

Thermomechanical Analysis

Basics of Thermomechanical Analysis with TMA 4000

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Introduction

Thermomechanical Analysis remains one of the most basic tools of material science. The new PerkinElmer TMA 4000, shown in Figure 1, continues the tradition of high sensitivity TMA in an attractively priced product.

The basis of TMA is the change in the dimensions of a sample as a function of temperature. A simple way of looking at a TMA is that it is a very sensitive micrometer.



Figure 1. TMA 4000 Thermomechanical Analyzer

Background

The need for a commercial TMA grew from hardness or penetration tests and was used on polymers in 1948¹. Subsequently, it has developed into a powerful tool in the analytical laboratory. TMA measurements record changes caused by changes in the free volume of a polymer². While engineers and rheologists tend to think of TMA data as defining changes in material behavior, polymer physicists and chemists may lean toward interpreting the data as changes in molar free volume. Changes in free volume, v_f , can be monitored as a volumetric change in the polymer; by the absorption or release of heat associated with that change; the loss of stiffness; increased flow; or by the change in relaxation time. The free volume of a polymer, v_f , is known to be related to viscoelasticity³, aging⁴, penetration by solvents⁵, and impact properties⁶.

The T_g in a polymer corresponds to the point in the expansion curve where the free volume begins to allow for greater chain mobility (Figure 2)⁷. Seen as an inflection or bend in the thermal expansion curve, this change in the TMA can be seen to cover a range of temperatures, for which the T_g temperature is a somewhat arbitrary indicator calculated by an agreed upon method (Figure 3). This fact seems to be not appreciated by inexperienced users, who often worry why perfect agreement isn't seen in the value of the T_g when comparing different thermal methods. The width of the T_g region can be as important an indicator of changes in the material as the actual temperature.

Experimentally, A TMA consists of an analytical train that allows precise measurements of position and can be calibrated against known standards. A temperature control system of a furnace, heat sink and temperature measuring device (most commonly a thermocouple) couples to the sample. Fixtures to hold the sample during the run are normally made out of quartz because of its low CTE, although ceramics and invar steels may also be used. Fixtures are commercially available for expansion, three-point bending or flexure, parallel plate, and penetration tests.

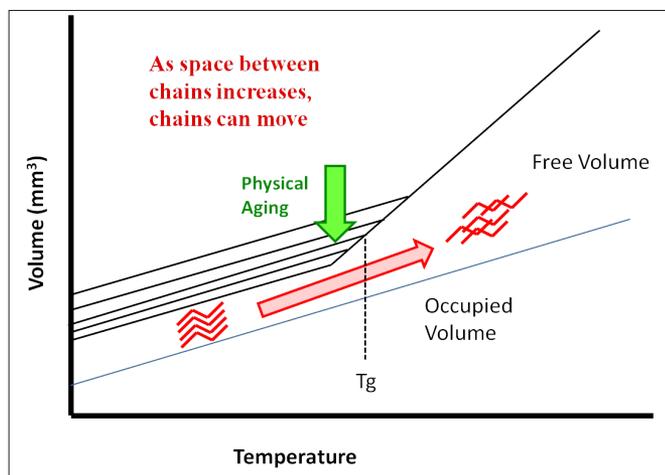


Figure 2. The increase in free volume is caused by increased energy absorbed in the chains, and this increased free volume permits the various types of chain movement to occur. Below the T_g various paths with different free volumes exist depending on heat history and processing of the polymer, where the path with the least free volume is the most relaxed.

Applications of TMA

TMA applications are in many ways the simplest of the thermal techniques. TMA merely measures the change in the height of the sample. The resultant information is useful in supplying information needed to design and process everything from chips to food products to motors. Because of the sensitivity of modern TMA, it is often used to measure T_g s that are difficult to obtain by DSC, for example those of highly cross-linked thermosets.

Expansion and CTE

TMA allows the calculation of the thermal expansivity⁸ from the same data set as used to calculate the T_g . Since many materials are used in contact with a dissimilar material in the final product, knowing the rate and amount of thermal expansion helps design around mismatches that can cause failure of the final product. This data is only available when the T_g is collected by thermal expansion, not by the flexure or penetration method. Different T_g values will be seen for each mode of testing⁹. The Coefficient of Thermal Expansion (CTE) is calculated on the linear sections of the curve as shown in Figure 3. Once this value is obtained, it can be used to compare to that of other materials used in the same product. Large differences in the CTE can lead to motors binding, solder joints failing, composites splitting on bond lines, or internal stress build up.

If the material is heterogeneous or anisotropic, it will have a different thermal expansions depending on the direction in which it has been measured. For example, a composite of graphite fibers and epoxy will show three distinct thermal expansions corresponding to the x, y, and z directions. Blends of liquid crystals and polyesters show a significant enough difference between directions that the orientation of the crystals can be determined by TMA¹⁰. Similarly, oriented fibers and films have a different thermal expansivity in the direction of orientation than in the perpendicular direction. This is normally addressed by recording the CTE in the x, y and z directions (Figure 4a).

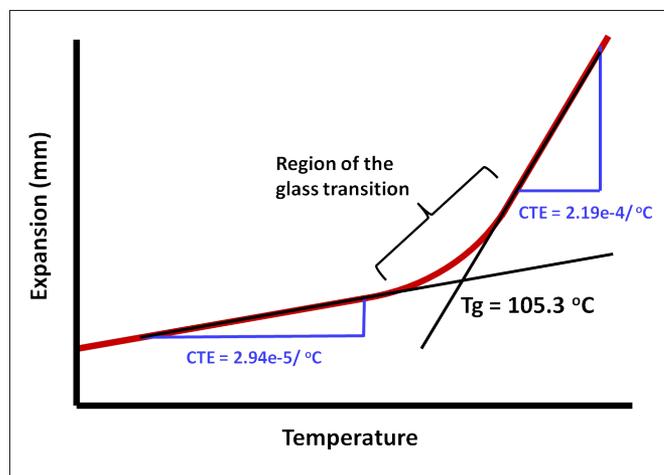


Figure 3. The glass transition and CTE of polystyrene is shown. The slopes of the baseline are used to calculate the CTE. The T_g is a region of between 90 and 110 °C, for which a T_g temperature is calculated as shown.

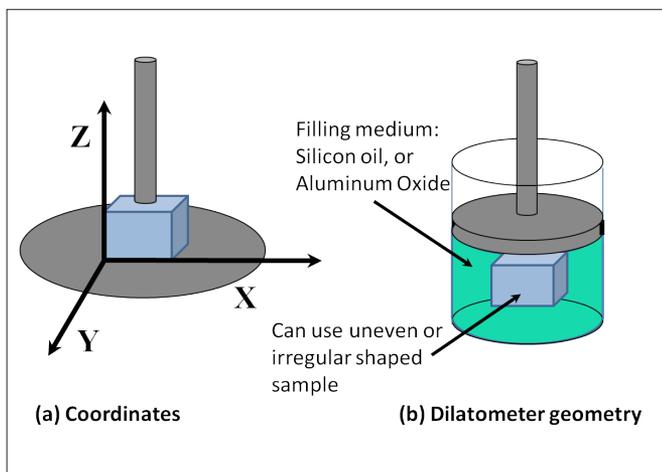


Figure 4. Heterogeneous samples require the CTE to be determined in the x, y and z planes (a) or in bulk to obtain a volumetric expansion in the dilatometer (b).

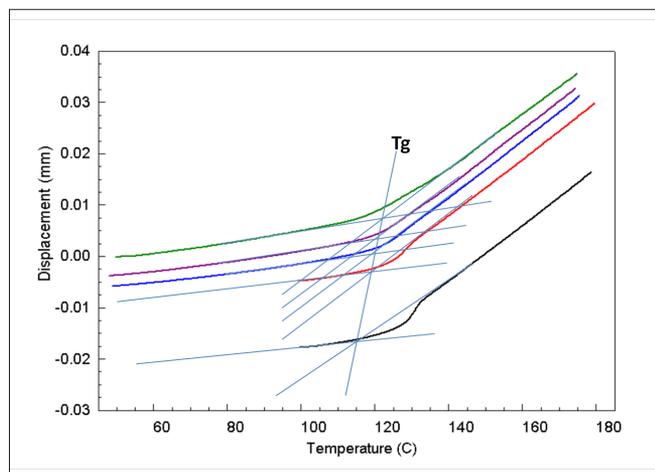


Figure 5. Effect of thermal history on the Tg of epoxy PC board: TMA 4000 data scanning at 5 °C/min after cooling at 40, 5, 2, .5 and .1 °C/min in the TMA. To compare to Figure 2 the data would be aligned at some temperature above the Tg region.

Dilatometry and Bulk Measurements

Another approach to anisotropic materials is to measure the bulk expansion of the material using dilatometry (Figure 4b). The technique itself is fairly old. It was used extensively to study initial rates of reaction for bulk styrene polymerization in the 1940s¹¹, an experiment, which is still used in thermal analysis class in the TMA. By immersing the sample in a fluid (normally silicon oil) or powder (normally Al_2O_3) in the dilatometer, the expansion in all directions is converted to a vertical movement, which is measured by the TMA. This technique has enjoyed a renaissance in the last few years because modern TMAs make it easier to perform than previously. It has been particularly useful for studying the contraction of a thermoset during its cure^{12,13}. The technique itself is rather simple: a sample is immersed in either a fluid like silicon oil or buried in aluminum oxide powder in the dilatometer and run thru the temperature cycle. If a pure liquid or a monomer is used, the dilatometer is filled with that liquid instead of the silicon oil or aluminum oxide.

Thermal History, Free Volume and Tg

In Figure 2 the glass transition is represented as the intersection of two straight lines. Above Tg the dimensional change is that of a liquid with all its molecular degrees of freedom. Below Tg the dimensional changes with temperature are those of an amorphous solid whose rotational and translational degrees of freedom have been frozen out. When a liquid is cooled rapidly (as often occurs in plastics processing) it results in a solid structure with more and larger voids than if the material is cooled slowly or allowed to sit for a long time in the low end of its Tg region. This latter case is called "physical aging", (as indicated by the green arrow in Figure 2). Amorphous material which is stored in its Tg temperature range will change mechanical properties, such as modulus, which will

affect its processing characteristics. The glass transition as measured by TMA using the intersection of the tangents above and below Tg indicate the extent of physical aging. If carried out in a dilatometer the extent of volume change can be measured (although in practice this may be a difficult measurement). Figure 5 shows an epoxy printed circuit board heated at 5 °C/min after cooling at 40 °C/min (top curve), 10 °C/min, 2 °C/min, 0.5 °C/min and 0.1 °C/min (bottom curve). The effect of the physical aging is to lower the Tg. Unlike measuring the Tg by DSC the Tg measured by TMA directly measures this physical aging effect¹⁴. Moreover it can be directly measured on the cooling curve (not shown in Figure 5 for simplicity) without loss of accuracy at slow cooling rates.

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