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Demonstrating the Effects of Processing on the Structure and Physical Properties of Plastic Using Disposable PETE Cups

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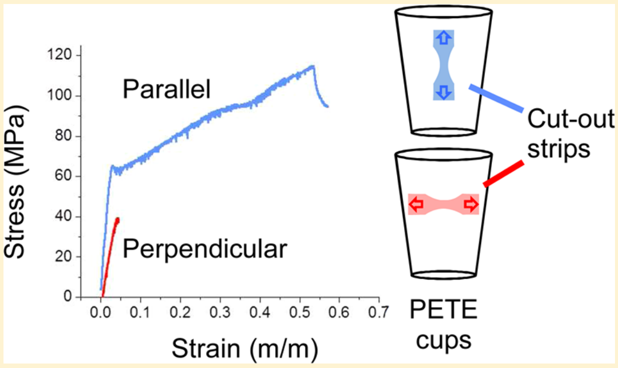
Ⓢ *Supporting Information*

ABSTRACT: An educational activity is described in which the structure and physical properties of disposable plastic cups were directly related to the method of processing. The mechanical properties of specimens cut from the walls of poly(ethylene terephthalate) (PETE) cups, oriented parallel and perpendicular to the thermoforming direction, were measured in tension. The parallel sample displayed greater elastic moduli, yield stress, and predominantly ductile deformation behavior compared to the relatively weaker and more brittle perpendicular sample. This observed mechanical anisotropy was related to the processing-induced orientation of polymer molecules within the cup. This activity, which is suitable as a classroom demonstration, short laboratory task, or an outreach activity, effectively demonstrates the relationship between polymer processing, structure, and properties without the use of large-scale melt processing equipment.



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■ INTRODUCTION

One of the most fundamental concepts that is taught in undergraduate polymer or organic chemistry courses is that the structures of the polymer molecules have a direct effect on the physical properties of bulk plastic materials, including degree of crystallinity, mechanical strength, and thermal resistance.[1−4] In material science courses, this discussion is expanded to include the important impact of processing on the plastic material's structure and physical properties.

The processing−structure−property relationships for plastic materials can be demonstrated with laboratory activities involving plastic manufacturing coupled with material characterization. For example, the mechanical properties of plastic films created by sheet extrusion can be strongly anisotropic and depend on the orientation of the film with respect to the processing direction.[5,6] This property−processing relationship is related to the microstructure of the film, as extrusion processing will result in preferential alignment of the polymer molecules within the film which increases the mechanical strength of the film in the extrusion direction.

This report describes a 1 h activity that uses disposable plastic cups to illustrate the effect of polymer processing on a plastic material's microstructure and properties without the use of sophisticated manufacturing equipment or time- and energy-intensive plastic melt processing laboratory tasks. Mechanical characterization was performed on samples from different regions of the plastic cups, and results were related to the differences in polymer microstructure of the regions which ultimately stem from the processing method used to manufacture the cup (which is typically thermoforming, described in the following section).

With its focus on how processing affects the cup's mechanical properties, this activity builds upon previously described laboratory exercises that focus on thermal properties of plastic bottles manufactured from blow molding.[7] This activity could be incorporated into an organic chemistry or polymer science course as a short, laboratory-based, hands-on activity or classroom demonstration or could be included as an introductory activity or outreach demonstration in a materials science course. To facilitate this, a complete description of the 1 h activity is recounted here and supplemental documents (including a preactivity handout for students, teacher instructions, and a number of short videos) have been created and are available in the Supporting Information.

■ BACKGROUND AND HYPOTHESIS

Disposable plastic drinking cups and soda bottles are commonly manufactured from poly(ethylene terephthalate) (PETE), a type of polyester that is the most widely recycled plastic in the U.S.[8] An estimated 45 pounds of PETE containers are used annually in each U.S. household. Interestingly, if all of the containers from a household were recycled, it would yield

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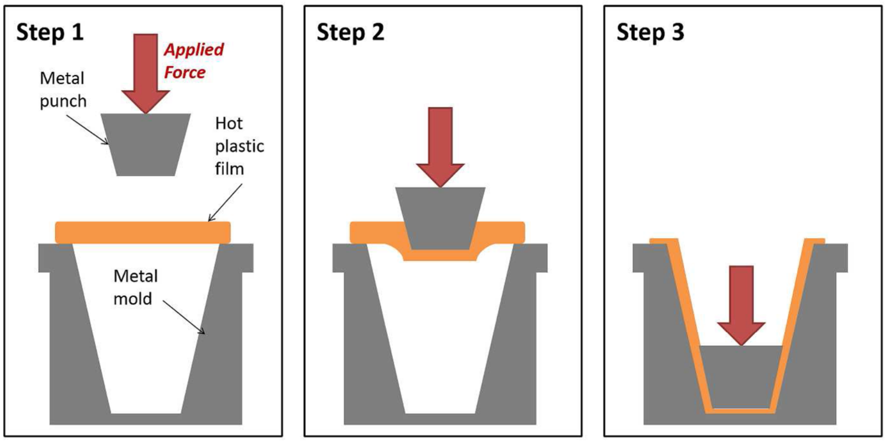

Figure 1. Cross-sectional schematic of mechanical matched-mold thermoforming process to create a plastic cup. Step 1: A hot plastic film is positioned above a metal mold containing a cup-shaped cavity. Step 2: A metal punch is brought into contact with the film by application of a downward force, and the plastic subsequently deforms around the punch. Step 3: The punch is pushed further into the film, causing it to stretch and deform, ultimately filling the mold and creating the cup.

enough polyester fiber to make 12 dozen large T-shirts or enough carpet for a 12-by-15 foot room.[9] However, in 2013, the U.S. recycling rate for PETE was only 31%.[10]

To create plastic cups by thermoforming, pellets of PETE are first heated above its melting temperature (T_m = 250−265 °C[11]) and extruded into a continuous plastic film. The film is then cooled to a temperature between 122 and 165 °C, known as the "thermoforming window" for PETE,[12] which is below T_m and above its glass transition temperature, T_g, which ranges from 67 to 125 °C depending on degree of crystallinity.[11] While at temperature, the film is expanded into a cylindrical cup-shaped mold cavity, typically assisted by applying a vacuum or mechanical pressure, which causes significant stretching of the film to form the walls of the cup (i.e., stretching in the forming direction).[12] The film is then cooled and hardened in the mold and subsequently released, forming a solid plastic cup. A schematic illustrating a basic mechanical thermoforming process is shown in Figure 1. In 2009, 1.4 billion pounds of PETE packages were produced in the U.S. and Canada, accounting for approximately 25% of the total thermoformed packages that were manufactured from all types of plastic resins.[13] More information on the recycling and life-cycle analysis of disposable plastic cups as well as educational videos on the thermoforming process is available in the Supporting Information.

Similar to the effect of processing on an extruded thin film, it is hypothesized that the processing-induced stretching of the PETE in the thermoforming direction will result in the development of anisotropic mechanical properties within the walls of the cup. To test this hypothesis, the activity described below will measure the mechanical strength of two samples from the walls of a PETE cup: (1) PETE specimens oriented parallel to the forming direction (i.e., vertical with respect to a properly oriented/"upright" cup, see Figure 2) and (2) PETE specimens oriented perpendicular or orthogonal to the forming direction. It is expected that the "parallel-cut" PETE specimens will exhibit greater strength and ductility than the "perpendicular-cut" PETE specimens and that this mechanical anisotropy is related to the degree of processing-induced orientation of the polymer molecules in the specimens.

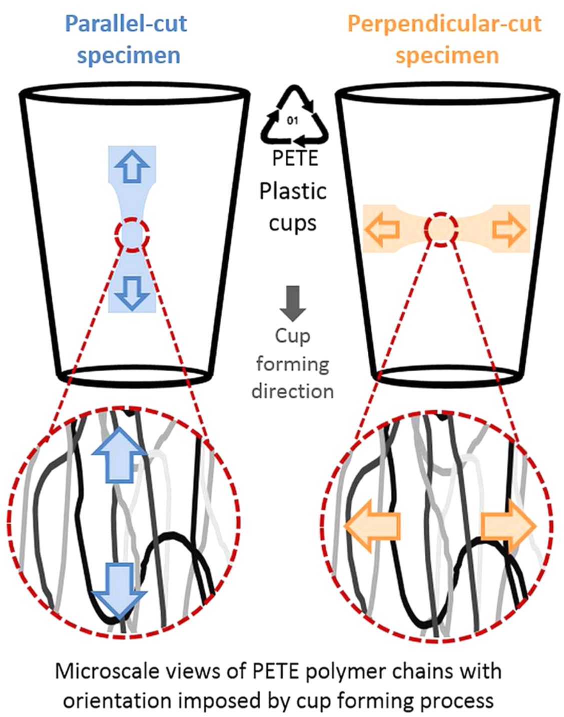

Figure 2. Schematic of PETE plastic cups, indicating the macroscale orientation of the parallel- and perpendicular-cut specimens on the cup walls as well as the microscale orientation of the polymer molecules within the specimens. Blue and orange arrows indicate the direction of the applied tensile forces during mechanical testing of the parallel- and perpendicular-cut specimens, respectively.

■ METHODS

Optically clear, smooth-walled, disposable PETE drinking cups (12 oz., SOLO brand) were obtained from a local grocery store. Using scissors, two samples ($n \geq 8$) of dog-bone style specimens were traced and cut from the walls of the cups in the vertical and horizontal directions (see Figure 3 for an example). These two sample sets will be subsequently referred to as "parallel" and "perpendicular", indicating the specimens' relative orientations to the forming direction. Mechanical tensile tests were performed on the parallel and perpendicular samples using an Interactive Instruments Tensile 1K Desktop Materials

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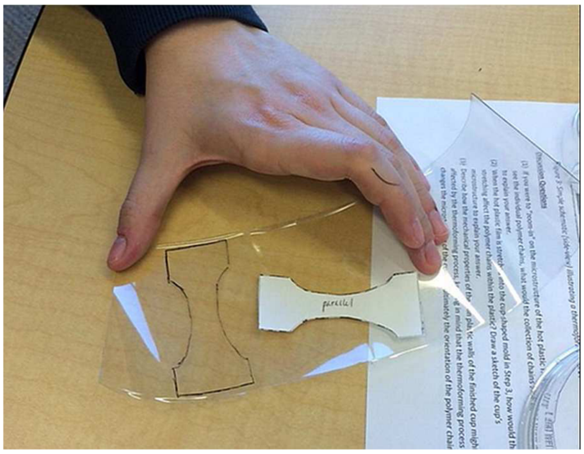

Figure 3. Trace of a dog-bone style, parallel-cut specimen on the flattened wall of a PETE plastic cup, prior to specimen cutting and tensile testing.

Tester (Scotia, NY, USA), a general purpose universal testing machine that was designed as an affordable alternative to servo-hydraulic systems. Strain rates of 1 in./min (0.42 mm/s) were employed for all specimens. Details on the experimental procedure and data analysis are included in the Supporting Information.

■ RESULTS

The parallel-cut specimens experienced ductile deformation behavior during mechanical testing, in which the applied tensile force caused the specimens to irreversibly stretch and elongate within the gauge (central) region. While there was no visible necking, significant strain stiffening was observed in the stress response. Representative stress−strain responses from parallel-cut specimens are shown in Figure 4a, and a video of a representative tensile test is included in the Supporting Information. Table 1 reports the average values of the Young's modulus (E, i.e., stiffness) and yield stress for the parallel sample.

In contrast to the parallel sample, specimens from the perpendicular sample primarily experienced brittle deformation behavior during mechanical testing. About 80% of the specimens experienced brittle fracture while the remaining 20% experienced ductile behavior. When brittle fracture occurred, the specimen would break cleanly in the gauge region. In some instances, pieces of the specimen would rapidly shatter into smaller shards. For the few specimens that behaved in a ductile manner, necking occurred in a similar fashion to the parallel-cut specimens. Representative brittle and ductile stress−strain responses from perpendicular-cut specimens are shown in Figure 4b and two videos separately capturing the ductile and brittle deformation behavior of perpendicular-cut specimens are available in the Supporting Information. The average Young's modulus and yield stress of the perpendicular sample were significantly reduced from the average modulus and yield stress of the parallel sample (see Table 1). Although 20% of the perpendicular-cut specimens displayed ductile behavior, the Young's modulus and yield stress of the ductile specimens were very similar to those of the brittle specimens (see curves in Figure 4b for comparison).

Table 1. Average Mechanical Properties of PETE Parallel and Perpendicular Sample Sets[a]

PETE Sample	Young's Modulus (GPa)	Yield Stress (MPa)	Strain at Failure (%)
Parallel	2.2 ± 0.2	67 ± 5	60 ± 7
Perpendicular	1.2 ± 0.2	38 ± 5	4.3 ± 1.0

[a]Error bars indicate ±1 standard deviation ($n \geq 8$ specimens for each sample). All specimens were tested at applied strain rates of 0.42 mm/s.

■ DISCUSSION

As reported in Table 1 and captured in Figure 4, the deformation response of the PETE samples strongly depended on the orientation of the specimens with respect to the forming direction: either parallel or perpendicular. The measured mechanical values were similar to results in the literature for semicrystalline PETE:[11] E = 2.4 GPa, ultimate tensile strength = 40 MPa, and strain at failure = 90%. In general, the parallel sample displayed ductile deformation behavior while the perpendicular sample displayed brittle deformation behavior. Statistical hypothesis testing assuming a T-distribution and 1% significance level revealed that the elastic modulus values of the parallel and perpendicular samples are statistically different, and the yield stress values of the two samples are also statistically different. The parallel sample displayed a greater elastic modulus, yield stress, and percent strain at failure compared with the perpendicular sample.

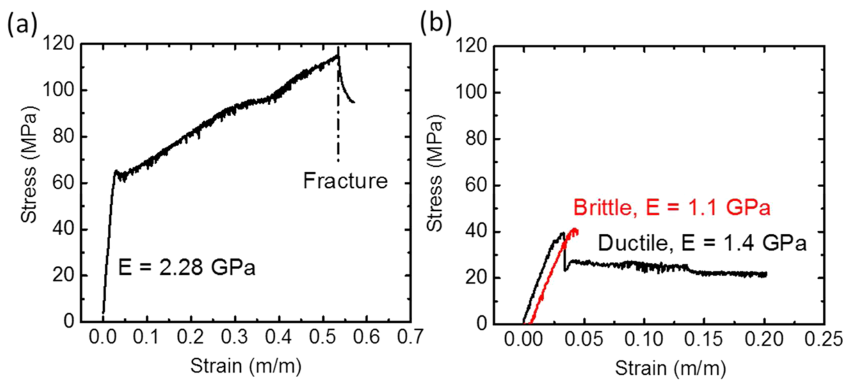

Figure 4. Stress−strain curves and Young's modulus (E) values for (a) a parallel-cut PETE specimen and (b) two perpendicular-cut PETE specimens, one exhibiting brittle fracture (red) and one exhibiting ductile necking (black). Specimens were deformed in tension at a strain rate of 0.42 mm/s.

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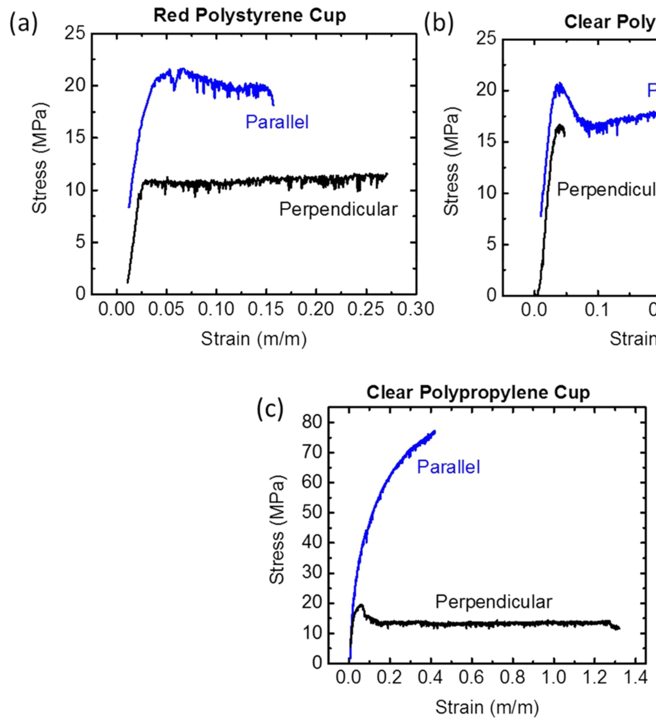

Figure 5. Stress–strain curves of three different types of plastic cups tested at a strain rate of 0.42 mm/s and $T = 25$ °C. In all plots, the blue curves show the behavior of the parallel-cut specimens and the black curves show the behavior of the perpendicular-cut specimens.

The increased stiffness, strength, and ductility of the parallel sample compared with the perpendicular sample are consistent with processing-induced orientation of the polymer molecules of the parallel-cut specimens in the direction of the applied tensile force (see Figure 2). During mechanical testing of a parallel-cut specimen, the applied force would therefore be directly supported at the molecular level by the relatively strong covalent bonds within the polymer backbone (with bond energies ranging from 30 to 100 $\times$ 10^{-20} J), whereas for a perpendicular-cut specimen, the applied force is resisted only by the relatively weak van der Waals interactions between neighboring polymer molecules (with bond energies of ~1 $\times$ 10^{-20} J, on the same order of magnitude as thermal energy, k_bT, at room temperature).[14−16] This mechanical anisotropy supports the starting hypothesis that the processing-induced stretching of the polymer molecules in the thermoforming direction will result in the development of anisotropic mechanical properties within the walls of the plastic cup.

An additional quick activity to provide further evidence of the processing-induced stretching of the polymer molecules in the cup's forming direction is described by Klein.[12] If a plastic cup is placed, inverted, in an oven at ~250 °F (121 °C), within minutes the walls of the cup will shrink and the cup will flatten into a disk-like shape. This change in shape is driven by the residual stresses within the walls of the plastic cup which are due to the thermoforming-induced stretching of the polymer molecules during fabrication. The polymer molecules essentially have a "memory" of their relaxed, unstretched (unprocessed) state, which they seek to return to when the cup is reheated in the oven at a temperature near its initial forming temperature.

■ CLASSROOM IMPLEMENTATION USING PETE PLASTIC CUPS

This 1 h activity was performed with a small mixed group of undergraduate materials engineering and first-year undergraduate engineering students at Purdue University. A full step-by-step description of the activity implementation is presented in the Teacher Instructions document available in the Supporting Information. Highlights are presented below.

First, students were asked by the instructor to read a document that presented basic information about the microstructure of plastic materials, the impact of applied forces on polymer molecules, and the thermoforming process that is typically used to make disposable plastic cups (see the Pre-Activity Reading and Discussion Questions in the Supporting Information). The students, even at the first-year undergraduate engineering level, believed that the thermoforming process would stretch the polymer molecules in the walls of the cup, such that the mechanical properties in the walls would be anisotropic. They predicted that testing samples cut from the walls in a direction parallel and perpendicular to the processing direction would exhibit different mechanical properties. A first-year student suggested that, "Sample B [the perpendicular sample] would fail first and be weaker, since there is nothing for the [applied] force to pull on." A third-year student agreed and suggested that, "Sample A [the parallel sample] would stretch more and be stronger, since the backbones of the chains are aligned along the length of the sample and would support the [applied] force."

Next, the students were each given a PETE cup and the supplies to trace and cut dog-done style specimens. The cut specimens displayed slightly different lengths (±5 mm) depending on the cutting and tracing skills of particular student, and some specimens had rougher edges than others. When the specimens' dimensions were measured with digital

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calipers, each student's specimen had a slightly different thickness, ranging from 0.26 to 0.30 mm, but the thickness was found to be constant for specimens cut from the same cup (within the resolution of the calipers, ±0.01 mm).

The instructor and an undergraduate researcher assisted the students in tensile testing their specimens and recording and analyzing the data. Six specimens were tested at a strain rate of 1 in./min. The three parallel-cut specimens exhibited ductile stress−strain behavior, very similar to the curve in Figure 4a, displaying relatively large yield stress values and elongations as well as significant strain stiffening. The three perpendicular-cut specimens displayed strongly brittle behavior, similar to the red curve in Figure 4b, with fracture occurring after only a few seconds of deformation and sometimes resulting in multiple fractures and fragments of PETE being ejected (hence the need for all participants to wear safety glasses during the activity). The difference in the stress−strain behavior and the failure speed and explosiveness of the perpendicular-cut specimens was particularly surprising to the students. Following testing, the differences in the stress−strain responses of the specimens were discussed and related to the hypothesized differences in the microstructure resulting from the alignment of the polymer molecules during thermoforming. After the activity, students were able to draw simple sketches of the cup and its microstructure, illustrating the processing-induced alignment of polymer molecules within the walls of the cup.

■ COMPARISON WITH OTHER TYPES OF PLASTIC CUPS

Following the same mechanical testing protocol for the PETE tensile tests of parallel- and perpendicular-cut specimens, three additional types of disposable plastic cups were tested (all purchased from a local grocery store): red-colored polystyrene (PS) cups, clear PS cups, and clear polypropylene (PP) cups. The stress−strain curves are displayed in Figure 5 with data reported in Table 2.

Compared to the PETE plastic cups, the PS and PP cups displayed relatively weaker mechanical properties, with lower modulus and yield stress values. The red PS cups displayed delamination during tensile testing, with the white inner lining visibly separating from the red outer film; thus, these cups should not be used for this activity. The clear PS cups behaved in a similar fashion to the PETE cups, with the parallel-cut specimens displaying ductile fracture and the perpendicular-cut specimens displaying brittle fracture (see Figure 5b). Unlike PETE, less strain stiffening behavior was observed during deformation of the parallel-cut PS specimen and the elastic moduli of the parallel- and perpendicular-cut PS specimens were more similar (0.61 and 0.79 GPa, respectively, see Table 2) compared to PETE specimens (2.2 and 1.2 GPa, respectively, see Table 1).

The clear PP cups displayed the most dissimilar behavior compared to the PETE and PS cups (see Figure 5c). For this reason, videos were captured of the PP specimens' deformation behavior and are available in the Supporting Information. For parallel-cut PP specimens, no clear yielding behavior was observed and the specimens displayed very uniform stretching (with no obvious necking) before failure. In contrast, the perpendicular-cut PP specimens displayed clear yielding behavior followed by extreme necking behavior and ductile elongation that continued until the maximum crosshead displacement of the mechanical tester was reached, and thus no failure was directly observed. Images of the parallel- and perpendicular-cut PP specimens following deformation are shown in Figure 6. Similar to PETE, the elastic modulus of the parallel-cut PP specimens (1.3 GPa) was approximately two times greater in magnitude than the modulus of the perpendicular-cut PP specimens (0.67 GPa).

The overall differences in the PP, PS, and PETE tensile properties may be due to the polymers' glass transition temperatures (T_g). PP typically has a T_g < 25 °C, ranging

Table 2. Calculated Tensile Properties of the Parallel- and Perpendicular-Cut Specimens Displayed in Figure 5

Sample	Young's Modulus (GPa)	Yield Stress (MPa)	Strain at Failure (%)	Observations during Test
Red PS cup				
Parallel	0.72	20	16	Ductile behavior, delamination
Perpendicular	0.72	11	27	Ductile behavior, delamination
Clear PS cup				
Parallel	0.61	20	38	Visible necking, ductile behavior
Perpendicular	0.79	16	4.6	Brittle behavior
Clear PP cup				
Parallel	1.30	No clear yielding	41	Ductile elongation, no visible yielding prior to failure[a]
Perpendicular	0.67	20	No failure	Visible necking and ductile elongation, no failure within testing limits[b]

[a]See the video PP-parallel-cut.avi in the Supporting Information. [b]See the video PP-perpendicular-cut.avi in the Supporting Information.

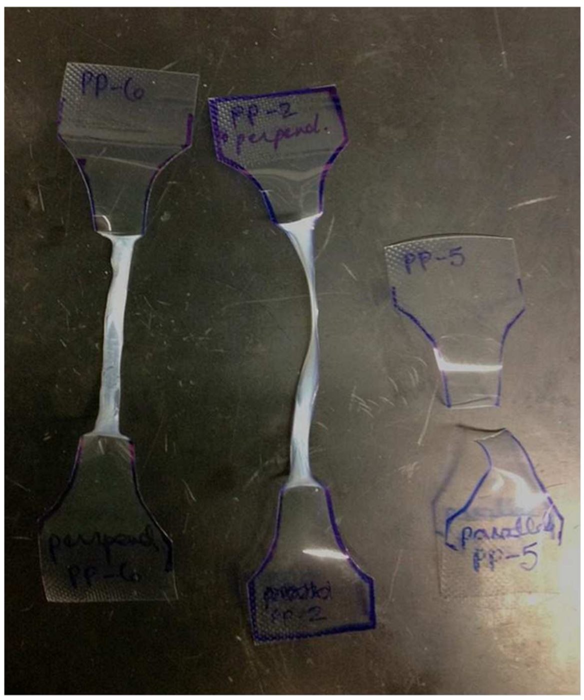

Figure 6. Image of two perpendicular-cut PP specimens (left, center) and a parallel-cut PP specimen (right) after tensile testing at a strain rate of 0.42 mm/s and T = 25 °C. The opaque neck region is most likely due to crazing.[5]

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from −13° to 7 °C depending on tacticity and degree of crystallization, while the reported T_g of semicrystalline PETE is about 80 °C and the reported T_g of PS is about 100 °C.[17] Thus, PP may only display brittle behavior during deformation at much faster strain rates or at subambient temperatures whereas brittle behavior can be observed for PETE and PS during deformation at room temperature. Depending on the knowledge level of the students who participate in this activity, it could be instructive to test both PETE and PP cups and ask the students to explain why the two cups display such different mechanical properties.

■ SUMMARY

Mechanical testing of specimens cut from the walls of disposable plastic cups revealed that processing of the cups had a statistically significant effect on the plastic's stiffness, strength, and ductility. The Young's modulus, yield stress, and ductility of the walls of PETE cups were observed to be significantly greater in the forming direction and reduced in the orthogonal direction. This mechanical anisotropy was due to the processing-induced orientation of the polymer molecules within the cup in the forming direction. This simple activity demonstrates the importance of processing on the final structure and physical properties of plastic objects.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00082.

PETE specimen tensile testing, parallel cut (AVI)
PETE specimen tensile testing, perpendicular cut, #1, ductile (AVI)
PETE specimen tensile testing, perpendicular cut, #2, brittle (AVI)
PP specimen tensile testing, parallel cut (AVI)
PP specimen tensile testing, perpendicular cut (AVI)
background and experimental procedure (PDF, DOCX)
glossary (PDF, DOCX)
teacher instructions (PDF, DOCX)
preactivity handout (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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