Characteristics of Tg Detection Using Micro Thermomechanical Analysis

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ABSTRACT

The detection of the glass transition (Tg) is a fundamental and important measurement in the thermal analysis of polymers. Thermomechanical analysis (TMA) is a basic technique that easily measures the Tg in many polymers. In TMA, a probe is placed on a sample surface and detects Tg by either expansion or penetration as the sample is heated. Recently, the advent of a new thermal analysis technique, Micro Thermal Analysis (μTA™), has introduced a thermomechanical technique based on detecting expansion or penetration with a thermal Atomic Force Microscopy (AFM) probe. This technique, termed μTMA™, can also detect Tg by penetration, but on cubic micrometer size volumes of material. As opposed to "macro" TMA, μTMA functions by heating the thermal probe. Characteristics of how this new technique detects Tg will be discussed.

INTRODUCTION

The glass transition temperature (Tg) is one of the most useful thermal parameters in characterizing a polymer. Many important properties can be correlated to Tg including molecular weight, crystallinity, degree of cure and hardness *(1)*.

Thermomechanical analysis (TMA) is a useful technique for detecting Tg. In a TMA experiment a probe is lowered onto the surface of a sample and the movement of the probe is measured as the sample is heated. With a load applied to the probe, a combination of modulus changes and expansion of the sample are observed. Depending upon the probe / sample contact area and the load applied, the Tg can be detected by either an upward (expansion) or downward (penetration) movement of the probe. With large contact areas and low forces expansion is primarily observed, whereas, for small contact areas and high forces penetration is primarily observed.

In Micro Thermal Analysis (μTA™) a tiny resistive thermal probe is mounted within an atomic force microscope (AFM) in place of the usual Si probe *(2-4)*. The thermal probe can collect images related to sample topography and thermal conductivity. Using the images as guides, points can then be selected for further examination by local thermal analysis (LTA). In this technique, the probe is positioned at the selected points and the temperature is ramped from a start to a

final temperature at very high ramp rates (5-25° C/s). Typically a few cubic micrometers are heated. By monitoring the vertical motion of the probe during heating, a curve analogous to a thermomechanical curve is collected. The technique is referred to as µTMA™ and is the focus of this paper. In addition, by plotting the power sent to the probe during a local thermal experiment a signal analogous to a DTA signal is collected and termed µDTA™. While neither signal is quantitative – only transition temperatures may be determined – the utility of the µTA technique lies in its ability to thermally characterize micrometer size volumes of material.

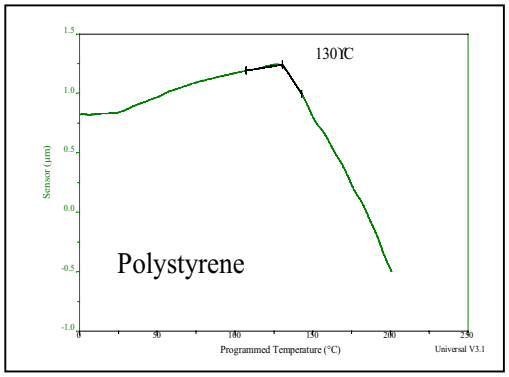
EXPERIMENTAL

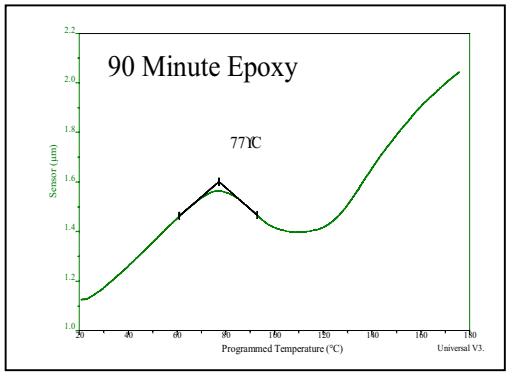
Two model systems were used to characterize how µTMA detects Tg: polystyrene and 90-minute epoxy. The polystyrene (PS) was in pellet form and distributed by the National Institute of Standards and Technology as a standard reference material (SRM 705a). Pellets were mounted on stainless steel metal stubs using double stick carbon black tape. These stubs were then mounted in the 2990 µTA for analysis.

The 90-minute epoxy was a standard commercial two-component epoxy consisting of a hardener and resin. The two components were mixed together on a small piece of aluminum foil and allowed to cure for one month prior to the experiments. The aluminum foil plus epoxy was then mounted on a stainless steel metal stub using double stick carbon black tape. The stub was then mounted in the 2990 µTA for analysis.

RESULTS AND DISCUSSION

Generally, the detection of Tg's by TMA appears differently for thermoset versus thermoplastic materials. For thermoplastic materials expansion is detected prior to the Tg and penetration into the sample at the Tg, whereas for thermoset materials expansion is detected prior to and after the Tg, with penetration at the Tg. These same types of curve characteristics are seen in µTMA also. Figures 1a and 1b illustrate these two types of characteristic Tg detection on polystyrene and 90 minute epoxy respectively. The figures show plots of probe deflection versus temperature. A positively sloping curve indicates that expansion of the probe/sample system is occurring while a negative slope indicates penetration due to softening of the surface.

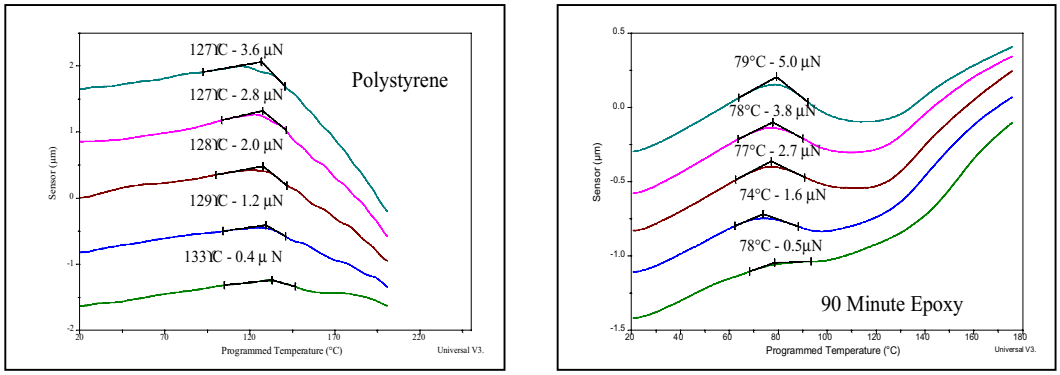




Figs. 1a and b. Tg detection on polystyrene and 90 minute epoxy respectively.

One difference between macro TMA experiments and µTMA experiments concerns the expansion portion of the curves. Quartz probes are used with macro TMA and these have very low thermal expansion. Therefore the expansion that is detected is mainly due to the sample. In µTMA experiments, however, the probe is made from platinum wire, and the expansion detected during a run includes the expansion of this wire.

In conventional TMA, the higher the force used the stronger the deflection at Tg. The same is true for µTMA. Figures 2 a and b show results for PS and 90 minute epoxy using increasingly higher forces. The forces are only estimates and are calculated using a rough spring constant of 1N/m and an initial cantilever deflection estimated by using a system-generated calibration constant. Table 1 quantifies the increase in deflection generated by a 3x increase in force.

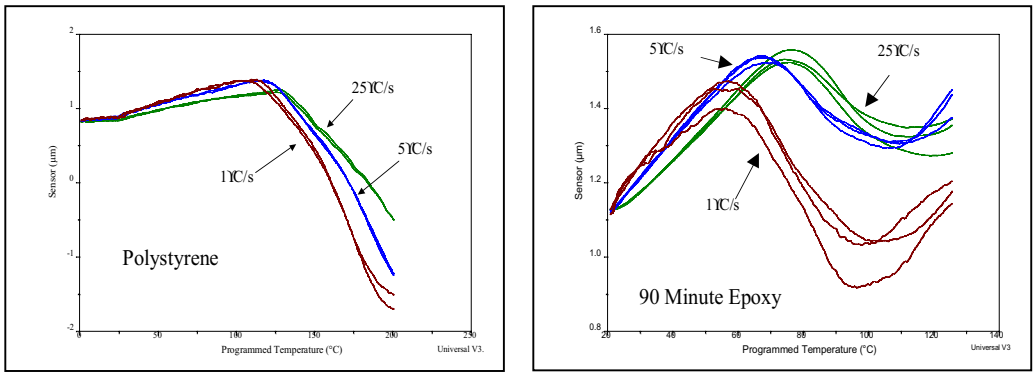


Figs. 2 a and b. Effect of increasing force on Tg detection.

Table 1

	Increase in Force	Increase in Deflection
Polystyrene	3x	2.5x
90 Minute Epoxy	3x	3x

Scan rate also has an effect on the detection of Tg with the Micro Thermal Analyzer using µTMA. There are three heating rate effects. As the heating rate is reduced the sensor deflection at Tg is increased, the signal to noise ratio is decreased and the transition temperature is shifted downward. Figures 3 a and b illustrate this. Again, these are typical of macro TMA experiments also.



Figs. 3 a and b. Effect of ramp rate on Tg detection.

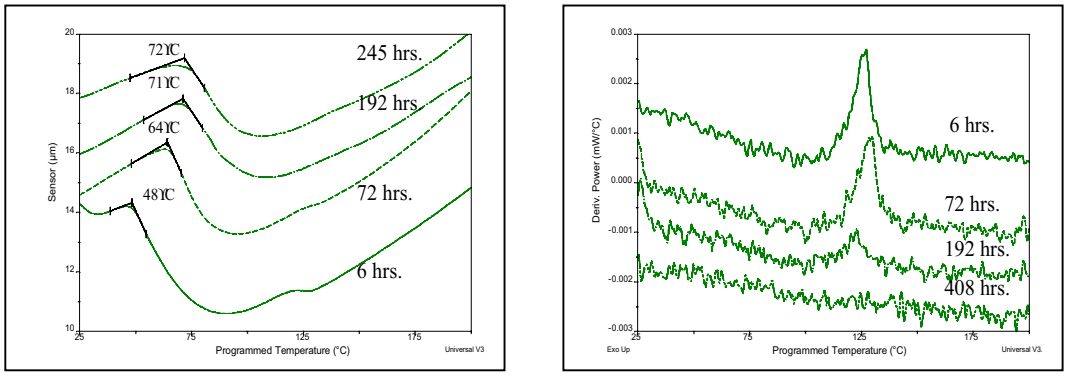
Table 2 below quantifies the effects seen with varying ramp rate for polystyrene.

Table 2

	25°C/s	5°C/s	1°C/s
Average Transition T (°C)	130	121	113
Average Pentration (μm)	1.63	2.58	2.98
Noise (nm)	<1	~3	~20

A unique aspect of the Micro Thermal Analyzer, as applied to curing systems, is its ability to collect both TMA and DTA data simultaneously. Both the shift in Tg and the decrease in the exotherm associated with curing can be detected and tracked – something macro TMA cannot do. Figure 4 shows an example for 90-minute epoxy.

Figure 4a indicates that the Tg shifts from 48°C to a stable value of 72°C in a span of about 245 hours. Figure 4b tracks the disappearance of the curing exotherm at 150°C over time. After 408 hours of curing the exotherm is no longer detectable.



Figs. 4 a and b. a. Shift in Tg versus curing time. **b.** Elimination of curing exotherm with curing time.

Because μTMA is a local technique – it analyzes only a few cubic micrometers of material – a distinct advantage over macro TMA is its ability to track changes in Tg laterally over a surface. Figure 5 shows three μTMA plots taken at three different positions on a polymer film (the derivative of the TMA signal is plotted for better observation of the Tg). The original surface was amorphous, but a conical dye was used to create a conical depression on the surface. It is reasonable to believe that the polymer chains might orient themselves at the point of highest force and therefore lose their amorphous nature. The data confirm this. Near the rim of the depression, the Tg is detectable. As the probe is moved towards the apex the Tg all but disappears. A distance of 1-2mm separates the rim from the apex

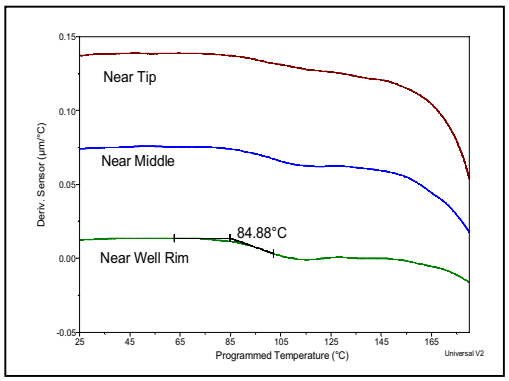


Fig. 5. Lateral tracking of changes in Tg on a polymer film surface.

CONCLUSIONS

Detection of Tg transitions by µTMA is not dramatically different than detection by macro TMA. Data from µTA experiments on polystyrene and 90-minute epoxy indicate that signal strength at the Tg increases with increasing force and with slower ramp rates. These observations also apply to macro TMA experiments. The noise level of the µTMA signal also increases with decreasing ramp rate, but not to a level that interferes with detection of the Tg.

However, detection of Tg by µTMA has some major advantages over conventional TMA for certain physical systems. Some of these advantages include the ability to analyze very small samples that may be impossible to analyze with macro TMA, and the ability to track changes in Tg over lateral distances.

Furthermore, detection of Tg's by µTA is unique in that with the added µDTA signal, simultaneous tracking the Tg and the curing exotherm of thermoset systems is possible. The µTMA signal will track changes in the Tg, while the µDTA signal will track changes in the curing exotherm.

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