

Measuring and Modeling the Rheological Data of Diglycidylether of Bisphenol-A During Polymerization for Finite Element Analyses

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ABSTRACT: Finite element analyses (FEA) of thermosets are often performed on the basis of rheological data for fully cured resin. For the FEA of thermosets during curing, a material model is established and a technique is demonstrated, which allows the rheological data of the linear viscoelastic material to be derived. As the moduli are sensitive to conversion, all measured properties are related to temperature and conversion. Therefore the basis for the rheological data has to be a suitable reaction kinetic. Based on the kinetics shear and compression properties are measured

independently and modeled mathematically with the focus to gain a formulation, which is suitable for FEA. The considered time constants are in the range between one second and one month as these times are relevant for the investigated relaxation times. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1868–1872, 2003

Key words: rheology; computer modeling; viscoelastic properties; resins; curing of polymers

INTRODUCTION

The curing of a filled thermoset leads to internal stress in the compound. This internal stress is caused by shrinkage during polymerization and differences in thermal expansion between filler and matrix. During polymerization of the thermoset, the stress increases because of the shrinkage and at the same time a stress relaxation takes place.

The main aim of this work is to calculate the internal stress of a filled thermoset dependent on both, temperature and conversion rate, by means of FEA during processing and annealing. Therefore a material model of the matrix for FEA is developed to enable such calculations. In dependence of conversion, time and temperature the parameters for the material model are experimentally obtained.

Fundamental for all rheological properties is the conversion of the thermoset. Therefore the reaction kinetics have to be known. For the investigated epoxy resin a suitable reaction kinetic is proposed by Wisanrakkit and Gillham.¹ The basis for this model is a unique relation between conversion and glass transition temperature of the thermoset. In this kinetic the

DiBenedetto^{2,3} equation is used. The formulation of Couchman⁴ provides a simple method to gain the parameters:

$$T_g = \frac{\lambda \cdot x}{1 - (1 - \lambda) \cdot x} \cdot (T_{g\infty} - T_{g0}) + T_{g0} \quad (1)$$

with $\lambda = \Delta c_0 / \Delta c_{p\infty}$, T_{g0} is the glass transition temperature of the uncured thermoset, $T_{g\infty}$ the glass transition temperature of the cured thermoset, Δc_0 the change in the isobaric heat capacity at T_{g0} , and $\Delta c_{p\infty}$ the change in the isobaric heat capacity at $T_{g\infty}$.

For the reaction rate one obtains⁵

$$\frac{dx}{dt} = k \cdot (1 - x)^2(x + B) \quad (2)$$

with the Rabinowich^{6,7} approach:

$$\frac{1}{k} = \frac{1}{k_T} + \frac{1}{k_d} \quad (3)$$

$$k_T(T) = k_0 \cdot e^{(-E/RT)} \quad (4)$$

$$k_d(T, T_g) = k_d(T) \cdot e^{\{[2303 \cdot C_1(T) \cdot (T - T_g)] / C_2 + |T - T_g|\}} \quad (5)$$

$k_d(T)$, $C_1(T)$, C_2 are material-specific parameters.

These equations are the reaction kinetics for an autocatalytic system. They enable a numerical integra-

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tion to calculate the conversion for any thermal history at any time.

EXPERIMENTAL

The materials used in these experiments are a diglycidylether of bisphenol-A (DGEBA) with an epoxy equivalent of 172 g/equivalent and the hardener is an isophorone diamine with an H-equivalent of 43 g/equivalent. The trade names are Ruetapox 0162 (resin) and Ruetadur SG (hardener), respectively, from Bakelite AG (Duisberg-Meiderich, Germany). The stoichiometric mixtures are stirred thoroughly and degassed by means of a vacuum. The cast samples were annealed according to the reaction kinetic to the specified conversion.

According to the Boltzmann superposition principle, it is possible to separate shear and compression properties.

$$\sigma_{ij} = \delta_{ij}s_h + s_{ij} \tag{6}$$

$$s_h = \frac{1}{3} \cdot (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \tag{7}$$

where δ_{ij} is the Kronecker symbol, and s_{ij} the stress deviator.

Therefore the mechanical properties are measured and modeled separately for shear and compression.

Shear properties

The shear properties are measured with a shear Rheometer RMS-800/RDSII from Rheometrics. The frequency range is between 0.01–10 Hz. Dependent on

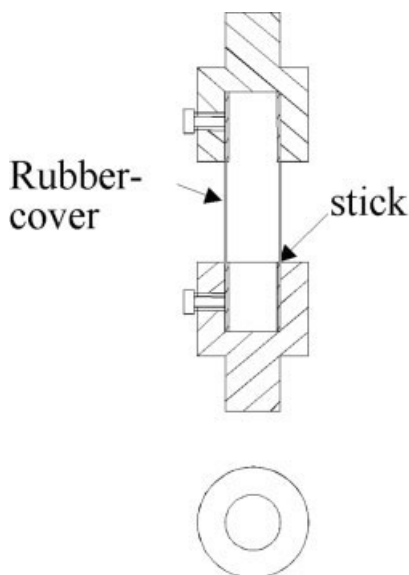


Figure 1 Test device for partially cured samples.

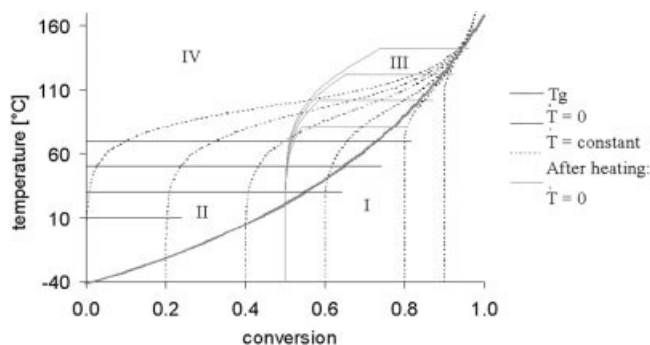


Figure 2 Domains with different reaction rates.

conversion and temperature different geometries of the specimens were used.

For samples below the gel point, a plate–plate assembly is used.

For samples with conversion over 80%, the “standard” geometry 4×10×40 mm³ is used.

For samples with conversions between 50 and 100%, a cylindrical sample with Ø 6 mm and height 10 mm is used (Fig. 1).

The cylindrical samples (Fig. 1) were molded separately in a upper and a lower metal ring and cured to a conversion of 50%. In this state the glass transition temperature is slightly above ambient temperature, so the samples are glassy. Both sides of the sample were mounted in the clamping device of the dynamic mechanical analyzer (DMA) and then glued together. With this procedure it is ensured that the sample is mounted without stress. The glue was an epoxy resin curing at ambient temperature. Dependent on the temperature cycle during the DMA the resin becomes liquid or gelled again. Therefore a rubber envelope was used to guarantee that the geometry is undistorted. The samples were heated up to the required temperature within 5 min and then held at a constant temperature. At the transition of T_g they become liquid again, since the gel point is at about 58% conversion.^{8–10}

The measurement of the complex shear modulus G^* has to be done for specified conversion at different temperatures. Therefore different temperature cycles have to be performed (Fig. 2). The thick grey line shows the glass transition temperature according to DiBenedetto’s equation .

The four different types of lines represent different techniques as to how the shear modulus can be measured, dependent on conversion and temperature. These four domains are as follows:

- I. Domain with material temperature below the glass transition temperature and therefore very small reaction rates ($\ll 1$ %/min). The material exhibits a high shear modulus with only a slight

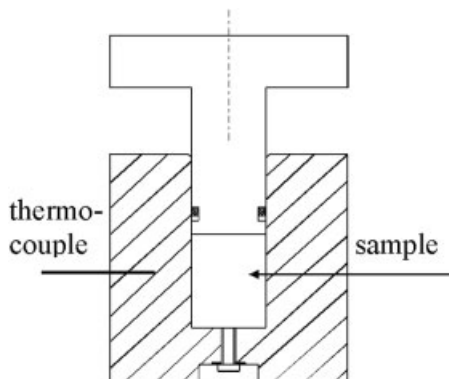


Figure 3 Device for compression testing.

dependence on conversion and can be measured with the cylindrical sample (Fig. 1).

- II. Domain where the material is liquid or gelled. The reaction rate is moderate ($<2\%$ /min). As the shear modulus is low the measurement can be performed isothermally in a plate–plate assembly.
- III. Domain with high reaction rate, and as the material is gelled it exhibits too high a modulus to use a plate–plate assembly but it is still too soft to use the standard geometry. The measurement is performed with the cylindrical sample (Fig. 1).
- IV. Domain with very high reaction rate. With none of the techniques described applicable as the allowed reaction rate is limited to 2% /min.

Compression properties

The compression properties are measured dependent on temperature and conversion in a test device according to Figure 3.

The fully cured samples are machined in a cylindrical shape, placed in the steel cylinder, and evacuated at 10^{-1} mbar. Within the vacuum chamber the remaining volume is filled with silicone oil. The compressibility of the silicone oil and the used resin is quite similar, and due to the low proportion of the oil ($<0.1\%$) the influence can be neglected.

The uncured thermoset can be measured at room temperatures without a considerable reaction rate. For elevated temperatures and higher reaction rates the thermal capacity of the steel is too high for a fast heating. Therefore the properties are estimated by uncured resin without hardener. For low temperatures the modulus for a resin hardener mixture and for pure resin was compared and a correction factor can be established.

The uncured material was filled in the cylinder under vacuum to prevent air inclusion.

RESULTS AND DISCUSSION

Shear properties

The shear properties were investigated for frequencies between 0.01 and 10 Hz at different temperatures and different conversion rates. For the FEA time constants between one second and one month are required. For each specified conversion, the storage and the loss modulus are measured at different temperatures. For thermorheologically simple material behavior, a frequency temperature shift is possible to expand the frequency range. With this technique it is possible to obtain data for frequencies that are not measurable in practice. Figure 4 shows such a shift for a fully cured resin at 160°C .

For modeling shear properties, a generalized Maxwell model is used. The model parameters, the rigidities G_i , and relaxation times λ_i , can be obtained by fitting the parameters according to eq. (8) and eq. (9) to the frequency dependent storage and loss modulus^{11,12}:

$$G' = \sum_{i=1}^n R_i(T_0) \frac{\omega^2 \cdot [a_T \cdot \lambda_i(T_0)]^2}{1 + \omega^2 \cdot [a_T \cdot \lambda_i(T_0)]^2} \quad (8)$$

$$G'' = \sum_{i=1}^n R_i(T_0) \frac{\omega \cdot [a_T \cdot \lambda_i(T_0)]}{1 + \omega^2 \cdot [a_T \cdot \lambda_i(T_0)]^2} \quad (9)$$

The relaxation times are chosen at logarithmic equidistance. The rigidities and the temperature shift factor a_T are obtained for different discrete conversions. To obtain the parameters for any conversion, a suitable interpolation method has been developed.

Figure 5 shows an example for the interpolation method. The shown curves represent a resin with 80% conversion and a fully cured resin. According to eq. (8) and eq. (9), a change in temperature leads to a shift

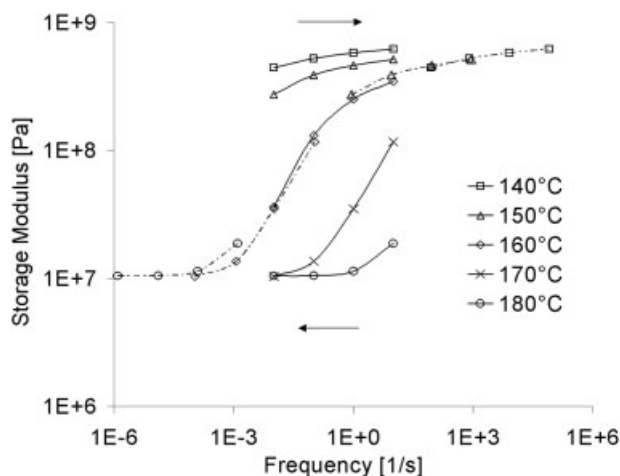


Figure 4 Time-temperature shift for fully cured resin.

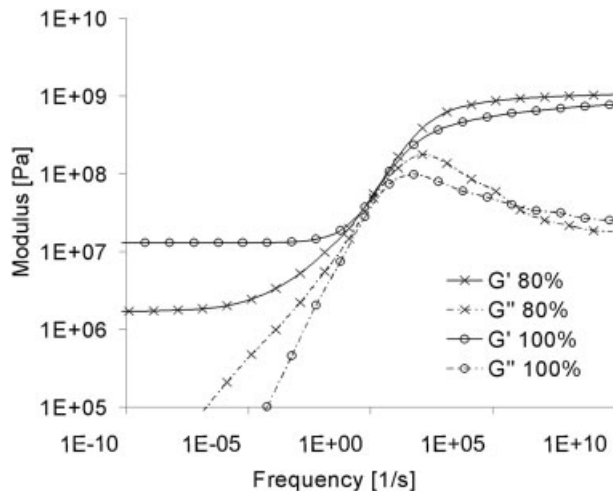


Figure 5 Curves shifted to their individual glass transition temperature.

along the frequency axis. For resins with (slightly) different conversion, the storage and the loss modulus are similar, except of a different glass transition temperature.

Therefore the curves from Figure 5 are not plotted for the same temperature, but for their individual glass transition temperature. The glass transition temperatures are calculated with the DiBenedetto equation. The rigidity of the Maxwell elements are interpolated for the same relaxation times. The resulting curve represents a resin with a conversion between 80 and 100%. This interpolated curve represents the properties at the glass transition temperature of the interpolated conversion. For other temperatures, the

modulus must be shifted according to eq. (8) and eq. (9) with a linear interpolated shift factor.

The curves for 80, 100, and the interpolated curves, here for 90%, all at a temperature of 120°C are shown in Figure 6.

Compression properties

Contrary to the viscoelastic shear properties, the bulk modulus, *K*, can be modeled elastically.^{12,13} The modeling of pressure-volume-temperature (pvT) data for thermoplastics is performed by the Tait equation.^{14,15} The Tait equation delivers the specific volume, *v*, dependent on temperature and pressure. This equation can be used below and above the glass transition temperature. In the softening region, this relation cannot be used.¹⁵

$$v(T, p) = v(T) \cdot \left[1 - C \cdot \ln \left(1 + \frac{p}{b_1} \cdot e^{T/b_2} \right) \right] \quad (10)$$

where *p* the hydrostatic pressure; and *C*, *b*₁, and *b*₂ are material-dependent parameters.

The compressibility is¹⁵

$$\frac{1}{K} = \kappa = - \frac{1}{v(T, p)} \cdot \left[\frac{\delta v(T, p)}{\delta p} \right]_T \quad (11)$$

This leads to

$$\frac{1}{K(T, p)} = \kappa(T, p) = \frac{(C/b_1) \cdot e^{(T/b_2)}}{[1 + (p/b_1) \cdot e^{(T/b_2)}] \cdot \{1 - C \cdot \ln[1 + (p/b_1) \cdot e^{(T/b_2)}]\}} \quad (12)$$

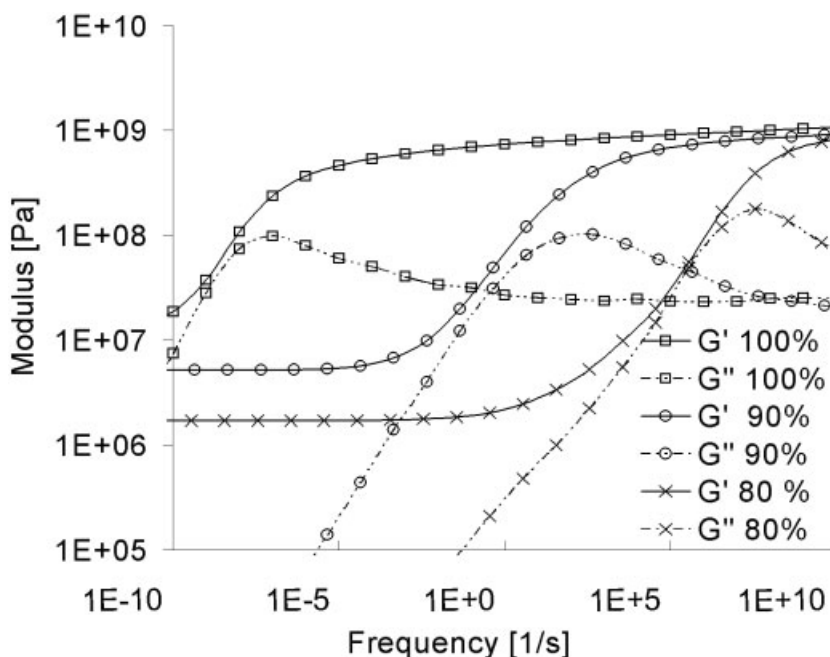


Figure 6 Modulus for different conversions at 120°C.

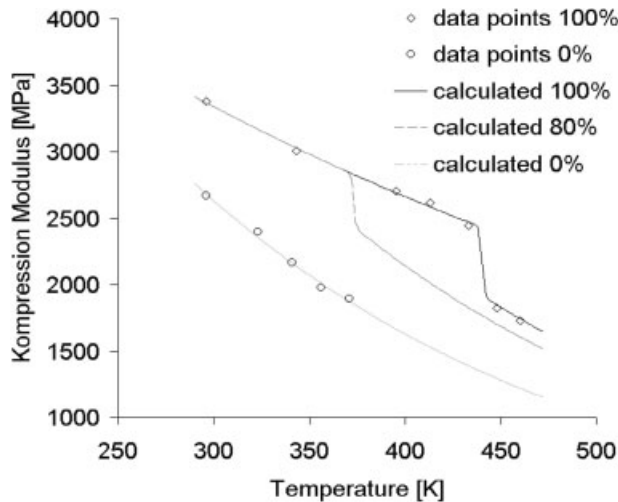


Figure 7 Comparison of calculated and measured data.

The compressibility monitored at ambient pressure leads to

$$K_l(T) = \frac{b_{1l}}{C_l} \cdot e^{-(T/b_{2l})} \quad (13)$$

$$K_g(T) = \frac{b_{1g}}{C_g} \cdot e^{-(T/b_{2g})} \quad (14)$$

The index g (glassy) is used for $T < T_g$ and the index l (liquid or gelled) for $T > T_g$.

The Tait equation and therefore eq. (13) and eq. (14) do not consider conversion. For $T < T_g$, it is assumed that there is no correlation between conversion and compressibility. The mechanical behavior in this domain is governed by secondary valence bonds, so there is only a slight dependence on conversion. For the glassy state, the factor C_g is set to 1. For the liquid, gelled, or rubbery state, a conversion dependence is introduced: $C_l = C_l(x)$.

Figure 7 shows the fitted Tait equations according to eq. (13) and eq. (14). For C_l , the following is found:

$$C_l = 1 - 0,3 \cdot x \quad (15)$$

Equation (15) delivers the linear interpolation between the measured values for $x=0$ and $x=1$. For a mathematical description, a step function between eq. (13) and eq. (14) is required. The Heavyside function is not suitable as it is discontinuous. As a suitable step function the hyperbolic tangent can be used. This leads to

$$K(x, T) = 0,5 \cdot \left\{ \frac{b_{1g}}{1} \cdot e^{-(T/b_{2g})} \cdot [\tan h(T_g - T) + 1] + \frac{b_{1l}}{C_l} \cdot e^{-(T/b_{2l})} \cdot [\tan h(T - T_g) + 1] \right\} \quad (16)$$

with T_g according to eq. (1) and C_l according to eq. (15).

The terms in round brackets are used as a toggle switch. Dependent on both, temperature and glass transition temperature, they enable or disable parts of the equation.

Figure 7 shows the measured data points together with the calculated modulus for conversions of 0, 80, and 100%.

CONCLUSION

The work presented enables investigation into viscoelastic material properties during polymerization. The obtained rheological data allows FEAs with consideration of conversion. Therefore a suitable generalized Maxwell model was implemented in the FEA. In difference to common generalized Maxwell models or to Prony series, the parameters of the model are dependent on conversion.

The rheological data considers the time-, conversion-, and temperature-dependent shear modulus, and the conversion- and temperature-dependent bulk modulus. Together with the shrinkage and the thermal expansion, this material model enables calculation of stress. This allows the calculation of optimized processing parameters and optimized annealing cycles with the aim of short annealing cycles and low internal stress in a specified temperature range. The calculated material properties were compared to mechanical testing and photoelasticity, and exhibits even for long times (weeks) a good approximation to the experimental results.

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