

Dielectric Changes During the Curing of Epoxy Resin Based on the Diglycidyl Ether of Bisphenol A (DGEBA) with Diamine

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The curing characteristics of diglycidyl ether of bisphenol A (DGEBA) with diaminodiphenylmethane (DDM) as a curing agent were studied using differential scanning calorimetry (DSC), rheometrics mechanical spectrometry (RMS), and dielectric analysis (DEA). The isothermal curing kinetics measured by DSC were well represented with the generalized auto-catalytic reaction model. With the temperature sweep, the inverse relationship between complex viscosity measured by RMS and ionic conductivity obtained from DEA was established indicating that the mobility of free ions represented by the ionic conductivity in DEA measurement and the chain segment motion as revealed by the complex viscosity measured from RMS are equivalent. From isothermal curing measurements at several different temperatures, the ionic conductivity contribution was shown to be dominant in the dielectric loss factor at the early stage of cure. The contribution of the dipole relaxation in dielectric loss factor became larger as the curing further proceeded. The critical degrees of cure, at which the dipolar contribution in the dielectric loss factor starts to appear, increases as isothermal curing temperature is increased. The dielectric relaxation time at the same degree of cure was shorter for a sample cured at higher curing temperature.

Introduction

Recently, we have witnessed the increased applications of epoxy resins in various areas.^{1,2} In particular, they are important as matrix resins for epoxy molding compounding (EMC) in semiconductor industry and advanced aerospace composite materials. In these applications, the molecular structure of cured epoxy resins decides final physical properties such as shrinkage, residual stress, impact strength, dielectric constant, and so forth.¹⁻³ Consequently, there is a need for more detailed understanding of the curing process and the structure-property relationship of cured epoxy resins in order to control the curing economically and to optimize the physical properties of final products.

It is difficult to characterize *in-situ* structural and rheological property changes during thermoset curing. With the development of dielectric analysis (DEA) technique, however, it is possible to monitor the entire curing process by measuring dielectric properties.⁴⁻¹⁰ Ionic conductivity is often compared with resin viscosity because it represents the mobility of free ions in a matrix medium, and thus the dielectric loss factor provides more information about the molecular motion.⁴⁻⁷ In this regard, the DEA technique would be powerful in examining the microstructure of the epoxy network during curing.

In studying curing kinetics, many different types of reaction kinetics including the auto-catalytic reaction have been frequently used to interpret thermal analysis data.¹¹⁻¹² Since the heats of reaction of epoxy with both primary and secondary amine groups are almost the same, the degree of cure is calculated based on the consumption of epoxy groups without distinguishing the reactions with primary and secondary

amines. It has, however, been reported that the reactivity ratio of primary to secondary amines with epoxies is not unity,¹¹⁻¹⁶ and the network structure of fully cured epoxy has been studied with different curing conditions.^{3,11-12} Dusek¹⁵ proposed that several factors including relative reactivity affect the network formation and the structure of cured epoxy resins and studied on model reactions using low functionality monomers. It is, however, still challenging to analyze the network structure of cured general epoxy resins experimentally.

The present study is concerned with the behavior of dielectric properties during curing reaction and the experimental evidence for the difference in the microstructure of cured epoxy networks. The ionic conductivity measured by DEA is compared with the complex viscosity obtained from RMS before gelation. To understand the curing mechanism, contributions of both ionic conductivity and dipole relaxation in the dielectric loss factor are examined at different cured states of epoxy.

Experimental Section

Materials. The epoxy resin used in this study was YD128 (a kind of DGEBA), supplied by Kukdo Chemical Co., and its epoxy equivalent weight is about 190. The content of Cl⁻ ion in the epoxy was reported to be about 0.05 wt%, and these impurity ions dominates the dielectric properties during the early stage of curing reaction. The epoxy resin was cured with 4,4'-diaminodiphenylmethane (DDM) curing agent purchased from Aldrich. All the mixtures of epoxy resin and curing agent were made in stoichiometric ratios. To lower the mixture viscosity and aid the intimate mixing between the added components, the mixture was initially stirred in a preheated oil bath at 50 °C for 30 min until clear fluid was

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obtained. The mixture was then degassed *in vacuo* to remove trapped air.

Curing Kinetic Study. Curing kinetics were obtained with DSC (TA 2010, TA Instruments) under nitrogen atmosphere. All the measurements were performed in hermetically sealed aluminum pans with sample weights ranging from 10 to 30 mg. The total heat of curing reaction, Q_{tot} , was estimated by the area of an exothermic peak in temperature scanning mode at a heating rate of 10 °C/min. The profiles of isothermal reaction exotherm were measured at 100, 110, 120, 130, and 140 °C. Isothermal DSC runs were stopped when no further exotherm is observed. The samples were then reheated from room temperature to 300 °C in temperature scanning mode again at a heating rate of 10 °C/min to detect any residual reactivity left in the isothermally cured samples. The extent of cure of the epoxy/amine mixtures under isothermal curing condition was estimated by the area under the exothermic peak as follows:

$$\alpha(t) = \frac{1}{Q_{tot}} \int_0^t dQ dt \quad (1)$$

where $\alpha(t)$ is the extent of cure at a given time, dQ is the heat release at an infinitesimal time increase dt , and Q_{tot} is the total heat of curing reaction, which is usually taken as the area of DSC exotherm of a temperature sweep.

Rheological Measurements. All rheological experiments were carried out using Rheometrics Mechanical Spectrometer, RMS 800 (Rheometrics Inc.). Curing reaction was monitored on a disposable aluminum parallel plate with a diameter of 25 mm. To determine the optimum experimental condition, preliminary frequency and strain sweeps were performed. Curing experiments were performed at a frequency of 20 rad/sec with a strain of 25%. The complex viscosity of a sample was monitored during curing reaction in temperature scanning mode at a heating rate of 2.5 °C/min.

Dielectric Measurements. Dielectric analyzer, DEA 2970 (TA Instruments), was used to obtain dielectric loss factor, ϵ'' , of epoxy/amine mixtures during curing reaction under both isothermal and temperature scanning conditions. To directly compare dielectric properties with complex viscosities determined from RMS, curing conditions were set to be the same as rheological measurements. ϵ'' was measured over a frequency range from 0.1 to 100,000 Hz. The frequency range was selected to allow collection of 16 data points within a period of 1 min. Comparing with time required in isothermal curing, which was about 30 min at 130 °C, this collection time is sufficiently short to assume the instantaneous snapshot of dielectric loss factor during the isothermal curing. Parallel plate electrodes were employed in measuring the dielectric data, and the gap between the electrodes was maintained at a fixed value of 0.5 mm.

Theoretical Background

Dielectric loss factor mainly consists of two parts as follows^{4-6,17}:

$$\epsilon'' = \epsilon''_{ion} + \epsilon''_{dipole}$$

$$\epsilon''_{ion} = \frac{\sigma}{2\pi f \epsilon_0} \quad (2)$$

where ϵ''_{ion} is the contribution from ionic conductivity, ϵ''_{dipole} is the contribution from dipole relaxation, σ is the ionic conductivity, f is the applied frequency in Hz, and ϵ_0 is the dielectric constant of vacuum (8.854×10^{-12} F/m).

The ionic conductivity σ is considered to reflect the mobility of free ions, and to be independent of applied frequency. At a low degree of cure, since the growing epoxy chains and/or networks are small and the viscosity of the resin is relatively low, the contribution from the ionic conductivity to dielectric loss factor is expected to be dominant and the dielectric loss factor is thus proportional to the reciprocal of applied frequency.⁴⁻⁶

As curing reaction further proceeds, the epoxy chains and/or networks grow even larger and the contribution from dipole relaxation comes into effect, which can be monitored as a peak in the dielectric loss factor.¹⁸⁻²¹ This peak is shifted to lower frequencies as the epoxy chains and/or networks continuously grow mainly due to the increased dipole relaxation time (or dielectric relaxation time, τ). To explain the frequency dependent behavior of ϵ''_{dipole} and to obtain the dielectric relaxation time (τ), ϵ''_{dipole} was fitted to the Havriliak-Negami model (equation (3)) which has widely been used to explain the dipole relaxation behavior of real polymeric systems^{8,17-25}:

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + (i\omega\tau)^\beta} \quad (3)$$

where $\epsilon^* = \epsilon' - i\epsilon''$, ϵ' and ϵ'' are the dielectric constant and the dielectric loss factor of a polymeric material, and ω is the applied frequency (rad/sec). ϵ_0 and ϵ_∞ is the static or relaxed permittivity and the unrelaxed or high frequency optical permittivity, respectively, and the difference between them, $\epsilon_0 - \epsilon_\infty$, is referred to as the dielectric strength, which is related to the total dipole moment concentration involved in the dielectric relaxation. The parameter β is related to the distribution of relaxation times. This dielectric relaxation time provides information about the chain dimension, *i.e.* the radius of gyration. Figure 1 shows the schematic dielectric loss factor curve in wide frequency range, and both the ionic conductivity contribution and the peak shift due to the change

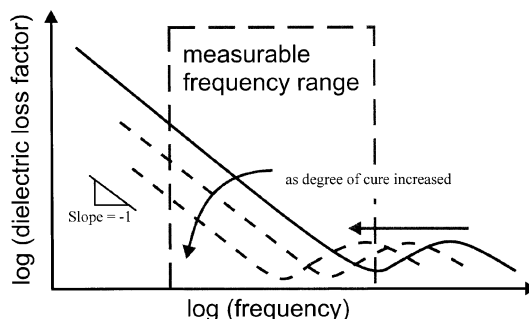


Figure 1. Schematic illustration of dielectric loss factor curves of a DGEBA/DDM mixture at different curing stages as a function of frequency.

in dipole relaxation are indicated with different degrees of cure.

Results and Discussion

Isothermal experiments were carried out at several different temperatures for DGEBA/DDM mixtures. Figure 2(a) shows the measured curing reaction rates (*i.e.*, symbols), which was calculated from the measured heat flow and the total heat as represented by equation (1), as a function of isothermal curing time. A generalized auto-catalytic kinetic model,^{2,11-12} which has been used by many researchers, was adopted to fit the experimental data:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \quad (4)$$

The parameters in this kinetic model, K_1 , K_2 , m , and n were obtained with fitting the data into the model with the Nelder-Mead simplex algorithm at each curing temperature. The Arrhenius type equations for the kinetic rate constants K_1

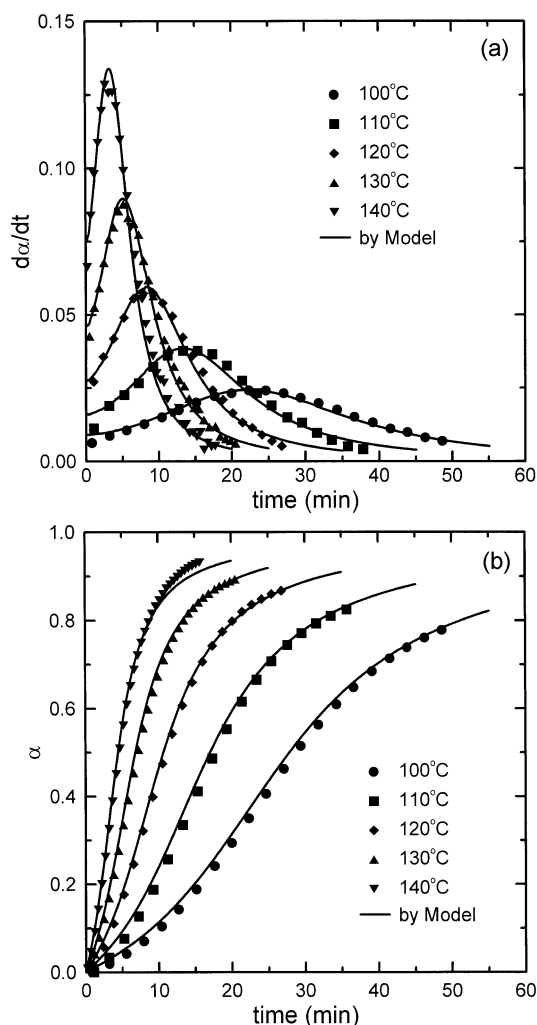


Figure 2. Isothermal curing data measured at several temperatures by DSC (symbols) and calculated fit (lines) using an auto-catalytic reaction given as equation (4) in text; (a) reaction rate, (b) degrees of cure.

and K_2 were employed to consider the temperature dependency:

$$K_i = K_{i0}\exp(-E_i/RT) \quad (5)$$

The parameters obtained from the fitting are $K_{10} = 2.8870 \times 10^7 \text{ sec}^{-1}$, $K_{20} = 3.8660 \times 10^6 \text{ sec}^{-1}$, $E_1 = 67891.97 \text{ J/mol}$, $E_2 = 51968.18 \text{ J/mol}$, $m = 1.3718$, and $n = 2.0103$. The solid lines in Figure 2(a) are the curing reaction rates calculated by the generalized auto-catalytic reaction model with these parameters and the corresponding degrees of cure as a function of time is also shown in Figure 2(b). Excellent agreement between experimental measurements and prediction from the reaction kinetic model implies that the degree of cure can be accurately estimated from the reaction kinetics.

Rheological and dielectric measurements were also performed in temperature scanning mode at a heating rate of 2.5 °C/min. The complex viscosity profile shows the typical pattern of curing reaction as shown in Figure 3. The complex viscosity initially decreases with increasing temperature before the onset of curing reaction. The decrease in complex viscosity in this region is due to increase in the mobility of component molecules. As curing reaction further proceeds, the complex viscosity passes through the minimum and then abruptly increases due to the increased molecular weight and the more extensive network formation. Ionic conductivity, which was calculated from the measured dielectric loss factor, is also plotted in Figure 3. The ionic conductivity is measured from the mobility of free ions such as Na^+ and Cl^- , which inherently exist in many commercial DGEBA epoxy resins as a byproduct of the reaction between epichlorohydrin and bisphenol A⁷. Since the viscosity of epoxy medium determines the mobility of free ions, the complex viscosity is proportional to the reciprocal of ionic conductivity.^{4,8} Figure 3 clearly demonstrates this relationship up to the abrupt increase in complex viscosity.

Since the heats of reaction of epoxy group with primary

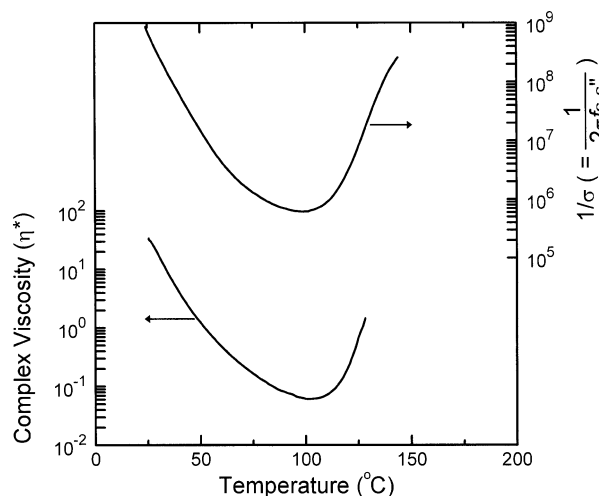


Figure 3. The complex viscosity, as measured from RMS, and the inverse of ionic conductivity, as obtained from DEA, plotted against temperature for a DGEBA/DDM mixture. The heating rate for the temperature sweep is 2.5 °C/min.

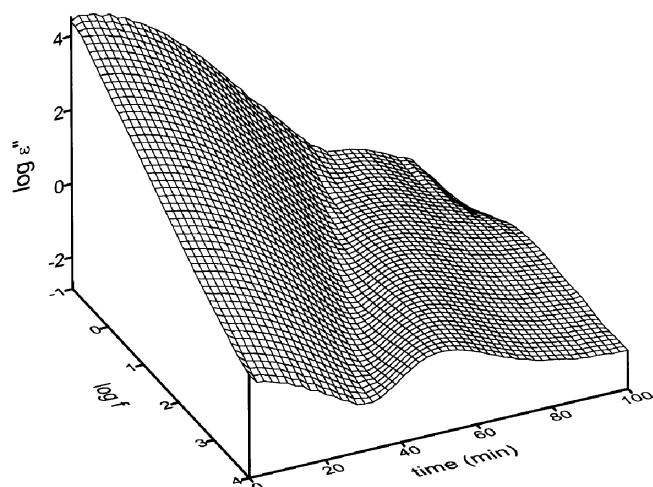


Figure 4. Real time dielectric loss factor as functions of both applied frequency and curing time during an isothermal curing at 90 °C for a DGEBA/DDM stoichiometric mixture.

and secondary amines of a curing agent are known to be almost the same,¹⁻² it is thus difficult to separate the extent of reactions of the primary and secondary amines using general thermal analysis. This in turn means that the final cured structure, which is the key factor for final physical properties,³ can not be predicted or examined with the auto-catalytic reaction kinetics based on thermal analysis. To compare the curing mechanism and the structure of epoxy network in different curing conditions, real time dielectric measurement was carried out for samples cured at several different isothermal temperatures. Figure 4 shows one example of three-dimensional feature of the dielectric loss factor, ϵ'' , for an isothermal curing at 90 °C as functions of both isothermal curing time and applied alternating frequency. Frequency dependency of ϵ'' shows a straight line with a slope of -1 in $\log \epsilon''$ vs. $\log f$ plot at the early stage of cure, meaning that the contribution from ionic conductivity to ϵ'' is dominant. As curing reaction further proceeds, the mobility of free ions decreases and at the same time the epoxy chains and/or networks grow leading to a situation where the contribution from the ionic conductivity decreases while the contribution due to the dipole relaxation increases. The increased contribution from dipole relaxation is manifested as a ridge in this figure. At curing temperatures of 100, 110, 120, and 130 °C, similar three-dimensional features of the dielectric loss factor were also obtained.

The frequency behaviors of ϵ'' at several cured states are plotted in Figures 5(a)-5(e) for isothermal cures at 90, 100, 110, 120, and 130 °C respectively. Since the frequency sweep of ϵ'' at each cured state took less than 1 minute which is a fairly short period compared with the total curing time, the frequency-dependent dielectric loss factor can be regarded as an instantaneous snapshot. In these figures, each degree of cure was estimated from the auto-catalytic reaction kinetics (equation (4)) with kinetic parameters obtained from the thermal analysis. In Figure 5(a), we note that the dielectric loss factor at a low degree of cure is initially propor-

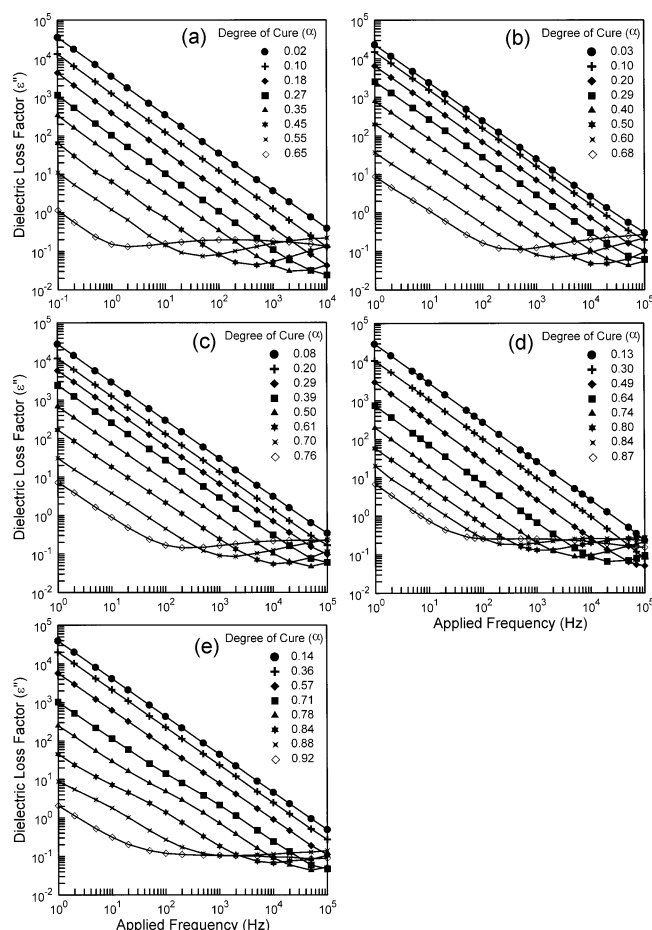


Figure 5. Frequency dependency of dielectric loss factors at several different cured states for an isothermal temperature of (a) 90 °C, (b) 100 °C, (c) 110 °C, (d) 120 °C, and (e) 130 °C.

tional to the reciprocal of applied frequency (*i.e.*, the slope in the plot of $\log \epsilon''$ vs. $\log f$ is exactly -1). When the degree of cure exceeds 0.27, the dielectric loss factor at high frequencies starts to deviate from the straight line, meaning that the epoxy chains and/or networks grow to a certain scale at which the contribution from dipole relaxation becomes detectable within the measured frequency range. As the mixture further reacts and the chains and/or networks become larger, the dipole relaxation time should be longer, which is represented in Figure 5(a) as the dielectric loss peak due to the dipole relaxation shifts toward lower frequencies.

The critical degrees of cure, defined to be the degree of cure at which the contribution of dipole relaxation comes in effect, increase as the isothermal curing temperature is increased; 0.27 for 90 °C, 0.29 for 100 °C, 0.39 for 110 °C, 0.49 for 120 °C, and 0.71 for 130 °C respectively. At these critical degrees of cure, viscosity at each cure condition is almost the same to be about 0.1 Pa·s, indicating the similar mobility. These critical degrees of cure are plotted as a function of curing temperature in Figure 6. When a mixture passes the critical degree of cure, the epoxy chains and/or networks will grow enough to show relaxation behavior within the measured frequency range. From the data given in Figure 6, it can be thought that, at a lower isothermal curing

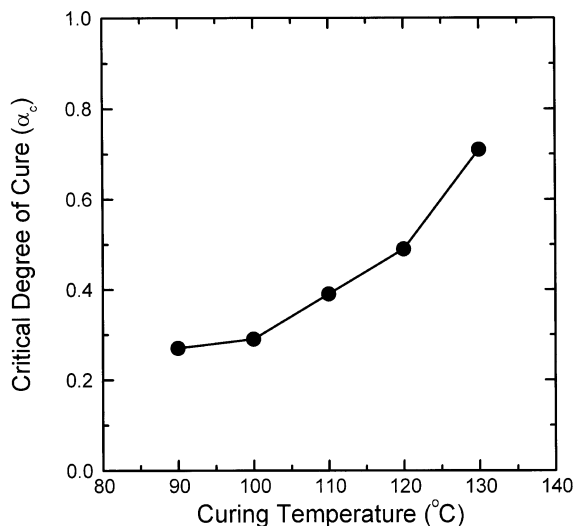


Figure 6. Critical degree of cure as a function of isothermal curing temperature. The critical degree of cure is defined to be the degree of cure at which the contribution from dipole relaxation in dielectric loss factor becomes important.

temperature, larger epoxy chains and/or networks are formed even at the earlier stage of cure compared with a higher temperature curing case: relatively longer linear chains or networks having less branches are preferred at a lower isothermal curing temperature even at the same degrees of cure. Linear polymers generally show higher viscosity than highly branched chains with the same molecular weight mainly due to the larger radius of gyration. The mobility of free ions is thus lower for the linear polymers and the contribution to the ionic conductivity in dielectric loss factor is reduced at a lower isothermal curing temperature. This can be supported by the reactivity difference of epoxy groups with primary and secondary amine groups. The reactivity ratio of secondary amines to primary amines is known far below unity for DGEBA/DDM system,^{12-13,16} and it can be changed with the isothermal curing temperature.^{15,16} The structure of epoxy chains can thus depend on the curing conditions. The structure of epoxy chains and/or networks can also be known by analyzing dipolar motion.

To examine the mobility of epoxy chain segments, the contribution from dipole relaxation was calculated from the measured dielectric loss factor by subtracting the contribution from ionic conductivity. Since the contribution from ionic conductivity is known to be inversely proportional to applied frequency as mentioned earlier (equation (2)), the least square fitted lines were subtracted from the measured dielectric loss factors given in Figure 5. The calculated contribution of dipole relaxation, ϵ''_{dipole} , in the dielectric loss factor is shown in Figure 7 for an isothermal curing at 90 °C. The dielectric relaxation time (τ), which represents the dominant segmental motion of polymer chains,^{17,21-24} was calculated at each cured state by using the Havriliak-Negami model as mentioned earlier (equation (3)). Figure 8 shows the estimated dielectric relaxation time, τ , for each degree of cure at isothermal curing temperatures of 90, 100, 110, and 120 °C. In this figure, we note that the relaxation times of

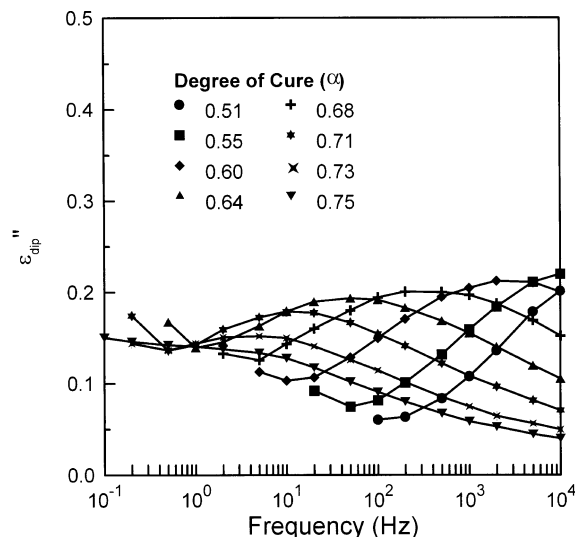


Figure 7. Frequency dependency of the calculated contribution from dipole relaxation in dielectric loss factor, after subtracting the contribution from ionic conductivity, at several cured states at an isothermal temperature of 90 °C.

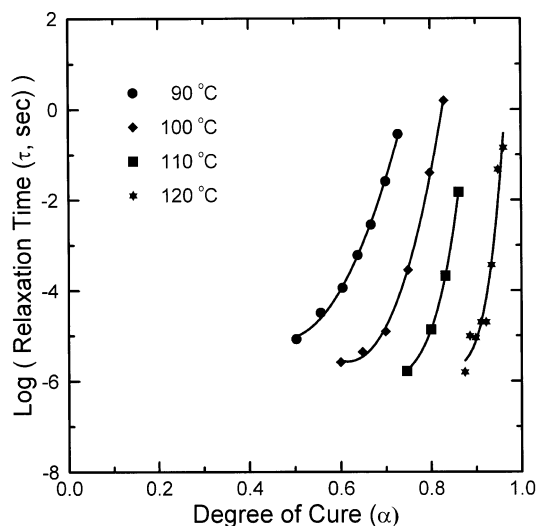


Figure 8. Dielectric relaxation times, estimated from the contribution from dipole relaxation in dielectric loss factor using the Havriliak-Negami model, as a function of degree of cure.

epoxy chains and/or networks estimated at higher isothermal curing temperatures are much smaller at the same degrees of cure. This means that the average length of dangling chains of a network or the average chain length between network junction points showing dominant relaxation phenomenon is shorter and the motion of chain segments is faster when the epoxy mixture is cured at a higher isothermal temperature leading to more compact cured structure.

One might argue that there exists the effect of measuring temperature on the relaxation times shown in Figure 8; the relaxation time of a polymer should be shorter at higher temperature even with the same molecular structure. The measuring temperature effect on relaxation time is, however, hard to directly measure mainly because epoxy resin is a highly reactive system. Since it has been known⁹ that the

temperature dependency of viscosity and dielectric relaxation time is comparable and the activation energies, when expressed with the Arrhenius equation, estimated from both viscosity and dielectric relaxation time have the same order of magnitude for polymers, the effect of measuring temperature on relaxation time can be estimated indirectly from that on viscosity. From our independent measurement of epoxy viscosity at different temperatures, the activation energy was estimated to be approximately 40 kJ/mol and this value is well compared to the reported value.⁷ It has also been known⁷ that the activation energy derived from dielectric relaxation time is nearly constant regardless of the chain length of linear DGEBA epoxy resin implying that the activation energy of the relaxation time can thus be estimated to be about 40 kJ/mol in present study when the effect of measuring temperature on relaxation time is concerned. Figure 8, however, shows that the activation energies of the relaxation times measured at each degree of cure lie between 300 and 500 kJ/mol although limited number of data is available. This value (300-500 kJ/mol) is certainly much larger than the activation energy (40 kJ/mol) only due to the change in measuring temperature with the same molecular structure. The comparison of the two activation energies implies that the structural effect on relaxation time is still quite important. This will be further verified in our forth coming paper dealing with the effect of curing history on dielectric properties measured at the same temperature: the relaxation times at the same degrees of cure become shorter even at the same measuring temperature if the DGEBA/DDM mixture is cured partially at the curing temperature higher than measuring temperature.

Summary

The curing characteristics of DGEBA/DDM mixture and effects on dielectric responses were investigated. In temperature scanning mode, the inverse relationship between complex viscosity and ionic conductivity is established indicating that the mobility of free ions and that of chain segments are equivalent before the onset of curing. In early state of isothermal curing, the dielectric loss factor is inversely proportional to applied frequency since the contribution from ionic conductivity is dominant. As the curing reaction further proceeds, however, the contribution from dipole relaxation comes into effect due to the decreased mobility of free ions and the larger size of epoxy chains/networks. The critical degrees of cure, defined to be the degree of cure above which the contribution from dipole relaxation becomes important, increased as isothermal curing temperature was increased. We also observed that the dielectric relaxation time estimated from

the dipolar contribution is also much shorter for higher curing temperature at the same degree of cure. We believe that this difference in dielectric responses originates from different cured structures obtained by changing curing temperatures, implying that the different reactivity of primary and secondary amines with epoxy affects the cured structure by varying curing temperature.

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