Using Modulated DSC® (MDSC®) to Separate an Enthalpic Recovery from a Glass Transition

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TA433

BACKGROUND

The glass transition is the temperature range where amorphous structure undergoes a change in mobility which can have a large effect on material properties. This transition is a reversible transition, unless there is some structure change in the material that would eliminate or obscure the transition. As a material is heated from below the glass transition temperature (Tg) through the Tg, the molecular mobility increases. Conversely, as a material is cooled from above the Tg through the Tg, the molecular mobility decreases.

There are several characterization techniques that can be used to measure a glass transition, including DSC, DMA, & TMA. DSC is routinely used due to speed and ease of sampling. As a material is heated (or cooled) through a Tg, there is a step transition in the DSC heat flow rate. This transition is typically analyzed to find the midpoint, and the midpoint is called the Tg. This midpoint can be determined in several ways with the half height method (half the height of the change in Cp) and the inflection point being the most common. Depending upon the thermal history of a material, the glass transition as seen in a DSC can be a simple step transition, or much more complicated and therefore harder to interpret. This application note will show how Modulated DSC® (MDSC®) can be used to improve the interpretation of these transitions.

DSC

Differential Scanning Calorimetry (DSC) is a technique that measures heat flow rate of a sample versus temperature, or versus time at a temperature. With typical samples sizes of 5-10 mg, and heating rates of 10-20 °C/min, DSC is a standard thermal technique to look at glass transitions, and other transitions of materials. As the molecular mobility increases upon heating through the Tg, the heat capacity (Cp) also increases. This step change in Cp, shows up as a step transition in heat flow.

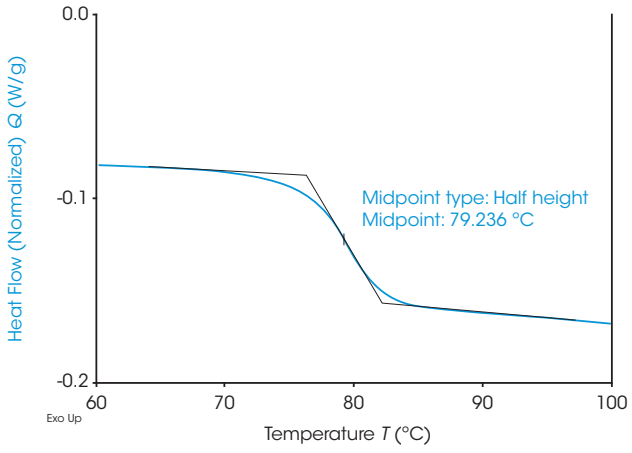

Figure 1. Simple Step change at Polymer Tg by DSC

Theoretically, the glass transition in a DSC scan is a simple step transition in the endothermic direction. This size of this step transition varies with the amount of amorphous structure, the sample size, and the heating rate. Figure 1 shows a simple step change occurring at a glass transition.

PEAK AT THE GLASS TRANSITION

Sometimes the transition is not so simple. Due to thermal history, and/or physical stresses, the step change may have a large endothermic peak instead of a simple step change. Sometimes this peak can be so large it can be misinterpreted as a melt instead of a glass transition. This peak is called an enthalpic recovery peak. Figure 2 shows an example of a material with an enthalpic recovery peak at the glass transition. The peak is commonly caused by a material being stored at a temperature below, but close to, the Tg [1]. In these cases, the material's temperature is close enough to the Tg that it has a little molecular mobility. Over time, the material can give up energy and move to a lower energy state. This is a time dependent event (Kinetic event) and occurs faster the closer to the Tg the sample is stored. Typically, if a material is stored more than 40 °C below the Tg, this occurs so slowly as to be negligible. As this lower energy material is heated through Tg, there is the normal increase in mobility that occurs at the Tg. In addition, the sample is in a lower energy state than expected and absorbs that energy as the molecular mobility increases. This energy absorbance shows up as an endothermic peak at the Tg.

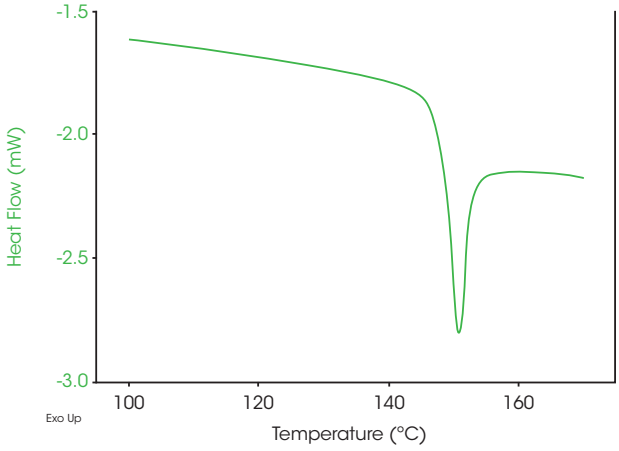

Figure 2. Example of a Polymer Tg with an Enthalpic Recovery Peak

The existence of this peak makes it difficult to determine the midpoint of the transition. In addition, these materials are at a lower energy state than normal with lower molecular mobility. This lower molecular mobility can shift the "apparent" Tg, to a higher temperature. One way to try and eliminate this enthalpic recovery peak is to heat the material 15-20 °C above the Tg, cool

down and then reheat. This can work; however, it is problematic for thermosets and materials that might change during this heating past the Tg. For instance, if the goal is to obtain the Tg of a thermoset after "x" hours of curing at room temperature, this typically won't work as the sample will advance the cure and the measured Tg on the second heat will be higher than on the first heat. This can also be an issue with some thermoplastics as some semi-crystalline thermoplastics will increase crystallinity when heated past the Tg.

For many materials, the answer is MDSC!

MODULATED DSC® (MDSC®)

Modulated DSC is a technique where a sinusoidal temperature modulation is overlaid on the normal heating rate of a DSC experiment.[2] MDSC is a standard feature on the Discovery DSC 2500, and all current TA Instruments DSC's including the new Discovery X3 DSC. MDSC allows the separation of Heat Capacity events from Kinetic events. As already mentioned, the glass transition is due to a change in heat capacity and the enthalpic recovery is a kinetic event. The output of a MDSC experiment includes the Total Heat Flow (the same as a standard DSC heat flow at the same underlying heating rate), Reversing Heat Flow (the heat capacity component of heat flow), and the Non-Reversing Heat Flow (the kinetic component of heat flow).[3] As a glass transition is a heat capacity event it will appear in the Reversing Heat Flow, and as the enthalpic recovery is a kinetic event it will appear in the Non-Reversing Heat Flow. Figure 3 shows the relationship between transitions and the MDSC signals.

MDSC Theory: Heat Flow Signals

$$\frac{dQ}{dt} = Cp\,\frac{dT}{dt} + f(T, t)$$

Total Heat Flow	Reversing Heat Flow	Non-Reversing Heat Flow
• All Transitions	• Heat Capacity • Glass Transition • Melting	• Enthalpic Recovery • Evaporation • Crystallization • Thermoset Cure • Denaturation • Decomposition • Some Melting • Chemical Reactions

Figure 3. MDSC Heat flow Signals and Transitions

MDSC Conditions:

A typical MDSC experimental procedure is listed below for the determination of a glass transition:

Data Storage Off
Equilibrate at 0 °C
Modulate ±1 °C every 60 seconds
Isothermal for 5 minutes
Data Storage On
Ramp 3 °C/min to 200 °C

The starting and final temperature should be adjusted as appropriate for the sample. A good starting point is at least 20 °C below any expected transitions, and a final temperature of at least 20 °C above any sample transitions. It is recommended that the final temperature be kept lower than the decomposition temperature of the material.

EXPERIMENTAL

The epoxy system used for this experiment was Araldite GY6010*/ Jeffamine® D230* epoxy resin/curing agent. The resin is a standard diglycidyl ether of Bisphenol A based epoxy (DGEBA), and the curing agent is a Polyetheramine. This system has a long (4-5 hour) "pot life" at room temperature. The "pot life" is the time the material is still workable (able to be poured, spread or applied) before it is cured.

The goal of the DSC experiment was to determine the Tg after the sample was cured for 72 hours at room temperature. Figure 4 shows the DSC scan, at 10 °C/min, of this material.

There are three events to point out.

1. The Tg can be seen in the step-change of the heat flow;
2. A large enthalpic recovery peak is seen; and
3. Additional curing and crosslinking upon heating above the Tg.

Even though the Tg can be seen it would be difficult to quantify the temperature due to the enthalpic recovery.

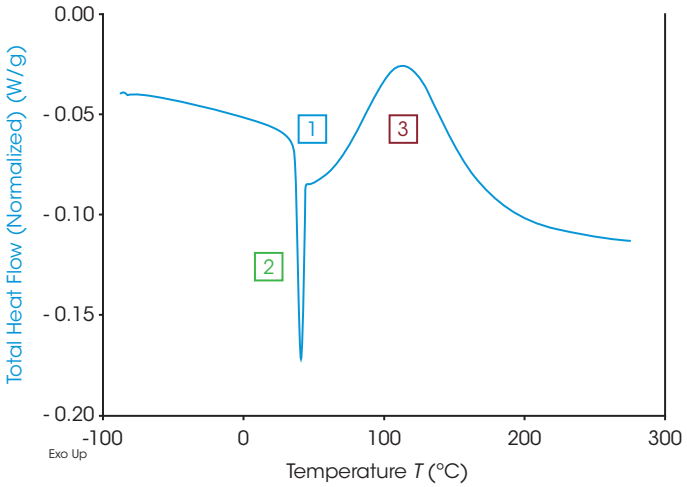

Figure 4. DSC of 72-hr cured epoxy

What is happening to make the DSC thermogram complicated?

This Tg appears to be between 25 °C and 50 °C. When the material is stored at room temperature it is below but close to the Tg. There is enough mobility for the sample to give up energy as discussed earlier, and therefore we see enthalpic recovery.

Why is there a residual crosslinking occurring after the Tg?

Recall that the epoxy was cured at room temperature. As the material crosslinks the Tg moves to higher temperatures. As the Tg rises to a temperature above the cure temperature, as clearly

occurred here, the sample goes through vitrification. This is the process of forming a “glass”, therefore dramatically lowering molecular mobility. This quenches the crosslinking reaction and the material does not fully cure. When the material is heated above the Tg, molecular mobility increases, and the curing will continue.

What if we do a Heat-Cool-Heat (H-C-H) experiment? Will that allow us to measure the Tg?

Since we know the material undergoes further crosslinking during the first heat, any H-C-H experiment will only show the Tg after the sample is cured from the first heat, and not the desired “as received” value.

As previously discussed, the Tg is a heat capacity transition, while enthalpic recovery and crosslinking are kinetic transitions. MDSC can separate the heat capacity from the kinetic transitions. Figure 5 shows the MDSC data of the material, using the conditions described earlier. The Total Heat Flow signal is very similar to the standard DSC curve in Figure 4, but with MDSC two more signals are also available. The Reversing Heat Flow curve shows a clearly defined Tg with a midpoint of 40.28 °C, while the Non-Reversing Heat Flow curve shows the enthalpic recovery and the additional crosslinking.

As mentioned earlier, the goal was to determine the Tg of the material after cuing at room temperature for 72 hours. MDSC shows this and the answer is approximately 40 °C.

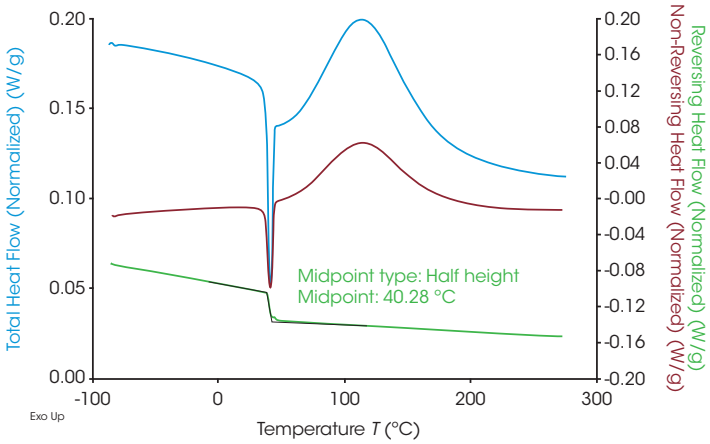

Figure 5. MDSC of 72-hr cured epoxy

CONCLUSION

DSC is commonly used to characterize a variety of materials exhibiting many different transitions. As DSC is relatively fast, and uses a relatively small sample, it is very often the first attempt to characterize these materials for thermal transitions. As shown, some transitions are not simple or clear in DSC. In cases where glass transitions are occurring around the same temperature as kinetic transitions, like an enthalpic recovery as shown in the paper, MDSC can separate these and allow for clearer interpretation of the data. MDSC is an important tool for the Thermal Analyst and is standard on all TA Instruments DSC’s – Discovery X3 DSC, Discovery DSC 2500, 250, & 25. The Discovery X3 DSC allows 3 samples to be run at the same time for added productivity and the comparison of data under the same conditions.

ACKNOWLEDGEMENT

This paper was written by Louis Waguespack, Applications Laboratory Manager, and Tianhong (Terri) Chen, Ph.D., Senior Applications Support Scientist at TA Instruments.

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