

RELATION OF THE CURE-DEPENDENT DIRECTIONAL AND VOLUMETRIC EXPANSIVITY OF 8552/S2 EPOXY + GLASS FIBER LAMINATES TO THE GLASS TRANSITION

Antje Stein, Bryan Bilyeu, and Witold Brostow
Laboratory of Polymers and Composites (LAPOM), Department of Materials Science,
University of North Texas, Denton, TX 76203-5310

Peter Butzloff
Chemical and Process Laboratory, Bell Helicopter Textron, Inc.,
P.O. Box 482, Fort Worth, TX 76101

Rickard Berggren and Vendela von Malmborg
Department of Chemical Engineering, Royal Institute of Technology, Kansli KKT,
Teknikringen 10, 100 44 Stockholm, Sweden

Abstract

The cure-dependent expansivity of a composite 8552/S2 epoxy resin with glass fiber has been investigated by Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA), and Pressure-Volume-Temperature (PVT) techniques. Two glass transition temperature models have been developed as a function of temperature and time. The first model is based on DSC measurements, the second on measurements of the loss modulus in DMA. A comparison of the modeled volume changes of unidirectional and bi-directional laminates was made to determine which approach might be better suited to predict volumetric changes.

Introduction

Glass fiber reinforced epoxy composites are of significant interest to research and to the automotive and aerospace industries. The cure process, which influences the mechanical and thermal properties of epoxy, has been extensively investigated¹⁻¹², but this does not mean that sufficient understanding has been achieved for all applications.

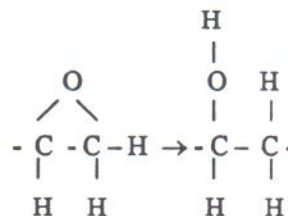
The development of structure-property relationships, including phenomenological models, can be used to model macroscopic changes due to molecular structure changes during cure. These may provide the basis for property optimization in terms of manufacturing parameters.

Several investigators have proposed glass transition temperature-extent of curing relationships¹⁻⁵. Cure temperature and time have been used to quantify the glass transition temperature as related to the extent of cure. Cure has also been related to changes in the free volume¹⁴.

Experimental

Materials

The composite material consists of 8552/S2 sulfone toughened epoxy and 66 weight % of glass fibers. The resin contains a highly reactive epoxy group:



at each end of the low-molecular weight polymer chain. Addition of an amine hardener produces the cross-linking which ensures a rigid structure. Unidirectional glass fibers are added for reinforcement.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry was performed on a Perkin Elmer DSC-7 apparatus to determine the cure-dependent glass transition temperature T_g . The uncured samples were heated to several cure temperatures: 100, 120, 140, 160 and 180°C at 40 K/minute, then held at a given temperature from 5 to 750 min. The samples were then cooled to 20°C at 40 K/min. A second scan was performed at 5 K/min to 250 °C to determine the glass transition temperature by the onset method.

Dynamic Mechanical Analysis (DMA)

The DMA equipment used was a Rheometrics Solid Analyzer model RSA-2. The test material was conditioned at isothermal temperature. The Glass Transition Temperature (T_g) was measured by Dynamic Mechanical Analysis (DMA) at 10 radians/second and at 10K/minute in 3-point bending at 0.1% strain with a strain offset of 5% displaced normal to the fiber reinforcement at the crosshead. The temperature of the loss modulus maximum was taken as the T_g , and the average of five determinations was used to determine T_g .

Pressure-Volume-Temperature Technique (PVT)

Measurement of the specific volume of a material as a function of pressure and temperature was performed on the GNOMIX PVT apparatus manufactured by GNOMIX Research, Inc., Boulder, Colorado.

The sample and the confining fluid (mercury) were contained in a rigid sample cell, one end of which was closed off by a flexible metal bellow. A linear variable differential transducer (LVDT) measured the motion of the bellow end as the temperature changed.

The volumetric expansivity of both unidirectional and bi-directional laminates was measured from 35 to 250°C at 4 K/min at isobaric pressures of 10, 15, and 20 MPa after constant pressure was attained.

Results and Discussion

Cure-Dependent Glass Transition Temperature Models

The DSC and DMA data were used to create the glass transition temperature model in the following form:

$$T_{g-\max} = f(\beta_{\max}(t, T)) \quad (1)$$

where $T_{g-\max}$ is the maximum obtainable glass transition temperature for the given isothermal temperature, and β_{\max} is the maximum obtainable extent of cure at the same temperature as limited by diffusion.

Glass transition temperatures vs. \ln time curves for different isothermal temperatures are shown in Figure 1 for DSC while those from DMA are shown in Figure 2. These data were used to calculate the activation energy E_a and the pre-exponential factor Z . The reaction rate follows first-order kinetics, so that the rate of conversion is proportional to the concentration of the uncured material:

$$d\beta_{\max} / dt = k(1-\beta_{\max}) \quad (2)$$

After separating variables, integration and taking the natural logarithms we obtain:

$$\ln \left(\int d\beta_{\max} / f(\beta_{\max}) \right) = \ln k(T) + \ln t \quad (3)$$

The left side of Equation (3) is a function of the conversion β_{\max} , and therefore a direct function of the glass transition temperature $T_{g-\max}$. Thus, Equation (3) can be rewritten as:

$$F(T_{g-\max}) = \ln k(T) + \ln t \quad (4)$$

The glass transition temperature $T_{g-\max}$ will vary at time t_1 for the cure temperature T_1 and with t_2 for the cure temperature T_2 as follows:

$$F(T_{g-\max}) = \ln k(T_1) + \ln t_1 = \ln k(T_2) + \ln t_2 \quad (5)$$

If t_1 and t_2 are the time to reach the same $T_{g-\max}$ (or respectively β_{\max}) at two different isothermal cure temperatures T_1 and T_2 , then the Arrhenius equation (5) may be applied, yielding:

$$\ln t_2 - \ln t_1 = \frac{E}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (6)$$

Equation (6) reveals that the difference between the \ln time to reach the same T_g for two isothermal temperatures is a constant factor a_T :

$$a_T = \ln t_2 - \ln t_1 \quad (7)$$

Given this result, the T_g vs. \ln time plots in Figures 1 and 2 were superposed by shifting all curves horizontally to a reference temperature. Since this operation was successful, we are dealing here with a kinetically controlled regime.

Deviations represent the start of the diffusion-controlled cure reaction. The resulting master curves are shown in Figure 3.

Arrhenius plots of the shift factors a_T vs. the reciprocal cure temperature T were fitted to a straight line, the slope of which is equal to the activation energy E_a divided by the gas constant R . The activation energy E_a and the pre-exponential factor Z of the DCS data yields $E_a = 27$ kJ/mol and $Z = 11$. The DMA data yields $E_a = 32.3$ kJ/mol and $Z = 23.4$.

In Figure 4 we show the glass transition temperatures T_g vs. extents of cure β for both methods are shown. The extent of cure was determined by use of the assumption of a one-to-one relationship between T_g and β :

$$\beta = 1 - \frac{T_{g\text{ ult}} - T_{g\text{ i}}}{T_{g\text{ ult}} - T_{g\text{ 0}}} \quad (8)$$

where $T_{g\text{ i}}$ is the instant glass transition temperature of reacting material, and $T_{g\text{ ult}}$ is the final glass transition temperature of the fully cured material. $T_{g\text{ 0}}$ is the glass transition temperature of the uncured material.

In Figure 4 the same linear relationship between $T_{g\text{ max}}$ and $\beta_{\text{ max}}$ for both methods is apparent as cure-dependent T_g model:

$$T_{g\text{ max}} / [\text{K}] = 205 * \beta_{\text{ max}} + 273 \quad (9)$$

To obtain the time-temperature-dependent T_g model, Equation (2) has been rearranged so as to express the extent of curing $\beta_{\text{ max}}$ explicitly:

$$\beta = 1 - \exp(-k(T)t) \quad (10)$$

By inserting Equation (10) into Equation (9), we obtain the following T_g model:

$$T_{g\text{ max}} / [\text{K}] = 205 (1 - \exp(-k(T)t)) + 273 \quad (11)$$

Figure 4 also reveals that this linear relationship between $T_{g\text{ max}}$ and $\beta_{\text{ max}}$ extends into the diffusion-controlled regions.

The modified form of the DiBenedetto relation^{6,13} for temperature and T_g normalized diffusion in reactive epoxy systems was found to be applicable for a comparison of changes of T_g to volumetric changes:

$$D = \frac{T_{g\text{ ult}} - T_{g\text{ max}}}{T_{g\text{ ult}} - T_{g\text{ 0}}} \quad (12)$$

where D is a diffusion constant.

It is understood that, as molecular mobility decreases during the course of reaction, the reaction rate slows

down¹⁴. The rate of the reaction is considered dependent on the temperature and the free volume. The glass transition temperature is also understood to be directly related to isothermal changes in free volume for a reacting polymer.

When $T_{g\text{ max}}$ is plotted against temperature in Figure 5, the characteristic extent of reaction, as limited by diffusion control, is seen to be a transition function and is not linear with temperature.

When the change in isothermal T_g with time is calculated, (dT_g/dt) , this reaction rate for DMA or for DSC based T_g can be subsequently normalized for each isothermal temperature data set.

The use of a normalized T_g reaction rate therefore permits each incremental reaction rate to be modified by the diffusion coefficient D , reflected by the change of D with temperature, to generate an apparent $T_{g\text{ app}}$ as follows:

$$T_{g\text{ app}} = T_{g\text{ sum}} / (1-D) \quad (13)$$

$T_{g\text{ app}}$ is substituted for T_g in the normalized reaction rate T_g model to determine the incremental normalized T_g reaction. This increment is denormalized by use of the Arrhenius relation of the rate factors for temperature, and the incremental result is added to the current T_g value.

$$T_{g\text{ sum}} = \Sigma (dT_g / dt) \quad (14)$$

DSC-based diffusion analysis applied to the cure reaction by use of the maximum cure at constant temperature also permits the determination of the diffusion constant (D). The logarithmic time corrected correspondence between cure and T_g may then be represented by the relation of the diffusion coefficient:

$$D = \frac{\beta_{\text{ ult}} - \beta_{\text{ i}}}{\beta_{\text{ ult}} - \beta_{\text{ 0}}} \quad (15)$$

where β_0 is the extent of cure of the unreacted material ($\beta_0 = 0$) and $\beta_{\text{ ult}}$ is unity ($\beta_{\text{ ult}} = 1$) by definition for the cured state. The GNOMIX volumetric measure of the instant volume V_i at a given time is similarly found under isothermal conditions by us of the initial volume V_0 , and the final volume V_f as follows:

$$D = \frac{V_f - V_i}{V_f - V_0} \quad (16)$$

If D may be equivalently determined for the equilibrium diffusion resulting from DMA, DSC, or sum total change in volume as measured by GNOMIX, then D may also be used to calculate the percentage volume change under aged or equilibrium isothermal conditions for any temperature.

Under non-equilibrium conditions, the isothermal decrease in volume with time as measured by GNOMIX at low pressures of 20 MPa is most comparable to the function of T_g increase as measured isothermally by DMA at the same temperature and at relatively low frequencies (see Figure 6). This relation is not so good at higher frequencies. A significant constant positive logarithmic time shift is required to make the same comparison for the cure reaction as a function of time, and an even greater correction is required for the determination of T_g by DSC as a function of time.

Conclusions

There is no preference of DSC or DMA for the ability to relate glass transition temperature to volume change for equilibrium isothermal conditions.

The glass transition temperature as determined by DMA at low frequencies was found to be best suited to relate to the non-equilibrium rate of change in volume at low constant pressures as demonstrated by the polymeric epoxy system evaluated due to the minimized time shift factor.

Acknowledgements

We are grateful to Gauri Patankar for her assistance with the DSC measurements, and to Perkin-Elmer Corp. for the equipment and other support.

References

- /1/ J. Gillham, *On the Cure and Properties of Thermosetting Polymers Using Torsional Braid Analysis*, Report for Johnson and Johnson Vision Products, Inc., Jacksonville, FL, 1996
- /2/ C. Guibe and J. Francillette, *Time-Temperature-Transformation Cure Diagrams*, J. Appl. Polymer Sci., 1996, 62, 1941
- /3/ R.A. Venditti and J.K. Gillham, *Anomalous Behavior of Thermosetting Systems After Cure vs. Chemical Conversion*, J. Appl. Polymer Sci., 1995, 56, 1687
- /4/ F.E. Arnold and S.Thoman, *B-Staging of Toughened Epoxy Composites*, International SAMPE Technical Conference, 1996

- /5/ G.Wisanrakhit and J.K.Gillham, *The Glass Transition Temperature as a Parameter for Monitoring the Isothermal Cure of an Amine-Cured Epoxy System*, Amer. Phys. Soc., 1990
- /6/ P. Chiou and A. Letton, *Reaction Kinetics and Chemoviscosity of a Thermoset Exhibiting Complex Curing Behavior*, Report for Polymer Science and Engineering Program, Mechanical Engineering Department, Texas A&M University College Station, TX, 1990
- /7/ A.Moroni, J. Mijovic, E.M. Pearce, and C.C. Foun, *Cure Kinetics of Epoxy Resins and Aromatic Diamines*, J. Appl. Pol. Sci., 1986, 32, 3761
- /8/ J. Mijovic, *Cure Kinetics of Neat Versus Reinforced Epoxies*, J. Appl. Pol. Sci., 1986, 31, 1187
- /9/ J. Barton, *The Application of Differential Scanning Calorimetry to the Study of Epoxy Resin Curing Reactions*, J. Adv. Pol. Sci., 1992, 111
- /10/ T.Kamon and H. Furukawa, *Curing Mechanisms and Mechanical Properties of Cured Epoxy Resins*, J. Adv. Pol. Sci., 1986, 80, 173
- /11/ G. Holmes and A. Letton, *Bisphenol-A Bimodal Epoxy Resins. Part I: The Dynamic Mechanical Characterization of a 6300 (340/22,500) Weight Average Molecular Weight System*, Pol. Eng. Sci., 1994, 34, 1635
- /12/ C. W. Wise, W. D. Cook, and A. A. Goodwin, *Chemico-Diffusion Kinetics of Model Epoxy-Amine Resins*, Polymer, 1997, 38, 3251
- /13/ E. A. Turi, *Thermal Characterization of Polymeric Materials (Volume 2)*, Academic Press, New York, 1997
- /14/ A. Ya. Gol'dman, *Prediction of the Deformation Properties of Polymeric and Composite Materials*, Amer. Phys. Soc., Washington, D.C., 1994

Key Words: Epoxy, Glass Transition, Diffusion, and Free Volume

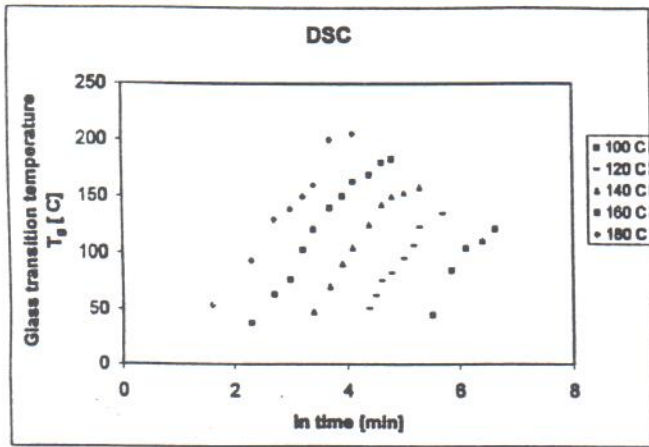


Figure 1: DSC glass transition temperatures dependent on time at several isothermal cure temperatures

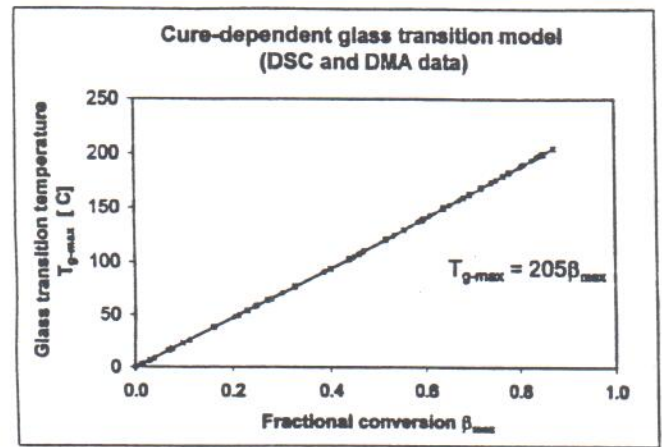


Figure 4: Maximum obtainable glass transition temperature vs. maximum extent of curing at the same isothermal cure temperature

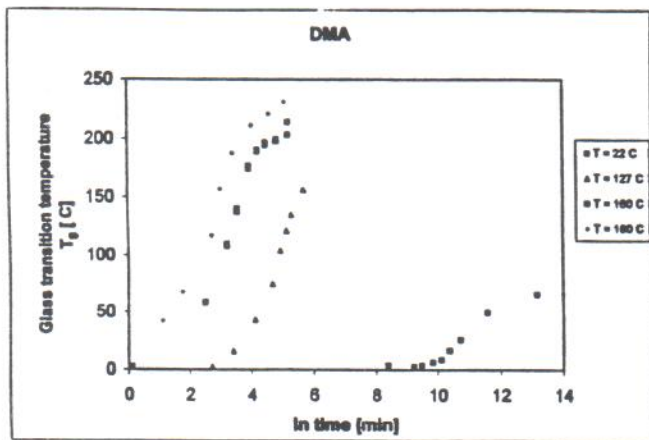


Figure 2: DMA glass transition temperatures dependent on time at several isothermal cure temperatures

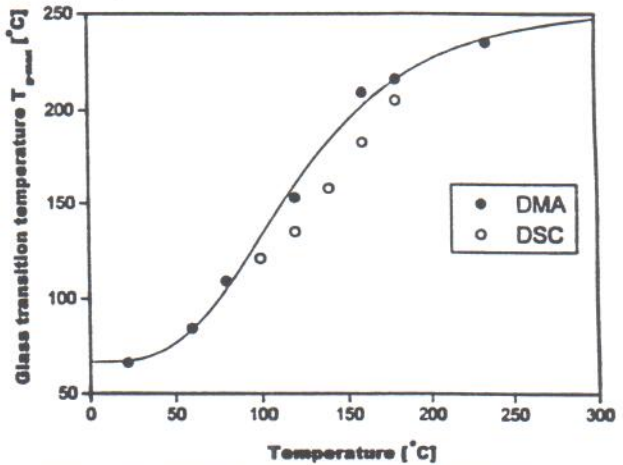


Figure 5: Maximum obtainable glass transition temperatures at several isothermal cure temperatures for DSC and DMA data

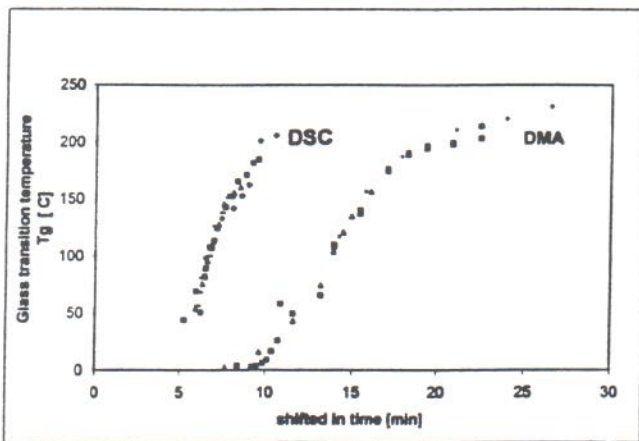


Figure 3: DSC and DMA master curves

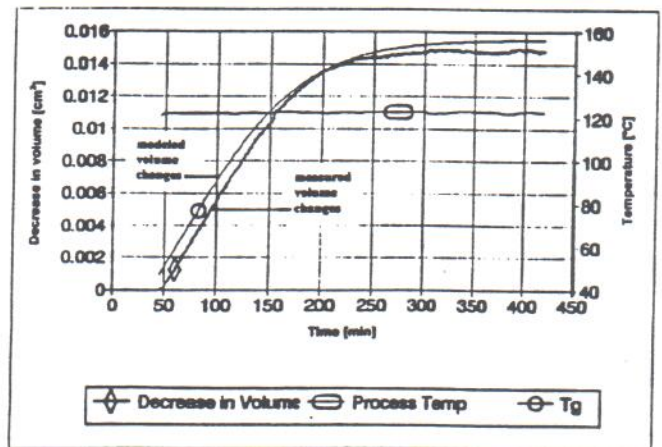


Figure 6: Measured and modeled volume changes vs. cure time (GNOMIX PVT measurements at isothermal cure temperature of 120°C and at pressure of 20 MPa)