

Determination of Glass Transition Temperature from Viscosity and Conductivity Measurements for an Epoxy–Amine System During Curing

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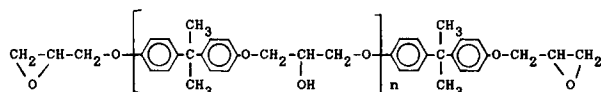
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SYNOPSIS

The melt viscosity and the direct current (dc) conductivity have been investigated for three bisphenol-A novolac-type epoxide oligomers (PGEBA_Ns) that have some branching in each molecule in comparison with the diglycidyl ether of bisphenol-A (DGEBA) oligomer without branching. The novolac-type PGEBA_N oligomer has an experimental relationship between the melt viscosity (η) and the dc conductivity (σ), $\sigma \cdot \eta^k = \text{const}$, which is the same form observed for the DGEBA oligomer. The exponent k has a linear relationship with the glass transition temperature (T_g) for the two types of oligomers with and without branching. The T_g dependence of k for the epoxide oligomers was used to analyze the T_g of a DGEBA–amine system that had some degree of branching in the molecule based on the bisphenol-A structure. The T_g of the DGEBA–amine system, which was calculated from the k that had been nondestructively determined from the viscosity and the conductivity measurements, was consistent with the T_g experimentally measured by differential scanning calorimetry (DSC). © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Dielectric analysis is widely used to monitor the curing process of epoxy resin systems since it is an effective and nondestructive measurement.^{1–4} The epoxide oligomer most frequently used is the diglycidyl ether of bisphenol-A (DGEBA), whose structural formula is shown below⁵:



The epoxide oligomer is composed of linear molecules with different molecular weights according to the variation in the repeating number (n) of the structural formula.

The DGEBA oligomer is considered to have a chemical structure similar to that of the reactive DGEBA–aromatic amine system before gelation

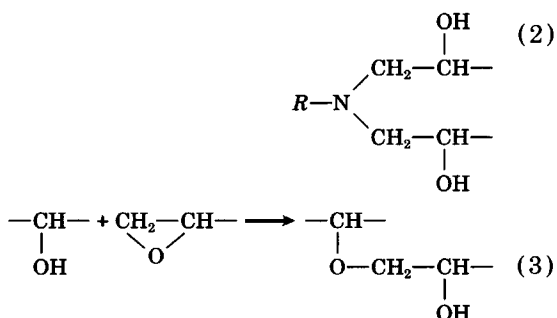
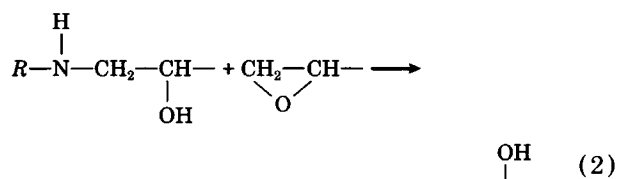
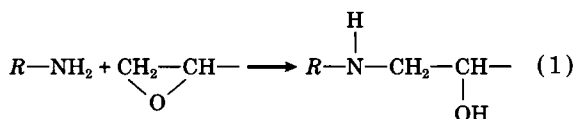
during curing. The dielectric data, collected on DGEBA oligomers, have been used to analyze the curing process of the epoxy–amine system in the dielectric cure monitoring.^{6–8} Bidstrup and co-workers⁶ used the conductivity data of the uncured epoxide oligomer to predict the glass transition temperature (T_g) of the curing system. In previous studies,^{7,8} the T_g of the DGEBA–aromatic amine system, which was calculated from the dielectric relaxation time (τ) using the relationship between τ and T_g for the DGEBA oligomers, coincided well with the T_g experimentally determined by differential scanning calorimetry (DSC) during the middle curing stage.

During the early curing stage, when the dipole relaxation of the curing system is negligible, the conductivity of the curing system can be obtained from the dielectric measurement.⁹ It is generally recognized that the dc conductivity (σ) of the curing system is inversely proportional to the viscosity (η), $\sigma \cdot \eta = \text{const}$, if the molecule of the curing system is regarded as a rigid spherical particle.^{9,10} This relationship between σ and η has also been applied to

the analysis of the epoxy resin curing system. Several researchers¹⁰⁻¹³ reported that the viscosity of the epoxy resin curing system had a good relationship with the conductivity, which was obtained from the dielectric measurement during the early stage of curing.

The DGEBA oligomer, which has been studied for analyzing the epoxy resin curing process, exhibits different viscoelastic behavior from polymers or monomers.¹⁴⁻¹⁶ In a previous work,¹⁵ it was reported that the dielectric relaxation time was not directly proportional to the viscosity for the DGEBA oligomer whose weight-average molecular weight (\bar{M}_w) was less than 2000. In addition, the experimental relationship between η and σ , $\sigma \cdot \eta^k = \text{const}$ ($0.63 \leq k \leq 1.12$), was derived for the DGEBA oligomers with different \bar{M}_w 's ($388 \leq \bar{M}_w \leq 2640$). This relationship is a comprehensive description of the generally accepted one, $\sigma \cdot \eta = \text{const}$, and indicates that the dc conductivity is not always inversely proportional to the viscosity for the epoxide oligomer. The exponent k depends on the T_g ($-18 \leq T_g \leq 54^\circ\text{C}$) of the oligomer and linearly decreases with an increase in T_g . The T_g dependence of k for the uncured DGEBA oligomer is expected to be applicable for the nondestructive analysis of the epoxy-amine curing process.

The DGEBA oligomer is composed of bisphenol-A-based linear molecules having no branching. The actual epoxy-amine curing system, however, has a chemical structure with some degree of branching in each molecule as shown in the following reactions [(1)-(3)] suggested by Shechter and co-workers¹⁷:



A bisphenol-A novolac-type multifunctional epoxide oligomer, the poly(glycidyl ether) of bisphenol-A

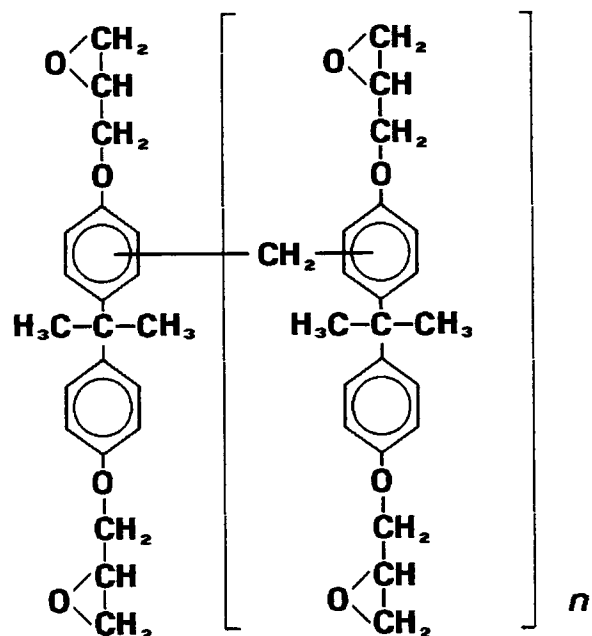


Figure 1 Chemical structure of poly(glycidyl ether) of bisphenol-A novolac (PGEBAN).

novolac (PGEBAN), has two side chains in every bisphenol-A backbone structure (Fig. 1). The viscosity and conductivity data for the branched PGEBAN in combination with the nonbranched DGEBA oligomer may provide useful information for a better understanding of the DGEBA-amine system that has some degree of branching. One of the main objectives of the work reported here was to evaluate the viscosity and the dc conductivity of the branched PGEBAN oligomer in comparison to those of the nonbranched DGEBA oligomer. Another objective was to apply the data, obtained for two types of uncured oligomers, to the analysis of an actual DGEBA-aromatic amine system in the dielectric cure monitoring.

EXPERIMENTAL

Materials

The PGEBAN oligomers used in this study were Epikote 157S65, 157S70, and 157S75, which were supplied by Yuka Shell Epoxy. The number-average molecular weights (\bar{M}_n 's) and the weight-average molecular weights (\bar{M}_w 's) for the three oligomers are from 766 to 936 and from 1570 to 2480, respectively. The characteristics of the samples are summarized in Table I. The novolac-type PGEBAN oligomer is manufactured by the direct addition of epichlorohydrin to bisphenol-A novolac in the pres-

Table I Properties for PGEBAN Oligomers and DGEBA

Epoxide Oligomer	T_g (°C)	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	Na ⁺ ^a (ppm)	Cl ⁻ ^b (ppm)
Epikote 157S65	19	766	1570	2.05	< 1	< 1
Epikote 157S70	25	827	2300	2.78	< 1	< 1
Epikote 157S75	28	936	2480	2.65	< 1	< 1
DGEBA	-18	340	340	1.00	< 1	< 1

^a Measured by atomic absorption analysis.
^b Measured by potentiometric titration with 0.01N silver nitrate.

ence of sodium hydride. The major ions in the PGEBAN oligomer are Na⁺ and Cl⁻ due to the manufacturing process as well as the DGEBA oligomer.¹⁴ The concentrations of ions for the three PGEBAN oligomers are given in Table I. Characterization of the oligomer was performed by the same method previously reported.¹⁴

The epoxy resin curing system was a stoichiometric mixture of DGEBA and 4,4'-diaminodiphenylmethane (DDM). The DGEBA was refined from Epon 825 (Shell Chemical) using the crystallization technique employed in a previous work.¹⁸ The characteristics of the DGEBA are listed in Table I.

Measurements

Viscosity measurements were performed using a cone and plate viscometer (MR-3; Rheology Engineering) equipped with a cone having a diameter of 3.2 cm and an angle of 2°, operating in the frequency range from 0.001 to 10 Hz. The temperature range studied was from 40 to 170°C. The temperature variations during the measurements were less than ±0.1°C.

The direct current (dc) conduction measurements were performed in a temperature range of 80–180°C using an apparatus that consisted of a dc power supply (TR300C; Takeda Riken), a vibrating reed electrometer (TR84M; Takeda Riken), and a pen recorder (EPR-200A; Toa Dempa). The measuring cell, a vertical parallel-plate type, was the same one used before.¹⁴

T_g was measured using a DuPont 9900 differential scanning calorimeter (DSC).

RESULTS AND DISCUSSION

Relationship Between Melt Viscosity and dc Conductivity for Epoxide Oligomer

Figures 2 and 3 show the temperature dependence of the melt viscosity (η) and the dc conductivity

(σ), respectively, for the three novolac-type PGEBAN oligomers. The relation between $\log \eta$ and $\log \sigma$ is plotted for the two PGEBAN oligomers, Epikote 157S65 and 157S75, in Figure 4. A linear relation is observed for each log-log plot, which leads to the following experimental equation between η and σ :

$$\sigma(T)[\eta(T)]^k = \text{const} \quad (4)$$

where $\sigma(T)$ is the dc conductivity at temperature T ($T_g \leq T \leq T_g + 100^\circ\text{C}$); $\eta(T)$, the melt viscosity at T , and k , the exponent. The relationship [eq. (4)] for the PGEBAN oligomer has the same form as that of the DGEBA one obtained during a previous study.¹⁵ The k value, which represents the slope of log-log plot between η and σ (Fig. 4), varies from 0.79 to 0.83 depending on the T_g of the PGEBAN oligomer (Table II). In Figure 5, the relationship between k and T_g is shown for the PGEBAN oligomer along with the DGEBA one previously studied.¹⁵ The exponent k was found to have a linear dependence on T_g in a T_g range below and around 50°C for the two types of oligomers with and without branching.

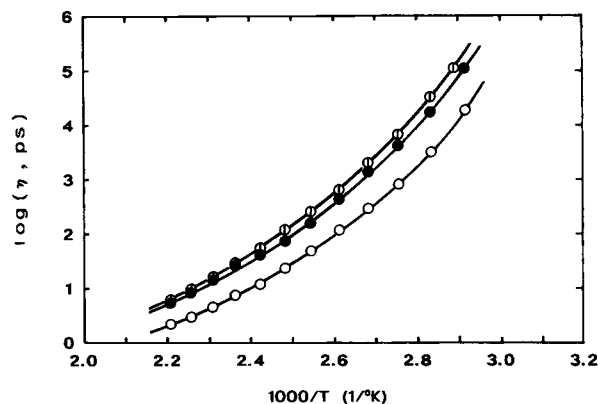


Figure 2 Temperature dependence of melt viscosity η for three PGEBAN oligomers: (○) Epikote 157S65; (●) Epikote 157S70; (⊙) Epikote 157S75.

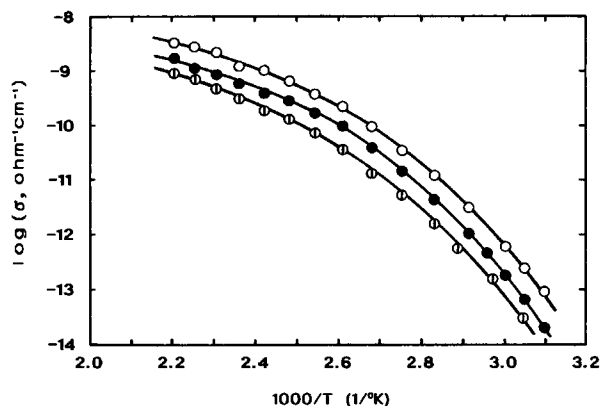


Figure 3 Temperature dependence of dc conductivity for three PGEBAN oligomers: (○) Epikote 157S65; (●) Epikote 157S70; (◻) Epikote 157S75.

Relationship Between Exponent k and WLF Parameter for the Epoxide Oligomer

It is generally recognized that the temperature dependence of the melt viscosity (η) is governed by the following WLF equation¹⁹:

$$\log \frac{\eta(T)}{\eta(T_g)} = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \quad (5)$$

where $\eta(T)$ is the melt viscosity at temperature T ($T_g \leq T \leq T_g + 100^\circ\text{C}$), while C_1 and C_2 are parameters.

On the other hand, the dc conduction above the T_g for the epoxide oligomer is considered to be caused by ions (their mobility and concentration), which are always present, to some extent, in commercial products. The major ions in the PGEBAN oligomer are Na^+ and Cl^- due to the manufacturing process. As shown in Table I, the ion concentrations are very low and regarded as similar among the three PGEBAN oligomers studied. The ionic mobility, therefore, plays a major role in the dc conduction of the oligomer. Since the mobility of an ion is closely re-

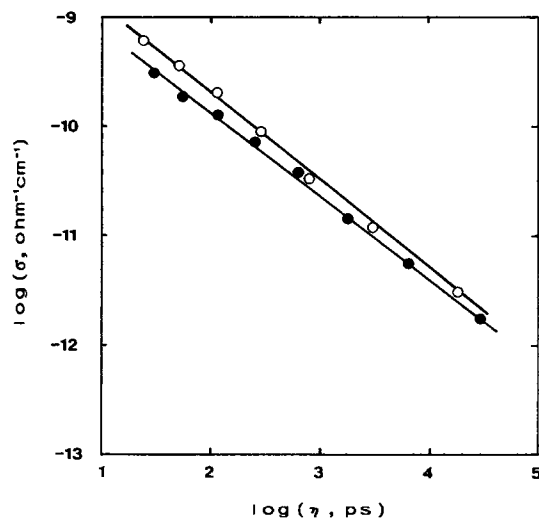


Figure 4 Relationship between $\log \eta$ and $\log \sigma$ for Epikote 157S65 and 157S75: (○) Epikote 157S65; (●) Epikote 157S75.

lated to the segmental mobility of the host oligomer, the temperature dependence of the dc conductivity for the epoxide oligomer will be expressed in the following WLF equation^{14,20}:

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C'_1(T - T_g)}{C'_2 + T - T_g} \quad (6)$$

where $\sigma(T)$ is the dc conductivity at temperature T ($T_g \leq T \leq T_g + 100^\circ\text{C}$), while C'_1 and C'_2 are parameters.

In a previous work,¹⁵ the meaning of k for the nonbranched DGEBA oligomer was already discussed; the k value is an indication of the segment and the ion mobilities and corresponds to the ratio of two WLF parameters for η and σ [eq. (7)]:

$$k = \frac{C'_1}{C_1} \quad (7)$$

Table II WLF Parameters and Exponents Between Melt Viscosity and dc Conductivity for PGEBAN Oligomers

PGEBAN Oligomer	WLF Parameters					
	Viscosity		Conductivity			
	C_1	C_2	C'_1	C'_2	k	C'_1/C_1
Epikote 157S65	15.03	56.43	12.26	53.80	0.83	0.82
Epikote 157S70	15.15	52.62	11.89	51.24	0.80	0.78
Epikote 157S75	14.85	55.30	11.54	49.04	0.79	0.78

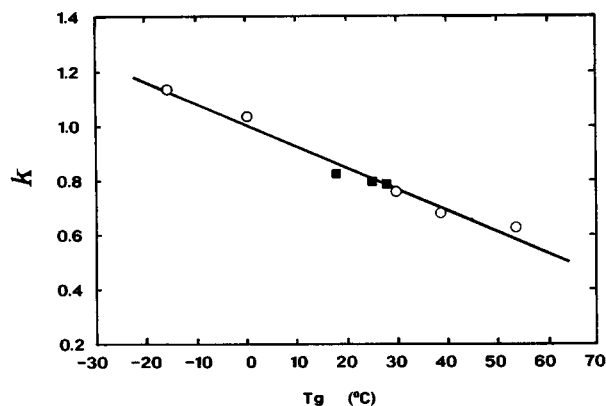


Figure 5 Relationship between exponent k and T_g for epoxide oligomers: (○) DGEBA; (■) PGEBAN.

where C_1 and C_1'' are the WLF parameters for η and σ , respectively.

To determine whether eq. (7) is applicable to the branched PGEBAN oligomer as well as to the non-branched DGEBA one, the temperature dependencies of η and σ were analyzed according to the WLF equation. The temperature dependencies of both η and σ for the PGEBAN oligomer were found to be governed by the WLF equations [eqs. (5) and (6)] already described. The WLF parameters and the exponents are summarized in Table II. The k value is very close to the ratio of the two C_1 parameters, C_1''/C_1 , for each PGEBAN oligomer, which is consistent with the result [eq. (7)] obtained for the DGEBA oligomer from a previous work.¹⁵ The C_1 parameters for the three branched PGEBAN oligomers are plotted as a function of T_g , along with those for the nonbranched DGEBA oligomers in Figure 6. Two types of oligomers with and without branching exhibit a similar tendency in the relationship between the C_1 parameters and T_g . As for another parameter, C_2 , the two C_2 parameters for each PGEBAN oligomer have similar values as summarized in Table II. This is the same behavior seen in the DGEBA oligomer without branching.^{14,15} If the two C_2 parameters for the same oligomer are equal to each other, eq. (7) can be numerically derived from eq. (4) and the two WLF equations [eqs. (5) and (6)].

The behavior of WLF parameters for the oligomer can be explained by describing the two parameters in the following forms according to the WLF equation combined with the free-volume theory developed by Cohen and Turnbull^{21,22}:

$$C_1 = \frac{\gamma v^*}{2.303 f_g v_m} \quad \text{and} \quad C_2 = \frac{f_g}{\alpha_f} \quad (8)$$

where γ is a numerical factor introduced to correct for overlap of the free volume; v^* , the critical volume large enough to permit a molecule to jump in after the displacement; v_m , the average molecular volume; f_g , the free-volume fraction at T_g ; and α_f , the thermal expansion coefficient of the free volume.

According to eq. (8), the C_2 parameter is determined by the characteristics (f_g and α_f) of an oligomer matrix or a host oligomer matrix only. The two C_2 parameters for each PGEBAN oligomer have similar values (Table II), which is consistent with the theory previously mentioned. On the other hand, the C_1 parameter reflects not only the characteristics of an oligomer (a host oligomer) matrix, but also the size of the moving unit that is expressed by the critical volume (v^*) for the transport of the oligomer segment or the ionic charge carrier. The ratio of the critical volume for the ion and the segment can be obtained by dividing one C_1 parameter by another for the same oligomer [eq. (8)]. Therefore, the exponent k , $k = C_1''/C_1$, is regarded as a measure of the mobilities of the ion and the oligomer segments. Figure 5 indicates that the oligomer with a larger T_g or \bar{M}_w has a smaller value of k . The behavior of k is interpreted in the following way: As already mentioned, three DGEBAN oligomers have the same kind and similar concentrations of ions (Table I). The critical volume for the ion transport is not very different among the oligomers because of the similar ion sizes, whereas the critical volume needed for the segment transport increases with an increase in T_g or \bar{M}_w . Thus, the exponent k , which represents the ratio of the critical volumes for the ion and the segment, has a value reflecting the T_g or \bar{M}_w of the oligomer.

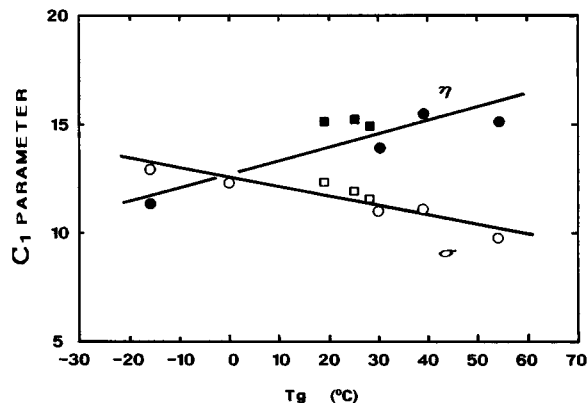


Figure 6 Plot of WLF C_1 parameters for η and σ vs. T_g of epoxide oligomer: (●) C_1 for η of DGEBA; (■) C_1 for η of PGEBAN; (○) C_1 for σ of DGEBA; (□) C_1 for σ of PGEBAN.

In Figure 5, the linear T_g dependence of k is observed for the uncured oligomers, PGEBA and DGEBA, whether the oligomer has branching or not. Therefore, the relation between k and T_g (Fig. 5) for two types of oligomers may be used to analyze the epoxy resin curing system that has some degree of branching in each molecule. The application of that relationship to the curing system will be discussed later.

Viscosity and Conductivity of the DGEBA-Aromatic Amine System During Curing

As already mentioned, the ionic conduction is attributed mainly to the dc conduction of the epoxide oligomer or to the epoxy resin curing system. During the early curing stage, when the dipole relaxation of the epoxy resin curing system is negligible, the dc conductivity (σ) is obtained from the dielectric loss (ϵ'') in the dielectric cure monitoring using the following relationship²³:

$$\epsilon'' = \frac{\sigma}{\omega E_0} \quad (9)$$

where ϵ'' is the dielectric loss; E_0 , the permittivity of free space (8.855×10^{-14} F/cm); and ω , the angular frequency.

In a previous study,¹⁹ the dc conductivity of the DGEBA-DDM system was determined from the dielectric measurement according to eq. (9) and was compared to the viscosity during the early stage of curing. The data, which were obtained for the DGEBA-DDM system in a previous study,¹⁸ were reexamined in terms of the relationship between η and σ , $\sigma \cdot \eta^k = \text{const}$, which would provide information on T_g through the exponent k .

Before applying this relationship to the analysis of the actual curing system, the value of the constant, $\sigma \cdot \eta^k$, was investigated. The values of the constant for the nonbranched DGEBA oligomers are obtained from the result of a previous study.¹⁴ Figure 7 shows $\log(\sigma \cdot \eta^k)$ as a function of T_g for three PGEBA and five DGEBA oligomers along with that for the DGEBA-DDM system at 70 and 80°C curing. The value of $\log(\sigma \cdot \eta^k)$ for the DGEBA-DDM system was calculated from the three factors, σ , η , and k , at the starting point of the curing reaction. The η and σ values at the starting point were estimated from the measured η and σ vs. curing time curves during the early stage of curing for the DGEBA-DDM system, because the initial η and σ for the curing system were difficult to measure by the measuring apparatus used in this study. The initial k

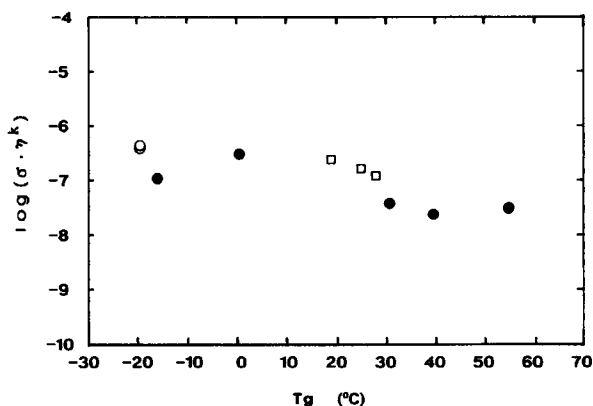


Figure 7 Relationship between $\log(\sigma \cdot \eta^k)$ and T_g for epoxide oligomers and DGEBA-DDM system: (●) DGEBA; (□) PGEBA; (○) DGEBA-DDM.

value ($k = 1.16$) was determined from the relationship between k and T_g (Fig. 5) for the epoxide oligomers using T_g ($T_g = -20^\circ\text{C}$) of the uncured DGEBA-DDM system. The $\sigma \cdot \eta^k$ values of the DGEBA-DDM curing system at the starting point are 3.69×10^{-7} and 3.86×10^{-7} for the two isothermal temperatures, 70 and 80°C, respectively. The constants for both the oligomers and the curing system appear to be similar in the T_g range below 20°C (Fig. 7). As indicated later (Figs. 9 and 10), from the actual T_g measurements, the T_g of the DGEBA-DDM system is less than 20°C during the early curing stage studied. The relationship between σ and η for the curing system was analyzed regarding the value of $\sigma \cdot \eta^k$ as a constant during each isothermal curing.

Figure 8 shows $\log \sigma$ and $\log \eta$ for the DGEBA-DDM system as a function of curing time at 70°C. The equation, $\sigma \cdot \eta^k = \text{const}$, was used to analyze the relationship between σ and η of the curing system. Figures 9 and 10 show the plot of k , along with the calculated T_g , as a function of curing time at 70 and 80°C, respectively. The T_g of the curing system was calculated from k using the linear relationship between T_g and k for the uncured epoxide oligomers (Fig. 5). The k value of the curing system decreases according to the progress of the curing reaction (Figs. 9 and 10). The calculated T_g as a function of curing time exhibits an inverse pattern of the behavior of k . The T_g of the curing system, which was experimentally measured by DSC at each curing temperature, was also plotted in Figures 9 and 10. A good agreement is observed between the calculated and measured T_g 's for the DGEBA-DDM system during each isothermal curing.

The T_g of the reactive epoxy resin system during curing cannot be nondestructively detected using

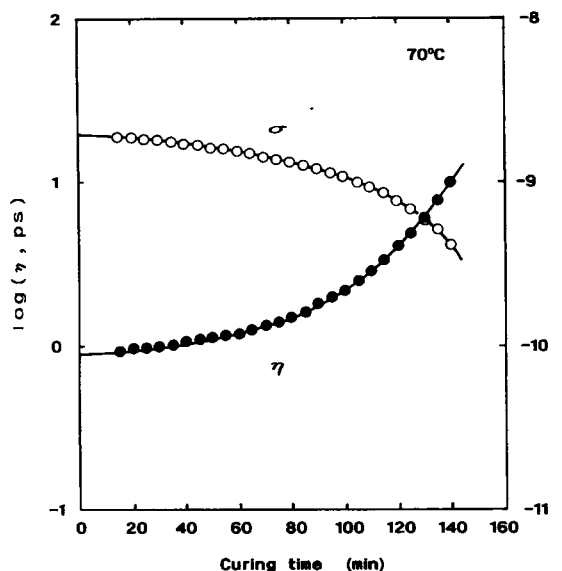


Figure 8 Viscosity η and dc conductivity σ as a function of curing time for DGEBA-DDM at 70°C: (●) η ; (○) σ .

commercially available measuring methods such as DSC. In a previous study,⁷ the T_g of the DGEBA-DDM system was calculated from the dielectric relaxation time (τ) detected by the dielectric cure monitoring during the middle curing stage at 80°C. The T_g of the DGEBA-DDM system, which was calculated from τ in a previous study,⁷ was plotted as a function of curing time at 80°C along with the

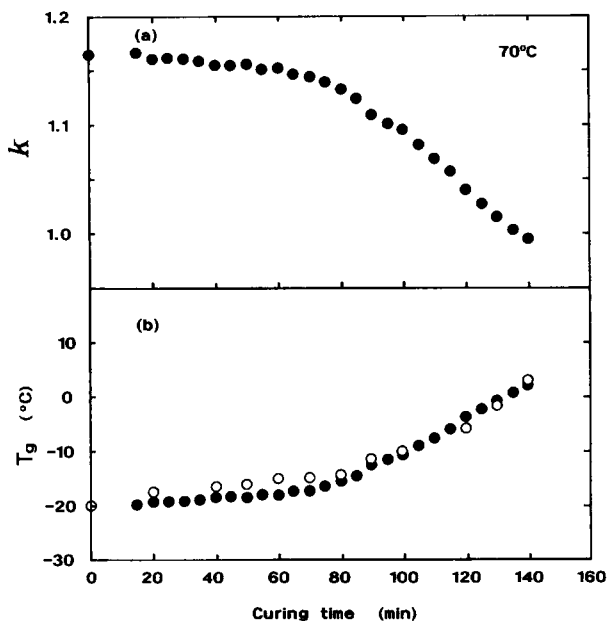


Figure 9 (a) Exponent k and (b) glass transition temperature as a function of curing time for DGEBA-DDM system at 70°C: (a) (●) k ; (b) (○) measured T_g ; (●) calculated T_g .

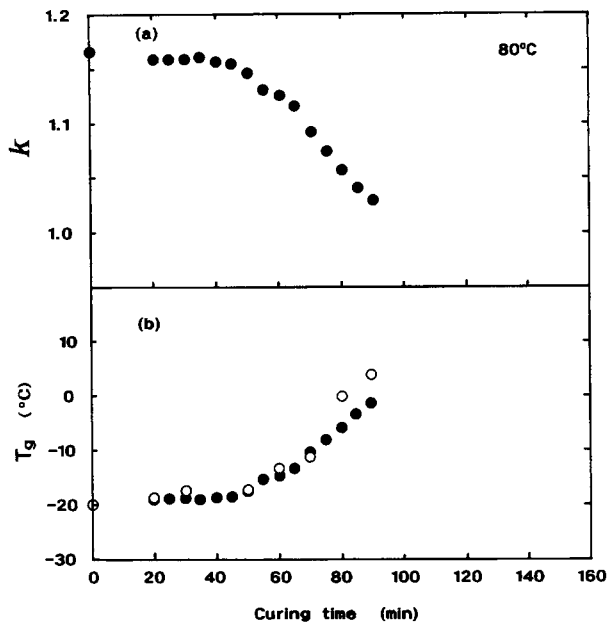


Figure 10 (a) Exponent k and (b) glass transition temperature as a function of curing time for DGEBA-DDM system at 80°C: (a) (●) k ; (b) (○) measured T_g ; (●) calculated T_g .

T_g determined from k in this study (Fig. 11). These calculated T_g 's, which were obtained from k and τ during the early and the middle curing stages, were compared with the T_g experimentally measured by DSC. The calculated T_g for the DGEBA-DDM system was found to coincide well with the actually measured one over a wide time range from the early to the middle curing stages (Fig. 11).

The on-line conductivity measurement was al-

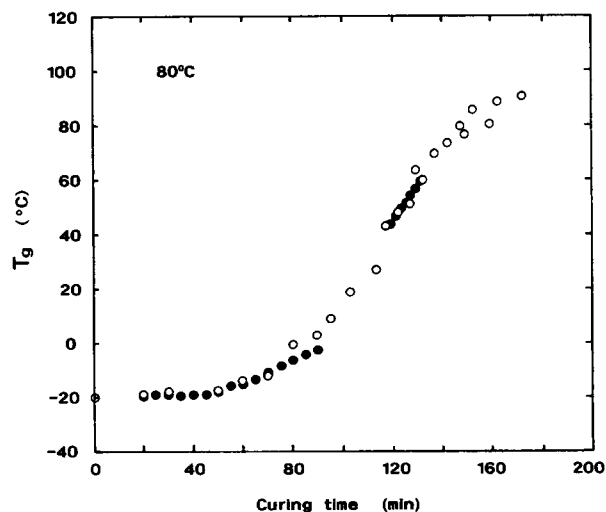


Figure 11 Glass transition temperature as a function of curing time at 80°C for DGEBA-DDM system: (○) experimental value; (●) calculated value.

ready applied to the prediction of the T_g or the degree of conversion for the epoxy resin curing system.^{6,24} The nondestructive determination of T_g from the conduction measurement was reported to be possible for the epoxy resin system using the modified WLF equation that described the conductivity as a function of curing temperature and T_g .^{6,24} The modified WLF equation,^{6,24} however, needs five estimated parameters to calculate the T_g of the curing system, which sometimes results in a large deviation from the actually measured T_g due to the accumulation of errors caused by the five parameters.

Generally, the combined measuring method provides more reliable information than does the single measuring one in the cure monitoring of epoxy resins. The simultaneous measurement of the viscosity and the dielectric property was developed by two groups of researchers.^{11,12} One is Gotro and Yandrasits¹¹ who investigated the laminating resin by mounting a microdielectric sensor in the bottom plate of a parallel-plate rheometer; the other is Lane and co-workers¹² who used a viscometer that had an electrically isolated parallel-plate test fixture. If this kind of simultaneous measurement is available, the T_g prediction method of this study, which is based on the combination of the viscosity and the dielectric measurements, may become a practical tool in the nondestructive analysis of the DGEBA-amine curing process.

CONCLUSIONS

The melt viscosity and the direct current (dc) conductivity have been investigated for three bisphenol-A novolac-type epoxide oligomers (PGEBANs) that have some branching in each molecule in comparison with the diglycidyl ether of bisphenol-A (DGEBA) oligomer having no branching. The following conclusions were obtained:

1. The novolac-type PGEBAN oligomer has an experimental relationship between the melt viscosity (η) and the dc conductivity (σ), $\sigma \cdot \eta^k = \text{const}$, which is the same form observed for the DGEBA oligomer. The exponent k has a linear relationship with the glass transition temperature (T_g) for the two types of oligomers with and without branching.
2. The T_g dependence of k for the oligomers was used to analyze the T_g of a DGEBA-aromatic amine system during the isothermal curing. The T_g of the DGEBA-aromatic amine system, which was calculated from the k that had been nondestructively determined from

the viscosity and the conductivity measurements, was consistent with the T_g experimentally measured by differential scanning calorimetry (DSC).

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