

# Volume Changes of an Epoxy Glass Fiber Composite as a Function of Cure and the Glass Transition Temperature

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## Abstract

Temperature and pressure-dependent volumetric changes of the 8552/S2 epoxy + glass fiber composite were investigated under constant conditions (PVT measurements) and related to the cure behavior of the reacting composite. A cure-dependent and, therefore, time-temperature-dependent glass transition temperature model based on measurements in Dynamical Mechanical Analysis and Differential Scanning Calorimetry was developed. Based on the glass transition temperature model and the PVT measurements, a model was created for determining the volume changes during cure. A comparison of the modeled with the measured volume changes was made to confirm the model.

## Introduction

The applied glass fiber reinforced epoxy composite is of significant interest to research and to the aviation and aerospace industries. The cure process, which influences the mechanical and thermal properties of epoxy, has been extensively investigated (1-11), but this does not mean that sufficient understanding has been achieved for all applications.

The development of structure-property relationships, including phenomenological

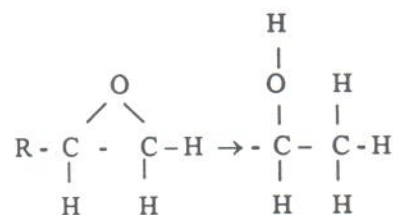
models, can be used to model macroscopic changes due to molecular structure changes during cure. These may provide the basis for property optimization in terms of manufacturing parameters.

Several investigators have proposed glass transition temperature-extent of curing relationships (1-5). 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 volume (13).

## 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. The fibers are orientated either unidirectional or cross-ply (bi-directional).

### *Differential Scanning Calorimetry (DSC)*

Differential Scanning Calorimetry was performed on a Perkin Elmer DSC-7 apparatus to determine the cure-dependent glass transition temperature  $T_{g,c}$ . The uncured samples were heated up to different isothermal cure temperatures of  $T = 100, 120, 140, 160$  and  $180^\circ\text{C}$  at  $40\text{ K/minute}$ , then held constant for cure times ranging from  $t = 5$  to  $750\text{ min}$ . The samples were then cooled down to  $20^\circ\text{C}$  at  $40\text{ K/min}$ . A second heating scan to  $250^\circ\text{C}$  was performed at  $5\text{ K/min}$  to determine the glass transition temperature ( $T_g$ ) by the onset method.

### *Dynamic Mechanical Analysis (DMA)*

Dynamic Mechanical Analysis was performed on a Rheometrics Solid Analyzer model RSA-2. The material was conditioned at isothermal temperatures of  $T = 22, 127, 160$  and  $180^\circ\text{C}$ . The glass transition temperature was measured in 3-point bending mode at a controlled amplitude of  $10\text{ radians/second}$  and at  $10\text{K/minute}$  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  $T_g$ .

### *Pressure-Volume-Temperature Technique PVT*

Measurement of the specific volume of a material as a function of pressure and temperature was performed on the 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 volume changed.

The volume changes of both unidirectional and bi-directional laminates were measured by heating up the uncured samples to isothermal cure temperatures of  $T = 100, 120, 140$  and  $160^\circ\text{C}$  at  $2\text{ K/minute}$  and isobaric pressures of  $P = 10, 20$  and  $50\text{ MPa}$  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  $\beta_{\max}$  is the maximum obtainable extent of cure at the same temperature as limited by diffusion.

Glass transition temperatures vs. In 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 1st-order kinetics where the rate of conversion is proportional to the concentration of the uncured material, as follows:

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

where  $k$  is the rate constant of the chemical

reaction. 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  $\beta_{\max}$ , 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  $\beta_{\max}$ ) at two different isothermal cure temperatures  $T_1$  and  $T_2$ , then the Arrhenius Equation (5) may be applied to yield:

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

where  $E_a$  is the activation energy of the chemical reaction and  $R$  the gas constant.

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

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

The  $T_g$  vs.  $\ln$  time plots in Figures 1 and 2 were superposable by shifting all curves horizontally to a reference temperature. Those data, which appeared to be superposable, represent the kinetically controlled regime.

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

Arrhenius plots of the shift factors  $a_T$  vs. the reciprocal cure temperature  $T$  were fitted with 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 the glass transition temperatures  $T_g$

$$\beta = 1 - \frac{T_{g-ult} - T_{g-i}}{T_{g-ult} - T_{g-o}}$$

vs. extents of cure  $\beta$  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  $\beta$ :

$$(8)$$

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

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

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

To obtain the time-temperature-dependent  $T_g$  model Equation (2) has been rearranged so as to express the extent of curing  $\beta$  explicitly:

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

By inserting Equation (10) into Equation (9) the time-temperature-dependent  $T_g$  model is as follows:

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

Figure 4 also reveals that this linear relationship between  $T_{g-\max}$  and  $\beta_{\max}$  extends into the diffusion-controlled region (14).

When  $T_{g-max}$ , 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 the temperature.

It is understood that as molecular mobility decreases during the course of reaction, the reaction rate slows down (13). 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.

The PVT data were used to create the volume changes model in the following form:

$$\Delta V = f(T, P, T_g(\beta)) \quad (12)$$

by calculating the  $T_g$  by inserting the extent of curing  $\beta$  at any time during the isothermal curing process into the  $T_g$  model in Equation (9). The extent of curing  $\beta$  can be calculated as follows:

$$\beta = 1 - \left[ \frac{(\Delta V_i - \Delta V_{end})}{(\Delta V_{max} - \Delta V_{end})} \right] \quad (13)$$

where  $\Delta V_i$  are the instant volume changes of partially cured material at different cure times,  $\Delta V_{end}$  are the volume changes of the maximum cured material at particular isothermal cure temperatures and  $\Delta V_{max}$  are the volume changes at reaching the isothermal cure temperature.

In Figure 6 the normalized volume changes  $\Delta V/V_0$  are plotted vs.  $T_g$  and pressure for the example of the bi-directional laminate at the cure temperature of  $T = 120^\circ\text{C}$ . Since  $T_g$  is temperature dependent, as demonstrated in Equation (11), the axis  $T - T_g$  expresses this interaction.

By fitting the curves for unidirectional as well as cross-ply laminates we obtain the following volume changes model:

$$\Delta V / V_0 = -0.0037 - 2 \cdot 10^{-4} \cdot P + 1.25 \cdot 10^{-4} \cdot T + C(T - T_g) \quad (14)$$

Below the glass transition, the coefficient  $C$  amounts to 1.6 while at and above the glass transition it equals to zero as apparent in Figure 6 as a flat curve. At the glass transition the curve has a kink.

The initial volume is calculated by dividing the initial mass of the composite by the density  $\rho$ , which amounts to  $\rho = 1.818 \text{ g/cm}^3$  for unidirectional laminates and to  $\rho = 1.873 \text{ g/cm}^3$  for bi-directional laminates.

For the model confirmation, in Figure 7 the modeled and measured volume changes are compared at the isothermal cure temperature of  $T = 120^\circ\text{C}$  and at the pressure of  $P = 20 \text{ MPa}$ , which apparently reveals the conformity of model and experiment.

## Conclusion

The glass transition temperature is a suitable materials property for determining the volume changes during cure of the 8552/S2 epoxy + glass fiber composite.

There is no preference of DSC or DMA for the ability to relate the glass transition temperature to the volume changes under 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 Bryan Bilyeu and Gauri Patankar for performing the DSC measurements, and to Perkin-Elmer Corp. for the DSC-7 apparatus and other support.

Further, we thank Rickard Berggren and Vendela von Malmborg for performing the Gnomix PVT measurements.

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