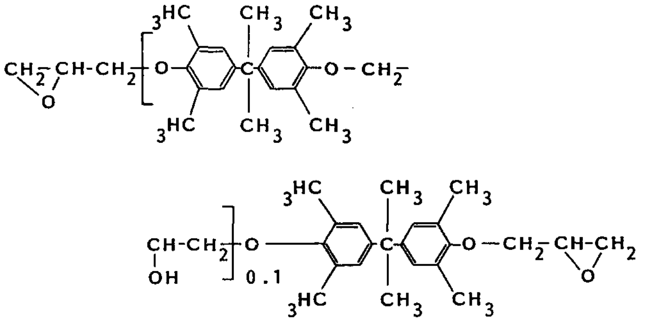
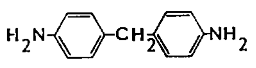
As bisphenol-A type resin, bisphenol-A diglycidyl ether (BADGE)



and tetramethyl bisphenol-A diglycidyl ether (TMBADGE) were used solely or mixed.



4,4′-Diaminodiphenylmethane (DDM) was used as a curing agent.



The curing agent was EP grade material and was used without further purification.

Measurements

The shapes and dimensions of the specimens for measuring the internal stress are shown in *Figure 1*. The steel ring on which the strain gauge (KFC-10-C1-11, Kyowa Electric Co. Ltd) was bonded by adhesive was placed on the mould coated with release agent. The epoxide resin mixture was cast in the space between the steel ring and the outer frame. As the curing of the epoxide resin proceeds, the steel ring is subjected to stress and raises the strain. The change of the strain δ_θ in the cooling process was measured and the internal stress σ_i was calculated using the equation[4]:

$$\sigma_i = Ed(\delta_\theta - \delta_t)/r$$

where E, d and r are the modulus, the thickness and the inside diameter of the steel ring, respectively. δ_t is the blank value of the thermal strain of the steel ring itself and is subtracted from the value of δ_θ to cancel the thermal expansion or contraction of the ring.

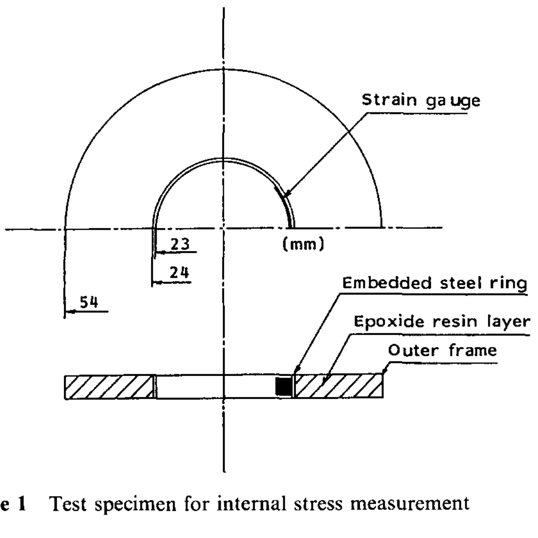


Figure 1 Test specimen for internal stress measurement

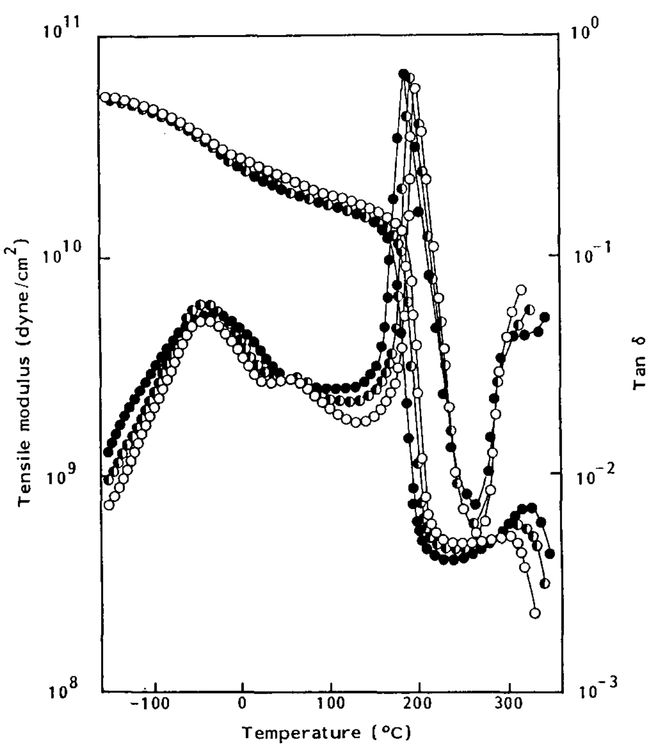


Figure 2 Dynamic mechanical properties of cured epoxide resins. TMBADGE/BADGE: (●) 0/100; (◐) 50/50; (○) 100/0. Measuring frequency: 10 Hz

The thermal expansion coefficient was calculated from the change in sample length by using a thermomechanical analyser (TMA CN8090 F1, Rigaku Electric Co. Ltd). The temperature range measured was from room temperature to 300°C and the heating rate was 5°C min^{-1}.

Dynamic mechanical properties were determined using 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^{-1} under atmospheric pressure.

RESULTS AND DISCUSSION

Dynamic mechanical properties

The dynamic mechanical properties of the bisphenol-A type resin system are shown in *Figure 2*. In this resin system, the increase in the ratio of branched resin slightly affects the modulus of the rubbery or the glassy regions and the glass transition temperature (T_g). These results show that the introduction of methyl branches into bisphenol-A type resin does not affect the mobility of network chains or free volume of the cured resins. The introduction of methyl branches must cause opposing effects on free volume: one effect is the increase in free volume by steric hindrance and the other effect is the decrease in free volume by filling the space between

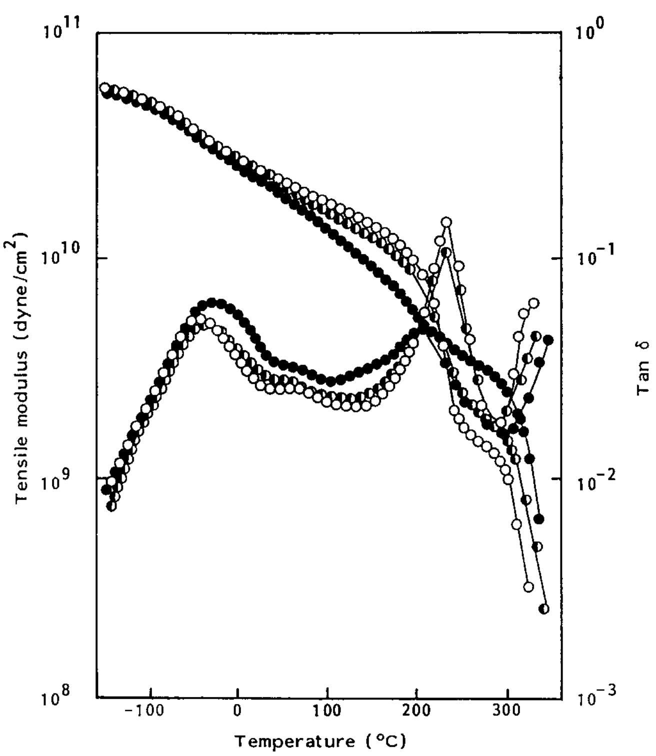


Figure 3 Dynamic mechanical properties of cured epoxide resins. TMBPDGE/BPDGE: (●) 5/95; (◐) 50/50; (○) 100/0. Measuring frequency: 10 Hz

network chains. In the case of bisphenol-A type resin, in which the phenylene rings are not in alignment and considered to have relatively large free volume compared with biphenol type resin, the two opposing effects on free volume are cancelled resulting in a small change in the modulus and T_g.

In contrast with the above resin system, the biphenol type resin system showed a dramatic change in modulus and tan δ (*Figure 3*). According to the increase in the ratio of branched resin, the modulus in the rubbery region decreased and the tan δ peak height in the glass transition region increased. These results show that the introduction of methyl branches into biphenol type resin increases the mobility of network chains in the rubbery region. On the other hand, the modulus in the glassy region increased according to the introduction of methyl branches. We have already reported[3] that, the resin system containing the tetramethyl biphenol structure has a very high rubbery modulus and a low glassy modulus compared with the bisphenol-A type resin system. This figure shows that the characteristic phenomena of biphenol type resin are enhanced by eliminating the methyl branches from their skeleton structure. In the biphenol type resin, the elimination of methyl branches could facilitate the alignment of the biphenol structure, and thus cause the decrease in free volume in the rubbery region. Accordingly, the biphenol type resin which has smaller amounts of methyl branch vitrifies through the non-equilibrium state from higher ambient temperature, and results in a larger free volume and lower modulus in the glassy region. The modulus in the glassy and rubbery regions *versus* mixing ratio of the resins is plotted in *Figure 4*. In the case of the bisphenol-A resin system, the modulus in the glassy and rubbery regions remains nearly constant regardless of the introduction of methyl branches. This is due to the cancellation of the opposing effects on the free volume by the introduction of methyl branches. In contrast to this system, in the case of the biphenol resin system, the modulus in the rubbery region decreased and in the glassy region increased. This is due to the increase in the mobility in the rubbery region with the introduction of methyl branches.

The peak height of tan δ *versus* the mixing ratio of the resins is plotted in *Figure 5*. In the case of the bisphenol-A type resin, the peak height of tan δ was unaffected by the introduction of methyl branches. However, in the case of the biphenol type resin, the peak height of tan δ increased with the introduction of methyl branches. These results also show that the introduction of methyl branches into biphenol type resin caused an increase in the free volume and mobility of network chains in the rubbery region.

Internal stresses

The change in the magnitude of the internal stress σ_i in the cooling process for bisphenol-A resin system is shown in *Figure 6a*. The internal stress in the cured systems is negligibly small in the rubbery region, and is generated near the T_g of each cured system. Then the stress increases in proportion to the decrease in temperature in the glassy region[5,6]. In this system, the internal stress is unaffected and is independent of the introduction of methyl branches. On the other hand, the internal stress for the biphenol resin system shown in

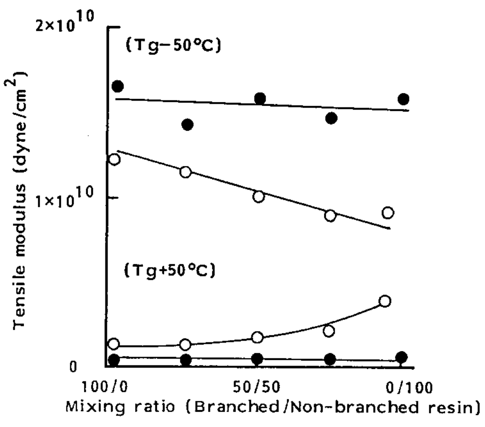


Figure 4 Tensile modulus of cured epoxide resins. Epoxide resin: (○) biphenol type; (●) bisphenol-A type

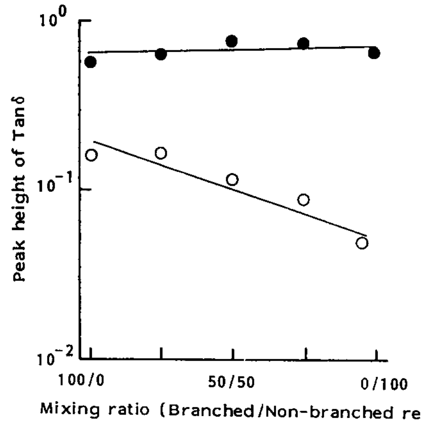


Figure 5 Peak height of tan δ at T_g. Symbols as in *Figure 4*

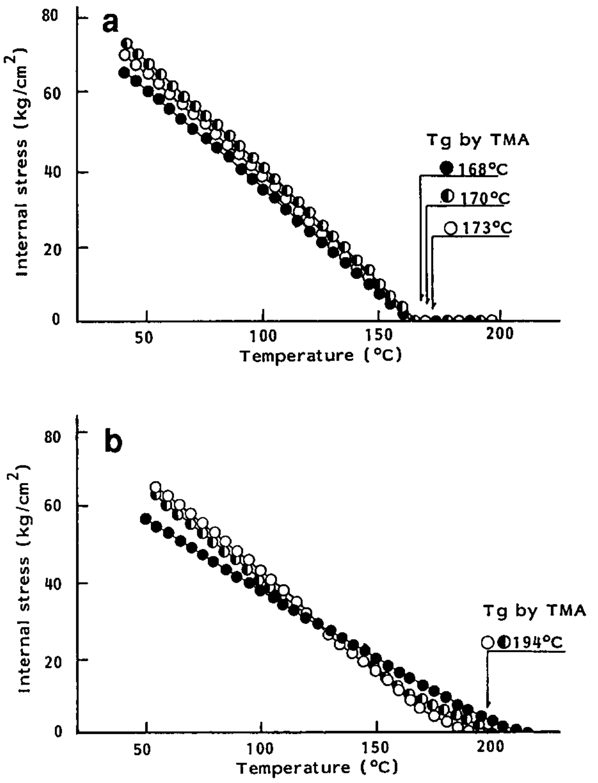


Figure 6 Internal stress of cured epoxide resins. Symbols as in (a) *Figure 2* and (b) *Figure 3*

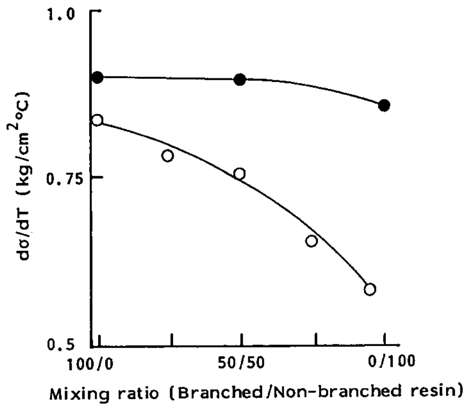


Figure 7 Increment in internal stress of cured epoxide resins. Symbols as in *Figure 4*

Figure 6b is different. The temperature at which the internal stress is generated decreases with the introduction of the branches, though the T_g of each sample is almost the same. This seems to be attributed to the decrease in the modulus of the rubbery region with an increase in the mobility of the network chains; and the increment ($d\sigma/dT$) of the internal stress increased with the introduction of the branches. This seems to be attributed to the increase in glassy modulus with the introduction of the branches. The increment in internal stress ($d\sigma/dT$) *versus* mixing ratio of the resins is plotted in *Figure 7*. All values of $d\sigma/dT$ of the biphenol resin system are lower than for the bisphenol-A resin system. This result shows that the introduction of the biphenol skeleton is effective in reducing the internal stress. In addition, though the introduction of the branches does not affect the increment ($d\sigma/dT$) in bisphenol-A type resin, the increment in the biphenol resin system is small with increasing ratio of the branch free resin. This phenomenon in the latter system seems to be attributed to the decrease of the modulus in the glassy region with increasing ratio of the branch free resin. In other words, the cured system with higher mobility in the rubbery region is packed more closely in the transition region resulting in the increase in the modulus in the glassy region.

Linear expansion coefficient

The internal stress arises from shrinkage of cured resin[5,6], so the linear expansion coefficient must contribute to the internal stress. The linear expansion coefficient of bisphenol-A and biphenol type resins is shown in *Figures 8a* and *b*, respectively. In any cured resin, the value of the linear expansion coefficient is low in the glassy region and high in the rubbery region. This is because the value of the linear expansion coefficient in the glassy region reflects the increase in occupied volume, and the value in the rubbery region reflects the increase in occupied and free volumes.

In the bisphenol-A type resin system, the values of the linear expansion coefficient in both the glassy and rubbery regions are only slightly affected by the introduction of methyl branches. Also, the introduction of methyl branches into this type of resin has little effect on the free volume of the cured resin. In the biphenol type resin system shown in *Figure 8b*, the values of the linear expansion coefficient in the rubbery region increased according to the introduction of methyl branches. This indicates the increase in free volume in

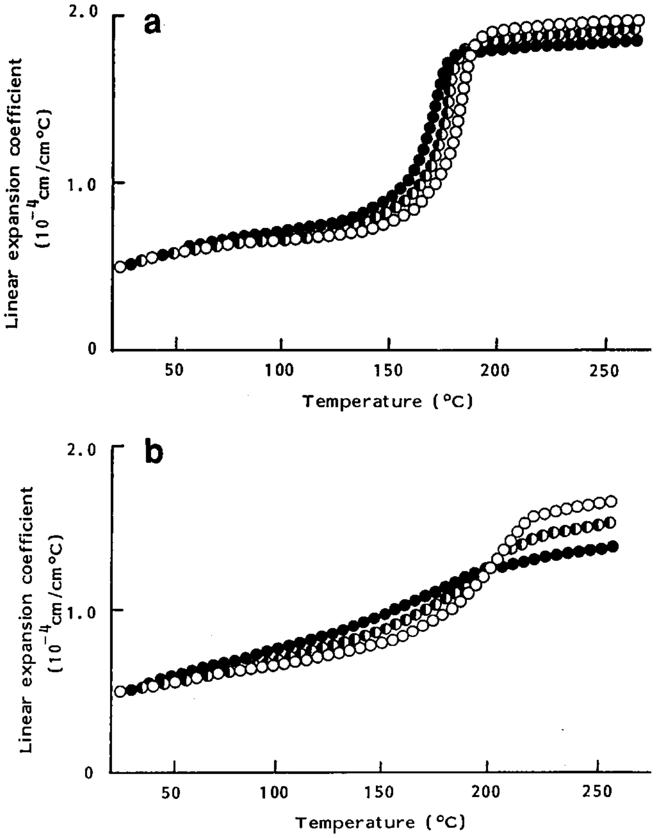


Figure 8 Linear expansion coefficient of cured epoxide resins. (a) Bisphenol-A type resins. Symbols as in *Figure 2*. (b) Biphenol type resins. Symbols as in *Figure 3*

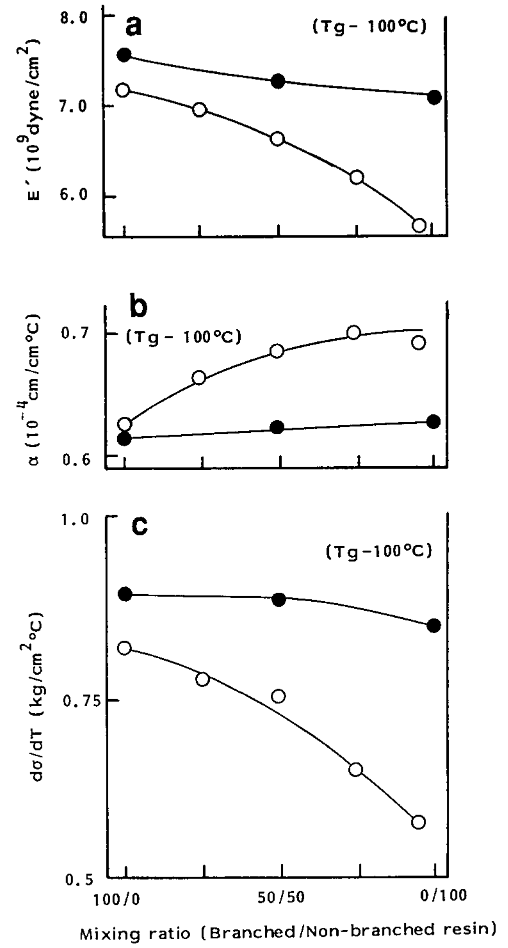


Figure 9 Relationship between mixing ratio of resins and (a) modulus, (b) coefficient of linear expansion and (c) increment in internal stress. Symbols as in *Figure 4*

the rubbery region due to steric hindrance. Moreover, the values in the glassy region decreased according to the introduction of the branches. This shows the decrease in free volume in this region with an increase in the concentration of methyl branches. It is also concluded from these results that the introduction of methyl branches into biphenol type resin decreases the mobility of network chains in the rubbery region and thus increases the free volume in the glassy region.

The relationship between the mixing ratio of resins, modulus and the linear expansion coefficient and increment in internal stress is shown in *Figure 9*. In the bisphenol-A type resin system, the increment in internal stress is unaffected by the introduction of methyl branches. This is because both the modulus and the linear expansion coefficient in the glassy region remain almost constant regardless of the introduction of branches. In contrast to this system, the increment in internal stress of the biphenol resin systems decreased with increase in the ratio of branch free resin regardless of the increase in the value of the linear expansion coefficient. This is due to the decrease in the modulus accompanied by the increase in free volume in the glassy region.

Mechanical properties

The temperature dependence of the tensile strength of the two resin systems is shown in *Figure 10*. In the bisphenol-A type resin, a dramatic decrease in tensile strength was observed around T_g and was slightly dependent on the introduction of methyl branches. On the other hand, the biphenol type resin system exhibited a gradual decrease in tensile strength over all the temperature range studied and considerable strength was retained even in the rubbery state. In addition, the strength in rubbery region increased according to the increase in ratio of branch free resin. This is due to the fact that the biphenol structure seems to have low mobility in the rubbery region and that the mobility is reduced with the increase in ratio of branch free resin. The elongation at break in tensile strength measurements is shown in *Figure 11*. In the case of bisphenol-A type resin, a maximum elongation was shown around T_g. This is due to the existence of a large glass transition in the system having a relatively high mobility in the network chain. On the other hand, in the case of the biphenol type resin system, no elongation peak was shown around T_g. This is due to the broad and small glass transition in the system having a low mobility in the network chain.

CONCLUSIONS

Bisphenol-A and biphenol type epoxide resins were cured with DDM and the effect of the introduction of methyl branches into the skeleton on the dynamic mechanical and thermal properties was investigated. The following conclusions were obtained:

1. Biphenol type epoxide resins have some characteristic phenomena, such as high rubbery modulus, low glassy

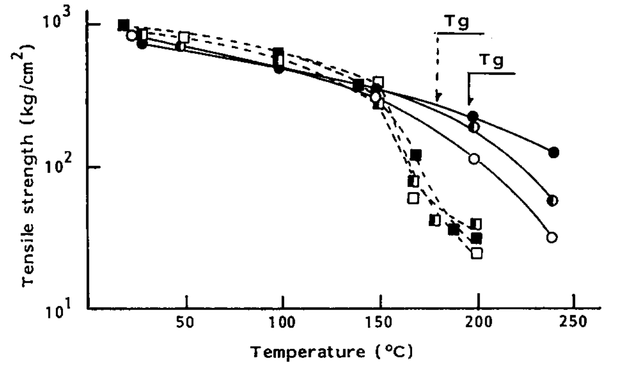


Figure 10 Tensile strength of cured epoxide resins. TMBADGE/BADGE: (■) 0/100; (◨) 50/50; (□) 100/0. TMBPDGE/BPDGE: (●) 5/95; (◐) 50/50; (○) 100/0

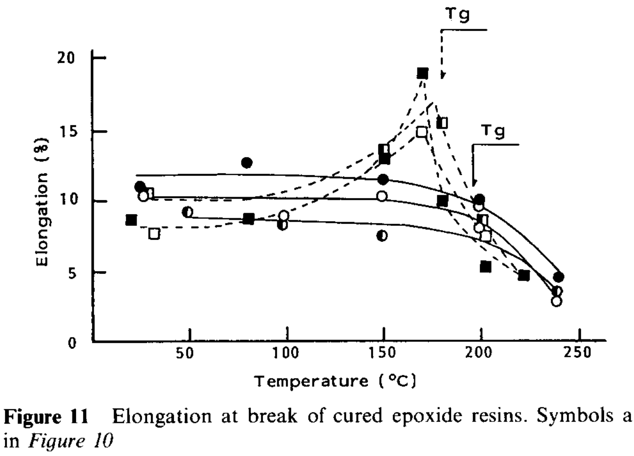


Figure 11 Elongation at break of cured epoxide resins. Symbols as in *Figure 10*

modulus and a broad glass transition, compared with bisphenol type epoxide resins.

2. These phenomena are strongly affected by the introduction of methyl branches into the skeleton structure of the biphenol type resin. Namely, the rubbery and glassy modulus of this type of resin decrease and increase with an increase in the amount of methyl branches, respectively.

3. We suggested that the peculiar phenomena of the biphenol type resin are explained as follows: biphenol type resin has a very low mobility in the rubbery region. Thus, the motion of the network segments in this type of resin is frozen in the larger free volume state, and thus the elastic modulus in the glassy region decreases. The introduction of methyl branches into this type of resin increases the free volume of networks in the rubbery region due to steric hindrance, and thus decreases the rubbery modulus.

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