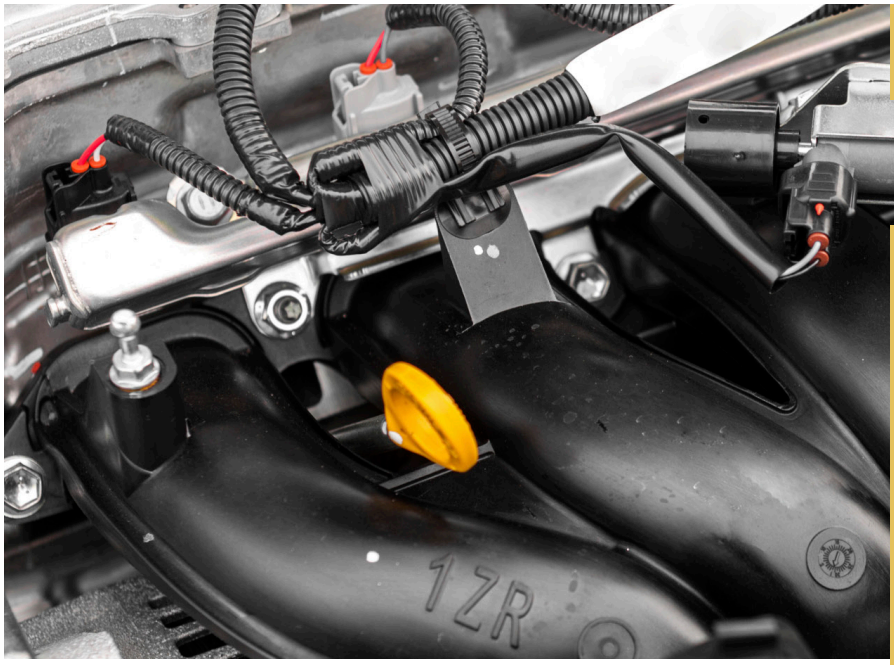

APPLICATION NOTE

Thermal Analysis

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Use of the TMA 4000 to Characterize Melting and Softening Points

Introduction

A fundamental property of a material—whether a plastic, a metal or ceramic—is its melting point. While a DSC can determine the temperature where the heat of crystalline melting takes place, or the heat capacity increases at the glass transition, it takes a mechanical analyzer to identify where the sample goes from being rigid to soft or flexible—i.e., where there is a dramatic decrease in modulus. Dynamic mechanical analysis (DMA) gives the widest range of quantitative data about changes in modulus, but often a much simpler test using thermomechanical analysis (TMA) is sufficient to qualify or quantify changes occurring in a material as it softens on heating.

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To accomplish this for a wide range of sample types, TMA utilizes several sample geometries using specialized probes for compression, flexure (bending) and extension. As a sample is heated to its melting point it deforms from the force applied by the probe. The TMA detects and records the changes in sample height as a function of temperature. This approach is also the basis for certain industry-specific melting point tests, many of which are now performed by TMA because of its simplicity and rapid test time.

The TMA 4000

The TMA 4000 analyzer is ideally suited to perform rapid and reliable melt test methods. Figure 1 shows a cross-sectional diagram of the instrument. From bottom to top here are the features it provides:

- The cold sink is cooled by a heat exchanger surface that allows tap water, a water circulator, or a mechanical refrigerator to be bolted on with a simple, single bolt. This allows flexibility for cost effective cooler choices based on your lowest temperature analysis need. Later, upgrading to a stronger cooler for lower temperature is also easy.
- The furnace which heats the sample is a full 40 mm in height, which provides an extremely wide uniform temperature zone. This means more accurate temperature control and temperature data. The furnace, well proven and extremely reliable is designed to go higher in temperature than its use in the TMA 4000.
- Fused Quartz furnace tube, sample platform and probes are heavier gauge and more robust than in competitive TMAs. Fused quartz has the lowest thermal expansion, and is more resistant to thermal shock than other materials.

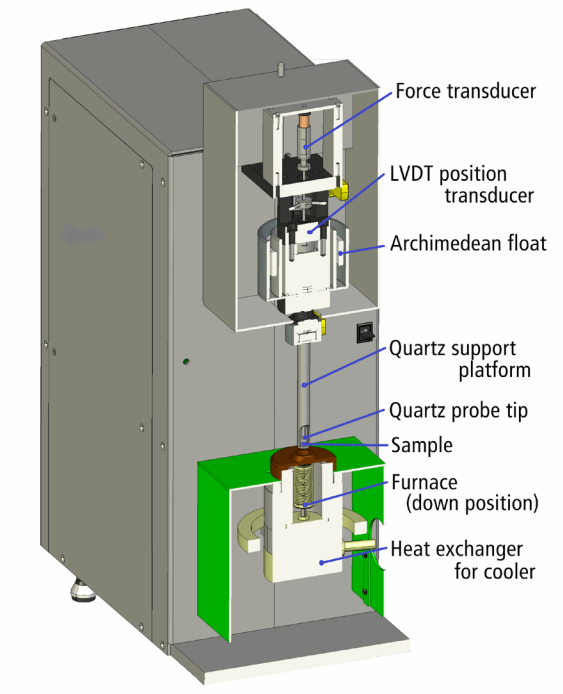

Figure 1. Cross-sectional diagram of the TMA 4000

- The position sensor, a linear variable differential transformer (LVDT) is high sensitivity and has a wide 12 mm linear detection zone. This provides sensitivity to small changes AND the ability to track large dimensional changes should they occur. The LVDT is temperature thermostatted to make its output independent of furnace temperature and laboratory temperature.
- An Archimedean float (wholly submerged) supports the weight of the sample probe and core rod. This provides damping of environmental vibration and protection of the quartzware from freefall during loading or power outage. Why don't other manufacturers provide this unique and useful feature?—because they would rather provide quasi-DMA functionality to their TMA.
- The Force transducer is also wide-range and linear and needs only to provide the up or down force selected by the TMA user (since it does not need to support the probe and core rod weight.)

Softening Under Compression

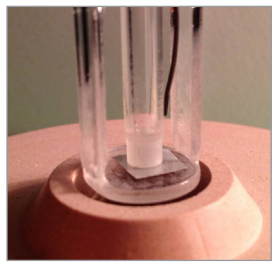

Figure 2. Expansion probe on can liner sample

The simplest form of softening point is to place a sample in the TMA, then lower a flat tip probe onto the sample with an applied force, then heat. (Figure 2) There are two different flat tip probes to choose from to select optimal applied stress.

Figure 3 shows the detection of the softening point of a liner on an aluminum beverage can. The resin lining is necessary to prevent reactions between the beverage and aluminum. The can fabricator can adjust the softening point, the glass transition, higher or lower in temperature using more or less of a heat cycle to advance the crosslinking reaction. This Tg adjustment allows optimiztion of throughput while attempting to meet requirements for flexibility, barrier maintenance and processing[1]. TMA offers a way to make this measurement despite the difficulty of limited sample to work with. Current research in this area is being applied to find replacements for the BPA-epoxy primers currently in use.

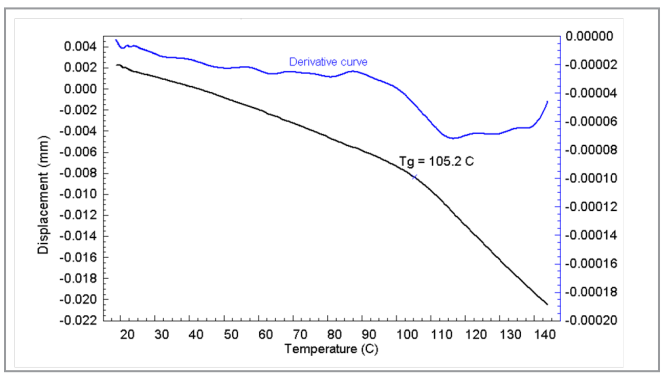

Figure 3. Detection of Tg of a food/beverage can lining.

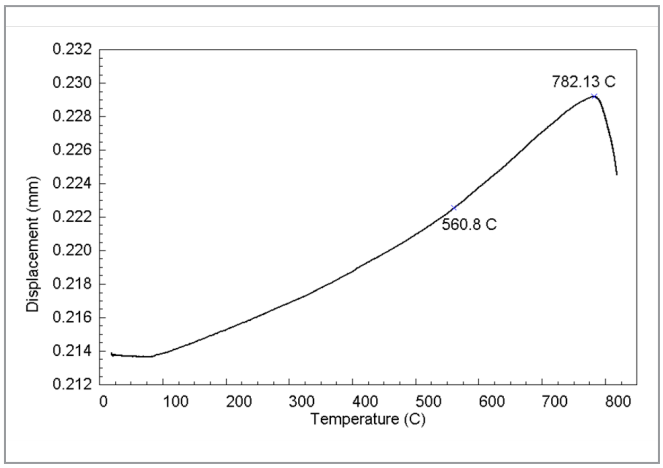

Figure 4. Softening point of a ceramic glaze—sample in a STA pan

Figure 4 shows the softening point for a ceramic glaze sample that had been run by simultaneous thermal analysis (STA). In this case the STA trace had shown evidence for two weak glass transitions, and running the sample in the TMA allowed confirmation of these events. This test can even be performed inside a DSC or STA pan with a loose-fitting lid to minimize cleanup. The first Tg in the STA correlated in the TMA with an increase in the coefficient of expansion, the second is the melt.

In the above tests the onset temperature of melting depends somewhat on the amount of force selected and the sample geometry. This test can be made less technique-dependent by using the sample and probe dimensions to calculate the stress which is being applied to the sample and the resultant strain associated with the probe displacement. Two examples of such a test are the Heat Deflection Under Load test, (e.g., ASTM D648 and ASTM E2092)[2] to obtain the Heat Deflection Temperature (HDT) and the Vicat softening temperature test (e.g., ASTM E2347)[3].

Heat Deflection Temperature

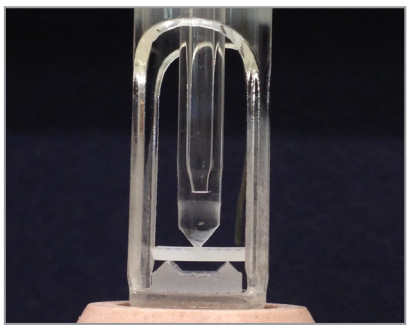

Figure 5. Diagram showing the geometry for the flexural analysis, or three point bending geometry used in the heat deflection test.

When it is desired to identify the temperature at which a sample material crosses a particular modulus threshold short of viscous flow the probe to use is the flexure probe. In this case a bar of sample of defined dimensions is laid across a pair of parallel knife edges. (Figure 5) The probe is lowered onto the sample centered between the two knife edges and a specified force is applied. The sample geometry and knife spacing allow calculation of the stress applied and the resultant strain. Standard test methods that employ this approach are ASTM D 648 and ASTM E2092 which simulate industry tests for the Heat Deflection Temperature (HDT), also known as the Deflection Temperature Under Load (DTUL). Figure 6 shows an example of this test on a sample of polystyrene. For this test the force applied to the sample is calculated based on sample dimensions for a stress of 66 psi or .445 Newtons. The output data is the temperature at which the strain is 0.20%. The displacement corresponding to this standard strain is based on the sample geometry and knife edge spacing. This test can identify where a material may have become sufficiently flexible that a mechanical piece will bend under load.

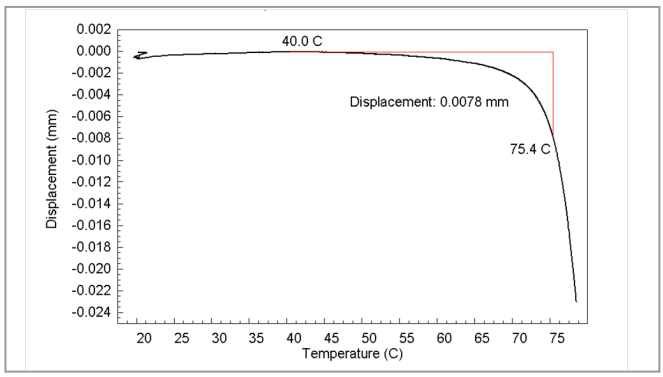

Figure 6. HDT/DTUL flexure test Heat Deflection at 66 psi (.455 N) of Polystyrene

Vicat Softening Temperature

To identify a temperature where a high localized stress results in penetration into the body of a component the Vicat test is used. In the TMA simulation of this test the force is concentrated on a small surface area of the sample using one of the penetration probes. (Figure 7) The Vicat test calls for identifying at what temperature the material softens to a specific value of Young's Modulus. Using the geometry of the sample and probe and using a maximum applied force of 200 grams results in a calculated penetration of 0.32 mm to achieve the Vicat A modulus. The temperature corresponding to this penetration is a TMA-simulated Vicat softening temperature. Figure 8 shows the testing of a highly-filled, porous architectural PVC material using the TMA 4000.

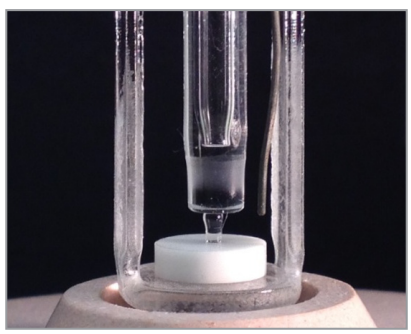

Figure 7. TMA geometry for simulated Vicat softening test

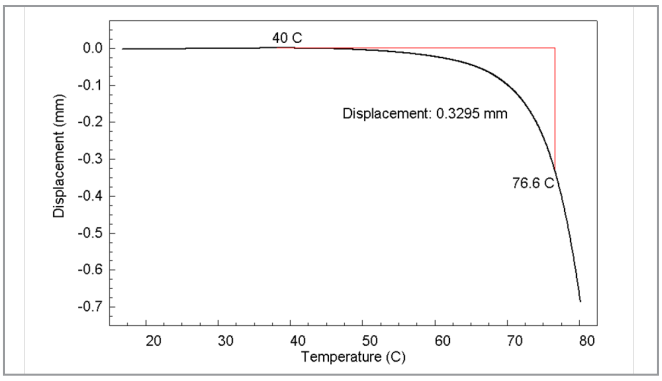

Figure 8. Softening point by a Vicat-type technique

Summary

The TMA 4000 has been evaluated over a wide range of applications including determining the melting and softening points of organics, metals, plastics and ceramics. It has the sensitivity to detect weak transitions or melting of thin layers, and the dynamic range to follow melting phenomena through 100% dimensional change. Since it is designed for simplicity and sturdiness, the TMA 4000 is ideal for use for routine testing using one of many industry-specific tests to quantify melting characteristics without needing to use rheological methods. Its robustness also makes it attractive for an educational setting.

References

1. Wicks, Z. W., et. al., Organic Coatings Science and Technology, Wiley, 2007
2. ASTM Standards, ASTM, Philadelphia, Pa, Standard Test Methods D-648 and E2092
3. ASTM Standards, ASTM, Philadelphia, Pa, Standard Test Methods D-1525 and E2347

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