Effects of Crosslinking on Physical Properties of Phenol–Formaldehyde Novolac Cured Epoxy Resins

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SYNOPSIS

To clarify the relationship between crosslinking density and physical properties of phenol-formaldehyde novolac cured epoxy resin and factors governing their physical properties, we studied various properties of cured resins having different crosslinking densities. The resins were prepared with various curing accelerators and raw epoxy resins having different molecular weights. We found that as the crosslinking density of a cured resin increases, glass transition temperature (T_g) rises and the relaxation time becomes longer. Furthermore, in the rubbery region, the coefficient of linear thermal expansion drops and the elastic modulus become larger, while, in the glassy region, the coefficient of linear thermal expansion, specific volume, water absorption, diffusion coefficient, and permeability all increase but the elastic modulus becomes smaller. The WLF analysis on the relaxation behaviors of typical cured resin showed that cured resin with a higher crosslinking density decreases in the fractional free volume. This behavior is completely opposite from the relationship predicted from the temperature dependency of specific volume. While the coefficient of thermal expansion of free volume decreases as the crosslinking density increases for the cured resin, it coincides well with the tendency predicted from the difference in coefficient of cubic thermal expansion in the rubbery and glassy regions of each cured resin. That the free volume obtained from WLF analysis shows a relationship opposite to the predicted free volume as based on the temperature dependency of specific volume is explained as follows: Namely, the free volume obtained from the WLF analysis is a hole free volume V_h which contributes to fluidity and V_h decreases with the crosslinking density. On the other hand, the free volume predicted from the specific volume is a sum of the interstitial free volume V_i and V_h. V_i increases with the crosslinking density and this V_i increase exceeds the decrease of V_h. Therefore, the free volume predicted from the specific volume increases with the crosslinking density. Consequently, the influence of free volume on the relationship between the crosslinking density and physical properties of cured resin can be interpreted as follows. As the crosslinking density increases on cured resins, T_g rises, the relaxation time is lengthened, and the coefficient of linear thermal expansion becomes smaller in the rubbery region because, as the crosslinking density increases, V_h decreases. Since crosslinking density increases on cured resins, the coefficient of linear thermal expansion, water absorption, diffusion coefficient, and permeability become larger, and the elastic modulus becomes smaller in the glassy region because, as the crosslinking density increases, V_i increases and, accordingly, molecular chain packing becomes looser; i.e., the specific volume increases. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resins have excellent thermal, mechanical, electrical, and chemical properties, ensuring their

applications in many industrial fields.[1] With thermosetting resins such as epoxy resins, crosslinking density is an important factor governing the physical properties of cured resin. Previous studies have investigated the effect of crosslinking on physical properties of cured resin, particularly focusing on amine or anhydride cured epoxy resins.[2-11] However,

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no unified interpretation has been given yet, in part because the methods of changing the crosslinking density are subjected to limitations and problems. There are four ways of changing the crosslinking density of epoxy resins:

1. Change in chemical structure of epoxy resin or hardener.
2. Change in equivalent ratio of epoxy resin and hardener.
3. Change in conversion.
4. Control of curing reaction mechanism.

The most popular method is 1, but its disadvantage is that the basic composition of the resin system changes, depending on the kind of epoxy resin or hardener used. Method 2 has the same problem. The approach using 3 is the simplest, and the change is readily implemented by adjusting the curing conditions, but it is still problematic, because semicured resins are thermally unstable, and making accurate measurements of the crosslinking density and physical properties of cured resin is difficult. Results of much research may have been interpreted in too complicated a manner, because epoxy resin, hardener, and equivalent ratio were changed over a wide range, the basic composition of the resin system was changed, and physical properties of cured resin were affected by various factors other than the crosslinking density.

We have carried out work on fundamental properties and practical characteristics of phenol–formaldehyde novolac cured epoxy resins, used as base resins for semiconductor packaging materials, and found that the crosslinking density of final cured resin differed greatly according to the kind of curing accelerator used for the curing reaction.[12-15] The variation in crosslinking density with the kind of accelerator may be attributed to accompanying change in the curing mechanism and conversion of the resin system.[16,17] In this case, the mixing ratio of epoxy resin and hardener is constant and the proportion of accelerator is almost negligible, i.e., 1–2 wt %. Therefore, the basic composition of cured resin may be regarded as almost the same. On the other hand, for semiconductor packaging material, o-cresol novolac type epoxy resin having the same iterative unit as the base resin is used.[14] We found that when changing the number of iterative units (i.e., molecular weight) of an epoxy resin such as this, the crosslinking density of the final cured resin also differed considerably.[18] Again, the basic composition of cured resin remained almost the same. This difference was attributed less to a variation in the cur-

ing mechanism or curing degree than to the difference in the number of functional groups per molecule of raw epoxy resin affecting the crosslinking density of the entire system in different ways.[19]

Now, we have studied the relationship between the crosslinking density and physical properties of cured resins prepared by changing the accelerator and molecular weight of raw epoxy resin. We also considered factors governing the various physical properties.

EXPERIMENTAL

Samples

Tables I and II list the chemical structures of resins and accelerators used for the experiments. Epoxy resins (Sumitomo Chemical) were o-cresol novolac type epoxy resin ESCN 195 series and brominated bisphenol A type epoxy resin ESB 400, and the hardener was phenol novolac resin PN (Nippon Kayaku). The mixing equivalent ratio of epoxy resin and hardener was 1/1. Figure 1 shows the characteristics of o-cresol novolac type epoxy resins used for the experiments. Epoxy resin having a molecular weight (M_w) of 2110 was used to study the influences of the accelerators, while resins having M_w of 1510, 2400, and 3210 were used to study the influences of molecular weight of raw epoxy resin. To maintain the basic structure of epoxy resin, we always used an epoxy resin of almost constant equivalent (within the range of 195–202). As accelerators, we used various bases and onium–borate compounds known to be effective in accelerating the curing reaction of phenol–formaldehyde novolac/epoxy resin systems. These compounds have different curing reaction accelerations, depending on their basicity and solubility in the resin. To get as close as possible resin curing reaction rates, that is, to have almost identical gelation times at the curing temperature, we adjusted the added amount within the range of 3.0–7.5 mmol. Each accelerator was dissolved in the hardener beforehand.

Preparing Cured Resin

Epoxy resin was melted by heating to 130–140°C. Hardener, containing a specified quantity of accelerator, was added to the melted epoxy resin, quickly mixed, degassed in vacuum, and then cured at 150°C for 2 h and at 180°C for 6 h. These conditions were found to give the highest T_g in a preliminary study which examined the change of T_g in cured resin after stepwise heating of resin components using various accelerators.

Table I   Composition of Epoxy Resins

	Chemical Structure	Parts
Epoxide	Polyglycidyl ether of o-cresol–formaldehyde novolac	90
	Diglycidyl ether of brominated bisphenol A	10
Hardener	Phenol–formaldehyde novolac resin	52
Accelerator	See Table II	0.4–2.5 (3.0–7.5 mmol)

Measurement Methods

Dynamic Viscoelasticity

To measure dynamic viscoelasticity, we used a viscoelastic spectrometer (Iwamoto, PRX-706). The sample was a cured resin ($\phi50$ mm, 5 mm thick) prepared as described above and then cut into strips $1 \times 4 \times 40$ mm long, with measurements made at a 30 mm chuck spacing. Crosslinking density $\rho_{(E')}$ was determined by using the kinetic theory of rubber elasticity as follows[20]:

$$\rho_{(E')} = E'/3\phi RT \qquad (1)$$

where E' is storage elastic modulus of cured resin at peak temperature of tan δ + 40°C, ϕ is a front factor (assumed as $\phi = 1$), R is the gas constant, and T is absolute temperature. The peak temperature of tan δ was taken as the glass transition temperature $T_{g(\text{VES})}$.

Coefficient of Linear Thermal Expansion

The coefficient of linear thermal expansion was measured for test specimens of $5 \times 5 \times 15$ mm length with a thermomechanical analyzer (Shinku Riko, TMA 1500). After placing the sample in the tester, it was preliminarily heated close to the glass transition temperature T_g at a rate of 10°C/min and then gradually cooled to get rid of water and distortion. Then, it was heated from room temperature to about 250°C at a rate of 2°C/min. The coefficient of linear thermal expansion was obtained from the

Table II Accelerators

Name	Chemical Structure	Properties
N-benzyldimethylamine (BDMA)	⟨C₆H₅⟩—$CH_2N(CH_3)_2$	Crystal liquid, bp 183–184°C
Tetramethylbutylguanidine (TMBG)	$N(C_4H_9)$ ‖ $(CH_3)_2N$—C—$N(CH_3)_2$	Crystal liquid, bp 173°C
N-methylpiperazine (MP)	HN⟨ ⟩N—CH_3	Crystal liquid, bp 138°C
2-Ethyl-4-methylimidazole (EMI)	[imidazole ring] —CH_3, HN—N, C_2H_5	Pale yellow liquid, bp 160–166°C/20 mm Hg
1,8-Diazabicyclo(5,4,0)-7-undecene (DBU)	[bicyclic N=C–N ring]	Pale yellow liquid, bp 100°C/4 mm Hg
Triphenylphosphine (TPP)	P—⟨C₆H₅⟩₃	White solid, mp 80.5°C
Tris-3-hydroxypropylphosphine (THPP)	$P(C_3H_6OH)_3$	Pale yellow liquid
Tris-2-cyanoethylphosphine (TCEP)	$P(C_2H_4CN)_3$	White solid, mp 94–96°C
Triethylammonium tetraphenylborate (TEA–TPB)	$(C_2H_5)_3HN·B$—⟨C₆H₅⟩₄	White solid, mp 195–200°C
2-Ethyl-4-methylimidazolium tetraphenylborate (EMI–TPB)	[imidazolium] —CH_3, HN═NH·B—⟨C₆H₅⟩₄, C_2H_5	White solid, mp 186–190°C
2-Ethyl-1,4-dimethylimidazolium tetraphenylborate (EDMI–TPB)	[imidazolium] —CH_3, CH_3N═NH·B—⟨C₆H₅⟩₄, C_2H_5	White solid, mp 233–236°C
1,8-Diazabicyclo(5,4,0)-7-undecenium tetraphenylborate (DBU-TPB)	[bicyclic] N═N·B—⟨C₆H₅⟩₄, H	White solid, mp 205–207°C
Methyltributylphosphonium tetraphenylborate (MTBP-TPB)	$(CH_3)(C_4H_9)_3P·B$—⟨C₆H₅⟩₄	White solid, mp 150–152°C
Methyltricyanoethylphosphonium tetraphenylborate (MTCEP-TPB)	$(CH_3)(NCC_2H_4)_3P·B$—⟨C₆H₅⟩₄	White solid, mp 206–208°C
Ethyltrioctylphosphonium tetraphenylborate (ETOP-TPB)	$(C_2H_5)(C_8H_{17})_3P·B$—⟨C₆H₅⟩₄	White solid, mp 72–76°C
Hexadecyltributylphosphonium tetraphenylborate (HTBP-TPB)	$(C_{16}H_{33})(C_4H_9)_3P·B$—⟨C₆H₅⟩₄	White solid, mp 140–142°C
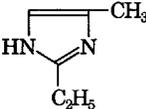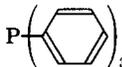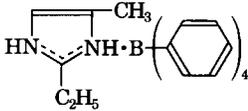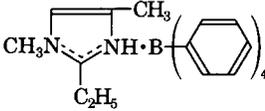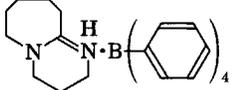
Table II *Continued*

Name	Chemical Structure	Properties
Tetrabutylphosphonium tetraphenylborate (TBP-TPB)	$\left(C_4H_9\right)_4 P \cdot B \left(\bigcirc\right)_4$	White solid, mp 232–234°C
Butyltriphenylphosphonium tetraphenylborate (BTPP-TPB)	$(C_4H_9)\left(\bigcirc\right)_3 P \cdot B \left(\bigcirc\right)_4$	White solid, mp 203–205°C
Tetraphenylphosphonium tetraphenylborate (TPP-TPB)	$\left(\bigcirc\right)_4 P \cdot B \left(\bigcirc\right)_4$	White solid, mp 282–285°C
Tetraphenylphosphonium butyltriphenylborate (TPP-BTPB)	$\left(\bigcirc\right)_4 P \cdot B \left(\bigcirc\right)_3 \left(C_4H_9\right)$	White solid, mp 175–178°C
Tetraphenylphosphonium tetrabutylborate (TPP-TBB)	$\left(\bigcirc\right)_4 P \cdot B \left(C_4H_9\right)_4$	Pale yellow solid, mp 87–89.5°C
Tetrabutylphosphonium tetrabutylborate (TBP-TBB)	$(C_4H_9)_4 P \cdot B (C_4H_9)_4$	Pale yellow solid, mp 62–62.5°C

thermal expansion quantity. The inflection point of thermal expansion was defined as glass transition temperature $T_{g(\mathrm{TMA})}$.

Specific Volume

The sample used was $5 \times 5 \times 15$ mm long. A mixture of carbon tetrachloride/ethanol having the same specific gravity as the sample was got by a sink and float method at 25°C. The mixture density was obtained by a vibrating density measuring instrument (Antonpaar, DMA-02C), and its reciprocal was used as specific volume of sample resin. The specific volume at high temperature was calculated using the coefficient of linear thermal expansion of cured resin obtained in (3).

Water Absorptivity

Using a precision balance, we periodically measured the weight of a sample ($5 \times 5 \times 30$ mm long), which had been dried beforehand at 120°C for 48 h, and then left at 60°C and 100% RH. The saturated water absorption Q_v was the water absorption at equilibrium after about 3000 h, and the diffusion coefficient D was obtained according to Fick's second law[21]:

$$q_v(t)/Q_v = 4\sqrt{Dt/l^2\pi} \tag{2}$$

where q_v is the water absorptivity in t h (168 h) and

l is the sample thickness (5 mm). Water permeability P was calculated by

$$P = Q_v \cdot D \tag{3}$$

RESULTS

Crosslinking Density of Cured Resins

As described in the Introduction, four different ways are conceivable for changing crosslinking density of thermosetting resins such as epoxy resin. When studying the relationship between crosslinking density and physical properties of cured resin and their governing factors, it is important to prepare a thermally stable fully cured resin without a change in its basic composition. So, we prepared cured resins having different crosslinking density by changing the kind of accelerator and molecular weight (number of iterative units n) of o-cresol novolac type epoxy resin. Table III and Figure 2 show calculated results of crosslinking density obtained, using a kinetic theory of rubber elasticity[20] with measurements of the dynamic viscoelasticity for each fully cured resin. When the accelerator and molecular weight of raw epoxy resin were changed, remarkably different crosslinking densities were obtained.

The reason why the crosslinking density of cured resin varies considerably according to the kind of accelerator may be the following. The curing reac-

Mw	1510	2110	2400	3210
Mn	830	1000	1120	1420
Mw/Mn	1.8	2.1	2.1	2.3
Epoxy equivalent(g/eq)	195	198	199	202
Melting point (℃)	65	75	81	88
Viscosity at 150℃ (P)	3.0	6.3	10.4	20.2
Line	————	– – – –	·—·—·	············
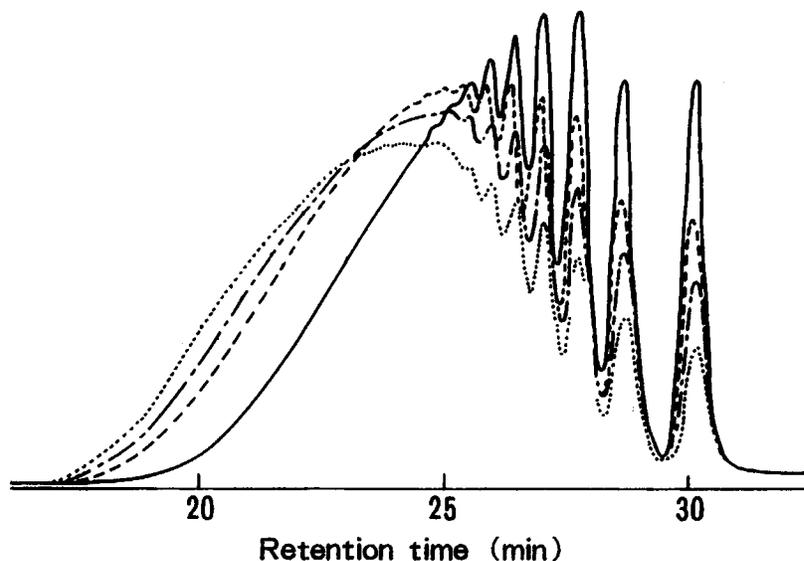
Figure 1   HLC chromatograms and properties of o-cresol novolac type epoxy resins.

tion of phenol–formaldehyde novolac cured epoxy resin is mostly attributable to the reaction of epoxy and phenolic hydroxyl groups.[16] Depending on the type of accelerator, however, reaction between epoxy groups and/or between epoxy and alcoholic hydroxyl groups may be caused by the curing accelerators.[17] Therefore, for some types of accelerators, the curing reaction mechanism differs, and the degree of lowering the reactivity of the functional group by topological steric hindrance also differs; both affect the degree of curing in the resin system. The difference in crosslinking density of cured resin according to the molecular weight of raw epoxy resin may be explained as follows: o-Cresol novolac type epoxy resins used for the experiments have the same iterative unit structure, and the epoxy equivalent remains unchanged regardless of the molecular weight. In this case, the curing mechanism and conversion may not change according to the molecular weight of raw epoxy resin, but the bonds between the iterative units of raw epoxy resin are regarded as the

a priori crosslinks. Therefore, if epoxy resins having higher molecular weight are used, they provide higher crosslinking density in the cured products.

Crosslinking Densities and Physical Properties of Cured Resins

Various studies have already been made on the relationship between crosslinking density and physical properties of amine or anhydride cured epoxy resin systems.[2-11] The studies made so far, however, changed the kinds of epoxy resin and hardener used and their equivalent ratio. Therefore, the basic composition of the resin system was changed. As the physical properties of cured resin are affected not only by the crosslinking density, but also the kind and concentration of remaining polar groups, cohesive energy between molecular chains, molecular chain rigidity, and other chemical structural factors, all these factors complicated understanding of the relationship between crosslinking density and

**Table III Dynamic Viscoelastic Properties and Crosslinking Densities
of Resins Cured Using Various Accelerators**

| Accelerator | Tan δ Peak | | E' (10^{10} dyn/cm^2)[a] | | | $\rho_{(E')}$[b] (10^{-3} mol/cm^3) |
	Value	Temp (°C)	20°C	$T_g - 60$°C	$T_g + 40$°C	
BDMA	0.552	181	3.31	2.30	0.78	6.35
TMBG	0.616	175	3.08	2.17	0.59	4.87
MP	0.558	178	3.19	2.35	0.63	5.17
EMI	0.375	215	2.56	1.89	1.37	10.40
DBU	0.415	201	2.47	1.83	1.01	7.89
TPP	0.507	195	2.85	2.16	0.91	7.16
THPP	0.422	202	2.97	1.96	1.07	8.33
TCEP	0.445	198	2.76	1.98	1.06	8.32
TEA–TPB	0.579	156	3.21	2.51	0.47	4.04
EMI–TPB	0.338	208	2.54	1.99	1.32	10.20
EDMI–TPB	0.423	199	2.78	1.85	1.08	8.46
DBU–TPB	0.507	184	3.56	2.36	0.81	6.55
MTBP–TPB	0.394	196	3.04	2.02	1.19	9.37
MTCEP–TPB	0.381	202	2.97	1.94	1.25	9.73
ETOP–TP	0.401	199	3.54	2.16	1.20	9.40
HTBP–TPB	0.372	202	2.72	1.83	1.30	10.12
TBP–TPB	0.435	193	2.60	1.91	1.03	8.16
BTPP–TPB	0.446	193	3.43	1.83	0.94	7.41
TPP–TPB	0.509	184	3.19	2.20	0.80	6.45
TPP–BTPB	0.382	205	2.45	1.80	1.31	10.10
TPP–TBB	0.493	194	2.69	1.90	0.96	7.16
TBP–TBB	0.372	205	2.35	1.76	1.31	10.10

[a] E' = storage elastic modulus.
[b] $\rho_{(E')}$ = crosslinking density.

physical properties of cured resin and factors governing their properties.[2–11]

We tried to keep the basic composition almost the same for cured resins, where the crosslinking density was changed depending on the kind of accelerator and molecular weight (number of units n) of o-cresol novolac type epoxy resin, and then we studied the effect of crosslinking density on the physical properties of cured resin.

Glass Transition Temperature

Figure 3 shows the relationship between T_g and crosslinking density of resins cured by different accelerators. Approximately 30°C separated $T_{g(\text{VES})}$ (peak temperature of tan δ of dynamic viscoelasticity) and $T_{g(\text{TMA})}$ (obtained from the inflection point of coefficient of linear thermal expansion). But between T_g and crosslinking density, there is a definite correlation; i.e., as the crosslinking density increases, T_g of resin containing the same segments rises. T_g of thermosetting resin is much influenced by crosslinking density ρ or molecular weight between

crosslinking points M_c and several relationships with T_g have been proposed.[22–24] It is known that the following equation[22] fits various thermosetting resins well:

$$T_g = K_1 \log K_2 \rho \qquad (4)$$

where K_1 is the degree of influence on the molecular chain motion by the crosslinking point and K_2 is a constant, dependent on interactions and rigidity of the main chain. For bisphenol A type epoxy resin with which anhydride, aliphatic or aromatic diamine, imidazole, etc. is used as hardener, K_1 is 50–110 and log K_2 is 3.7–5.9.[25]

For our phenol–formaldehyde novolac cured epoxy resin K_1 and log K_2 are 111 and 3.9, respectively, indicating the influence of the crosslinking point on the molecular chain mobility is relatively large.

Coefficient of Linear Thermal Expansion

Figure 4 shows the relationship between the crosslinking density and coefficient of linear thermal ex-
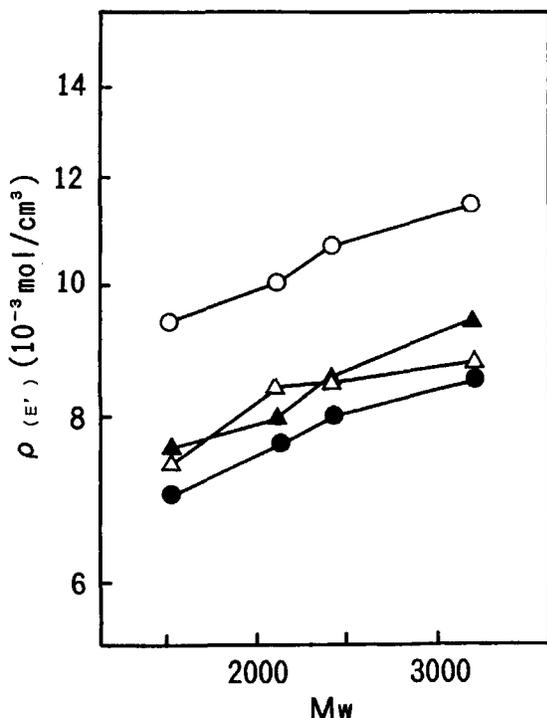
Figure 2 Crosslinking densities ($\rho_{(E')}$) of resins cured using various epoxy resins having different molecular weight (M_w). Accelerator: (O) EMI; (●) MP; (△) TPP; (▲) TPP–TPB.
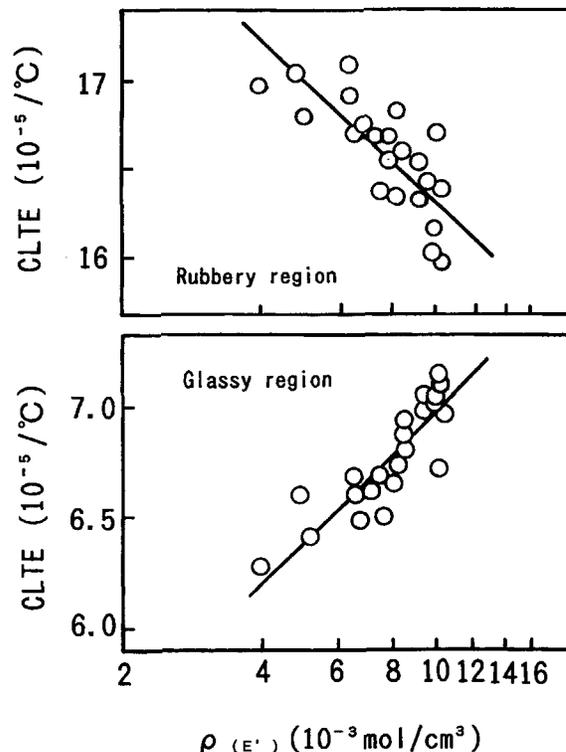
Figure 4 Coefficient of linear thermal expansion (CLTE) vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various accelerators.
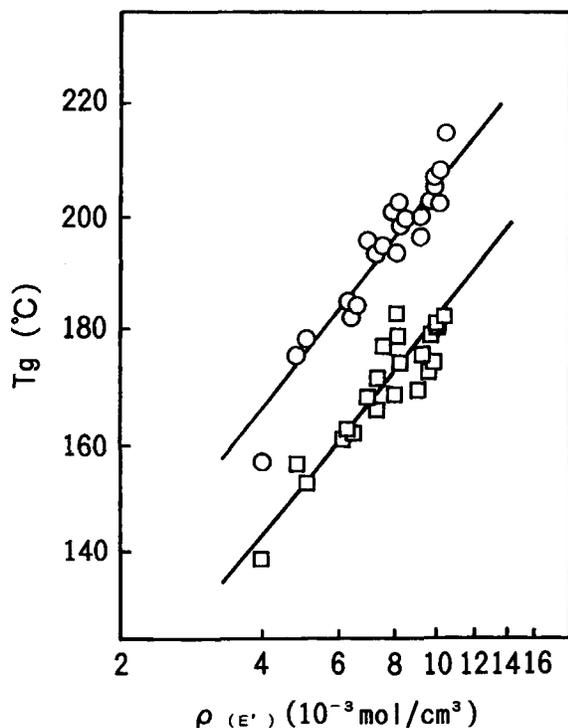
Figure 3 T_g vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various accelerators: (O) $T_{g(VES)}$; (□) $T_{g(TMA)}$.

pansion for resins cured using various accelerators. In the rubbery region (190–250°C), the coefficient decreases as the crosslinking density of cured resin increases. In the glassy region (50–140°C), on the other hand, it tends to increase with the crosslinking density. It is very interesting that the relationships between the coefficient of linear thermal expansion and crosslinking density are opposite according to whether the measurement temperature was higher or lower than T_g.

The fact that a cured resin having a high crosslinking density gives a small coefficient of linear thermal expansion can easily be understood by reasoning that the crosslinking point mutually pulls molecular chains under a micro-Brownian motion, thereby preventing the molecular chains from expanding with rising temperature. However, there has been no report that cured resin having a high crosslinking density gives a large coefficient of linear thermal expansion, and this is a very singular phenomenon. It cannot be explained by thermal equilibrium theory. To understand this phenomenon, it would be necessary to analyze the relationship between the crosslinking density and molecular chain packing status or fractional free volume.

Elastic Modulus in Glassy Region

Figure 5 shows the relationship between the cross-linking density and elastic modulus at $T_{g(VES)}$ −60°C for resins cured with various accelerators. From the kinetic theory of rubber elasticity, the elastic modulus in the rubbery region should increase as the resin crosslinking density increases. The high elastic modulus in the rubbery region for a cured resin of high crosslinking density is a peculiarity of the entropy elastic modulus. In the glassy region, however, the elastic modulus decreases as the crosslinking density increases. This relationship in the glassy region indicates that the influence by the crosslinking point on the elastic modulus is completely different from the rubbery regions.

Specific Volume

Figure 6 shows the relationship between the cross-linking density and specific volume at $T_{g(VES)}$ −60°C for resins cured with various accelerators. The specific volume of each cured resin tends to increase as the crosslinking density increases. Supposing that the elastic modulus in the glassy region depends on the specific volume, this relationship is reasonable. All these results suggest that, for cured resins having

Figure 6   Specific volume at $T_{g(VES)}$ −60°C vs. cross-linking densities ($\rho_{(E')}$) of resins cured using various accelerators.

high crosslinking densities, the molecules are loosely packed in the glassy region.

Water Absorptivity

Next, we studied the relationship between the crosslinking density and water absorptivity when resins cured with different accelerators were left at 60°C and 100% RH. As shown in Figure 7, higher crosslinked resins tend to have a higher saturated water absorption, diffusion coefficient, and permeability. Murakami et al.[26] and Danieley and Long[27] reported that the saturated water absorption depends on the interaction between water molecules and polar groups in network chains. By contrast, Gupta et al.[28] and Wang and Broutman[29] noted that the mobility of water molecules in a cured resin largely depends on the free volume and that the free volume size and distribution have a considerable effect on the initial water absorption rate in particular. On the other hand, Diamant et al.[9] reported that the coefficient of moisture diffusion into epoxy resin depends on four main factors as follows: (i) the polymer network structure; (ii) the polymer polarity, determining polymer–moisture affinity; (iii) the physical morphology of the polymer; and (iv) the

Figure 5   Elastic modulus (E') at $T_{g(VES)}$ −60°C vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various accelerators.

Figure 7 Water absorptivity at 60°C/100% RH vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various accelerators.

moduli within the frequency range of 1–100 Hz at different temperatures around T_g for each cured resin. The relaxation behavior differs considerably according to the crosslinking density of the cured resin; i.e., the higher the crosslinking density of the cured resin, the higher the temperature at which the relaxation occurs, and the smaller the temperature and frequency dependency of the relaxation. Figure 9 gives composite curves got by applying the temperature–time conversion rule to the relaxation elastic modulus of each cured resin (reference temperature 201°C). Cured resins having a higher crosslinking density have a transition region at a lower frequency or at a longer time, so that the relaxation occurs over a wide time scale. It is also characterized by a smaller relaxation strength (difference in elastic modulus between glassy and rubbery states).

End Group Effects on Physical Properties of Cured Resins

So far, we have shown that, for phenol–formaldehyde novolac cured epoxy resins, the crosslinking density depends on the kind of accelerator and its causes large variations in physical properties of cured resin. Cured resin whose crosslinking density is changed by the kinds of accelerators may lead to differences in kind and concentration of residual unreacted functional groups or of produced polar groups due to the difference in the curing mechanism and conversion of resin system. However, it is suggested that, for cured resins of different crosslinking densities, the molecular chain packing state and fractional free volume are substantially different. To clarify the influence of these factors on the physical properties of cured resin, we studied the relationship between the crosslinking density and physical properties of cured resin on samples prepared by using four kinds of o-cresol novolac type epoxy resin having different molecular weight (number of iterative units n) and four kinds of typical accelerators. The results are shown in Figures 10–14.

T_g goes up as the crosslinking density increases. The coefficient of linear thermal expansion decreases in the rubbery region and increases in the glassy region as the crosslinking density increases. As the crosslinking density increases in the glassy region, the elastic modulus decreases and the specific volume increases. The saturated water absorption, diffusion coefficient, and permeability increase with the crosslinking density. The relationships between the crosslinking density and various properties of the cured resin are the same as when the crosslinking

development of microdamage. They also emphasized that it is difficult to predict which of these factors or a combination thereof dominates the moisture diffusion process into a given epoxy resin. The difference in the crosslinking density of resins cured by various accelerators is attributable to the difference of the curing mechanism and the conversion. Therefore, for each cured resin, the concentration of unreacted epoxy and phenolic hydroxyl groups, or alcoholic hydroxyl groups produced by the curing reaction may be different. On the other hand, the difference in the crosslinking density may cause a big difference in the free volume and packing state of cured resin molecules. So, it is not clear which of these factors affects the water absorptivity examined here. More consideration is given to this later.

Relaxation Behavior

Relaxation behavior was analyzed for cured resins, prepared using four typical curing accelerators to give remarkably different crosslinking densities. Figure 8 shows measured storage and loss elastic

Figure 8 Relaxation behavior of typical cured resins having different crosslinking densities.
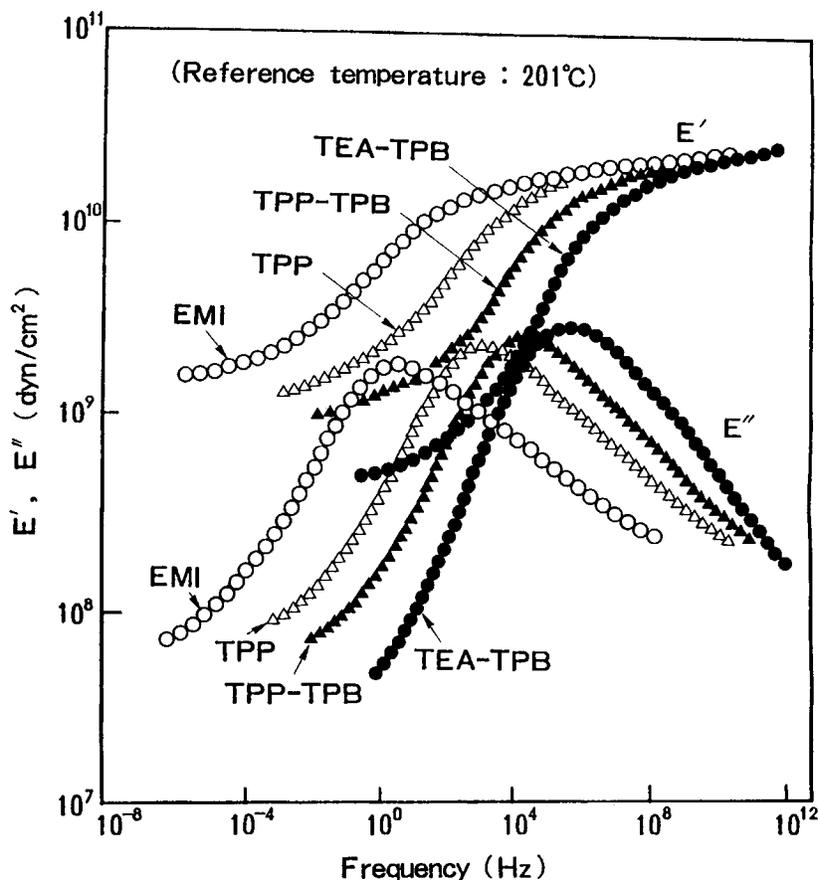
Figure 9   Composite curves of cured resins having different crosslinking densities.

density is changed by using different curing accelerators.

Cured resin using different accelerators may differ in the kind and concentration of residual polar groups due to the difference in the curing mechanism and conversion of resin system. On the other hand, cured resin prepared by changing the molecular weight (number of iterative units n) of raw epoxy resin may differ less in the kind and concentration of residual polar groups, because the curing mechanism and conversion of this resin system are not affected by the molecular weight of raw epoxy resin remarkably. Nevertheless, both resin systems indicate the same tendency. This suggests that the properties of cured resin depend more on the crosslinking density than on the kind or concentrations of polar groups in the cured resins. Further, for samples which had very different crosslinking densities, we made infrared analyses and tried to get a quantitative evaluation of the residual functional groups, but found no significant difference. There-

fore, the difference in the amount of residual functional groups in each sample may be negligibly small.

Summary of Experimental Results

The above studies identified the relationships summarized in Table IV between the crosslinking density and various properties of phenol–formaldehyde novolac cured epoxy resins. Namely, as the crosslinking density increases, T_g rises and the relaxation time becomes longer. The coefficient of linear thermal expansion decreases in the rubbery region, but increases in the glassy region with the crosslinking density. As expected, elastic modulus increases in the rubbery region, but decreases in the glassy region with the crosslinking density. On the other hand, the specific volume decreases in the rubbery region, but increases in the glassy region as the crosslinking density increases. Finally the saturated water absorption, diffusion coefficient, and permeability increase as the crosslinking density increases.
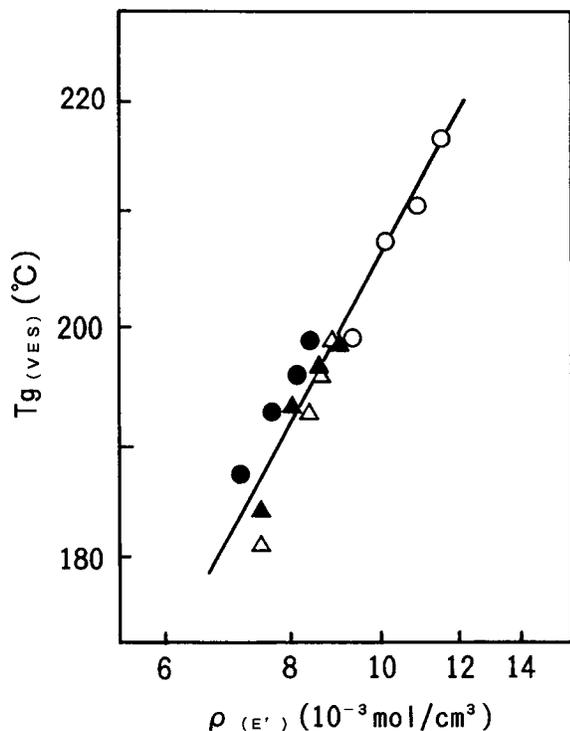
Figure 10 $T_{g(\text{VES})}$ vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various raw epoxy resins and accelerators. Accelerator: (O) EMI; (●) MP; (△) TPP; (▲) TPP–TPB.

The relationship between crosslinking density and physical properties of cured resin was studied mainly for amine and anhydride cured epoxy resin systems[2–11]; however, the physical properties of the cured resins in question are limited, and there are no cases where the relationship with various properties has been studied with the detail of the present paper. There are no reports either which show dependence of the coefficient of linear thermal expansion of cured resins on the crosslinking density and that the relationship between them is opposite in the rubbery and glassy regions. The relationship between crosslinking density and water absorptivity was studied by numerous investigators[9,26–30]; but the same resin gave different results,[30] and there was no unified conclusion as to a relationship. As to why cured resin properties differed with crosslinking density, the free volume and the kind or concentration of residual polar groups were cited, but they did not sufficiently justify the relationship with a series of properties.

So, we observed why the crosslinking density brought about such a difference in physical properties of cured resin.

FACTORS GOVERNING THE CURED RESIN PROPERTIES

Influence of Free Volume Estimated from Specific Volume

To understand the influence of free volume on the relationship between crosslinking density and physical properties of cured resin, we first examined the temperature dependency of the specific volume of various cured resins. The results indicate that the specific volume decreases in the rubbery region, but increases in the glassy region as the crosslinking density increases. Figure 15 shows the relationship between crosslinking density and specific volume at $T_{g(\text{TMA})}$ of resin cured with various accelerators. The specific volume tends to increase as the crosslinking density increases.

To interpret this behavior, Figure 16 gives a schematic representation of the specific volume change during the curing schedule of two resin types having remarkably different crosslinking densities, although their basic resin compositions are the same.
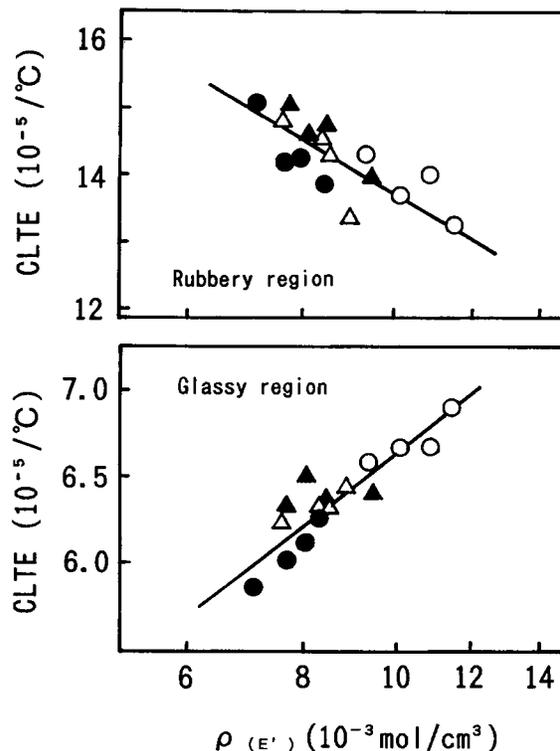
Figure 11   Coefficient of linear thermal expansion (CLTE) vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various epoxy resins and accelerators. Accelerator: (O) EMI; (●) MP; (△) TPP; (▲) TPP–TPB.
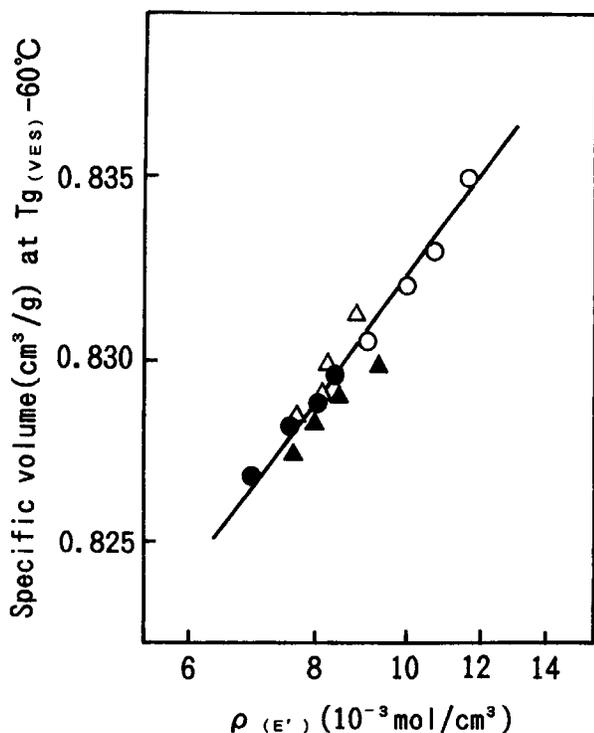
Figure 12 Elastic modulus (E') at $T_{g(\mathrm{VES})}$ $-60°C$ vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various epoxy resins and accelerators. Accelerator: (○) EMI; (●) MP; (△) TPP; (▲) TPP–TPB.

Resin I represents the resin system which gives cured resin having a higher crosslinking density, and Resin II represents the system for a lower crosslinking density. The representation is based on results of temperature dependency of specific volume in cured resins.

The high crosslinking density of Resin I is due to its larger conversion and it has a large shrinkage in curing and a small specific volume at the curing temperature (rubbery region). Resin II, with the low crosslinking density because of its smaller conversion, has a small shrinkage in curing and a large specific volume in the rubbery region. In the cooling process, for Resin I, molecular motion is frozen at a relatively large specific volume due to a strutting of the crosslinking points. For Resin II, freezing of molecular motion takes place only when its specific volume becomes small enough because of a smaller constraint action on the molecular motion by the crosslinking points. Then, in the glassy region, Resin I has a large specific volume and the specific volume at $T_{g(\mathrm{TMA})}$ may increase with the crosslinking density. The basic composition of these resins is the same, except for a slight variation in the amount of

accelerator. Therefore, the occupied volumes of the cured resins can be regarded as equal and the differences in specific volume may be due to differences in free volume.

According to the theory of the iso-free-volume, the fractional free volume at T_g is constant at 2.5% regardless of the kind of substance. However, results suggest that the fractional free volume differs according to constraints of molecular motion caused by the number of crosslinking points and the way of crosslinking, at least for highly crosslinked epoxy resins.

Then, we considered the relationship between physical properties and this free volume of cured resin. For three-dimensionally crosslinked polymers, molecular chains are in micro-Brownian motion, with mutual pulling by crosslinking points and its influence is considered stronger as there are more crosslinking points. Therefore, as the crosslinking density increases the expansion of molecular chains caused by the temperature rise may be constrained and T_g may rise, the relaxation time may become longer, and the coefficient of linear thermal expansion in the rubbery region may decrease. In glassy
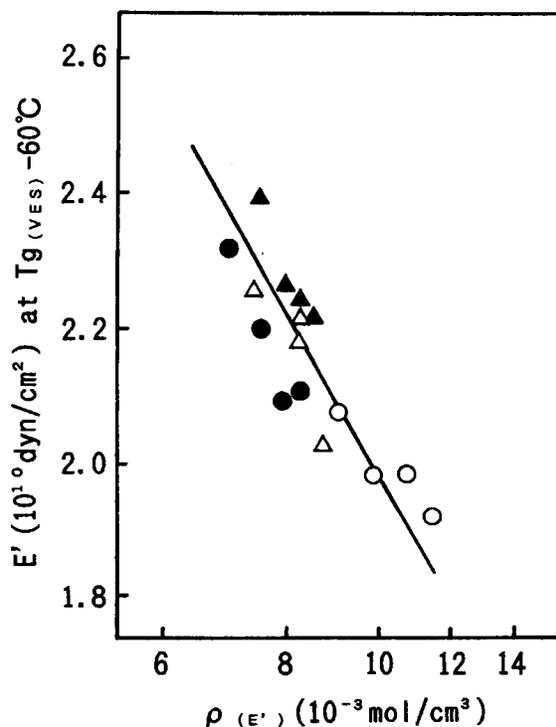
Figure 13 Specific volume at $T_{g(\mathrm{VES})}$ $-60°C$ vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various epoxy resins and accelerators. Accelerator: (○) EMI; (●) MP; (△) TPP; (▲) TPP–TPB.

regions, however, the micro-Brownian motion of the molecular chain is frozen where the free volume is large due to strutting of crosslinking points.

Generally, the thermal expansion of a substance is a combination of thermal expansion of both occupied volume and free volume. The fact that a cured resin of a high crosslinking density such as Resin I gives a large coefficient of linear thermal expansion in the glassy region can be justified by the large free volume. A cured resin of high crosslinking density has a small elastic modulus and large water absorption, diffusion coefficient, and water permeability. These phenomena are understandable considering that the free volume of cured resin is large.

Influence of Free Volume via WLF Analysis

The free volume of polymer material can also be obtained by WLF analysis.[31] The WLF equation (5)
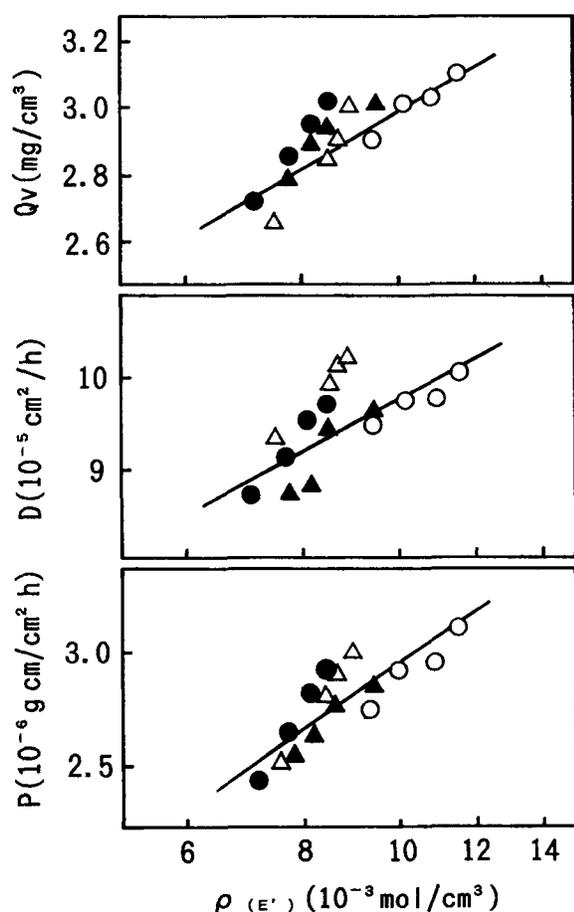
Figure 14 Water absorptivity at 60°C/100% RH vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various epoxy resins and accelerators. Accelerator: (O) EMI; (●) MP; (△) TPP; (▲) TPP–TPB.

Table IV Effects of Crosslinking on Physical Properties of Cured Epoxy Resins

Property	Trend[a]
Crosslinking density	↗
Glass transition temperature	↗
Relaxation time	↗
Coefficient of linear thermal expansion	
Rubbery region	↘
Glassy region	↗
Elasticity	
Rubbery region	↗
Glassy region	↘
Specific volume	
Rubbery region	↘
Glassy region	↗
Water absorption	
Glassy region	↗
Diffusion of water	
Glossy region	↗
Permeation of water	
Glossy region	↗

[a] Arrow directions indicates tendency of the increase/decrease.

is an empirical equation derived from a free volume concept:

$$\log a_T = -\frac{C_1^g(T - T_g)}{C_2^g + T - T_g}$$

$$= -\frac{(1/2.303 f_g)(T - T_g)}{(f_g/a_f) + T - T_g} \tag{5}$$

The WLF equation is valid up to temperatures approximately 100°C higher than T_g. More accurate parameters C_1^g and C_2^g can be obtained in eq. (5) by selecting a reference temperature higher than T_g. For the reference temperature T_0, eq. (5) is expressed as

$$\log a_T = -\frac{C_1^0(T - T_0)}{C_2^0 + T - T_0} \tag{6}$$

For the parameters in eqs. (5) and (6), there are the following relationships:

$$C_1^g \times C_2^g = C_1^0 \times C_2^0 \tag{7}$$

$$C_1^g = \frac{C_1^0 \times C_2^0}{C_2^0 + T_g - T_0} \tag{8}$$

$$C_2^g = C_2^0 + T_g - T_0 \tag{9}$$

Equation (6) can be transformed to

$$\frac{T - T_0}{\log a_T} = -\frac{C_2^0}{C_1^0} - \frac{1}{C_1^0}(T - T_0) \tag{10}$$
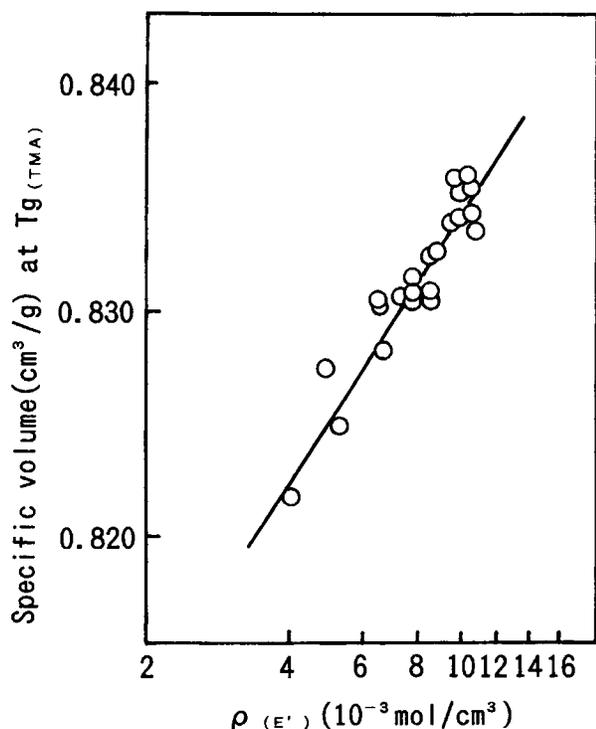
Figure 15 Specific volume at $T_{g\,(\text{TMA})}$ vs. crosslinking densities ($\rho_{(E')}$) of resins cured using various accelerators.

Based on eq. (10), we measured the relaxation characteristics of cured resin, applied the temperature–time conversion rule to them to obtain a_T and plotted the relationship between $(T - T_0)/\log a_T$ and $T - T_0$. From the gradient of the linear function and intercept of the linear function at $T = T_0$, we obtained parameters C_1^0 and C_2^0. Equations (8) and (9) give C_1^g and C_2^g. From eq. (5), there are relationships $C_1^g = 1/2.303\,f_g$ and $C_2^g = f_g/\alpha_f$. Then, we can obtain the fractional free volume at T_g (f_g) and the coefficient of thermal expansion of free volume in the rubbery state (α_f).

So, we carried out the WLF analysis based on the relaxation behavior of cured resins having remarkably different crosslinking densities prepared using four typical accelerators. Figure 17 shows the shift factor a_T in the relationship of $(T - T_0)/\log a_T$ vs. T. All the cured resins have a good linear relationship within the range where the temperature is several tens of degrees higher than T_g, and the temperature dependency of a_T of each cured resin follows the WLF equation. Then using the above method, we obtained each parameter of the WLF equation and f_g and α_f. These results are given in Table V. $C_1^g \times C_2^g$ of each cured resin is between 700 and 1200, which is close to the universal value 900 ($C_1^g = 17.44$, $C_2^g = 51.6$).[31,32] On the other hand, f_g is between 0.032 and 0.048, which is slightly larger than the universal

value 0.025, and α_f is between $3.6 \times 10^{-4}/°C$ and $6.1 \times 10^{-4}/°C$, which is near the universal value $4.8 \times 10^{-4}/°C$.

Figure 18 shows the relationships between f_g and α_f of each cured resin and between the specific volume at T_g, the difference in the coefficient of cubic thermal expansion around T_g, and crosslinking density. The relationships of crosslinking density and difference in coefficient of cubic thermal expansion around T_g, crosslinking density, and α_f show the same tendency. The difference in coefficient of cubic thermal expansion around T_g and α_f decreases as the crosslinking density increases. Therefore, the thermal expansion of free volume may have been reflected on the thermal expansion of specific volume observed macroscopically. However, while the specific volume at T_g increases with the crosslinking density, f_g decreases as the crosslinking density increases. Namely, the intermolecular space obtained by subtracting the occupied volume from the specific volume is not reflected at all on f_g. To clarify the influence of f_g on various physical properties of cured resin and crosslinking density, the relationship between specific volume and f_g must be further considered.

Relationship between Specific Volume and f_g

The relationship between the crosslinking density and various physical properties in the glassy region of cured epoxy resin is justified by considering the difference of free volume estimated from the specific
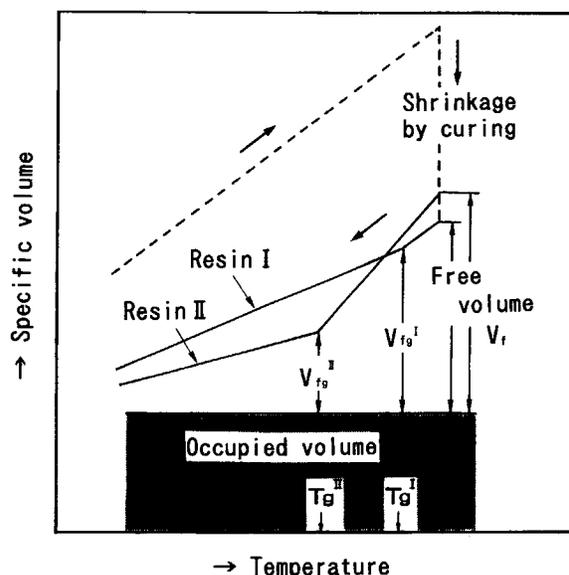
Figure 16 Schematic representation of specific volume change of epoxy resins during the curing schedule.
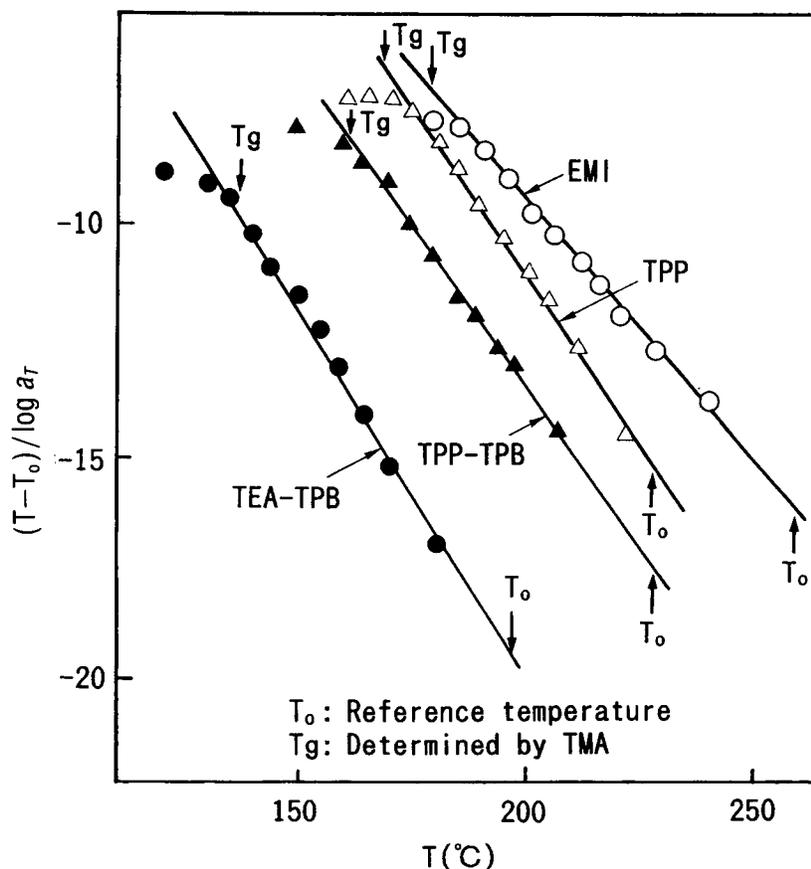
Figure 17 $(T - T_0)/\log a_T$ vs. T plots of cured resin having different crosslinking densities.

volume. However, the relationship between the crosslinking density and f_g obtained by WLF analysis is opposite the tendency expected from the specific volume, and it has been found that f_g is not reflected on the specific volume of cured resin. So, we proceeded to examine the reason for this.

Generally, specific volume V is expressed by the sum of occupied volume V_0 and free volume V_f as in

$$V = V_0 + V_f \qquad (11)$$

Free volume V_f is considered to consist of two terms V_h and V_i as shown in Figure 19[33]:

$$V_f = V_h + V_i \qquad (12)$$

where V_h is a hole or vacant site caused when mixing liquid molecules, which may greatly affect the fluidity and viscosity. On the other hand, V_i is an interstitial free volume caused by thermal expansion due to anharmonic vibration and may not affect the fluidity and viscosity. While the free volume esti-

Table V   Results of WLF Analysis of Cured Resins Having Different Crosslinking Densities

Sample (Accelerator)	A (TEA–TPB)	B (TPP–TPB)	C (TPP)	D (EMI)
$\rho_{(E)}$ (10^{-3} mol/cm^3)	4.04	6.45	7.16	10.4
C_1^g	9.1	11.1	11.4	13.6
C_2^g	78.7	76.5	79.2	88.9
$C_1^g C_2^g = C_1^0 C_2^0$	720	843	895	1226
f_g	0.048	0.039	0.038	0.032
α_f ($10^{-4}/°C$)	6.1	5.1	4.8	3.6
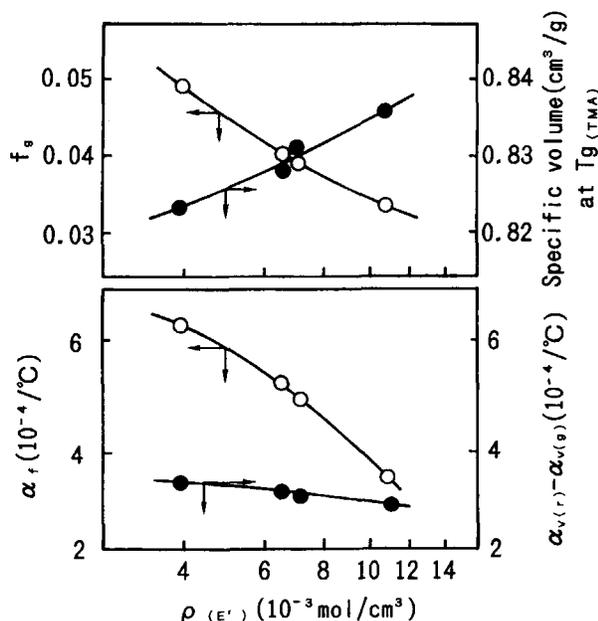
Figure 18 Free volume and coefficient of thermal expansion of free volume vs. $\rho_{(E')}$ of cured resin having different crosslinking densities.

mated from the specific volume is considered to be composed of V_h and V_i, f_g obtained as a parameter of molecular motion (relaxation time) by WLF analysis is considered to correspond to V_h.

When interpreting the free volume in this way, the relationship between macroscopic free volume estimated from the specific volume and f_g obtained by WLF analysis is not contradictory, and the influence of free volume on the relationship between the crosslinking density and various physical properties of cured resin can be explained as follows: Namely, a highly crosslinked resin has a long relaxation time in the viscoelastic spectra, and its high T_g may be because V_h governing the fluidity and viscosity becomes smaller as the crosslinking density increases. For a highly crosslinked resin, the specific volume is large in the glassy region with a large coefficient of linear thermal expansion, large water absorptivity and a small elastic modulus. This may be because the interstitial free volume V_i directly affecting the specific volume increases with the crosslinking density.

The above results suggest that, for a highly crosslinked 3-dimensional network polymer such as phenol–formaldehyde novolac cured o-cresol novolac type epoxy resin, the crosslinking point acts to block close packing of molecular chains. Namely, when micro-Brownian motion freezes, the crosslinking point props up toward the frozen direction at an inherent bond angle, thereby separating the molecular chains from each other. Therefore, the molec-

ular chain packing becomes looser in the glassy region, and the specific volume or interstitial free volume increases as the crosslinking density increases. In the glassy region, such a cured resin may have a large coefficient of linear thermal expansion and water absorptivity and a small elastic modulus.

To understand the characteristics and properties of 3-dimensionally crosslinked high polymers better, reports have focused on the size and distribution of the free volume, heterogeneity in network structures in crosslinked high polymers, and the like.[34-42] For example, Yu and Sung[39] attempted to interpret the change in distribution and size of free volume before and after curing epoxy resins. Wu and Bauer[40] looked at network heterogeneity of epoxy resins using a neutron scattering method.

CONCLUSIONS

The relationships between crosslinking density and physical properties of phenol–formaldehyde novolac cured o-cresol novolac epoxy resins and factors governing it were studied and the following conclusions were reached.
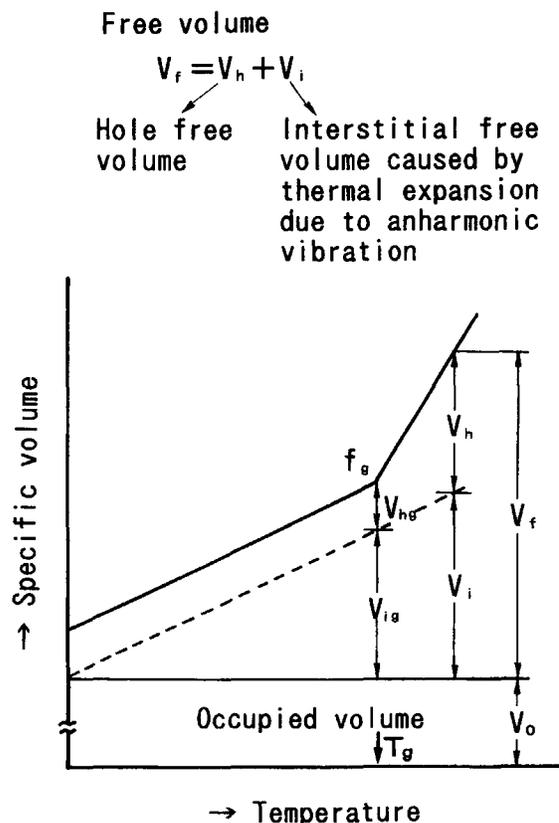
Figure 19 Schematic representation of composition of free volume.

1. The influence of the crosslinking point on various physical properties of cured resin differed considerably between rubbery and glassy regions. This relationship could be explained by considering two free volumes, hole free volume V_h and interstitial free volume V_i.

2. As the crosslinking density increased, T_g rose and the relaxation behavior shifted to longer times. This may be because, as the crosslinking density increased, the hole free volume V_h contributed to a fluidity decrease.

3. In the glassy region, highly crosslinked resin had a large specific volume, coefficient of linear thermal expansion, water absorption, diffusion coefficient and permeability, and a small elastic modulus. These reflected the crosslinking density increase of cured resin; the interstitial free volume V_i directly affected the specific volume increases, thereby making the molecular chain packing looser.

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