TA Instruments

Thermal Analysis & Rheology

THERMAL SOLUTIONS

MEASUREMENT OF AGING EFFECTS ON AMORPHOUS PET

PROBLEM

In amorphous polymers, such as polyethyleneterephthalate (PET), it is common for an enthalpic relaxation to be present just above the glass transition. This relaxation, which has been described in the literature using several names including stress relaxation, volume relaxation, and middle endothermic peak, is endothermic and increases in size with longer aging times at increased temperatures (1,2). Hence, measuring the size of this relaxation is of interest because end-use applications such as wear-dated carpet fibers and packaging are affected by changes in internal polymer structure due to aging. Differential scanning calorimetry (DSC) has traditionally been used to evaluate the glass transition in amorphous polymers. Unfortunately, as shown in Figure 1, overlap of the glass transition and the enthalpic relaxation is often sufficient to make interpretation difficult and measurement of the energy associated with the relaxation essentially impossible even using sigmoidal baseline treatments to account for baseline shifts.

SOLUTION

Modulated DSC™ is a new technique which subjects a material to a linear heating method which has a superimposed sinusoidal temperature oscillation (modulation) resulting in a cyclic heating profile. Deconvolution of the resultant heat flow profile during this cyclic heating provides not only the "total" heat flow obtained from conventional DSC, but also separates that "total" heat flow into its heat capacity-related (reversing) and kinetic (nonreversing) components. Thus, modulated DSC provides all the same benefits as conventional DSC plus several unique benefits including:

- *Separation of complex transitions into more easily interpreted components*
- *Increased sensitivity for detection of weak transitions*
- *Increased resolution of transitions without loss in sensitivity*
- *Measurement of heat capacity and heat flow from a single experiment*
- *Determination of initial crystallinity in polymers*
- *Determination of thermal conductivity*

Figure 1. ENTHALPIC RELAXATION OF PET

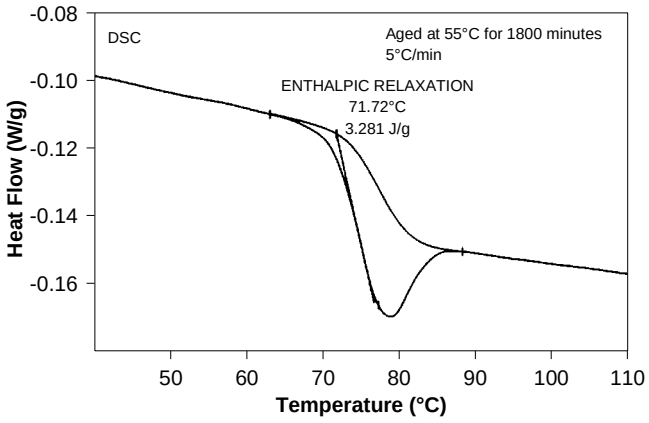
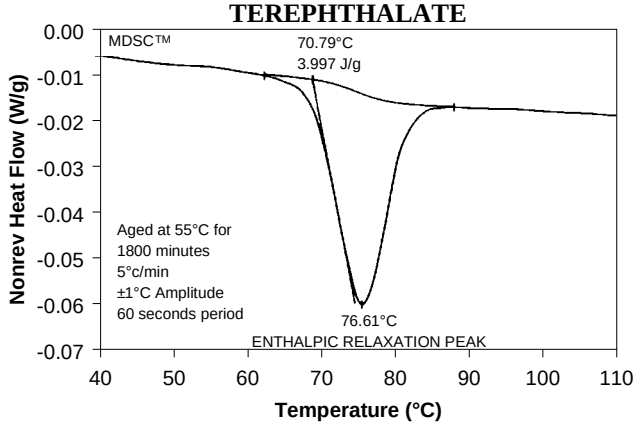


Figure 2. AGED POLYETHYLENE TEREPHTHALATE



Modulated DSC™ offers a better method for separating the glass transition and the associated relaxation because the glass transition is a reversing phenomenon in modulated DSC and the enthalpic relaxation is a nonreversing event. Figure 2 shows the level of separation and quantitation possible from the modulated DSC results. Using a series of PET samples aged for known periods of time at a specific end-use temperature (55°C in the examples shown in Figure 3), it is possible to construct a correlation curve between aging and the size of the enthalpic relaxation. In this case, the best fit (Figure 4) is described by the equation $\Delta H = -0.562 \ln(t_{55}) + 1.21$ where t_{55} = the effective age in minutes and ΔH = the endothermic relaxation enthalpy in J/g. This correlation curve can subsequently be used to estimate the effective age (time since production) of the polymer.*

REFERENCES

1. B. Wunderlich, Thermal Analysis, Academic Press, 207 (1990).
2. M. Todoki, Polymer Data Handbook (Japanese), Society of Polymer Science, Baifuu-kan, 684-703 (1986).

Figure 3. PET's ENTHALPIC RELAXATION vs AGE

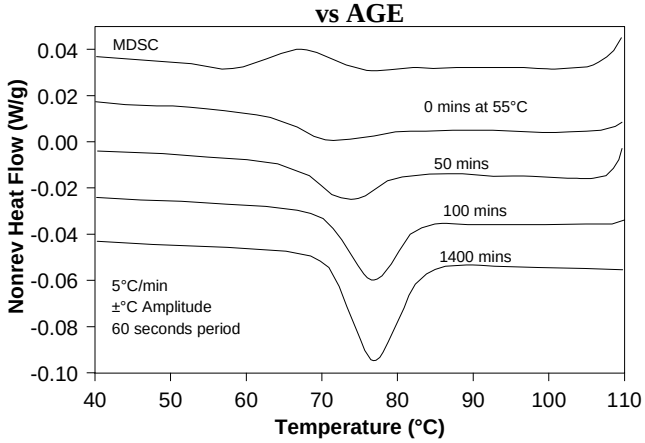
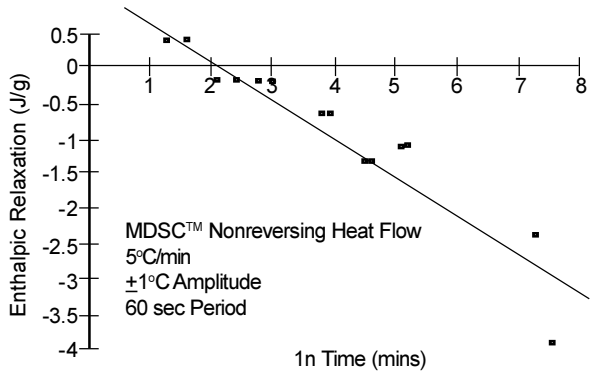


Figure 4. EFFECT OF AGING PET AT 55°C



*The quantitative measurement of the heat flow associated with the enthalpic relaxation from the nonreversing heat flow is affected by the period (frequency) of modulation. Hence, constant conditions must be used when comparing materials as described in this brief.

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