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BIODEGRADABLE PLASTICS FROM MILK PROTEINS

Executive Summary

This study explores biodegradable plastics for the manufacture of keycards to open doors into hotel rooms or other commercial buildings. The keycards are imprinted with a magnetic stripe or bar code with the appropriate security for admittance. Clients have expressed a strong desire to replace the current polyvinyl chloride (PVC) keycards with an environmentally friendly version of the plastic substrate. PVC keycards have a relatively short lifetime and are discarded after 10 or fewer reuse cycles, creating a persistent pollutant in landfills. A biodegradable material, which is broken down by microorganisms after disposal, would help the manufacturer demonstrate environmental stewardship.

A group of protein solids, derived from milk and soy raw materials, was screened as a possible source of a stable plastic. The process of denaturing those proteins must furthermore yield a plastic that could be fabricated into sheets of 30-mil thickness to be cut and slit into the final keycard dimensions. Of all the proteins tested, caseinates in the form of either sodium or calcium salts gave the best results. Simply heating the samples in water produced viscous, gummy resins, which could be cast and dried into thin, transparent films. These firm plastic layers showed good adhesion when laminated with paper. The dried plastics were quite water-resistant and could be heated to about 300 deg. F, before they would begin to char.

Interesting composites were obtained by combining denatured sodium or calcium caseinate with two other locally available byproducts: (1) natural rubber crumbs and (2) shredded coated-paper milk cartons. Layered, sandwich structures were produced by adding the casein resinous dopes to the other components and allowing the mixtures to dry. These combinations had good structural integrity and might be of further interest as reinforced plastics, which are 99-100% biodegradable.

STUDIES ON BIODEGRADABLE PLASTICS

Introduction

This search and experimentation was begun in late 2007 in response to a request from PLI, a high-volume producer of plastic hotel keycards, to help find a biodegradable plastic. Public concern is being directed toward life cycle characteristics of products made from synthetic plastics. There is much interest in replacing discarded plastics derived from petroleum products, which remain persistent environmental pollutants, with materials that are naturally degraded by microbial activity.

Considerable effort to recycle post-consumer plastic items in recent years has diverted millions of tons of plastics from landfill wastes, resulting in value-added secondary products. In spite of these worthwhile results, higher levels of landfill avoidance still remain to be achieved. Even for those plastics, that account for the great majority of recycled polymers, certain fractions are unusable. For example, thermoformed polyethyleneterephthalate (PET) disposable containers have a different melt index than that of blow-molded PET and are therefore excluded from recycling. Other possible recycling candidates have been treated with additives that reduce intrinsic viscosity to levels too low for certain processes and applications. Outside of the market for recycled PET and high density polyethylene (HDPE) and much smaller amounts of polypropylene, other high-volume plastic wastes, such as polyvinyl chloride (PVC) and polystyrene, are sent to Asia or are hauled to municipal landfills.[1]

The reputation of PVC has been particularly maligned by activists for environmental sustainability, such as Greenpeace and the Center for Health, Environment & Justice. The latter claims that PVC is dangerous to human health and the environment throughout its entire life cycle – from the factory, to the home, and even into the trash.[2]

Biodegradability as a Building Block of Sustainability

This research program was launched in support of sustainability concerns toward synthetic plastics, especially those which are not in the mainstream of recycling. The work began with a search for environmentally friendly plastics, which, after disposal in landfills, would undergo microbial decomposition. The Asheville manufacturer, PLI, which currently uses PVC as a substrate for its products, is interested in finding an appropriate biodegradable plastic to replace the PVC core stock. The material must withstand processing temperatures up to 320°F without discoloration or distortion. It must also be either photoprintable or adhere to a printed PVC cover sheet after lamination.

Commercial Examples of Compostable Polymers

Those commercial polymers from agriculturally based raw materials, such as polylactic acid (PLA)[3] made from corn-derived dextrose, Mirel[4] also from corn sugar, SpudWare[5] from potato and corn starch plus soy oil, have had limited acceptance in the marketplace.

These materials are disposed of as a shredded component of well-designed and managed composting operations. Other new plastics, whose manufacturers claim biodegradability, are (1) Ecoflex[6] made from adipic acid, butanediol, and terephthalic acid and (2) Ecovio[6] , which also contains 45% corn-derived PLA. Polyglycolic acid, a polymer made from formaldehyde and carbon monoxide, is used in specialty applications, such as medical sutures, and is considered environmentally friendly. As a barrier layer in PET bottles, PGA breaks down chemically during the bottle recycling process.[8]

Since PLA has been available in manufactured quantities for a few years, it has already been tested as a possible substitute in the PLI process for keycard production. It was found to be thermally unstable and charred and deformed during the heating and vacuum cycle. Although PLA is compostable, it does not spontaneously biodegrade and, thus, fell short of the desired goal.

Plastics Derived from Milk Proteins

Attention was then shifted to reports in literature from the dairy research industry, some of which dated back to before 1950. A detailed investigation of casein-based plastics was completed in 1942 by researchers in the Department of Dairy Industry, University of Wisconsin, Madison, WI. This study was supported by a quality button manufacturer to evaluate the use of these plastics for commercial buttons.[9] Rennet casein, coagulated from skimmed milk, was converted into a transparent plastic through application of heat and pressure to denature the moistened casein. The plastic product was immediately extruded into a die to give a uniform strip, which could be tested for color and light transmission. A variety of conditions and post-treatments was examined to determine the important variables in generating a clear, transmissive plastic. It was determined that the amount of residual fats in the casein extracts contributed directly to the discoloration and decrease in light transmission of the resulting plastics. Earlier studies had shown the relation of sugars in the samples to color development in milk products.

With background observations from the previous work, the current investigation was conducted by denaturing milk and whey protein samples from 8 samples of milk, whey, and casein samples generously supplied by Main Street Ingredients, La Crosse, WI.[10] These materials are most often used in cheese manufacture. Because no specially built cell for protein denaturation of the type used in the previously cited study was available for this work, the denaturation was done simply by brief heating in a microwave oven. Samples of the starting proteins were suspended in water, well-stirred, and then heated to a foamy, frothy consistency. The product plastics separated as swollen, gummy resins, which hardened when isolated and dried. Those plastics, which gave the highest yields of the most attractive products, were also combined with some other solid wastes from industries in the area to produce interesting composites.

Raw materials, glassware, and plastics from denatured proteins.

The denatured protein plastics, including those samples combined with other waste materials, were allowed to dry and harden as flat, thin samples for evaluation. Results of the experiments with all the protein samples are summarized in the following table.

MILK EXTRACT SUBSTRATE	YIELD % of SOLID	PLASTIC CHARACTERISTICS	COMMENTS
Milk protein isolates	Very small	Separates as gelatinous lumps, thin layer on filter paper	Brittle, colorless solid
Whey protein concentrate	Low yield	Pale yellow solid; insoluble in strong organic solvents (DMF, NMP, iPA)	Chars when heated to 350 deg F.
Whey protein isolate	90%	Granular solid separates; filters easily; product is amorphous but is unlike other gummy, sticky products	Does not swell into a film-forming resin in hot water
Milk protein concentrate	Low yield	Clear plastic layer clings to filter paper	Solid stiff and brittle
Casein rennet	59% solid product	Very sticky white solid rapidly turns brown from apparent bioactivity	Strong, unpleasant odor during drying; dry solid malodorous
Soy protein isolate	No solid product	Reaction mixture and products water soluble	Barely perceptible coating of product on filter paper; not isolable
Calcium caseinate	86%	Transparent plastic	Adheres tenaciously to filter paper; insoluble
Calcium caseinate + shredded milk carton	84%	Straw-colored, foamy plastic with core of shredded paper milk carton	Interesting composite with good adhesion
Sodium caseinate	81-94%	Straw-colored solid; adheres well to paper	Gummy product in water; dries hard, insoluble
Sodium caseinate + shredded milk carton	88%	Good sandwich structure with shredded paper core; total 0.6% polyethylene from milk carton	Composite has good adhesion; 99.4% biodegradable
Sodium caseinate + natural rubber crumb	99%	Good hardened dispersion of rubber in plastic	Adhesion good; mixture 100% biodegradable

In summary, from this assortment of samples and tests, denatured caseinate salts showed most promise. When heated to a stage of frothy agglomeration, the aqueous slurries of either sodium or calcium caseinate produced thickened resins; these viscous dopes could easily be cast into flat molds and dried into thin films or layers of hard plastic. The yields of isolable plastics from the caseinates were good, even with such a rudimentary technique, which consisted of hand mixing, limited stirring, and heating to a foamy consistency. No opportunity existed for good temperature control.

In contrast, the whey protein concentrates and isolates, as well as the milk protein concentrates and isolates, all gave gummy or granular agglomerates under the same conditions of heating and stirring. When dried, these sticky products accounted for very poor yields of denatured protein.

Physical Properties of Plastic Products

The general behavior of the plastics was much the same, regardless of the raw material used. All were insoluble in polar organic solvents, such as dimethyformamide (DMF), N-methyl pyrrolidinone (NMP), and 2-propanol (or isopropyl alcohol, iPA), even when heated to boiling. All the dried plastics could be heated to about 320° F, before discoloration began to occur. Further heating to 350° F caused significant charring. The denatured protein plastics were insoluble in water.

Two raw materials, soy protein and casein rennet, were not evaluated further after the initial screening experiments. Soy protein gave no solid product, when heated in water to denature the protein. The casein rennet, when denatured as in the other experiments, gave a discolored, foul-smelling lump of gummy product. The unpleasant odor persisted throughout the drying period, and the dried product also had a repulsive odor.

Composites from Caseinate Proteins and Other Available Byproducts

Biodegradable composites, prepared from the two most promising casein samples gave interesting combinations. Sodium or calcium caseinate could be combined with shredded milk cartons[11] directly from the denaturation mixture. The two-component mixture showed good adhesion and could be formed into thin layers with the shredded paper carton as the central core and top and bottom layers of casein plastic. Sodium caseinate was also combined with shredded natural rubber crumbs[12]. Similarly, a composite with good adhesion was obtained with the rubber crumbs dispersed throughout the casein plastic.

Upper left photo: Casein plastic/paper composite cast in Pyrex form.
Lower photo: Casein/crumb rubber composite; casein/shredded milk carton composite

Conclusions

These experiments with biodegradable protein plastics demonstrated the capacity of milk protein fractions to generate sturdy, chemically stable, formable plastics. Further studies would require appropriate equipment to make and mold the plastics under controlled conditions. A system with well-regulated applications of heat, pressure, and immediate extrusion, as described in Ref. 9, would be recommended. The physical properties of the plastics from this screening have shown that they are not sufficiently thermally stable for the intended application. The lamination step involved in plastic keycard manufacture would thermally degrade the plastics developed in this study. However, there may be other applications, particularly those requiring a formable, biodegradable plastic with good adhesion to other components, for which these materials could be considered.

Experimental

All samples were denatured in water the same way, according to the following procedure. A 15g sample of the protein was suspended in 50 ml distilled water and stirred thoroughly by hand in a tall open beaker. The mixture was heated 30 sec in a 1200w microwave oven at full power. The frothy resin was stirred down, until all lumps were moistened and then heated again for 30 sec in the microwave. If an easily isolable solid resulted, this was filtered and allowed to dry at room temperature or outside in the sunlight. If a gelatinous lump or a syrupy resin was obtained, this was cast as a film-former into a 10 cm Petri dish or into another small flat form. The water was allowed to evaporate, and the plastic layer was flattened intermittently with gentle pressure during the drying process. For the casein composites with other materials, the second component was added during the casting step, and the combination was dried together. All of the dried samples released easily from the form.

REFERENCES AND ENDNOTES

1. Tullo, Alex H., C&EN, Oct. 15, 2007.

2. McCoy, M., C&EN, Aug. 18, 2008.

3. Natureworks is produced by Cargill

4. Mirel is produced by Metabolix/ADM partnership

5. Spudware is a registered trademark of Excellent Packaging & Supply

6. Ecoflex and Ecovio are manufactured by BASF in Ludwigshafen, Germany.

7. PGA will be manufactured in Belle, W. Virginia, by Japanese firm, Kureha.

8. McCoy, M. C&EN, Apr. 28, 2008, p. 28.

9. Fick, H. F. and Sommer, H. H., Dept. of Dairy Industry, University of Wisconsin, Madison, WI, “ Factors Affecting the Color and Clarity of Casein Plastics.” Article available on the Internet.

10. We are grateful to Mr. Aaron Jordi, Main Street Ingredients, PO Box 54603, La Crosse, WI, for arranging the selection and shipment of these samples.

11. The post-consumer milk cartons were manufactured by Evergreen Products in Canton, NC, and supplied by Stephen Wolfe of Wolfe Research and Development, Inc.

12. The natural rubber fines were from a waste stream from Day International in Arden, NC, which produces high-quality rubber rollers and mats for the printing industry.