

Characterization of Polymers by TMA

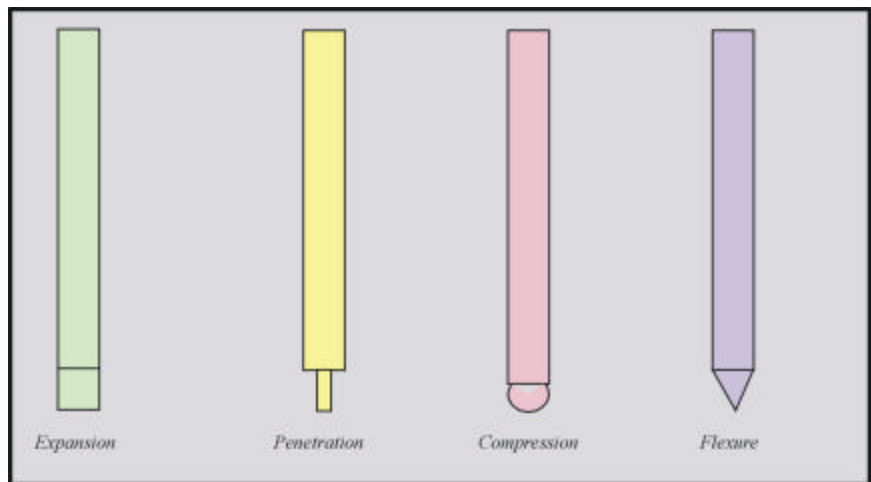
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Thermomechanical analysis (TMA) is one of the important characterization techniques in the field of thermal analysis. With TMA, the dimensional properties of a sample are measured as the sample is heated, cooled or held under isothermal conditions. The loading or force applied to the sample can be varied with TMA. The technique is used to assess the following important properties of polymers:

- Softening temperatures or Tg(s)
- Melting temperatures
- Stress relief effects at Tg
- Coefficients of thermal expansion (CTE)
- Dimensional compatibilities of two or more different materials
- Onset of foaming
- Relative degree of cure of thermosets
- Composite delamination temperatures
- Percent shrinkages of films and fibers
- Shrinkage forces
- Effectiveness of cling of films
- Testing of coatings on metals, films, optical fibers and electrical wires
- Assessment of transverse versus machine orientational properties of films

With the TMA technique, a number of different probe configurations are offered in order to

Figure 1. TMA probe configurations.



optimize the test conditions for a specific sample and/or application. The TMA probes offered by PerkinElmer include expansion, penetration, compression, flexure, extension and dilatometry. Some of the probe geometries are represented in Figure 1.

The most commonly used TMA probe is the expansion probe. This probe rests on the surface of the test specimen under low loading conditions. As the sample expands, during heating, the probe is pushed up and the resulting expansion of the sample is measured. Displayed in Figure 2 are the TMA results obtained on an epoxy – fiberglass printed circuit board sample at the

glass transition temperature (Tg) using the expansion probe.

At the glass transition event, the epoxy matrix exhibits a significant change in slope due to an increase in its rate of expansion. The onset temperature of this change in expansion behavior is the Tg of the resin. TMA is significantly more sensitive than DSC for the measurement of Tg of crosslinked or filled materials, such as composites.

One of the benefits of using the expansion probe is that coefficients of thermal expansion (CTE) can be easily measured by TMA. The CTE is a quantitative assessment of the expansion of a material over a temperature interval. When

Figure 2. Measurement of Tg of epoxy printed circuit board.

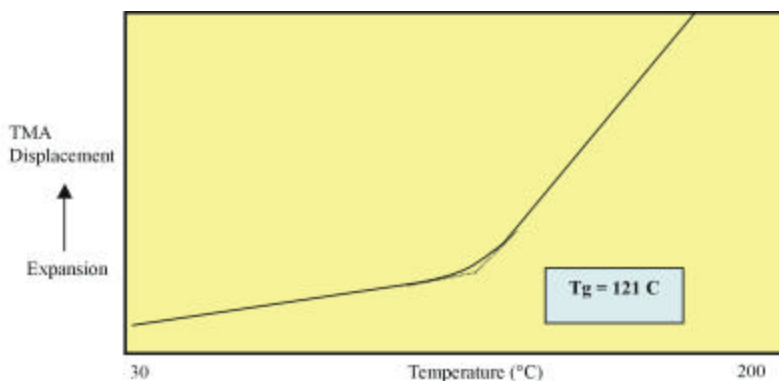


Figure 3. TMA results on epoxy PCB showing assessment of coefficients of thermal expansion.

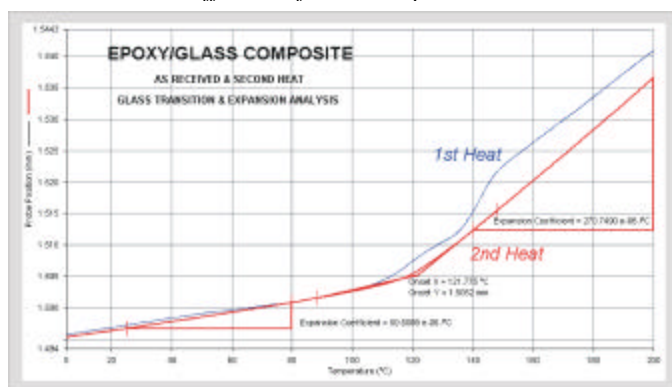
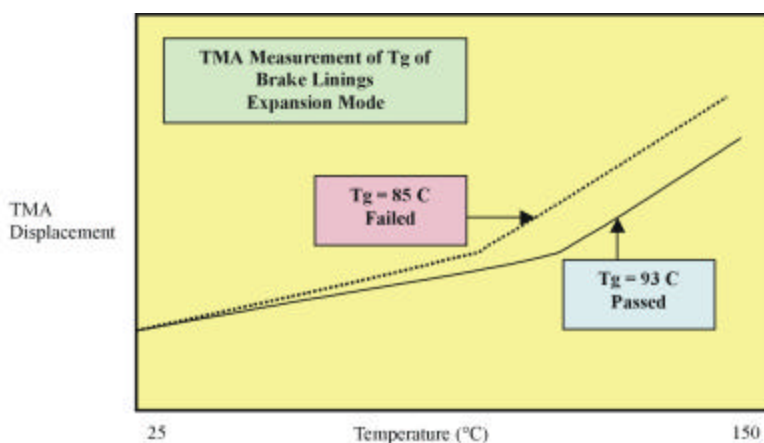


Figure 4. TMA expansion results on brake linings.



manufacturing products that contain two different materials, it is oftentimes critical to ensure that the materials will have CTE values that are identical to avoid the build-up of thermal stresses or to prevent leaks or component malfunctions. Displayed in Figure 3 are the CTE values measured on an epoxy printed circuit board below and above Tg.

Below Tg, the printed circuit board has a CTE value of 50.5 $\mu\text{m}/\text{m}^\circ\text{C}$, while above Tg, the value of the CTE increases to 270.7 $\mu\text{m}/\text{m}^\circ\text{C}$. For electronic materials, it is important that the other associated components have similar expansion coefficients to prevent the build-up of thermal stresses during operation. For example, better product lifetimes of electronic flip-chip packaging can be obtained on solder joints by ensuring that the CTE values of the solder and the epoxy underfill are identical.

Figure 3 also shows the effects of residual thermal stresses on the TMA measurements. During the 1st heating segment, the TMA expansion results show the occurrence of an undulation in its expansion behavior in the region near Tg. This reflects the release of stresses, which are frozen-in during processing. When the printed circuit board sample is cooled, and then reheated, a simple change in expansion rate is observed at Tg which indicates that the material is now free of thermal stresses or other thermal history related effects.

The high sensitivity of the TMA technique allows it to detect weak transitions that may not be observed by DSC. An example is the characterization of brake linings, which are highly filled and crosslinked. The TMA expansion



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Figure 5. TMA penetration probe results on electrical coil wire.

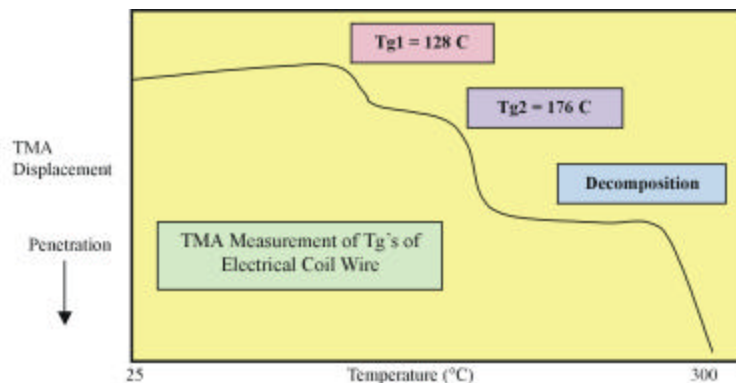


Figure 6. TMA penetration results on crosslinked and non-crosslinked polyethylene.

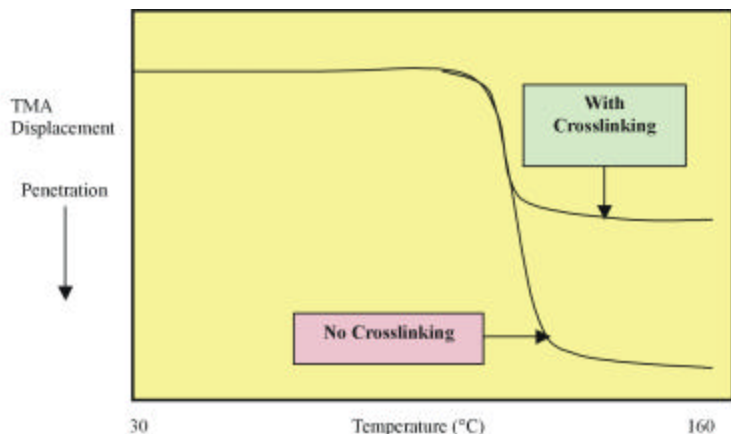
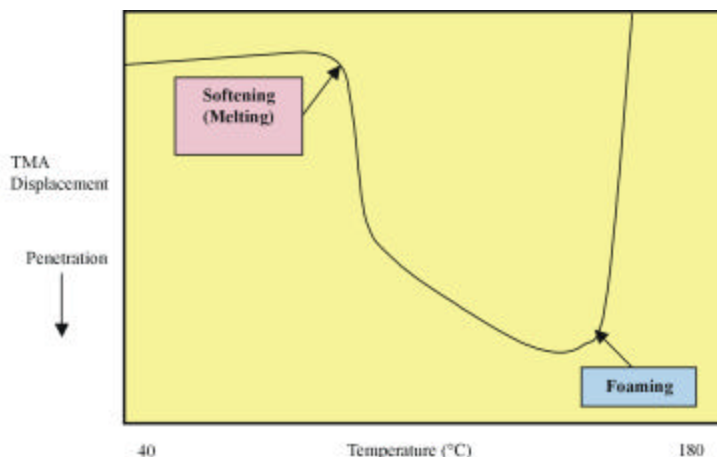


Figure 7. Characterization of LDPE foam by TMA compression mode.



results displayed in Figure 4 demonstrates that the TMA can detect the glass transition temperature associated with these highly filled materials.

The TMA penetration probe provides another means of assessing glass transition temperatures. When performing measurements with the penetration probe, loading is added to the probe so that it moves down through the material as it softens. The penetration probe is useful for measuring the glass transitions of coatings on a substrate. Displayed in Figure 5 are the TMA penetration results generated on a wire sample with two coatings. The wire is used to produce electrical motor coils and the inner coating prevents electrical contact between adjacent wires and the outer coating is used to bond the coil.

The TMA penetration results show that the outer coating has its Tg at 128 C and that of the inner coating occurs at 176 C. The decomposition of the resin is observed at approximately 260 C.

The penetration probe provides excellent data on the softening properties of thermoplastics. Shown in Figure 6 are the TMA penetration results on crosslinked and non-crosslinked polyethylenes. The sample with crosslinking exhibits a smaller degree of penetration due to the higher viscosity in the liquid region above the melting point.

In the next applications example, a sample of foam blown polyethylene was characterized using the compression mode of the TMA. The results are displayed in Figure 7.



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Figure 8. TMA extension results on polyester partially oriented fibers.

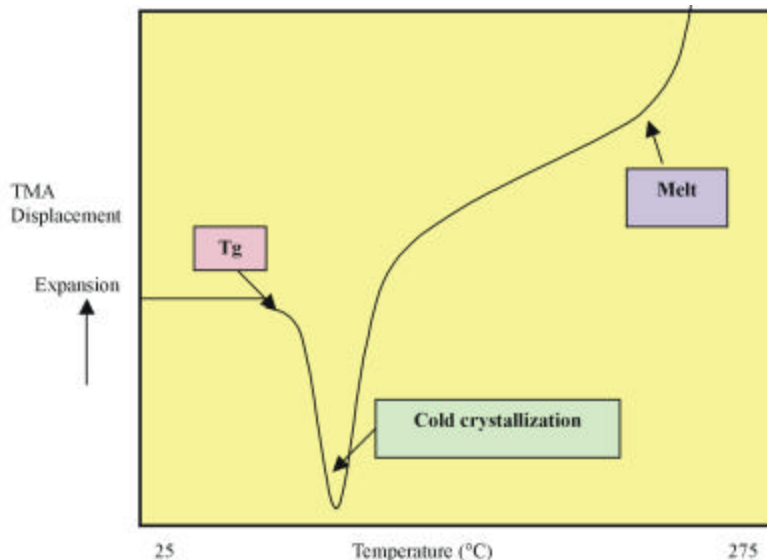
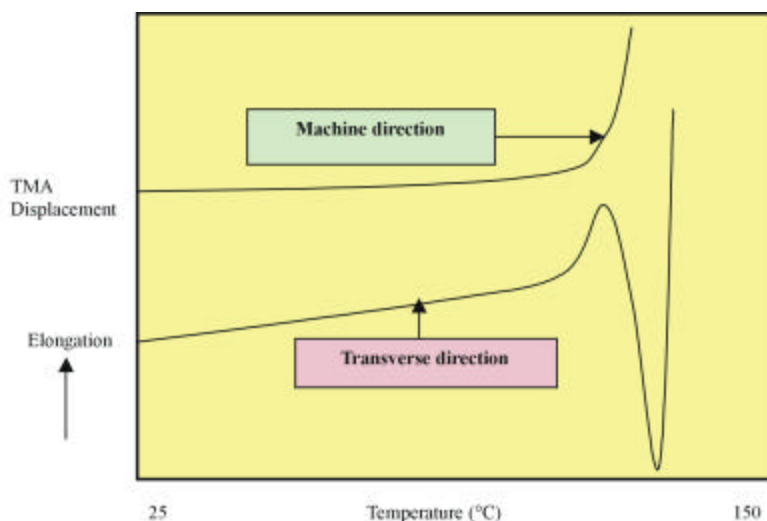


Figure 9. TMA results on biaxially oriented HDPE film in machine and transverse orientations.



The TMA results show that the LDPE sample undergoes a small amount of expansion between 40 and the melting temperature. At approximately 100 C, the sample melts and the lightly loaded probe

penetrates the sample and a rapid decrease in the thickness of the sample is observed. A quasi-linear response is obtained in the viscous region above the melting point and the slope of this reflects the degree

of crosslinking achieved by the resin. Upon further heating a large increase in the expansion of the polymer is observed and this reflects the swelling causes by the release of the nitrogen gas from the blowing agent. These results demonstrate that the TMA results can provide valuable information on the melting temperature, relative crosslink density and foaming temperature.

For the characterization of films and fibers, the TMA extension mode yields excellent results. With the extension mode of analysis, the sample is clamped between two fixtures which then hangs in the TMA sample tube. Displayed in Figure 8 are the TMA extension results generated on a sample of polyester (PET) partially oriented yarn.

The polyester yarn sample undergoes its glass transition event at approximately 75 C as reflected by the large amount of shrinkage or contraction that occurs beginning at this temperature. With continued heating, the amorphous phase in the fibers undergoes cold crystallization, which tends to stabilize the properties of the fibers. As crystallization takes place, the fibers undergo elongation. As the sample temperature approaches 250 C, the crystalline phase of the PET fibers melts, and substantial elongation takes place. TMA provides valuable characterization information on fibers and yarns including heat set or texturing temperatures, percent shrinkages, shrinkage forces and defect analysis.

The properties of oriented films are best studied using the extension mode of the TMA. In the next example, a sample of biaxially oriented high density polyethylene



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(HDPE) film was characterized by TMA. Test specimens were cut in the machine and perpendicular directions (transverse) in order to study the effects of processing on the biaxially stretched film.

Displayed in Figure 9 are the TMA results generated on the biaxially oriented HDPE film in the machine and transverse orientations using the extension mode.

In the transverse direction, the film sample expands slightly up to 133 C, where rapid shrinkage or contraction occurs due to the frozen-in orientation which has been imposed on the film in that orientation. At about 138 C, the film undergoes elongation due to the melting of the crystalline phase since the film is no longer able to support any load. In the machine direction, the film undergoes gradual expansion until sample melting occurs at 134 C, producing rapid elongation. The TMA results demonstrate that the biaxially oriented film exhibits distinctly different shrinkage/elongation characteristics depending on how the sample is cut and mounted in the TMA. There is apparently a high degree of orientation in the transverse direction as compared to the machine direction, due to the particular processing conditions employed in the production of the film.

The PerkinElmer TMA 7 provides state-of-the-art performance for the characterization of the dimensional properties of materials. The instrument offers the following key features to provide the best possible TMA results:

- High resolution (3 nanometer) strain detector for the measurement of even the smallest or most subtle dimensional changes
- Electromagnetic probe control (rather than less performing springs) which provides constant, load force regardless of sample dimensional changes
- Computer-controlled loading (or force application) which eliminates the use of weights, improving reproducibility of results
- Temperature-controlled detector (LVDT) for the elimination of baseline variability and better accuracy and reproducibility
- Automated cooling capability using ACA (automated cooling accessory) for ease of use and improved subambient performance
- Wide temperature range (-170 to 1000 C) using a single furnace eliminating the need for time consuming furnace changes

- Multiple probe types (including expansion, penetration, compression, flexure, extension and dilatometry) to permit the successful analyses of a wide range of samples and applications
- One-touch automated probe control for simplifying probe positioning and to provide the highest possible reproducibility of TMA results

Summary

TMA provides valuable characterization information on the dimensional properties of a wide range of materials. Used either alone or in conjunction with other thermal analysis techniques (DSC, TGA, DMA or thermoconductivity), the technique provides a large amount of valuable information on polymers and other materials which is difficult or even impossible to obtain by other analytical techniques. TMA offers a higher degree of sensitivity as compared to DSC for the detection of the Tg of highly filled or highly crosslinked materials, such as composites, printed circuit boards or brake linings. The state-of-the-art PerkinElmer TMA 7 provides outstanding results on a wide variety of materials and applications for both research as well as quality assurance uses.

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