FREQUENTLY ASKED QUESTIONS

Thermomechanical Analysis

TMA 4000

A Beginners Guide to TMA 4000

Thermomechanical Analysis (TMA) is one of the most fundamental analysis techniques as it measures a very basic property of materials. On the simplest level, it measures softening the point or glass transition (Tg) as do tests like Vicat, Softening, and heat deflection point. All of these can be approximated in a Tg, and all tell you where a material changes from stiff to flexible. In addition, TMA allows you to measure the coefficient of thermal expansion, a property where mismatching it or not compensating for it can lead to failures in electronics, to motors, to food packaging.

This guide answers the basic questions asked by scientist and technicians new to the techniques, gives advice on how to understand TMA data, and introduces a bit of the theory behind it (without a lot of math). Hopefully, this will make the technique more understandable and more useful to practitioners.

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Q A What is Thermomechanical Analysis?

Thermomechanical Analysis (TMA), is a technique that measures changes in sample size as a function of temperature, time and load. This measurement can detect a change in size from expansion or contraction of the sample as well as a softening or deformation of the sample. Data from these experiments helps you predict how materials will respond when used in different temperature conditions.

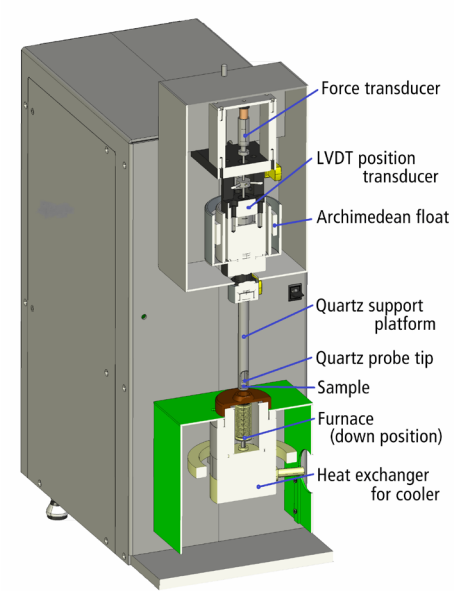

Figure 1. Cross section of the TMA 4000 showing the major components.

Q A How does TMA work?

TMA can be conceptualized as a caliper in an oven. A TMA applies a controlled load to a sample that sits in a temperature and atmosphere controlled environment. The sample is normally in a low expansion fixture like fuzed quartz, borosilicate glass, or ceramic. Above this sits the analytical train consisting of the force motor, LVDT, and upper probe. Force is normally applied by an electronic force motor although weights can also be used. Ideally the force applied is very close to zero so that the expansion of the material occurs without any restrictions. An LVDT (linear variable differential transducer), which is ideally temperature controlled, is used to measure changes in size. To assure quality measurements, the TMA 4000 uses an Archimedean float system to balance the weight of the analytic train. See Figure 1.

Q A What can TMA do for you?

TMA allows you to understand how your materials respond to heat. This can be very important for processing and for final applications. TMA can measure how much your material expands with temperature change (Coefficient of Thermal Expansion, or CTE), the temperature at which the glass transition occurs, or when other changes happen in the material. TMA is about 10 times more sensitive to the presence of a transition than even HyperDSC (also called Fast Scanning Rate DSC). If your material sees various temperatures in operation, TMA is an important tool you should be using.

Q A What kinds of materials can I measure?

TMA can be used on a wide range of materials from hard solids to rubbers, from thin films run in an extension fixture to liquids and gels run in a dilatometer. Materials studied include muscle tissue and polymers, ceramics and gels, or metals and curing systems. As all materials have a CTE, the technique is applicable to a wide range of industries. (There are some zero and negative CTE materials, but they tend to be rare, highly engineered, and exhibit this unusual behavior only in a narrow temperature range.)

Q A What is CTE?

When a material expands, we measure this expansion as a function of the sample height. We convert this to a normalized value for expansion called either coefficient of thermal expansion (CTE) or isobaric expansivity. This is done by dividing the change in length by the initial length times the temperature change:

$$\alpha = \frac{\Delta L}{L * \Delta T}$$

This value is normally on the order of parts per million, so for aluminum alpha is 22.4 x 10^{-6}/°C. An example is shown in Figure 2. This can be considered a measurement of the free volume of a material. It is sometimes called linear expansion, or LCTE, to distinguish it from volumetric expansion as measured in a dilatometer.

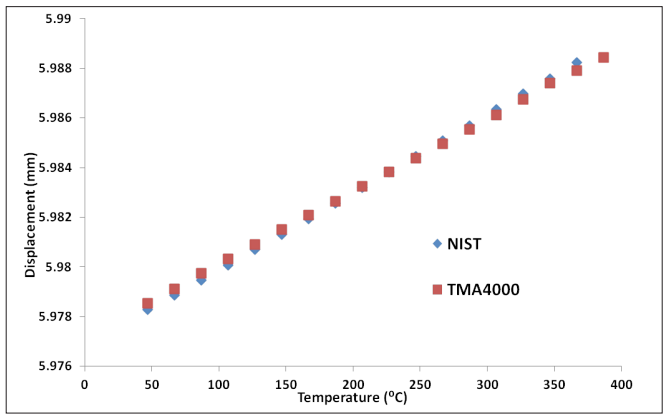

Figure 2. The measured values for a borosilicate glass are plotted with the NIST supplied ones. This increase in expansion comes from the free volume.

Q What is free volume?

A If we think of atoms as hard spheres, and compressed until there is no more space between, this can be considered the occupied volume of a material and the volume at absolute zero. As temperature increases the atoms move more, and the space that they can move in is the free volume of the material. The increase of the free volume with temperature is what creates the expansion we measure with CTE. (Figure 3)

Q Why is free volume so important?

A Free volume explains why materials expand on heating. In addition, it can explain how materials change with transitions as the changes needed for side chain mobility or chain movements in polymers or in crystalline phase changes in materials require increases in the free volume. This means that TMA can detect these changes and measure transitions like the glass transition (Tg) or heat set temperature in a fiber. This can appear like the glass transition does as a change in the slope of the line, so that a material has a different CT above and below the transition, explaining why so many material properties change at the Tg. In addition, contraction of the free volume in polymers allows us to explain things like enthaplic overshoot at the glass transition in polymers, increased packing with aging, and other properties. (Figure 3)

Q How do you know the CTE is accurate?

A You calibrate the CTE by using known standards like aluminum, silver, or borosilicate glass. These materials allow you to determine the expansion of the fixtures and analytical train. As much as possible, we use low expansion materials like fused quartz or ceramics for the TMA's fixtures. Because CTE is dependent on temperature, we control the temperature of the LVDT to prevent that from changing during the run.

Q What is the glass transition?

A The glass transition or Tg (pronounced T-G) is where an amorphous material changes from rigid to flexible or fluid. It's caused by movements in 3-6 carbons of the polymer backbone and causes a large change in the free volume, and hence the CTE, when it occurs. Depending on the heat history it can be a smooth transition or noisy.

It is worth noting that in TMA the fact that the term glass transition refers to a region of behavior and not a temperature is clearly visible. The Tg temperature is taken as the intersection of the tangents from the CTE lines above and below the transition (Figure 4). However, the entire area where the material departs from those tangents can be considered part of the Tg. This region of change is why DSC, TMA, and DMA values for the Tg don't agree: the different instruments are sensitive to different properties and they also have agreed upon definitions of how the Tg temperature is determined.

Q What about other types of transitions?

A Besides the glass transition found in amorphous polymers and glasses, we can see solid-solid transitions and changes in crystalline forms , eutectic and eutectoid transitions in metals, and stress induced transitions to name a few. An example of the last type would be the overshoot at the Tg one see in the DSC or the heat set temperature in a fiber.

Q What is the heat set?

A When making fabrics from polymers, the material is heated above the glass transition and distorted to give the fiber the feel like that of a natural fiber, which is called a hand. When dyeing a fabric, we need to heat above the Tg so the dye molecules can get into the fiber but stay below the heat set so we don't erase the hand. In the TMA, the heat set appears as a bump in the expansion curve with little to no difference in CTE above or below. As we are erasing this trapped stress and the heat history that caused it, the heat set is irreversible.

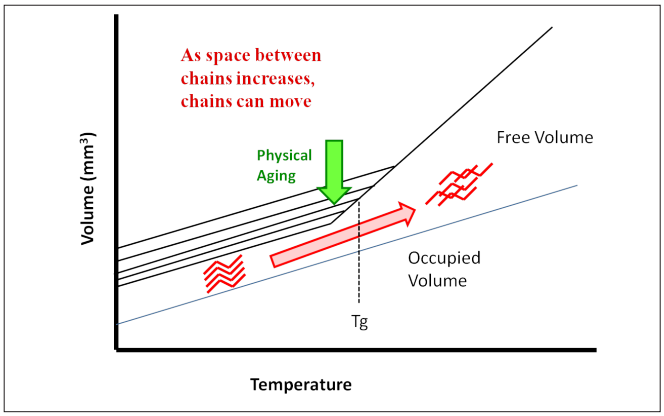

Figure 3. Free Volume in polymers is an basic principle for understanding behavior.

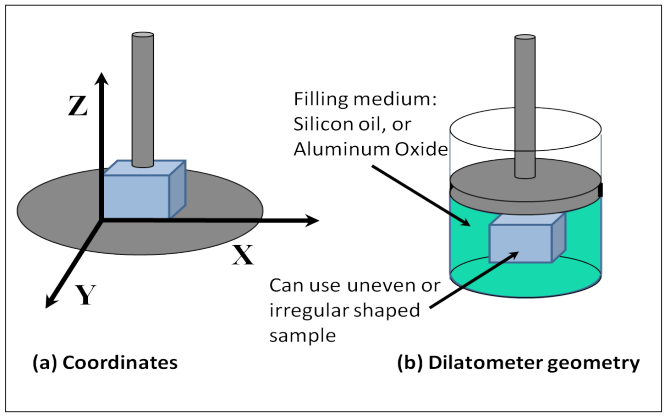

Figure 4. The glass transition and CTE of polystyrene is shown. The slopes of the baseline are used to calculate the CTE. The Tg is a region of between 90 and 110 °C, for which a Tg temperature is calculated as shown.

Q How do you run films and fibers?

A Films and fibers are run using specialized clamps and under a tensile, or pulling, force. For CTE, we use just enough force to keep the sample from collapsing under its own weight. For more industry specific tests, a known load may be required.

Q Why worry about shrinkage?

A When materials cure or dry, their volume is normally reduced. This can be significant as in amine epoxy system where curing results in shrinkage of 5-6%: compensating for this much loss in a thick part can be tricky. Shrinkage leads to porosity and internal cracking as well as stress build-ups in the material. One approach to measuring shrinkage is to run the sample in a dilatometer, where it can freely contract and the contraction measured. .

Q What is dilatometer?

A A dilatometer is either a specialized form of TMA designed for large mass samples or a fixture used in a TMA to measure volumetric expansion. Normally in a TMA, we measure only the linear expansion and so for non-homogeneous materials, we measure x, y, and z directions. Sometimes, however, the sample is too irregular to treat as a cube or not solid enough to hold its own weight (a gel or a liquid) and we can confine it in a dilatometer and measure the volumetric change. As a dilatometer confines the sample, which may be immersed in oil or packed in alumina, the volumetric expansion is converted to a vertical movement of the plunger and measured by TMA. (Figure 5)

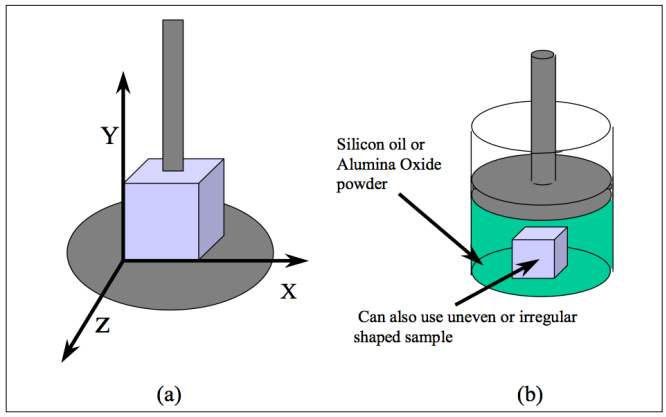

Figure 5. Heterogeneous samples require the CTE to be determined in the x, y and z planes (a) or in bulk to obtain a volumetric expansion in the dilatometer (b).

Q What is penetration used for?

A Penetration tests are an import from more primitive mechanical testing methods that identified the Tg of a material as it's softening point. Many of these tests applied a known load to a sample and heated it until the probe indented the sample, giving the upper operating temperature of the material. Some materials specifications still require it. In addition, it is a way to measure Tg on an oddly shaped sample.

Q Why do we do flexure tests?

A Flexure is the geometry used in another popular mechanical test, and testing using the TMA to determine the heat deflection point is still commonly used. In flexure, the sample is suspended across two jaws and force applied to the center, causing it to deflect when the material softens as it approaches the Tg.

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