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by

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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.

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DIELECTRIC ANALYSIS OF THE CURE OF THERMOSETTING EPOXY/AMINE SYSTEMS

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INTRODUCTION

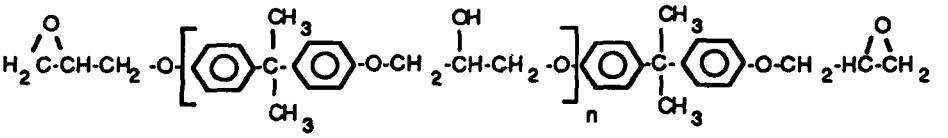
The use of dielectric measurements to monitor the cure of thermosetting polymers dates back to the pioneering work of Kienle and Race in 1934 [1]; a review of the literature may be found in [2]. In 1966, Olyphant [3] recognized that the changes in the dielectric properties during cure are related to 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.



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, σ, was determined from loss factor, ε'', using the relation

$$\varepsilon'' = \sigma / \omega\varepsilon_0 \qquad (1)$$

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 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 σ 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],

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

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

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} $(ohm\text{-}cm)^{-1}$ 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 x 10^{-16} $(ohm\text{-}cm)^{-1}$. 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],

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

where α 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.

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

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

where T_{g0} is the glass transition of the unreacted material and α 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 T_g, while at the start of cure the temperature may be as much as 170° above T_g. 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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REFERENCES

[1] Kienle, R.H. and Race, H.H., Trans. Electrochem. Soc., 65, 87 (1934)

[2] Senturia, S.D. and Sheppard, Jr., N.F., Adv. Polym. Sci., 80, (1986), in press.

[3] Olyphant, Jr., M., Insulation, 13, 37 (1966)

[4] M.L. Williams, R.F. Landel and J.D. Ferry, J. Am. Chem. Soc., 77, 3701 (1955)

[5] Sheppard, Jr., N.F., Ph.D. Thesis, Massachusetts Institute of Technology, 1986, unpublished.

[6] Lee, H. and Neville, K., Handbook of Epoxy Resins, McGraw-Hill, New York, 1967

[7] LeMay, J.D., Swetlin, B.J., and Kelly, F.N., in Characterization of Highly Cross-Linked Polymers, S.S. Labana, ed., American Chemical Society, Washington, D.C., 1984; and personal communication

[8] N.F. Sheppard, D.R. Day, H.L. Lee and S.D. Senturia, Sensors and Actuators, 2, 263 (1982)

[9] Davidson, D.W. and Cole, R.H., J. Chem. Phys., 19, 1484 (1951)

[10] T. Miyamoto and K. Shibayama, J. Appl. Phys., 44, 12 (1973)

[11] K. Arai and A. Eisenberg, J. Macromol. Sci. - Phys., B17(4), 803 (1980)

[12] A. Killis, J-F. LeNest, H. Cheradame and A. Gandini, Makromol. Chem., 183, 2835 (1982)

[13] H. Cheradame, IUPAC Macromolecules, Ed. by H. Benoit and P. Rempp, Pergamon Press, Oxford and New York, 1982.

[14] Fava, R.A. and Horsfield, A.E., Brit. J. Appl. Phys. (J. Phys. D), Ser. 2, 1, 117 (1968)

[15] Vogel,H., Physik. Z., 22, 645 (1921)

[16] Sourour, S. and Kamal, M.R., Thermochimica Acta, 14, 41 (1976)

[17] Sheppard, Jr., N.F., Coln, M.C.W and Senturia, S.D., Proc. 30th SAMPE Symposium, 1243, Reno, NV, April 1985

[18] Adabbo, H.E. and Williams, R.J.J., J. Appl. Polym. Sci., 27, 1327 (1982)

[19] J.B. Enns and J.K. Gillham, J. Appl. Polym. Sci., 28, 2567 (1983)

Table 1 - Epoxy Resin Properties and WLF Parameters

Resin	EEW[a]	n	T_g(K)[b]	C_1	C_2(K)	Log($\sigma(T_g)$)	T_g-C2
EPON X22	172	0	254	10.2	34	-15.7	220
EPON 825	175	0	254				
EPON 828	185	0.2	256	10.3	30	-16.1	226
EPON 834	380	0.6	269	10.1	49	-15.4	220
EPON 1001	490	2.3	315	11.5	92	-14.1	223
EPON 1002	660	3.4	324	10.1	71	-14.7	243
EPON 1004	900	5.1	334	11.3	82	-15.3	252
EPON 1007	1880	12.1	352	10.3	83	-14.5	269
Average				10.5		-15.1	236

a From [6] for n<1, [7] for n>1
b Measured using DSC at 10 K/min.

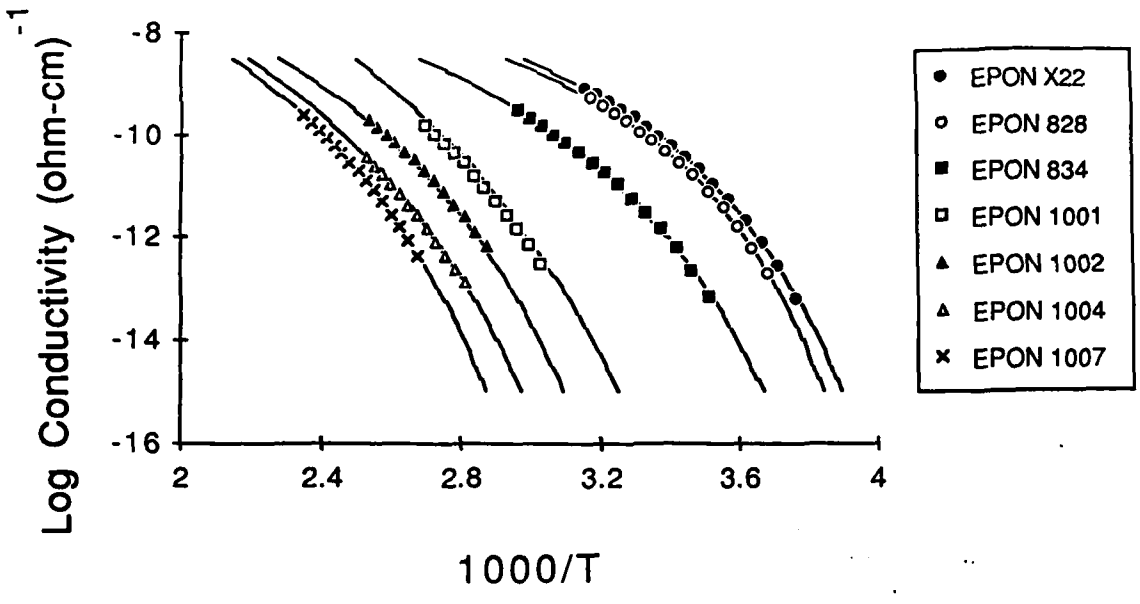


Figure 1 - Arrhenius plot of the conductivity of EPON epoxy resins. Data points represent experimentally measured values; solid curves are WLF equation calculated using parameters presented in Table 1.

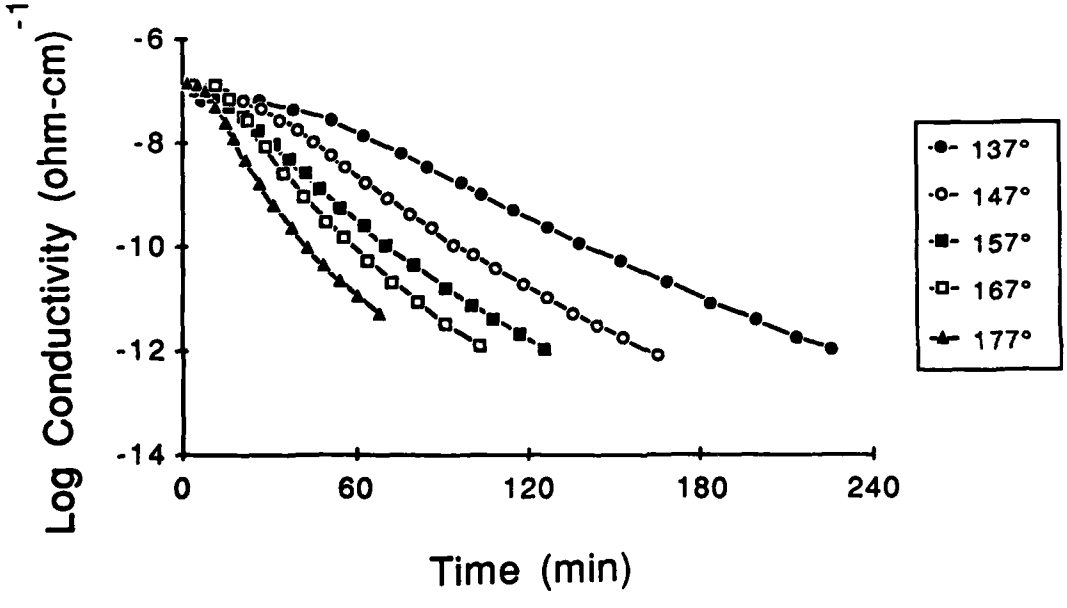


Figure 2 - Experimentally measured conductivity versus time for EPON 825 resin cured isothermally with diamino diphenyl sulfone.

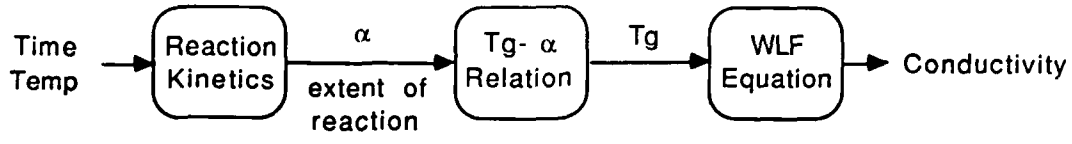


Figure 3 - Schematic illustration of model used to calculate conductivity during epoxy cure.

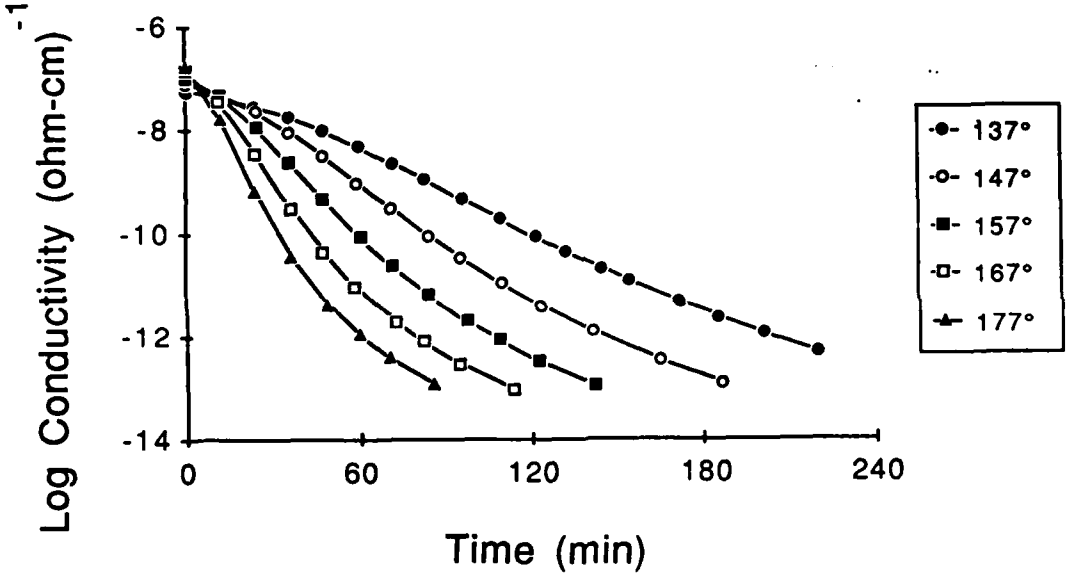
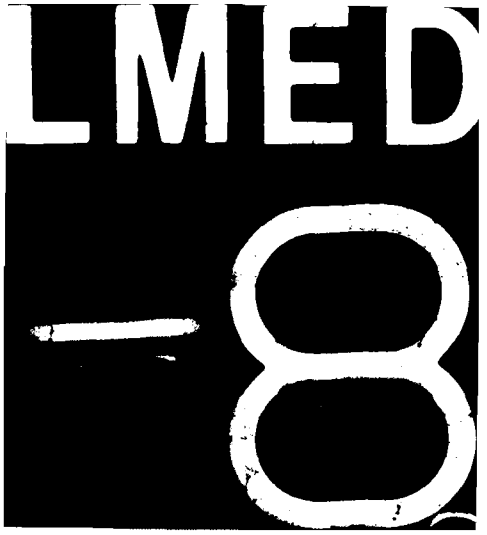


Figure 4 - Calculated conductivity versus time using the model of Figure 3, for EPON 825 resin cured isothermally with diamino diphenyl sulfone.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