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USE OF THERMAL ANALYSIS TECHNIQUES FOR EXAMINING BLOW-MOLDED PET BOTTLE SPECIMENS

C. D. Wingard

NASA/MSFC, Mail Code EH32, Marshall Space Flight Center, Alabama 35812, USA

Abstract

Eight samples from different areas of stretch-blow-molded poly(ethylene terephthalate) [PET] bottles, including a PET resin control, were tested by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). The glass transition temperature (T_g) was found to linearly decrease about 6°C from zero to 45 percent initial crystallinity. Measurements of T_c (crystallization temperature, DSC) and film tension modulus (TMA) were related to crystallization rate during stretch-blow-molding. The TMA linear coefficients of thermal expansion and shrinkage were shown to be important for blow-molding temperature control.

Keywords: glass transition, hot-fill, initial crystallinity, shrinkage, stretch-blow-molding

Introduction

The Technology Transfer Office at the NASA/Marshall Space Flight Center (MSFC) provides consulting/expertise through engineers and scientists to private companies to assist in solving technical issues. A manufacturer that produces stretch-blow-molded PET bottles by the hot-fill method sought assistance from NASA/MSFC via thermal analysis testing to better understand the influence of the T_g and percent crystallinity on the shrinkage control for the hot-fill (85–90°C) and blow-molding (95–110°C) processes. The blow-molding process is performed first, followed by the hot-fill process for the pasteurization of non-carbonated liquids such as fruit juices and sports drinks. Each bottle preform is made by injection-molding the PET resin near 280°C (the melting temperature is near 250°C). During blow-molding, each preform is heated to a temperature about 20°C above its T_g. Stretch-blow-molding occurs at very high speeds (40–70 m min^{-1}), causing deformation of each preform that produces orientation and crystallization to form the bottle. The stretching process also freezes some inner stress in the amorphous regions of each bottle to allow for proper bottle shrinkage. The neck region of the blown PET bottle should be purely amorphous, and the bell and panel regions should have about 25–30% crystallinity to minimize shrinkage (by cooling to the hot-fill temperature) and softening due to the influence of the T_g at the hot-fill temperature. The T_g and T_c (crystallization temperature) as measured by DSC are critical for both the injection molding and blow molding processes. The processing window is (T_c–T_g); the wider this window the better for process control. The T_g of PET does not change very much, but T_c may vary as much as 30°C if the PET resin used

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in bottle processing comes from different suppliers. This variation in T_c can also have a significant effect on the crystallization rate of stretch-blow-molded bottles.

The hot-fill process is performed about 5 to 10°C above the T_g, and each blown bottle is quenched from 85 to 23°C with cool water for shrinkage control. The shrinkage in cooling from blow-molding to hot-fill should be about 1% by volume; in cooling from hot-fill the shrinkage should be less than 2%, based on bottle dimensional measurements. Thermomechanical analysis (TMA) data at various temperatures can be related to the shrinkage of the PET bottles after blow-molding and hot-fill, and can be useful for blow-molding temperature control and bottle design references.

The manufacturer supplied the Nonmetallic Materials Branch at NASA/MSFC with eight samples which included the neck, bell and panel regions of 32 oz. and 64 oz. bottles, and a PET resin control, for DSC (T_g, initial crystallinity and aging) and TMA (thermal expansion and shrinkage, film tension modulus) testing. These bottle samples were from rejects that did not sustain the hot-fill process, and were from bottles that were kept in storage at uncontrolled temperature and humidity for about three months before being tested at MSFC.

There are several factors that can lead to finished PET bottle rejections: (a) Each bottle preform can age rapidly (e.g., within one week of production) because it is purely amorphous, resulting in a blown bottle that may be too brittle. The critical enthalpy of aging as measured by DSC is about 3 J g^{-1} for oriented and unoriented sheet PET (1), which indicates the onset of brittle failure; (b) Bottle preform design is critical in determining proper material distribution for achieving the optimum bottle thickness and material modulus (stiffness); (c) The higher the stretch-induced crystallinity in each blown bottle, the less amorphous regions, resulting in less hot-fill shrinkage and less chance of bottle rejection. If necessary, the crystallinity can be increased by a heat-set procedure for a short time in the mold shortly after the bottle is blown. The panel region of each blown PET bottle is where the label is placed, but if there is too much shrinkage the bottle cannot be labeled properly.

Most of the recent papers in the literature report the measurement of properties of oriented PET sheet, rather than the stretch-blow-molded bottles. Mukherjee and Jabarin [1] reported aging characteristics below the T_g by DSC. Maruhashi and Asada [2] reported shrinkage and crystallinity as a function of draw ratio at 85–95°C. The literature indicates that semi-crystalline polymers such as PET may show an increase in T_g of the amorphous regions as crystallization develops and reduces the total chain mobility. However, the T_g may be unaffected by the presence of crystallites if they are more widely spaced [3]. Recent data from the TA Instruments Dynamic Mechanical Analyzer (DMA 2980) on 10 micron PET films showed an increase in T_g and modulus with increasing crystallinity [4].

Experimental methods

All of the thermal analysis data by DSC and TMA were obtained with an argon gas sample purge. The DSC data was obtained with a TA Instruments 910 DSC. A typical DSC experiment on a PET sample was:

1. Initial temperature scan from 25 to 300°C at 10°C min^{-1}.

2. Cool from 300 to 25°C at 10°C min^{-1}.
3. Reheat from 25 to 300°C at 10°C min^{-1}.
4. Quench cool sample on an aluminum block at room temperature, then reheat from 25 to 300°C at 10°C min^{-1}.

Each PET sample was crimped in a non-hermetic aluminum DSC sample pan. The average DSC sample weight was 15.1 mg (std. dev.=4.3 mg) for 40 PET specimens tested. From 1 to 5 PET specimens per sample type were tested on the DSC to show reproducibility of the T_g and initial crystallinity (step 1 above only). Initial crystallinity of each PET sample was calculated from the DSC heat of melting, and was compared with the crystallinity of each sample type calculated from a density air/water weight method. The density data was obtained with an analytical balance in NASA/MSFC's Space Sciences Laboratory. After air weight measurements were made, the PET samples were immersed in distilled water by allowing the water to boil vigorously for about 15 min to remove bubbles from the sample surfaces.

The TMA data was obtained with two TA Instruments modules: 943 TMA (expansion/shrinkage data) and 2940 TMA (modulus data in the film tension mode). A typical TMA experiment on a PET bottle sample for expansion/shrinkage data was:

1. Heat sample from 25 to 110°C at 5°C min^{-1}.
2. Observe shrinkage for natural cool down of the sample from 110 to 25°C with the TMA furnace still intact. It is not possible to use cold water in contact with the TMA furnace for cooling as is done for shrinkage control of the blow-molded PET bottles.

The expansion/shrinkage data was obtained with a macro (wide) expansion probe (6.0 mm dia.) loaded with a 2 g weight. Bottle specimens were cut that were straight vertically but with some curvature so they stood upright under the expansion probe.

The TMA 2940 was used in the film tension mode for determining the modulus (stiffness) of several flat PET bottle samples [e.g., 4.8 mm by 19.1 mm (0.75 in by 0.188 in)] as a function of temperature and sample thickness. The modulus for each sample was calculated from the initial slope of stress/strain data (based on force/dimension change data from the TMA 2940). A typical TMA experiment on a PET bottle sample for film tension data was:

1. Equilibrate at 25°C.
2. Force at 0.05 Newtons (N).
3. Ramp force 0.05 N min^{-1} to 0.4 N.
4. Increment 10°C.
5. Repeat segment 2 till 85°C.

Results and discussion

DSC and density data

For DSC testing, the initial crystallinity was calculated from the observed heat of melting relative to that in the literature for 100% crystalline PET, an average value of 135 J g^{-1} [5]. If necessary, the observed heat of cold crystallization from the initial temperature scan of a sample was subtracted from the observed heat of melting before calculation of the percent crystallinity (as shown in Fig. 1 for the 32 oz. Powerade neck). More specifically, the initial crystallinity of each PET sample was based on a "thermodynamic" method for connecting the DSC baseline between the two equilibrium liquid regions just above the T_g and above the peak melting tem-

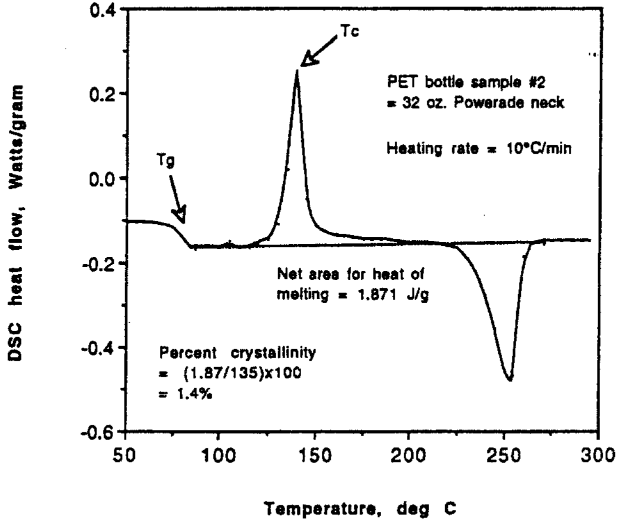


Fig. 1 Initial DSC heating scan on a PET blow-molded bottle sample with minimal crystallinity

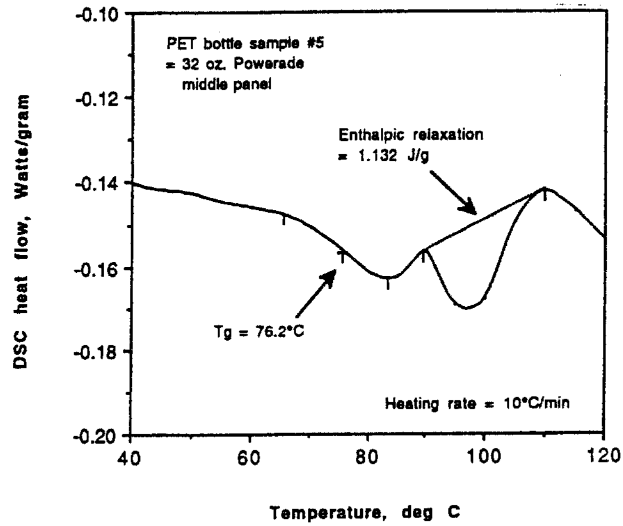


Fig. 2 Initial DSC heating scan on a PET blow-molded bottle sample showing an endothermic relaxation just the T_g

perature, T_m [6]. Although this method works best for PET that is highly amorphous (Figure 1 for one of two neck samples tested, with 1.4% crystallinity) or is made amorphous by quench cooling from the melt, the method also worked fairly well for the initial temperature scans on the bottle samples. The average initial crystallinity ranged from 8.5% (neck sample) to 34.6% (top bell sample) for the bottle samples, with a value of 44.5% for the PET resin.

The initial crystallinity of each PET sample type was also calculated from the density of each sample from the air/water weights, and the densities of pure amorphous and crystalline PET [7]. These crystallinity values averaged within 5% of those determined from DSC data.

Figure 2 shows an endothermic enthalpic relaxation just past the T_g in a DSC scan on one of the bottle samples. This endotherm ranged from about 0.3 to 1.4 J g^{-1} for the bottle samples, and a plot of the endotherm energy *vs.* ambient laboratory aging time (up to one year) went through a slight maximum for several bottle samples. Recall that if this endotherm energy reaches about 3 J g^{-1}, it results in the onset of brittle failure of the PET [1]. The T_g's from the initial DSC scans ranged from 79.8°C (neck sample) to 71.8°C (top bell sample). In Fig. 3, the T_g and heat flow change at T_g are plotted *vs.* initial crystallinity. Although the correlation is not very strong, the T_g linearly decreased about 6°C from 0 to 45% initial crystallinity. The heat flow change at T_g more clearly decreased from low to high crystallinity. The trends

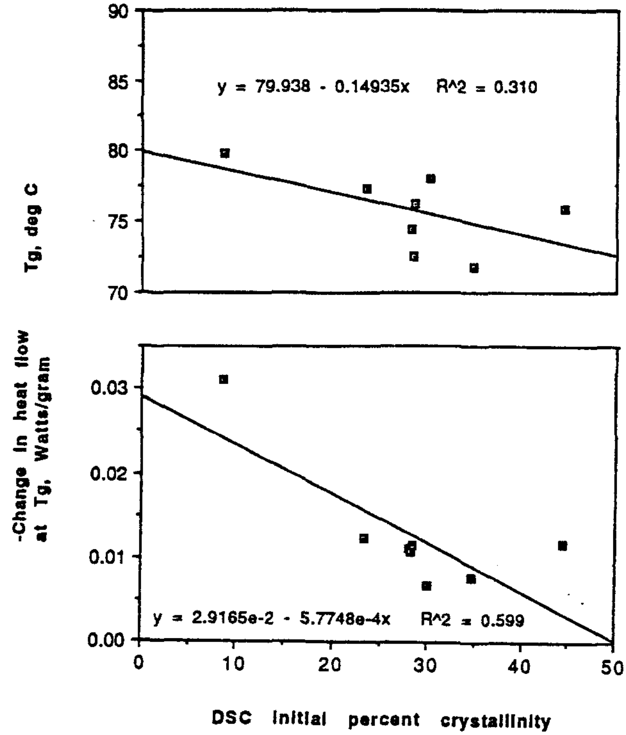


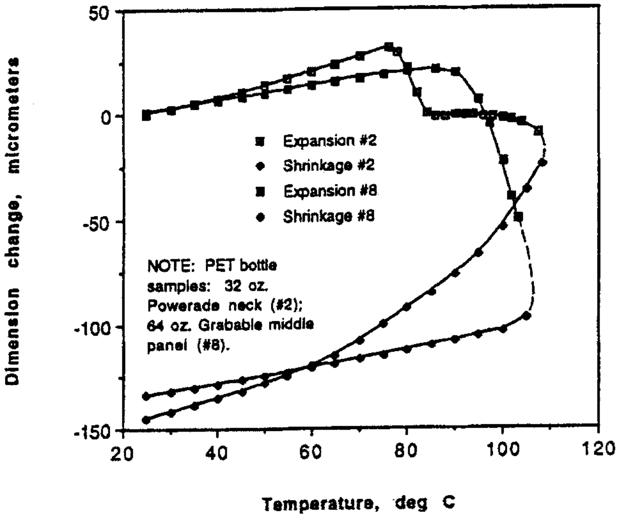
Fig. 3 Glass transition temperature (T_g) and heat flow change at T_g *vs.* crystallinity of PET samples for initial DSC heating scans

in Fig. 3 were also observed when each PET sample was cooled at 10°C min^{-1} from the melt following heating at 10°C min^{-1}.

For the controlled cooling from the melt, the peak crystallization temperature (T_c) was observed for each PET sample. For 32 oz. Powerade bottle samples, the T_c averaged 185°C; for 64 oz. Grabable bottle samples, the T_c averaged 163°C. This data implies that these two different size bottles were made from different PET resins. The data also implies that the 32 oz. bottle had almost a 20% higher crystallization rate than the 64 oz. bottle, based on literature data on amorphous PET for the growth rate of spherulites at several crystallization temperatures by hot stage optical microscopy [8].

TMA data

Two specimens from the 32 oz. Powerade neck sample and three specimens from the 64 oz. Grabable middle panel were heated from 25 to 110°C in the TMA, then allowed to cool naturally to 25°C with the TMA furnace still intact. Representative expansion/shrinkage data from these runs is shown in Fig. 4, with the sharp decrease in the expansion curves at 77 to 85°C due to the influence of the T_g. Between 25 and 85°C, the expansion/shrinkage for the neck sample and middle panel sample were about 0.4% and 0.2%, respectively. The linear coefficients of thermal expansion and shrinkage were each about twice as high for the neck sample than for the middle panel sample, reflecting about 0 and 30% crystallinity for the neck and middle panel regions, respectively. Although the rate of shrinkage was much higher for the neck sample, both sample types had about 1.5–2.0% total shrinkage (based on sample height) after natural cooling from 110 to 25°C. The TMA expansion/shrinkage data shows that rate of shrinkage could be strongly influenced by blow-molding temperature control.



NOTE: PET bottle samples: 32 oz. Powerade neck (#2); 64 oz. Grabable middle panel (#8).

Fig. 4 TMA expansion and shrinkage data for two PET blow-molded bottle samples with low and high crystallinity

In the TMA film tension mode, one sample each from the 32 oz. Powerade bottle (middle and bottom panels) and one sample from the 64 oz. Grabable middle panel were tested as a function of temperature. The resulting modulus *vs.* temperature data showed that: (a) the 32 oz. middle panel had a modulus about twice that of the 64 oz. middle panel at 25°C, although the 64 oz. sample was about 60% thicker; and (b) the 32 oz. middle panel sharply decreased in modulus at 35°C, but the 64 oz. middle panel decreased very little in modulus up to 75°C. These results may reflect the implied higher crystallization rate for the 32 oz. bottle than for the 64 oz. bottle based on DSC data, and thus a more thermally stable 64 oz. bottle produced at a lower crystallization rate.

Conclusions

The DSC initial crystallinity of eight samples from different regions of stretch-blow-molded PET bottles averaged 8 to 35%. The initial crystallinity by a density method averaged within 5% of that by the DSC method. With increasing crystallinity of the bottle samples, the T_g slightly decreased but the change in heat flow at the T_g clearly decreased. For ambient laboratory aging of the bottle samples up to one year, the energy of a DSC enthalpic relaxation just past the T_g was no more than half of the energy required for onset of brittle failure in the PET material. For samples from 32 oz. and 64 oz. PET bottles, differences in the crystallization temperature (T_c) and modulus determined by DSC and TMA techniques, respectively, could be due to different crystallization rates during processing for the two bottle sizes. The linear coefficients of thermal expansion and shrinkage for a bottle neck sample (very minimal crystallinity) were about twice those of a middle panel sample (30% crystallinity), but the total shrinkage from 110 to 25°C was about the same for both samples.

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