A Laboratory To Demonstrate the Effect of Thermal History on Semicrystalline Polymers Using Rapid Scanning Rate Differential Scanning Calorimetry

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Semicrystalline polymers are characterized by the existence of ordered domains within the otherwise disordered structures constituted by long coiled chains. The presence of the crystalline domains has a significant impact on the thermal, mechanical, and physical properties of a polymer (1). High-density polyethylene (HDPE) is more crystalline than low-density polyethylene (LDPE) and exhibits greater hardness, higher tensile modulus, and a higher melting point (1). Considering the commercial and technological significance of polymers, an understanding of the range of factors that influence crystallinity in polymers is crucial for engineering and science students.

The thermal behavior of a polymer can also be significantly influenced by its morphology. Amorphous polymers do not exhibit a melting transition; rather, they are characterized by a transformation from a glassy state to a liquid-like state known as the glass transition. Semicrystalline polymers exhibit a glass transition and also a melting transition as the crystalline domains are disrupted at higher temperatures. Furthermore, depending on processing conditions and heating rate, semicrystalline polymers may also recrystallize during heating. Semicrystalline polymers may be characterized by various techniques such as X-ray diffraction (XRD), optical microscopy, and differential scanning calorimetry (DSC). However, DSC remains a preferred method because it facilitates complete characterization of the various thermal transitions in these materials.

DSCs are used to measure temperatures and heat flow associated with thermal transitions in materials. Significant advances in thermal instrumentation over the past few years have enabled development of commercial DSCs capable of attaining faster heating and cooling rates. These DSCs enable characterization of subtle and complex thermal events and also extend the measurement range of a conventional DSC by facilitating ballistic cooling or heating rates, which are encountered in polymer processing (2–6). The use of the rapid scanning rate DSC (Project RHC, TA Instruments) in a materials science laboratory course for characterizing the thermal behavior of poly(ethylene terephthalate) (PET) obtained from a beverage bottle is described here. Iler and co-workers (7) used PET, due to its widespread commercial use and because it exhibits a rich variety of transitions, for laboratory demonstrations of polymer behavior, which enhanced student understanding of semicrystalline behavior. In a recent article, D’Amico and co-workers (8) described a student exercise involving measurement of differences in crystallinity of PET samples obtained from the neck and the body of a PET bottle using DSC. However, unlike the previously described student experiments, the goal of this laboratory was to provide a detailed picture of the effect of thermal history on the behavior and properties of a semicrystalline polymer.

The laboratory described here involved examining the effect of parameters such as heating rate and isothermal annealing time or temperature on the thermal behavior of PET. The RHC-DSC was particularly useful for these experiments because all the tests could be conducted using the same sample by rapidly heating the material above the melting temperature to 280 °C, followed by cooling to −150 °C at 500 °C min⁻¹, which ensured that the material was amorphous prior to each test. The laboratory was conducted by dividing each section into six groups of 3–4 students. The rapid heating and cooling rates of the RHC-DSC proved to be valuable in enabling more experiments over the 2-h time frame in comparison to a conventional DSC.

Instrumentation

The experiments described in this work were performed using an RHC-DSC from TA Instruments. The rapid rates attained in the RHC-DSC are made possible through infrared heating elements for heating and a liquid nitrogen cooling system for cooling (9). The temperature and heat flow calibrations were performed using a reference indium sample at 500 °C min⁻¹. The sample pans employed in the DSC had a diameter of 1.6 mm and are almost 10 times smaller than a typical DSC pan to minimize the effect of thermal gradients. The sample and pan masses were weighed accurately with a PerkinElmer AD2 microgram balance.

Materials

The PET required for the tests was obtained from the body of a used beverage bottle that had been rinsed with water prior to use. The dry strips were wiped with a tissue prior to cutting for sample preparation. A small specimen (0.1–0.2 mg) was cut and inspected under an optical microscope prior to weighing with the DSC sample pan.

Hazards

The sample preparation involves cutting thin slices of the PET film using a razor blade. Sufficient care must be exercised to ensure that the sample is held in a stable manner while cutting the specimen to avoid injuries.

Experimental Section

The laboratory was designed to examine the effect of heating rate and isothermal annealing conditions on the thermal transitions observed in PET. Prior to each test, the polymer was
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preconditioned by heating to 280 °C at 500 °C min⁻¹, followed by cooling the sample melt to −150 °C at 500 °C min⁻¹, which rendered the polymer completely amorphous. The laboratory was divided into three modules.

Module 1

The effect of heating the preconditioned amorphous sample to 280 °C at two different rates of 500 °C min⁻¹ and 20 °C min⁻¹ was examined.

Module 2

The preconditioned amorphous sample was annealed over various times (7 and 10 min) at 125 °C. Following the annealing period, the sample was quickly quenched to −150 °C at 500 °C min⁻¹ and immediately heated to 280 °C at 500 °C min⁻¹ to examine the effect of the isothermal annealing times.

Module 3

The effect of annealing the sample for 10 min at 125 and 130 °C was examined. Following the annealing period, the sample was quickly quenched to −150 °C at 500 °C min⁻¹ and immediately heated to 280 °C at 500 °C min⁻¹ to examine the effect of the isothermal annealing temperatures.

Results

The thermal response observed upon heating the preconditioned PET to 280 °C at 500 °C min⁻¹ is shown in Figure 1. PET is rendered completely amorphous upon preconditioning and exhibits only a glass transition upon heating at 500 °C min⁻¹ because the rapid heating rate employed does not facilitate recrystallization upon heating. The glass transition is represented by a step change in heat flow in Figure 1, signaling a transition of the polymer from a glass-like to a liquid-like state. The onset of glass transition is found to be at 80.7 ± 1.2 °C based on six measurements, which is in agreement with the range of values reported by Iler and co-workers (7). In contrast, when the preconditioned amorphous PET is heated to 280 °C at 20 °C min⁻¹, a cold crystallization exotherm and a melting endotherm are observed as shown in Figure 2. In this instance, the heating rate of 20 °C min⁻¹ is sufficiently slow for development of some ordered domains or crystallites within the polymer chains. It is noted that the degree of crystallinity can be further increased by employing heating rates slower than 20 °C min⁻¹.

The heat flow curves obtained upon heating to 280 °C at 500 °C min⁻¹ after an isothermal hold at 125 °C for 7 and 10 min and at 130 °C for 10 min are compared in Figure 3. The heat flow curves exhibit a glass transition and a small endotherm prior to the actual melting endotherm. In general, the low-temperature endotherm for PET has been reported around 10−30 °C above the isothermal crystallization temperature, in agreement with the results of this work. The origin for the occurrence of the second peak in between the glass transition and the actual melting peak has been discussed extensively in the literature (10–13) and attributed to various reasons such as melting of lamella with different thickness and a melt-recrystallization mechanism, which suggests that some crystals formed during isothermal annealing undergo partial melting in order to be perfected or recrystallized and then melt again, leading to multiple melting endotherms (14). Some studies (15, 16) have attributed the low-temperature melting peak to the existence of a third phase known as the rigid-amorphous phase. The rigid-amorphous phase was first
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reported by Menczel and Wunderlich (17) when the amorphous and crystalline fractions did not account for the entire composition in several polymers. The rigid-amorphous phase is typically observed after isothermal treatments above the glass-transition temperature, when amorphous regions in the vicinity of crystalline domains attain some order leading to a decrease in their mobility (16, 18). In recent work, based on temperature modulated DSC (TM-DSC) measurements, Righetti and co-workers (19 20) proposed that the low-temperature endotherm arises from a partial crystallinity, liquid-like state.

For the isothermal histories shown in Figure 3, the degree of crystallinity, \( w_c \), is obtained as

\[
  w_c = \frac{\Delta H_f}{\Delta H_f^c}
\]

where \( \Delta H_f \) is the enthalpy of fusion (melting) of the semicrystalline material and is obtained as the sum of the enthalpy of both melting endotherms in this work. \( \Delta H_f^c \) is the enthalpy of fusion of a completely crystalline polymer and is reported to be 140.1 J/g for PET (7). The value of \( w_c \) increases from 14.7% to 19.8% upon increasing the isothermal annealing time from 7 to 10 min at 125 °C. For an annealing period of 10 min, a further increase in \( w_c \) from 19.8% to 20.7% is observed upon increasing the annealing temperature from 125 to 130 °C. Although \( w_c \) at 130 °C was higher than the value of \( w_c \) at 125 °C, the standard deviation was ±1%, based on six measurements, indicating that the difference might be within the error of the measurements. The onset of the glass transition appears to shift slightly toward higher temperatures with annealing time and temperature, as indicated in Figure 3. In this work, the intensity and the peak temperatures of the low-temperature endotherm increases with increasing annealing time and temperature, as shown in Figure 3, in agreement with the work of Song (16). However, the crystalline melting peaks do not shift significantly with annealing time or temperature and is found to be 227.2 ± 1 °C, based on six measurements. We note that some differences exist between the melting point reported in this work and values reported in the literature, 246–248 °C (7, 8), for samples obtained from PET bottles. The origins for some of the differences between this work and previous reports on PET bottles may be attributed to the measurement rate and crystallization temperature or history.

Summary and Student Evaluation

In this lab, the students examined the transformation of semicrystalline PET into an amorphous polymer through cooling and heating at ballistic rates. The students also observed the introduction of multiple melting behaviors through isothermal annealing. Hence, the experiments designed in this laboratory enabled the students to observe and characterize the wide range of thermal transitions exhibited by PET as a consequence of varying the thermal treatments.

A survey conducted at the end of the course revealed an overall favorable opinion among the students of the RHC-DSC lab. The results indicated that 91% of the students preferred the rapid scanning DSC lab over a conventional DSC lab conducted in the previous week of the same course because it facilitated more experiments over a short period of time and because the students did not have to wait for a long time between tests for the instrument to cool down. However, only 27% of the respondents felt that the RHC-DSC was easier to use compared to a conventional DSC particularly owing to challenges involved in the preparation of small samples required for these tests. The students were provided with a literature article (10) that described the origins of multiple melting behaviors in PET along with previous studies in the literature of the same phenomenon. Encouragingly, 86% of the students agreed that their understanding of polymer crystallinity improved after this lab and were unanimous in recommending that this lab should be an integral part of the materials science laboratory course in the future. The course consisted of 12 laboratory exercises in different areas of polymer processing and characterization, and the RHC-DSC lab was listed among the top 5 best laboratories by 64% of the students.

Although it is expected that higher heating and cooling rates will continue to be incorporated in modern thermal analysis, DSCs with rapid cooling or heating capabilities are not yet in widespread use. However, most materials science and engineering departments have access to a DSC instrument. In that regard, it is noted the experiments described in this article, especially those involving isothermal annealing, can be performed in a conventional DSC using slower heating and cooling rates, although the duration of the laboratory would have to be suitably longer.

Acknowledgment

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Literature Cited

15. Lu, X. X.; Cebe, P. Polymer 1996, 37, 4857.

Supporting Information Available

Student laboratory instructions; student survey questionnaires. This material is available via the Internet at http://pubs.acs.org.