

PROPERTIES OF THERMOSETTING POLYMERS DURING CURE

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Abstract

The mechanical/rheological behavior of thermosetting polymers during cure is not fully understood. Today's computer simulations of thermoset processing make use of models based on ad hoc approximations which simply relate the strength properties of thermosets linearly to the degree of cure. However, these assumptions are not valid when modeling thick parts where phase change is temperature and space dependent and significantly contributes to the build-up of residual stresses in the final part. Within this research project presented in this paper, the thermomechanical material characterization as a function of cure of an unsaturated polyester resin was developed with the use of dynamic mechanical analysis and differential scanning calorimetry.

Introduction

In recent years, the need for production of large, lightweight, strong and stiff parts has made fiber reinforced polymers an important industrial material. The quality of fiber reinforced parts are highly influenced by the filling process and processing conditions. Material properties of such parts are greatly affected by fiber orientation, formation of knit lines, etc. One major concern in the design of plastic parts is the change of the part's shape and dimension due to shrinkage and warpage. Shrinkage and warpage result from material inhomogeneities caused by flow induced fiber orientation, curing, poor thermal mold lay-out, and processing conditions.

Shrinkage and warpage are directly related to residual stresses which result from locally varying strain fields that occur during the curing or solidification stage of a manufacturing process (1). Such strain gradients are caused by non-uniform thermomechanical properties and temperature variations inside the mold cavity. These are, in great part, a result of the transient thermodynamic processes that take place during the curing stage of the matrix material during molding. On the other hand, strain gradients are also created by process dependent phenomena such as the fiber orientation that occurs during flow, poor thermal mold lay-out and by combining or sandwiching different types of materials such as when manufacturing copper clad epoxy/glass fiber composites widely used by the printed circuit board industry.

The objective of this study is to conduct experimentation, modeling, analysis and process simulation of the thermomechanical behavior of thermoset composite parts. More specifically, the thermomechanical

qualification and characterization of a thermoset unsaturated polyester matrix is to be achieved. The measured dynamic and static properties of thermosetting polymers are used to model the thermomechanical behavior of composites during the manufacturing process.

Material Characterization

During the compression molding process, the material properties of fiber reinforced thermoset composites become highly anisotropic. This is due to the fiber orientation distribution induced by the molding process. Three major topics in the materials area have been of great interest in the past: mechanical, thermomechanical properties and stress analysis of fiber reinforced composites (1-8).

For an in-depth study of flow, heat transfer, and strength of fiber reinforced thermoset resins, the detailed constitutive models that relate physical properties are required. Such models include viscosity, curing and stress-strain relations during processing and cure.

Viscosity

Here, for unsaturated polyester resins found in SMC and BMC materials, the cure is slow enough that it does not play a role in the viscosity during flow. Hence, a generalized Newtonian model is justified. The deviatoric stress tensor τ needed for flow calculations include shear

thinning effects and temperature dependencies which can be written as

$$\tau = \eta(\gamma, T) \dot{\gamma}, \quad (1)$$

where the viscosity can be modeled using the Bird-Carreau equation written for amorphous materials as

$$\eta = \frac{K_1 \alpha_T}{\left[1 + K_2 \dot{\gamma} \alpha_T \right]^{K_3}}. \quad (2)$$

The temperature dependence of the viscosity is taken into account with the WLF shift expressed as

$$\ln \alpha_T = \frac{8.86(K_4 - K_5)}{101.6 + K_4 - K_5} - \frac{8.86(T - K_5)}{101.6 + T - K_5}, \quad (3)$$

where the constants K1-K5 represent the material dependent constants for the Carreau-WLF model.

This model takes into account the shift of the transition point between newtonian and power law behavior at a specific temperature of the polymer melt. Figure 1 presents experimental data (9) and calculated data with the use of the Bird-Carreau equation with a WLF temperature shift.

Curing Reaction

Any molding process of fiber reinforced thermosets begins when the uncured matrix/fiber material at room temperature is placed inside a heated mold. The mold is then closed, forcing the material to flow and consolidate. At this point, complex heat transfer processes take place, as the material cures and solidifies.

The amount of heat liberated by the reaction is usually taken as a measure of the degree of cure, assuming that the fractional conversion is proportional to the number of bonds formed in linking the chains together, and that each bond releases the same amount of heat (10). Thus the fraction conversion, also called the degree of cure, can be defined as

$$c = \frac{Q}{Q_T} \quad (4)$$

Where Q_T is the heat of reaction and Q is the amount of heat released up to the current time which can be defined by

$$Q = \int_0^t \dot{Q} dt \quad (5)$$

The degree of cure or conversion, c , equals zero when there has been no reaction, and it equals one when the reaction is complete. Thus, the cure is a field quantity that varies in space and time. The rate of heat generated during curing can be expressed as

$$\dot{Q} = Q_t \frac{dc}{dt}, \quad (6)$$

where dc/dt is the time rate of change in the degree of cure represented by an empirical model such as the one proposed by Kamal and Sourour (11,12). For stepwise isothermal cure of a thermoset resin, the cure rate equation has the form

$$\frac{dc}{dt} = (d_1 + d_2 \cdot c^m)(1 - c)^n, \quad (7)$$

where $c=0$ at $t=0$, m and n are constants and the terms d_1 and d_2 contain the temperature dependence of the curing rate as

$$d_1 = a_1 e^{-\frac{b_1}{RT}}, \quad (8a)$$

and

$$d_2 = a_2 e^{-\frac{b_2}{RT}}. \quad (8b)$$

where a_1 , a_2 , b_1 , and b_2 are material based constants, T is the absolute temperature and R is the universal gas constant.

To determine the constants described in the above equations, a non-linear regression fit based on the Levenberg-Marquardt method was developed (13). The Levenberg-Marquardt method is a method which varies smoothly between the inverse-Hessian method and the steepest descent method and has become the standard of nonlinear least-squares routines. As an example, the fit for a generic unsaturated polyester system is presented in this paper. The heat of reaction was determined by monitoring the curing reaction via isothermal differential scanning calorimetry (DSC) to complete conversion.

The isothermal reaction rate profiles of an unsaturated polyester resin measured at three isothermal temperatures is shown in Fig.2. Good agreement between the lines, which indicate the results from the model prediction, and the symbols, which indicate the experimental measurements, is observed. Results from the model indicate that at a high activation temperatures the reaction develops much faster than when the activation temperature is at a low temperature. Moreover, the model predicts the initiation stage at the various activation temperatures quite well. The numerical values of the six constants obtained from the curve fitting program are listed in Table 1.

The comparison between the experimental and computational conversion of the unsaturated polyester system with respect to time is shown in Fig. 3. The conversion is calculated using the kinetic model along with the constants obtained from the curve fitting program. Good agreement between experimental data and predictions can be found in Fig. 3.

Stress-Strain Relations

Once a thermoset composite part begins to solidify, residual stresses start to build-up. A simplified model which can be used to predict these residual stresses has been developed by Sun, Davis and Osswald (14). To present this model, the processing of a simple plate is considered. As a plate cures, it develops a solidified layer at the outer walls that continues to grow until the whole plate has hardened. At any instant in time, t , a location within the plate which has reached a degree of cure of 80% is considered solid and capable of withstanding residual stresses. The strength properties of the composite are calculated using an ad hoc model that linearly relates the elastic constants of the elasticity tensor to the degree of cure.

Solving for the residual stress distribution requires that the energy equation be solved, while satisfying the force balance equation within the solidified material.

The strain at any time and position is usually defined as the sum of its elastic, thermal and viscous components as

$$\epsilon(t) = \epsilon_E + \epsilon_{th} + \epsilon_v + \epsilon_c. \quad (9)$$

The elastic strain, ϵ_E , is simply a function defined by Hooke's Law. The thermal strain, ϵ_{th} , occurs after the material reaches an 80% degree of cure and is a function of the thermal expansion coefficient. The viscous strain, ϵ_v , is the strain the layer undergoes just before solidifying due to thermal contraction and viscous flow. The viscous strain occurs under a negligible stress and is not felt by the layer that has just solidified. Each layer has a different viscous strain equal to the overall strain of the plate, $\epsilon(t)$, the instant that layer solidified, thus the viscous strain is a function of space. The curing strain, ϵ_c , is a linear function of the degree of cure and includes the shrinkage of the material due to the cross-linking reaction. To solve for the total strain of the plate, the stresses must approach equilibrium and sum up to zero as (15)

$$\int_{-L}^L \sigma(z, t) dz = 0. \quad (10)$$

Molding induced residual stresses which occur due to inhomogeneities through the part thickness, in addition to the in-plane inhomogeneities discussed earlier, were also included in past simulation work. The most important factors which contribute to residual stress build-up and thus lead to warping and surface waviness are:

- Differences in temperature between the upper and lower mold surfaces due to poor mold lay-out.
- Irregular curing caused by the one-sided heating of the molding compound when it is placed inside the mold, before flow begins.
- Usage of sandwiched materials such as the combination of SMC with random and uni-axial fibers.

All of these aspects were taken care of by the use of equivalent moments applied on the surface of the structure through the part thickness. For example, temperature differences between the upper and lower mold surfaces. The effect of this temperature gradient was replaced with an equivalent moment that lead to part warpage.

In order to understand the complicated phenomena of shrinkage and warpage arising during curing of an unsaturated polyester/glass component, the residual stresses in a planar part was examined. In this case, the residual stress build-up is reduced to a one-dimensional problem where the stress distribution along the thickness direction was calculated. In particular, it is of interest to evaluate the effect of part thickness on the residual stress build-up. The material properties of unsaturated polyester resin were used in the simulation with a mold temperature of 150 °C and a charge temperature of 20 °C. Results for the residual stress distribution of varying part thicknesses are shown in Fig. 4. Parabolic stress distributions are predicted with the interior regions in tension and the exterior regions in compression. This results from an outside to inside cure history of the plate. It can be seen from Fig. 4 that an increase in thickness results in an increase of the corresponding residual stress distribution. The dramatic

increase in residual stresses from a 5 mm to a 7 mm thick part is of particular interest. This clearly demonstrates the significant influence that the plate thickness has on the formation and evolution of the residual stresses.

Experimental Results

Reological measurements used to quantify the progression of mechanical properties during cure remains a difficult problem due to the reaction rates and the broad range of properties the materials exhibit during the curing process. Various methods may need to be used at different stages during the curing spectrum. At early states of cure, methods such as torsional braid analysis (TBA), dynamic spring analysis (DSA) and torsional impregnated cloth analysis (TICA) have been used to measure the mechanical properties of thermoset materials, however, results from such experiments are difficult to interpret and repeat. On the other hand, dynamic mechanical analysis (DMA) has shown success in the characterization of thermoset materials at later stages of the curing reaction (16).

In order to determine the stress-strain relation as a function of temperature and degree of cure, several samples with varying degree of cure were molded. Since the exothermic reaction can be related to the degree of cure, the degree of cure of a molded sample can be determined by measuring its residual exothermic heat of reaction. The material modulus was found using DMA results. For example, DSC results on a 3 mm thick plate pressed from a BMC matrix at 100°C for 590 seconds, indicate a 44% degree of cure. The DMA results for a specimen from this plate, shown in Fig. 5, indicates a negligible modulus for the material at the 100°C pressing temperature. This result indicates a trend of the modulus as a function of cure. It appears that the modulus does not become significant until at least a 50% degree of cure is reached. This result implies that under realistic molding conditions, a minimum level of 50% cure must be achieved for any significant material strength. Another interesting aspect of the DMA test is the increase in modulus starting at 100°C. This is due to the acceleration in the rate of cross-linking during the test once the original molding temperature is exceeded. The influence of the degree of cure on the modulus of a polyester resin is shown in Figure 6 for 100°C tests. It should be pointed out that 100°C is above the glass transition temperature for all samples tested resulting in a low modulus.

Several press times were used at each molding temperature to produce plates at varying degrees of cure. An advantage of making thinner plates is that the molding process temperature can be considered as isothermal, making characterization of the material more precise. It should also be noted here that while the low temperatures used for these material characterization analyses are not typical of actual processing temperatures, they are necessary due to the fast exothermic polymerization reactions which occur at standard processing temperatures within the range of 150 to 175°C. Therefore, the material properties will be characterized at the lower temperatures and a WLF type shift factor will be used to extrapolate the material model for actual processing temperatures.

Conclusions

The influence of the degree of cure during molding on the material properties of thermoset materials is substantial to the development of residual stresses. It has been shown that the kinetic cure model proposed by Kamal and Sourour accurately predicts the degree of cure with the use of constants determined from the curve fitting program based on the Levenberg-Marquardt method. The curve fitting program developed within this research project renders a practical tool that can be used on a daily basis in today’s thermosetting industry.

In the literature, the evolution of the mechanical properties has been qualitatively modeled with the use of a linear relation between the strength properties and the degree of cure that assumes that the unsaturated polyester is a solid at 80% conversion. However, it has been demonstrated that this relationship between material strength and the degree of cure is infact not linear. DMA has been successfully used to quantify the mechanical properties of unsaturated polyester at higher degrees of conversion, however, properties at lower degrees of conversion are still difficult to measure.

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References

1. Osswald, T.A. and S.C. Tseng, “Flow and Rheology in Polymer Composites Manufacturing”, ed. S.G. Advani, Elsevier, New York, 1995.

2. Woebcken, W., *Kunststoffe*, **12**, 460-465, 1952.

3. Halpin, J.C., *Comp. Mater.*, **3**, 732-734, 1969.

4. Halpin, J.C., K. Jerine and J.M. Whitney, *J. Comp. Mater.*, **5**, 36-49, 1971.

5. Chen, C.Y. and C.L. Tucker, *J. Reinf. Plast. Comp.*, **3**, 120-129, 1984.

6. Woebcken, W., *Kunststoffe*, **8**, 373-381, 1959.

7. Kabelka, J. and G.W. Ehrenstein, *Kunststoffe*, **5**, 537, 1987.

8. Schneider, W., *Kunststoffe*, **61**, 273, 1971.

9. Lee, L.J., L.F. Marker and R.M. Griffith, *Polym. Comp.*, **2(4)**:209-218, 1981.

10. Isayev, A.I. ed., “Injection and Compression Molding Fundamentals”, Marcel Dekker, Inc., 1987.

11. Kamal, M.R. and S. Sourour, *Pol. Eng. Science*, **13(1)**, 1973.

12. Barone, M.R. and D.A. Caulk, *Int. J. Heat Mass Transfer*, **22**, 1979.

13. Sun, E.M., University of Wisconsin-Madison, *Ph.D. Thesis*, 1996.

14. Sun, E.M., B.A. Davis and T.A. Osswald, *50th SPI Conf. Proc.*, **15-B**, 1995.

16. Osswald, T.A. and G. Menges, “Materials Science of Polymers for Engineers”, Hanser Verlag, Munich, 1995.

15. Dealy, J. and K. Wissbrun, “Melt Rheology”, Van Nostrand Reinhold, New York, 1990

$a_1=4.87 \cdot 10^{36}$	sec^{-1}
$a_2=2.13 \cdot 10^9$	sec^{-1}
$b_1=286.91$	$\text{KJ} \cdot \text{mol}^{-1}$
$b_2=76.42$	$\text{KJ} \cdot \text{mol}^{-1}$
$m=1.9$	
$n=1.28$	

Table 1. Numerical values of the six constants in kinetic model for an unsaturated polyester system.

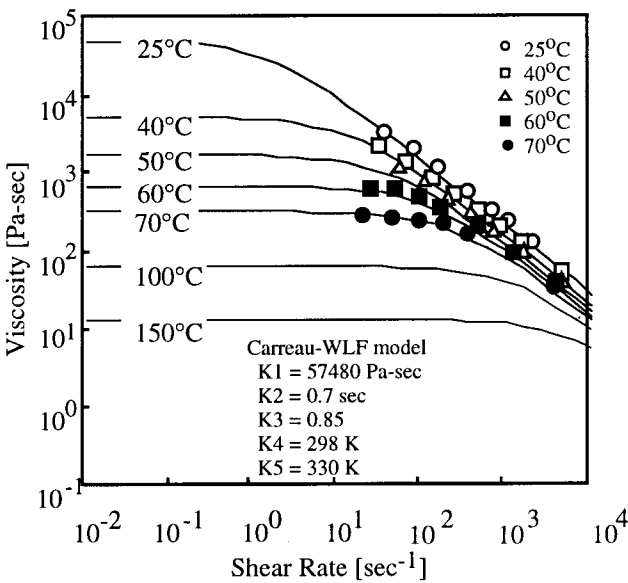


Figure 1. Experimental and calculated viscosity curves.

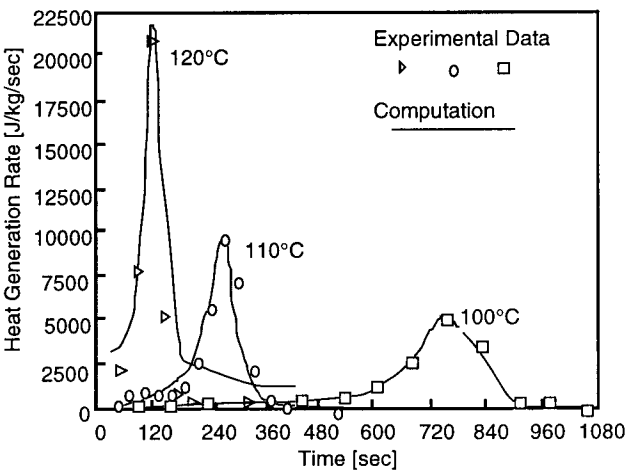


Figure 2. Isothermal reaction rate profiles of an unsaturated polyester resin.

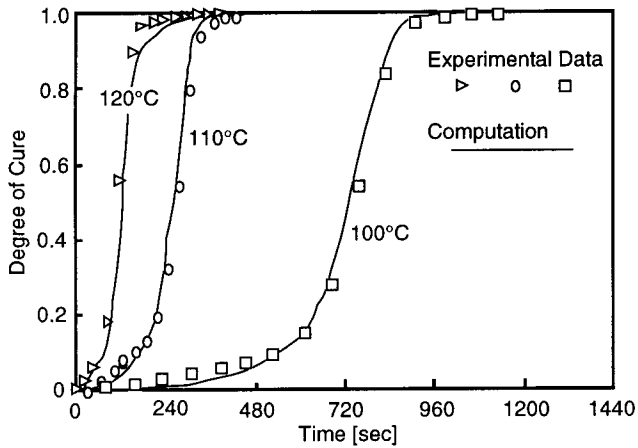


Figure 3. Experimental and predicted degree of cure with time for the unsaturated polyester system.

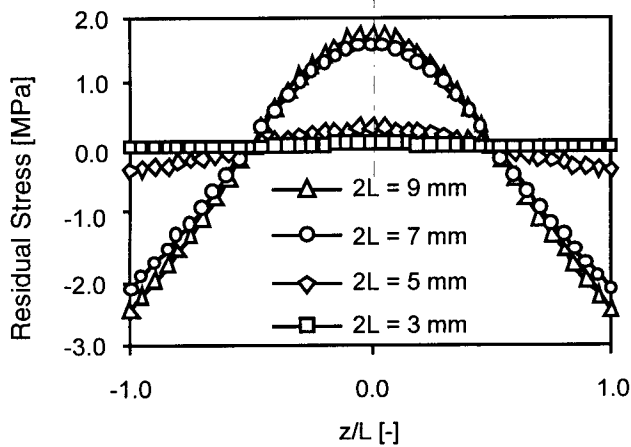


Figure 4. Residual stress distribution of varying plate thickness. (11)

Key Words: Thermosetting Polymers, Cure, Properties

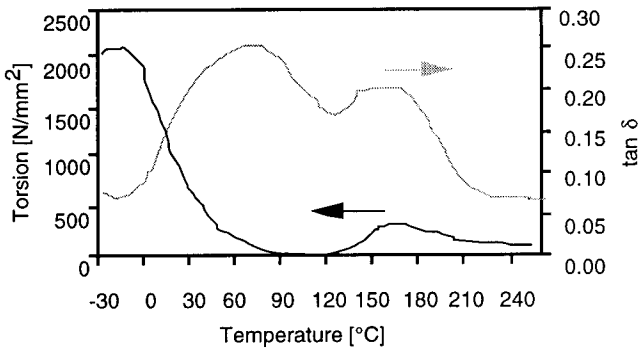


Figure 5. DMA result of a 3 mm thick specimen with a 44% degree of cure measured in DSC. Molding conditions: $T_m=100\text{ }^{\circ}\text{C}$, $t_m=590\text{ seconds}$, $P_m=40\text{ bar}$.

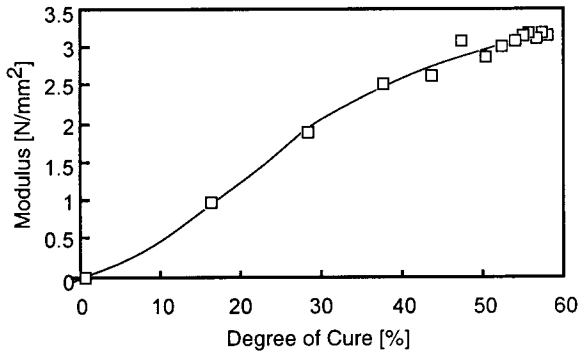


Figure 6. Modulus as a function of cure of a BMC matrix based on isothermal test at $100\text{ }^{\circ}\text{C}$.