

Blending of Poly(lactic acid) and Starches Containing Varying Amylose Content

Tianyi Ke, Susan Xiuzhi Sun, Paul Seib

Department of Grain Science and Industry, Kansas State University, Manhattan, Kansas 66506

Received 21 June 2002; accepted 9 December 2002

ABSTRACT: Four dry corn starches with different amylose content were blended at 185°C with poly(lactic acid) (PLA) at various starch:PLA ratios using a lab-scale twin-screw extruder. Starch with 30% moisture content also was blended with PLA at a 1:1 ratio. Each extrudate was ground and dried. The powder was mixed with about 7.5% plasticizer, and injection molded (175°C) into test tensile bars. These were characterized for morphology, mechanical properties, and water absorption. Starch performed as a filler in the PLA continuous matrix phase, but the PLA phase became discontinuous as starch content increased beyond 60%.

Tensile strength and elongation of the blends decreased as starch content increased, but no significant difference was observed among the four starches at the same ratio of starch:PLA. The rate and extent of water absorption of starch/PLA blends increased with increasing starch. Blends made with high-amylose starches had lower water absorption than the blends with normal and waxy corn starches. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3639–3646, 2003

Key words: blends; plastics; biodegradable

INTRODUCTION

Advances in petrochemical polymer technology have brought considerable benefits to mankind. However, they also have brought ecological problems as a result of the nondegradable materials used for disposable items. Finding durable plastic substitutes, especially for short-term packaging and disposable applications, has become important in order to minimize effects on the ecosystem.

Starch has been considered a low-cost alternative to petroleum in production of disposable plastics.^{1,2} Starch by itself was plasticized and shaped into consumer items,^{3–6} but plasticized starch alone swells and deforms on exposure to moisture. To address this, starch was blended with petroleum polymers to increase biodegradability.^{7–9} However, articles made from starch/petroleum blends are only partially degradable. In the 1990s, blending starch with biodegradable synthetic polymers became the target. These blends would be fully degradable, but their ability to withstand moisture is still an issue. Starch has been blended with poly(caprolactone) (PCL),^{10–14} polyhydroxybutyrate (PHB), poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV),^{15–21} and poly(lactic acid) (PLA).^{22–29}

PLA has been studied extensively for tissue engineering and drug delivery systems³⁰ because of its good biodegradability^{31–33} and mechanical proper-

ties.³⁴ Semicrystalline PLA is preferred in cases where high mechanical strength and toughness are required.^{32,35} These properties have made PLA attractive for disposable and biodegradable plastic substitutes. In our previous work, methods of blending starch with PLA are investigated, along with starch ratio, starch moisture content, blend heat treatment, plasticizers, and coupling agents—all of these variables affected blend properties.^{24–26}

Starch contains two major polymers—nearly linear amylose and branched amylopectin. When blending starch and PLA, the properties of amylose and amylopectin at or near starch granule surface would affect properties of blends. Furthermore, the water sensitivity of plastics containing starch has always been a key issue because starch takes up water and swells. The swelling of corn starch decreases with amylose content. Therefore, amylose content may be key to improving moisture resistance of blends. In this study, four corn starches with different amylose levels were blended with PLA. Morphology, mechanical properties, and water absorption of blends were characterized.

EXPERIMENTAL

Materials

Four corn starches containing amylose contents of approximately 0, 28, 50, and 70% by weight were used in this study. Percentage of amylose were reported by the supplier. Amioca (0% amylose), Hylon V (50% amylose), and HylonVII (70% amylose) were obtained from National Starch and Chemical Company (India-

Correspondence to: X. Sun (xss@ksu.edu).

napolis, Indiana), and normal corn starch (Silver Medal Pearl-1100, 28% amylose) was purchased from Cargill, Inc. (Minneapolis, MN). The PLA was obtained from Shimadzu, Inc. (Tokyo, Japan). It was polymerized mainly from L-lactic acid and had a molecular weight of about 120,000 Dalton. Mechanical properties and water absorption of pure PLA was reported in previous studies.^{24,29,38} The plasticizer acetyltriethyl citrate (Citroflex A2) was obtained from Morflex, Inc. (Greensboro, NC).

Blend preparation and experimental design

Each of the four granular starches was dried in an oven at 130°C for about 2 h. The PLA was ground into particles of about 2 mm. The dried starches and ground PLA were premixed using a stand mixer (Ultra Power Kitchen Aid, St. Joseph, MI) at ratios (w/w) of 1:4, 2:3, 1:1, 3:2, and 7:3 (starch:PLA) at ambient conditions; the mixtures were stored in polyethylene zip-lock plastic bags. The mixtures were blended in a lab-scale corotating, conical twin-screw extruder (TW-100, Haake, Paramus, NJ) with a screw diameter of 19.1 mm, a length to diameter ratio of 25:1, and with a normal constant pitch screw and constant flight depth. A mixture was fed into the feeding funnel by hand, and was extruded through an 8 mm diameter rod die with at a temperature profile of 120°C (zone 1, near to the feed inlet), 185°C (zone 2), 185°C (zone 3), and 185°C (at the die). The screw speed was fixed at 100 rpm, and the output rate was about 15 g/min. The extruded rods were cut into short cylinders of about 10 mm in length and then were ground into small particles of about 2 mm using a Wiley mill (Model 4 Laboratory Mill, Thomas-Wiley Company, Philadelphia, PA). The ground blends were dried again in the oven at 110°C for 24 h before molding.

An injection-molding machine (Boy 22S, Boy Machines, Postfach, Germany) at a molding temperature of 175°C was used to prepare tensile bars according to Standard Method ASTM D638-91. Acetyltriethyl citrate (7.5% based on dried extrudate) was mixed with each ground extrudate to increase flowability of the material in the mold. Tensile bars were stored in plastic bags for a week at room temperature, and then were conditioned for 48 h in a chamber [50% relative humidity (RH), 23°C] before mechanical analysis. The results reported for mechanical properties testing were averages of five tensile bars.

To compare granular starch with gelatinized starch in a blend, the moisture content (MC) of each of the four starches was adjusted to 30% by adding distilled water to each starch and allowing the hydrated starch to stand several hours in a sealed container. According to previous research,²⁴ starch with 30% MC was almost completely gelatinized when blending with PLA at about 185°C. The moisturized starch samples were blended with PLA at a ratio at 1:1 (dried starch:PLA). Extruded products were dried at 130°C for 2 h before processing into specimens for testing.

Scanning electron microscope

Microstructures of the fractured samples from tensile testing, as well as samples' surface characteristics, were observed using a Hitachi S-3500N scanning electron microscope (SEM) (Hitachi Science Systems, Ltd., Ibaraki, Japan) at an accelerated voltage of 20 kV. Molding surface of samples also was observed.

Mechanical analysis

Tensile tests were performed with an Instron testing machine (Model 4465, Canton, MA) according to the ASTM D638-92 test method with a crosshead speed of 5 mm/min and a gauge length of 30 mm. All samples were pre-conditioned for 48 h at an ambient temperature of 23°C and 50% RH. Tests were performed under these same conditions.

Starch gelatinization measurement

For the extrudates made with starches at 30% moisture content at 1:1 (dried starch: PLA) ratio, starch was isolated from the blends by extracting the PLA from the ground samples with chloroform for 24 h. The mixture was filtered using filter paper, and the residue was washed repeatedly with chloroform. The separated starch was dried and stored in a dessicator. Differential scanning calorimetry (DSC) was used to estimate gelatinization degree measurement. The degree of gelatinization was calculated according to the method described by Potente et al.³⁶:

$$G = (1 - \Delta H_G / \Delta H_0) * 100$$

where G is the degree of starch gelatinization, ΔH_G is the DSC enthalpy of the gelatinized starch extracted from the blends, and ΔH_0 is the DSC enthalpy of native starch.

Water absorption

Water absorption was determined using the ASTM test method D570-81. Tensile bars were weighed and then immersed in distilled water at ambient temperature for 45 days. The samples were removed from the soaking tank at specified intervals and blotted gently with tissue paper to remove excess water on the surface, weighed, and then placed back into the soaking tank for the next measurement. Each measurement was done in triplicate.

RESULTS AND DISCUSSION

Scanning electron microscope

Hylon V was selected to illustrate SEM results. Selected SEM pictures are presented in Figure 1 for the blends with various starch and PLA ratios. The re-

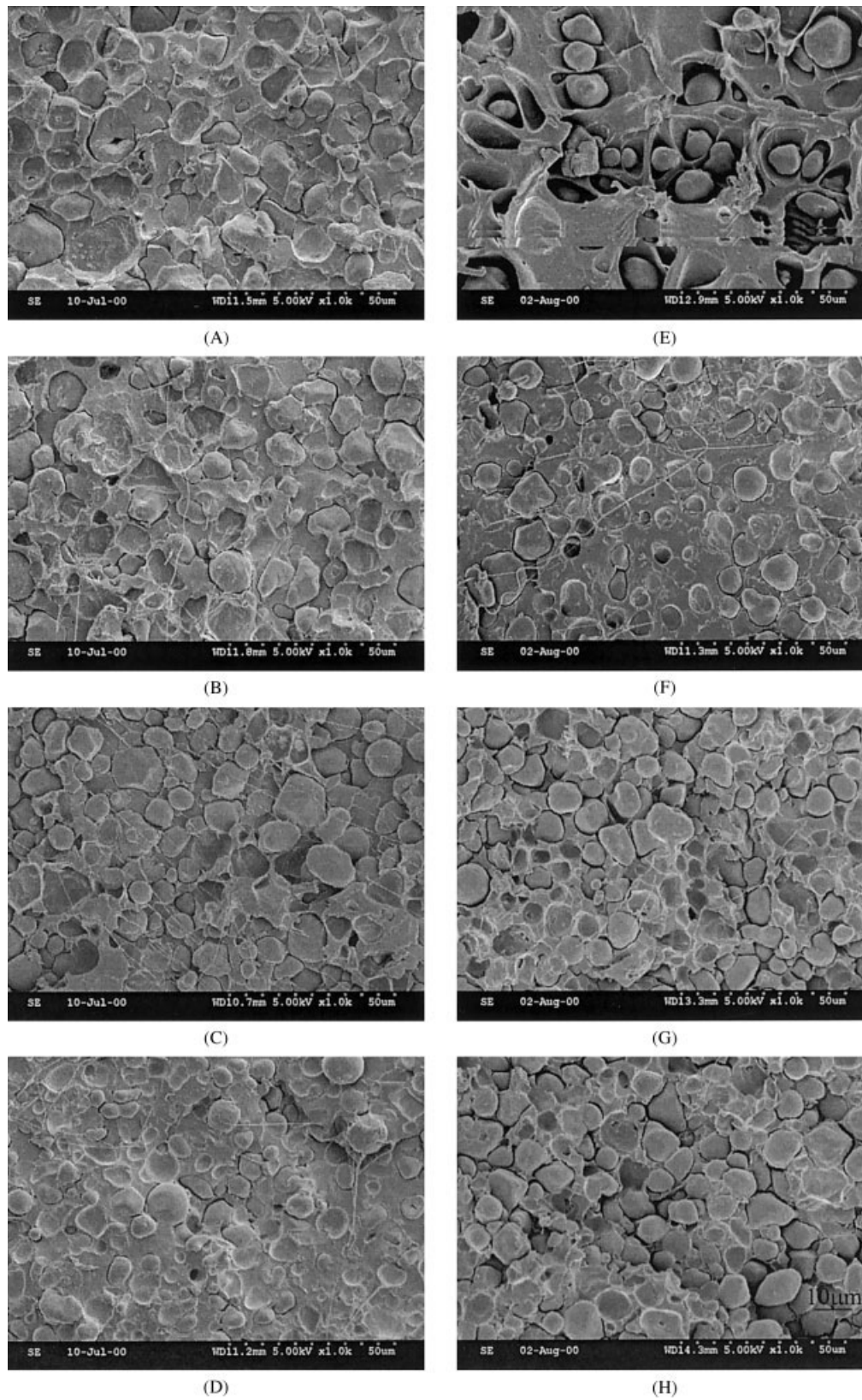


Figure 1 SEM pictures of fractured tensile bars of PLA and starch—(A) Amioca, (B) corn starch, (C) Hylon V, (D) Hylon VII at 50:50 blending ratio—and of PLA and Hylon V starch at various ratios (starch:PLA)—(E) 20:80, (F) 40:60, (G) 60:40, (H) 70:30.

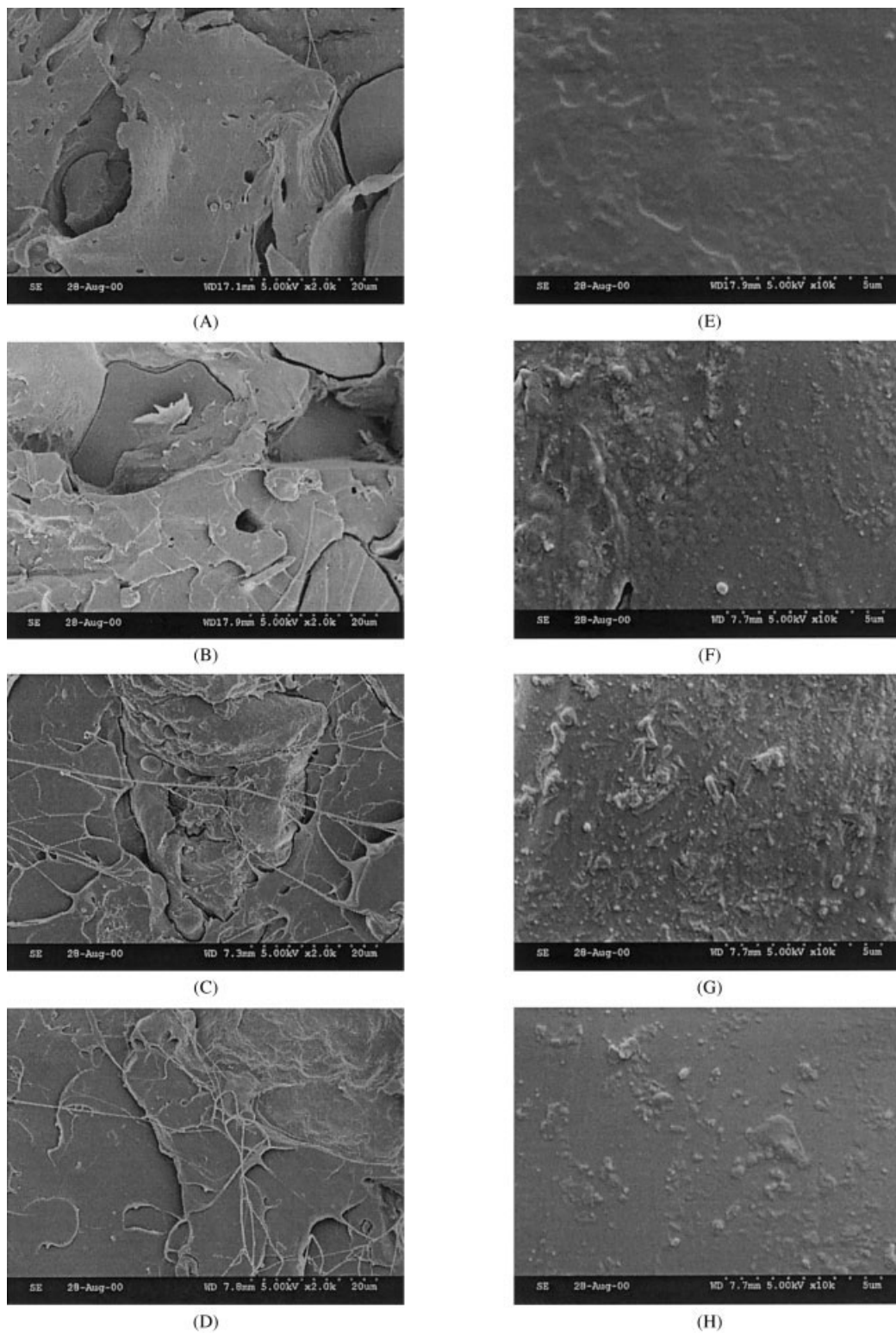


Figure 2 SEM pictures of fractured tensile bars of PLA and gelatinized starch (50:50, w/w) with 30% moisture content (A) Amioca, (B) cornstarch, (C) Hylon V, (D) Hylon VII; and of molding surface (E) Amioca, (F) cornstarch, (G) Hylon V, (H) Hylon VII.

maining starches had SEM pictures with similar characteristics and are not shown. PLA was the continuous phase with starch as a filler in the two-phase system.

Starches of differing amylose content largely retained their granular structure in the extrudates. Their sizes were similar, averaging approximately 15 μm , which

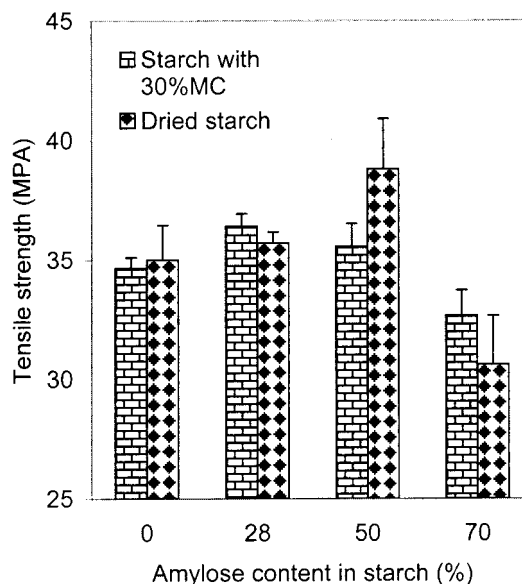
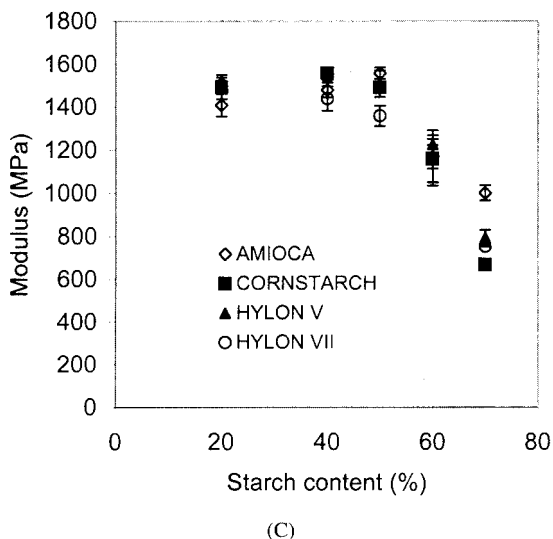
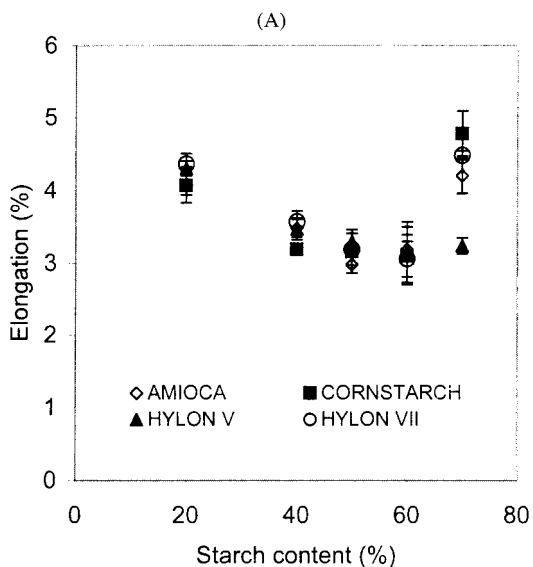
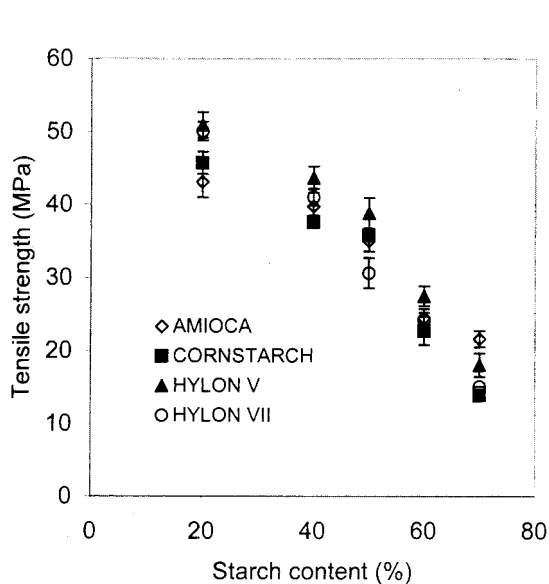


Figure 4 Tensile strength of starch:PLA (50:50, w/w) blends containing 30% moisture content.

indicated little difference among the starches in the blends [Figure 1(A–D)]. PLA phase was continuous at low starch content (<40%) [Fig. 1(E)], but became discontinuous as the starch content increased to >50% [Fig. 1(G and H)]. Space gaps were observed between starch granules and PLA phases in the blends at all the different weight ratios of blends, indicating that adhesion between the starch and PLA was poor.

Almost no starch granules were observed under SEM in the fractured surface of samples made from starches with 30% MC [Fig. 2(A–D)]. However, some particulate material (about or less than 1 μm) was observed on the molding surface of some samples [Fig. 2(E,F)], indicating that the starch had been gelatinized and highly destructurized. According to DSC measurement, starch was completely gelatinized in these samples from all four starches used (data not shown), which was in agreement with the SEM observation.

Mechanical properties

Starch performed as a filler in the PLA matrix, as was observed from the SEM photomicrographs. As the blends were subjected to an external tensile load, the PLA matrix was the main load-bearing phase. As the starch content increased, the effective cross-sectional area of the PLA continuous phase was reduced, resulting in decreased strength, elongation, and modulus [Fig. 3(A–C)] regardless of starch type and composi-

Figure 3 Tensile test properties of starch:PLA blends at various ratios: (A) tensile strength, (B) elongation, and (C) Young’s modulus.

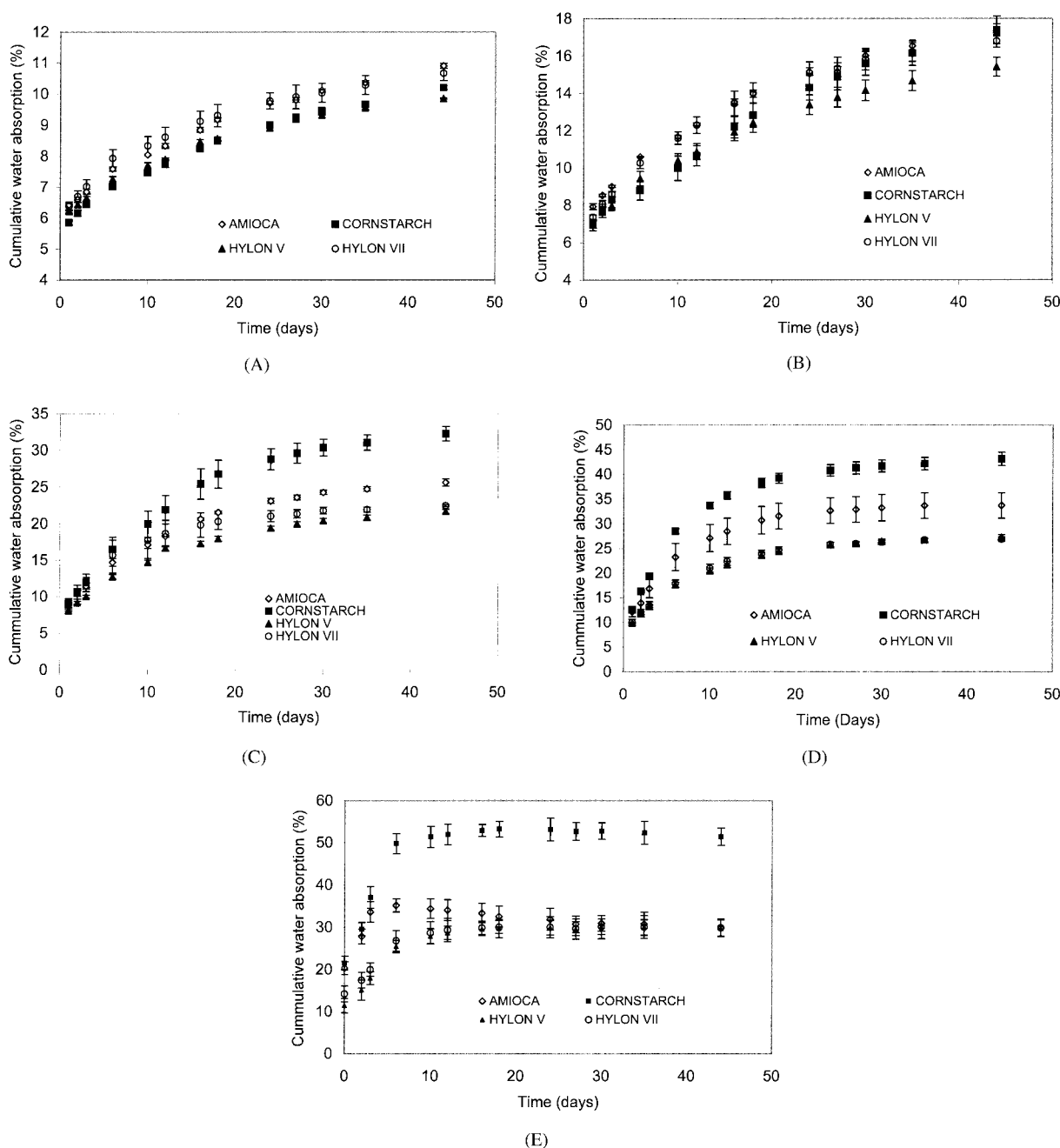


Figure 5 Water absorption of blends at various ratio of starch:PLA: (A) 20:80, (B) 40:60, (C) 50:50, (D) 60:40, (E) 70:30.

tion. The blend containing Hylon V with 50% amylose had the highest tensile strength among the four starches at all blending ratios except for 70% starch [Fig. 3(A)]. The blends containing the other three starches did not show significant differences in tensile strength. Elongation decreased as starch content increased, but at 70% starch content, elongation increased [Fig. 3(B)]. The increase in elongation at 70% starch was attributed to relatively high plasticization of PLA because of a higher ratio of plasticizer to PLA in the blend. The changing ratio of plasticizer to PLA

also was a factor in the observed decrease in tensile strength. Modulus of the blends increased slightly as starch content increased up to 40%, and then the modulus decreased as starch content increased above 50%. This is likely because of the discontinuity of the PLA matrix and the effect of the much higher proportion of plasticizer [Fig. 3(C)].

Generally, no significant differences in mechanical properties were observed between the blends prepared from dried starch and the starch with 30% MC (Fig. 4, elongation and modulus are not shown). The

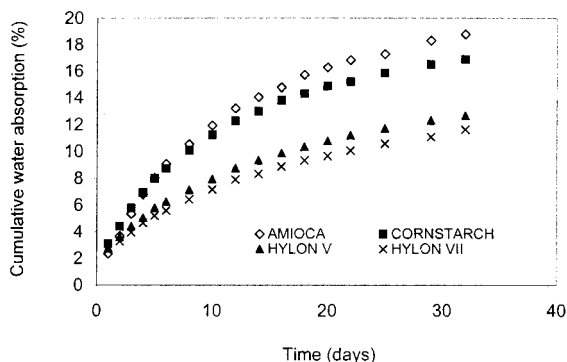


Figure 6 Water absorption of starch/PLA (50/50, w/w) blends containing 30% moisture content.

blends prepared from 0, 28, and 50% amylose corn starches had similar tensile strengths, and the blends from 70% amylose corn starch had the lowest tensile strength. Young's modulus and elongation of all blends made from starch with 30% MC ranged from 1540 to 1630 MPa and 4.2 to 4.4%, respectively.

Water absorption

Water absorption rate of all blends was fast in the first few days, and then leveled off [Fig. 5(A–E)]. Water absorption increased as starch content increased. This is because starch is a hydrophilic polymer and PLA is hydrophobic. Meanwhile, a shorter time was required to reach equilibrium as starch content increased because the discontinuity of the PLA matrix phase increased. At high starch content, water could saturate the surface of the blends easily, and also penetrated into the blends through voids and was absorbed easily by the starch, resulting in higher water absorption in a shorter time.

Blends with 40% or less starch had similar water absorption regardless of starch type and amylose content [Fig. 5(A,B)]. The equilibrium cumulative water absorption was 9–11% for the blend made from 20% starch and about 15–18% from 40% starch. As starch content increased beyond 50%, the blends made from corn starch with 28% amylose had highest cumulative water absorption, reaching up to 30% (at 50% starch), 40% (at 60% starch), and 53% (at 70% starch) [Fig. 5(C–E)]. The second highest cumulative water absorption was in blends made from waxy corn starch (0% amylose). Blends made from the high amylose (50 and 70%) corn starch showed similar water absorption behavior at all levels. The blends at 70% starch content for all four starches were saturated in 6 days [Fig. 5(E)], and the water absorption dropped slightly as soaking time increased because some starch was leached away from the test bar.

The various starch types produced distinct water absorption proportions. At starch content <40%, dif-

ferences were not pronounced because of the continuous PLA phase inhibiting water penetration into a blend. Therefore, similar water absorption was observed for all types of starches. However, as starch content increased, the water absorption of blends was in the order: normal corn starch > waxy maize > 50% amylose corn starch > 70% amylose corn starch. Although amylopectin contains more crystal structure than amylose, waxy (0% amylose) starch granules are well known to absorb more water upon soaking than amylose containing starch due to its large branched molecules with about 75% amorphous structure.³⁷ However, the PLA blends with waxy corn starch had lower water absorption than those with normal corn starch (about 75% amylopectin). It appears the normal corn starch underwent more mechanical damage than waxy maize starch during extrusion with PLA, perhaps because the 28% amylose made the normal corn starch granule stiff. For blends with gelatinized starch, water absorption increased as amylopectin content increased, which was as expected. The crystalline region of starch was melted upon gelatinization, and swelling of amylopectin played a main role in water absorption.

CONCLUSION

The water resistance was improved without affecting mechanical properties as increasing amylose above 50%. No significant difference in mechanical properties was observed among starches with varying amylose content, except that the blend containing 50% amylose had slightly greater strength. Water absorption of the blends was affected by amylose content. Absorption increased as starch content increased, and the blends containing 50 and 70% amylose corn starch had lower water absorption than the blends containing 0 and 28% corn starch. Blends prepared from gelatinized starch showed similar mechanical properties and water absorption behavior as those prepared from granular starch.

References

1. Doane, W. M. In *New Crops, New Uses, New Markets*; U.S. Department of Agriculture: Washington, DC, 1992; p 47.
2. Bastioli, C. *Starch/Stärke* 2001, 53, 351.
3. Lay, G.; Belling, B.; Rehm, J.; Stepto, R. F.; Krozingen, B.; Thom, M.; Sachetto, J.-P.; Lentz, D. J.; Silbiger, J. U.S. Pat. 5,095,054, 1992.
4. Tomka, I. Switzerland Eur. Pat. Appl. 542,155, 1993.
5. Wiedmann, W.; Strobel, E. *Starch/Stärke* 1991, 43, 138.
6. Yu, J.; Chen, S.; Gao, J.; Zheng, H.; Zhang, J.; Lin, T. *Starch/Stärke* 1998, 50, 246.
7. Doane, W. M. *Starch/Stärke* 1992, 44, 293.
8. Griffin, G. J. L. In *Chemistry and Technology of Biodegradable Polymers*; Griffin, G. J. L., Ed.; Chapman & Hall: London, 1994; pp 18–47.

9. Shogren, R. L.; Fanta, G. F.; Doane, W. M. *Starch/Stärke* 1993, 45, 276.
10. Doi, Y.; Fukuda, K. *Biodegrad Plast Polym* 1994, 437.
11. Koenig, M. F.; Huang, S. J. *Polymer* 1995, 36, 1877.
12. Krishnan, M.; Narayan, R. U.S. Pat. 5,500,465, 1996.
13. Schroeter, J.; Hobelsberger, M. *Starch/Stark* 1992, 44, 247.
14. Tokiwa, Y.; Ando, T.; Suzuki, T.; Takeda, T. *ACS Polym Mat Sci Eng* 1990, 63, 742.
15. Imam, S. H.; Gordon, S. H.; Shogren, R. L.; Greene, R. V. *J. Environ Polym Degrad* 1995, 3, 205.
16. Imam, S. H.; Chen, L.; Gordon, S. H.; Shogren, R. L.; Weisleder, D.; Greene, R. V. *J Environ Polym Degrad* 1998, 6, 91.
17. Kontis, M. A.; O'Brien, G. S.; Willett, J. L. *J Environ Polym Degrad* 1995, 3, 97.
18. Ramsay, B. A.; Langlade, V.; Carreau, P. J.; Ramsay, J. A. *Appl Environ Microbiol* 1993, 59, 1242.
19. Shogren, R. L. *J Environ Polym Degrad* 1995, 3, 75.
20. Willett, J. L.; O'Brien, G. S. In *Cereals: Novel Uses and Processes*; Campbell, G. M., et al., Eds.; Plenum Press: New York, 1997.
21. Zhang, L.; Deng, X.; Zhao, S.; Huang, Z. *Polym Int* 1997, 44, 104.
22. Ajioka, M.; Enomoto, K.; Yamaguchi, A. U.S. Pat. 5,444,107, 1995.
23. Jacobsen, S.; Fritz, H. G. *Polym Eng Sci* 1996, 36, 2799.
24. Ke, T.; Sun, X. S. *Cereal Chem* 2000, 77(6), 761.
25. Ke, T.; Sun, X. S. *J Appl Polym Sci* 2001, 81, 3069.
26. Ke, T.; Sun, X. S. *Trans ASAE* 2001, 44(5).
27. Kim, S. H.; Chin, I.-J.; Yoon, J.-S.; Kim, S. H.; Jung, J. S. *Korea Polym J* 1998, 6, 422.
28. Park, J. W.; Lee, D. J.; Yoo, E. S.; Im, S. S.; Kim, S. H.; Kim, Y. H. *Korea Polym J* 1999, 7, 93.
29. Wang, H. M.S. thesis, Kansas State University, 2001.
30. Huang, S. J. In *Polymers—Biomaterials and Medical Applications*; Kroschwitz, J. J., Ed.; Wiley & Sons: New York, 1989.
31. Leenslag, J. W.; Pennings, A. J.; Bos, R. R. M.; Rozema, F. R.; Boering, A. *Biomaterials* 1987, 8, 311.
32. Nakamura, T.; Hitomi, S.; Watanabe, S. J. *Biomed Mater Res* 1989, 23, 1115.
33. Reed, A. M.; Gilding, D. K. *Polymer* 1981, 22, 494–498.
34. Engelberg, I.; Kohn, J. *Biomaterials* 1991, 12, 292.
35. Hay, D. L.; Von Fraunhofer, J. A.; Chegini, N.; Mastersin, B. J. *J Biomed Mater Res* 1988, 22, 179.
36. Potente, H.; Liu, J.; Rucker, A. *Starch/Stärke* 1996, 48, 171.
37. Tester, R. F.; Morrison, W. R. *Cereal Chem* 1990, 67(6), 551.
38. Wang, H.; Sun X.; Seib P. A. *J Appl Polym Sci* 2001, 82, 1761.