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Anisotropic Thermal Behavior of Silicone Polymer, DC 745

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Abstract: In material applications, it is important to understand how polymeric materials behave in the various environments they may encounter. One factor governing polymer behavior is processing history. Differences in fabrication will result in parts with varied or even unintended properties. In this work, the thermal expansion behavior of silicone DC 745 is studied. Thermomechanical analysis (TMA) is used to determine changes in sample dimension resulting from changes in temperature. This technique can measure thermal events such as the linear coefficient of thermal expansion (CTE), melting, glass transitions, cure shrinkage, and internal relaxations. Using a thermomechanical analyzer (Q400 TMA), it is determined that DC 745 expands anisotropically when heated. This means that the material has a different CTE depending upon which direction is being measured. In this study, TMA experiments were designed in order to confirm anisotropic thermal behavior in multiple DC 745 samples of various ages and lots. TMA parameters such as temperature ramp rate, preload force, and temperature range were optimized in order to ensure the most accurate and useful data. A better understanding of the thermal expansion of DC 745 will allow for more accurate modeling of systems using this material.

Introduction

In many systems, important components are manufactured out of polymeric materials. Therefore, it is important to understand how these materials behave in the various environments to which they might be exposed. One factor governing such behavior is processing history. Thermoplastics are generally processed via molding or extrusion.[1] In both cases, the raw polymeric material is heated, forced into a specified shape, and then cooled so that it retains that shape. These methods can cause the polymer chains to align (Figure 1).[2] Generally, this sort of alignment produces polymeric material with mechanical and/or thermal anisotropy.

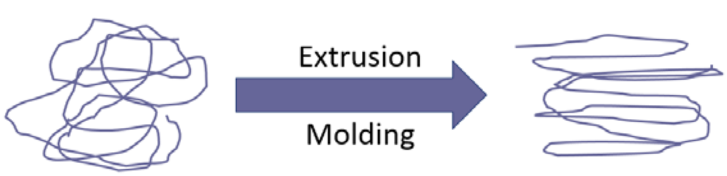

Figure 1. Schematic of an extruded or molded polymer chain. Note that properties measured parallel to the alignment can yield different values than those measured perpendicular.[2]

In this work, a thermomechanical analyzer is used to study the anisotropic thermal behavior of molded silicone polymer, DC 745. Thermal mechanical analysis (TMA) measures changes in sample dimensions resulting from changes in temperature.[3] This technique is commonly used to measure thermal events such as the linear coefficient of thermal expansion (CTE), melting, and glass transitions.[1] Figure 2 illustrates the general components of a TMA instrument. In this technique, a sample sits on a quartz stage and a quartz probe is placed in contact with the sample surface.[4] As the sample is heated or cooled, it expands or contracts accordingly. A linear variable differential transformer (LVDT) is able to measure the displacement of the probe, and thus the change in sample dimensions, with a resolution of 0.1 μm.[5]

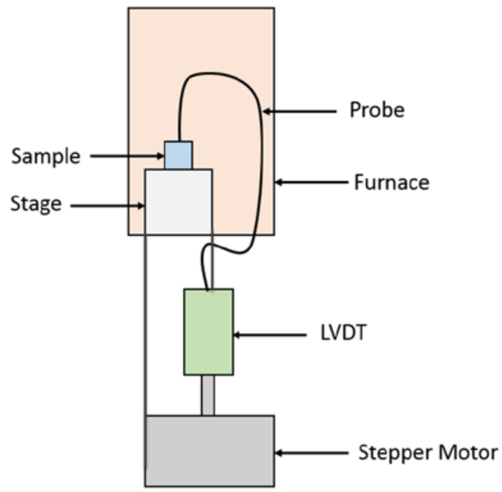

Figure 2. General schematic of a thermomechanical analyzer (TMA).[4]

TMA yields a plot of dimensional change (μm) versus temperature (°C). The linear coefficient of thermal expansion (CTE) is calculated by dividing the slope of the plot by the original dimension of the sample (Equation 1).[6] Materials with a large CTE value expand or contract more as temperature changes than materials with a small CTE value.

$$\alpha = \frac{1}{L_0} \cdot \frac{\Delta L}{\Delta T}$$

Equation 1. Calculation for the coefficient of thermal expansion (α) where ($\Delta L/\Delta T$) is equal to the slope of the dimensional change vs. temperature plot and L_0 is equal to the original dimension of the sample.

In assembled systems, many components are often tightly packed together. It is important that these components are made of materials with similar CTE values in order to avoid product failure, leaks, or a build-up of thermal stress.[7] Therefore, understanding thermal behavior is crucial. In this study, TMA experiments were designed in order to probe the thermal behaviors of DC 745 samples of various lots and ages. TMA parameters such as temperature range, temperature ramp rate, and preload force were optimized to ensure the accurate measurements.

Experimental

Samples. Four cubes of DC 745 silicone polymer material, representing various ages and lots, were obtained and labelled A, B, C, and X. The three unique faces of the cubes were carefully labeled as top/bottom, radial, or circumferential direction, respectively.

TMA instrumentation. A TA Q400 EM instrument with an expansion probe (2.54 mm diameter) was used. During the instrumental sequence, the sample was allowed to equilibrate at 20°C for 5 minutes. Then it was cooled to the minimum temperature and allowed to equilibrate for 10 minutes. Finally it was heated to the maximum temperature and allowed to equilibrate for 5 minutes. The measurements were conducted under a nitrogen purge with a flow rate of 50 mL/min.

In order to produce accurate and consistent results, the effect of load and heating rate on the measured CTE values was explored and optimal parameters were selected. The load of the probe on the sample surface was varied from 0.01 to 0.5 N. The temperature ramp rate was varied from 0.5 to 5°C/min.

Before starting the measurements, the TMA instrument was calibrated using an aluminum standard from TA instruments, following the TA calibration method.

Results & Discussion

Effect of Temperature Ramp Rate

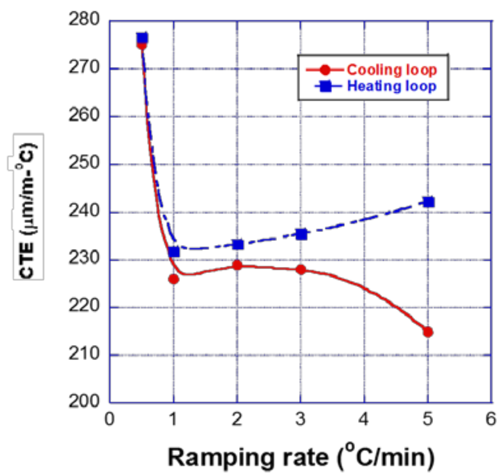

Figure 3. Effect of temperature ramp rate on the CTE's of Sample X in the cooling (15 to -25°C) and heating (-25 to 15°C) segments.[8]

To explore the effect of temperature ramp rate on the measured CTE value, sample X was tested using ramping rates from 0.5 to 5°C/min. The CTE was calculated using TA universal software in both the cooling (15 to -25°C) and heating (-25 to 15°C) segments. Ideally, the materials should be expanding or contracting at the same rate, regardless of whether the sample is being heated or cooled. However, the calculated CTE values in the heating and cooling segments begin to diverge as the ramping rate is increased (Figure 3).[8] This is due to a phenomenon common in polymeric materials known as thermal lag. Polymers have low thermal conductivities; therefore when the temperature of the air around the materials is increased, it takes time for the material itself to reach that temperature.[9] For the TMA of polymeric materials, it is important to use a temperature ramp rate where the material is not experiencing thermal lag so that the measured CTE values are as accurate as possible. Therefore the slowest ramp rate of 0.5°C/min was chosen for these experiments.

Effect of Applied Force (Stress)

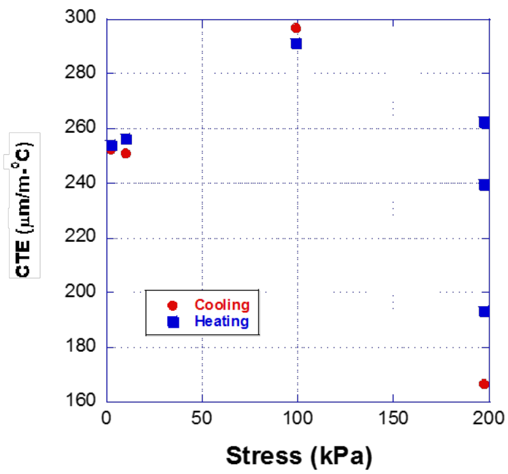

Figure 4. Effect of applied probe force on the CTE's of Sample X in the cooling (15 to -25°C) and heating (-25 to 15°C) segments.[8]

To explore the effect of applied force by the TMA probe on the measured CTE value, sample X was tested using loads of 0.01 to 0.5 N. The CTE was calculated using TA universal software in both the cooling (15 to -25°C) and heating (-25 to 15°C) segments. Ideally, the probe should apply sufficient force to maintain contact with the sample, but not so much that the sample is being deformed. As illustrated in Figure 4, the measured CTE values for the cooling and heating segments begin to vary greatly as the applied stress is above 100 kPa.[8] This is because the higher applied forces severely deform the sample and might damage the internal structure. It is important to maintain the original condition of the material, therefore, a low applied stress of 0.05N (<20 kPa) was selected.

Determination of Temperature Range

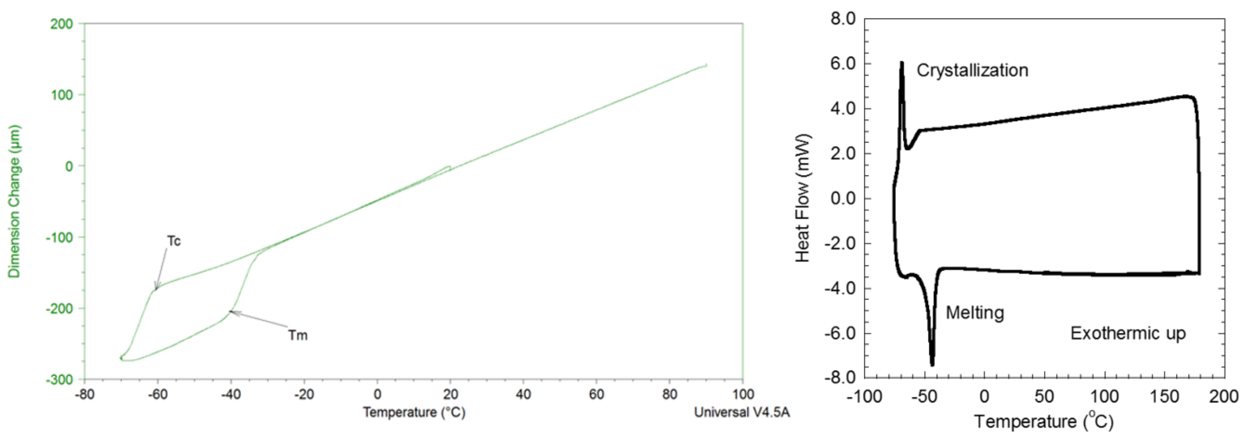

Figure 5.a. TMA plot for DC 745 demonstrating a loop in the sample's dimensional change between -35°C and -70°C (left); b. DSC for DC 745 indicating a phase transition at -50°C (right).[8]

Originally, the temperature range of interest for DC 745 material was -70°C to 90°C. As demonstrated in Figure 5.a., TMA for this range produced a loop in the dimensional change between -35°C and -70°C. DSC, as shown in Figure 5.b., confirmed that this loop is the result of a phase transition. As the sample is cooled, it crystallizes at approximately -60°C, causing the sample dimension to shrink. When the sample is reheated, it melts at approximately -40°C and the sample dimension expands.[10] In order to prevent this phase change from affecting the original CTE value, a temperature range of -30°C to 60°C was chosen for the TMA experiments.

Anisotropic Thermal Expansion

Figures 6-8 present the CTE values (left) and TMA results (right) of several samples in three directions. The results indicate that the DC 745 samples of different lots and ages exhibit anisotropic thermal behavior. In all cases, the CTE value in the circumferential direction is approximately 40 μm/(m·°C) less than in the radial or top/bottom direction. Interestingly, the direction with the highest CTE value and the reversibility of the heating/cooling segments vary from sample to sample. This is probably due to subtle differences in processing history and the alignment of the polymer chains. The heterogeneity of the materials may also contribute to this variation.

Sample A		
Ramping direction	**Test Direction**	**CTE [μm/(m°C)]**
Cooling	Top/bottom	253.9
Heating	Top/bottom	253.2
Cooling	Bottom/top	238.9
Heating	Bottom/top	247.1
Cooling	Circumferential	207.7
Heating	Circumferential	212.1
Cooling	Radial	222.9
Heating	Radial	231.1

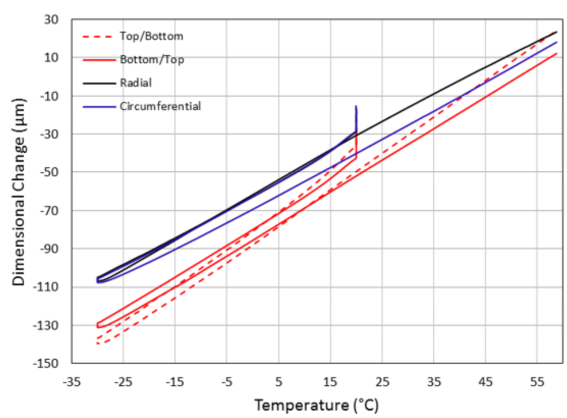

Figure 6.a. Calculated CTE values (left); b. TMA plots (right) for Sample A.

Sample B		
Ramping direction	**Test Direction**	**CTE [μm/(m°C)]**
Cooling	Top/bottom	285.2
Heating	Top/bottom	289.1
Cooling	Bottom/top	257.2
Heating	Bottom/top	263.5
Cooling	Circumferential	231.8
Heating	Circumferential	238.1
Cooling	Radial	335.8
Heating	Radial	339.6

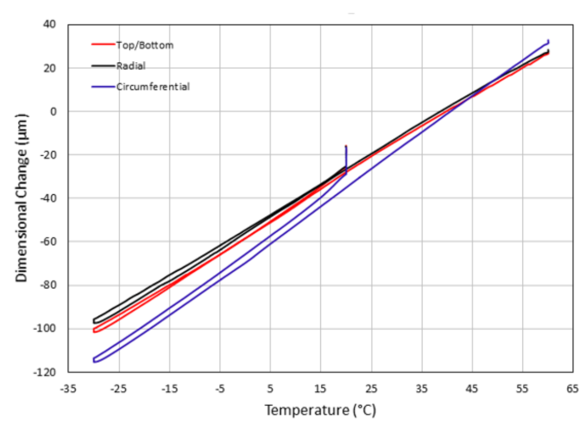

Figure 7.a. Calculated CTE values (left); b. TMA plots (right) for Sample B.

Sample C		
Ramping direction	Test Direction	CTE [µm/(m°C)]
Cooling	Top/bottom	266.0
Heating	Top/bottom	285.2
Cooling	Circumferential	212.9
Heating	Circumferential	212.1
Cooling	Radial	274.1
Heating	Radial	279.3

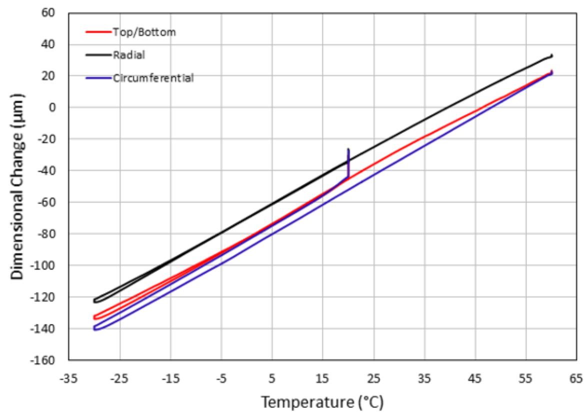

Figure 8.a. Calculated CTE values (left); b. TMA plots (right) for Sample C.

Conclusion

In summary, TMA experiments were designed in order to study anisotropic thermal behavior in silicon polymer DC 745 samples of various ages and lots. Exploratory work determined that the experimental parameters should consist of a 0.5°C/min ramp rate, 0.05 N preload force, and a temperature range between -30°C and 60°C. TMA experiments confirmed thermal anisotropy in three different DC 745 samples. In all cases, the CTE value in the circumferential direction was approximately 40 µm/(m·°C) less than these in the radial and top/bottom directions. It is important to understand and properly model this anisotropic thermal expansion when components made out of DC 745 material are used inside compacted system. Overlooking this anisotropic behavior can produce unexpected results in the systems using DC 745.

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