# Mechanical Performance Studies on Extruded Cornstarch-Based Plastic Manufactures

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ABSTRACT: Twin-screw extrusion of cornstarch produces a strong, yet readily biodegradable plastic material. Because of the brittleness of these cornstarch plastics, ASTM standard methods did not apply, and an alternative sample grip was developed. A suitable method for the tensile testing of extruded cornstarch plastics of differing feed composition (amylose content, cross-linking, plasticizer) and processing conditions (temperature) was developed, and quantitative values of tensile strength, strain, elastic modulus, and energy were obtained. The mean tensile strength of these materials ranged from 667 to 4148 psi, which is in the range of values for low-density polyethylene and high-density polyethylene. The high amylose content cornstarch plastics extruded at high temperatures demonstrated greatest strength. Wet/dry studies of the pure cornstarch materials showed them to degrade readily with extended exposure to water, but immersion in water for 1 h in room temperature ( $17^{\circ}$ C) water did not, as measured by standard tensile tests, adversely affect their strength, but made them more ductile, less stiff and tougher. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2147–2154, 1999

Key words: cornstarch plastics; amylose; cross-linking; plasticizer

### **INTRODUCTION**

Growing concern over the environmental impact of waste disposal in increasingly expensive landfills has prompted studies into methods of reducing the volume of waste. Although plastics represent just 20-24% of the volume of garbage in landfills,<sup>1</sup> they are denounced as the culprits causing these landfill problems. One method being studied to reduce the load on landfills and ease the stigma surrounding plastics is the development of biodegradable packaging. An ultimately biodegradable material will undergo mineralization into microbial biomass and be removed from the environment as carbon dioxide and water in aerobic conditions or methane and carbon dioxide in anaerobic conditions.<sup>2</sup> Changing over from petroleum-based plastics to plantbased ones may have a protective effect on the environment by reducing the amount of litter and, Roper and Koch<sup>3</sup> predict, by decreasing the volume of wastes by at least 10%.

Biodegradable polymers are not a novel idea. Attempts at making corn zein plastics were made by Quaker Oats, Corn Products Refining Company, and others as early as the 1930's.<sup>4</sup> More recently, researchers have been incorporating starch into the composition of petroleum-based plastics, although the biodegradability of the final result has been called into question.<sup>5–8</sup>

The incentive to produce plastic materials using starch is starch's ultimate biodegradability. Synthetic polymers resist biodegradation because naturally occurring microorganisms have not evolved enzyme systems capable of attacking them, whereas natural polymers, such as starch,

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are readily biodegradable by microbial action.<sup>9</sup> This advantage was partially demonstrated in the starch–plastic blends.

Strantz and Zottola<sup>10</sup> studied the degradation of cornstarch-containing polyethylene films by starch-degrading enzymes and found that the incorporation of cornstarch into the petroleumbased polyethylene did not increase degradability because the starch was not accessible as a substrate for microbial growth. Gould and colleagues<sup>11</sup> studied formulations of starch/[poly-(ethylene-co-acrylic acid)] and starch/[poly(ethylene-co-acrylic acid) and low-density polyethylene] blends and found that the starch was subject to microbial attack, thereby decreasing the tensile strength of the starch-plastic composites, but the petroleum components forming the matrix were not affected by microbes. Similar results were found by Roper and Koch<sup>12</sup> in their study of polyethylene and polypropylene containing 6-20% starch.

Perhaps the best way to get a truly biodegradable plastic is the development of a plastic made solely of natural polymers. Previous research seeking to produce pure starch polymers was unsuccessful because of product instability caused by loss or degradation of plasticizers<sup>13</sup> and equipment difficulties when the pressure and torque necessary for the high-starch extrusion exceeded the capacity of the extrusion equipment.<sup>14</sup> Other researchers have produced extruded starch plastics of all-natural polymers, but were unable to perform tensile tests because the extrudates were too soft or brittle<sup>15</sup> or became distorted after conditioning.<sup>16</sup> Successful attempts at producing starch plastics made of purely natural polymers and testing for their mechanical properties have been made using soy isolate,<sup>17</sup> soy protein,<sup>18</sup> dialdehyde starch and zein,<sup>19</sup> waxy maize starch,<sup>20</sup> and potato starch.<sup>21,22</sup> The latter studies on waxy maize and potato starch examined the effects of water content/crystallinity and molecular mass, respectively, on mechanical properties of the starch extrudates. Data for the influences of crosslinking, amylose content, and extrusion temperature on the mechanical properties of extruded starch plastics are not available.

This article evaluates the performance of extruded cornstarch-based plastics suitable for nonpermanent uses, such as packaging, disposable containers, or single-use items. The extruded cornstarch plastics varied in composition (common cornstarch, crosslinked common cornstarch, common cornstarch with plasticizer, 50% amylose cornstarch, 50% amylose cornstarch with plasticizer, 70% amylose cornstarch, crosslinked 70% amylose cornstarch, and 70% amylose cornstarch with plasticizer) and processing conditions (low, high, and higher extrusion temperatures). The extruded plastic materials were very brittle, and testing as specified by the American Society for Testing Materials (ASTM) standards for sheet, plate, and molded plastics (ASTM D-638)<sup>23</sup> was impossible. Therefore, the first part of this study involved developing a methodology for testing the cornstarch plastics. The study proceeded to determine the mechanical properties of the plastics, to examine their moisture stability, and to establish which formulations are the best.

# **EXPERIMENTAL**

# Materials

Cornstarch samples were made in a separate phase of the project by the research group of Dr. Graciela Wild Padua and Luping Ning.<sup>24</sup> Seventeen samples were produced by extrusion of eight cornstarch feeds at three different extrusion temperatures, as shown in Table I. Crosslinking of the cornstarch was accomplished by treatment with phosphorus oxychloride, and palmitate monoglyceride was added at a 2% level as a plasticizer.

# **Tensile Testing**

The intention of this study was to test the cornstarch materials using an Instron model 1011 (Instron Corp., Canton, MA), according to ASTM standards for sheet, plate, and molded plastics (ASTM D-638)<sup>25</sup>; but, because of the materials' brittleness, the samples broke between the pressure of the tensile tester's pneumatic clamps. To eliminate this problem, the ASTM procedure was modified to fit the samples directly into the upper grip coupling and the base grip adapter of the tensile tester's crossheads.

Cornstarch materials were prepared by first autoclaving while pressed between two perforated metal sheets to soften and flatten the samples and then die-cutting them. Autoclaving was done at  $275^{\circ}$ F ( $135^{\circ}$ C) for 3 min in a Castle Steam Sterilizer (Sybron Corp., Rochester, NY), then the materials were cut immediately in the dimensions specified as specimen type I by ASTM D-638. Cut samples were left to dry pressed between the metal sheets for 24 h.

	Extrusion Temperature			
Cornstarch Feed	Low (max. 80°C)	High (max. 120°C)	Higher (max. 130°C)	
30% amylose cornstarch (30)	1	8		
Crosslinked 30% amylose cornstarch ( $\times$ 30)	2	9		
Plasticized 30% amylose cornstarch (P30)	3	10		
50% amylose cornstarch (50)	4	11		
Plasticized 50% amylose cornstarch (P50)		12		
70% amylose cornstarch (70)	5	13	16	
Crosslinked 70% amylose cornstarch ( $\times$ 70)	6	14	17	
Plasticized 70% amylose cornstarch (P70)	7	15		

Table I Feed Compositions and Processing Treatments of Extruded Cornstarch Plastics

To position the cornstarch polymers in the tensile tester, cut samples were suspended between two epoxy-filled polypropylene culture tube closures (Bacti-Capall, size 18 mm, Manufactured by Oxford Labware, St. Louis, MO) fit with screw eyes. The screw eyes connected directly to the base grip adaptor and upper grip coupling on the crossheads of the Instron (Fig. 1).

Tensile tests were run within the ASTM-recommended speed range at a crosshead speed of 0.5 in min<sup>-1</sup> (12.7 mm min<sup>-1</sup>). Values for yield strength and tensile strength, strains at peak and break, modulus of elasticity or Young's modulus, and total energy-to-break (area under the stressstrain curve) were measured and calculated using Series IX Automated Materials Testing Systemversion 6.04 (Instron Corp., Canton, MA). Each sample's thickness was measured using a digital micrometer (Enco, model no. 600-2321). The thick-



**Figure 1** Modified ASTM D-638 method for testing cornstarch plastics.

ness of samples ranged from  $0.0410 \pm 0.00369$  to  $0.0986 \pm 0.01660$  in. (1.04-2.44 mm). The number of available samples that could successfully be cut to the ASTM D-638 specifications was limited; so, the number of replicates for each cornstarch sample varied from 6 to 10.

#### Water Immersion

As a preliminary measurement of environmental degradability of the cornstarch plastics, samples were placed in boiling water for several minutes and in tap water for 6 h, and, in both trials, the materials virtually disintegrated. However, a biodegradable polymer is useless if it degrades before it can serve its intended purpose; so, the cornstarch materials were tested for water stability under typical short-term conditions (i.e., in room temperature water for 1 h). Plastics consisting of 70% amylose cornstarch were extruded and tested as follows.

Ten samples were autoclaved, cut, and set in epoxy-filled culture tube caps, as above. After the epoxy dried, the prepared samples were put into room temperature water (63°F/17°C) for 1 h. Wet samples were removed from the water bath after 1 h and then immediately tensile tested using the same method. A set of 10 dry samples was prepared and tested as a control sample.

# **RESULTS AND DISCUSSION**

From these experiments, values for various mechanical properties of the cornstarch-based plastics were obtained, and the effects of composition and extrusion temperature on the mechanical properties were studied. Table II gives values of

	Yield Strength	Tensile Strength	Strain at Peak	Strain at Break	Elastic Modulus	Energy- to-Break
Units	Psi	Psi	%	%	Ksi	lb/in
Range	179–3300	667 - 4148	3.62 - 6.95	3.62 - 6.87	48-125	0.60-4.84
Materials with highest values <sup>a</sup>	P30/high 50/high 70/high ×70/high	50/high 70/high ×70/high	P30/high 50/high 70/high ×70/high	P30/high 50/high 70/high ×70/high	50/high 70/high	P30/high 50/high 70/high ×70/high

Table II Mechanical Property Data for Extruded Cornstarch Plastics

50 = 50% amylose cornstarch; 70 = 70% amylose cornstarch; P30 = plasticized 30% amylose cornstarch;  $\times 30 = crosslinked 30\%$  amylose cornstarch;  $\times 70 = crosslinked 70\%$  amylose cornstarch; low = low temperature; and high = high temperature.

the ranges of the data collected from these tensile tests and the materials giving the highest values for each mechanical property. Figure 2 shows a typical stress-strain curve for the cornstarch plastics, compared with ones of polystyrene and high-density polyethylene tested at room temperature according to ASTM D-638 standards.

Figures 3 through 8 are graphical representations of the tensile testing data and show relationships between feed composition, processing conditions, and mechanical properties. Statistical analyses of the data were performed by using a general linear model and the least significant differences method ( $\alpha = 0.05$ ) of version 6.10 of the SAS<sup>®</sup> System (SAS Institute, Inc., Cary, NC). These results are also shown in Figures 3 through 8. The large standard deviations found are attributed to the variable nature of the starch polymeric materials themselves and to irregularities occurring in the fabrication process. Extrusion



**Figure 2** Comparison of typical stress-strain curves of synthetic plastics and cornstarch plastics: (A) polystyrene, (B) cornstarch plastic, and (C) high-density polyethylene.

artefacts introduce heterogeneity into the materials that would act as sites for initiation and/or propagation of failure, contributing to the inconsistent behavior observed in the tensile tests.

Table II shows that the 50% amylose cornstarch, 70% amylose cornstarch, and crosslinked 70% amylose cornstarch, all processed at high temperature, have the best combined mechanical properties. To lend some significance to this data, the ranges of tensile strengths, strains, and elastic moduli values obtained in mechanical testing are compared with those given by Flinn and Trojan<sup>26</sup> for various petroleum-based plastics in Table III. The strain values achieved by the cornstarch plastics are much lower than those found for the synthetic plastics, but some tensile



**Figure 3** Composition and processing effects on yield strength of extruded cornstarch plastics. Numbers above bars are standard deviations. Different superscript lowercase letters indicate significant differences in yield strength between feed compositions at the 95% confidence level. Different uppercase letters indicate significant differences in yield strength between temperature treatments at the 95% confidence level.



**Figure 4** Composition and processing effects on tensile strength of extruded cornstarch plastics. Numbers above bars are standard deviations. Different superscript lowercase letters indicate significant differences in tensile strength between feed compositions at the 95% confidence level. Different uppercase letters indicate significant differences in tensile strength between temperature treatments at the 95% confidence level.

strength and modulus values of the cornstarch plastics exceeded those of low-density and highdensity polyethylene. The causes of failure of the cornstarch plastics will be studied in future work and, with further work, materials with mechanical properties similar to polypropylene may be attainable.



**Figure 5** Composition and processing effects on strain at peak of extruded cornstarch plastics. Numbers above bars are standard deviations. Different superscript lowercase letters indicate significant differences in strain at peak between feed compositions at the 95% confidence level. Different uppercase letters indicate significant differences in strain at peak between temperature treatments at the 95% confidence level.



Figure 6 Composition and processing effects on strain at break of extruded cornstarch plastics. Numbers above bars are standard deviations. Different superscript lowercase letters indicate significant differences in strain at break between feed compositions at the 95% confidence level. Different uppercase letters indicate significant differences in strain at break between temperature treatments at the 95% confidence level.

Analysis of the processing parameters reveals what gave the materials listed in Table II their superior qualities:

• *Extrusion Temperature:* Generally, processing a feed at a higher temperature resulted



**Figure 7** Composition and processing effects on elastic modulus of extruded cornstarch plastics. Numbers above bars are standard deviations. Different superscript lowercase letters indicate significant differences in elastic modulus between feed compositions at the 95% confidence level. Different uppercase letters indicate significant differences in elastic modulus between temperature treatments at the 95% confidence level.



**Figure 8** Composition and processing effects on energy-to-break of extruded cornstarch plastics. Numbers above bars are standard deviations. Different superscript lowercase letters indicate significant differences in energy-to-break between feed compositions at the 95% confidence level. Different uppercase letters indicate significant differences in energy-to-break between temperature treatments at the 95% confidence level.

in a stronger, more ductile material. In the cases in which statistical significance was found, the material produced at the higher temperature performed better. This is believed to be a result of a greater degree of starch gelatinization in the materials. With increasing extrusion temperature, the disruption of granules by gelatinization is enhanced.<sup>27</sup>

• *Increasing Amylose Content:* Generally, increasing amylose content did not make a significant difference in mechanical properties. When significant differences were found between feeds, the mechanical properties' values of the higher amylose content feeds were greater than that of the lower amylose con-

tent feeds, probably because the linear structure of amylose leads to greater orientation of molecules within the material. This is in agreement with the results of George and colleagues.<sup>28</sup> With lower amounts of the branched fraction, amylopectin, the molecules can more easily slide past one another and are less likely to be entangled in the branches, which can cause breakage.

- Crosslinked Starch Feed: Starch was chemically modified with phosphorous oxychloride to alter the nature of interactions between the polysaccharide chains to produce a crosslinked starch. This procedure was done to improve the processibility of the starch by preventing its expansion upon extrusion and to get a high viscosity, cohesively strong product.<sup>29</sup> However, generally, the crosslinked starch made little difference in the performance of materials. In the cases in which statistical significance was found, the crosslinked cornstarch performed significantly poorer than its unmodified counterpart. Shah and colleagues<sup>30</sup> attribute this adverse effect to the brittleness that results from the crosslinking treatment.
- Addition of Plasticizer: Palmitate monoglyceride was added at a 2% level to act as a plasticizer of the cornstarch feedstock. Plasticizers are added to plastics to keep them soft and viscous, by acting as an interchain lubricant to allow molecules to slide freely over one another.<sup>31</sup> In the cornstarch plastics, adding the plasticizer made a statistical difference in the higher amylose-content cornstarches and, in these cases, the materials without the lipid had better mechanical properties. The plasticizers' detrimental effect on mechanical properties of the higher amylose cornstarches can be attributed to

# Table IIIComparison of Mechanical Properties of Extruded Cornstarch Plasticsto Values from Literature

	Tensile Strength (psi)	Strain at Break (%)	Elastic Modulus (ksi)
Extruded cornstarch plastics	667 - 4148	3.62-6.87	48-125
Low-density polyethylene <sup>a</sup>	2000	90-800	25
High-density polyethylene <sup>a</sup>	4000	15 - 100	120
Polypropylene <sup>a</sup>	5000	10-700	200

<sup>a</sup> Values from R. A. Flinn and P. K. Trojan, Engineering Materials and Their Applications, Houghton Mifflin Co., Boston, 1981.



**Figure 9** Effects of water immersion  $(17^{\circ}C \text{ water for } 1 \text{ h})$  on mechanical properties of extruded cornstarch plastics. Numbers above bars are standard deviations. Asterisk after the mechanical property indicates significance between wet and dry treatments at the 95% confidence level. YS = yield strength; TS = tensile strength; StrPk = strain at peak; StrBk = strain at break; Mod = elastic modulus; E = energy.

the greater linear structure found in these samples. Increasing the amylose content in the samples gave better mechanical properties by allowing the molecules to slide past each other more easily; but, addition of the lipid provided too much lubrication and the molecules lacked the steric hindrance to stay together.

• Water Immersion: The effects of water immersion on extruded 70% amylose cornstarch plastics is shown in Figure 9. Yield strength and tensile strength both decreased on water immersion, but not significantly at the 95% confidence level. The strains at peak and break both showed a significant increase after soaking, showing the material to be more ductile after being in water. Elastic modulus significantly decreased after the immersion, whereas the energy-to-break increased significantly and the material was, therefore, tougher.

# **CONCLUSIONS**

From this study, it was concluded that cornstarch-based materials with mechanical properties comparable to present petroleum-based plastics are achievable, with the strongest materials being made of 50% amylose, 70% amylose and crosslinked 70% amylose cornstarch, all extruded at high temperatures. The pure cornstarch materials are readily degraded by extended exposure to water, but immersion in water for 1 h in room temperature water did not seem to adversely affect their strength, but made them more ductile, less stiff, and tougher.

Future work will concentrate on finding the causes of failure in these cornstarch-based materials to provide direction toward the improvement of their mechanical properties. Furthermore, it would be useful to perform biodegradability studies according to established standards, work toward producing more consistent materials, and experiment with the materials' molding capabilities.

#### REFERENCES

- 1. Rathje, W.; Murphy, C. Smithsonian, 116 (July, 1992).
- Palmisano, A. C.; Pettigrew, C. A. Bioscience 1992, 42, 680.
- 3. Roper, H.; Koch, H. Starch/Strke 1990, 42, 123.
- 4. DuBois, J. H. Plastics History U.S.A., Cahners Publishing Company, Inc., Boston, 1972.
- Gould, J. M.; Gordon, S. H.; Dexter, L. B.; Swanson, C. L.; in Agricultural and Synthetic Polymers, Glass, J. E.; Swift, G.; Eds., American Chemical Society, Washington, D.C., 1990, Chap. 7.
- Holton, E. E.; Asp, E. H.; Zottola, E. A. Cer Foods World 1994, 39, 237.
- Strantz, A. A.; Zottola, E. A. J Food Prot 1992, 55, 736.
- Vaida, U. R.; Bhattacharya, M. J Appl Polym Sci 1994, 52, 617.
- Aminabhavi, T. M.; Balundgi, R. H.; Cassidy, P. E. Polym Plast Tech Eng 1990, 29, 235.
- Strantz, A. A.; Zottola, E. A. J Food Prot 1992, 55, 736.
- Gould, J. M.; Gordon, S. H.; Dexter, L. B.; Swanson, C. L. in Agricultural and Synthetic Polymers, Glass, J. E.; Swift, G. Eds., American Chemical Society, Washington, D.C., 1990, Chap. 7.
- 12. Roper, H.; Koch, H. Starch/Stärke 1990, 42, 123.
- 13. Roper, H; Koch, H. Starch/Stärke 1990, 42, 123.
- Vaida, U. R.; Bhattacharya, M. J Appl Polym Sci 1994, 52, 617.
- 15. Shogren, R. L.; Swanson, C. L.; Thompson, A. R. Starch/Stärke 1992, 44, 335.
- Onteniente, J. P; Etienne, F.; Bureau, G.; Prudhomme, J. C. Starch/Stärke 1996, 48, 10.
- 17. Paetau, I.; Chen, C. Z.; Jane, J. Ind Eng Chem Res 1994, 33, 1821.

- Shilling, C. H.; Babcock, T.; Wang, S.; Jane, J. J Mater Res 1995, 10, 2197.
- 19. Spence, K. E.; Jane, J.; Pometto, III, A. L. J Env Polym Degrad 1995, 3, 69.
- van Soest, J. J. G.; de Wit, D.; Vligenthart, J. F. G. J Appl Polym Sci 1996, 61, 1927.
- van Soest, J. J. G.; Benes, K.; de Wit, D. Starch/ Stärke 1995, 47, 429.
- 22. van Soest, J. J. G.; Benes, K.; de Wit, D. Polymers 1996, 16, 3543.
- American Society for Testing Materials, in Annual Book of ASTM Standards, Vol. 08:01, 1993, p. 163.
- Padua, G. W.; Wei, L. S.; Ning, L. in Book of Abstracts, 1995 Institute of Food Technologists Annual Meeting, Anaheim, CA, 1995, p. 41.
- American Society for Testing Materials, in Annual Book of ASTM Standards, Vol. 08:01, 1993, p. 163.

- Flinn, R. A.; Trojan, P. K. Engineering Materials and Their Applications, Houghton Mifflin Co., Boston, 1981, p. 404.
- Tayeb, J.; Valle, G. D.; Barres, C.; Vergnes, B. in Food Extrusion Science and Technology, Kokini, J. L.; Ho, C. T.; Karwe, M. V. Eds., Marcel Dekker, Inc., New York, 1992, p. 41.
- 28. George, E. R.; Sullivan, T. M.; Park, E. H. Polym Eng Sci 1994, 34, 17.
- Rutenberg, M. W.; Solerek, D. in Starch: Chemistry and Technology, Whistler, R. L.; BeMiller, J. N.; Paschall, E. F. Eds., Academic Press, Orlando, FL, 1984, p. 311.
- Shah, P. B.; Bandopadhyay, S.; Bellare, J. R. Polym Degradation Stab 1995, 47, 165.
- Hanlon, J. E. in Handbook of Package Engineering, Technomic Publishing Co., Inc., Lancaster, PA, 1992, Chap. 1.