ELSEVIER

Thermochimica Acta 392–393 (2002) 299–302

thermochimica acta

www.elsevier.com/locate/tca

Examination of interphase thermal property variance in glass fiber composites

Matthew S. Tillman, Brian S. Hayes, James C. Seferis*

Department of Chemical Engineering, University of Washington, P.O. Box 351750, Seattle, WA 98195-1750, USA

Received 19 January 2001; accepted 4 May 2001

Abstract

In an effort to understand the implications of the fiber/matrix interphase on the performance of aerospace grade composite materials, a study was performed to examine the properties of the interphase region on the micro-scale. An epoxy resin was cured with several curing agent systems to evaluate the material based variations in experimental detection of glass transitions with scanning thermal microscopy (SThM). After an appropriate material was selected, glass fibers with different finishes were impregnated with an epoxy/amine resin system, and the properties of the interphase regions were examined using scanning thermal microscopy.

Keywords: Interphase thermal property; Glass fiber composites; Fiber center

1. Introduction

For many years, the study of fiber reinforced composite materials has focused on structure–property relationships that could be developed to describe the heterogeneity that existed in these materials. With the development of the process–structure–property methodology by Seferis and Theocaris in the 1980's [1], the focus of material evaluation changed to include the effects of processing parameters on the final characteristics of polymeric composites. The evaluation and characterization of micro-scale material structure–property changes with variation in processing conditions has led to an increased understanding of the effect of the interphase region on the performance of composite materials.

The reasons for the formation of this interphase region have been examined in depth by many researchers. An inclusive review of this material is presented by Hughes [2], while another presentation is given by Theocaris [3]. It is in this volume that Theocaris presents his concentric cylinder model for the development of interphases in composite materials, in which the properties of the interphase are a function of radial distance away from the fiber. While mechanical testing has been used to infer the presence of interphase regions for many years, until recently it had not been possible to directly evaluate the localized thermal properties of the interphase region.

With the development of the atomic force microscope (AFM), new tools were added to the evaluation of interphase phenomena. The development of scanning thermal microscopy (SThM) provided a tool with which the thermal properties of materials can be evaluated on a very small scale [4,5]. While initial studies illustrated the importance of sample preparation and material

* Corresponding author. Tel.: +1-206-543-9371; fax: +1-206-543-8386.
E-mail address: seferis@cheme.washington.edu (J.C. Seferis).

0040-6031/02/$ – see front matter
PII: S0040-6031(02)00113-2

selection in micro-thermal analysis (μTA) [6,7], further work has shown that the technique was quite capable of detecting variations in the glass transition temperature (T_g) [8]. In previous work, these methods have been used to evaluate the variation in interphase properties of a commercial thermosetting resin system impregnated in carbon and glass fibers [9].

The purpose of this work was to evaluate the interphase properties of a simple epoxy/amine thermosetting composite system using active thermal atomic force microscopy. This required the selection of an appropriate resin through analysis of several material responses to μTA. Through this knowledge, it was possible to select a resin system that could be used for evaluation of the influence on the interphase region of glass fiber finish.

2. Experimental

Before evaluation of the fiber/matrix interphase region could be undertaken, a suitable resin was required for ease of evaluation. Since thermosetting resins can provide difficulty for analysis with micro-scale thermal analysis technics [7], several resins were evaluated for their glass transition behavior. In an effort to keep the formulation of these resins from unduly influencing the results of the analysis, simple resin formulations were used. A diglycidylether of bisphenol-A (Epon 828 from Shell Chemical) was cured with 80% of the stoichiometric amount of the following curing agents: methylene dicyclohexylamine (Amicure® PACM from Air Products), triethylene pentamine (Ancamine® TEPA from Air Products) and triethylene tetramine (Ancamine® TETA from Air Products). A resin was also made with a stoichiometric amount of TETA. Resin plaques were cured at a pressure of 620 kPa (80 psig) and a 1.39 °C/min (2.5 °F/min) ramp to 121 °C (250 °F), a 2 h hold at 121 °C, and a 1.39 °C/min cool down to room temperature.

The suitability of each material was judged based on evaluation by both dynamic mechanical analysis (DMA) and μTA. The DMA evaluation of the T_g for each material was performed using a TA Instruments DMA 2980 in single cantilever beam mode with a frequency of 1 Hz and an oscillation amplitude of 10 μm while the temperature was ramped from 25 to 250 °C at 5 °C/min. The T_g was evaluated as the onset of the drop in the storage modulus. To evaluate the T_g on the micro-scale, cross-sections of each resin were polished. Final surface polishing was done using 0.3 μm Al_2O_3 grit to ensure a surface roughness of less than 300 nm. The polished specimens were then examined using a TA Instruments 2990 μTA. Using the modulated local thermal analysis (LTA) mode of the μTA, the probe temperature was ramped from 50 to 350 °C at rates of 10 and 25 °C/s. For all experiments detailed in this paper, the μTA temperature was modulated with an amplitude of 2 °C at a frequency of 2.2 kHz, and data was collected at a rate of 150 data points/s.

To evaluate the influence of glass fiber finish on the interphase region in thermosetting composites, several commercial glass fabrics with proprietary finishes from BGF Industries were used and were labeled fibers 1, 2 and 3. The analysis of isolated fiber/matrix interactions was accomplished by manufacturing resin plaques that contained a single yarn of glass fiber. In these plaques, the yarn was tensioned in a mold, and the mold was filled with resin. These plaques were cured using the curing conditions specified above for the neat resin specimens. The plaques were then cross-sectioned, polished and analyzed with the μTA as described above.

Suitable locations for interphase analysis were selected on the basis of several thermal and topographical scans, conducted at a temperature of 100 °C, a scanning frequency (scan velocity/scan length) of 2 Hz and a resolution of 200 lines per scan. These scans were concentrated on isolated fibers that had been forced apart from the yarn during cure. Once a fiber was selected for analysis, local thermal analyses were performed at various radial distances from the fiber center.

A series of these experiments was performed on each laminate. Glass transition temperatures were obtained by evaluating the onset point of the drop in the micro-TMA signal [4], corresponding to a softening of the matrix material. These temperatures were then normalized based on each specimen's bulk T_g ($T_{g,bulk}$) as determined through μTA measurements far from the fibers. This accounts for probe and specimen based heat transfer effects that shift the measured T_g to higher temperatures than the actual T_g [6,7], and allows relative decreases in T_g to be measured.

To normalize the T_g values, Eq. (1) was used.

$$T_{g,normalized} = \frac{T_g}{T_{g,bulk}} \quad (1)$$

Following this, the distance from the center of the fiber was normalized using Eq. (2). Distances were measured using the position coordinates of the selected LTA locations (X_{LTA} and Y_{LTA}), the coordinates of the fiber center (X_{fc} and Y_{fc}), and the radius of the fiber in question (R), which was determined using topographic feature measurement functions integrated in the μTA controller software.

$$\frac{r}{R} = \frac{\sqrt{(X_{LTA} - X_{fc})^2 + (Y_{LTA} - Y_{fc})^2}}{R} \quad (2)$$

3. Results and discussion

3.1. Suitability analysis of thermosetting resins

Before evaluating the effects of fiber finish on the interphase properties of composite systems, it was necessary to formulate a simple thermosetting polymer that would ensure easily measured results. In this fashion, experimental variations due to fiber/matrix interactions could be isolated from experimental effects due to poor reproducibility. In order to determine the best resin/curing agent system for analysis with the micro-thermal analyzer, it was necessary to evaluate the reproducibility of the glass transitions measured using this technique. Using two ramp rates, it was possible to compare the effectiveness of the μTA for the detection of material transitions for each material. As shown in Fig. 1, the reproducibility of the 80% TETA cured and 80% PACM cured materials were very high, while the 80% TEPA and 100% TETA materials showed very poor performance. As shown in Fig. 2, the glass transition temperature of the 80% TETA material was much lower than the other materials as measured by DMA and μTA. Because of this analysis, it was determined that the 80% TETA material was the most suitable resin for further analysis.

3.2. Fiber/matrix interphase evaluation

Through examination of the cross-sectioned resin plaques with imbedded glass fibers, it was possible to evaluate the localized glass transition temperatures at various radial distances from the glass fibers. Through normalization of this data, it was possible to compare the results for several different fiber finishes, allowing the evaluation of finish influence on fiber/matrix interphase formation. As shown in Fig. 3, the interphase behavior of the various fiber/matrix systems was quite distinct.

While it should be noted that interphase properties are dependent on the epoxy resin, curing agent, and fiber system, it is clear that the interaction of the uncured matrix with various glass fiber finishes produced dramatic results. Since the matrix material and

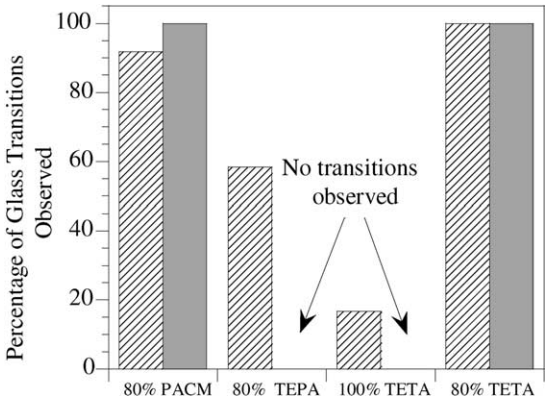

Fig. 1. Micro-thermal evaluation of experimental reproducibility for various curing agents. 10 °C/s μTA ramp rate (hatched) and 25 °C/s μTA ramp rate (solid).

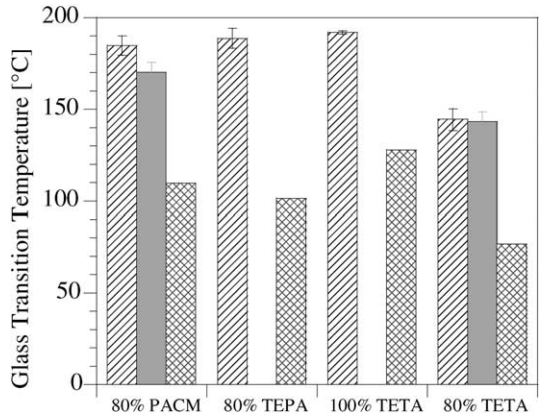

Fig. 2. Measured glass transition temperatures for various curing agents. 10 °C/s μTA ramp rate (hatched), 25 °C/s μTA ramp rate (solid) and DMA (cross-hatched).

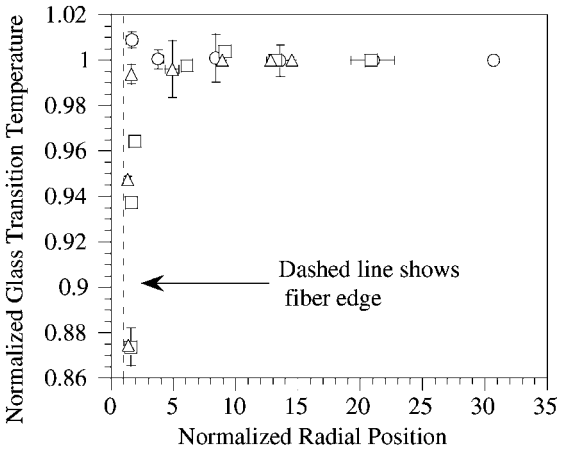

Fig. 3. Glass transition temperature variation within the interphase. 80% TETA resin with fibers 1 (circles), 2 (squares) and 3 (triangles).

cure profiles were constant in this set of experiments (S.D. for DMA, T_g measurements was less than 1%), we can draw several interesting conclusions based on the results presented in Fig. 3. As can be seen, interphase behavior was not observed for fiber 1. While this does not rule out the possibility of an interphase existing for this fiber type, it does restrict its size. Since no reduction in T_g was measured, for an interphase to be present, it must be smaller in dimension than the μTA probe contact diameter (on the order of 0.5 μm).

In addition, the interphase regions of fibers 2 and 3 had different dimensions. The data presented in Fig. 3 illustrates the fact that the interphase region from fiber 2 was much larger than that from fiber 3. The most likely cause for this is that TETA had a higher affinity for the surface finish of fiber 2, so more curing agent migrated in the direction of the fiber. To quantify this difference, the data presented in Fig. 3 representing the interphase region was linearly regressed using a least-squares algorithm. This data is presented in Table 1, where α is the normalized interphase dimension ($\alpha = R_{\text{interphase}}/R$) and $T_{g,min}/T_{g,bulk}$ is the hypothetical normalized T_g at the fiber surface.

As can be seen from Table 1, linear regression provides a method for comparison of interphase dimensions and variation in T_g. This may be a method for comparing the interphase regions of dissimilar materials, and correlating the micro-scale interphase properties to macroscopic thermal and mechanical properties.

Table 1
Linearly regressed interphase properties

Fiber	α	$T_{g,min}/T_{g,bulk}$
1	0.0	1.00
2	2.1	0.78
3	1.7	0.81

4. Conclusion

In the reinforcement of epoxy/amine thermosetting polymers with glass fibers, the fiber finish plays a critical role in determining the interphase properties of the material. As has been shown, the finish used to treat the fibers can determine the interphase dimension as well as the decrease in T_g near the fibers. In addition, μTA has been shown to be an effective tool for interphase analysis, providing a unique, quantitative method of measuring the thermal properties in the interphase region.

Acknowledgements

Support for this work was provided by the industrial sponsors of the Polymeric Composites Laboratory at the University of Washington. The authors wish to extend special thanks to BGF Industries for their support and cooperation.

References

[1] J.C. Seferis, P.S. Theocaris, Interrelations between Processing, Structure and Properties of Polymeric Materials, 1984.
[2] J.D.H. Hughes, Comp. Sci. Technol. 41 (1990) 13.
[3] P.S. Theocaris, The Mesophase Concept in Composites, 1987, p. 292.
[4] A. Murray, T. Lever, M. Reading, D. Price, Mater. World 6 (10) (1998) 615.
[5] A. Hammiche, M. Reading, H.M. Pollock, M. Song, D.J. Hourston, Rev. Sci. Instrum. 67 (1996) 4268.
[6] M.S. Tillman, T. Takatoya, B.S. Hayes, J.C. Seferis, J. Thermal Anal. and Calorimetry 62 (2000) 599.
[7] M.S. Tillman, T. Takatoya, B.S. Hayes, J.C. Seferis, in: Proceedings of the Fourth Mediterranean Conference on Calorimetry and Thermal Analysis, 1999, p. 122.
[8] M.S. Tillman, J.C. Seferis, in: Proceedings of the Forty-fifth SAMPE Symposium, 2000, p. 1029.
[9] M.S. Tillman, B.S. Hayes, J.C. Seferis, J. Applied Polymer Science 80 (2001) 1643.