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Thermal and Mechanical Analysis of Polyurethane Memory Foam

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Some mattresses and pillows manufactured recently exhibit the unusual properties of viscoelastic slabstock foam, marketed as memory foam. These properties include a delayed and damped response to an applied force, and the ability to both absorb energy and to flow to minimize stresses. Many other polymeric materials display similarly complex viscoelastic properties at elevated temperatures at which compression properties may be a problem for processing. Analyzing this material offers a chance to use dynamic mechanical analysis (DMA) to characterize a material whose room temperature viscoelastic properties are unusual, and yet familiar.

Analysis of polyurethane memory foam starts out with understanding the properties of polyurethane (PU). The cross-linking of polyol results in a block structure having amorphous and crystalline domains. The amorphous domain contributes flexibility and impact properties to the end product, and the crystalline domain contributes strength and resilience.

Differential scanning calorimetry (DSC) has been used with other techniques to determine the fraction of material in each of the phases and the softening properties of each phase, and to quantify how these fractions are affected by thermal history. This paper focuses on three chemically similar foam products, the technique of Modulated Differential Scanning Calorimetry (MDSC™) (**TA Instruments,** New Castle, DE) to characterize the "soft segment" domain, and the use of DMA to characterize the foam characteristics.

The materials analyzed were two samples of viscoelastic slabstock foam and a conventional polyurethane bolster pillow foam. From a material safety data sheet on the memory foam, the material is described as the fully cross-linked product of polyhydroxy polyol, toluene di-isocyanate, catalysts, surfactants, pigments, and water. In a recent conference on polyurethane foams, a problem cited in the processing of memory foam is "a narrow processing latitude," and possible end-product deficiencies are "resilience, temperature sensitivity, permanent sets, changes with age/use, and poor hand/feel."[1] Many of these potential end-use deficiencies can be identified by means of thermal and mechanical analysis.

Figure 1 Q1000 DSC (a) and RSA III DMA (b).

Instrumentation

The Q1000 DSC (**TA Instruments**) (*Figure 1a*) was selected to generate the DSC and MDSC data. This instrument employs Tzero Technology™ (**TA Instruments**), which effectively minimizes instrumental contribution to the DSC output.[2] For example, it corrects for cell asymmetry in order to produce a straight, empty pan baseline. As applied to MDSC, Tzero minimizes the contribution of the pan and sensor mass to the reversing signal, thus improving calibration and shortening analysis time.[3] Use of the refrigerator cooling system (RCS) permitted DSC operation starting at –90 °C. Thermogravimetric analysis (TGA) was also used to confirm weight loss processes on the DSC thermal curve.

For rheological analysis, the RSA III dynamic mechanical analyzer (**TA Instruments**) (Figure 1*b*) was selected for the following reasons: By using a DMA in compression, instead of a rotational rheometer, the foam samples could be analyzed using parallel plate fixtures, thus avoiding any difficulties associated with clamping. By selecting the RSA, with transducers on both sides of the sample, instead of a classical stress-controlled DMA, the limitations associated with the inertia of the drive system can be minimized. This allows a wider range of frequencies and time scales to be meaningfully investigated, which more completely characterizes the foam. Also, using the RSA III allowed operation within the viscoelastic region, which required measurements employing a strain of less than 2%.

The three foam samples—one conventional polyurethane pillow foam and two memory foam samples—were prepared using a dual parallel razor tool. The resulting samples had a height of approx. 5.5 mm and were mounted in an 8-mm-diam parallel plate fixture. Sample loading consisted of raising the probe, inserting the cube of foam, then lowering the probe.

Results

Figure 2 shows the DSC and TGA curves of a memory foam sample run at

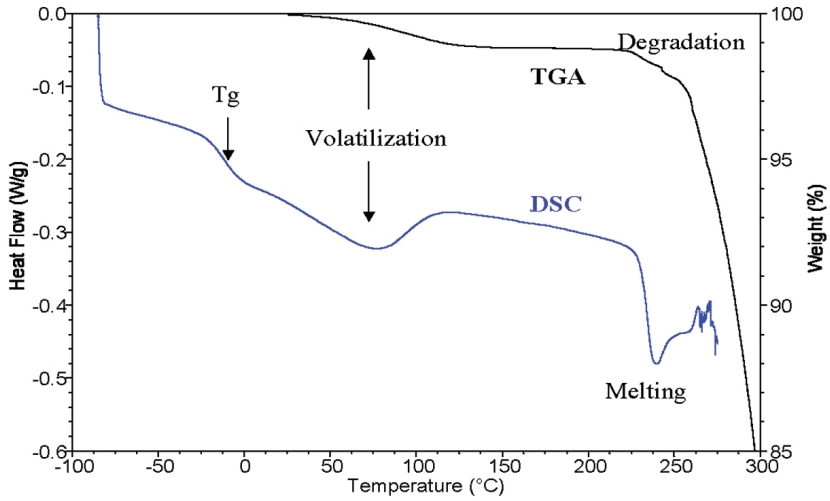

Figure 2 *Memory foam sample scanned at 10 °C/min by DSC and TGA.*

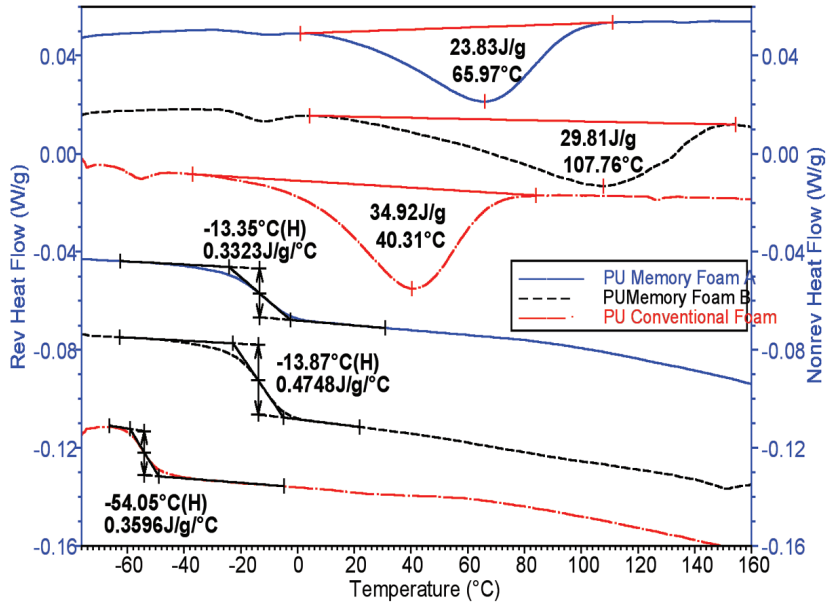

Figure 3 *Use of MDSC to obtain Tg and volatilization data for conventional polyurethane and memory foam polyurethane samples.*

10 °C/min. The curves of all three samples are qualitatively very similar and show a subambient glass transition, followed by a broad volatilization endotherm, followed by melting accompanied by decomposition. To characterize the soft segment phase, one needs to determine the temperature and change in heat capacity at Tg, and for the hard segment phase, the onset and latent heat of crystalline melting. However, when DSC is used, the heats of volatilization and decomposition interfere with the measurements. This analysis can be performed by MDSC, which separates thermodynamic processes (Tg and melting) from kinetic processes, such as volatilization and decomposition.[4]

Figure 3 shows the MDSC of the three foam samples over the low-temperature region. In each case, the reversing signal shows glass transitions bracketed by straight baseline. This allows the temperature and heat capacity change, proportional to the soft segment fraction, to be made accurately and unambiguously. The broad volatilization endotherm falls entirely on the nonreversing signal, where it can be independently measured.

The Tg midpoint temperatures for the two memory foam samples are the same within experimental error, but the changes in specific heat capacity are quite different. Since the change in Cp at Tg is proportional to the quantity of material in that amorphous phase, memory foam B, the softer of the two, can be seen to contain 43% more material in the low-temperature (soft segment) phase than memory foam A.

Mechanical properties

The mechanical properties of a foam are determined not only by the chemical constituents and molecular morphology of the polymeric material but also by the cell size, wall thickness, and pore size between adjacent cells. In the case of the memory foam, the pore size is particularly critical since the damped response to a change in stress is in part regulated by gaseous flow through constricted cell pores. Isothermal DMA is uniquely able to characterize end-use performance (the time-dependent modulus) of the materials.

Figure 4 shows the conventional and memory foam samples analyzed using a 1-min stress relaxation test in which a strain of 1% is applied and the stress required to hold this strain is monitored. Note that the modulus of the conventional foam is nearly constant with time, but for the memory foam samples the modulus drops exponentially with time. When the strain is first applied (the first point is at 0.01 sec), the modulus of the memory foam samples is three times greater than for the conventional foam. Within a few seconds, however, the modulus of the memory foam is less than that of the conventional foam. Other data taken at 15 and 35 °C show that the modulus of the conventional foam is roughly independent of temperature, while that of the memory foam at short intervals is almost an order of magnitude higher at the lower temperature. This has ramifications for the use of memory foam in cushioning applications below room temperature. For instance, it shows that at 15 °C the initial hardness of a pillow made of these memory foams would be comparable to that of modeling clay.

While the above strain sweep tests clearly show the time dependence of the overall modulus, they do not give information on whether applied energy is stored, as it is in a perfectly elastic substance, or substantially dissipated, as it is in a viscoelastic material near the glass transition. To obtain this information one must use a dynamic (modulating) stress or strain.

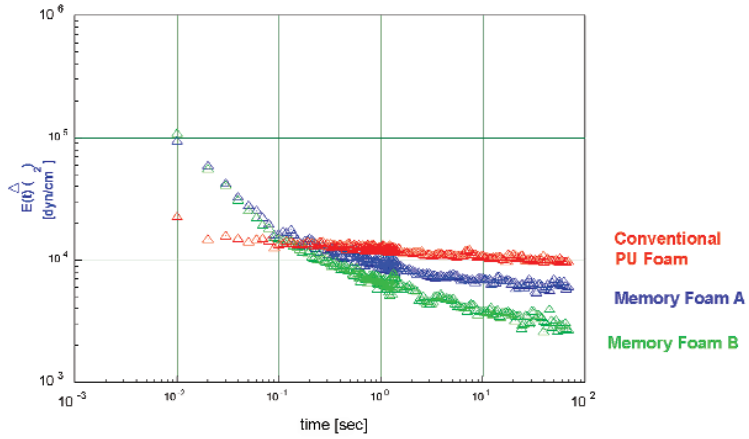

Figure 4 DMA stress relaxation test of conventional polyurethane foam and memory foam samples.

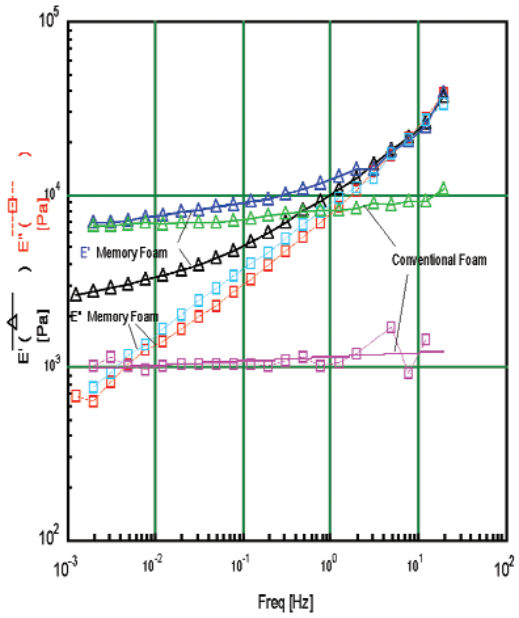

Figure 5 Storage and loss modulus for conventional polyurethane and memory foam samples at 25 °C.

From the phase response of the sample to the modulating strain, the resultant modulus can be broken up into an in-phase, storage (elastic) component, E′, and an out-of-phase, loss (flow) component, E″. This loss modulus, E″, is especially important when the foam is being utilized for sound or vibration damping. It is also important to the supportive feel of a mattress or pillow made of memory foam.

Figure 5 shows the storage and loss modulus of the three samples as a function of frequency of modulation. The sample is placed between the parallel plates and the amplitude of modulation is held constant while the frequency is decreased from 20 Hz down to 0.002 Hz. From these data it can be seen that the conventional foam has a very low loss modulus (pink curve) at all frequencies. This material would be a very poor absorber of sound or vibration and would have high resilience. For the memory foam, the loss component is comparable in magnitude to the elastic component at high frequencies, and more than an order of magnitude greater than that for the conventional foam. Similar to the results from the stress relaxation data, the dynamic data indicate a higher storage modulus for the memory foam than for the conventional foam at high frequencies (short time intervals) and lower modulus at low frequencies. A difference can also be seen between the two memory foam samples, namely, the storage modulus of memory foam B (black curve) continues to drop with time (at low frequencies). This indicates that it would offer much less steady-state support as a mattress or pillow foam.

Conclusion

Analysis by MDSC allows the characterization of hard and soft segment phases of polyurethane formulations even when there is loss of volatiles. From the heat capacity change at Tg, the amount of material in an amorphous phase can be quantified, and when the melting can be separated from decomposition, the enthalpy of melting is a measure of the amount of crystalline phase.

From DMA, the time-dependent mechanical characteristics of a foam can be quantified as a function of frequency, time, strain, and temperature. While there may not seem to be a direct correlation from pillow foam to a polymer melt, similar tests can be used with a DMA or (rotational) rheometer to characterize viscoelastic behavior in a wide range of materials, even the complex viscoelastic properties of a polymer melt.

References

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