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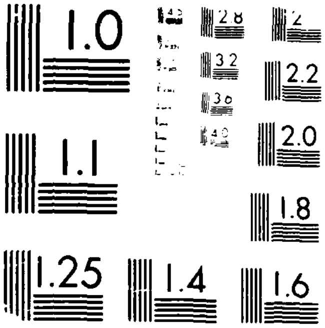

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CORRELATION BETWEEN DIELECTRIC AND STRUCTURAL PROPERTIES DURING EPOXY CURE

by

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

The relationship between the dielectric properties and the molecular structure of a commercial epoxy resin, Ciba-Geigy's MY720, is reported. The ionic conductivity σ was measured at several temperatures by microdielectrometry and correlated with the structural parameter, the glass transition temperature T_g, through a modified Williams-Landel-Ferry formulation where C_1 is a constant and C_2 and $\log \sigma(T_g)$ are assumed to be a linear functions of T_g

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The C_1 constant was found to be equivalent at various temperatures for the MY720 resin, MY720 resin plus curing agent at non-curing temperatures, and a commercial prepreg material (MY720 plus curing agent plus proprietary ingredients). The C_2 value was similar for the first two materials but substantially larger in magnitude for the prepreg material. Comments on these results based on theoretical considerations and problematic experimental procedures are offered.

INTRODUCTION

The measurement of dielectric properties has potential use as an on-line cure monitor for epoxy resins since it is one of the few characterization techniques that can be performed in real time and can follow the complete transformation from liquid resin to a glassy solid [1]. The pertinent literature relating to the dielectric measurements has been reviewed by Senturia and Sheppard [2]. The references on commercial epoxy systems in this review, while containing interesting and valuable insights into monitoring the cure of these epoxies, do not generally discuss the present concept that ionic conductivity is one of the better monitors of the resin cure and ignore the blocked electrode effects caused by these ions. More recent work [3,4] does consider these factors, but the relationship between dielectric properties, structural changes, and mechanical properties has not been established for commercial resin systems. A better understanding of these relationships would be of considerable value in the application of dielectric measurements to process monitoring and control.

Ions are present in epoxy monomers as a residue from the synthesis process. The electrical conductivity σ resulting from these ions can be expressed by the following equation

$$\sigma = \sum_i n_i q_i \mu_i \tag{1}$$

where n_i is the number of ions of species i per unit volume with a charge magnitude q_i and mobility μ_i. For a given system, the ion concentration and ionic charge are fixed and as a result, the conductivity is a function of the ion mobility. The ion mobility, in turn, is a direct function of the polymer segment mobility which decreases as the polymer cures.

There is considerable evidence [5-8] that the Williams-Landel-Ferry (WLF) formulation [9], which was initially developed to relate polymer segment mobility to the material mechanical properties, could also apply to the ionic conductivity. Sheppard and Senturia [2,10] studied the temperature dependence of ionic conductivity for a homologous series of bifunctional epoxy resins (without crosslinker) of varying molecular weight. Analysis of this neat resin data revealed that while the WLF constant C_1 is independent of molecular weight of the resin, the C_2 value and the reference conductivity [log $\sigma(T_g)$] can be represented by a simple linear dependence on the glass transition temperature T_g of the resin. Therefore the WLF relation for ionic conductivity can be rewritten:

$$\log \sigma(T) - [C_5 + C_6 T_g] = \frac{C_1[T - T_g]}{[C_3 - C_4 T_g] + [T - T_g]} \qquad (2)$$

where $[C_5 + C_6 T_g]$ replaces $\log \sigma(T_g)$ and $[C_3 - C_4 T_g]$ replaces C_2. This relation has also been applied to model ionic conductivity changes during the cure of a bifunctional epoxy resin with a tetrafunctional amine [11].

In this study, the relationship between the ionic conductivity and the glass transition temperature was determined for a commercial tetrafunctional epoxy resin first without any additives, then with a curing agent at low non-curing temperatures, and finally under typical curing conditions.

EXPERIMENTAL

Two epoxy systems were used for this study: Ciba-Geigy MY720 resin and a commercial MY720-based prepreg solution. The MY720 resin consists of ~80 % tetraglycidyl diamino diphenyl methane [Fig. 1] plus other by-products and impurities [12]. The prepreg solution contains the MY720 resin, diamino diphenyl sulfone crosslinker [Fig.1], and other proprietary ingredients dissolved in a mixed methyl ethyl ketone-acetone solvent. For studies involving the prepreg solution, the bulk of the solvent was removed by evaporation in an oven at ~29" Hg vacuum and 70°C.

The first set of experiments involved determining the effect of temperature on ionic conductivity. 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. The electrode area of the microdielectrometry sensor is 2 x 3.5 mm. A single drop of the test material was placed on the dielectric sensor surface. The sensor was then place in a gas chromatograph oven preheated to the measurement temperature. The permittivity ε' and the dielectric loss factor ε'' were measured at frequencies ranging from .005 - 10,000 Hz. The conductivity σ was determined from the loss factor, at frequencies where a log-log plot of the loss factor versus frequency has a slope of -1, using the relation

$$\varepsilon'' = \sigma / \omega \varepsilon_0 \qquad (3)$$

where ω is the angular frequency and ε_0 is the permittivity of free space (8.85×10^{-14} Farads/cm). To insure the test material did not change during the experiment due to chemical reaction or degradation, ionic conductivity measurements were performed at temperatures of less than 155°C for the MY720 resin (without crosslinker) and 115°C for the prepreg (with crosslinker). The glass transition temperatures for the MY720 resin and for the prepreg were measured using a Perkin-Elmer DSC 4.

The second experiment involved correlating ionic conductivity changes with changes in the glass transition temperature during the isothermal cure of the MY720-based prepreg material. The cure experiment was performed by placing two microdielectrometer sensors, each covered with a small quantity of the prepreg material, into a small chamber to which a vacuum could be applied. In addition, small quantities (10-20 mg) of the prepreg material were loaded into hermetically sealed aluminum DSC pans. The DSC pans and the vacuum chamber containing the sensor were then inserted in a Carver Model 2518 hydraulic lab press. This press was used only to provide a conveniently shaped and accessible isothermal environment. A typical industrial cure schedule was used. The press temperature was ramped at 3°C per minute to 116°C, and this temperature was held for two hours. Approximately midway into the two hour temperature hold, the dielectric loss factor stabilized and a ~28" Hg vacuum was then applied to the chamber to remove residual solvent from the prepreg material. This vacuum was maintained through the remainder of the cure. After the two hour hold, the temperature was ramped at 3°C per minute and then held at the designated cure temperature. The permittivity ε' and the dielectric loss factor ε'' were measured at even decades of frequency over a range of .1 - 10,000 Hz every five minutes for the entire cure cycle. Ionic conductivity was determined from the loss factor measurements using Equation 3. At particular stages during the cure, several DSC pans were removed from the press and quenched by placement in a -20°C freezer. The glass transition temperature for these quenched samples was measured by DSC. T_g was defined as the midpoint in the DSC transition curve.

RESULTS AND DISCUSSION

The first set of experiments involved measuring the temperature dependence of ionic conductivity for non-curing (i.e. systems where T_g remained constant) epoxy resins. MY720 resin is primarily composed of the tetrafunctional epoxy TGDDM and contains no crosslinker. Hence, it is possible to measure conductivity for this resin at temperatures greater than 120°C without changing the system as a result of crosslinking. The ionic conductivity of MY720 was scanned at temperatures ranging from 0°C to 155°C (Figure 2). The glass transition temperature for this resin was determined to be -7°C as measured by DSC. The best fit, by a nonlinear least squares method, of the data to the WLF relation (Equation 2) is illustrated by the solid line, and the resulting WLF constants are listed in Table I.

The temperature dependence of ionic conductivity was also measured for a commercial MY720-based prepreg material. Since the prepreg contained a crosslinker and hence would react at higher temperatures, the measurement temperature did not exceed 115°C. The results of the temperature scan for the prepreg are shown in Figure 3. The T_g of the prepreg was 1°C as measured by DSC. The solid line in Figure 3 represents the best fit of the data to Equation 2. The resulting WLF constants are listed in Table I.

Previously published values [11] of the best fit WLF constants for a homologous series of diglycidyl ether of bisphenol A (DGEBA) resins are also listed in Table I. The agreement between the WLF constants for the three systems is good, especially considering the large number of constants and the form of the WLF equation. This can be explained by exploring the physical significance of the WLF constants. In application of the WLF model to ionic conduction, the C_1 constant is proportional to the critical free volume for ion transport [2,10]. This value is independent of the resin structure because of the small size of the ionic impurities relative to the resin molecules. Since sodium and chloride ions are the principal charge carriers for all three systems, large differences between best fit C_1 values would not be expected. Through entropic arguments [10], the C_2 value is related to the T_g and the Vogel Temperature T_2 (i.e. the temperature at which the conductivity appears to go to zero). Sheppard [10] approximated the C_2 value as being linearly dependent on T_g. The C_2 values for the MY720 resin and the MY720-based prepreg material show approximately the same T_g dependency. The slight variations in C_2 values MY720 and the DGEBA systems might be accounted for by differences in structure between these two epoxy resins. The log $\sigma(T_g)$ best fit values show the same dependency on T_g for all three systems. However, the magnitude of log $\sigma(T_g)$ at a given glass transition temperature is different. This may be a result of different levels of ionic contamination between the resin systems.

The second set of experiments involved correlating the changes in ionic conductivity with changes in the glass transition temperature during the cure of the MY720-based prepreg material. Two sensors were used at each cure temperature to monitor conductivity during the polymerization. Figure 4 presents ionic conductivity as a function of reaction time at cure temperatures ranging from 157°C to 187°C. Scatter in the data is a result of variation between the measurements of the two sensors. Early in the cure, conductivity decreases very rapidly. As the cure proceeds, an inflection point is observed which marks the slowing of the reaction. The T_g data from DSC analysis at particular stages in the polymerization are shown in Figure 5 as a function of cure time and temperature. The thermal transition in the DSC scans were broad, making accurate determination of T_g difficult. This can be noted in Figure 5 by the scatter in glass transition temperatures obtained for a given reaction time. The correlation between the conductivity and T_g is shown in Figure 6 for each of the cure temperatures. The solid lines represent the best fit of the WLF model, and the constants are listed in Table 2. Note that the conductivity vs. $(T-T_g)$ data at 157°C does not correspond with the behavior observed at the other cure temperatures. This may be the result of a different reaction mechanism occurring at the lower temperature.

As with the temperature dependence of σ for the non-curing systems, the WLF equation accurately models the behavior of the glass transition temperature during the prepreg cure. In addition, the C_1 values for the prepreg cure agree with the values obtained by measuring conductivity for the MY720 resin and prepreg at non-curing temperatures (Table I). This was as expected since the C_1 value should depend only on the size of the ionic impurities. However, the best fit values of C_2 and log $\sigma(T_g)$ for the prepreg cure are significantly different from those reported in

Table I. One possible explanation is that the vacuum applied on the sensor during cure removed some additional solvent which was not removed from the samples in the DSC pans. In this case, the Tg measurements obtained at a particular reaction time (Figure 5) would not necessarily correspond to the conductivity measurements (Figure 4). This would not affect the material-independent C_1 value, but could substantially change the T_g dependent C_2 and log $\sigma(T_g)$ terms. Work is in progress to determine if the sample contained in the DSC pans is exposed to the same conditions as the material on the sensor.

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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., Advances in Polymer Science, **80**,1 (1986).

[3] Gotro, J. and Yandrasits, M., SPE Technical Papers, **33**, 1039 (1987).

[4] Bidstrup, W.W. and Senturia, S. D., SPE Technical Papers, **33**, 1035 (1987).

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

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

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

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

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

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

[11] Bidstrup, S. A., Sheppard, Jr., N.F. and Senturia, S. D., SPE Technical Papers, **33**, 987 (1987).

[12] Hagnauer, G. L. and Pearce, P.J., Effects of Impurities on Hydrolytic Stability and Curing Behavior, in R. Bauer (ed.), "Epoxy Resin Chemistry II", ACS Symposium Series **221**, 190 (1983).

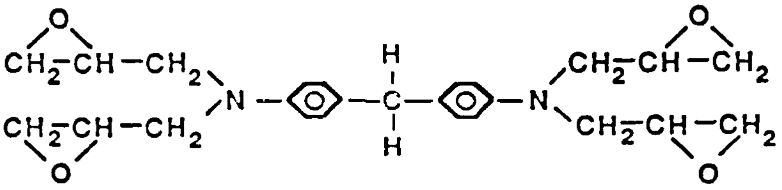
TABLE I
WLF CONSTANTS FOR NON-CURING EXPERIMENTS

	MY720 RESIN	PREPREG MATERIAL	DGEBA RESIN [11]
C_1	10.4	9.5	10.5
C_2	$-141 + .69\ T_g$	$-143 + .68\ T_g$	$-109 + .58\ T_g$
$\mathrm{LOG}\ \sigma(T_g)$	$-18.7 + .013\ T_g$	$-18.0 + .015\ T_g$	$-19.2 + .013\ T_g$

TABLE 2
WLF CONSTANTS FOR CURING EXPERIMENTS

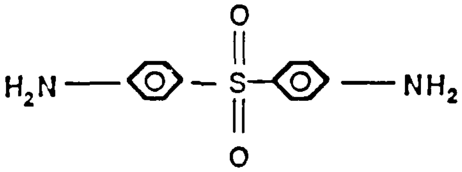
	157°C	167°C	177°C	187°C
C_1	10.0	9.5	9.5	9.6
C_2	$-376 + 1.4\ T_g$	$-594 + 1.9\ T_g$	$-716 + 2.4\ T_g$	$-529 + 1.9\ T_g$
$\mathrm{LOG}\ \sigma(T_g)$	$-21.8 + .022\ T_g$	$-22.0 + .023\ T_g$	$-22.0 + .023\ T_g$	$-21.9 + .023\ T_g$

EPOXY RESIN



Tetraglycidyl Diamino Diphenyl Methane
(TGDDM)

AMINE CROSSLINKER



Diamino-Diphenyl Sulfone
(DDS)

Figure 1. Chemical structure of resin and crosslinker.

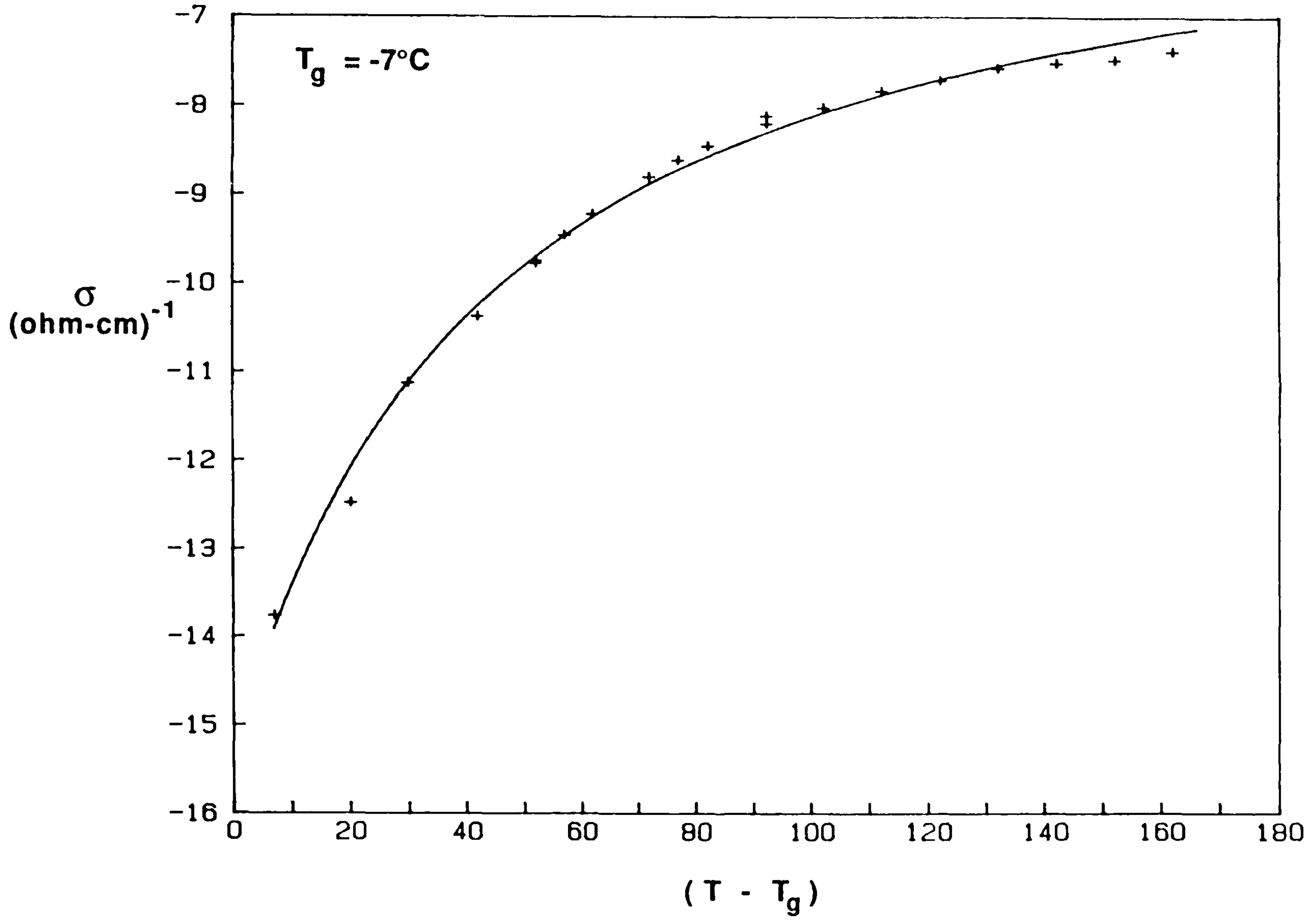


Figure 2. Conductivity versus the difference between the measurement temperature T and the glass transition temperature Tg for MY720 resin.

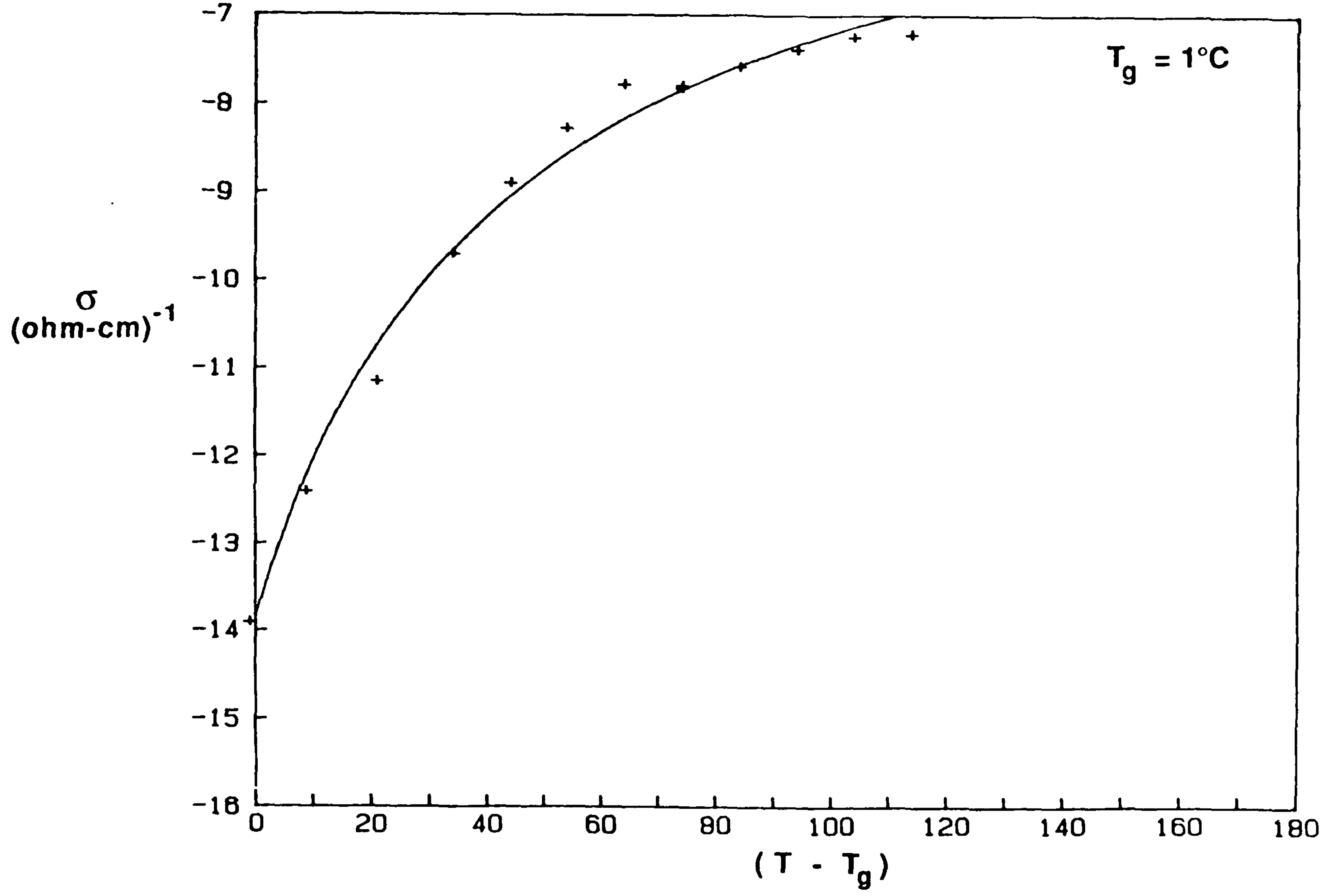


Figure 3. Conductivity versus the difference between the measurement temperature T and the glass transition temperature Tg for MY720-based prepreg material

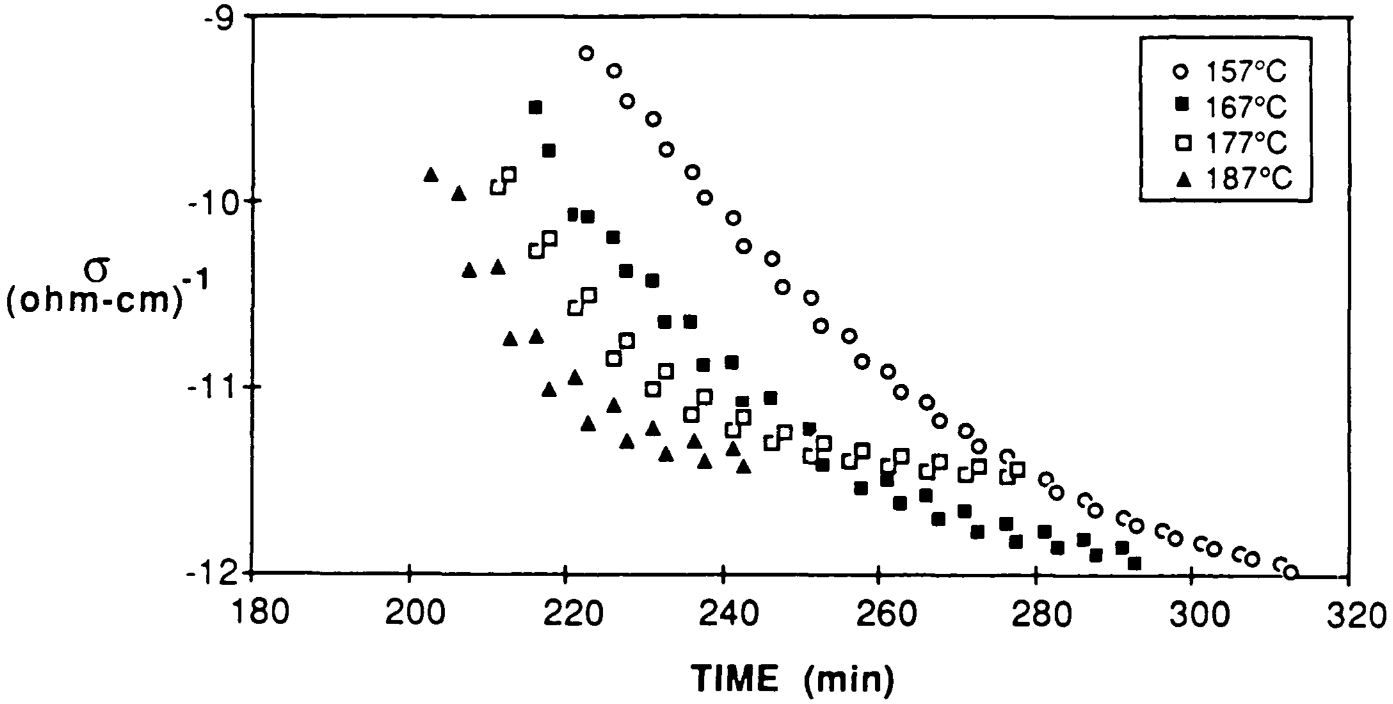


Figure 4. Measured conductivity versus cure time for MY720-based prepreg solution. Cure temperatures range from 157°C - 187°C.

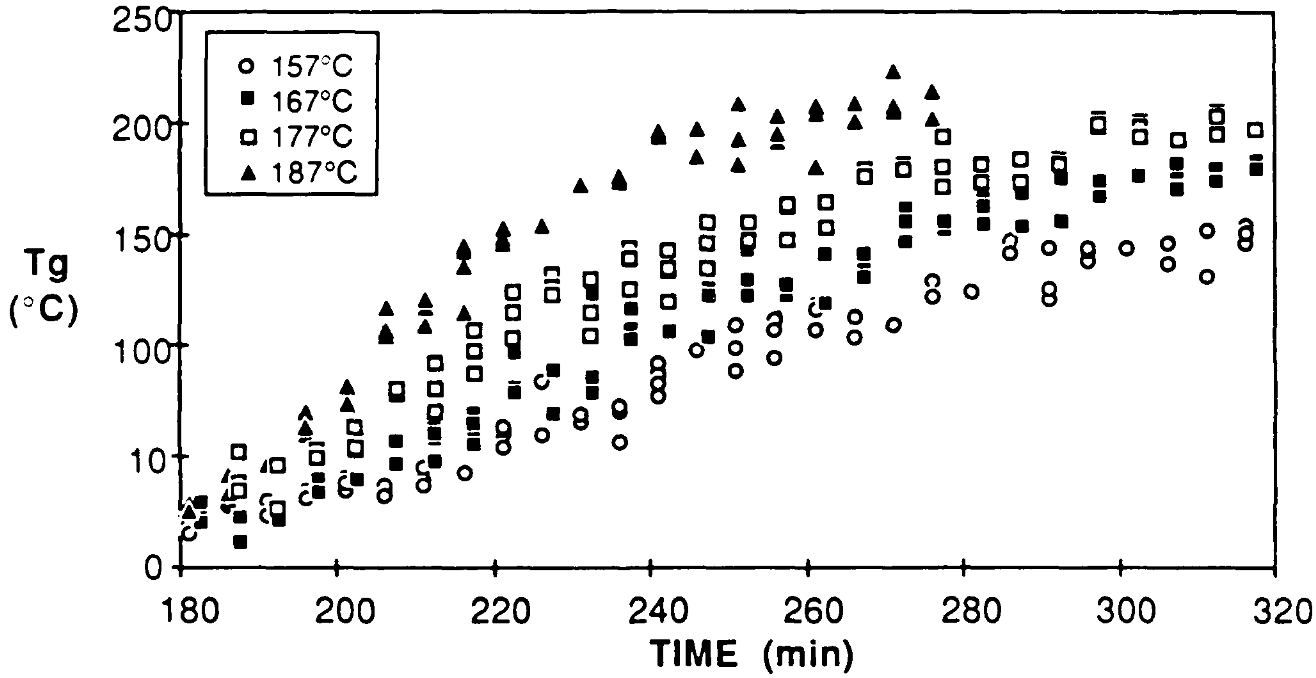


Figure 5. Glass transition temperature versus cure time for MY720-based prepreg solution. Cure temperatures range from 157°C - 187°C.

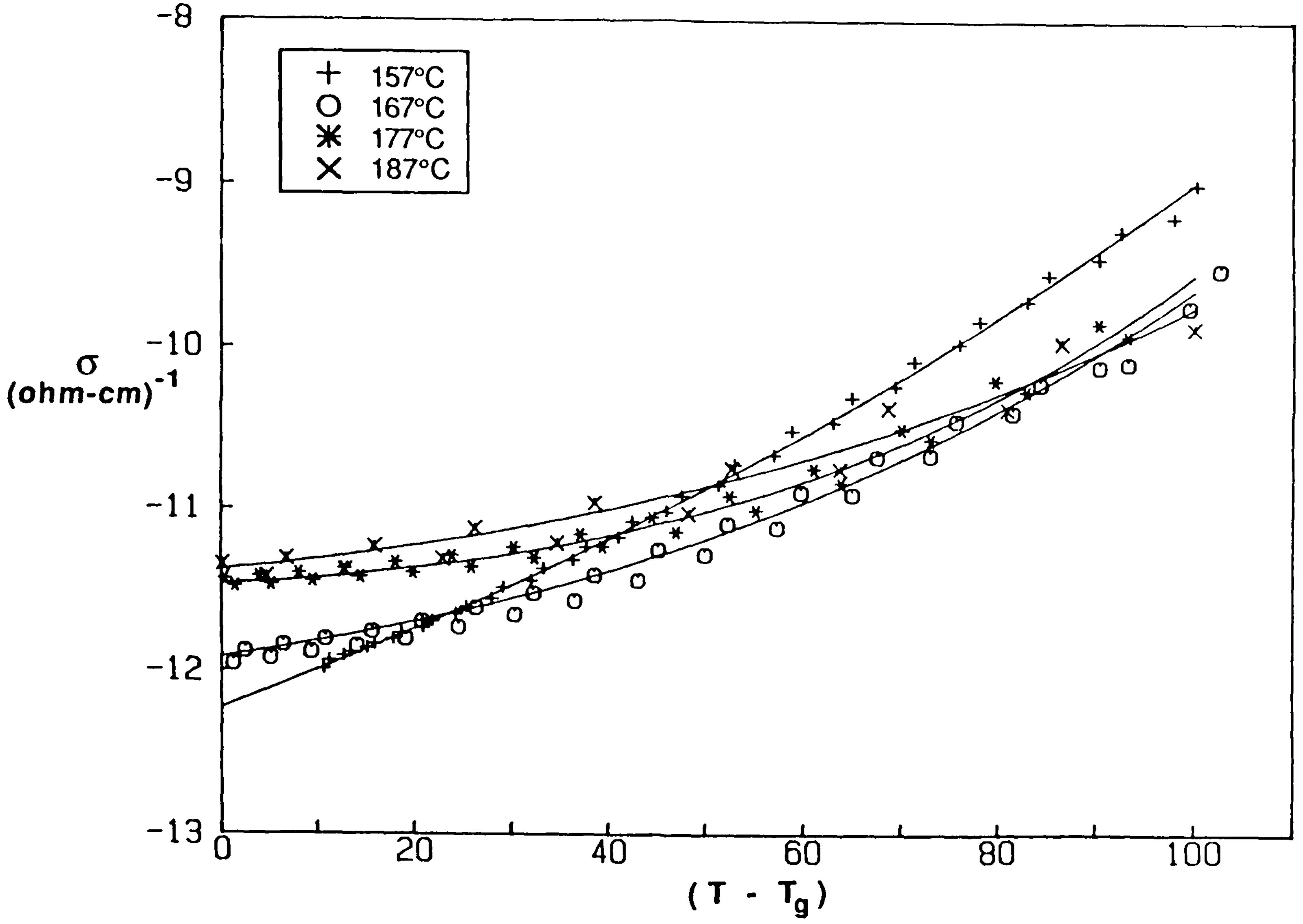


Figure 6. Conductivity versus (T-Tg) for cure temperatures ranging from 157°C - 187°C. The solid line represents the best fit of the WLF equation.

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