Dielectric Relaxation During Isothermal Curing of Epoxy Resin with an Aromatic Amine

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SYNOPSIS

The isothermal curing behavior of an epoxy resin system has been monitored by a dielectric measurement whose sensor consisted of a vertical parallel-plate cell based on a three-terminal method. The materials used in the isothermal cure were the diglycidyl ether of bisphenol-A (DGEBA), which was purified from Epon 825 by recrystallization, and 4,4′-diamino diphenyl methane (DDM). A dielectric relaxation was observed during each isothermal cure at temperatures of 70, 80, 90, and 100°C, which were below the glass transition temperature (T_g) of the reactive DGEBA–DDM system at the gel point. The relaxation is considered to be caused by the transformation from a liquid state to an ungelled glassy state as a result of an increase in molecular weight because gelation followed by a rubbery state did not exist in the temperature range studied. The dielectric relaxation for the DGEBA–DDM system fits the empirical model of the Havriliak–Negami equation. The T_g of the DGEBA–DDM system, which was estimated from the dielectric relaxation time, agreed with the one experimentally determined by differential scanning calorimetry (DSC).

INTRODUCTION

Dielectric analysis is one of the most effective procedures for investigating the curing process of epoxy resin at the point of nondestructive testing. In this analysis the dielectric constant (ϵ') and dielectric loss (ϵ'') can be obtained as a function of the curing time over a wide range of frequencies. Dielectric loss, mainly caused by ionic conduction in the early stage of cure, has a good correlation with viscosity before gelation. Several studies[1-5] have concentrated on proving the relationship between dielectric loss and viscosity during cure. In a previous work[5] the authors reported a good correlation between dielectric loss and viscosity during cure for an epoxy resin system that consisted of the diglycidyl ether of bisphenol-A (DGEBA) and 4,4′-diamino diphenyl methane (DDM).

As for the middle stage of cure, it was reported in several papers[6-10] that a peak was observed in the dielectric loss or the dissipation factor versus curing time curve. Delmonte[6] attributed a peak observed in the dissipation factor to gelation. Adamec[7] pointed out that the peak is due to the transition of the reactive resin system into the glassy state. Senturia and Sheppard[9] discussed Cole–Cole diagrams for the relaxation process of epoxy resin system during curing. Lane and co-workers[10] calculated the dielectric relaxation time from the angular frequency at the peak in the dielectric loss by assuming that the modified Debye model[11] was applicable to the DGEBA–polyamide system with a distribution of the relaxation time.

DGEBA oligomers of varying molecular weights are considered to have similar chemical structures to the reactive DGEBA–aromatic amine system before gelation. The useful information for the DGEBA curing process may be obtained from the dielectric study on the α-relaxation process of the DGEBA oligomer. Sheppard and Senturia[12] reported that dielectric α-relaxation processes for several DGEBA oligomers were described by the Kohlrausch–Williams–Watts (KWW) relaxation function. In a previous work[13] the authors have studied dielectric properties for a series of DGEBA oligomers with different molecular weights by taking into account the molecular distribution of the oligomer, and have found that the dielectric α relaxation of the oligomers fitted the empirical model of the Havri-

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Table I Properties for DGEBA and DGEBA Oligomers

DGEBA Oligomer	T_g (°C)	$\bar{M}_n$[a]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
DGEBA	−18	340	340	1.00
Epon 825	−17	352	354	1.01
Epikote 1003	45	1250	2078	1.66
Epikote 1005	59	1413	2759	1.95
Epikote 1007	69	2215	3903	1.76

[a] Number-average molecular weight.
[b] Weight-average molecular weight.

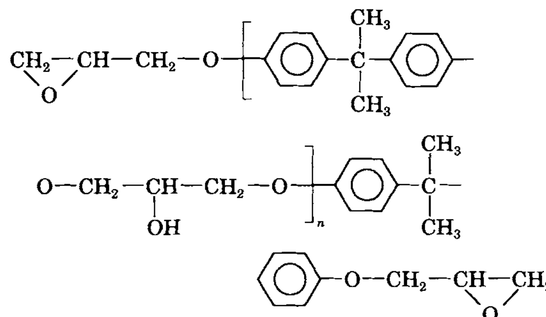
liak–Negami equation.[14] This study focused on the careful analysis of the relaxation process of the DGEBA–DDM system during isothermal cure on the basis of the relaxation behavior of DGEBA oligomers.

EXPERIMENTAL

Materials

The epoxy resin system used in this study was a stoichiometric mixture of the diglycidyl ether of bisphenol-A (DGEBA) and 4,4′-diamino diphenyl methane (DDM). DGEBA was refined from Epon 825 (Shell Chemical) by a crystallization technique using a mixture of methylethylketone (MEK) and ethylalcohol as the solvent. The resin system was the same one used in a previous study.[5]

Three oligomers of DGEBA with different weight-average molecular weights ($2078 \leqq \bar{M}_w \leqq 3903$) were investigated for understanding the curing behavior of the DGEBA–DDM system. The structural formula of the oligomer is



The epoxide oligomer has different molecular weights according to the variation in the repeated

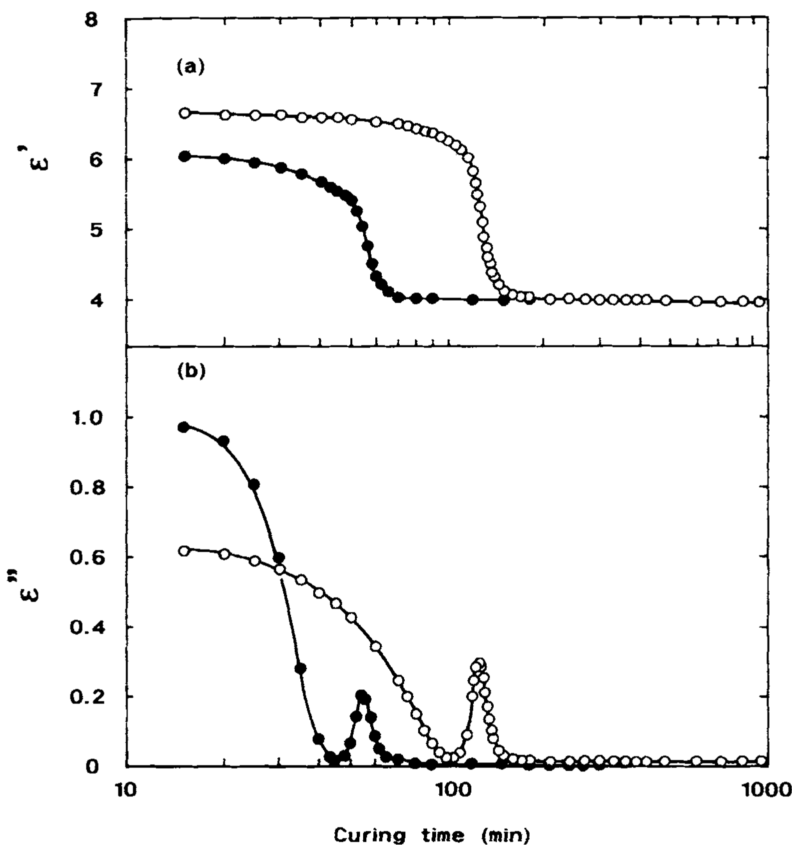


Figure 1 (a) Dielectric constant ε′ and (b) dielectric loss ε″ versus log (curing time) for DGEBA–DDM system at 10 kHz: (○) 80°C cure, (●) 100°C cure.

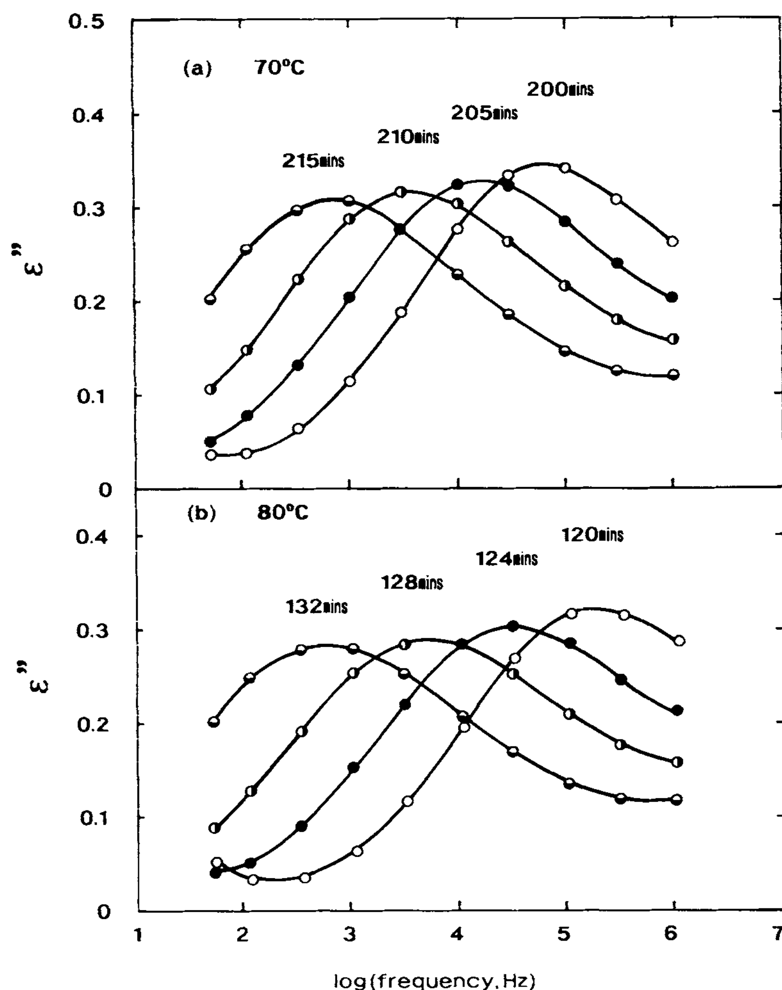


Figure 2 Dielectric loss ϵ'' versus log (frequency) for DGEBA–DDM system: (a) at 70°C cure and (b) at 80°C cure.

number, n, indicated in the structural formula. The three oligomers used in this study, Epokote 1003, 1005, and 1007, were manufactured at Yuka Shell Epoxy. The characteristics of the oligomers are given in Table I together with those of DGEBA and Epon 825.

Measurements

Dielectric measurements were performed using an inductive ratio arm bridge-type apparatus (TR-1100; Ando Electric) with a frequency range of 50 Hz to 1 MHz. The measuring temperatures were 70, 80, 90, and 100°C for monitoring the cure of the DGEBA–DDM system and in the range 40–180°C for investigating the oligomers. A vertical parallel-plate cell with three terminal electrodes, developed during previous studies,[5,13] was used to measure the samples. Samples for curing were prepared by mixing DGEBA with a stoichiometric amount of DDM at each isothermal temperature after preheating each sample at that same temperature.

The glass transition temperature (T_g) was measured using DuPont 9000 differential scanning calorimeter (DSC). The temperature scan was at a rate of 20°C/min. The T_g was determined as the intersection point of the baseline and the transition one in the heat flow versus temperature curve.

RESULTS AND DISCUSSION

Changes in Dielectric Properties During Cure

Isothermal curing behaviors of the DGEBA–DDM system at temperatures of 70, 80, 90, and 100°C were examined by the dielectric measurement. Figure 1 shows dielectric constant (ϵ') and dielectric loss (ϵ'') as a function of the logarithm of time (15–960 min)

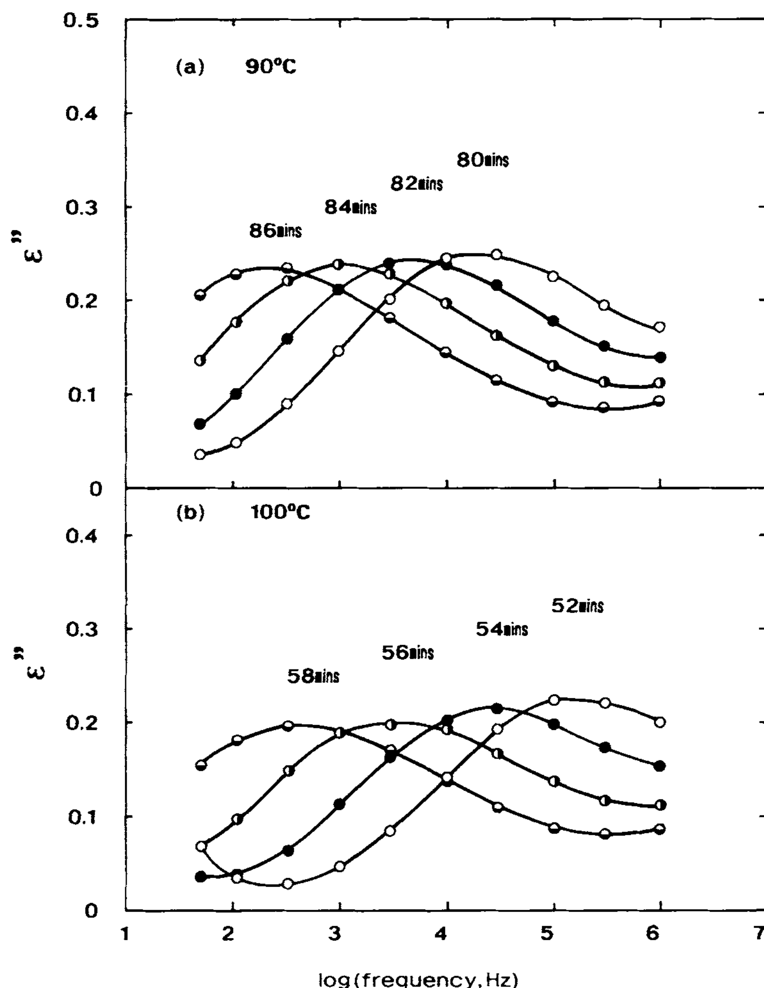


Figure 3 Dielectric loss ϵ'' versus log (frequency) for DGEBA–DDM system: (a) at 90°C cure and (b) 100°C cure.

for the 10-kHz frequency at two isothermal temperatures, 80 and 100°C. In the early stage of cure ϵ'' changes from a high value to a low one similar to the inverse of the viscosity versus time curve. After the bottom of ϵ'', a peak is observed at the curing time when a sudden decrease in the dielectric constant occurs. Similar behaviors were observed at the other two curing temperatures, 70 and 100°C. Figures 2 and 3 show the plots of ϵ'' versus the logarithm of frequency in the relaxation regions at the four temperatures.

Generally, dielectric loss has two components; one is due to dipole orientation and the other is caused by ionic conduction. The following simple relation can be expressed:[15]

$$\epsilon'' = \epsilon''_d + \frac{\sigma}{\omega E_0} \qquad (1)$$

Table II Glass Transition Temperatures for DGEBA–DDM System at Various Curing Conditions

Curing Temperature (°C)	Glass Transition Temperature T_{g0}[a] (°C)	T_{gi}[b] (°C)	$T_{g\infty}$[c] (°C)
70	−10	89	180
80	−10	95	180
90	−10	106	179
100	−10	111	178

[a] Glass transition temperature for unreacted DGEBA–DDM system.
[b] Curing condition; 16 h at each isothermal temperature.
[c] Curing condition; 16 h at each isothermal temperature + 5 h at 200°C.

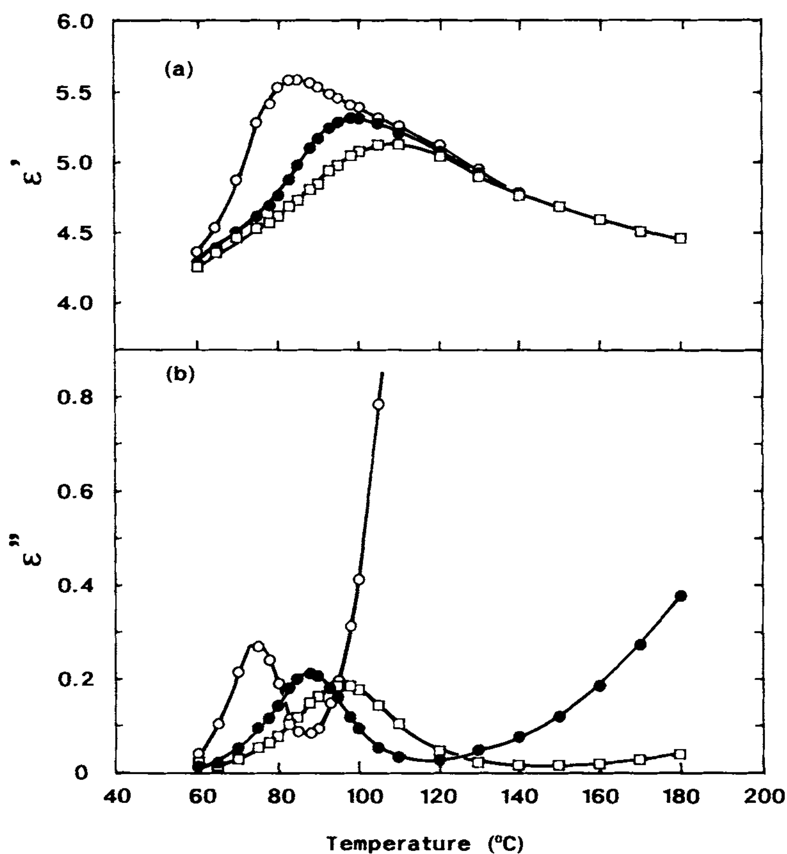


Figure 4 Temperature dependence of (a) ϵ' and (b) ϵ'' for Epikote 1005 at three frequencies: (○) 50 Hz, (●) 1 kHz, (□) 10 kHz.

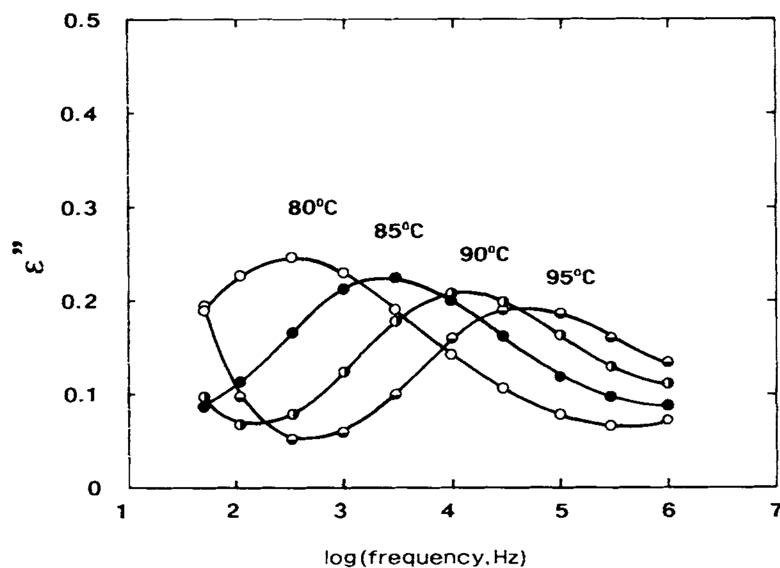


Figure 5 Frequency dependence of ϵ'' at various temperatures for Epikote 1005 in the α-relaxation region.

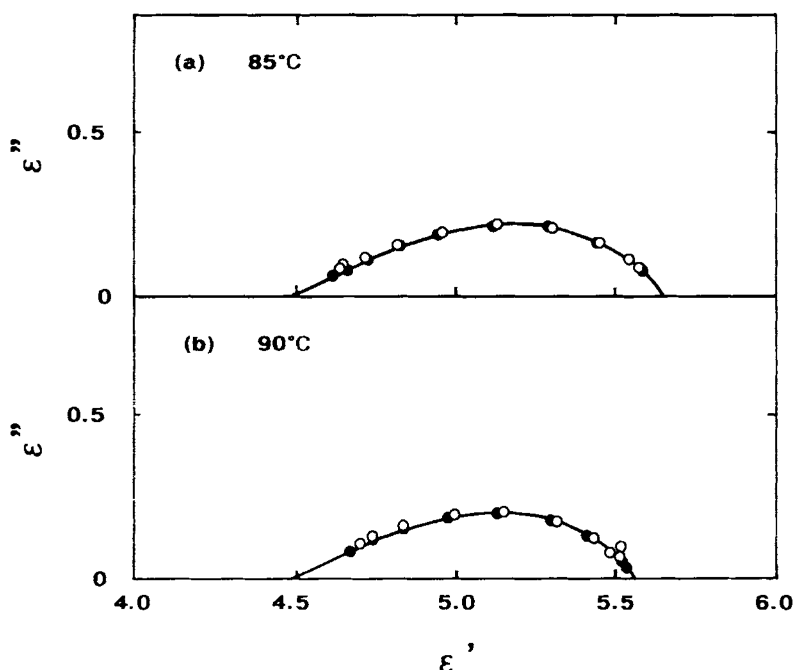


Figure 6 Cole–Cole arcs for Epikote 1005: (a) at 85°C and (b) at 90°C; (○) experimental value, (●) calculated value.

where ϵ_d'' is a dipolar component, σ is dc conductivity, E_0 is the permittivity of free space (8.555×10^{-14} F/cm), and ω is angular frequency.

The contribution of the ionic component is overwhelming compared to the dipole one in the early stage of cure. The large ionic component is due to the large ionic mobilities that result from the segmental mobility. As mentioned in other papers,[1-5] ϵ'' has a good correlation with ionic conduction in the early stage of cure. On the other hand the contribution of the dipole orientation becomes large with the progress of cure because the motion of ions through the matrix resin is gradually restricted. Peaks of ϵ'' in Figure 1 are considered to be caused by the dipole orientation.

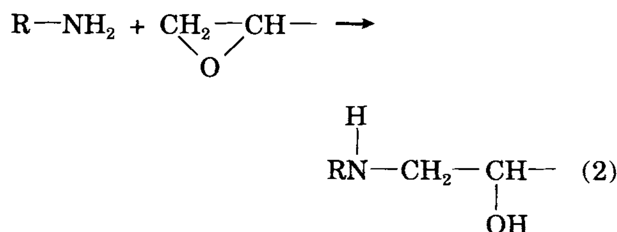
Babayevsky and Gillham[16] proposed that isothermal cure of thermosetting resins was characterized by gelation and vitrification as a result of the increase in molecular weight of the reactive system. Gelation corresponds to the transformation from a liquid to a rubbery state while vitrification involves a transformation from a liquid or rubbery state to a glassy state. If the curing temperature of an epoxy resin system is below the T_g of the resin system at gel point, no rubbery state exists because of the occurrence of vitrification prior to gelation. The vitrification in this case corresponds to the liquid-to-ungelled glass transformation. According to the torsional braid analysis (TBA) by Babayevsky and Gillham,[16] the T_g of the DGEBA–DDM system at gel point is about 110°C. Table II shows the measured values of T_g for the DGEBA–DDM system in the three states; one is the unreacted state, another is the isothermal curing state, and the last is the fully cured state. After an isothermal cure, the T_g of each cured DGEBA–DDM system has a higher T_g value than the isothermal temperature, as shown in Table II. Since T_g increases from −10°C in the unreacted state with the increase in molecular weight of the system, the glass transition (or the vitrification) takes place when the value of T_g reaches the curing temperature.

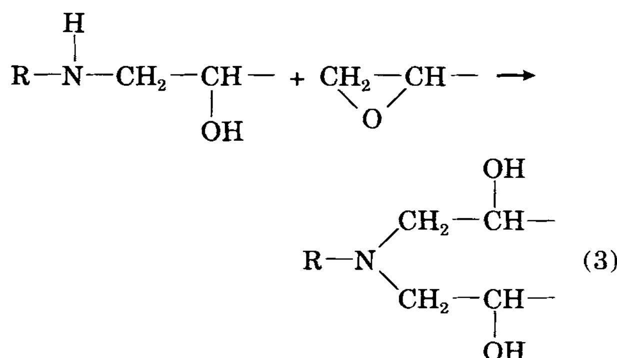
There is only one transition for the DGEBA–DDM system during each isothermal cure in the temperature range from 70 to 100°C, which is below the T_g (110°C) of the system at gel point. That is the liquid-to-ungelled glass transformation. Adamec[7] pointed out that the peak in the dissipation factor indicated the transition of the resin into the glassy state. The peak in ϵ'' for the DGEBA–DDM system in this study is considered to result from the α relaxation by the transformation from a liquid to ungelled glassy state.

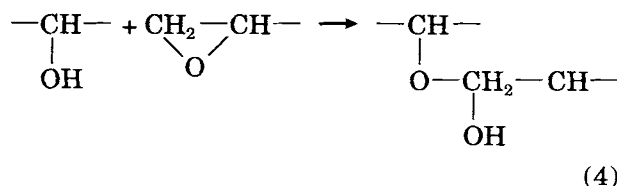
Schechter and co-workers[17] suggested that there were three possible reactions [Eqs. (2)–(4)] in epoxy resin with diamines as follows:

Table III Parameters of the Havriliak–Negami Equation for Epikote 1005

Temperature (°C)	ϵ_0	ϵ_∞	$\epsilon_0 - \epsilon_\infty$	α	β	Relaxation Time (s)
80	5.75	4.46	1.29	0.39	0.49	1.5×10^{-3}
85	5.65	4.49	1.16	0.39	0.50	2.3×10^{-4}
90	5.56	4.49	1.06	0.40	0.50	4.4×10^{-5}
95	5.49	4.50	0.99	0.40	0.49	1.2×10^{-5}







Bell[18] reported that in the reaction between DGEBA and DDM the primary amine reaction (2) was approximately 7–12 times as fast as the secondary amine reaction (3) due to steric hindrance and that reaction (4) was negligible. Therefore, the DGEBA–DDM system before gelation may be a mixture of linear molecules with branches and those without ones. DGEBA oligomers consist of linear molecules without branches as previously shown. A dielectric study of DGEBA oligomers may provide useful information for better understanding the relaxation process of the DGEBA–DDM system because of the structural similarity between them with regard to the molecular linearity and the aromatic (bisphenol-A) backbone.

Dielectric Study of DGEBA Oligomers

In a previous work[13] dielectric properties for a series of DGEBA oligomers ($388 \leqq \bar{M}_w \leqq 2640$) were investigated. The dielectric relaxations for the oligomers were fitted to the following empirical model of the Havriliak–Negami equation:[14]

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{[1 + (i\omega\tau)^{1-\alpha}]^\beta} \tag{5}$$

where

$\epsilon^*(\omega)$ = the complex dielectric constant
ϵ_∞ = high-frequency limit to the dielectric constant
ϵ_0 = low-frequency limit to the dielectric constant
ω = angular frequency
τ = relaxation time
α = distribution parameter
β = skewness parameter
i = square root of -1.

The Williams–Landel–Ferry (WLF) equation was found to be applicable to the temperature dependence of the dielectric relaxation time (τ), which was calculated from Eq. (5), for each oligomer at temperatures above T_g.

The dielectric data in a previous work[13] are insufficient to precisely analyze the DGEBA–DDM curing process because of the relatively small $\bar{M}_w$'s of DGEBA oligomers studied ($388 \leqq \bar{M}_w \leqq 2640$). Dielectric properties for additional three DGEBA oligomers, Epikote 1003, 1005, and 1007 ($2078 \leqq \bar{M}_w \leqq 3903$), were examined in order to obtain further information to understand the α-relaxation process of the DGEBA–DDM system. Figure 4 shows the dielectric behavior of an oligomer, Epikote

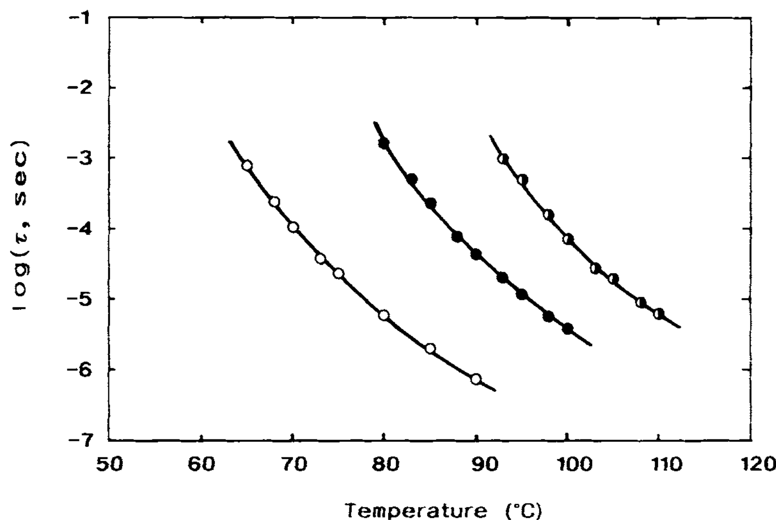


Figure 7 Temperature dependence of relaxation time τ for three oligomers: (○) Epikote 1003, (●) Epikote 1005, (◑) Epikote 1007.

1005, for three frequencies over a temperature range of 60–180°C. In Figure 5 the dielectric loss, ϵ'', of Epikote 1005 was plotted as a function of frequency at several temperatures in the relaxation region. Cole–Cole plots for the oligomer are shown in Figure 6, comparing calculated values with experimentally obtained ones. The dielectric relaxation process for Epikote 1005 can be expressed by the Havriliak–Negami equation as well as the oligomers studied in the previous work.[13] Parameters in Eq (5) for Epikote 1005 are listed in Table III. Two other oligomers are also fitted to the equation. Figure 7 shows the temperature dependence of the dielectric relaxation time, which was calculated from Eq. (5) for each oligomer.

The following WLF equation[19] can be applied to the temperature dependence of the dielectric relaxation time (τ) for amorphous thermoplastic polymers for temperatures between T_g and $T_g + 100°C$.

$$\log \frac{\tau(T)}{\tau(T_g)} = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \tag{6}$$

where T is the temperature, T_g is the glass transition temperature, and C_1, C_2 are parameters.

The temperature dependence of the DGEBA

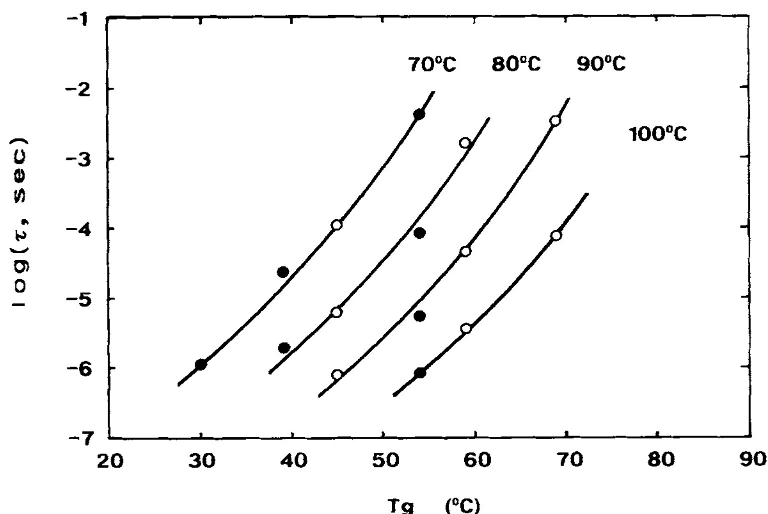


Figure 8 Relationship between relaxation time τ and T_g for DGEBA oligomers at four temperatures: (○) this work, (●) previous work.

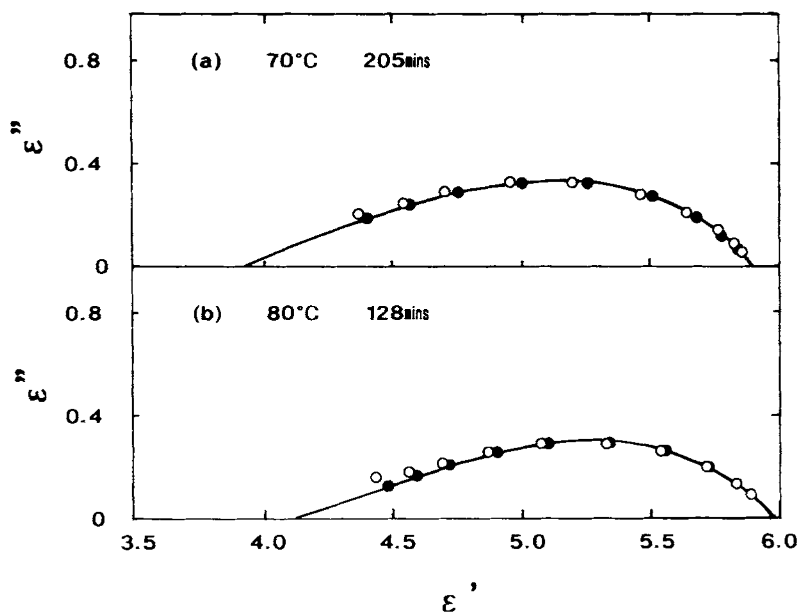


Figure 9 Cole–Cole arcs for DGEBA–DDM system: (a) at 70°C cure and (b) at 80°C cure; (○) experimental value, (●) calculated value.

oligomer has been found to fit the WLF equation in a previous work.[13] The WLF equation also expresses the relationship between τ and T_g at a specific temperature, T, because τ at $T_g[\tau(T_g)]$ and parameters, C_1 and C_2, have a constant value, respectively, for the same oligomer. Therefore the T_g dependence of τ at a specific temperature for DGEBA oligomers can be obtained from the temperature dependences of τ for a series of DGEBA oligomers with different T_g's. Since the reactive DGEBA–DDM system in the ungelled state may be a mixture of branched or nonbranched linear molecules based on the bisphenol-A backbone, the relationship between τ and T_g for the DGEBA–DDM system can be estimated from that for DGEBA oligomers, which have similar structures.

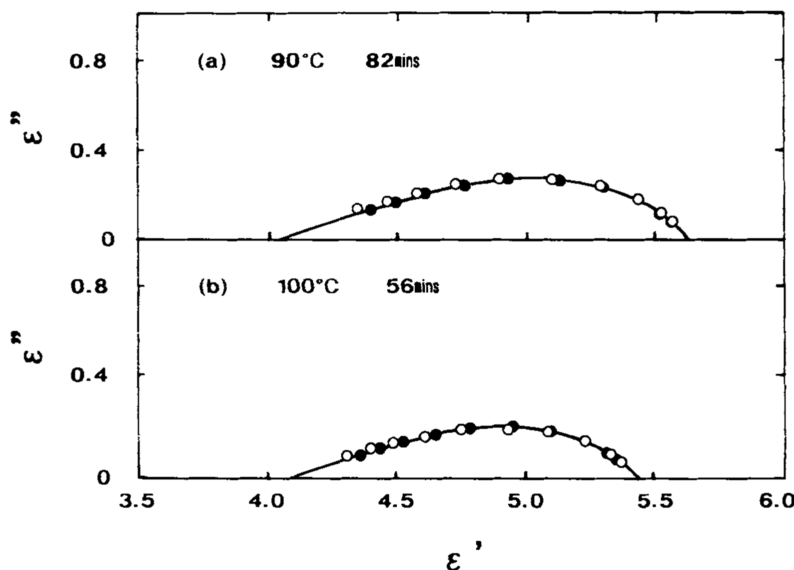


Figure 10 Cole–Cole arcs for DGEBA–DDM system: (a) at 90°C cure and (b) at 100°C cure; (○) experimental value, (●) calculated value.

Table IV Parameters of the Havriliak–Negami Equation for DGEBA–DDM System

Curing Condition							
Temperature (°C)	Time (min)	ϵ_0	ϵ_∞	$\epsilon_0 - \epsilon_\infty$	α	β	Relaxation Time (s)
70	200	5.93	3.87	2.06	0.40	0.38	1.3×10^{-5}
	205	5.90	3.88	2.02	0.41	0.39	4.1×10^{-5}
	210	5.87	3.89	1.98	0.42	0.40	2.0×10^{-4}
	215	5.84	3.90	1.94	0.43	0.40	9.4×10^{-4}
80	120	6.04	4.10	1.94	0.40	0.38	5.3×10^{-6}
	124	6.01	4.11	1.90	0.42	0.39	2.7×10^{-5}
	128	5.98	4.12	1.86	0.43	0.40	1.6×10^{-4}
	132	5.95	4.13	1.82	0.45	0.42	1.2×10^{-3}
90	78	5.66	4.04	1.62	0.42	0.38	1.2×10^{-5}
	80	5.65	4.05	1.60	0.44	0.39	4.1×10^{-5}
	82	5.63	4.06	1.57	0.45	0.40	1.4×10^{-4}
	84	5.62	4.07	1.55	0.47	0.42	6.4×10^{-4}
100	52	5.45	4.07	1.38	0.41	0.37	6.1×10^{-6}
	54	5.44	4.08	1.36	0.43	0.38	3.1×10^{-5}
	56	5.43	4.09	1.35	0.45	0.39	2.1×10^{-4}
	58	5.52	4.10	1.32	0.46	0.40	1.7×10^{-3}

Figure 8 shows the logarithm of τ versus T_g curves for DGEBA oligomers in the temperature range of 70–100°C by combining the data obtained from both a previous work[13] and the present one. If τ for DGEBA–DDM system is measured during isothermal cure, the T_g of the system can be predicted from the relation given in Figure 8. The relations in Figure 8 are useful for the quick determination of T_g because the T_g of the epoxy resin system cannot be directly detected nondestructively during cure.

Dielectric Relaxation Time and T_g during Cure

Figures 9 and 10 show typical Cole–Cole plots for the DGEBA–DDM system during four isothermal temperatures. The dielectric relaxation during cure is also governed by the Havriliak–Negami equation, whose parameters and relaxation times are given in Table IV. The relaxation times are plotted as a function of time for four curing temperatures in Figure 11. The curves in Figure 11 resemble those

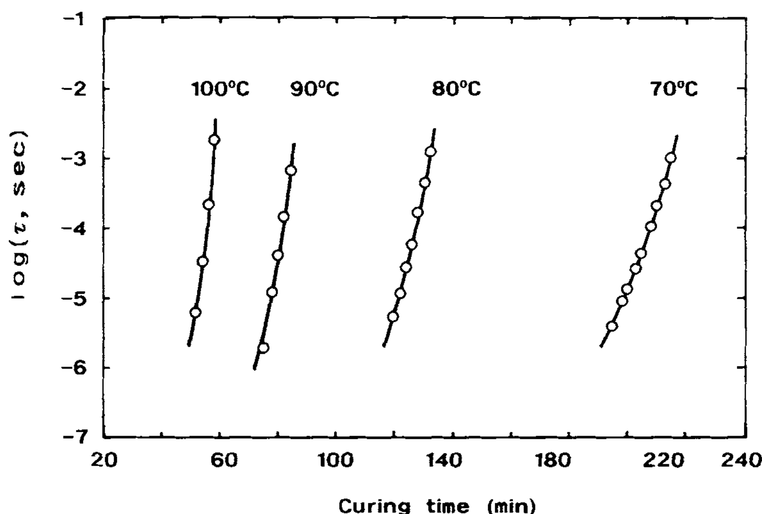


Figure 11 Relaxation time τ as a function of curing time for DGEBA–DDM system at four temperatures.

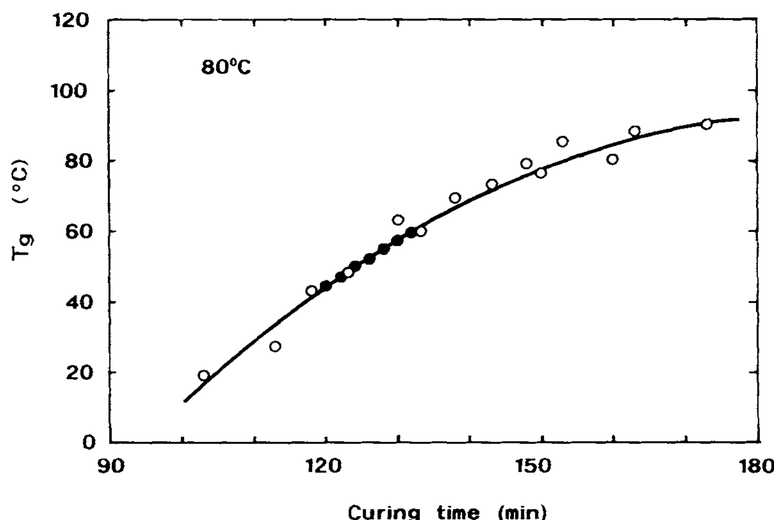


Figure 12 Glass transition temperature as a function of curing time at 80°C for DGEBA–DDM system: (○) experimental value, (●) calculated value.

for viscosity versus curing time as reported in several papers,[20-23] which is understandable when considering the general assumption that relaxation time is proportional to viscosity for most polymers.

The dielectric relaxation time cannot be directly used as a kinetic term in the cure analysis because of the temperature dependence. The T_g is temperature independent and is one of the reliable indications that represent the degree of cure as shown by Mijovik and Lee.[23] As previously noted, the T_g of the reactive epoxy resin system can be predicted from the dielectric relaxation time through the relations in Figure 8.

In order to verify the validity of the T_g prediction from τ through the relations in Figure 8, the T_g of DGEBA–DDM system during curing was measured by DSC.[23-26] The T_g data from the DSC analysis are shown in Figure 12 as a function of cure time at 80°C, compared to the predicted T_g from τ. The estimated T_g agreed very closely with the one experimentally obtained by DSC as shown in Figure 12. Therefore, the relationship between τ and T_g for the DGEBA oligomer is considered to be useful in the nondestructive determination of T_g for the reactive DGEBA–DDM system through the dielectric monitoring.

CONCLUSIONS

The isothermal curing behavior of the DGEBA–DDM system was monitored using a dielectric measurement. A dielectric relaxation was observed during each isothermal cure at temperatures of 70, 80, 90, and 100°C, which were below the glass transition temperature (T_g) of the reactive DGEBA–DDM system at the gel point. The following conclusions were obtained.

1. The relaxation is considered to be caused by the transformation from a liquid state to an ungelled glassy state as a result of an increase in molecular weight.
2. The dielectric relaxation for the DGEBA–DDM system fits the empirical model of the Havrikliak–Negami equation.
3. The T_g of the DGEBA–DDM system, which was estimated from the dielectric relaxation time, agreed with the one experimentally determined by differential scanning calorimetry (DSC).

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