

Starch–Poly(vinyl alcohol) Foamed Articles Prepared by a Baking Process

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ABSTRACT: Composite foam plates were prepared by baking a mixture of granular starch and aqueous poly(vinyl alcohol) (PVOH) solution inside a hot mold. Foam strength, flexibility, and water resistance were markedly improved by addition of 10–30% PVOH to starch batters. The improvement in strength at low humidity was greater for partially (88%) hydrolyzed PVOH while strength at higher humidities improved most with fully (98%) hydrolyzed PVOH. Foam flexibility increased with higher PVOH molecular weight. Scanning electron micrographs of the surface of the foams revealed a phase-separated morphology in which swollen starch granules were embedded in a matrix of PVOH. The starch component was gelatinized (melted) during baking while the PVOH component crystallized to a high degree during baking. Crosslinking agents such as Ca and Zr salts were added to starch batters to give further increases in water resistance. Respirometry studies in soil showed that the starch component of starch–PVOH foams biodegraded relatively rapidly (weeks) while the PVOH component degraded more slowly (months). Baked foams prepared from starch and PVOH have mechanical properties that are adequate for use as packaging containers over a wide range of humidity. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2129–2140, 1998

Key words: starch; poly(vinyl alcohol); foam; biodegradable; packaging

INTRODUCTION

The use of starch as a biodegradable, renewable base material for disposable articles such as plates, utensils, and bags is desirable as an envi-

ronmentally friendly alternative to the present use of nondegradable, nonrenewable petroleum based plastics such as polyethylene and polystyrene.^{1–5} Although the latter can be recycled, this is often difficult and expensive due to contamination of plastic articles with food and collection costs. Totally biodegradable starch-based plastics can be composted into a useful mulch rather than being entombed in landfills.

Starch consists of a mixture of about 25% amylose, a nearly linear polymer of α -1,4 anhydroglucose units, and amylopectin, a highly branched polymer consisting of short, α -1,4 chains linked by α -1,6 bonds. In the native state, starch exists

Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name USDA implies no approval of the product to the exclusion of other that may also be suitable.

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as 5–60- μm diameter granules with amylopectin providing a crystalline framework. Starch is widely available and, at a cost of \$0.25–0.60/kg, is less expensive than polyethylene and polystyrene (\$0.80–1.50/kg) and is readily biodegradable.^{2,3,6–8} The use of this material as a substitute for plastics has, however, been severely limited due to its brittleness and hydrophilicity.^{9–12} Articles made from starch are weak and brittle at low humidity and swell and deform upon exposure to moisture, making them unsuitable for most packaging applications.¹³ After being extrusion-processed with water into a sheet, corn starch, for example, has a tensile strength of 40 MPa and an elongation to break of 9% at 50% humidity compared to 20 MPa and 3% at 20% humidity.¹³

Poly(vinyl alcohol) (PVOH) is a biodegradable synthetic polymer, which has excellent strength and flexibility^{14,15} and costs \$2.70–3.10/kg.¹⁶ The tensile strength and elongation of PVOH are approximately 80 MPa and several hundred percent, respectively, at 50% humidity. As humidity decreases, tensile strength increases and elongation decreases. PVOH can be dissolved in hot water and, hence, is used in applications such as textile sizing, paper coatings, and water-soluble film.

Previous work has shown that addition of PVOH improves the strength and flexibility of gelatinized starch. Young¹⁷ found that films cast from aqueous solutions of amylose or high amylose starch and PVOH had higher strength and elongation to break at 23 and 50% humidity than films cast from starch alone. Otey and Mark¹⁸ found similar improvement in mechanical properties for films cast from solution mixtures of normal (27% amylose) cornstarch and PVOH and also incorporated formaldehyde as a crosslinking agent. A water-resistant coating comprised of a polyurethane and polyvinyl chloride was also described. Bastioli et al.¹⁹ and Lay et al.²⁰ described the extrusion of starch, PVOH, and water into a homogeneous melt, followed by molding. Some improvement in dimensional stability at high humidities was claimed. LaCourse and Altieri²¹ described the extrusion of modified high amylose starches, water, and up to 10% PVOH into expanded foam.

A process for preparing shaped foam articles from starch has recently been described.^{22–24} This involves baking a starch–water batter in a hot mold. A starch formed article is formed as the starch gelatinizes, expands, and dries. While such products are useful for some applications, it would be desirable to increase the strength, flexibility,

and water resistance of starch foams to expand the range of applications. This article describes baked starch–PVOH foamed articles, which have improved strength, flexibility, and water resistance and thus are better suited for use as food packaging and serving articles. Relationships between the structure, morphology, and mechanical properties of the foams are described.

EXPERIMENTAL

Materials

Potato starch was unmodified food grade from Avebe America, Princeton, NJ, and had a moisture content of 12–18%. Corn starch was Buffalo 3401 from CPC International, Englewood Cliffs, NJ, and had a moisture content of 10–12%. PVOH polymers were obtained from Air Products, Inc., Allentown, PA. Moisture contents were reported to be 2–4%. The percentage of hydrolysis (mol % of vinyl alcohol, with the remainder being vinyl acetate) and weight-average molecular weight (M_w) of the PVOH polymers were as follows.

Airvol No.	Percent Hydrolysis	M_w
350	98.3	124–186,000
325	98.3	85–146,000
540	88.6	124–186,000
523	88.2	85–146,000

An aqueous solution of zirconium acetate (22% ZrO_2 , pH 3.8) was obtained from Magnesium Elektron, Flemington, NJ. Guar gum and magnesium stearate were from Sigma Chemical, St. Louis, MO.

Preparation of PVOH Solutions

10 and 15% aqueous solutions of PVOH were prepared by adding 800 or 1200 g of PVOH and 6000 g of distilled water to a 10-L resin flask equipped with an air stirrer, condenser, heating mantle, and thermometer. The mixture was stirred and heated at 85°C for about 3 h and then poured into a plastic jug for storage at room temperature. Water was added to bring the final solution weight to 8000 g.

Preparation of Foam Trays

Starch and magnesium stearate (2% by weight of starch + PVOH) were first mixed using a Kitchen Aid mixer with a wire whisk attachment. Magnesium stearate acts as a mold release agent, preventing sticking of starch to the mold. For batters containing no PVOH, guar gum (1% by weight of starch) was also added to prevent settling of the starch. PVOH solution and/or water were then added so as to give the desired level of PVOH and a total solids content of 33%. When zirconium acetate solution was added to the batter, pH was first adjusted to 4.8 with 1M acetic acid. Mixing was continued for 20–30 min. Starch foam trays were prepared using a lab model baking machine (model LB TRO) supplied by Franz Haas Machinery of America, Richmond, VA. This machine essentially consists of two heated steel molds, the top of which can be hydraulically lowered to mate with the bottom half for a set amount of time. Dimensions of the mold were 217 mm long, 134 mm wide, 19 mm deep, and 3 mm (plate separation). Baking temperatures were set at 200–205°C. Actual temperatures at the mold surface were about 10°C lower, as measured using a Temp-Sure Digital Pyrometer TS-200. Baking times were the minimum required to avoid a soft or bubbled tray and varied from about 80–140 s.

Testing of Trays

Trays were equilibrated at 5, 20, 50, 85, and 95% relative humidity (RH) at 23°C for 7 days prior to mechanical testing. An Electro-tech Systems environmental chamber, model 518, was used for 5% RH. The 20 and 95% RH environments were achieved by placing saturated solutions of sodium acetate and disodium hydrogen phosphate, respectively, in large glove boxes. For 85% RH, a Hotpack constant humidity oven was used. Equilibration at 50% RH and testing was carried out in a special room maintained at that humidity. Humidities were checked in each environment using a Vaisala humidity meter HMI 31, which was calibrated with saturated LiCl and NaCl. Trays maintained humidities other than 50% were placed in Ziplock polyethylene bags and then were removed one by one for testing.

Mechanical testing was performed using an Instron model 4201 Universal Testing Machine equipped with a cylindrical probe (35-mm diameter) and a cylindrical base (80-mm inside diameter). The probe was lowered onto the tray until a

load of 0.5 N was reached and then lowered at 30 mm/min. Parameters calculated were the maximum force (F_m) and deformation to F_m (L_m). Flexural moduli in the three-point bending mode were determined following ASTM D790 using samples cut to 75 × 25.4 mm in size and a 50.8-mm support span. Data reported are an average of tests of 4–8 trays. Tray densities were estimated from the ratio of weight of a section to the volume (using ruler and calipers).

Water resistance tests were performed by first weighing a tray equilibrated to 50% RH, adding 100 mL of distilled water at 23°C, waiting 25 min, pouring off the water and reweighing the tray.

Scanning Electron Microscopy

Tray samples were mounted on aluminum stubs with graphite-filled tape and vacuum-coated with gold-palladium. Specimens were then examined with a JEOL JSM 6400V scanning electron microscope.

X-ray Diffractometry

X-ray diffraction (XRD) analysis of the surface of starch foam trays was performed with a Philips 1820 diffractometer operated at 40 kV, 30 mA with graphite filtered CuK_α radiation, and a theta compensating slit. Data were acquired in 0.05-degree two-theta, 4-s steps.

Respirometry

Starch-PVOH trays (2 g, 10% moisture) were cut into 1-cm squares and placed into 250-mL glass bottles with 100 g of prairie topsoil (Bluestem Products, Cedar Rapids, IA). A sample of Airvol 350 (coarse granular, particle size ~ 1 mm) as obtained from the manufacturer was also tested. The soil contained 0.9% N, had a pH of 7.9, and was adjusted to 60% moisture. Samples were maintained at 23°C with a water bath. CO₂ production and O₂ consumption was monitored over time with a Micro-oxymax respirometer (Columbus Instruments, Columbus, OH). Net CO₂ production was calculated by subtracting the total CO₂ produced by a soil sample alone from the value for a sample. Values given are the average of two duplicate sample chambers and are normalized to the total amount of C in the samples. At the end of the 80-day test period, the moisture contents of the soil + samples were 53–58%. pH values of soil and soil + samples were about 7.9

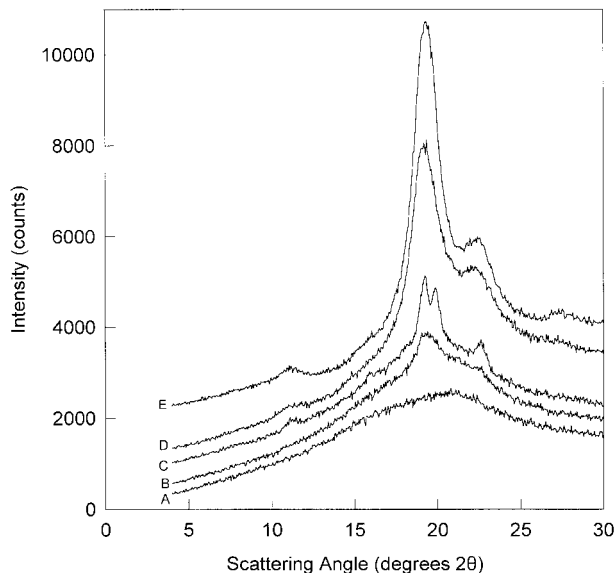


Figure 1 X-ray diffractometer scans of the surfaces of foam trays composed of (A) potato starch, (B) potato starch with 20% Airvol 523, (C) potato starch with 20% Airvol 325; also (D) powdered Airvol 523 and (E) powdered Airvol 325.

before and after testings. Samples for Fourier transform infrared (FTIR) analysis were pulverized in liquid nitrogen using a Wig-L-Bug Amalgamator, mixed with KBr, and pressed into pellets. Spectra were obtained using a Nicolet Impact 410 spectrometer.

RESULTS AND DISCUSSION

Morphology

XRD scans of the surface of starch–PVOH foams plates, as well as PVOH powders, are presented in Figure 1. A tray made with potato starch alone has a single broad intensity maximum, indicative of an amorphous structure. This is expected since the temperature of the batter during initial stages of baking (100–110°C) was greater than the melting temperature of the crystalline potato starch (~66°C).²⁵ A tray made with potato starch and 30% Airvol 325 has crystalline diffraction maxima, which occur at similar scattering angles to those of pure 325 but are somewhat narrower in width. This indicates that the PVOH is mostly phase-separated from the starch and that the crystalline domain size is rather large. The latter is probably due to the annealing of PVOH, which occurs during the latter stages of baking when the

tray dries (to ~2–3% moisture) and heats to near the mold temperature (~190°C). This is somewhat below the melting temperature of 98% hydrolyzed PVOH (~230°C),¹⁵ so crystallization would be expected to be rapid. Trays made with potato starch and 30% Airvol 523 have much smaller crystalline PVOH peaks. This is expected because the greater numbers of acetate groups tend to interrupt the crystalline domains of the PVOH, and the mold temperature is close to the melting temperature of 88% hydrolyzed PVOH (185°C). Potato starch foams containing 10 and 20% PVOH had proportionally smaller crystalline peaks (data not shown). Foams prepared from corn starch and PVOH had X-ray scans that were similar to potato starch and PVOH.

Interestingly, it has been observed that starch–PVOH foam plates do not stick to the steel molds despite the fact that PVOH is a known adhesive and becomes quite soft above its glass transition temperature (80°C). The crystallinity that develops in PVOH as it is heated and dried in the mold is probably responsible for this property.

Scanning electron micrographs of potato starch foam plates with and without 20% 350 are shown in Figure 2. Cross-sectional views [Fig. 2(A,B)] show that both foams have dense outer skins with small cells and less dense interiors with large cells. The outer skin is more dense because, being close to the hot mold, the starch paste dries rapidly and therefore cannot expand very extensively. The interior of the foam contains mostly large, open cells due to the large amounts of steam venting outside the mold and consequent cell rupture.

Some remnants of swollen starch granules can be seen on the surfaces of the foams, especially those containing PVOH [Fig. 2(C,D)]. The presence of the viscous PVOH solution probably acts as a mechanical resistance, thereby slowing granule swelling somewhat during baking. For foams containing 20% PVOH, some fibers of what is likely PVOH can be seen to be stretched between starch granules. Thus, starch granules and fragments are probably surrounded and bound together by a continuous phase of predominantly PVOH. The interior of the foams [Fig. 2(A,B)] appears more homogeneous. Starch near the surface of the mold dries rapidly so that there is less time for starch gelatinization and granule fragmentation to occur, while granular swelling in the interior is more extensive. Since it has been observed that starch dispersions in which the granules have been completely disrupted (by jet-cook-

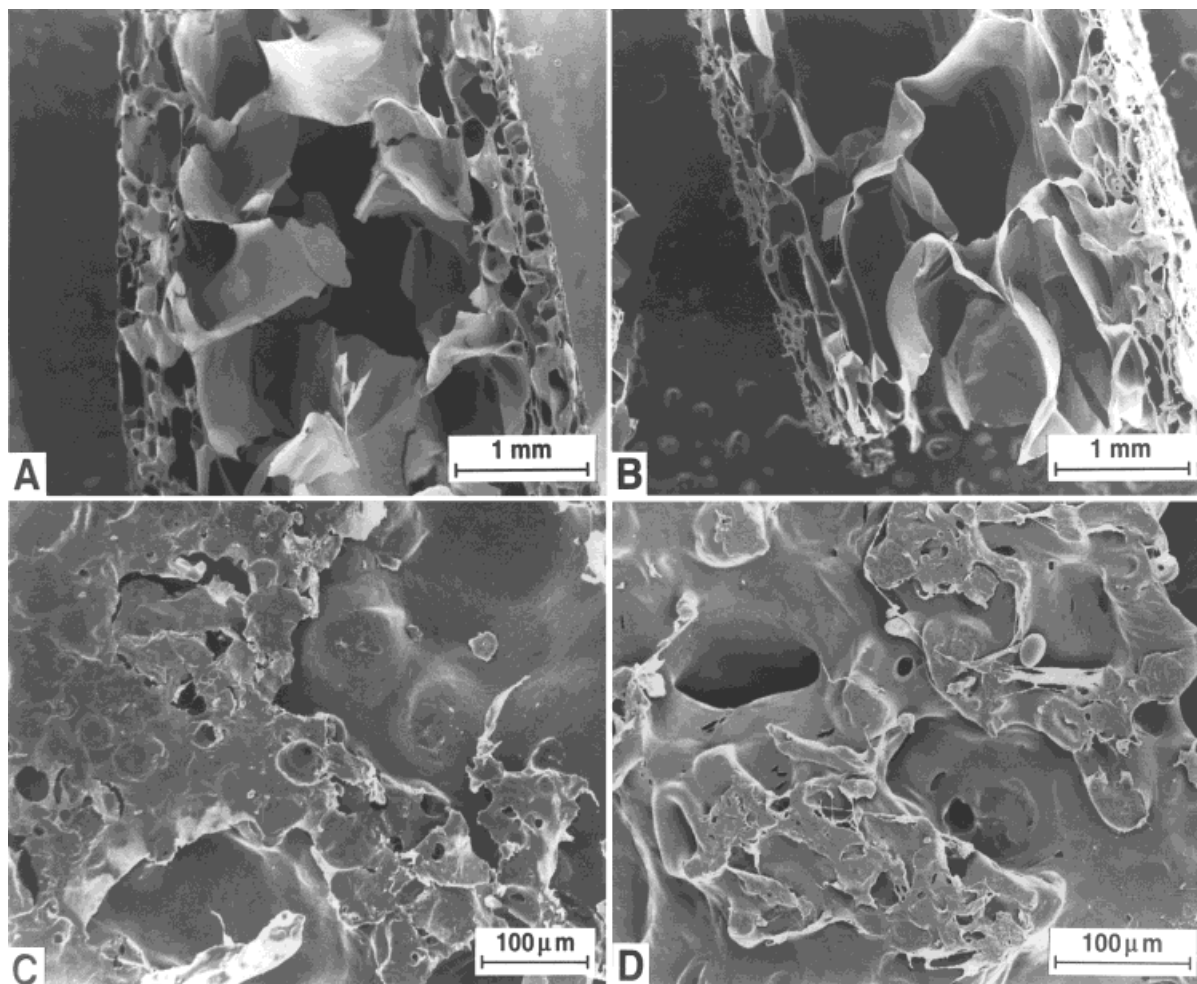


Figure 2 Scanning electron micrographs of cross sections of (A) potato starch and (B) potato starch-20% Airvol 350 foam trays and surfaces of (C) potato starch and (D) potato starch-20% Airvol 350 foam trays.

ing, for example) do not foam during baking,²⁴ it is reasonable to conclude that smaller granular fragments are still abundant in the interior of the foams. Previous microscopy studies have also shown that starch-water slurries heated to boiling contain many swollen granules and granule fragments.²⁶

There have been few studies of the compatibility and morphology of starch-PVOH composites. Information from solution mixtures indicate that these two polymers are largely incompatible.^{2,27} This is supported by the X-ray data above showing PVOH crystallinity. Good mechanical properties of cast and extrusion-blown films suggests, however, that there is at least mechanical compatibility.^{18,28} Starch-PVOH foams prepared by the baking technique appear to be rather unique due to arrangement of starch granule fragments in a dis-

continuous phase and PVOH in a more continuous matrix. This probably results from the low degree of shear or mixing that occurs during the baking process as well as starch-PVOH incompatibility. Extruded starch-PVOH films and foams undergo intense mixing in the extruder, which usually completely disrupts the starch granules and would be expected to result in more homogeneous dispersions of starch and PVOH.

Mechanical Properties

The effects of PVOH level, type, and humidity on the strength (F_m) of starch-PVOH foam trays are given in Figure 3. For all formulations, F_m tends to be greatest near 50% RH. At low humidities, brittleness and crack formation lead to lower strengths, while at high humidities, the plasticiz-

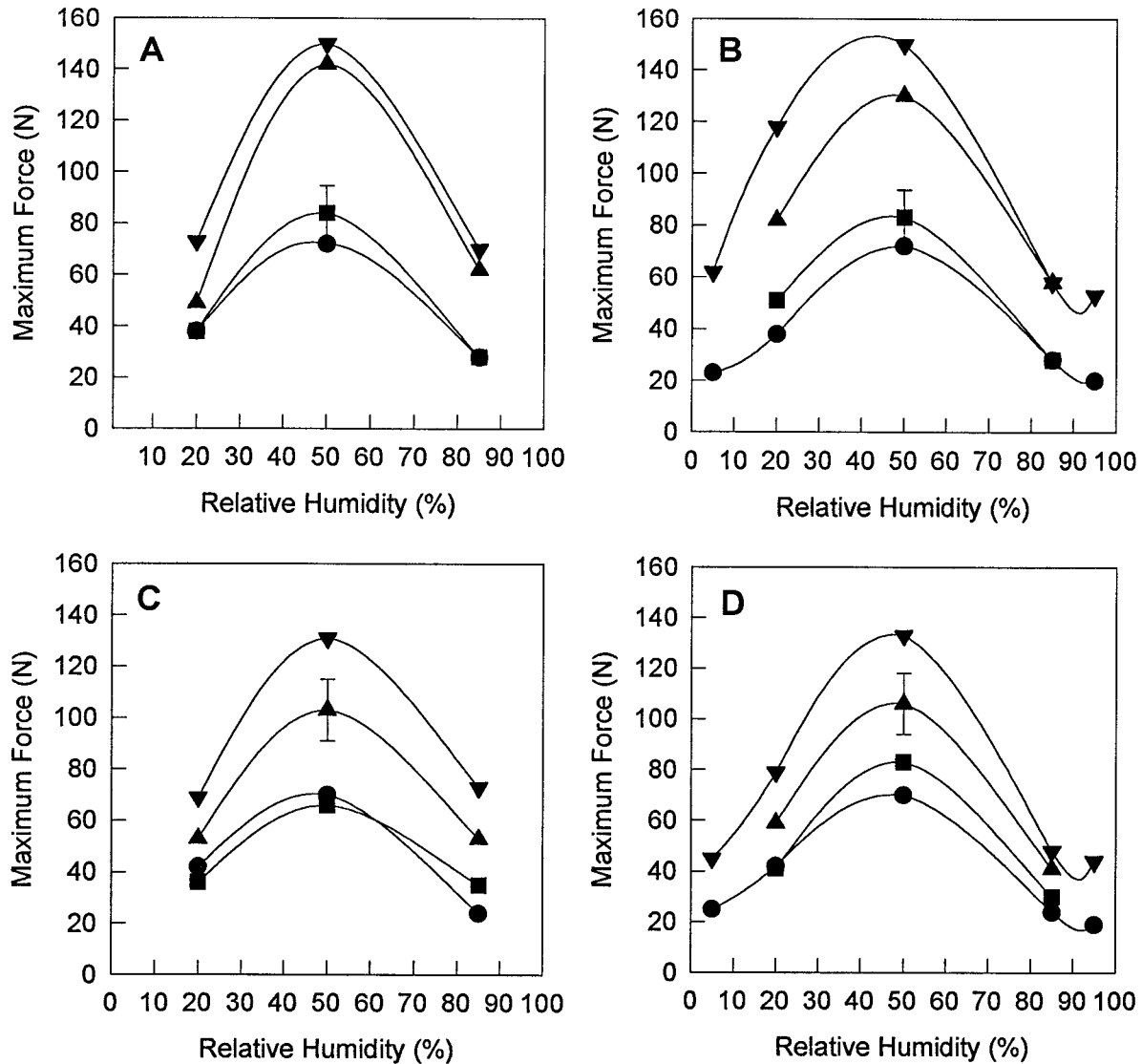


Figure 3 Strengths of foam trays composed of (A) potato starch–Airvol 325, (B) potato starch–Airvol 523, (C) corn starch–Airvol 325, and (D) corn starch–Airvol 523: (●) 0% PVOH, (■) 10% PVOH, (▲) 20% PVOH, and (▼) 30% PVOH.

ing effects of large amounts of absorbed water lower strength. For potato starch–Airvol 325 trays [Fig. 3(A)] at humidities of 50% and above, F_m increases rapidly as the level of PVOH increases from 10 to 20%. Little additional increase in F_m is observed above 20% PVOH. One explanation might be that 20% PVOH may be sufficient to completely surround and bind together the starch granule fragments. For 20% humidity, however, a more continuous increase in F_m with %PVOH is seen.

Data for potato starch–Airvol 523 trays [Fig. 3(B)] are similar to those containing 325, except strengths at low humidities are higher and

strengths at high humidities are slightly lower. These results are not surprising since it is known that PVOH films having a lower degree of hydrolysis (88%) are more flexible¹⁵ and, when blended with brittle starch, would tend to reduce brittle failure seen at low humidities. On the other hand, PVOH having a lower degree of hydrolysis is also more water-soluble, leading to lower strengths at high humidities.

Foams made from corn starch and PVOH [Fig. 3(C,D)] generally have strengths that are lower than those for potato starch and PVOH. This is probably reflects the lower molecular weight of corn starch amylose and amylopectin²⁹ and,

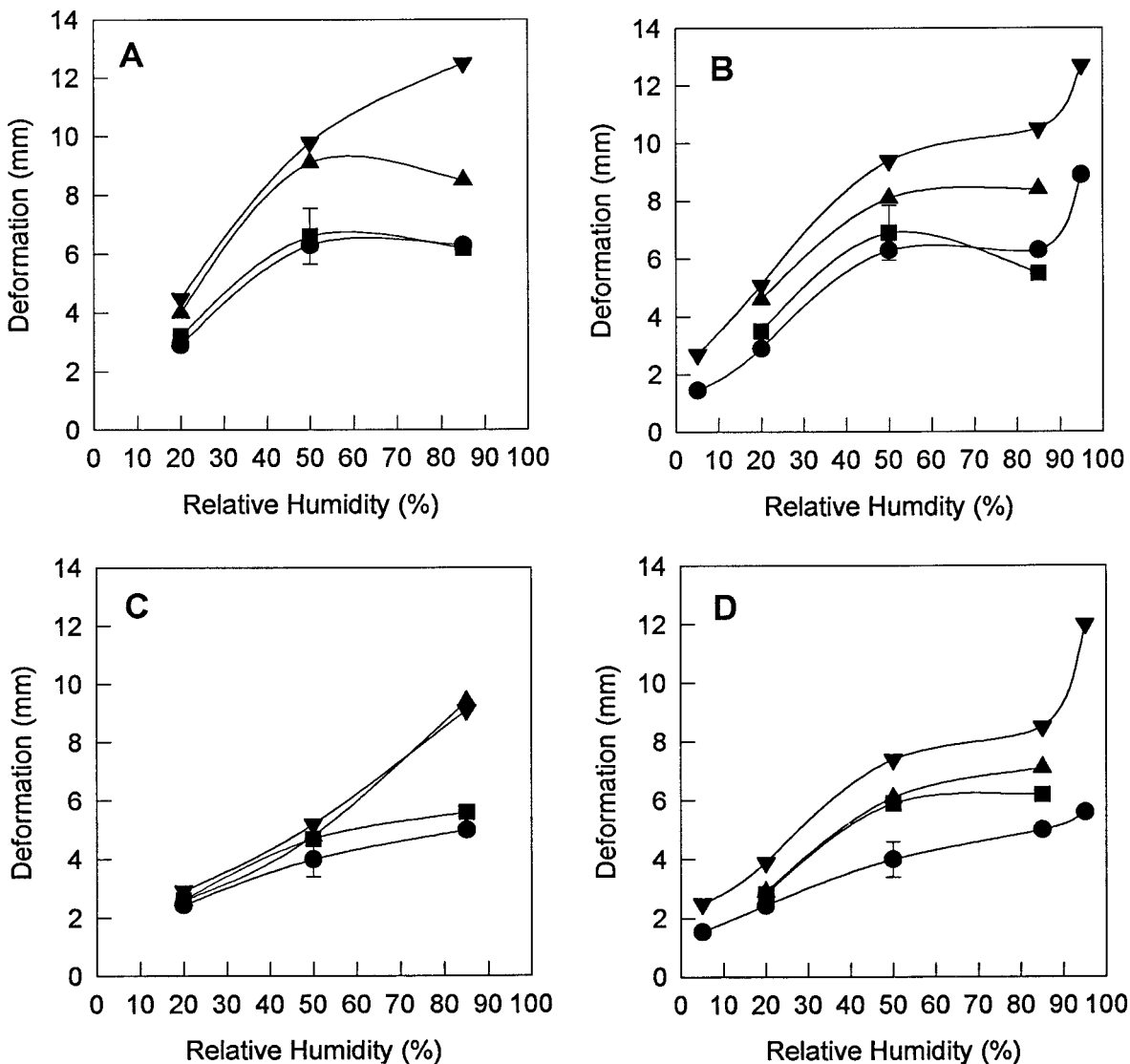


Figure 4 Deformation at yield of foam trays composed of (A) potato starch–Airvol 325, (B) potato starch–Airvol 523, (C) corn starch–Airvol 325, and (D) corn starch–Airvol 523: (●) 0% PVOH, (■) 10% PVOH, (▲) 20% PVOH, and (▼) 30% PVOH.

hence, the lower mechanical strength of corn starch than potato starch.³⁰ It may also be possible that since corn amylose leaches out of the granule more readily than potato amylose in hot water,^{26,31} the PVOH phase may contain more corn amylose and, hence, be less flexible.

Deformation (Lm) data or flexibility of the foam plates are presented in Figure 4. Lm generally increases with increasing humidity due to the plasticizing effect of added water at high humidities. Paralleling the strength data, values of Lm for potato starch [Fig. 4(A,B)] seem to undergo a large increase as PVOH increases from 10 to 20%. Values of Lm at low humidity are somewhat

higher for potato starch–20% 523 trays than for those made with 325. This is consistent with the known greater flexibility of the 88% hydrolyzed PVOH (523). Corn starch–PVOH trays [Fig. 4(C,D)] have lower Lm than those made with potato starch.

The effect of PVOH molecular weight on the mechanical properties of potato starch–20% PVOH foam trays is shown in Table I. Lm seems to be consistently higher for trays made with the higher-molecular-weight PVOH. The largest improvement was for trays containing 98% hydrolyzed PVOH at 20% RH. This trend parallels that seen for pure PVOH in which tensile strength

Table I Effect of Poly(vinyl alcohol) Molecular Weight and Relative Humidity (RH) on the Mechanical Properties of Potato Starch–Poly(vinyl alcohol) 4/1 Foams

PVOH Type	Hydrolysis (%)	M_w	20% RH		50% RH		85% RH	
			Fm (N)	Lm (mm)	Fm (N)	Lm (mm)	Fm (N)	Lm (mm)
325	98.0–98.4	85–146,000	49	3.9	141	9.1	63	8.5
350	98.0–98.4	124–186,000	64	4.8	142	9.6	61	9.0
523	87.0–89.0	85–146,000	82	4.5	130	8.2	57	8.4
540	87.0–89.0	124–186,000	75	4.8	135	8.7	59	8.8

and elongation to break increase with increasing molecular weight.¹⁵ For comparison, mechanical properties of a commercially available expanded polystyrene foam plate are given in Table II. Strengths of starch foams containing 20% PVOH are similar to the polystyrene foam at 50% RH and are somewhat lower at 20 and 80% RH. Flexibilities are greater for starch–PVOH foams than polystyrene foam at 50 and 80% RH and are slightly lower for starch–PVOH foams than polystyrene foam at 20% RH.

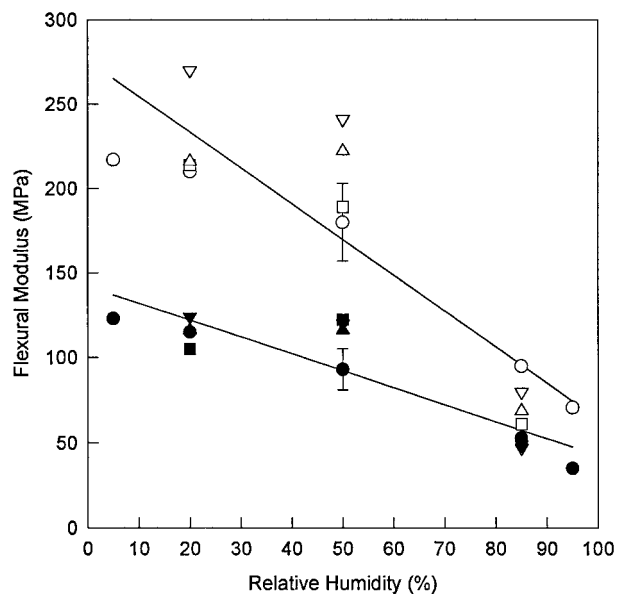
The effect of PVOH level and humidity on the flexural modulus or stiffness of starch foams is shown in Figure 5. Modulus declines with increasing humidity due to the plasticizing effect of the additional water. The presence of 10–30% PVOH in potato and corn starch foams does not appear to significantly affect the moduli. Corn starch foams, however, have moduli almost twice as large as those prepared from potato starch. Part of the reason for the difference is that corn starch foams have a higher density than potato starch foams (Fig. 6). Although data are not available, potato starch may also have a higher equilibrium moisture content than corn starch at a given water activity or humidity. Note in Figure 6 that the density of starch–PVOH foams does not change significantly with PVOH content so that density is not a factor in the changes in mechanical properties with PVOH level seen in Figures 3 and 4.

The effect of crosslinking agents on the strength (Fm) of potato starch–PVOH foams is shown in Table III. Zirconium salts form strong,

water insoluble complexes with hydroxyl-containing polymers, particularly after heating and drying.³² As an indication of the interaction of zirconium acetate with PVOH, the viscosities of starch–20% Airvol 325 batters increased from 120 poise (no Zr acetate) to 190 and 310 poise in the presence of 0.55 and 1.1% zirconium acetate, respectively. Strengths of the starch–PVOH foams, particularly at low humidity, increase as zirconium acetate content increases. For example, values of Fm at 20% RH are 89 and 129% larger for foams containing 0.55 and 1.1% zirconium acetate, respectively, than for those without crosslinking agent. Foam density is slightly higher (13, 29%) for foams containing zirconium acetate (0.55, 1.1%) than those without. This is due to the reduced rate of gelatinization and swelling of

Table II Mechanical Properties of a Commercial Expanded Polystyrene Foam Plate

Density (g/cm ³)	Fm (N)	Lm (mm)	Flexural Modulus (MPa)
0.10	130	5.2	280

**Figure 5** Flexural modulus of potato starch foam trays having (●) 0, (■) 10, (▲) 20, and (▼) 30% Airvol 325 and of corn starch foam trays having (○) 0, (□) 10, (△) 20, and (▽) 30% Airvol 325.

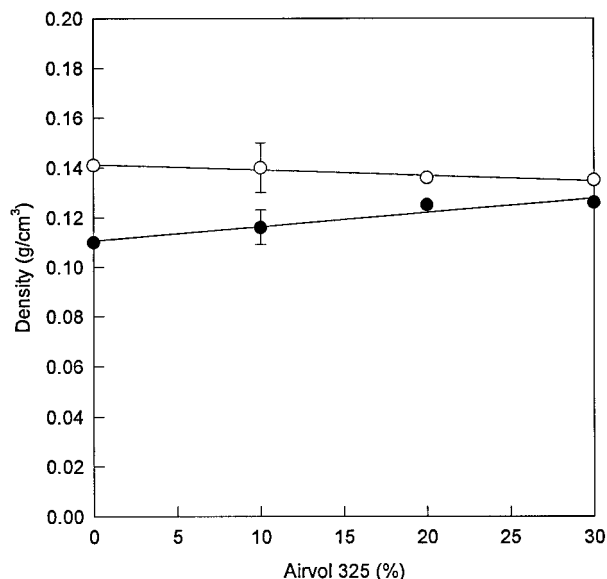


Figure 6 Densities of foam trays composed of (●) potato starch–Airvol 325 and (○) corn starch–Airvol 325.

the starch as it becomes crosslinked. Crosslinking probably increases the effective molecular weight of the starch and PVOH, thus increasing the force needed to cause crack and fracture formation to occur. There also may be less intermixing of the starch and PVOH when a crosslinking agent is present due to higher viscosities of the starch and PVOH phases. This would result in the continuous, load-bearing phase being richer in the stronger PVOH.

Calcium hydroxide is also known to form complexes with PVOH¹⁵ and starch.³³ Data in Table II show that Fm at 20 and 85% RH also improves with addition of Ca(OH)₂. Foam densities for foam trays containing Ca(OH)₂ are even higher than those for zirconium acetate, possibly due to the interaction of Ca with the phosphate groups present in potato starch. Since starch–PVOH foams are baked into their final shape *in situ*,

crosslinking agents can be added, which greatly enhance strength and water resistance. This would be difficult or impossible in extrusion processing since a heavily crosslinked composition would be extremely viscous and could not flow through an extrusion barrel.

Water Resistance

Water absorption (Table IV) decreases with increasing levels of Airvol 325 but increases with increasing levels of 523. This is because 98% hydrolysed PVOH (325) is highly crystalline and cold-water-insoluble, while 88% hydrolysed PVOH (523) is less crystalline and cold-water-soluble. Addition of polyvalent metal salts to the formulations greatly decreased water uptake of the baked foam trays. Water absorption was tested by adding 100 mL of water to a tray and waiting 25 min. Potato starch–Airvol 325 trays made with 0.5% Ca(OH)₂ gained only 27% water while similar trays made with 0.55% zirconium acetate gained 26% water. After the 25-min exposure to water, the surfaces of these trays were slightly soft but the tray remained rigid and useful. In contrast, a tray made with pure potato starch gained over 100% water and became so weak that it would tear or rupture when moved.

Respirometry

Plots of carbon dioxide released versus time for potato starch–Airvol 350 trays are given in Figure 7. For a potato starch tray, 82% of the carbon in the sample was released after 80 days in soil at 23°C. This value normally represents complete biodegradation since some carbon will always be incorporated in microbial cell components. For trays containing 10 and 20% Airvol 350, 73 and 65%, respectively, of the carbon was mineralized in 80 days. Visible pieces of trays containing 20%

Table III Effect of Crosslinking Agents on the Mechanical Properties of Potato Starch–Airvol 325 4/1 Foams

Crosslinking Agent	Amount (%)	Foam Density (g/cm ³)	20% RH		50% RH		85% RH	
			Fm (N)	Lm (mm)	Fm (N)	Lm (mm)	Fm (N)	Lm (mm)
None	0	0.137	49	3.9	141	9.1	63	8.5
Zr acetate	0.55	0.156	87	2.9	158	5.1	71	8.0
Zr acetate	1.1	0.180	108	3.8	174	5.2	78	7.8
Ca(OH) ₂	0.5	0.210	107	2.5	146	3.5	105	7.3

Table IV Effect of PVOH and Crosslinking Agents on the Water Absorption of Potato Starch–Poly(vinyl alcohol) Foams

PVOH Type	Amount PVOH (%)	Crosslinking Agent	Amount (%)	Weight Gain ^a (%)
None	0	none	0	111
325	10	none	0	83
325	20	none	0	75
325	20	Zr acetate	0.55	26
325	20	Zr acetate	1.1	23
325	20	Ca(OH) ₂	0.5	27
523	10	none	0	184
523	20	none	0	145

^a Percentage of weight gain in the tray after exposure to water at 23°C for 25 min. Average standard deviation for weight gain was 13%.

350 were left in the soil after 80 days. These pieces contained predominantly PVOH based on FTIR spectra of the residue (Fig. 8). They had the same length and width (1 cm) as before soil exposure but were much thinner. Scanning electron micrographs (Fig. 9) show that the less-dense center of the tray appears to have been digested away, leaving the two surface layers. The surface layers appear to consist of a continuous phase of PVOH with holes left from the digestion of the starch. Addition of Ca(OH)₂ appears to cause more extensive degradation of a starch–PVOH tray. Figure

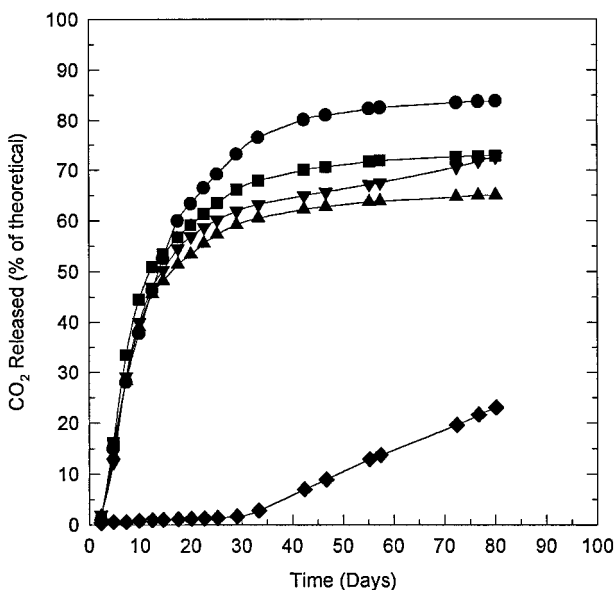


Figure 7 Carbon dioxide released during biodegradation of potato starch foam trays having (●) 0, (■) 10, (▲) 20% Airvol 350, (▼) 20% Airvol 350 and 0.5% Ca(OH)₂, and granular (◆) Airvol 350 in soil at 23°C.

7 also shows that Airvol 350 alone does biodegrade in soil but at a slower rate than starch.

The degradation of PVOH involves the enzymatic oxidation of 1,3 diol moieties to β -diketones followed by a hydrolytic chain cleavage which is also enzyme mediated.^{34,35} Organisms degrading PVOH are thought to all be mesophilic (optimum temperature 35°C). It is also known that 98% hydrolyzed PVOH degrades much more slowly than 88% hydrolyzed PVOH since the former is insoluble in water at room temperature and, therefore, less accessible to enzymes.³⁶ Extrusion blending of starch with Airvol 325 greatly increased the rate of biodegradation of the PVOH presumably due to the greater accessibility of PVOH in the blend.³⁶ In baked starch–PVOH foams, the enhancement in rate of degradation due to the starch may be less since the morphology is more phase-separated than in extrusion blended materials. Previous studies³⁷ have suggested that crosslinking agents enhanced biodegradability of starch–PVOH films, in agreement with our results for Ca(OH)₂.

CONCLUSIONS

The factors that most limit the use of starch in foamed plastic applications are brittleness and loss of strength at low humidity and poor resistance to water. By adding PVOH, starch foams with much improved strength and flexibility at low humidity have been prepared. The good mechanical properties appear to result from a morphology in which the PVOH occupies the continuous phase. Although somewhat inferior to ex-

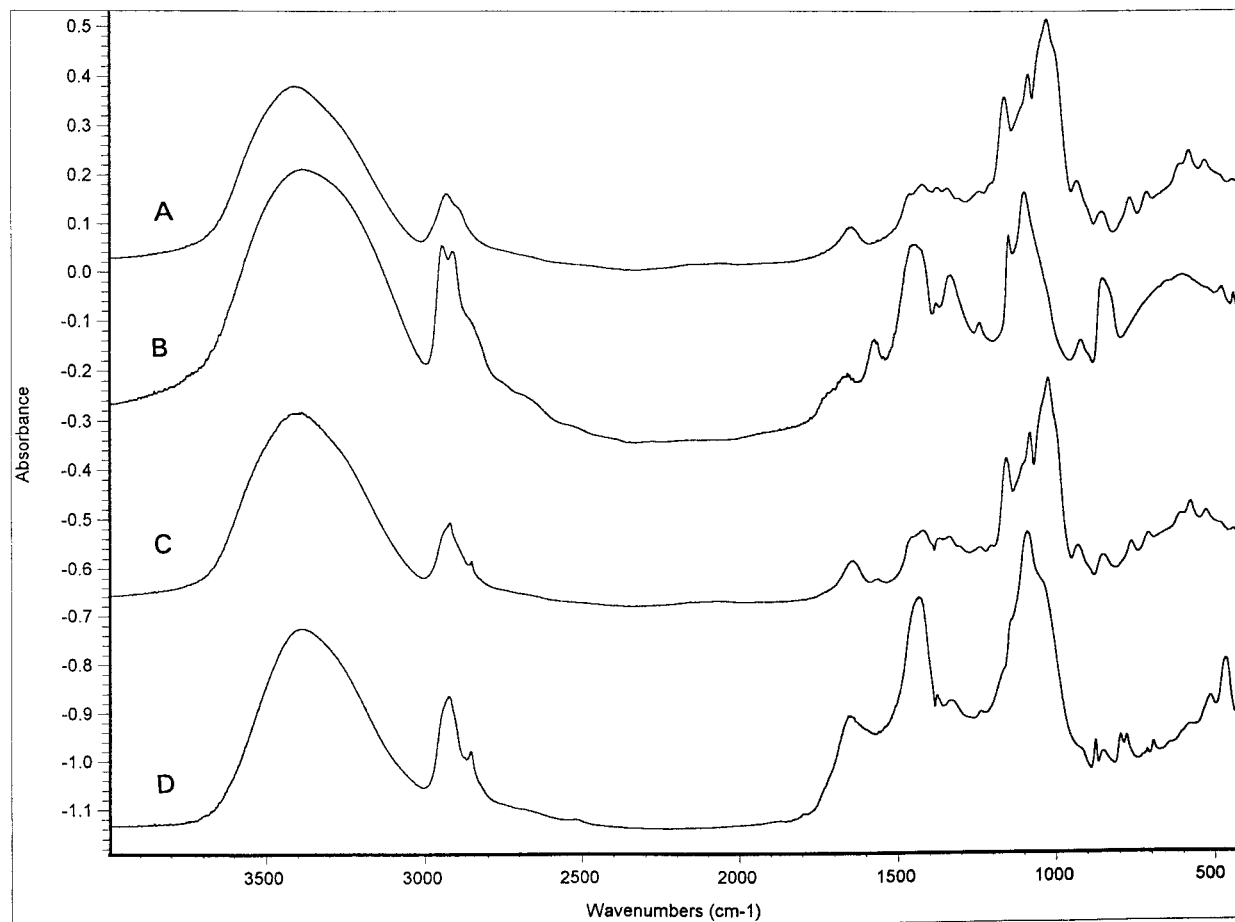


Figure 8 FTIR spectra of (A) starch, (B) Airvol 350, (C) potato starch-20% Airvol 350, and (D) potato starch-20% Airvol 350 after 80 days in soil at 23°C.

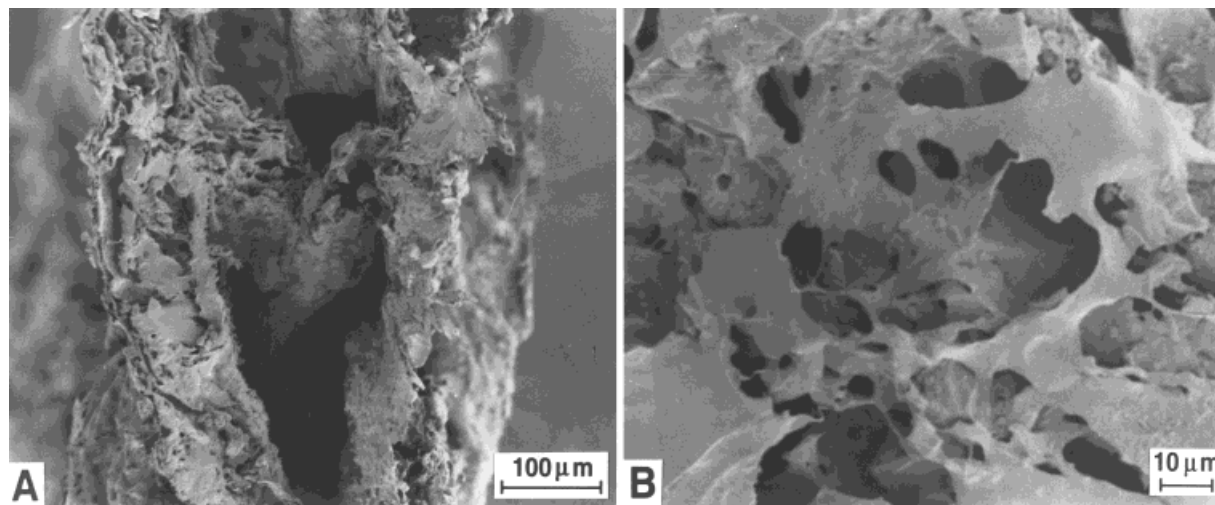


Figure 9 Scanning electron micrographs of (A) cross section and (B) surface of potato starch-20% Airvol 350 foam tray after 80 days in soil at 23°C.

panded polystyrene foam, starch–PVOH foams have mechanical properties that are acceptable for many applications, such as disposable plates, cups, clamshells, and other packaging. The desired strength, flexibility, or stiffness can be tailored by formulating with different PVOH level, PVOH type, starch type, batter solids level,³⁸ and crosslinking agent. Water resistance can be increased by addition of crosslinking agents or by applying an outer coating of a hydrophobic, biodegradable polymer.

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