A BULK MODULUS MODEL FOR AN EPOXY + GLASS FIBER COMPOSITE AS A FUNCTION OF PRESSURE AND TEMPERATURE

Antje Stein
Laminate Products/ Semiconductors Packages Research Group, Johnson Matthey Advanced Circuits, Inc., 3965 Meadowbrook Road, St. Louis Park, MN 55426, USA
formerly of
Laboratory of Polymers and Composites (LAPOM), Department of Materials Science, University of North Texas, Denton, TX 76203-5310, USA

Witold Brostow, Prakaipetch Punchaipetch, and Syed Maswood
Laboratory of Polymers and Composites (LAPOM), Department of Materials Science, University of North Texas, Denton, TX 76203-5310, USA

Abstract

Temperature and pressure-dependent volumetric changes of the 8552/S2 epoxy + glass fiber composite were investigated by a Pressure-Volume-Temperature (PVT) technique. The Hartmann equation of state was used to develop a model for prediction of the bulk modulus as a function of both pressure and temperature. This model describes the experimental data very well over a wide range of temperatures and pressures.

Introduction

The glass-fiber reinforced epoxy composite we have investigated is of significant interest to research as well as other industries such as the aviation and aerospace industries. The mechanical and thermal properties are more important for these industries rather than other properties. One significant property is certainly the bulk modulus, which is the reciprocal of the isothermal compressibility.

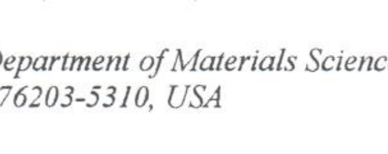
The mathematical modeling of structure-property relationships, including phenomenological models, can be used to predict macroscopic changes due to molecular structure changes. There are numerous papers that relate the bulk modulus to various equations of state (9-13).

However, a model based on the process parameters pressure and temperature would simplify the material property optimization by the manufacturing personnel. Therefore, the present work describes the development of a Bulk Modulus Model for the 8552/ S2 laminate.

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:



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 unidirectionally or bi-directionally (cross-ply).

Pressure-Volume-Temperature Technique (PVT)

Specific volume of a material as a function of pressure and temperature was measured on the PVT apparatus manufactured by Gnomix Research, Inc., Boulder, Colorado (14,15).

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 cured laminates were measured at temperatures between T = 100 to 200°C at a heating rate of 4 K/minute. The pressure was varied from P = 10 to 200 MPa in increments of 10 MPa. The samples were previously cured at T = 140°C and a pressure of P = 20 MPa.

Results and Discussion

For the development of the bulk modulus model we considered the Hartmann equation of state (1-6) as suitable. This equation is known to provide reliable results for polymer solids, melts and liquids (4,5) and reads:

$$P'' \cdot V''^{5} = T''^{3/2} - \ln V'' \qquad (1)$$

V" denotes the reduced volume, which is defined as follows:

$$V'' = V / V^{*} \qquad (2)$$

V is the specific volume. The volume V consists of two parts, namely the free volume V_f and the characteristic volume V* for a given material, the so-called incompressible volume:

$$V = V^{*} + V_f \qquad (3)$$

P is the pressure and T the thermodynamic temperature, while P* and T* are, similar to V*, characteristic parameters for the given material and obtainable from the PVT measurements and defined by equations analogous to equation (2):

$$P'' = P / P^{*} \qquad (4)$$

$$T'' = T / T^{*} \qquad (5)$$

T* characterizes the average strength of intersegmental interactions. P* is a complicated function of the spatial structure of the material.

By rearranging the Hartmann equation (1) to P explicitly we obtain:

$$P = \frac{\left(\frac{T}{T^{*}}\right)^{3/2} - \ln\left(\frac{V}{V^{*}}\right)}{aV^{5}} \qquad (6)$$

where

$$a = \frac{1}{P^{*} V^{*5}} \qquad (7)$$

The bulk modulus k_B is defined as follows:

$$k_B = -V \left|\frac{\delta P}{\delta V}\right|_T \qquad (8)$$

We obtain the bulk modulus model by deriving equation (6) from (8):

$$k_B = \left\{ \frac{P^{*} V^{*6}}{V^{6}} \left[1 + 5\left(\left(\frac{T}{T^{*}}\right)^{3/2} + \ln\left(\frac{V}{V^{*}}\right) \right) \right] \right\} \qquad (9)$$

where the characteristic parameter P*, determined from PVT maps (see Figures 1 and 2), depends on the applied pressure and temperature. P* can be calculated with the following equation:

$$P^{*} = (a_0 + a_1\,T)\,P^{2} + (b_0 + b_1\,T)\,P + c_0 \qquad (10)$$

Plots of P* against P were the basis for determining the polynomial equation (10).

Equation (10) was inserted into equation (9) for determining the bulk modulus k_B:

$$k_B = \left\{ \frac{\left[(a_0 + a_1\,T)\,P^{2} + (b_0 + b_1\,T)\,P + c_0 \right] V^{*6}}{V^{6}} \right\} * \left[1 + 5\left(\left(\frac{T}{T^{*}}\right)^{3/2} + \ln\left(\frac{V}{V^{*}}\right) \right) \right] \qquad (11)$$

which allows the calculation of the bulk modulus by inserting the manufacturing parameters pressure and temperature.

The mean values for the characteristic parameter V* and the T* in equation (11) are listed in Table 1 for the particular composite:

Characteristic Parameters	unidirectional	bi-directional
V^* [cm^3/g]	0.510	0.516
T^* [K]	4398	5485

Table 1: Characteristic parameters of the bulk modulus model in equation (11) for 8552/S2 laminates

The values of the coefficients in equation (11) are listed in Table 2:

Coefficients	unidirectional	bi-directional
a_0	207	270
a_1	-2	-2
b_0	-4420	-6251
b_1	45	62
c_0	-86	-63

Table 2: Coefficients of the bulk modulus model in equation (11) for 8552/S2 laminates

In equation (11), the specific volumes V for the cured unidirectional and bi-directional samples are $V = 0.56$ cm^3/g and $V = 0.52$ cm^3/g, respectively.

Conclusions

A bulk modulus model has been developed based on the Hartmann equation of state and Gnomix PVT measurements. Using equation (11) provides good results over wide temperature and pressure ranges. Hence, the equation has predictive capabilities. Equation (11) allows the prediction of the bulk modulus of the particular composite by inserting the manufacturing parameters pressure and temperature. We presume the model can be used for other materials also.

The Gnomix PVT data provided the volume changes and, therefore, the characteristic parameter of the bulk modulus model V*, P*, and T* of the 8552/S2 epoxy + glass fiber laminates dependent on pressure and temperature. The volume of the laminate decreased due to the completion of the curing process as well as the migration of voids and small air pockets. The incompressible volume V* as well as T* are independent of the processing parameters while P* depends on the applied pressure and temperature.

Since the volume changes are caused by curing as well as voids and air migration, the general bulk modulus k_B has to be separated into the two parts k_{B1} and k_{B2}:

$$k_B = k_{B1} + k_{B2} \qquad (12)$$

The bulk modulus k_{B1} is due to the void migration and depend on pressure, cure time and temperature while k_{B2} is due to curing and depend only on the cure time and temperature. The two parts of the bulk modulus are also dependent on the fiber orientation.

References

/1/ B. Hartmann
Proc. Can. High Polymer Forum **22,** 1983, 20

/2/ B. Hartmann and M. A. Haque
J. Applied Phys., **58,** 1985, 2831

/3/ B. Hartmann and M. A. Haque .
J. Applied Polymer Sci. **30,**1985,1553

/4/ W. Brostow, J. V. Duffy, G. F. Lee, and K. Madejczyk
Macromolecules **22,** 1989, 2761

/5/ Y. M. Boiko, W. Brostow and A. Y. Goldman, A. C. Ramamurthy
Macromolecules **36,** 1995, 1383

/6/ L. M. Thomas and J. Stanker
Phys. Stat. Sol. (b) **189**, 1995, 363

/7/ M. Kumar
Phys. Stat. Sol. (b) **196**, 1996, 209

/8/ D. Tabor
Polymer **35,** 1994, 2759

/9/ B. R. Djordjevic and M. F. Torpe
J. Phys.: Condens. Matter **9**, 1997. 1983

/10/ M. Kumar
Physica B **222**, 1996, 229

/11/ R. Simha and E. Papazoglou
Polym. Comp. **10**, 1989, 409

/12/ L. Sodomka and J. Sodomka
Int. Sci. Techn. **21**, 1994, 69

/13/ H. Ledbetter
Phys. Stat. Sol. (b) **181**, 1994, 81

/14/ P. Zoller, P. Bolli, V. Pahud, and H. Ackermann
Rev. Sci. Instrum. 1976, **49**, 948

/15/ P. Zoller
PVT Manual Version 5.01
Gnomix Research, Inc., 3809 Birchwood Drive, Boulder, CO 80304, USA, 1990

Keywords: bulk modulus, epoxy + glass fiber laminate, Hartmann equation of state, volume changes

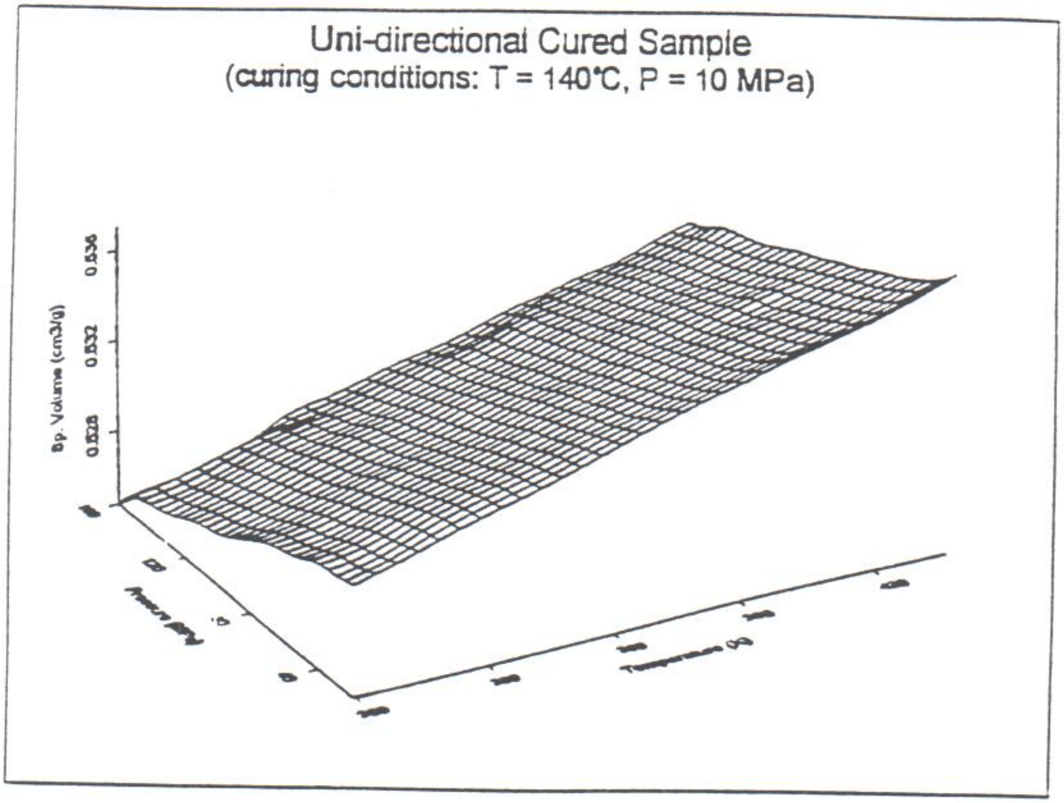


Figure 1: Pressure- Volume-Temperature map of unidirectional cured 8552/S2 laminate

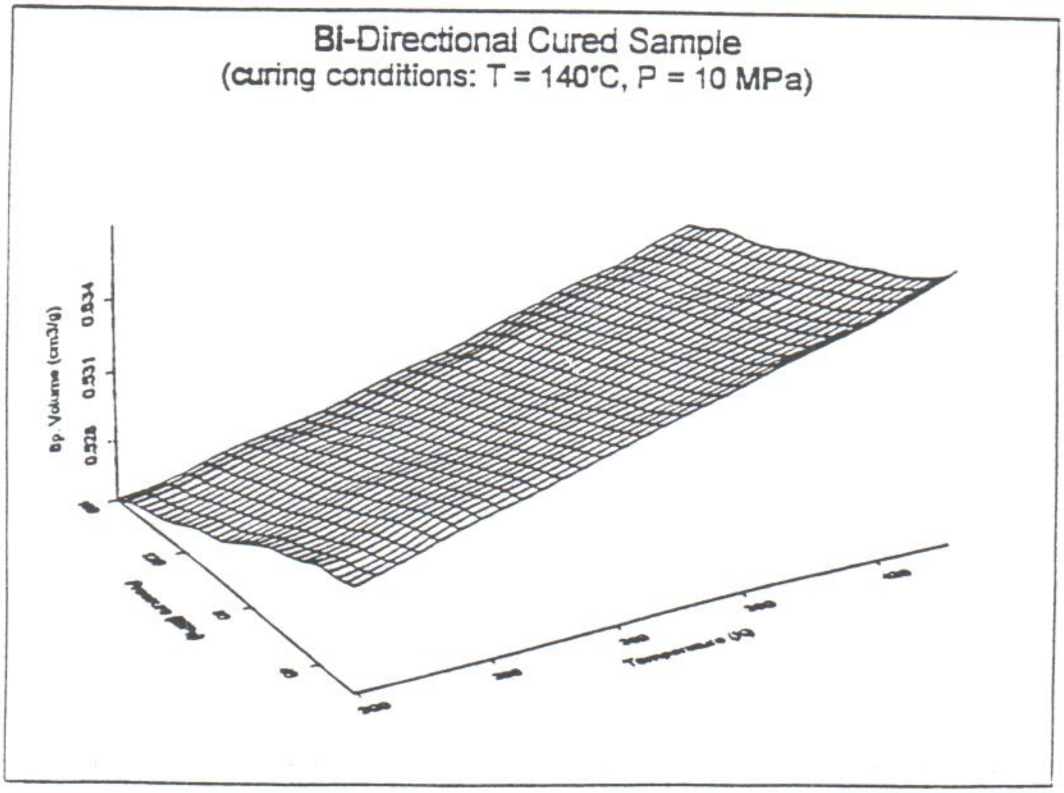


Figure 2: Pressure- Volume-Temperature map of bi-directional cured 8552/S2 laminate