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INFLUENCE OF POLYMER SPECIMEN STRUCTURE ON THE REPRODUCIBILITY OF MICRO-THERMOMECHANICAL TRANSITIONS

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Abstract

Glass transitions of amorphous polystyrenes with low polydispersity were evaluated using the modulated Local Thermal Analysis mode of the TA Instruments 2990 μTA and evaluating the thermomechanical signal. Transition temperature variance and fraction of transitions measured were compared for high molecular mass thermosetting materials and the melt of Nylon 6.6. The transition reproducibility was found to decrease as the molecular size of the polymer samples increased. Reproducibility also decreased for thermosetting materials when the experimental ramp rate was decreased. Heat transfer within the specimen was evaluated using finite element analysis, allowing scaling of microscale experimental results for comparison to bulk transitions.

Keywords: microscale heat transfer, micro-thermal analysis, thermosetting polymers

Introduction

Atomic force microscopy (AFM) has paved the way for a variety of methods for quantitative surface analysis. Many attempts have been made to incorporate thermal imaging in AFM systems [1–5]. This was finally realized in an efficient manner following the development work by Dinwiddie *et al.* [6, 7], followed by Price *et al*. [8]. Using an AFM probe constructed of Wollaston Process wire (R=2.5 μm), the developmental team fashioned a device that simultaneously acted as a resistive thermocouple and an electric heating element. These probes are packaged with a modified ThermoMicroscopes Explorer AFM in two commercially available systems: the TA Instruments 2990 μTA and the ThermoMicroscopes Explorer PolymerSystem.

As with AFM, the probe tip is in contact with the specimen using a feedback control loop to maintain a constant load on the surface. When in contact with the test surface, a voltage is applied across the leads of the cantilever, heating the probe tip. As such, the μTA is capable of analyzing materials in two modes of operation:

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two-dimensional scanning (2DS) and local thermal analysis (LTA). Through the composite methodology developed by Seferis and Theocaris [9], an understanding of the processing-structure-property relationships in polymers relates material properties in the laboratory to the performance of those materials on the manufacturing scale. These process-structure-property relations are developed through variations in material processing coupled with integrated thermal and mechanical testing. In the case of heterogeneous materials, 2DS can be used to elucidate the structural features of a material. However, the real interest lies in obtaining microscale analyses of property variations through LTA.

Local thermal analysis involves modifying the probe temperature according to a programmed thermal ramp. By comparing the electrical power response of the active probe to a reference probe, power compensated differential thermal analysis (DTA) can be performed on a sample with a theoretical size of several cubic μm [10]. In addition to the μDTA signal, the vertical position of the probe can be evaluated as a function of temperature, giving a micro-thermomechanical signal (μTMA). 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 increases the signal to noise ratio, allowing for easier analysis of data. LTA differs from macroscale thermal analysis in that the thermal probe used with the microscope acts as both a heating element and a temperature sensor, while the two are separate on a DTA or a DSC.

Craig and others have used m-LTA to examine microscale transitions in various thermoplastic materials and pharmaceuticals [8, 11–14]. Using the onset of troughs and peaks in the first derivative of the modulated temperature phase, they identified the glass transition, recrystallization, and melt of the materials. The results of these experiments correlated well to similar experiments performed using DSC. In addition, the use of 2DS in these two-phase systems allowed the researchers to evaluate the phase morphology of the materials.

However, when we attempted to reproduce such work using aerospace thermoset materials, glass transition temperatures (T_g) were not easily detected [15]. Furthermore, the reproducibility of these transitions was low. It was assumed that this was a result of the differing nature of transitions in thermoplastics and thermosets. Since isolated regions of thermoset materials can be very highly crosslinked, and have very few free end groups, the sampling volume of any thermal analysis technique plays a role in determining whether or not a transition will be detected. For bulk thermal analysis techniques such as DSC and TMA, this is not a problem since sample volumes are large enough to have a reasonably even distribution of crosslink densities. However, for the small theoretical sample volume of an LTA experiment, some thermosetting materials may not show any thermal transitions.

There were three areas of focus for this work. First, it was desired to explore the fraction of transitions observed for polymeric materials of various molecular mass and crosslink densities. Second, the influence of temperature ramp rate on the fraction of transitions observed and on the temperature of transitions was examined for a commercial aerospace epoxy system and a thermoplastic. Finally, the thermal behavior of a representative polymer was modeled using finite element analysis of the heat transfer phenomena.

Experimental

To evaluate the variance in reproducibility with changes in molecular size and structure, LTA was performed on polystyrene standards of two molecular masses: 18.700 g mol^{-1} (Aldrich Catalogue number 32.774-3) and 212.400 g mol^{-1} (Aldrich Catalogue number 32.778-6). Nylon 6.6 (Aldrich Catalogue number 18.112-9) with an unknown polydispersity was also evaluated. These Nylon samples were premelted in a TA Instruments 2910 DSC and cooled slowly to ensure a high degree of crystallinity. As such, it was possible to measure the melting transition of the Nylon using the micro-thermal analyzer.

This was followed by analysis of a model epoxy resin plaque (Epoxy Resin A) designed to have a mid-range crosslink density. This system consisted of diglycidyl ether of bisphenol A (DGEBA), Epon 828 from Shell Chemical, and was cured with dicyandiamide and diuron. Finally, LTA was performed on two commercial epoxy/carbon fiber composite systems: Hexcel F593 and F263. These specimens were prepared as ten ply laminates, and cured at 450 K and 653 kPa. The LTA's were then performed on the toolside of the cured laminate, which is covered by a resin rich layer suitable for analysis. For these experiments examining reproducibility, all thermal analyses were performed using a heating ramp from 298 to 623 K at 25 K s^{-1}.

Following this analysis, LTA was performed on cured laminates of Hexcel F593 and Nylon 6.6 disks to evaluate the effects of heating rate on transition measurement. For this study, heating rates of 5, 10, 15, 20 and 25 K s^{-1} were used as the temperature was ramped from 348 to 623 K.

All data in this study was collected using a TA Instruments 2990 Micro-Thermal Analyzer with a TopoMetrix thermal probe (TopoMetrix model number 1615-00). Probe temperature calibration was performed using room temperature (295 K) and the melting points of Nylon 6.6 (T_m=540 K) and benzoic acid (T_m=395 K). Each reference temperature was sampled with the Micro-Thermal Analyzer four times, and the probe resistance obtained at the softening point of the material (as measured through the drop in the TMA signal) was set to the material transition temperature obtained using a TA Instruments 2910 DSC ramped at 5 K min^{-1} with no temperature modulation. A linear interpolation of probe resistance as a function of temperature was used to provide a calibration curve over the temperature range of interest. For all experiments detailed in this paper, the LTA temperature was modulated with an amplitude of 2 K at a frequency of 2.2 kHz, and data was collected at a rate of 150 data points per second. Average transition temperatures and fractions of measured transitions are based on a minimum of ten measurements for thermoplastics and a minimum of 55 measurements for thermosets.

Finally, the specimen heat transfer during an LTA was modeled using NASTRAN software from the MacNeal-Schwendler Corporation. The effects of variation in probe contact radius, heating rate, and specimen thermal diffusivity on the heat transfer within the specimen were evaluated. The model was evaluated for tip radii (R) of 0.5, 1.0, 2.5 and 5.0 μm at a heating rate of 25 K s^{-1} and a thermal diffusivity (α) of $8.3\cdot10^{-9}$ m^2 s^{-1}. This was followed by evaluation of a tip radius of 1.0 μm and $\alpha=8.3\cdot10^{-9}$ m^2 s^{-1} for heating rates of 10, 15, 20 and 25 K s^{-1}. Finally, the effect of variance in α was evaluated using a constant probe radius of 1.0 μm and a 25 K s^{-1} heating rate, with values of $8.3\cdot10^{-9}$, $4.2\cdot10^{-8}$, $8.3\cdot10^{-8}$, and $1.3\cdot10^{-7}$ m^2 s^{-1}. Through symmetry, the finite element model was reduced to one fourth of a cubic specimen. The model used is shown graphically in Fig. 1, along with the form of the heat transfer equation that was solved. The boundary conditions were given such that the tip contact area was in thermal equilibrium with the tip, and the free surface of the sample was at 298 K. From this, the difference in temperature between the free surface and all points in the interior of the sample was calculated. This was plotted as $\Delta T_{\text{specimen}}$ as a function of ΔT_{probe} where $\Delta T_{\text{specimen}}$=(specimen temperature at a depth of 1 μm)–(298 K). And ΔT_{probe}=(contact area temperature)–(298 K).

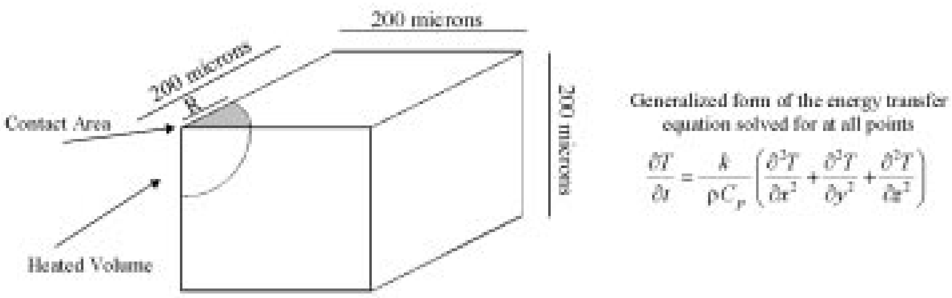

Fig. 1 Finite element model used to solve for the temperature profile in LTA specimens as a function of time

Results and discussion

When analyzing a material's response to the thermal ramp, the sensor position and derivative of power were plotted as a function of programmed temperature. For a thermosetting material such as F593, a glass transition is characterized by a step change in the sensor signal, or a large shift in the thermal expansion of the specimen, as shown in Fig. 2. Evaluating material transitions in this manner is equivalent to microscale thermomechanical analysis (μTMA) as detailed by Murray *et al.* [16]. As with TMA, the μTA provides information about the thermal expansion before and after a material transition. Unlike TMA, the μTA can qualify the power required to effect this transition. As such, it has the capability of simultaneously evaluating the thermomechanical and qualitative thermochemical behavior of the specimen, resulting in a combination of TMA and DTA. Additionally, the μTA is able to evaluate these properties at various microscale locations within the specimen.

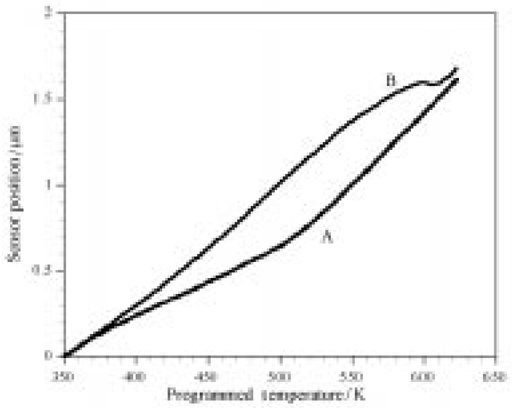

Fig. 2 μTMA data for two LTA experiments with F593 showing glass transitions resulting in change in thermal expansion (A) and a step change in the sensor signal (B)

As such, micro-thermal analysis should be a useful tool for measuring variance in glass transition temperatures throughout a composite material. However, when preliminary experiments were performed, glass transitions were not observed at every LTA location selected. To confirm this finding, the aforementioned experiments were performed. The results of these experiments are shown in Table 1.

Table 1 Fraction of LTA measurements yielding a transition, and the corresponding average transition temperatures

Sample	Signal		Transition temperatures			
	μDTA/%	μTMA/%	μDTA/K	μTMA/K	DSC/K	DMA/K
18k MW PS	100	100	415	417	365	–
212k MW PS	100	100	406	409	365	–
Nylon 6.6	100	100	547	548	540	–
Epoxy Resin A	68.8	93.8	428	429	391	–
Hexcel F593	12.1	15.5	503	554	–	454
Hexcel F263	0	9.5	–	476	–	460

The information presented in Table 1 confirms the preliminary assumption that the number of transitions detected decreased with crosslink density. As can be seen, transitions were measured in all three thermoplastic materials for all of the experiments performed. However, the measured melting point of the Nylon material was offset from its preset calibration value by nearly 10 K. This is due to the correlation of Nylon softening temperature with the melt temperature measured in a DSC. As further experiments have elucidated, a better calibration can be obtained through the correlation of thermoplastic melting temperatures (as measured through DSC) to the corresponding drop in the DTA signal measured through micro-thermal analysis [17].

As the crosslink density was increased to that of a medium crosslink density thermoset (Resin A), the fraction of measured transitions declined, and then decreased further when the specimen was changed to the highly crosslinked aerospace epoxy systems (F263 and F593). Since bulk T_g also provides a rough correlation of crosslink density for thermoset systems, the macro-thermal analysis data collected show that the number of transitions measured using micro-thermal analysis decreased as the crosslink density of the thermosets increased [18]. In addition, the surface T_g measured with the μTA increased with the increases in the bulk T_g. Finally, it is important to note that the fraction of transitions detected with the μDTA signal decreased faster than the fraction of transitions detected with the μTMA signal. Since the μTMA signal was calculated from the AFM force feedback signal, it was expected to have detection limits in the range of nanometers, while the changes measured were on the order of μm. On the other hand, the μDTA signal was measured directly from the current supplied to the probe and had detection limits on the order of milliwatts. Unfortunately, for the volumes of sample being evaluated, material transitions also had enthalpies on the order of milliwatts, reducing the effectiveness of the μDTA signal.

Table 2 presents information on the temperature based reproducibility of micro-thermal measurements. As can be seen, the thermoplastic materials display transition measurements with very low standard deviations, indicating that the transitions are highly reproducible. Interestingly enough, the temperature reproducibility of the thermosetting materials is not much worse than the thermoplastics. Only three of the measurements for thermosetting materials have standard deviation values that are set well apart from the thermoplastics (the F593 μTMA signal and both F263 signals). Since the standard deviations for most of the materials are similar, it reinforces the idea that the results of LTA performed on thermosetting materials are highly dependent on the localized structure of the material. From this, we can gather that the LTA experiment is not sampling enough material to effect a transition in the highly crosslinked thermosets.

Table 2 Standard deviation for temperature averages reported in Table 1

Sample	Standard deviation of transition temperatures			
	μDTA/K	μDTA/%	μTMA/K	μTMA/%
18k MW PS	10.8	2.6	10.4	2.5
212k MW PS	10.7	2.6	2.2	0.5
Nylon 6.6	8.6	1.6	2.8	0.5
Epoxy Resin A	4.2	1.0	6.4	1.5
Hexcel F593	10.2	2.0	47.7	8.6
Hexcel F263	–	–	50.8	10.7

By changing the thermal ramp of the LTA for F593 and Nylon 6.6, the fraction of transitions measured was altered. As shown in Table 3, for the thermosetting material, increasing the ramp rate increased the fraction of transitions observed. A lower heating rate tends to smooth out thermal transitions. In the case of micro-thermal analysis of thermosets the transitions observed were small step changes or small shifts in thermal expansion. It was likely that the same fraction of transitions were occurring for all experiments, but they went unnoticed for the experiments at lower heating rates. This was not a problem for the melt of the Nylon. Since the melt was a very strong transition in both signals, the smoothing effects of the varying heating rate did not affect the observance of the transitions. As such, it is advantageous to perform experiments with the highest ramp rate possible when evaluating thermosetting materials. Unfortunately, the scatter in the data was too large to draw any conclusions about the effects of heating rate on the measured temperature of transition for the thermoset. However, the transition temperature for the Nylon is very reproducible, regardless of ramp rate.

Table 3 Fraction of LTA measurements yielding a transition and the corresponding average transition temperatures with variance in ramp rate

Ramp rate/ °C s^{-1}	F593 transitions				Nylon 6.6 transitions			
	μDTA/ %	μTMA/ %	μDTA/ K	μTMA/ K	μDTA/ %	μTMA/ %	μDTA/ K	μTMA/ K
5	0.0	0.0	–	–	100	100	549	548
10	0.0	2.0	–	561	100	100	546	547
15	3.8	9.4	558	499	100	100	539	546
20	5.7	7.5	579	558	100	100	549	548
25	12.1	15.5	503	554	100	100	549	548

As shown in Table 1, the observed values for the glass transition temperatures were significantly higher when measured through LTA than when measured through traditional bulk thermal analysis. Furthermore, the data presented in Table 3 indicates that the number of transitions measured was dependent upon the ramp rate, while the transition temperature appears to have had no correlation to ramp rate. To account for these apparent discrepancies, it was necessary to examine the heat transfer in small volumes of the specimens during LTA experiments.

Evaluation of the temperature profiles within the sample showed several interesting features. Initially, a representative value of thermal diffusivity was used to simulate polystyrene. To effectively evaluate the finite element model, the temperature at various depths within the specimen was plotted as a function of surface temperature (programmed probe temperature). A depth of 1 μm was selected for further analysis. This depth was selected to give a representative volume needed to thermally observe a transition in thermoset materials.

Figure 3 displays the results of changing probe radius on the heating efficiency of the experiment. As can be seen, the specimen temperature only followed the probe temperature closely for a large probe radius. While this condition may be met in thermoplastic materials, where the probe was forced into the specimen as the surface melts, it was certainly not the case in thermoset materials, where the surface remains relatively rigid before and after the glass transition. This serves to explain the shift in the glass transition temperatures observed for the thermoset systems. When enough of the specimen was at a high enough temperature to undergo a thermal transition, the probe was already at a much higher temperature.

As shown in Fig. 4, the heating correspondence between the surface and the specimen at depth is not a strong function of heating rate. This is in line with the small sample size involved in the experiment. Since the thermal sampling volume is so small, the material can react quickly to rapid changes in temperature imposed on the specimen surface. This is reinforced by the data presented in Fig. 5, showing the ef-

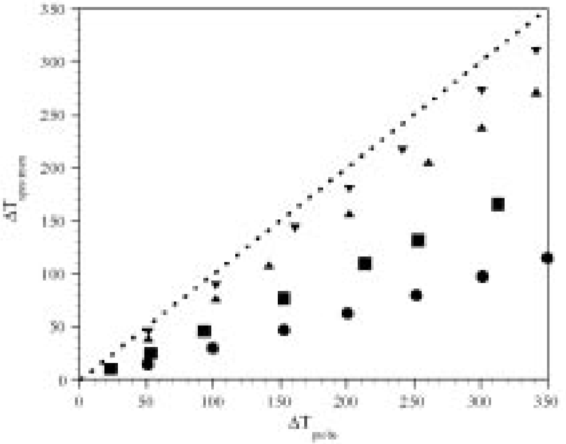

Fig. 3 Specimen temperature at a depth of 1 μm as a function of probe temperature, showing heating efficiency dependence on contact radius, with probe radii of 0.5 (●), 1.0 (■), 2.5 (▲), 5.0 μm (▼), and ideal heating (dashed line).

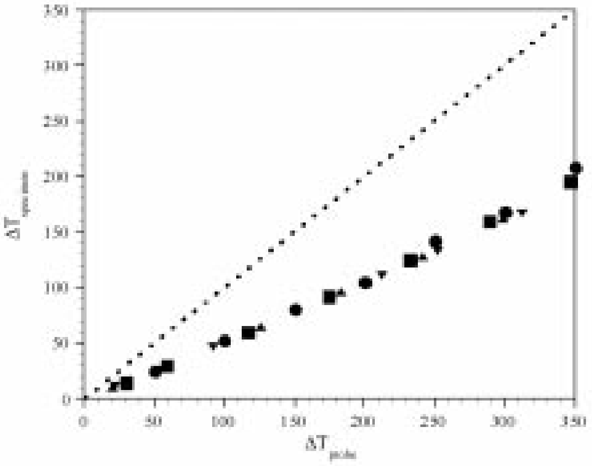

Fig. 4 Specimen temperature at a depth of 1 μm as a function of probe temperature, showing heating efficiency dependence on heating rate, with heating rates of 10 (●), 15 (■), 20 (▲), 25 K s^{-1} (▼), and ideal heating (dashed line)

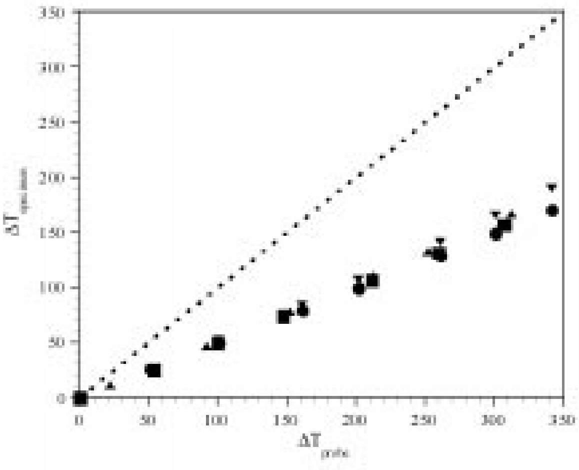

Fig. 5 Specimen temperature at a depth of 1 μm as a function of probe temperature, showing heating efficiency dependence on specimen thermal diffusivity, with α values of $8.3\cdot10^{-9}$ (●), $4.2\cdot10^{-8}$ (■), $8.3\cdot10^{-8}$ (▲), $1.3\cdot10^{-7}$ $m^2\ s^{-1}$ (▼), and ideal heating (dashed line)

fect of varying the thermal diffusivity of the sample. In this graph, it is clearly observed that changing the thermal properties of the sample has little effect on the heating efficiency for the experiment, indicating that the small sample size allows rapid thermal equilibrium.

This model helps verify the conclusions drawn from Tables 1 and 3: that the fraction of transitions observed is highly dependent on the molecular size of the specimen, and that the temperature ramp rate does not affect the measured transition temperature, but does serve to smooth out measurable transitions in thermoset materials.

Conclusions

In the analysis of polymeric composite materials, the simultaneous evaluation of processing-structure and processing-property relations provides a wealth of knowledge regarding the behavior of these materials. With the technology of micro-thermal analysis, it is now possible to access both of these important relations with one instrument. However, there are material and technique based limitations to this instrument, particularly in the area of probe reliability. As was shown through finite element analysis, the contact area between the probe and substrate plays a critical role in the generation of meaningful data. As such, specimen preparation is critical for this technique, as is the elimination of inconsistencies save for those present in the material itself. The use of this technique to analyze thermosetting materials may provide useful knowledge. However, this knowledge must be generated by methods different from those developed for the analysis of thermoplastic materials. As we have shown, the response of thermosetting and thermoplastic materials to this type of analysis is quite different. Collectively, in this study micro-thermal analysis was found to be a feasible technique for evaluating polymeric materials, and future refinement through finite element modeling should provide additional information regarding the process-structure-property relations of polymers and composites.

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