

Mechanical Properties of Acid-Cured Epoxide Resins with Different Network Structures

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Synopsis

Static and dynamic mechanical properties of cured epoxide resins based on ester bonds, ether bonds, or a mixture of ester and ether bonds were investigated. Their network structures were estimated from the results of gel content before and after saponification, and conversion of functional groups. It was found that cured epoxide resins based on a mixture of ester and ether bonds indicate intermediate properties between the resins based on ester bonds and the resins based on ether bonds. Both dynamic and static mechanical properties were strongly affected by their network density and their segmental structures suggested in this paper.

INTRODUCTION

There are many epoxide resin oligomers, curing agents, and catalysts which have well-identified structural schemes. Their purities are quite high, and reactions between epoxide resins and curing agents seem to be carried out in stepwise fashion. Epoxide resin systems are, therefore, useful for evaluating the reaction process of the chains before and after hardening compared with other thermoset resin systems.

We have studied the correlations between the structure and dynamic mechanical properties and/or static mechanical properties by using various epoxide resin oligomers¹⁻³ cured with aliphatic diamines,⁴⁻⁸ aromatic diamines,^{2,3,9} aliphatic dicarboxylic acids,^{10,11} alicyclic and aromatic polycarboxylic acids,¹² and some polymeric curing agents.¹³⁻¹⁵ It is known that, in order to get high conversion of epoxy groups, it is necessary to cure at relatively high temperature over a long period. Under this condition, ether bonds tend to be formed concomitantly in amine-cured or acid-cured epoxide resin networks.^{10,11,16} It is, therefore, observed in general that a network based on both ether and ester bonds or a network based on both amino and ether bonds is formed in these cured resins.^{10,16} Because of the complex network structures, it is difficult to realize what kind of structure mainly cause their specific properties. As a result of our experimental investigation, it has been found that a tertiary amine accelerates the reaction to form ester bonds and yet depresses the reaction to form ether bonds¹⁰ in acid-cured epoxide resins. Salicylic acid accelerates the reaction to form amino bonds and yet depresses the reaction to form ether bonds¹⁶ in amine-cured epoxide resins. It has also been well known that epoxide resin oligomers are able to form an ether network structure by using a catalyst.¹⁸⁻²⁰ This fact is also supported by our experimental results.^{10,11,16}

In this paper, cured epoxide resins based on ester bonds, ether bonds, or a mixture of ester and ether bonds were prepared on the basis of the results mentioned above.^{10,11} The correlations between structure and dynamic mechanical and/or static mechanical properties were discussed for these epoxide resins.

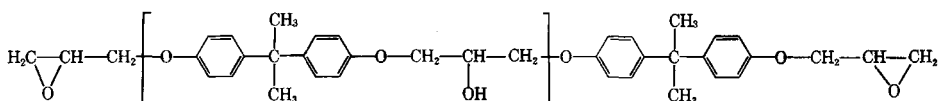
EXPERIMENTAL

Cured epoxide resin samples were prepared from a bisphenol-type epoxide resin (Epikote 828, Epoxy equiv 190 ± 5 , $\bar{M}_n = 380$) and various dibasic acids expressed by the general equation $\text{HOOC}-(\text{---CH}_2\text{---})_p\text{---COOH}$, such as adipic acid ($p = 4$), azelaic acid ($p = 7$), sebacic acid ($p = 8$), decanedicarboxylic ($p = 10$), and tetradecanedicarboxylic acid ($p = 14$). *N,N*-dimethylbenzylamine (DMBA) was employed both as a catalyst and as an accelerator. Their chemical structures and molecular weights are listed in Table I. The epoxide resin was obtained commercially, having been made by standard preparation techniques, and other chemicals used were reagent grade. The epoxide resin and one of the dibasic acids were mixed stoichiometrically; 1 mol of epoxy groups corresponds to 1 mol of carboxyl groups. The resin is mixed with 22.0 mol % (10 phr) of DMBA acting as a catalytic curing agent, or with 1.39 mol % (1 phr) used as an accelerator. The epoxide resin mixture with DMBA was cured for 10 h at 130°C, and the mixture without the accelerator was cured for 21 h at 130°C. The catalytically cured epoxide resin with DMBA was prepared by heating for 2 h at 80°C and then for 6 h at 180°C. These curing conditions were determined from the observation that no further reaction of functional groups and no more changes in mechanical properties were taking place with additional heating.

Dynamic mechanical properties were measured with a torsion pendulum (RD-1100AD Rhesca Co., Ltd.) in free vibration, at less than 3.0 Hz frequency,

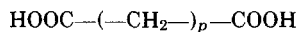
TABLE I
Chemical Structures of Epoxide Resin, Curing Agents, and Catalyst and Accelerator

Epoxide resin: Bisphenol A DGE ($n = 0.1$, Epikote 828)



Curing agents

α,ω -dicarboxylic acids:



Mol wt

$p = 4$: adipic acid	146
$p = 7$: azelaic acid	188
$p = 8$: sebacic acid	202
$p = 10$: decanedicarboxylic acid	230
$p = 14$: tetradecanedicarboxylic acid	286

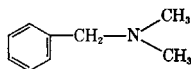
Catalyst and

accelerator:

N,N-dimethylbenzylamine (DMBA)

Mol wt

135



between -150°C and 200°C with a heating rate of $1^{\circ}\text{C}/\text{min}$. The measurement was carried out on the basis of ASTM D 2236-70.

The stress-strain properties were measured by use of an Instron Tensile Tester at a crosshead speed of 10 mm/min in accordance with ASTM D 1708-79.

The reaction rate of epoxy group was determined by the method of Shimazaki²¹; a solution made up of 0.2*N* pyridine-hydrochloride, isopropyl alcohol, and distilled water in the ratio of 2:2:1 was refluxed over the samples for 4 h and then the swollen samples were titrated with 0.5*N* sodium hydroxide. To determine the conversion of carboxyl groups, the resins swollen in methyl ethyl ketone were titrated with the same sodium hydroxide solution.²¹

Gel measurement was carried out by using tetrahydrofuran as a solvent in a manner similar to Kenyon and Nielsen.²² The solvent was changed every 4 days, and, after the samples were kept in the solution for 3 weeks at room temperature, the samples were dried under vacuum conditions at 80°C until a constant weight was reached. The gel content of the samples was obtained by comparing their original weight with the gel weight.

Hydrolysis of the samples in alkali was carried out by using the method of Lunak and Krejcar²³; the powdered samples were boiled in 0.5*N*-KOH-ethanol solution for 5 h and then washed with distilled water. After the samples were extracted with tetrahydrofuran, gel content was measured by comparing their original weight with the gel weight.

RESULTS AND DISCUSSION

Network Structure. Table II shows various properties of bisphenol type epoxide resins cured with one of the five aliphatic α,ω -dicarboxylic acids having different numbers of the methylene chain repeat units, or cured with one of these acids and DMBA acting as accelerator, and catalytically cured with DMBA.

Conversion of epoxy groups for the acid-cured resins with DMBA reaches 92–97%, regardless of the different *p* values of the dibasic acid used as curing agents. The networks are completely hydrolyzed in alkali (Table II), and they are expected to be made up of ester bonds. In detail, the matrix consists of 65–72% network structure and the rest is a linear structure based on ester bonds (hereafter called the ester network system). Conversion of epoxy groups for the catalytically cured resin is 95% with a gel content of the resin of 97%. After saponification the gel content of the resin is 94%. This resin is known to be composed of an ether network structure^{11,16,18–20} (hereafter called the ether network system). The epoxide resins cured only with dicarboxylic acids show 90–95% conversion of epoxy groups and the gel content of the resins is 90–93%. It is, however, observed that the nonsaponification fraction of the resin is 3–37% and the saponified portion of the resin has a 56–87% gel content. Namely, 56–87% of the matrix is based on ester network chains, 7–10% on linear ester chains, and 3–37% on ether network chains. This system will be termed the ether-ester network system. On the basis of the results described above, structural schemes are assumed as shown in Figure 1.

Dynamic Mechanical Properties of Cured Epoxide Resins with Different Structures. Dynamic mechanical properties for the ester network

TABLE II
Various Properties of Cured Epoxide Resins^a

Curing agents and catalyst	DMBA ^b added (mol %)	Conversion ^c of epoxide group (%)	Gel fraction of cured resins (%)	Gel fraction of saponified resins (%)	Network based on ester bonds (%)	Network based on ether bonds (%)	Linear structure (%)
Ester network systems							
Adipic acid	1.39	92	70	0	70	0	30
Azelaic acid	1.39	93	72	0	72	0	28
Sebacic acid	1.39	94	71	0	71	0	29
Decanedicarboxylic acid	1.39	90	64	0	64	0	36
Tetradecanedicarboxylic acid	1.39	97	65	0	65	0	35
Ether-ester network systems							
Adipic acid	0	90	93	37	56	37	7
Azelaic acid	0	89	93	27	66	27	7
Sebacic acid	0	95	90	3	87	3	10
Decanedicarboxylic acid	0	92	90	3	87	3	10
Tetradecanedicarboxylic acid	0	95	90	3	87	3	10
Ether network system							
<i>N,N</i> -Dimethylbenzylamine	22.0	95	97	94	0	94	6

^a Epoxide resin: bisphenol A DGE ($n = 0.1$, Epikote 828).

^b Accelerator and catalyst: *N,N*-dimethylbenzylamine (DMBA).

^c Titration analysis.

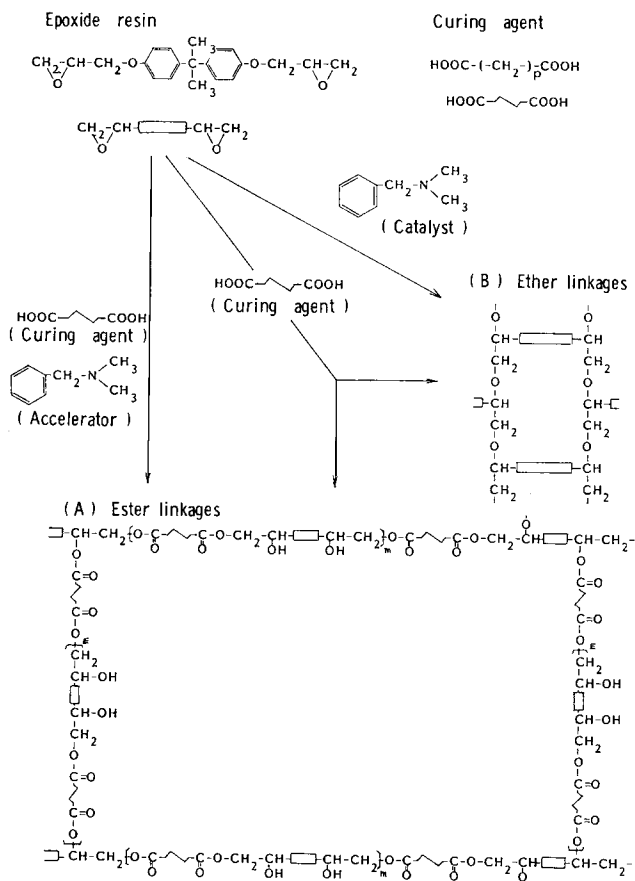


Fig. 1. Structural schemes of cured epoxide resins.

system and the ether network system are shown in Figure 2. The temperature at which a maximum reduction in shear modulus (G) occurs or at which $\tan \delta$ is maximum would be expected to be nearly equal to the glass transition temperature (T_g). G of the ether network system is largest in both glassy ($>T_g$) and rubbery ($\gg T_g$) region. The high values of T_g and low $\tan \delta_{\max}$ indicate that segmental motion in the matrix is strongly restricted. Data for G of the ester network system are relatively low throughout the entire temperature range, and, with increasing p , G decreases and $\tan \delta_{\max}$ increases. It is obvious that the network density decreases with increasing p , and segmental motion is not much restricted (described later in detail). It is observed from the $\tan \delta$ data shown in Figure 2 that the ether network system has a relaxation peak at -70°C , this due to motion of ether bonds,¹⁶ while the ester network systems have a relaxation peak at -50°C , due to the motion of hydroxy ether moieties formed by the reaction between epoxy group and carboxyl group. The ester systems with $p > 7$ have a γ -relaxation peak around -140°C interpreted as the motion of more than six methylene units.¹⁶

Dynamic mechanical properties of the ether-ester network systems are shown in Figure 3. The values of G for this system are lower than these of the ether

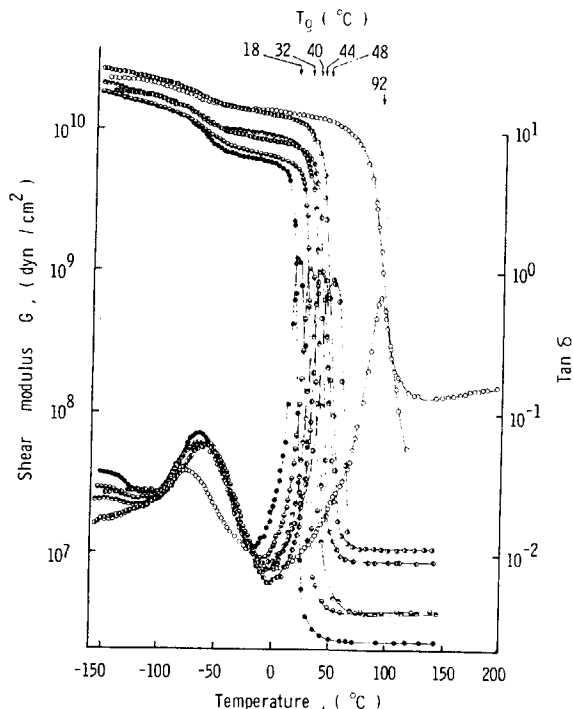


Fig. 2. Dynamic mechanical properties of cured epoxide resins composed of ether and ester bonds. Ester network systems: (●) adipic acid ($p = 4$); (◐) azelaic acid ($p = 7$); (◑) sebacic acid ($p = 8$); (◒) decanedicarboxylic acid ($p = 10$); (◓) tetradecanedicarboxylic acid ($p = 14$). Ether network system: (○) *N,N*-dimethyl-benzylamine (DMBA). Epoxide resin: bisphenol A DGE ($n = 0.1$, Epikote 828).

network system throughout the entire temperature range, and with increasing p of the dibasic acid used G decreases the $\tan \delta_{\max}$ increases.

Network Density and Glass Transition Temperature. In principle, the crosslink density ν can be obtained from modulus values in the rubbery region in Figures 2 and 3 by use of the theory of rubber elasticity.^{24,25} ν is plotted against p for both the ester and ether network systems as shown in Figure 4(A). It is noted that ν increases nearly linearly with decreasing values of p in both plots. This fact suggests that the epoxide resin oligomers react in a regular way with the acid curing agents to form network chains.

Figure 4(B) shows the relation between ν and T_g for all the systems. T_g strongly depends on the ν ; T_g increases with increasing ν for both the ester network system and the ether-ester network system.

Hence it is concluded that crosslink density is governed by the number of methylene units in curing agents. In addition, T_g of the cured systems is affected not only by their crosslink density but also by their network structure.

Network Structure and Mechanical Properties. Figure 5(A) shows the temperature dependence of tensile strength σ_B for the ester network system (adipic-acid-cured epoxide resin with DMBA), the ether-ester network system (adipic-acid-cured epoxide resin without accelerator), and the ether network system (catalytically cured epoxide resin with DMBA). It is obvious from the

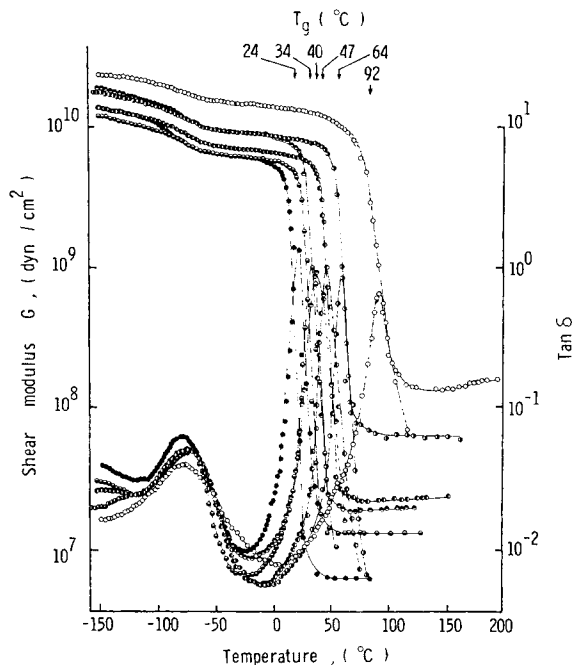


Fig. 3. Dynamic mechanical properties of cured epoxy resins composed of ether and ester bonds. Ether-ester network systems: (●) adipic acid ($p = 4$); (●) azelaic acid ($p = 7$); (●) sebacic acid ($p = 8$); (●) decanedicarboxylic acid ($p = 10$); (●) tetradecanedicarboxylic acid ($p = 14$). Ether network system: (○) *N,N*-dimethylbenzylamine (DMBA). Epoxide resin: bisphenol A DGE ($n = 0.1$, Epikote 828).

figure that σ_B varies little with temperature in glassy region, decreases rapidly around T_g , and again exhibits no change with temperature in the rubbery region. These three curves are superimposed upon each other with respect to the reference temperature, T_g , as shown in Figure 5(B). It has been observed that the shift method with respect to T_g is effective in analyzing physical properties such as mechanical^{2,4,6,7,12} static and dynamic properties fatigue,¹¹ friction,²⁶ and shrinkage due to curing or internal stress.⁸ The temperature dependence of the shifted σ_B for the ether network system, the ester network system, and the ether-ester network system is reasonably well represented by a single line in the T_g region and below T_g . Above T_g , σ_B increases in order of the ester network system, the ether-ester network system, and the ether network system in the same order as the order of the ν [Figs. 4(A) and 4(B)]. It is, therefore, inferred that σ_B is strongly related to ν .

Figure 6(A) shows temperature dependence of elongation at break, ϵ_B , and Figure 6(B) shows the superimposed ϵ_B with respect to T_g . These samples have a peak, $\epsilon_{B_{\max}}$, around T_g and the $\epsilon_{B_{\max}}$ increases in the order of the ether network system, the ether-ester network system, and the ester network system. In other words, increase of ν for the systems shows decreasing $\epsilon_{B_{\max}}$.

In order to correlate these results, the temperature of $\epsilon_{B_{\max}}$ is plotted against T_g in Figure 7 for 26 cured epoxy resin systems. They are systems with different structural oligomers,¹⁻³ aliphatic-diamine-cured systems, polyethylene-

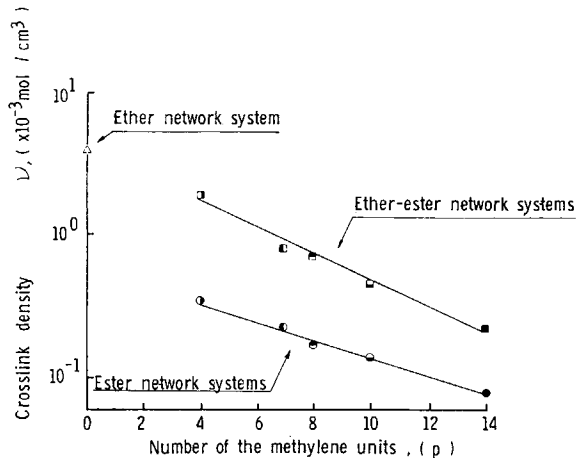


Fig. 4(A). ν vs. number of the methylene units (p) of cured epoxide resins. (1) Ester network systems: (○) adipic acid ($p = 4$); (○) azelaic acid ($p = 7$); (●) sebacic acid ($p = 8$); (⊙) decanedicarboxylic acid ($p = 10$); (●) tetradecanedicarboxylic acid ($p = 14$). (2) Ether network system: (Δ) *N,N*-dimethylbenzylamine (DMBA). (3) Ether-ester network systems: (▣) adipic acid ($p = 4$); (▣) azelaic acid ($p = 7$); (▣) sebacic acid ($p = 8$); (▣) decanedicarboxylic acid ($p = 10$); (▣) tetradecanedicarboxylic acid ($p = 14$). Epoxide resin: bipshenol A DGE ($n = 0.1$, Epikote 828).

polyamine-cured systems,⁴⁻⁸ aromatic-diamine-cured systems,^{2,3,9} and alicyclic or aromatic-dicarboxylic-acid-cured systems.¹² These cured epoxide resins used in Figure 7 are listed in Table III. These data follow a straight line with a slope of 45°. It is, therefore, noted that the temperature of $\epsilon_{B\max}$ is in fair agreement with T_g for these cured systems.

Temperature Dependence of Mechanical Properties. The influence of the network structure on σ_B and ϵ_B for adipic-acid-cured epoxide resins was studied in the last section. In this section, dibasic acids with the number of repeat units $p = 4, 7, 8, 10$, and 14 are employed to change the ν of the matrix, and correlations between ν and mechanical properties are discussed.

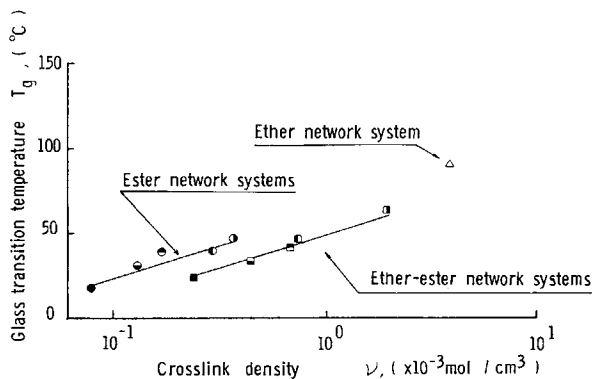


Fig. 4(B). T_g vs. ν of cured epoxide resins. Same legend as Figure 4(A). Epoxide resin: bisphenol A DGE ($n = 0.1$, Epikote 828).

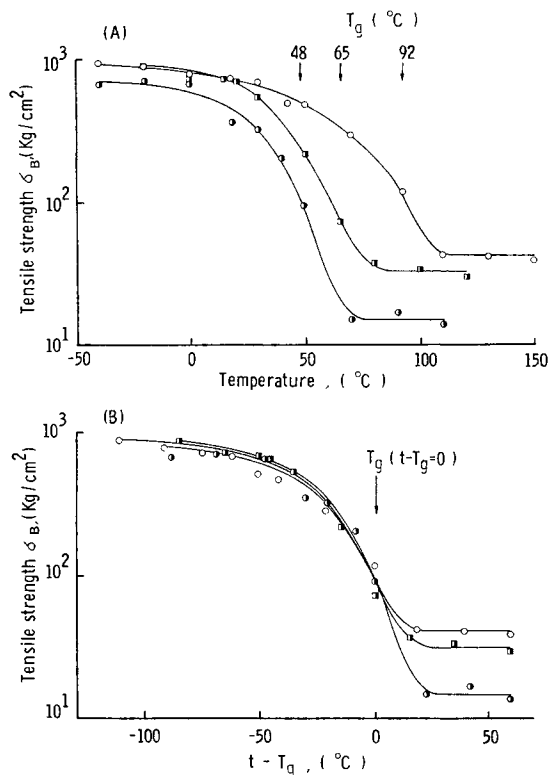


Fig. 5. Tensile strength of cured epoxide resins. Curing agent: adipic acid ($p = 4$); accelerator and catalyst: *N,N*-dimethylbenzylamine (DMBA). Epoxide resin: bisphenol A DGE ($n = 0.1$, Epikote 828); (●) ester network system; (○) ether network system; (□) ether-ester network system.

Figure 8(A) shows the relationship between σ_B and ν . Because of the scattering of data around T_g , σ_B at $T_g - 50^\circ\text{C}$ is plotted against ν . A fairly good correlation is obtained between σ_B and ν for ten different cured systems. In the same manner, the relationship between ϵ_B and ν is plotted in Figure 8(B). It is observed that the plot of ϵ_B vs. ν gives a single line, while ϵ_B depends on ν in the low- ν region, but is independent on ν in the high- ν region.

Estimation of Network Structure. Table IV shows ν and the molecular weight between crosslinks, \bar{M}_c , for various cured resins having different network structures. These values are obtained by using the rubber elasticity theory. Since the \bar{M}_c is 270 for the ether network system [Fig. 1(B)] and the \bar{M}_c estimated from the structural scheme is 280, a good agreement is observed between the two values. On the contrary, the ester network system has no ether bonds (Table II) and its \bar{M}_c varies from 2900 to 12,000 with p increasing from 4 to 14. These values are not unusually large, since $\bar{M}_c = 13,000$ for the epoxide resin-nylon system has been reported before.¹³⁻¹⁵

The number of ester chain repeat units, m , for ester networks is estimated to be 5-18 (Table IV). Thus low T_g , low modulus, low tensile strength, large loss tangent, and large elongation of the matrix are to be expected in the series of network structures evaluated here. When the p of the curing agent varies from

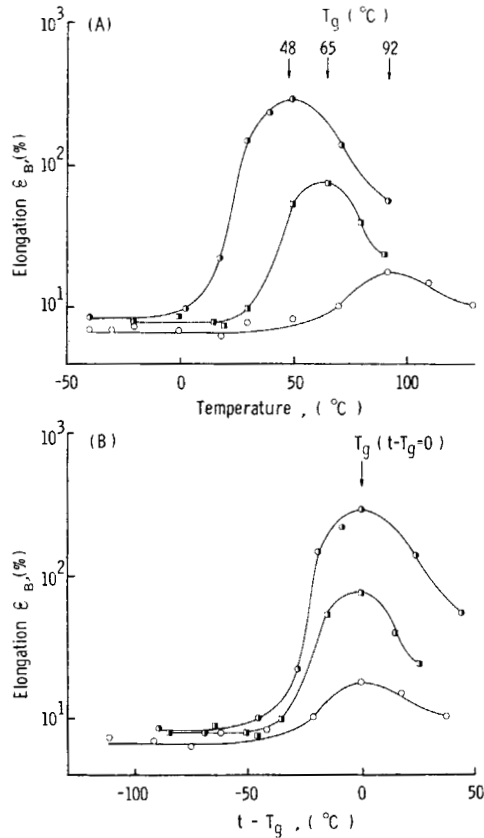


Fig. 6. Elongation at break for cured epoxide resins. (1) Curing agent: adipic acid ($p = 4$). (2) Accelerator and catalyst: *N,N*-dimethylbenzylamine (DMBA). (3) Epoxide resin bisphenol A DGE ($n = 0.1$, Epikote 828). Same legend as Figure 5.

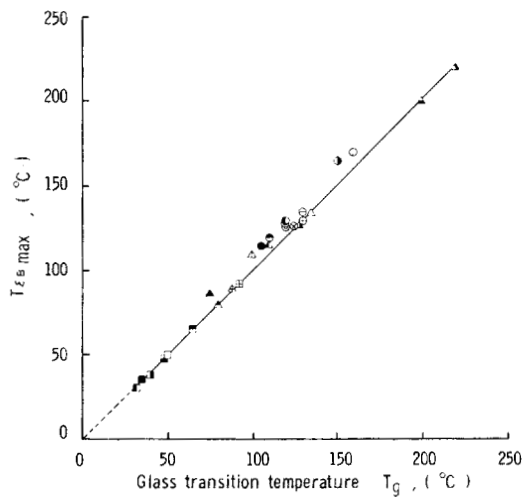


Fig. 7. $T\epsilon_{B\max}$ vs. T_g of cured epoxide resins.

TABLE III
List of the Cured Epoxide Resins used in Figure 7

Epoxide resins	Curing agents
⊙ DGEBA ($n = 0.1$)	4,4'-Diaminodiphenylmethane (DDM)
⊙ DGEBA ($n = 1.0$)	
⊙ DGEBA ($n = 2.0$)	
⊙ DGEBA ($n = 3.7$)	
● DGEBA ($n = 8.8$)	
▲ Tetraglycidyl- <i>m</i> -xylenediamine	
▲ Tetraglycidyl-1,3-bis(aminomethyl)cyclohexane	
⊖	$m = 0$
⊕	$m = 1$
⊗	$m = 2$ H ₂ N—(—CH ₂ CH ₂ NH—) _{<i>m</i>} —
⊙	$m = 3$ —CH ₂ CH ₂ NH ₂
⊖	$m = 4$
Δ	$m' = 2$
▲	$m' = 4$
Δ	$m' = 6$ H ₂ N—(—CH ₂ —) _{<i>m</i>} —NH ₂
▲	$m' = 10$
▲ DGEBA ($n = 0.1$)	$m' = 12$
Δ	Phthalic anhydride
▲	Hexahydrophthalic anhydride
□	$p = 4$
■	$p = 7$ HOOC—(—CH ₂ —) _{<i>p</i>} —COOH
■	$p = 10$
■	$p = 4$
■	$p = 7$ HOOC—(—CH ₂ —) _{<i>p</i>} —COOH/DMBA
■	$p = 10$
■	<i>N,N</i> -Dimethylbenzylamine (DMBA)

TABLE IV
Proposed Structure of Cured Epoxide Resins

Curing agents and catalyst	ν^a $\times 10^{-3}$ (mol/cm ³)	\bar{M}_c^b	Probable structures		
			Ester linkages	Ether linages	m^c
Ester network systems					
Adipic acid	0.37	2900	70	0	5.0
Azelaic acid	0.30	3700	72	0	7.0
Sebacic acid	0.17	7300	71	0	12.2
Decanedicarboxylic acid	0.13	8500	64	0	13.9
Tetradecanedicarboxylic acid	0.08	12,000	65	0	18.2
Ether-ester network systems					
Adipic acid	2.00	550	56	37	0.3
Azelaic acid	0.75	1500	66	27	1.9
Sebacic acid	0.70	1600	87	3	2.1
Decanedicarboxylic acid	0.45	2400	87	3	3.4
Tetradecanedicarboxylic acid	0.24	4500	87	3	6.2
Ether network system					
<i>N,N</i> -Dimethylbenzylamine	3.98	270 ^d	0	94	—

^a Crosslink density.

^b Obsd. by dynamic mechanical measurement.

^c Number of repeat units between crosslinks.

^d \bar{M}_c : Obsd: 270; Calcd: 280.

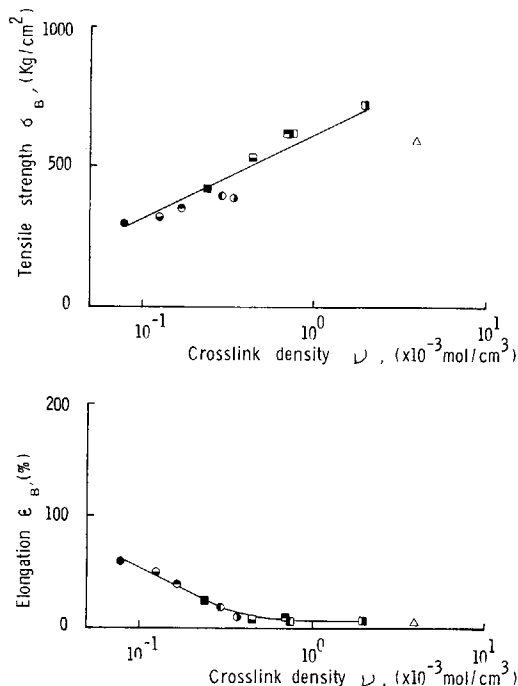


Fig. 8. Tensile strength and elongation vs. ν of cured epoxide resins. Some legend as Figure 4(A).

4 to 14, the ether network fraction in the ether-ester network system changes from 37% to 3% (Table II). The m for the ether-ester network system in Figure 1 is estimated to be from 0 to 6 by considering the contribution of the ether network ($\bar{M}_c \doteq 270$), which comprises from 3% to 37% of the ether-ester network.

The good correlations between ν and mechanical properties obtained here [Figs. 8(A) and 8(B)] suggest the importance of understanding the network structure. From various measurements, structural schemes which may be regarded as a key to discovering the relation between physical properties and network structure are successfully estimated here.

CONCLUSION

Bisphenol-type epoxide resins cured catalytically, or with one of the five, α , ω -dicarboxylic acids acting as curing agents, with or without DMBA as an accelerator, are used to form structures based on ester bonds, ether bonds, or a mixture of ester and ether bonds. The static and dynamic mechanical properties of these cured resins were investigated.

Based on the experimental results, we reached the following conclusions.

1. The ester network system showed low shear modulus, low tensile strength, low T_g , large $\tan \delta$, and large elongation at break. With the increasing number of methylene units p , of dicarboxylic acid used, the tensile strength and T_g decreased, while $\tan \delta$ and elongation at break increased. The high mobile network structure due to ester bonds induced these inherent properties.

2. The dense network structure of the ether networks system, in which the segmental motion is strongly restricted, induced high shear modulus, high tensile strength, high T_g , low $\tan \delta$, and low elongation at break.

3. Since the dicarboxylic-acid-cured epoxide resins without an accelerator showed intermediate properties between the ester network system and the ether network system, it is convenient to imagine the system as being composed of a mixture of ether and ester bonds.

4. The crosslink density in all cured resins was governed by the p values of the dicarboxylic acid used, and T_g was governed by both crosslink density and segmental structure of the network. In addition, it was found that tensile strength and elongation at break depend on the crosslink density and that the maximum elongation at break was obtained at T_g .

5. The structural schemes for the cured resins were estimated from the reaction mechanism between oligomers and curing agents. These structural schemes were useful in elucidation of the properties of the resins.

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