An Introduction to Polymer Processing, Morphology, and Property Relationships through Thermal Analysis of Plastic PET Bottles

Exercises Designed To Introduce Students to Polymer Physical Properties

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Polymer science and other materials-related disciplines represent important areas of work and academic research for chemistry graduates (1). Due to the ubiquitous presence of polymers, even within fields where they are not the principal focus, an understanding of their synthesis, structure, and properties is important. Unfortunately, many small college and university chemistry programs lack the enrollment and resources to justify a course extensively committed to the study of polymers. This article describes a set of demonstrations and experiments involving a polymer product that can be incorporated into traditional chemistry courses. Through thermal analyses of poly(ethylene terephthalate) (PET) bottles, students are introduced to the relationships between processing, morphology, and physical properties of polymer materials.

The physical properties of a polymer are primarily dependent upon its morphology,1 which in turn is dependent upon prior thermal and mechanical treatment, that is, on its processing history (2). Through thermal analyses of PET bottles and preforms,2 students investigate the relationships between physical properties, morphology, and processing of polymer materials. Although the complete set of exercises incorporates differential scanning calorimetry (DSC), important relationships can be demonstrated with just PET bottles and a laboratory oven. A “real-world” problem-solving experience is provided through a multiweek lab project in which students assume the roles of analytical chemists for a hypothetical PET bottle manufacturer.

The PET bottle was chosen as the subject for the following reasons.

• Familiarity: Students generally enjoy gaining a deeper understanding and knowledge of items and phenomena they encounter on a regular basis. PET bottles are used as containers for a variety of products such as carbonated beverages, bottled water, sport-drinks, and juices; therefore, they are familiar to most students. An additional benefit of studying and working with the PET bottle is that it can help students develop an appreciation for the extensive research and engineering that are involved in something as common and seemingly simple as a plastic bottle.

• Ease of Analysis: The PET bottle lends itself to a relatively fast, simple, and broad range of thermal analysis techniques. For example, a PET bottle will undergo dramatic physical changes simply by heating it from room temperature to about 150 °C. Also, PET is a crystallizable polymer that can exhibit discernible melting, crystallization, and glass transition events in a single DSC thermogram over a practical temperature range.

• Variety of Morphologies and Properties: Due to its processing history, a PET bottle shows distinctly different morphological features (amorphous, crystalline, oriented) in different regions of the same bottle. As a result, the various types of physical properties exhibited by the polymer in these different regions can be studied in the context of polymer morphology.

In summary, PET bottles are effective pedagogical tools for studying processing, morphology, and properties of polymers, and specifically how these determine or depend on structure at the molecular level.

Materials

Virgin PET bottles and preforms were provided by Amcor Whitecap LLC (1140 31st Street, Downers Grove, IL 60515). However, non-virgin samples of the different types of bottles used in the experiments can easily be obtained from PET recycle centers or purchased with product in them from stores. Preforms and bottles can also be purchased from Educational Innovations Inc. (362 Main Avenue, Norwalk, CT 06851). The types of bottles and preform used in the experiments are shown in Figure 1.

Hazards

In preparing PET samples for DSC analysis, students cut small pieces from the different bottle areas. A small pair of wire cutters works well but can sometimes result in small polymer pieces being “shot” in random directions. Therefore, students must wear safety goggles during sample preparation.

The Exercises

Exercise I: A Simple Demonstration of Processing–Morphology–Property Relationships in PET Bottles

A PET preform and bottle are placed in an oven at about 150 °C for 5 to 10 minutes. Students observe that the bottle returns to the size and shape close to that of the preform. As described more completely in the Supplemental Material, reheating the bottle above its glass transition temperature, \( T_g \), allows molecules oriented by stretch-blow molding to re-
turn to the random coil conformation. Also, the finish (threaded part) and base regions of the bottle will acquire an opaque appearance owing to the formation of crystalline regions as a result of the heating. This simple experiment can be run as part of a lab period or as a classroom demonstration in first year as well as more advanced chemistry courses to introduce processing–morphology–property relationships in polymers.

**Exercise II: Investigating Processing–Morphology–Property Relationships in PET Bottles through DSC Analysis**

This set of experiments builds on the previous exercise by providing a more quantitative study of the concepts. Students carry out DSC analyses on samples from different regions (sidewall and thread area) of different types of PET bottles (types A–C in Figure 1) and a type A bottle preform. Specific sample types can be assigned to different students and the data shared in order to achieve a typical 3–4 hour lab experience. The experiments provide \( T_g \) and percent crystallinities, which students use to assess the morphological state (amorphous, crystalline, oriented) of the polymer in the various bottle and preform regions. These results furnish insight into the effects that bottle fabrication have on the polymer morphology and physical properties.

**Exercise III: A PET Bottle Field Problem**

This is a multiweek project that involves approximately four to eight hours of lab work depending on the level of student involvement in the experimental setup. In this exercise students assume the roles of analytical chemists trying to solve a bottle performance problem for a hypothetical PET bottle manufacturer. The company's bottles are used for beverages, such as fruit juices, that are heat pasteurized (bottling the product at or near 80°C). It has become clear that a unique set of performance problems exists with the PET bottles during summer months. These problems are costing the company a great deal of money and may eventually result in the loss of a major juice bottler as a customer. It is believed that the warehouse environmental conditions within which the bottles are stored prior to bottling may be a contributing factor to the problems. For the exercise, PET bottles (type B in Figure 1) are stored for two to four weeks under simulated warehouse "summer" and "winter" conditions. Through analyses (DSC, percent water content measurements and other tests that the students may design) the students identify the cause(s) for the differences in performance between "summer" and "winter" bottles and then suggest solutions.

Exercises I–III can be modified and used independently as demonstrations, typical one-week laboratory episodes, or combined into a more lengthy laboratory project. We have found that Exercises I–III combined as a semester project for an instrumental analysis course gave students the type of in-depth, investigative, and problem-solving experiences often encountered by chemists in an industrial setting. The exercises would also be appropriate for a polymer chemistry lab course. The Supplementary Material provides theoretical and background information that, with instructor assistance, can be used by students to help them understand and interpret the results of their experiments with the PET bottles.

Also, students doing Exercise III are given references to two other documents that they are told may provide useful information for solving the assigned problem (3, 4).

**Student Data and Expected Student Learning**

**Exercise I: A Simple Demonstration of Processing–Morphology–Property Relationships in PET Bottles**

Figure 2 shows a bottle before and after being placed into a 150°C oven for about 5 minutes. The thermal treatment has resulted in two distinct changes in the bottle. One is the dramatic change in the bottle’s size and shape close to that of the preform from which it was stretch-blow molded. This result can be explained in terms of the

Figure 2. (Left) Type A bottle before and after 5 minute 150°C thermal treatment. (Right) Type A preform before and after 5 minute 150°C thermal treatment.

Figure 1. (A) The preform (left) and bottle (right) for carbonated soft drinks. (B) Heat-set type bottle used for hot-filled beverages. (C) Heat-set type bottle with post-crystallized (annealed) finish. Note the opaque appearance of the finish region of bottle C; the finish region is the threaded part of the bottle on which the cap is applied.

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polymer chain’s preferred random-coil conformation in the absence of stress. The fabrication process (stretch-blow molding) results in orientation of the polymer molecules in the bottle sidewalls. The orientation and its associated stress are locked into the bottle in part by vitrification (cooling the polymer below its glass transition temperature). Upon reheating the bottle to a temperature above its $T_g$, the amorphous molecules have sufficient mobility to relieve the stress and return to the higher entropy, random-coil conformation. This results in the bottle moving towards the non-oriented preform shape and size. The opaque appearance of the finish and base regions of the bottle is due to the presence of crystalline structures in these regions produced by the thermal treatment. The size of the crystalline domains is such that they effectively scatter visible light and thereby produce the observed white appearance.

Important questions for students to pursue, related to polymer morphology, are “Why does the bottle stop short of returning fully to the preform dimensions?” and “Why does the change in optical clarity occur throughout the entire preform but only in certain regions of the bottle?” (5–7). Responses to these questions are in the Supplemental Material.\textsuperscript{w}

Exercise II: Investigating Processing–Morphology–Property Relationships in PET Bottles through DSC Analyses

Figure 3 shows a PET DSC thermogram representative of the type used for the analyses in Exercise II. The results, presented in Table 1, clearly show that the percent crystallinity of the bottle sidewall region increases relative to that of the preform as a result of the stretch-blow molding process. Both the bottle sidewalls and the post-crystallized finish show high degrees of crystallinity. However, there is a distinct difference in the optical clarity of these two regions. The sidewalls are clear whereas the post-crystallized thread area is opaque. This difference in clarity should suggest, to the student, different types of crystal morphologies. Through their analyses of these data students should learn the important role that the polymer morphology and resulting properties produced by the stretch-blow molding and postcrystallization processes play in a PET bottle’s appearance, strength, barrier properties, thermal stability, and ultimate utility as a container for juices, carbonated soft-drinks, and other food products. Another interesting polymer-morphology related question for students to investigate is “Why is the glass transition temperature of the bottle sidewalls higher than that from the other bottle and preform regions?” (8, 9). A response to this question is in the Supplemental Material.\textsuperscript{w}

Exercise III: PET Bottle Field Problem

Table 2 presents the results of the bottle analyses for Exercise III. As a result of their higher relative humidity storage condition the “summer” bottles have higher water contents and significantly lower glass transition temperatures than the “winter” bottles. The average glass transition temperature of the summer bottles is below the pasteurization temperatures used during bottling. This means that the amorphous regions of the bottle will have long-range mobility (will flow) and therefore be less mechanically stable during filling. Because of this, the thread area can move (flow) under the stress of cap application and prevent a tight seal from forming. Also, the lower $T_g$ of the sidewalls of the summer bottles will make them more susceptible to shrinkage under hot-filling conditions. That is, as seen in Exercise I, taking an oriented bottle above its $T_g$ will result in it contracting back toward the size and shape of the non-oriented preform from which it was stretch-blow molded. The percent crystallinities do not appear to be affected by the different humidity conditions.

Overall, students understand the connection between warehouse humidity conditions, water content of the polymer, glass transition temperature, and bottle performance. From these data and their knowledge of the relevant processes (stretch-blow molding, postcrystallization, and bottling) students could propose a number of reasonable solutions to solve the bottle performance problem.
Conclusions

The PET bottle is an effective tool for introducing polymer concepts as well as the relationships between polymer processing, morphology and properties. Exercise I has been used as a classroom demonstration in the general and physical chemistry courses. We have found that by working through Exercise III the instrumental analysis students learn basic polymer structure–property relationships while developing a multidisciplinary approach to problem solving. Learning to connect the chemistry they are typically taught in the classroom and laboratory to other disciplines in "real-world" situations is a skill that will serve them well after graduation. These exercises would also be appropriate for a polymer chemistry lab course.

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Supplemental Material

Instructions for the students and notes for the instructor are available in this issue of JCE Online.

Notes

1. A polymer’s morphology refers to the structural form adopted by its collection of molecular chains. For example, crystalline, amorphous, and oriented states involve different arrangements and associations of a polymer’s chains and thus different morphologies.

2. A preform is the injection-molded piece from which a PET bottle is formed by the stretch-blow molding process.

Literature Cited