Physical Aging and Fragility of Amorphous Polyethylene Terephthalate

R. Bruce Cassel, Ph.D.
TA Instruments, 109 Lukens Drive, New Castle, DE 19720, USA

ABSTRACT

Physical aging of amorphous polyethylene terephthalate (PET) pre-forms is a source of difficulties in the processing of PET containers. Amorphous PET is characterized through cooling experiments at different rates to quantify the glass transition temperature, physical aging and fragility by differential scanning calorimetry (DSC).

INTRODUCTION

Polyethylene terephthalate (PET) is a ubiquitous packaging material used for bottles, containers and package wrap. Its excellent qualities of optical clarity, high strength and impact fracture resistance make it the material of choice for an increasing range of products. These properties are achieved through blow molding of the amorphous material above the glass transition temperature (Tg) where the material is rubbery and capable of flow. The blow molding produces orientation strain-related "seeds" and strength building crystallization. The quality of the finished product depends upon the mechanical treatment during processing and on the viscoelastic properties of the PET at the processing temperatures. The viscoelastic properties are a function of molecular weight distribution, additives and thermomechanical history. Naturally, rheology and thermal analysis testing play a significant role in the development of PET formulations and in trouble shooting problems that arise during processing. One such problem is changes in the viscoelastic properties of PET pre-forms during processing due to physical aging.

How thermal and mechanical properties change with temperature as a material is heated through the glass transition region may be determined using differential scanning calorimeter (DSC) and dynamic mechanical analysis (DMA) or rheology. When an amorphous material is maintained ten or twenty Celsius degrees below Tg, it appears solid and unchanging. In fact, if it is close enough to Tg, it undergoes slow changes in thermodynamic and viscoelastic properties, referred to as physical aging.

While physical aging occurs to some degree with all amorphous materials, the degree to which it occurs (*i.e.*, how far below Tg a material must be stored to be stable) varies by an order of magnitude depending on the material (*1*). Predicting physical aging

for a particular material, quantifying it and looking for ways to modify it are reasons for carrying out the DSC analyses.

Figure 1 shows a sample of amorphous PET heated through the glass transition region after being cooled at 0.2 °C/min. Heat capacity is displayed on the Y-axis and temperature on the X-axis. The peak in the heat capacity curve is an enthalpic recovery peak produced by the physical aging of cooling slowly through the glass transition

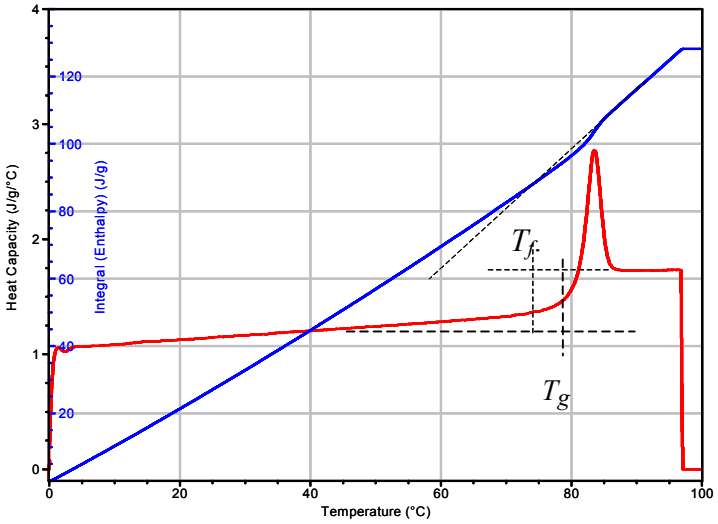

Figure 1 - Heat Capacity and Enthalpy Curve of PET Through the Tg Region Showing Constructs

region. Storing the PET at a temperature somewhat below Tg causes a similar effect.

The term "fragility" is used to describe the sensitivity of a material to physical aging. Fragility is defined by equation 1 and may be measured by DSC (*1*).

$$m_{\Delta h} = -\,(d \log \beta_c)/(d(T_{f,ref}/T_f)), \qquad \text{(eq. 1)}$$

where

β_c	is the prior cooling rate,
T_f	is the fictive temperature measured in heating, and
$T_{f,ref}$	is the reference fictive temperature, and
$m_{\Delta h}$	is the fragility parameter.

The glass transition temperature is a somewhat arbitrary value assigned to the glass transition region as defined by a particular procedure. In general, the value of Tg depends on the analytical technique, for example, calorimetry, volumetric analysis, or rheology. It also depends on the time scale of the measurement, *e.g.*, the DSC heating rate, or Modulated DSC® or DMA frequency. And it depends on the previous thermal (and mechanical) history of the sample.

One definition of Tg that has particular utility for determining fragility is the fictive temperature (T_f) (*2,3,4*). The fictive temperature is defined as the extrapolated intersection of the pre-transition and post-transition DSC heat flow baselines transposed to enthalpy units. To obtain relative enthalpy one integrates the DSC specific heat capacity curve, (or heat flow curves, provided that all instrumental curvature has been removed). There is also an equivalent graphical method of obtaining T_f directly from the DSC trace (*5*). Figure 1 shows the T_f on a DSC heat capacity trace and its integral.

The unique property of the fictive temperature is that it is independent of the DSC heating rate used to measure it. Hence, it gives a value for Tg that depends only on the previous cooling rate through the glass transition region, determining the enthalpy state of the material below Tg. So while there is an arbitrary aspect of any glass transition assignment, the use of the fictive temperature is more fundamental since it removes the time dependence of the measurement, leaving only the time dependence of the sample's thermal history, that genuinely affects the characteristics of the material, as physical aging demonstrates.

While the method of determining T_f is straightforward from a theoretical standpoint it presents considerable practical difficulty because it requires extrapolation to intersection of two slightly curved enthalpy lines. And it is very dependent on achieving straight, reproducible instrument baselines.

EXPERIMENTAL

A Q1000 DSC with Advanced Tzero™ Technology is used for this analysis. This DSC and sensor technology is described in a number of publications (*6*). The capabilities of this technology are particularly useful for this method. For example, the temperature scale is that of the pan holding the sample. Hence, all thermal lag is already addressed in the abscissa temperature data. This allows data to be compared at different heating and cooling rates with confidence that the DSC is calibrated for all these conditions (*7*).

Since determining the fictive temperature requires an extrapolation across the glass transition interval, it is essential that the baseline be devoid of instrumental slope or curvature. The Q Series™ DSC cell makes possible this capability. Rapid equilibration and fast cooling rates are also necessary, and both these characteristics are available using the Q Series™ DSC. Additionally, since the instrumental baseline has been removed from the DSC output the signal can be fully normalized into units of heat capacity, the fundamental thermodynamic property of the material being measured.

The collection of data for this analysis is accomplished with a single, overnight,

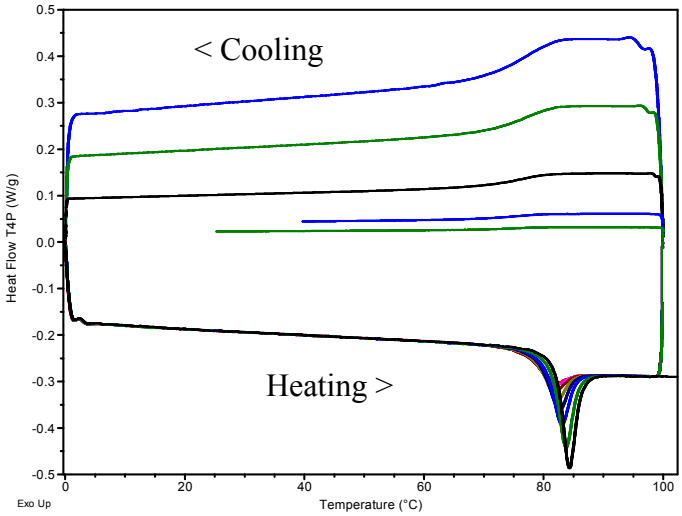

Figure 2 - DSC Data for Fragility Calculation, Showing Cooling at Multiple Rates and Heating at 10 °C/min

multiple-step program that alternately conditions the sample through the glass transition region at successive cooling rates and alternately measures the fictive temperature at a fixed rate, here 10 °C/min. Figure 2 shows much of the raw data for this analysis, both

on heating and cooling. (The method used in this procedure is presented in the appendix.)

In PET, the glass transition is sufficiently close to ambient temperatures that physical aging is an established problem. The storage of PET pre-forms for only a few days can produce sufficient physical aging to change the blow molding characteristics.

The encapsulated 15 mg crystalline PET sample (taken from a blow molded snack food container) was heated to 300 °C in nitrogen in the DSC to melt it. The sample is then removed and placed on a conductive surface at room temperature "quench" cooling it. This rapid cool-down prevented crystallization of the sample, thus "trapping" it in the amorphous state. Subsequent manipulation of the sample stays well below the cold crystallization temperature of PET.

Table 1. Glass Transition of PET after cooling

Cooling Rate (°C/min)	Fictive (°C)	Mid Pt. (°C)
15	76.42	77.91
10	75.53	77.95
5	74.66	77.98
2	73.82	78.23
1	73.03	78.61
0.5	72.1	79.03
0.2	71.23	79.99
0.1	70.17	80.67

RESULTS AND DISCUSSION

The Tg results may be seen in Figure 3 and Table 1. The sample is cooled at the indicated cooling rate through the glass transition interval then immediately heated at 10 °C/min, as shown in Figure 2. The glass transition is measured at the indicated cooling rates using the midpoint-by-half-height glass transition assignment protocol (*8*). The Tg is measured in the subsequent heating step using both the fictive temperature method (used for the fragility calculation) and the midpoint method.

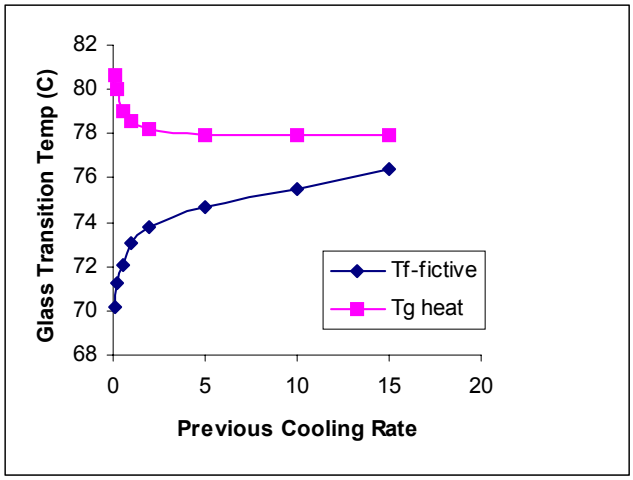

Figure 3. Effect of Cooling Rate on the Glass Transition of PET

The fictive Tg in Table 1 is lower after slow cooling. This is consistent with the changes in other physical properties that accompany physical aging, namely, increased mobility at lower temperatures. In contrast, the standard (mid-point) Tg method does not show this trend at 10 °C/min because of retardation caused by the physical aging. (If heated at a much slower rate, or if measured during the cooling cycle, the midpoint Tg would be seen to be much closer to the fictive temperature.)

For ordinary glass transition analyses, the midpoint method has the advantage of having lower sensitivity to physical aging changes and therefore more likely to give a material-dependent measure of the Tg region midpoint. The conventional method also minimizes extrapolation, which amplifies errors in positioning Tg constructs.

Using Equation 1 and the fictive glass transition data in Table 1, the fragility parameter, $m_{\Delta h}$, is determined using a least squares best fit, to be 127 ± 4. Using equation 1, the physical aging for three weeks (a cooling rate through Tg of 0.001 ºC/min) predicts a T_f of 66 ºC. This indicates a softening point more than 10 Celsius degrees lower than what would be indicated by a conventional DSC Tg test.

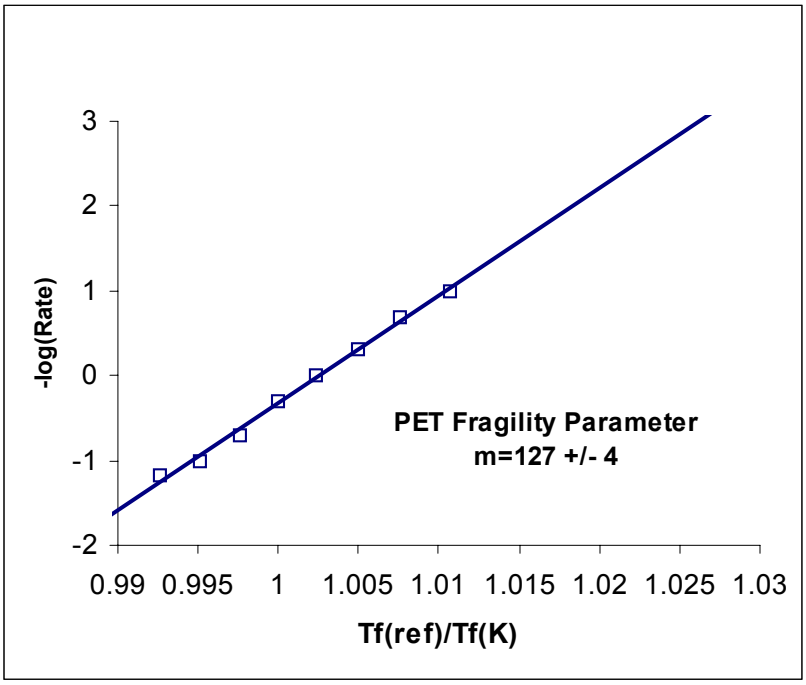

Figure 3 - Fragility Plot of PET

SUMMARY

A method is described to determine the fragility of a PET package material. (Fragility is a measure of the stability below the glass transition.) The Q1000 with Advanced Tzero™ Technology has considerable advantage for this analysis because of its improved temperature control, accuracy, and baseline stability. This approach could be extended to allow determination of the fragility parameter for other PET formulations to assess the effect of changes in molecular weight distribution and additives on the tendency of PET to physical aging.

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KEYWORDS

differential scanning calorimetry, glass transition, polyesters, thermoplastic polymers

APPENDIX

DSC Method

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TA Instruments Thermal Analysis
Instrument DSC Q1000 V6.2 Build
208
Module DSC Standard Cell FC
Operator BC
Demo\ta\Data\DSC\a-sucrose-Tg-
cooling.004
ProcName Multi-cool-Ramp
Sample sugar fragility
Size 19.900 mg
PanMass 23.620 23.000 mg
PanResist Automatic Automatic
K/W
Method Multi-cool-Ramp
Comment for fragility calc
Xcomment Pan: Aluminum
Xcomment Gas1: Nitrogen 10.0
ml/min
Exotherm Up
Nsig 18
Date 16-Apr-2002
Time 23:05
1: Equilibrate at 140.00 °C
2: Isothermal for 4.00 min
3: Ramp 25.00 °C/min to -30.00
°C
4: Isothermal for 3.00 min
5: Mark end of cycle 0
6: Isothermal for 3.00 min
7: Ramp 15.00 °C/min to 140.00
°C
8: Isothermal for 2.00 min
9: Mark end of cycle 0
10: Isothermal for 2.00 min
11: Ramp 15.00 °C/min to -30.00
°C
12: Isothermal for 3.00 min
13: Mark end of cycle 0
14: Isothermal for 3.00 min
15: Ramp 15.00 °C/min to 140.00
°C
16: Isothermal for 2.00 min
17: Mark end of cycle 0
18: Isothermal for 2.00 min
19: Ramp 8.00 °C/min to -30.00
°C
20: Isothermal for 2.00 min
21: Mark end of cycle 0
22: Isothermal for 2.00 min
23: Ramp 15.00 °C/min to 120.00
°C
24: Sampling interval 2.00
sec/pt
25: Isothermal for 3.00 min
26: Mark end of cycle 0
27: Isothermal for 3.00 min
28: Ramp 5.00 °C/min to -15.00
°C
29: Isothermal for 2.00 min
30: Mark end of cycle 0
31: Isothermal for 2.00 min
32: Ramp 15.00 °C/min to 100.00
°C
33: Isothermal for 2.00 min
34: Mark end of cycle 0
35: Isothermal for 2.00 min
36: Sampling interval 2.00
sec/pt
37: Ramp 2.00 °C/min to 10.00 °C
38: Isothermal for 2.00 min
39: Mark end of cycle 0
40: Isothermal for 2.00 min
41: Ramp 15.00 °C/min to 100.00
°C
42: Isothermal for 2.00 min
43: Mark end of cycle 0
44: Isothermal for 2.00 min
45: Ramp 0.50 °C/min to 20.00 °C
46: Isothermal for 2.00 min
47: Mark end of cycle 0
48: Isothermal for 2.00 min
49: Ramp 15.00 °C/min to 100.00
°C
50: Isothermal for 2.00 min
51: Mark end of cycle 0
52: Isothermal for 2.00 min
53: Sampling interval 10.00
sec/pt
54: Ramp 0.25 °C/min to 20.00 °C
55: Isothermal for 2.00 min
56: Mark end of cycle 0
57: Isothermal for 2.00 min
58: Sampling interval 0.50
sec/pt
59: Ramp 15.00 °C/min to 140.00
°C
60: Isothermal for 2.00 min
61: Ramp 4.00 °C/min to 85.00 °C
62: Sampling interval 10.00
sec/pt
63: Ramp 0.10 °C/min to 25.00 °C
64: Sampling interval 0.50
sec/pt
65: Isothermal for 2.00 min
66: Ramp 15.00 °C/min to 140.00
°C
67: Isothermal for 4.00 min
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