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DIELECTRIC ANALYSIS OF THE CURE OF THERMOSETTING
EPOXY/AMINE SYSTEMS

by

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Dielectric Analysis of the Cure of Thermosetting Epoxy/Amine Systems

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The conductivity of seven epoxy resins of varying molecular weights were studied (without hardener) as a function of temperature. In addition, a low molecular weight resin was cured isothermally with an aromatic amine hardener and the conductivity was measured as a function of cure time. The conductivities of the resins without hardener obey a Williams-Landel-Ferry relation, and by incorporating a cure-dependent glass transition temperature into this relation, the observed behavior of the resin-plus-hardener system can be modeled.
INTRODUCTION

The use of dielectric measurements to monitor the cure of thermosetting polymers dates back to the pioneering work of Kienle and Race in 1934 [1]; a review of the literature may be found in [2]. In 1966, Olyphant [3] recognized that the changes in the dielectric properties during cure are related to the change in the glass transition temperature that accompanies the curing reaction. A better understanding of this relationship would be of considerable value in the application of dielectric measurements to the processing of epoxies.

In this work, the conductivity of seven epoxy resins of varying molecular weights were studied (without hardener) as a function of temperature. In addition, a low molecular weight resin was cured isothermally with an aromatic amine hardener, and the conductivity was measured as a function of cure time. The conductivities of the resins without hardener obey a Williams-Landel-Ferry (WLF) relation [4], and by incorporating a cure-dependent glass transition temperature into this WLF equation, the observed behavior of the resin-plus-hardener system can be modelled.

EXPERIMENTAL

The epoxy resins used were seven commercial samples of diglycidyl ether of bisphenol-A (DGEBA) resins (see Table 1) [5]. The structural formula of DGEBA is presented below, but does not illustrate that the higher molecular weight samples may be branched. Prior to use, the resin samples were heated under vacuum to remove water and other volatiles. The samples for the curing study were prepared by dissolving a stoichiometric
amount of diamino diphenyl sulfone in EPON 825 heated to 120°C, then rapidly cooling the mixture.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CH} \\
\text{O} & \quad \text{CH}_3 & \quad \text{O} & \quad \text{CH}_2 & \quad \text{O} \\
\text{H}_2 & \quad \text{C} & \quad \text{CH}_2 & \quad \text{O} & \quad \text{O} & \quad \text{CH}_2 & \quad \text{O} & \quad \text{CH}_3
\end{align*}
\]

Diglycidyl ether of bisphenol-A (DGEBA)

The dielectric measurements were performed using microdielectrometry [7], which utilizes a silicon integrated circuit sensor having a comb electrode pattern, amplifying circuitry, and a semiconductor diode for temperature measurement. The electrode area of the microdielectrometry sensor is 2 x 3.5 mm, requiring resin samples of less than 10 mg. For resins without hardener, the temperature was increased from approximately T_g-30°C to T_g+70°C in discrete steps of 4°C. At each temperature, the dielectric permittivity and loss factor were measured at 26 frequencies in the range of 0.1 to 10,000 Hz. For cure experiments, the sample was rapidly heated to the cure temperature, and measurements were periodically taken at 0.1, 1, 10, 100, 1000 and 10000 Hz. The conductivity, \( \sigma \), was determined from loss factor, \( \varepsilon'' \), using the relation

\[
\varepsilon'' = \frac{\sigma}{\omega \varepsilon_0}
\]

(1)

where \( \omega \) is the angular frequency and \( \varepsilon_0 \) is the permittivity of free space, evaluated at frequencies where a log-log plot of loss factor versus frequency has slope of -1.
RESULTS

Conductivity of resins without hardener

Figure 1 is an Arrhenius plot of the conductivities of the seven DGEBA resin samples, without hardener. The apparent activation energy for conduction, the slope of log $\sigma$ versus $1/T$, increases as the temperature decreases toward $T_g$. This temperature dependence has been observed in the conductivities of liquids [9] and polymers [10-13], and can be described by the Williams-Landel-Ferry (WLF) equation [4],

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + T - T_g}$$  \hspace{1cm} (2)

This equation has been widely used to model relaxation processes in glass-forming materials near $T_g$.

To determine the empirical constants $C_1$ and $C_2$, the standard WLF test plot procedure [4] was used. The results are presented in Table 1, and were used to draw the solid curves on Figure 1. The $C_1$ constant is independent of the EEW of the resin, with an average value of 10.5. The $C_2$ constant ranges from 30 to 90, increasing with increasing molecular weight. The extrapolated conductivity at the glass transition temperature, $\sigma(T_g)$, is on the order of $10^{-15}$ (ohm-cm)$^{-1}$ and appears to increase slightly with increasing MW of the resin.

Conductivity versus cure time and temperature

Figure 2 presents the log of the conductivity versus cure time at isothermal cure temperatures ranging from 137°C to 177°C. The conductivity at the start of cure increases with increasing temperature, as was observed for the neat resins. During cure, the conductivity 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.
DISCUSSION

**WLF Constants**

The thermal expansion of free-volume has been proposed to account for the behavior described by the WLF equation [4]. In models for ionic conduction, the $C_1$ constant is proportional to a critical free-volume for ion transport [12,13]. The results presented above are consistent with this model, as the charge carriers in all of the epoxy resins are sodium and chloride ions remaining from the synthesis of the resin [14]. Note in Table 1 that while $C_2$ varies considerably, $T_g - C_2$ is a relatively weak function of the molecular weight of the resin, with an average value of 236 K. The difference $T_g - C_2$ is the temperature at which the conductivity appears to go to zero, and is often referred to as the Vogel temperature [15]. The extrapolated conductivity at $T_g$ is also a weak function of $MW$, with an average value of $8 \times 10^{-16} \text{ (ohm-cm)}^{-1}$. The fact that the three parameters, $C_1$, $T_g - C_2$, and $\sigma(T_g)$ describing the conductivity of the epoxy resins without hardener are relatively independent of molecular weight suggests that the conductivity of the curing system can be described by a WLF equation in which $T_g$ is the only cure dependent parameter. The following section presents a model to support this idea.

**Modelling of Cure Data**

Figure 3 illustrates schematically a model for the conductivity of the curing epoxy. First, the kinetics of the epoxy/amine reaction are used to predict the extent of epoxy conversion, $a$, as a function of cure time and temperature. Next, a structure-property relation is used to determine $T_g$ for a given conversion. The resulting $T_g$ is substituted into the WLF equation (Eqn. 2), using the average of the parameters $C_1$, $T_g - C_2$, and $\sigma(T_g)$ determined for the EPON resins.
Reaction kinetics. The reaction of an epoxide with a primary amine curing agent is autocatalytic in nature, and described by the following rate equation [16],

$$\frac{d\alpha}{dt} = (K_1 + K_2 \alpha)(1 - \alpha)^2$$  \hspace{1cm} (3)

where $\alpha$ is the extent of conversion and $K_1$ and $K_2$ are experimentally determined rate constants. In a previous study of the cure kinetics of the resin system used in this work, the rate constants were found to be [17],

$$K_1 = 1.28 \times 10^5 \exp(-72,500/RT)$$

and,

$$K_2 = 2.25 \times 10^4 \exp(-60,000/RT)$$

where the activation energies are expressed in J/mole.

$T_g$ - $\alpha$ relation. Adabbo [18] and Enns [19] have described a model to relate $T_g$ of epoxy systems to conversion. This model takes the form,

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(E_x/E_m - F_x/F_m)\alpha}{1 - (1 - F_x/F_m)\alpha}$$  \hspace{1cm} (4)

where $T_{g0}$ is the glass transition of the unreacted material and $\alpha$ is the extent of conversion. The parameters $E_x/E_m$ and $F_x/F_m$ are, respectively, the ratio in the crosslinked state to that in the unreacted state of the segmental mobility and the lattice energy. The values of $E_x/E_m$ and $F_x/F_m$ were estimated from the curing data to be 0.3 and 0.18, respectively. Work is underway in our laboratory to determine these parameters experimentally. The $T_g$ obtained from Eqn. 4 is used in the WLF equation, as described earlier.

Cure modelling results. Figure 4 illustrates the behavior of the conductivity during isothermal cures predicted by Eqs. 2-4. Comparison to Figure 3 indicates that the model does an excellent job at representing the changes in the conductivity with time and cure temperature, including the increase in slope and subsequent inflection point. The agreement is not
quantitative, however, and there are a number of possible reasons. The parameters used in
the WLF equation are estimates determined from the resins without hardener and at
temperatures within 70° of Tg, while at the start of cure the temperature may be as much as
170° above Tg. The segmental mobility and lattice energy parameters are also estimates, and
the kinetic model (Eqn. 2) breaks down late in cure. While further study is required to refine
each of the component models of Figure 3, the success of the model as a whole demonstrates
the promise of dielectric measurements for process monitoring and control.

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1984; and personal communication
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(1982)


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<th>n</th>
<th>$T_g$(K)b</th>
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a From [6] for n<1, [7] for n>1
b Measured using DSC at 10 K/min.
Figure 1 - Arrhenius plot of the conductivity of EPON epoxy resins. Data points represent experimentally measured values; solid curves are WLF equation calculated using parameters presented in Table 1.

Figure 2 - Experimentally measured conductivity versus time for EPON 825 resin cured isothermally with diamino diphenyl sulfone.
Time Reaction
Temp Conductivity
Figure 3 - Schematic illustration of model used to calculate conductivity during epoxy cure.

Figure 4 - Calculated conductivity versus time using the model of Figure 3, for EPON 825 resin cured isothermally with diamino diphenyl sulfone.