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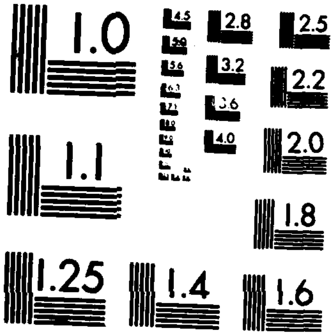
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WLF MODEL FOR CONDUCTIVITY CHANGES DURING EPOXY/AMINE CURE

by

Sue Ann Bidstrup, Norman F. Sheppard, Jr.,
and Stephen D. Senturia

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

DGEBA epoxy resin is cured isothermally with an aromatic amine hardener, and ionic conductivity is measured as a function of frequency, reaction time and cure temperature. At specific stages in the cure, small samples from the reacting mixture are quenched and then analyzed for the glass transition temperature by differential scanning calorimetry. The behavior of conductivity with the changing glass transition temperature during isothermal cure is found to be consistent with the WLF behavior of a series of neat epoxy resins of various glass transitions but with changing temperature.

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INTRODUCTION

The use of ionic conductivity measurements to monitor the cure of thermosetting polymers dates back to the pioneering work of Kienle and Race [1] in 1934. For epoxies, Fava [2] proposed that sodium and chloride ions are the charge carriers, the origin of these ions being the reaction used to synthesize the epoxy resin. Assuming that the concentration of these ionic impurities does not change during cure, the changes in conductivity can then be interpreted in terms of changes in ion mobility. This in turn is related to the mobility of polymer chains. Hence, the presence of these ionic impurities may actually provide a useful probe to monitor the cure of the resin system. A better understanding of the relationship between ion mobility and structural changes during polymerization would be of considerable value in the application of conductivity measurements to the processing of epoxies.

The Williams-Landel-Ferry (WLF) equation [3], which is widely used to describe the temperature dependence of mobility-related material properties, has the form

$$\log a_T = \frac{C_1(T-T_s)}{C_2 + (T-T_s)} \qquad (1)$$

where the shift factor a_T is defined as the ratio of the property of interest at temperature T to the same property at reference temperature T_s, often taken to be the glass transition temperature T_g. C_1 and C_2 are constants, originally thought to have universal values, but it is now accepted that these constants are material dependent. A number of workers [4-7] have described the viscosity of thermosetting polymers by incorporating the cure dependence of T_g into the WLF relation. Since viscosity and resistivity (the reciprocal of conductivity) are correlated prior to gelation, one might expect that the conductivity also tracks polymer mobility through a WLF equation. This has led us to propose a WLF model for the conductivity changes during epoxy cure, based on measurements of the temperature dependence of epoxy resins without hardener [8-10].

This work demonstrated the use of a WLF equation to model the temperature dependence of the conductivity in a homologous series of DGEBA epoxy resins of varying molecular weights. Figure 1 is an Arrhenius plot of the ionic conductivity σ for the DGEBA resins. The apparent activation energy for conduction increases with decreasing temperature, characteristic of behavior described by the WLF equation. Analysis of this data revealed that while the WLF constant C_1 is relatively independent of the molecular weight of the resin, the C_2 constant and the reference conductivity $\sigma(T_g)$ are material dependent. By expressing this material dependence in terms of a simple linear dependence on the T_g of the material, a pseudo-WLF equation was constructed to describe the conductivity of the epoxy resins in terms of T and T_g. Using an empirical kinetic model relating T_g to cure time, Sheppard [8,10] used this WLF relation to model ionic conductivity changes during the cure of DGEBA resin with a tetrafunctional amine. However, a simultaneous measurements of both T_g and ionic conductivity changes during polymerization are needed to refine the WLF model for curing systems.

In this study, a low molecular weight epoxy resin is cured isothermally with an aromatic amine hardner, and the conductivity is measured as a function of reaction time and cure temperature. At specific stages in the cure, small samples from the reacting mixture are quenched and then analyzed for the glass transition temperature by differential scanning calorimetry (DSC). In this manner, the change in dielectric properties can be directly correlated with the build-up of network structure during polymerization. The ionic conductivity is modeled as a function of the cure temperature and T_g using a WLF relation.

EXPERIMENTAL

The system used for this study consists of diglycidyl ether of bisphenol A (DGEBA) cured with 4,4' diaminodiphenyl sulfone (DDS). Commercial grade DGEBA was obtained under the trade name DER 332 (Dow) and was purified by recrystallization. The curing agent DDS was used as received (~99% purity) from the Aldrich Chemical Company. Samples were prepared by mixing purified DGEBA crystals with a stoichiometric amount of DDS. The mixture was then heated in a 120°C oil bath, and stirred rapidly for approximately one minute until both components are dissolved. Then the sample was quickly removed from the oil bath and quenched in an ice bath. Samples were used immediately after preparation.

The dielectric measurements were performed using a Micromet Instruments Eumetric System II Microdielectrometer, which utilizes a silicon integrated circuit sensor having a comb electrode pattern, amplifying circuitry and a semiconductor diode for temperature measurement [11]. The electrode area of the microdielectrometry sensor is 2 x 3.5 mm. A single drop of the epoxy-amine material was placed on the dielectric sensor surface. In addition, small amounts (10-20 mg) of epoxy-amine sample were loaded into hermetically sealed aluminum DSC pans. The sensor and DSC pans were placed into a tray, and then inserted in a Carver Model 2518 hydraulic lab press preheated to the cure temperature. The cure is performed under a blanket a nitrogen. The permittivity ε' and the dielectric loss factor ε'' were measured at even decades of frequency over a range of 1 - 10,000 Hz throughout the cure. The conductivity σ was determined from the loss factor using the relation,

$$\varepsilon'' = \sigma/\omega\,\varepsilon_0 \qquad (2)$$

where ω is the angular frequency and ε_0 is the permittivity of free space, evaluated at frequencies where a log-log plot of loss factor versus frequency has a slope of -1. In addition, at various stages in the reaction, some of the DSC pans were removed from the press, and quenched by placement in a -20°C freezer. The T_g for these quenched samples was determined using a Perkin-Elmer DSC 4 with a scan rate of 10°C/min.

RESULTS AND ANALYSIS

Figure 2 presents the ionic conductivity versus cure time at isothermal cure temperatures ranging from 145°C to 173°C. This behavior is similar to that reported previously [8-10]. At the start of cure, σ increases with increasing temperature. During cure, σ decreases slowly at first, then more rapidly. As the cure proceeds, an inflection point is observed, which marks the slowing of the cure reaction. The shapes of the curves at different temperatures are similar, but accelerated in time at higher cure temperatures. The Tg data from the DSC analysis at various cure times for isothermal cures ranging from 145°C to 173°C are shown in Figure 3. The correlation between the measured values of σ and T_g are shown in Figure 4.

The goal of this work was to investigate whether the cure data of Figure 4 would obey a WLF equation similar to that found for the temperature dependence of σ in non-curing neat epoxies. For the series of neat epoxy resins with varying molecular weight, Sheppard [8, 10] has found that the ionic conductivity can be modeled with a pseudo-WLF equation assuming a linear dependency of C_2 and $\log \sigma(T_g)$ with T_g. Therefore, the WLF relation (Equation 1) can be rewritten:

$$\log a_T = \log \sigma(T) - [C_5 + C_6 T_g] = \frac{C_1 (T - T_g)}{C_3 + C_4 T_g + (T - T_g)} \qquad (3)$$

where $C_5+C_6T_g$ replaces $\log \sigma(T_g)$ and $C_3+C_4T_g$ replaces C_2. The data of Figure 4 were fit to Equation 3 by a nonlinear least-squares method. The resulting WLF constants are shown as the right hand column of Table 1. The corresponding constants obtained from Sheppard's neat-epoxy data of Figure 1 are shown in the left-hand column. The agreement between the WLF constants is not good; however, because of the large number of constants and the form of the WLF equation, it turns out that the least-square fitting procedure is relatively insensitive to simultaneous variations of several parameters. To illustrate this, the least-square fit of the WLF equation to the cure data is shown in Figure 5 along with a single curve (the dashed line) calculated from the set of constants for neat epoxies, evaluated at 145°C. The neat-resin WLF equation comes close to the curing data at 145°C; hence, the numerical variation between the sets of WLF constants is not of great significance. Further work is clearly required before the specific values of constants obtained from these cure experiments can be given physical significance. As a step in that direction, experiments are in progress to measure $\sigma(T_g)$ directly, which will clarify the C_5 and C_6 values independent of the remaining constants.

The principal conclusion is that the behavior of $\sigma(T, T_g)$ with a changing T_g during isothermal cure is consistent with the WLF behavior of a set of neat epoxies of various T_g but with changing temperature. This not only supports the validity of using a WLF approach for analyzing the data, but demonstrates that forms like Equation 3 can be used to model both the temperature and glass transition temperature dependences of curing systems, making the conductivity a useful probe for process monitoring and control.

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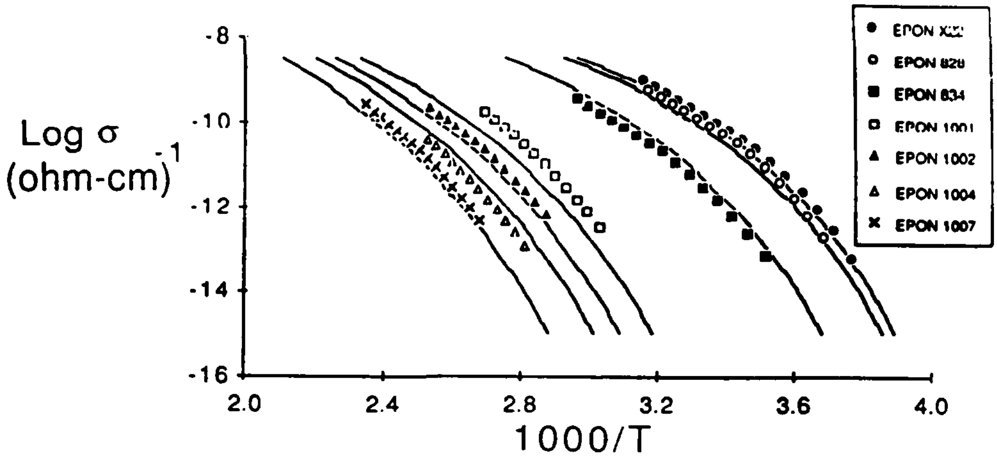

Figure 1. Arrhenius plot of the conductivity of DGEBA epoxy resins [10]. Data points represent experimentally measured values; solid curves are the resin WLF equation calculated using the parameters listed in Chart 1.

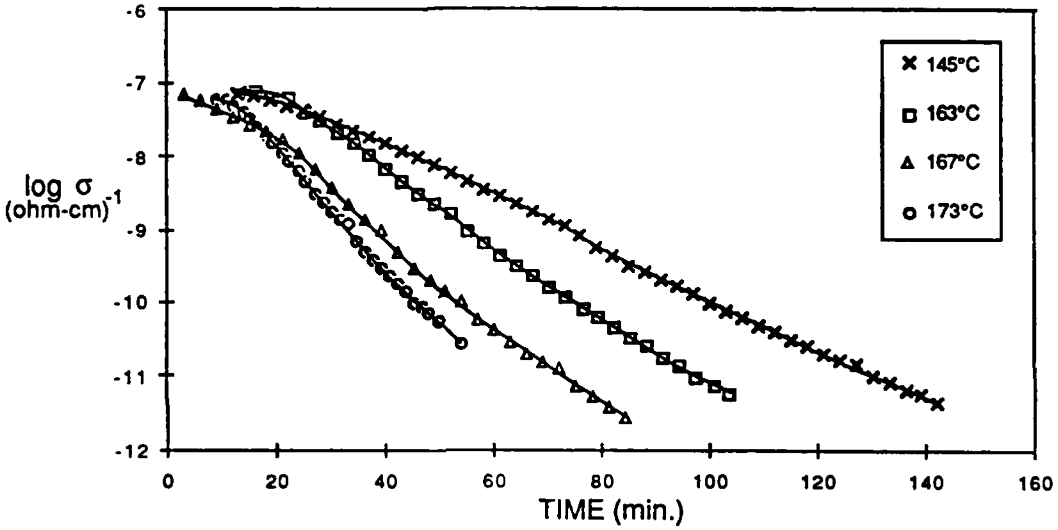

Figure 2. Experimentally measured conductivity versus cure time for DGEBA resin cured isothermally with diamino diphenyl sulfone.

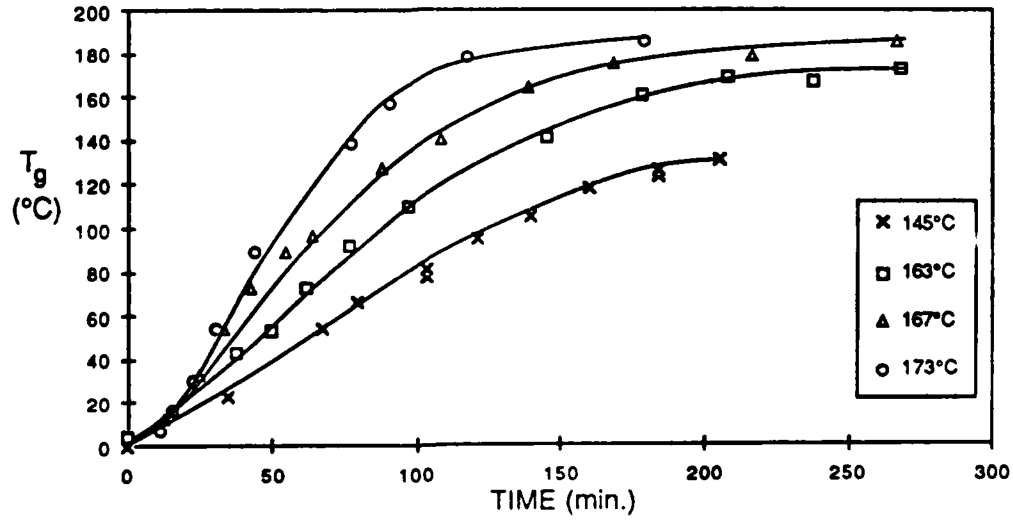

Figure 3. Experimentally measured glass transition temperature versus time for DGEBA resin cured isothermally with diamino diphenyl sulfone

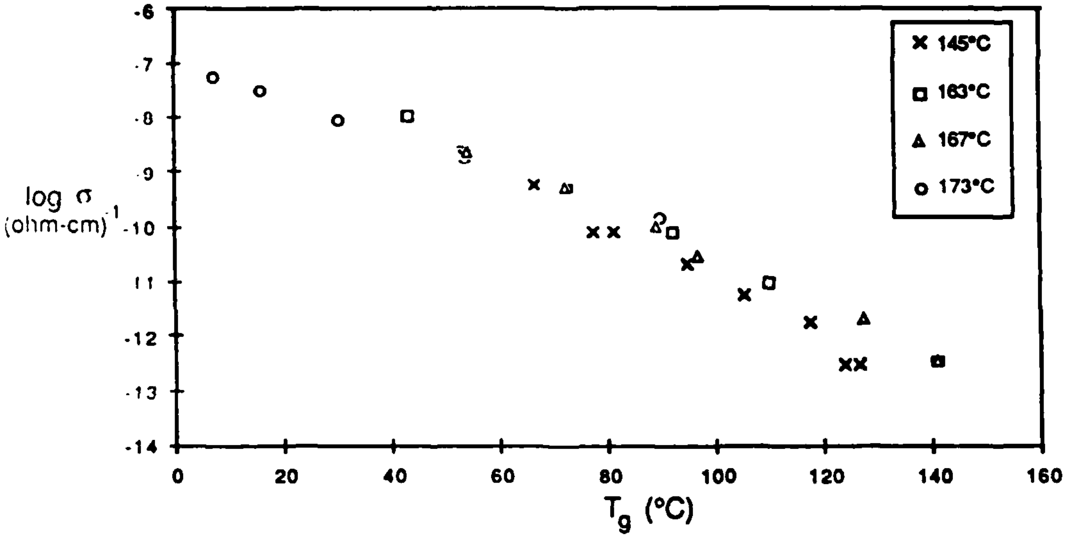

Figure 4. Conductivity versus the glass transition temperature for the DGEBA resin cured isothermally with diamino diphenyl sulfone.

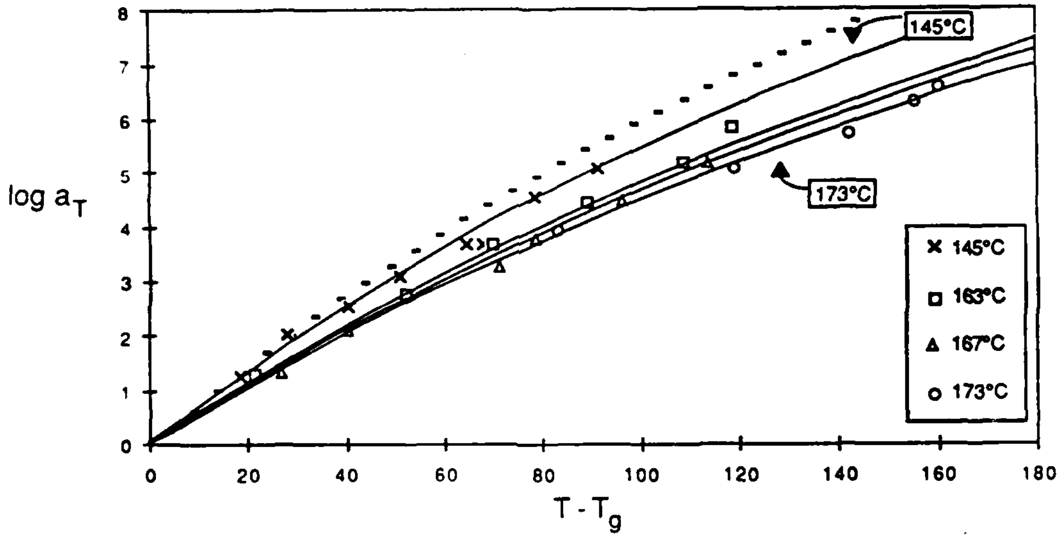

Figure 5. The shift factor versus the difference between the cure and glass transition temperatures, for the DGEBA resin cured isothermally with diamino diphenyl sulfone. Solid curves represent the WLF equation calculated using the cure system parameters listed in Table 1. The model prediction for the epoxy resin system at 145°C is illustrated by the dashed line.

TABLE 1

WLF Constants for Resin and Curing Systems

	RESIN SYSTEM [10]	CURE SYSTEM
C_1	10.5	5.5
C_3	-109	-243
C_4	.58	.77
C_5	-19	-14
C_6	.013	.0004

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