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Determination of volume changes during cure *via* void elimination and shrinkage of an epoxy prepreg using a quartz dilatometry cell

Summary — Volumetric changes were eliminated in processing of a glass fiber reinforced epoxy prepreg; two components from void elimination and the crosslinking reaction itself were isolated. A quartz dilatometry cell inside a Thermomechanical Analyzer (TMA) was used to measure the volume changes. Compression was applied at a temperature higher than the resin glass transition temperature to isolate the void elimination volume change, whereas the change due to reaction shrinkage was observed at a longer time at the cure temperature. Uniaxial and biaxial composite prepregs were studied. Each sample exhibited an approximately 0.5% volume change due to crosslinking. Void elimination varied with temperature, pressure and fiber orientation. Several interesting trends are evident in the present results. Higher pressure results in higher void elimination. Lower cure temperatures produce higher void elimination, except that high temperatures show some increase due to low viscosity before curing locks in the structure. Biaxially oriented fibers show higher void elimination than do uniaxial at low cure temperatures, but at higher temperatures the values are similar. The volume changes due to void elimination in the composites examined varied from 6% [biaxial, 100°C, 10 psi (*ca.* 0.07 MPa)] to 1% [uniaxial, 160°C, 5 psi (*ca.* 0.035 MPa)].

Key words: quartz dilatometry cell, thermomechanical analyzer, volume changes, void elimination and shrinkage of epoxy prepregs.

Prepregs are commonly used in the manufacture of fiber-reinforced composites. Prepregs consist of a mixture of epoxy resin and curing agent in a specific ratio along with any modifiers or additives, coated onto fibers. These prepreg sheets are made into multilayer composites by hand or machine layup. Typically, they are processed in a two-step operation. The uncured composite is compression molded until the voids and air pockets between the layers are squeezed out and the part has been staged, what implies that it is structurally rigid enough to maintain the molded shape. This stage, referred to as C-stage typically corresponds to gelation. Since the composite has a semirigid structure, final processing is done in an autoclave by using heat. Although shrinkage does occur during the final processing from the C-stage to full cure, the quality of the composite in terms of structure and void content is determined in the early stages. Prediction of the change in volume during the

compression molding step is important in minimizing void content and ensuring proper fiber to resin structure; as a result of too little prepreg in the mold, the voids are not eliminated; too much prepreg leads to resin squeezing out while fibers remain and a change in position.

The volume change during processing is due to two events: squeezing out interlaminar voids left from initial layup of the prepreg sheets and from the shrinkage of the epoxy due to the crosslinking reaction itself. The total volume change from both events combined is relatively easy to measure by using a dilatometry cell [1] as shown in Fig. 1; many times this combined value is used to determine preliminary processing parameters. However, it is possible to separate the two events and to quantify both values independently and thus to realize the inherent shrinkage of the material and the amount due to a specific prepreg layup technique. Interla-

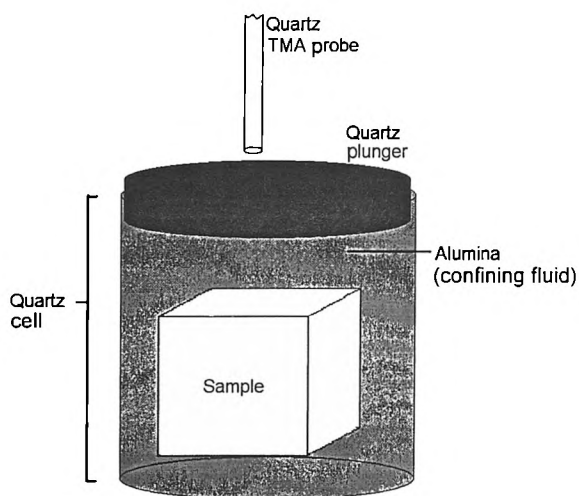


Fig. 1. A typical quartz dilatometry cell showing the cell and the plunger and a sample confined in alumina

minar voids tend to be squeezed out during the compression phase of compression molding, with pressure and temperature as important determinants for the rate of void elimination. Also, different layup orientations and techniques produce different amounts of voids. On the other hand, the chemical shrinkage from the reaction itself depends on the crosslink density; thus, the rate of chemical shrinkage depends on the rate of the reaction.

By heating the prepreg to a temperature above the glass transition temperature of the resin, applying pressure, and then heating to the curing temperature, the two events show distinct regions in the resulting data. When the pressure is applied above the glass transition temperature, there is a sharp drop in volume, corresponding to void elimination. Afterwards, the prepreg is quickly heated to the curing temperature, at which point the reaction proceeds and a broad volume change is observed corresponding to chemical shrinkage.

The force applied to the plunger of the dilatometry cell will have an effect on the expansivity observed. A series of pressures can be used to calculate the bulk modulus of the composite to eliminate the uncertainty of this pressure dependence. The objective of the present work is to separate the effects just described.

EXPERIMENTAL

The glass fiber reinforced prepreg was Hercules 8552-R2 (Hexcel, Inc.). Sheets, 1 mm thick, of premixed tetraglycidyl 4,4-diaminodiphenyl methane (TGDDM) and 4,4'-diaminodiphenylsulfone (DDS) with 66 weight % uniaxial glass fiber were made into both uniaxial and biaxial composites by hand layup and cut into 4 x 4 x 4 mm cubes.

A Perkin-Elmer Dynamic Mechanical Analyzer (DMA-7e) was used in the static force mode to measure the change in height of the plunger on a 7-mm diameter quartz dilatometry cell (Perkin-Elmer accessory # 319-0461).

The sample was suspended in a medium of alumina particles, which acted as a confining fluid inside the dilatometry cell [2, 3]. A quartz probe and ice coolant were used in the DMA. The holding temperature where pressure was applied was 80°C for 10 minutes and the curing temperatures were 100, 120 and 160°C. The pressures applied were 1.33 and 2.65 N corresponding to 5 and 10 psi (ca. 0.035 and 0.07 MPa) respectively.

Sample loading and baseline subtraction were done by following the manufacturer's recommendations [4]. The sample was placed on a layer of alumina powder in the dilatometry cell so that the bottom and the sides of the sample were not in contact with the cell. Alumina powder was poured over the sample until the cell was completely full. Compression and agitation were used to force the excess of alumina through the overflow vent until the plunger was at the starting position. The loaded cell was measured for linear change in time during the pressure and heating cycle described above. After the measurement the sample was removed, alumina was added until the weight of the loaded cell matched that of the previous run less the sample weight. This cell with alumina only was run under the same conditions as the one with the sample and was subtracted from the sample run to eliminate the small expansion of the alumina powder.

RESULTS

A series of graphs like the representative one shown in Fig. 2 were compiled for different cure temperatures, pressures and fiber orientations. In Fig. 2, the sample at

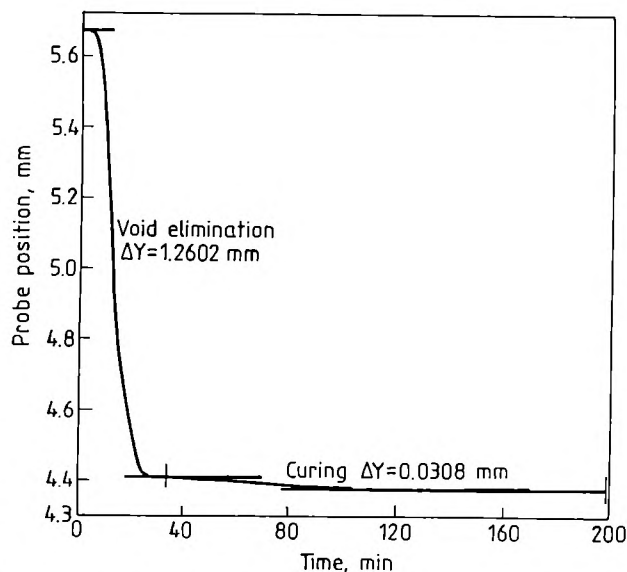


Fig. 2. The height of dilatometer plunger during compression and isothermal cure (probe height) versus time; the initial drop in height upon application of the force of 2.65 N through the probe results in an isotactic pressure of 10 psi (ca. 0.07 MPa) and the gradual shrinkage due to the crosslinking reaction

80°C shows a sharp drop in volume upon application of pressure [2.65 N = 10 psi (ca. 0.07 MPa)] corresponding to the interlaminar void elimination. On heating to the cure temperature (140°C), the volume change levels at a constant value. During the curing isotherm, a slow and broad decrease in volume is evident, corresponding to shrinkage associated with the crosslinking reaction in the epoxy resin.

The results of the series of experiments used to calculate volume change as a percent of the original volume are presented in Fig. 3 and 4. Figure 3 verifies that the

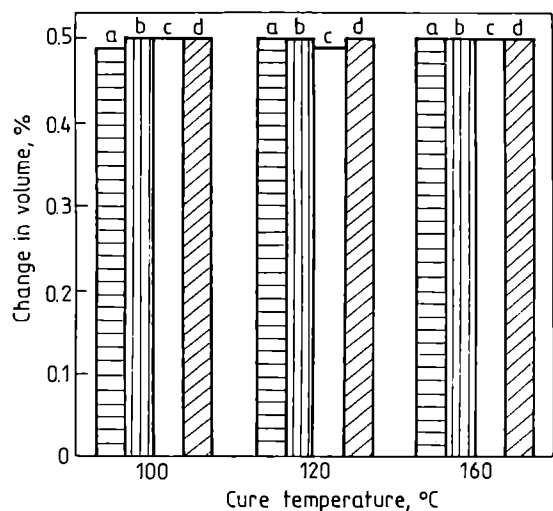


Fig. 3. Results from the series of experiments showing consistency in the second volume decrease due to crosslinking of the resin; a — biaxial, 5 psi (ca. 0.035 MPa), b — biaxial, 10 psi (ca. 0.07 MPa), c — uniaxial, 5 psi (ca. 0.035 MPa), d — uniaxial, 10 psi (ca. 0.07 MPa)

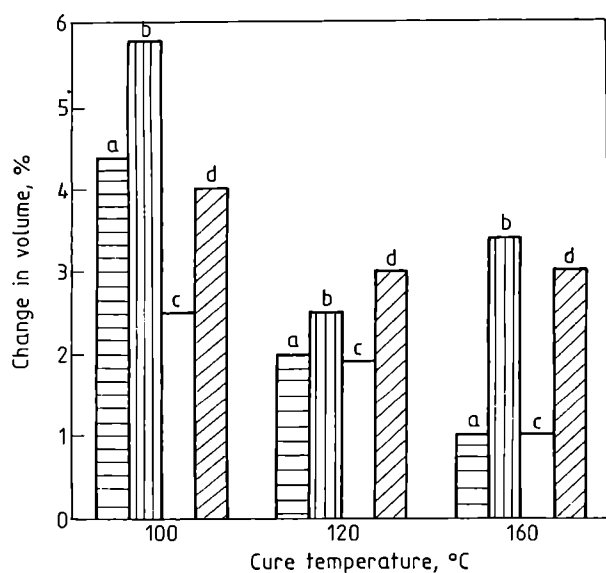


Fig. 4. Results from the series of experiments showing important trends in the relationship between void elimination and cure temperature and pressure for both biaxial and uniaxial fiber orientations (for symbols, see Fig. 3)

shrinkage due to crosslinking of the resin is consistently 0.5% in each experiment. This also confirms that the second volume change is indeed due to resin shrinkage and is independent of orientation, pressure and temperature. On the other hand, Fig. 4 shows the initial volume change upon application of pressure at the holding temperature of 80°C. The point at which the sharp drop flattens and the broad decrease begins was identified as the gel point of the resin by comparing the glass transition temperature values of aborted runs by differential scanning calorimetry (DSC) to previous reaction kinetics of this material [5].

The trends evident in Fig. 4 give insight into the minimization of voids during processing of an epoxy prepreg composite by adjusting processing temperature and pressure and the effects of fiber orientation. The greatest void elimination is seen to occur at low cure temperatures and high pressures, with biaxial composites demonstrating larger volume changes than the uniaxial ones. Lower cure temperatures allow the time necessary for interior voids to migrate. In contrast, high temperatures tend to lock the structure and seal the escape routes of the voids. However, high temperatures produce lower initial viscosity which corresponds to higher than expected void migration, as seen in the results at 120 and 160°C. High pressure tends to squeeze the voids out faster and also compress the trapped interior voids until the structure is secured in the compressed state by crosslinking. While we expect the uniaxial composites to compact more efficiently than the biaxial ones, the uniaxial ones will show a smaller volume change, since they have a lower initial void content after layup. Consider stacking wooden sticks both biaxially and uniaxially, then pressing the stacks flat. We would expect the biaxial ones to change more in volume although the uniaxial ones will be more compact.

CONCLUDING REMARKS

Characterization of the cure process of this epoxy prepreg by calorimetric studies has been presented elsewhere [6]. The present work is a part of a larger program of investigation and modification of epoxies. Thus, we are using hydroperoxides to modify epoxies [7—9].

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REFERENCES

1. Sibilja J. P.: "A Guide to Material Characterization and Chemical Analysis", VCH, New York 1988, p. 217; Wunderlich B.: "Thermal Analysis", Acade-

- mic Press, New York 1990, p. 311; Speyer R. F.: "Thermal Analysis of Materials", Marcel Dekker, New York 1993, p. 165; Wunderlich B.: The Basis of Thermal Analysis in "Thermal Analysis of Polymeric Materials", Ed., E. Turi, Academic Press, New York 1997.
2. Menard K. P.: "Dynamic Mechanical Analysis", CRC Press, Boca Raton, Florida 1999, p.58.
 3. Menard K. P.: Thermal Transitions and their Measurement in "Performance of Plastics", Ed., W. Brostow, Hanser, Cincinnati 2000.
 4. Perkin-Elmer, LLP: "Instructions for Dilatometer Accessory", 0993-9318 1996.
 5. Bilyeu B.: "Cure Kinetics and Processing Parameters of Neat and Reinforced High Performance Epoxy Prepregs", M. S. Thesis, University of North Texas, Denton 1999.
 6. Bilyeu B., Brostow W., Menard K. P.: *Polym. Compos., in press.*
 7. Bratychak M., Brostow W.: *Polym. Eng. Sci.* 1999, **39**, 8.
 8. Bazyliak L., Bratychak M., Brostow W.: *Mater. Res. Innov.* 1999, **3**, 132.
 9. Bazyliak L., Bratychak M., Brostow W.: *Mater. Res. Innov.* 2000, **3**, 218.

KALENDARZ IMPREZ

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7—12 lipca 2002 r. Pekin, Chiny. „39th International Symposium on Macromolecules”.

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