Analysis of Polymeric Composite Interphase Regions With Thermal Atomic Force Microscopy

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ABSTRACT: Previous work on the characterization of interphase regions in thermosetting composite systems has focused on the inference of an interphase layer from effects noticed through macroscale mechanical and thermal testing. With the development of atomic force microscopy and active thermal probes for this technique, it is now possible to examine material thermal properties on a much smaller scale. Variations in microscale thermal properties of an aerospace-grade thermosetting resin system were evaluated for carbon and glass fiber reinforcement, using the modulated local thermal analysis mode of a TA Instruments 2990 μTA. The variations observed clearly demonstrate the presence of a soft interphase layer in the glass material and underline the importance of fiber–matrix interactions during the formation of the interphase. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1643–1649, 2001

Key words: composites; thermosets; interphase; thermal microscopy

INTRODUCTION

For many years, the study of fiber reinforced composite materials has focused on the structure–property relations 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 during the 1980s,[1] the focus of material evaluation changed to include the effects of processing parameters on the final characteristics of polymeric composites. To this end, the evaluation and characterization of microscale material structure–property changes with variation in processing conditions have 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. Several inclusive reviews of this material are presented by Hughes, as well as by Shorthall and Yip,[2–4] while a comprehensive presentation is given by Theocaris.[5] It is in this volume that Theocaris presents his models for the development of interphases in composite materials, one of which is presented in Figure 1. In this model, which represents the interphase as a cylinder around the fiber, the resin properties vary in the radial direction in the interphase layer. However, the boundary conditions of the layers are such that the fiber and matrix properties do not vary with radial position.

Interestingly enough, a considerable body of work has been amassed regarding the inference of fiber interphase properties from the measurement of mechanical tests.[6–11] In some cases, these mechanical tests have been related to thermodynamic/kinetic models that provide a theoretical description of resin property variance near the fiber surface.[12,13] Although no clear evaluation of

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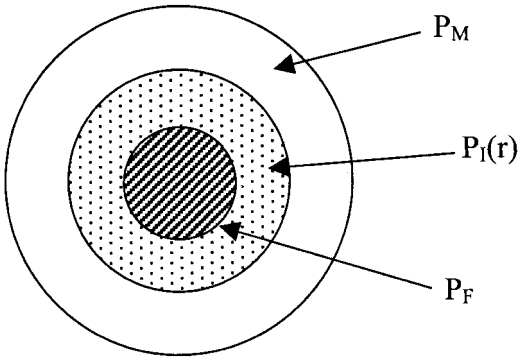

Figure 1 Transverse schematic of the three-layer interphase model proposed by Theocaris.

the structure of the matrix interphase had been performed, there was evidence to support variation of resin structure near fibers. This came primarily through the use of infrared (IR) spectroscopy of substrates coated with epoxy-based resins.[14–16] This type of isolated evaluation does not provide the structure for interphase regions within laminated structures, but it clearly shows that carbon fibers have a measurable effect on the curing kinetics of epoxy based resin systems.

With the development of the atomic force microscope (AFM),[17] new tools were added to the evaluation of interphase phenomena. This methodology, based on the use of mechanical force to probe the structure and properties of a specimen, has found widespread application in nanoscale materials science. In analysis of composite materials, the use of normal stiffness measurements to evaluate the resin modulus near the carbon fiber have been very successful, showing a clear link between the formation of the interphase layer and the mechanical and structural properties of the resin.[18,19] The growth of additional applications for atomic force microscopy has resulted in a large body of research focusing on the acquisition of microstructural knowledge of various materials.

The development of scanning thermal microscopy (SThM) has allowed researchers to evaluate the microscale thermal properties of materials. The use of a passive thermal probe to evaluate heat generation in small-scale devices has been very successful.[20–24] This technique uses a nanofabricated thermocouple to evaluate variations in temperature with a resolution of <100 nm.[21,23] Although this technique has found numerous applications in electronics research, it is limited because of the passive nature of the scanning probe. As such, it is unable to detect property-based variations on the microscale.

The development of an active thermocouple probe for use in SThM by Dinwiddie and coworkers has revolutionized the field of microscale materials analysis.[25–27] Using an SThM probe manufactured of wire made by the Wollaston process (5 micron diameter Platinum core surrounded by a 75-μm-diameter silver sheath), the developers produced a device that acted simultaneously as a miniature thermocouple and a resistive heating element. When this probe is coupled with an AFM, it is possible to resolve material differences based on thermal properties instead of mechanical force.

As in the case of traditional AFM, the probe is held in contact with the specimen using a feedback control loop to maintain a constant load on the surface. Using a separate feedback loop to maintain the probe at a fixed temperature,[28] it is possible to raster the cantilever over the surface of the specimen and generate a thermal map of the material. This provides information about the localized thermal conductivity of the specimen, and allows for visualization of the microscale heterogeneity in composite materials. This method is referred to as two-dimensional thermal scanning (2DThS).

In addition, 2DThS can be used to examine the subsurface morphology of a system. Through a modulation of the probe temperature in the 2DThS mode of operation, Reading and others found that the thermal probing depth could be varied by changing the frequency of modulation.[28,29] This type of analysis has been used to examine metallic structures beneath the surface of polymeric materials, and to observe dynamic behavior in polymeric blends.

Once the microscale morphology of a specimen has been evaluated, localized variations in thermal properties can be evaluated using local thermal analysis (LTA). Local thermal analysis involves modifying the probe temperature according to a programmed thermal ramp. By comparing the response of the active probe to a reference probe, differential thermal analysis (DTA) can be performed on a sample with a size of several cubic microns (μm^3).[30] Much like macroscopic thermal analysis techniques, a sinusoidal variation in the temperature can be superimposed on the nominal temperature profile, resulting in a modulated LTA (m-LTA). This addition of a sinusoidal modulation to the linear temperature ramp allows a lock-in amplifier to increase the signal-to-noise ratio, facilitating data analysis. A distinct difference exists between macroscale

thermal analysis techniques and the use of LTA, since the thermal probe acts as both a heating element and a temperature sensor, while the two are separate on a DTA or a DSC. As is the case with macroscale modulated thermal analysis, the phase angle and modulation amplitude play a role in evaluating materials.

Craig and others have used m-LTA to examine microscale transitions in various thermoplastic materials and pharmaceuticals.[31–35] Using the onset of troughs and peaks in the first derivative of the modulated temperature phase, these investigators identified the glass transition, recrystallization, and melting of the materials. The results of these experiments correlated well to similar experiments performed using DSC. In addition, the use of 2DThS in these two-phase systems allowed the researchers to evaluate the phase morphology of the materials.

The development of active probe SThM technology provides an exciting new method for the analysis of composite materials.[36,37] Through the composite methodology developed by Seferis,[1,38,39] an understanding of the processing–structure–property relationships in a polymeric composite relates material properties in the laboratory to the performance of those materials on the manufacturing scale. Since microthermal analysis allows microstructure exploration of the processing–structure–property relationship, it has become a useful tool in understanding polymeric composites.

In this respect, the thermal AFM is a unique instrument. The experimental techniques described above provide a method of simultaneously accessing both the processing–structure and processing–property relations through the use of 2DThS and LTA, respectively. The additional ability to analyze microscale changes in material properties such as the glass transition temperature (T_g) and thermal expansion unlock a new level of information for the study of interphase behavior.

The purpose of this work was to evaluate the interphase properties of a commercial aerospace composite system using active thermal atomic force microscopy. This was realized through the exploration of process–structure–property relations on the microscale, and the relation of observed effects to thermal analysis performed on the macroscale. Finally, the resulting interphase analysis was interpreted with respect to the lifecycle performance of composite materials in the aircraft environment.

EXPERIMENTAL

To evaluate the microscale presence of interphase regions in aerospace composites, materials were chosen to permit elimination of the effects of resin variation. To accomplish this, a commercial aerospace-grade material was used that is available with a single resin impregnated into a wide variety of fiber types. Two 20-ply laminates were constructed of this material with the fiber reinforcement as either an 8 Harness Satin 7781 style fiberglass or a plain-weave Toray T300 carbon fiber. To prevent the formation of voids due to air entrapment, the laminates were debulked between plies during lay-up. These laminates were cured simultaneously in a Lipton autoclave as per the manufacturers curing recommendations, which call for a pressure of 310 kPa (45 psig) and a 2.78°C/min (5°F/min) ramp to 177°C (350°F), a 2-h hold at 177°C, and a 2.78°C/min cool-down to room temperature.

To ensure resin consistency between the two materials used, laminates were examined for their macroscopic thermal behavior using a TA Instruments 2980 DMA. To evaluate the T_g of the materials, the instrument was used in a single-frequency oscillatory mode with a temperature ramp of 5°C/min from room temperature to 250°C, a frequency of 1 Hz, and an oscillation of 10 μm. The T_g was evaluated from the onset of the drop in the storage modulus.

To evaluate changes in the T_g near the fibers in these materials, cross sections of each laminate were polished. Final surface polishing was done using 0.3-μm Al_2O_3 grit. The polished specimens were then examined using a TA Instruments 2990 microthermal analyzer (μTA) with a TopoMetrix thermal probe (TopoMetrix model 1615-00). Probe temperature calibration was performed using room temperature (23°C) and the melting points of PETG (T_m = 165°C), Nylon 6 (T_m = 210°C), Nylon 6,6 (T_m = 247°C), and Nylon 4,6 (T_g = 277°C). A linear interpolation of probe resistance as a function of temperature was used to provide a calibration curve over the temperature range of interest. Using the modulated LTA mode of the μTA, the probe temperature was ramped from 50°C to 350°C at a rate of 25°C/s. For all experiments detailed in this article, the LTA temperature was modulated with an amplitude of 2°C at a frequency of 2.2 kHz, and data were collected at a rate of 150 data points per second.

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 focused on the edge of fiber tows that were near a pocket of resin in the cured laminate. From these scans, fibers were selected if they were near a resin-rich region that could be evaluated easily using LTA. It was important to select fibers near these resin rich regions so that a bulk T_g could be obtained to normalize the T_g near the fiber.

A series of these experiments was performed on each laminate. T_g values were obtained by evaluating the onset point of the drop in the micro-TMA signal, 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.[37] To normalize the T_g values, the following equation was used.

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

The distance from the center of the fiber was then 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), determined using topographic feature measurement functions integrated in the μTA controller software.

$$\frac{r}{R} = \frac{[(X_{LTA} - X_{fc})^2 + (Y_{LTA} - Y_{fc})^2)]^{1/2}}{R} \quad (2)$$

RESULTS

To ensure that the matrix material from the two systems had the same constituents, the results from the DMA analysis were evaluated as compared to the manufacturer's product specification. As shown in Figure 2, the DMA results indicate that the materials have identical T_g values when evaluated using a macroscopic thermal analysis technique, and that this value corresponds to the T_g provided by the manufacturer. However, the

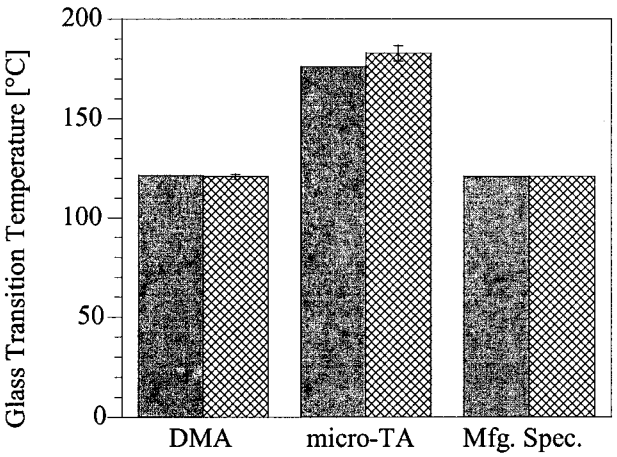

Figure 2 Measured glass transition temperatures (T_g) for commercial aerospace resin system on glass (solid gray) and carbon (cross-hatched).

T_g values obtained using the μTA are shifted to a higher temperature than those obtained using the DMA. This is the result of contact area dominated heat transfer effects on the microscale that artificially increase the temperatures measured using the μTA.[37,40,41] As discussed previously, this is the reason for normalization of the measured $T_g$values obtained using the μTA.

Using the 2DThS mode of the μTA, it was possible to visualize the structure of the cured carbon and glass laminates near the edges of fiber tows. As shown in Figure 3, the carbon and glass materials have different sizes and packing densities in the cured composite. Also, it is worth noting that while the region of carbon reinforced material shown below would make an excellent candidate for LTA (due to the large resin region to the right of the fiber bed), the presence of transverse oriented fibers prevents LTA from being performed on the glass material.

The evaluation of the glass transition variation with radial position from a fiber in the glass fiber-reinforced material is presented in Figure 4. As shown, the T_g of the material drops near the fiber surface to approximately 85% of the bulk value. This result supports the soft interphase theory presented by several investigators.[6,12,13] Whereas most research in the past has focused on the development of interphases for carbon fibers, Tsai and coworkers[6] have found evidence for a soft interphase in glass fiber materials.

In the case of the carbon fiber material, presented in Figure 5, the interphase is not as evident. The small drop in T_g near the fiber is most

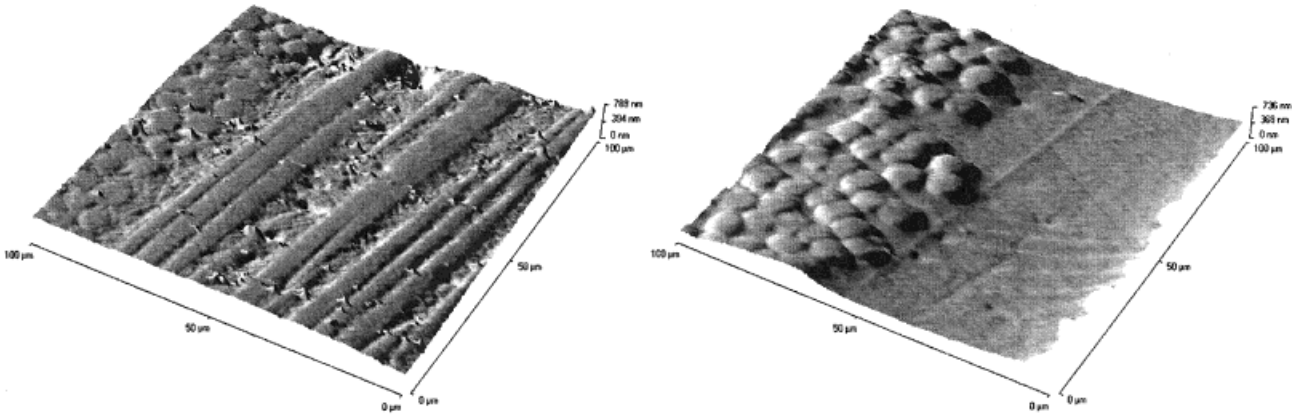

Figure 3 Topographical analyses of experimental laminates with glass (left) and carbon (right) reinforcement.

likely due to scatter introduced through data normalization. Since no clear interphase behavior was observed, the logical conclusion must be drawn that the interphase dimension is smaller than the minimum probe resolution for this technique.

DISCUSSION

In evaluating the importance of this finding, it is important to understand these results in relation to the end uses of these materials. As such, development of an understanding for the role of composites in the aircraft environment has been crucial. With the lower T_g of the resin matrix near the glass fibers, we have evidence that this aerospace resin system displays a long-range, soft interphase when it is impregnated and cured in glass fibers. In terms of durability, a soft interphase would result in lowered mechanical properties near the fibers in a laminate.[42] Since the matrix material nearest the fibers is expected to transfer the load from fibers to bulk matrix when the material is stressed, a lower strength and stiffness in this region will lead to reduced load transferring efficiency and possibly failure near the fibers. Of course, any failure near a fiber will tend to propagate down the length of the fiber at high speed, causing large scale fibrous delamination and part failure.

In addition, because the interphase region around the glass fibers has lower crosslink density than that of the bulk matrix, it is more susceptible to moisture ingression. Unfortunately, this will also lead to a lowering of the mechanical properties, and hasten the failure of a part. As such, intimate knowledge of the properties of the interphase region, as well as the subsequent ability to control those properties is of paramount importance in designed composite structures.

Alternatively, in the case of the carbon material, one expects the loads on the composite to be transferred more uniformly, and with greater efficiency. Since the interphase is relatively small, and regions close to the fiber exhibit the same T_g as the bulk, the interphase region must have less of an effect on the mechanical performance of this material than it does in the case of the glass-reinforced material.

On a broader scale, because the soft interphase region is large, and less efficient at transferring

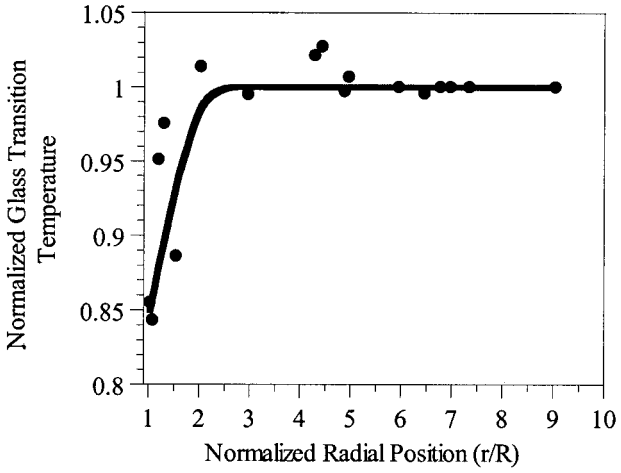

Figure 4 Observed decrease in glass transition temperatures (T_g) near glass fibers for commercial aerospace resin system.

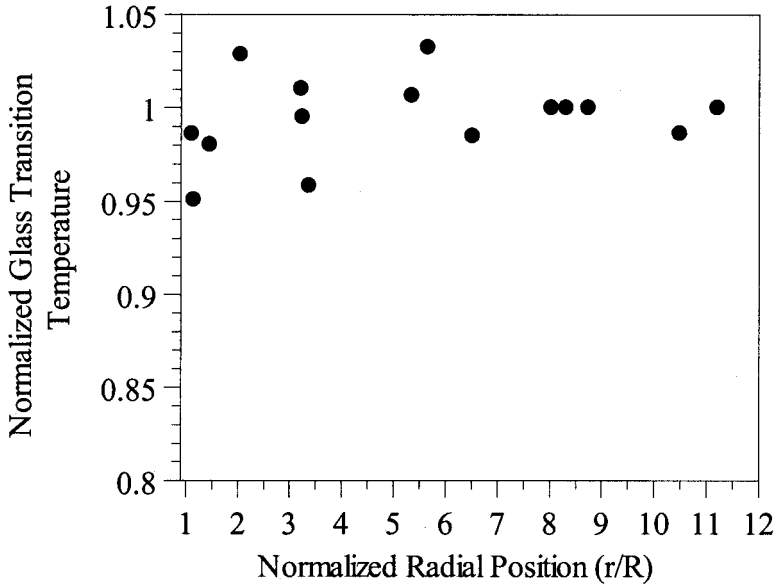

Figure 5 Observed decrease in glass transition temperatures (T_g) near carbon fibers for commercial aerospace resin system.

loads, the overall mechanical performance of a component will be decreased. As such, it is important to understand the phenomena that lead to the formation of interphase regions in composite materials, and thereby tailor the interphase for maximum performance. Now that the technology of active thermal AFM has been used to evaluate the presence of the interphase, characterization of various material interphases is no longer a matter of inferring their presence from mechanical tests.

CONCLUSIONS

The interphase thermal properties of a commercial aerospace composite resin system were evaluated. It was found that fiber type plays a significant role in the generation of the interphase. Microthermal analysis was employed to provide an effective method of measuring variations in glass transition temperature in near fibers in the cured laminates, and these data confirmed the presence of a soft interphase near glass fibers, but did not reveal the presence of an interphase near the carbon fibers. Collectively, this work provides a new methodology for directly evaluating the interphase thermal properties of composite systems, and clearly demonstrates the degree to which these systems can affect the performance of composite materials.

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