Measuring the Glass Transition of Amorphous Engineering Thermoplastics

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ABSTRACT

DSC is a useful tool for characterizing the glass transition region of amorphous thermoplastics. The Q1000 DSC, with its Advanced Tzero™ Technology, provides improved specific heat data obtained directly from a single run. It also provides improvements in Modulated DSC® capability for glass transition analysis of amorphous thermoplastic alloys and their constituent homopolymers.

BACKGROUND

Amorphous thermoplastics have especially desirable properties of optical clarity and impact resistance. For example, polycarbonate (PC) is used for eyeglasses and compact disk storage media, and acrylonitrile-butadiene-styrene terpolymer (ABS) is used for sports equipment and telephone housings. Unlike semi-crystalline

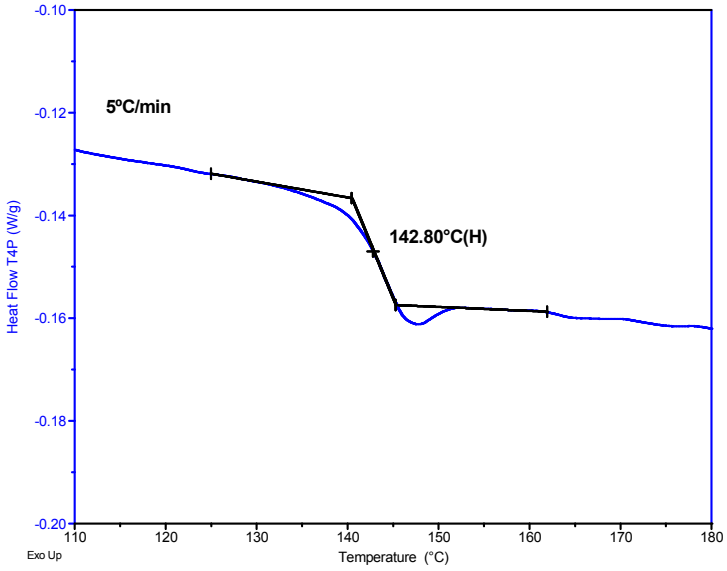

Figure 1 – Glass Transition of Polycarbonate

thermoplastics that derive their physical properties from a mix of amorphous and crystalline structures, amorphous thermoplastics derive their mechanical properties solely from the characteristics of their amorphous phases. The amorphous phase is obtained by cooling a liquid under conditions that do not permit crystallization. Such cooling produces a solid without the long-range molecular order of a crystal. When heated, an amorphous solid undergoes softening over the glass transition region. Over this temperature range (of several tens of Celsius degrees) typically, the strength, hardness, storage modulus, *etc*. change by several orders of magnitude. The glass transition also results in an increase in volume, heat capacity, coefficient of expansion and molecular mobility. The glass transition temperature range is often adjusted during formulation to improve the physical properties, *e.g*., strength, flexibility or impact resistance, at the service temperature of the finished product.

Differential scanning calorimtery (DSC) has long been used to quantify the glass transition temperature range by analyzing the heat flow to the sample specimen resulting from the change in heat capacity as shown for PC in Figure 1. Typically, a single temperature, called the glass transition temperature (Tg), is taken to represent the temperature range over which the glass transition takes place. Various industries have different preferences for this point (midpoint, inflection point, onset, *etc*.) so that high quality data analysis software provides several options for performing this determination. Additionally, the glass transition has a kinetic component so the value of Tg depends on how the measurement is made and on which physical property is being measured (*1*). For DSC, the experimental variables include the heating (or cooling) rate, the previous thermal treatment of the sample, and the use of temperature modulation to separate thermodynamic and kinetic components.

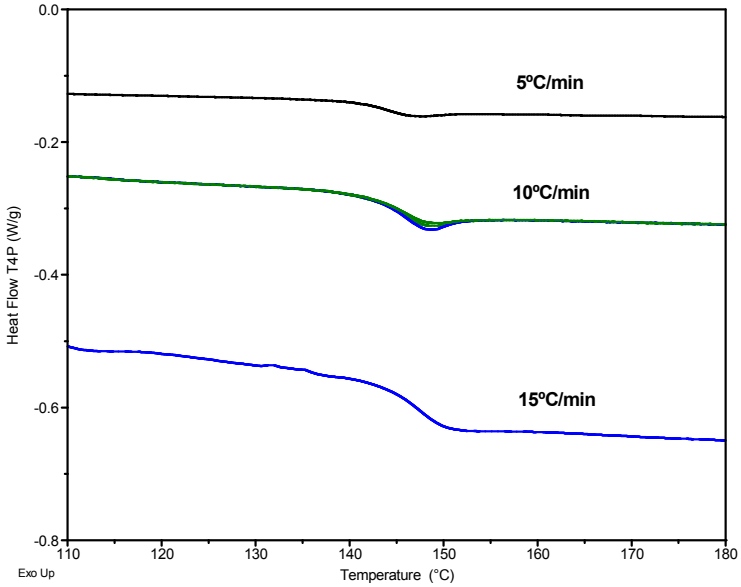

Figure 2 – The Glass Transition of Polycarbonate at Three Heating Rates. The 10 ºC/min Data is from Three Samples Cooled at 5, 10 and 20 ºC/min.

EXPERIMENTAL

A TA Instruments Q1000 DSC, equipped with a Refrigerated Cooling System (RCS), is used to collect this data. The Q1000 uses a novel sensor and signal treatment that removes the distortion caused by the DSC cell itself on the heat flow to the sample specimen (*2, 3*). The result is straighter baselines, sharper transitions, less thermal lag error, and less dependence of the DSC results on the details of the experimental conditions, such as the heating rate, sample size, and encapsulation (*4*).

The polycarbonate test specimen is cut from a commercial CD-ROM used for computer for data storage. The acrylonitrile-butadiene-styrene terpolymer and ABS-PC blends are obtained from a resin suppler in the form of mechanical analysis test bars. Sample size is 10 to 20 mg. Initial runs are performed on samples "as received" and rerun data is analyzed after ballistic cooling from the previous run.

RESULTS AND DISCUSSION

Figure 2 shows DSC results for polycarbonate obtained at three different, commonly used heating rates after creating a common thermal history by cooling at 10 ºC/min. The displacement from the zero heat flow line is proportional to the heating rate, as is the change in this signal upon traversing the glass transition interval. Thus, for weak or broad glass transitions a fast heating rate is preferred. For this sample the data could be taken equally well at slower rates thus avoiding possible temperature gradients in the sample. The middle curve also show the overlay of three test specimens cooled at 5, 10 and 20 °C/min.

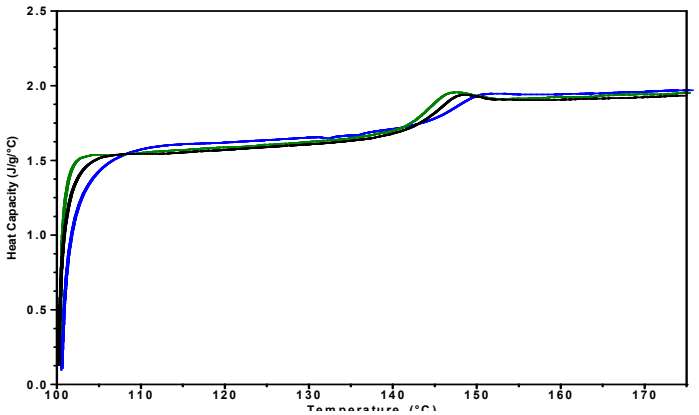

Figure 3 – Polycarbonate Heat Capacity at 5, 10 and 20 °C/min

One of the benefits of presenting experimental data in the form of specific heat capacity is that data taken at different heating rates can easily be compared as shown in Figure 3. Advanced Tzero™ Technology provides the ability to determine specific heat capacity directly so that there is no need to make multiple runs to obtain this data. Changing between the presentation in Figure 2 and Figure 3 is only a change of displayed units, not in data treatment. This is because the Q1000 DSC removes the slope, offset and curvature component that normally distorts the DSC data. The single curve Cp data in Figure 3 is obtained without subtracting a baseline and obtains the same Cp data before and after the transition shows that these deleterious baseline effects have all been

removed through the use of the Tzero signals. The fact that the Cp data varies with heating rate within the glass transition region is a predictable variation due to the kinetic aspect of the glass transition.

In formulating an amorphous thermoplastic to obtained desired improvements in physical properties, it is possible to shift the glass transition region, or to add an additional amorphous phase. Shifting the glass transition is achieved by incorporating another miscible polymer (or monomer) into the amorphous phase through co-polymerization or blending. When two polymers are partially miscible, the Tg of the mixed amorphous phase will shift between the Tg's of the two homopolymers more or less proportionally to the amount of each component in the mixture. When two polymers are not completely miscible there will be two glass transitions, one for each amorphous phase. By controlling the amount of the two components in the copolymer or polymer blend, the glass transition(s) can be shifted to adjust the physical properties of the formulati

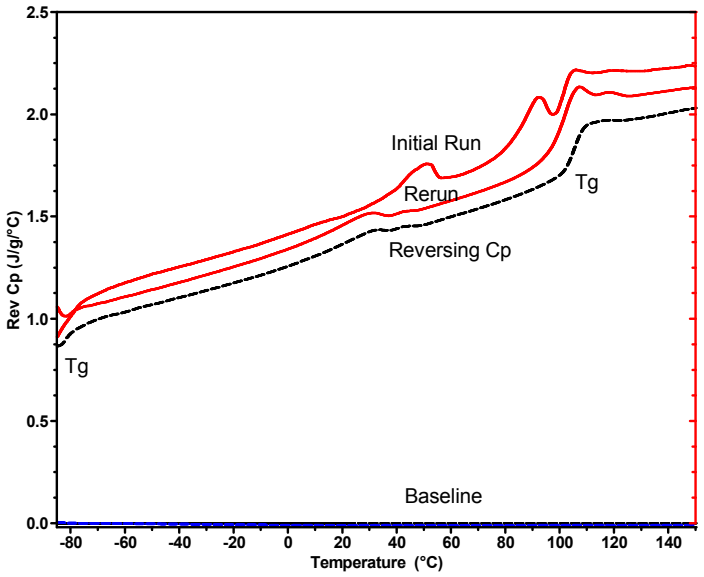

Figure 4 – Heat Capacity of ABS, Initial Heat, Reheat and Reheat Reversing Signal

Acrylonitrile-butadiene-styrene terpolymer is a high performance thermoplastic containing two amorphous phases; a rubbery phase provided by butadiene, and a strength-lending styrene-acrylonitrile (SAN) copolymer two-component phase. It has two glass transitions. The low temperature glass transition is due to the butadiene phase, and the high temperature one is due to the SAN phase. The ratio of A to B to S determines the properties of ABS from essentially a hard rubber to a shock-resistant high-modulus material.

Bair and coworkers showed that careful glass transition measurements are useful for determining the amount of these components in the terpolymer and therefore provide a tool for assessing the quality of ABS formulations (*5*). Bair's work found limited utility, however, due to the need to straighten the instrumental baseline of the then available instruments and to manually generate the heat capacity data. Advanced Tzero™ Technology and/or MDSC® meets these needs and renders Bair's approach practical. Figure 4 shows the use of the Q1000 DSC with an RCS cooling accessory to determine the transitions in ABS. Because the low temperature transition is around –80 ºC, it is (just barely) within the range of the mechanical refrigerator of the RCS, therefore it was

not necessary to use a liquid nitrogen-cooling accessory to make these measurements. Also shown on this plot at the bottom of the figure is the DSC baseline. One necessity for accurate Tg measurements is a flat baseline since any underlying instrumental curvature will introduce error in the Tg. The slope in the Cp data is due to the actual increase in the test specimens heat capacity with temperature and is not an instrument-induced artifact.

The dashed line in Figure 4 is the rapidly reversing Cp data taken from an MDSC experiment. The use of MDSC is recommended for interpreting complex DSC curves since it provides confirmation of the interpretation and isolates the Tg. That is, in Figure 4 the rapidly reversing curve shows an unambiguous sigmoidal change in Cp at the glass transition thus enabling the accurate determination of Tg.

The third amorphous engineering thermoplastic analyzed is a PC-ABS "alloy" containing a blend of polycarbonate and ABS copolymer and other additives to improve the interface between the two. When run by traditional DSC, the thermal curve shows a superimposition of endotherms and glass transitions such that it is difficult to accurately determine Tg. To improve the accuracy of the Tg measurements the analysis was carried out by MDSC. In this way the kinetic components appear on the nonreversing signal while the heat capacity components, which are to be analyzed, appear on the reversing signal. The conventional heat capacity obtained at constant heating rate (without the MDSC modulation) is the sum of these two curves.

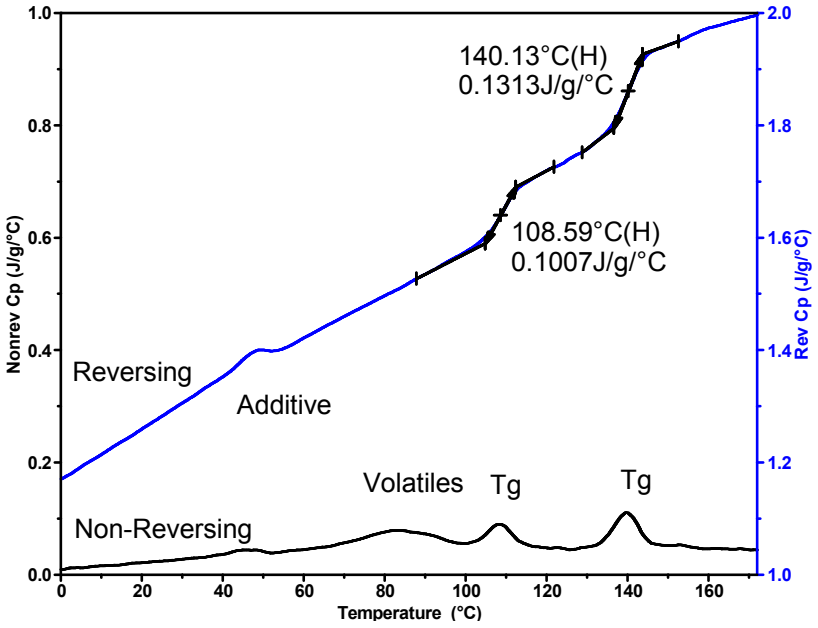

Figure 5 - MDSC® of PC-ABS Alloy

Based on the ratio of the specific heats capacities at 0 ºC this material is a 50/50 % mixture. If there were no miscibility between the phases then the blend would

look like a simple addition of the two DSC curves. If there were complete miscibility there would be one Tg roughly midway between the SAN and PC glass transitions. If there were partial miscibility then the glass transitions of the mixed amorphous phases would be between the two Tg's of the components, exactly what is observed.

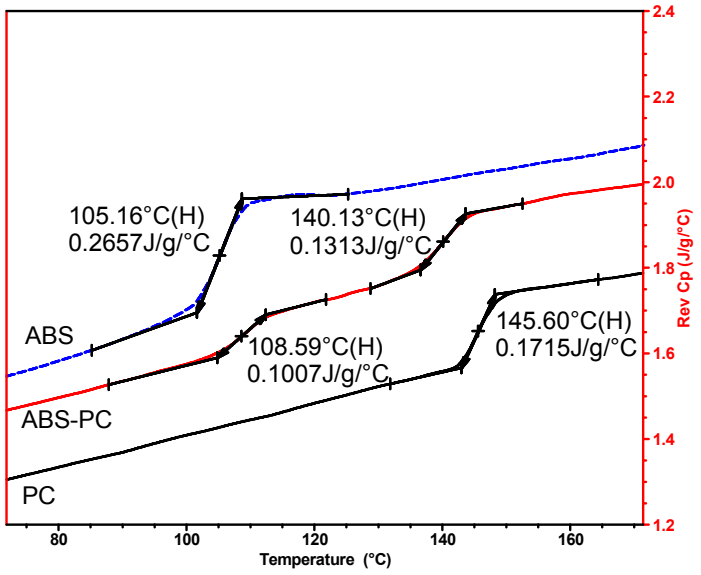

Figure 6 – Reversing Heat Capacity for PC, ABS and PC-ABS Alloy

Assuming that the shift in Tg's is proportional to the amount of each component then the amorphous phase with the lower Tg is 8 % PC and 92 % SAN, and the amorphous phase with the higher Tg is 13 % SAN and 87 % PC. By improving the miscibility of the amorphous phases the formulation increases the bonding across the phase boundaries and improves the physical properties of the blend. The thermal curves showing the Tg determinations are shown in Figure 6. Further insight may be able to be obtained from use of the change in heat capacity, that occurs over each of the glass transition interval, be proportional to the amount of material in each of these phases. While this approach would be valid for the case where the ABS and PC components are from the same stock in the blend and homopolymers, in this case the analysis is only illustrative because the components are not known in detail.

SUMMARY

DSC is a useful tool for characterizing amorphous thermoplastics by determining the glass transition temperatures. This technique is especially useful in the characterization of copolymers and blends where this information may be directly applied to determining the formulation changes required to improve physical properties., The Q Series™ DSCs offer improved technology, namely, straighter baselines, improved sensitivity, compensated thermal lag and faster MDSC capability for making these determinations

REFERENCES

1. Assignment of the Glass Transition, Special Technical Publication 1249, R. J. Seyler (Ed.), American Society for Testing and Materials, West Conshohocken, PA, **1984**.
2. L. E. Waguespack and R. L. Blaine, "Design of a New DSC Cell with Tzero™ Technology", *Proceedings of the 29th Conference of the North American Thermal Analysis Society*, **2001**, pp. 720-727.
3. R. L. Danley and P. A. Caulfield, "DSC Resolution and Dynamic Response Improvements Obtained by a New Heat Flow Measurement Technique", *Proceedings of the 29th Conference of the North American Thermal Analysis Society*, **2001**, pp. 673-678
4. R. L. Danley and P. A. Caulfield, "DSC Baseline Improvements by a Heat Flow Measurement Technique", *Proceedings of the 29th Conference of the North American Thermal Analysis Society*, **2001**, pp. 667-672.
5. X. Quan, H. E. Bair and G. E. Johnson, *Macromolecules*, **1989**, 22, p.4631.

KEY WORDS

differential scanning calorimetry, glass transition, heat capacity, modulated differential scanning calorimetry, thermoplastic polymers

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