JOURNAL OF CHEMICAL EDUCATION

Activity

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From Lobster Shells to Plastic Objects: A Bioplastics Activity

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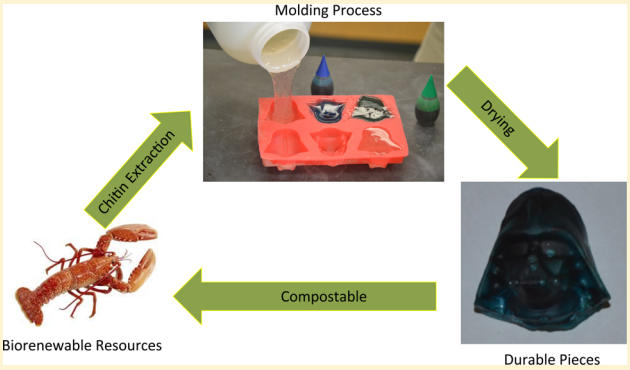
Supporting Information

ABSTRACT: A multiple day activity for students to create large-scale plastic objects from the biopolymer chitin (major component of lobster, crab, and shrimp shells) is described. The plastic objects created are durable and made from benign materials, making them suitable for students to take home to play with. Since the student-created plastic objects are sourced from biomass and fully compostable, the activity provides an opportunity to discuss depleting petrochemical resources and biorenewable feedstocks as well as issues of biodegradation vs persistence.



KEYWORDS: *Green Chemistry, General Public, Elementary/Middle School Science, High School/Introductory Chemistry, Public Understanding/Outreach, Polymer Chemistry, Hands-On Learning/Manipulatives*

The demand for biodegradable materials[1] for commercial products has been rising in step with awareness of environmental impacts from plastic pollution.[2] Similarly, knowledge of declining oil reserves[3] has driven a demand for materials sourced from biorenewable feedstocks.[4] While some petroleum-derived polymers can biodegrade (ecoflex),[5] many cannot (PET, PS). On the other hand, some polymers synthesized with biomass-derived feedstocks (castor bean oil → Polyamide 11) are not biodegradable, while many others are (lactic acid → polylactic acid).[6] Despite the significant effort put into transforming and isolating lactic acid from biomass,[7] and processing it into a usable polymer,[8] production of polylactic acid (PLA) has soared in recent years because it is both sourced from biorenewable feedstocks and fully compostable.[9]

To better retain the chemical complexity of the biomass feedstocks and with less need for transformation and processing, the use of highly abundant biopolymers such as chitin or cellulose would represent an even more ecologically benign material (Figure 1).

Despite the impressive mechanical properties of chitinous[10] materials (insect cuticle, nacre, and crustacean exoskeleton), little effort has been made to incorporate chitin into materials for commercial products. Some advances have been made with chitosan (deacylated chitin, Figure 2) fabrication for thin films, microfluidic devices, and surgical wound dressings.[11] Chemical alteration of the polymer,[12] blending with petrochemical polymers,[13] or freeze-drying[14] have been the most successful approaches for incorporation into materials, yet have failed to produce a viable, high-volume industrial application. Despite the lack of a high-volume industrial application on the scale of its abundant natural supply, chitin and chitosan derived materials are used in smaller-scale niche applications[15] such as immunology,[16,17] hemostasis and wound healing,[18,19] tissue regeneration,[20] drug delivery,[21,22] antioxidants,[23] antimicrobial agents,[24] gene therapy,[25] and heavy-metal remediation.[26−29] In

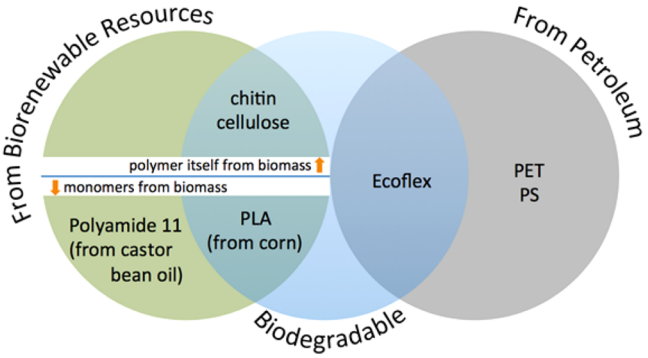


Figure 1. Sourcing and biodegradation of common polymers.

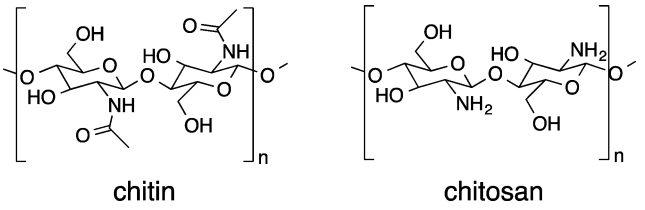


Figure 2. Chitin and chitosan.

Published: August 21, 2015

DOI: 10.1021/acs.jchemed.5b00108
J. Chem. Educ. 2015, 92, 1882−1885

2014, Fernandez and Ingber[30] used chitosan to generate large-scale functional objects such as cups, egg cartons, clips, and chess pieces. The chitosan was first dissolved in dilute aqueous acetic acid, then either precipitated with aqueous sodium hydroxide or the solvent was slowly evaporated at slightly elevated temperatures. The material generated by slow evaporation of the solvent displayed far superior physical properties, so we modeled this educational activity on their evaporative technique.

Our procedure does not rely on any sophisticated apparatus and can use chitosan (as Fernandez and Ingber used) or the more naturally abundant, highly acylated analogue, chitin, which has not yet been used for the creation of durable, large-scale objects. This activity adds to the vast array of activities and demonstrations for the synthesis and modification of polymers from petrochemical feedstocks (such as the nylon rope activity[31−34] and many more), but has a rare focus on the use of a biorenewable feedstock,[35,36] which will be important as we train a generation of scientists with less petroleum reserves at their disposal.

AUDIENCE

Grade school audiences learning about plastic recycling may find appealing the concepts of material sourcing from nature and biodegradation. Older audiences may be able to consider in more detail concepts such as phases of matter, and dissolving. Teachers can run the activity as part of their normal curriculum, or instead, science outreach volunteers could animate the activity in schools, libraries or after school programs. In cases where this activity may not specifically overlap with course curriculum topics, it can still be a valuable contribution to science or environment-themed after school programs. The sourcing of chitin as the biopolymer for plastic formation may have the most impact for students in areas where chitin is readily available as a result of a local industry (lobster from the Northeastern United States, shrimp from the Gulf coast, or crab from the Pacific Northwest).

ACTIVITY

A solution of chitin or chitosan (30 g, or 1/3 cup) in 1 L of dilute acetic acid (1−5%) or white vinegar (∼5% acetic acid) is prepared in a wide mouth bottle, which is capped and shaken to ensure a homogeneous solution. For off-white clear colorless pieces (Figure 3A), this solution can be poured directly into molds. For colored pieces (Figure 3B,D,E), the solution can be poured into smaller containers and mixed with food coloring, and these solutions poured into molds. The molds should be left at 30−40 °C by placing them on or near a gentle heat source (near a radiator or space heater, or on a seedling heating mat) to allow the solvent to evaporate. As the solvent evaporates, a thin positive replica of the mold is left behind. Depending on the heat and the depth of the mold, this drying process can take 1−4 days and will generate relatively thin pieces (Figure 3A,D). Instead, for thicker plastic pieces (Figure 3B,E) the mold can be refilled daily or when approximately half the solvent volume has evaporated. Even for refilling colored pieces, the noncolored chitin solution can be used; the original dye will diffuse into the newly added solution. Typically, 4 chitin-solution refills will suffice to generate a reasonably thick and durable plastic piece. If the activity is started on a Monday, and refilled each subsequent day until Friday, fully hardened pieces can be removed from the mold on Monday. For even thicker pieces, fine sawdust can be used as a filler in the chitin solution (Figure 3C). Instructors can view the video (Supporting Information) of manipulating single layered pieces and thicker pieces for a comparison of durability to decide whether the extra time required for thicker pieces is worthwhile for their purposes. The activity also works with larger molds (Supporting Information); however, if running this activity with many participants, we suggest the more common smaller molds given the price of chitin ($81.30/100 g: Sigma-Aldrich) or chitosan ($54.10/50 g: Sigma-Aldrich). A detailed materials list and procedure is provided in the Supporting Information.

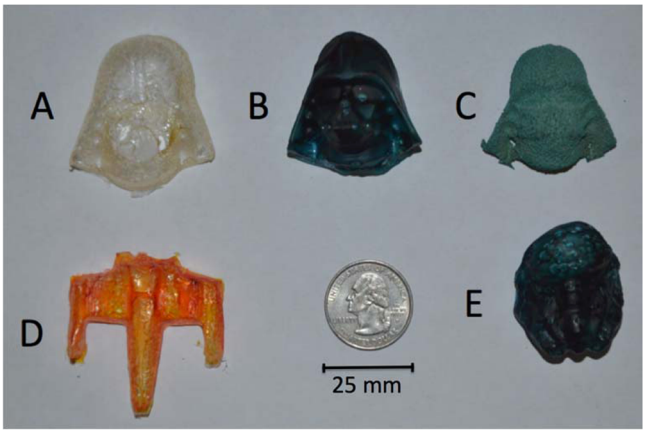


Figure 3. (A) Thin, undyed object made with only 1 mold-full of chitin solution. (B) Thicker, dyed object refilled daily with new chitin solution for 4 days. (C) Solid object made with fine sawdust as a filler. (D) Thin, dyed object made with only 1 mold-full of chitin solution. (E) Thicker, dyed object refilled daily with new chitin solution for 4 days; this mold lacked well-defined edges, so the piece shriveled considerably.

HAZARDS

This activity contains very little hazard. Chitin is a nontoxic biodegradable natural feedstock often used as a food supplement. Vinegar also is nontoxic. The most significant hazard is the gentle heat source. Heat sources such as a seedling heating mat should not be an issue, but fire safety precautions should be considered with more powerful heaters. The small chitin/chitosan pieces should be kept away from children under the age of 3, since they may be a choking hazard (although the pieces readily redissolve in acidic media, as in the mouth).

DISCUSSION

Animating the activity for groups of 6−10 grade school students at a local library, we had success framing the activity in the context of material sourcing and biodegradation in comparison to petrochemical-based plastics. Before the hands-on experience, we began the activity by asking the students:

(a) if they knew what plastics are
(b) if they knew where the material for most plastic bottles come from
(c) if plastic bottles break down in nature
(d) if they know what "biodegradable" means and
(e) if they have ever heard of bioplastics

Many of the students knew what plastics are, but did not know that most plastics are derived from oil. For the most part, the students knew that many plastics do not readily break down

DOI: 10.1021/acs.jchemed.5b00108
J. Chem. Educ. 2015, 92, 1882−1885

in nature, citing litter problems on the beach and on the street. Although few had heard of bioplastics, many could link "biodegradable" to composting. Upon understanding that most plastics come from oil, and do not break down easily, the students were receptive to the idea of making plastics from biological material that would otherwise go to waste. Although the drying of most molded pieces takes several days, we also cast a small film during the course of the activity by simply putting a few drops of chitosan solution onto wax paper (which sat on a seedling heating mat). The drops evaporated in the course of the activity, providing the students an idea of the process before they left. This served as a good preview, but the students were far more enthusiastic about their molded plastic objects. We did not attempt to subject the material to biodegradation since the likely several month process we felt would be beyond the time frame of the students' attention span, but for classes who do have the time, this activity could dovetail quite nicely with a module on composting (although we have not studied the rate of decomposition). Despite not composting our pieces, the students took our word that this biologically derived material could be broken down and reabsorbed by nature. We were able to impress upon the students how petrochemical derived plastics are inexpensive to manufacture, but that the costs of their widespread use (i.e., pollution) go beyond just the simple monetary price tag.

As a precaution to instructors, we should note that the evaporation of the acetic acid solution gives off a significant vinegar smell. Letting the acetic acid evaporate near an open window should help keep the odors out of the room, but if outside conditions preclude this option, then other arrangements should be made. When we animated this activity at a local library in the early spring, it was too cold to leave the windows open, and we did not want the library smelling like vinegar. Thus, we brought the molds back to our lab to allow the acetic acid to evaporate, and returned the dried pieces to the library for the students to pick up at their convenience.

Although the report that served as the model for our procedure used only chitosan (deacylation degree 80.46 ± 0.6%), we found that for our purposes chitin also worked. We cannot comment on the molecular level organization or specific measurements of material strength for chitin vs chitosan. However, we can say that they both cast relatively durable plastic objects suitable for children to play with. Given the greater solubility in aqueous acetic acid solutions that comes with higher degrees of deacylation in chitin/chitosan systems,[37] we assume that the chitosan (deacylation degree 75−85%) derived pieces may be stronger than the chitin derived pieces. We noticed that chitin did not as readily dissolve in the aqueous acetic acid as did the chitosan, but still cast reliable objects. Instructors can therefore decide for their purposes whether a potentially weaker piece is worth the demonstration of directly using the polymer derived from lobster and shrimp shells, or if they would rather use the modified polymer for a potentially stronger piece. Similarly, the original report used 1% acetic acid solution for the dissolution of chitosan. We found this to work for both chitin and chitosan systems, but to simplify the procedure, we found that distilled white vinegar (∼5% acetic acid solution) also worked for both chitin and chitosan systems.

SUMMARY

The activity outlined here represents, to the best of our knowledge, the first fabrication of durable large-scale objects from chitin, as well as the adaptation of industrially relevant chitosan and chitin object fabrication methods to an educational audience. With the use of a compostable biopolymer as the molding material, the activity can open dialogues on topics of pollution, biodegradation, materials sourcing, and petroleum feedstocks vs biomass feedstocks.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00108.

Instructor notes (PDF, DOCX)
Detailed materials lists and procedure (PDF, DOCX)
Movie of chitin pieces (ZIP)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Kate Anderson of Beyond Benign for fruitful discussion as well as Colby College and the National Science Foundation (SMA-1415189) for financial support.

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DOI: 10.1021/acs.jchemed.5b00108
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