

Starch-Based Plastic Foams From Various Starch Sources¹

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ABSTRACT

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Corn, tapioca, wheat, rice, and potato starches were extruded with 30% polystyrene and 5% magnesium silicate or 1% polycarbonate or 0.5% azodicarbonamide in a single screw C. W. Brabender laboratory extruder at 140°C barrel temperature, 140 rpm screw speed, and 16% starch moisture content on dry weight basis. The foams did not show presence of either free starch or polystyrene. The components were well

grafted as was confirmed by X-ray diffraction patterns of extrudates and water solubility indexes. The expansion, unit density and water solubility index of the extrudates depended on source of starch and the type of additive. In general, tapioca and corn starches gave the best products with any of the additives.

Plastic foams are used extensively as cushioning materials for the protection of fragile products during transportation and handling. Although useful and desirable for many purposes, the indestructibility of petroleum-based plastics is a growing concern because of their accumulation in the environment. Efforts have been made to provide suitable alternatives to replace these plastics with biodegradable polymers (Altieri and Lacourse 1992; Bhatnagar and Hanna 1993; Bhatnagar and Hanna 1995a,b; Wang et al 1995). These biodegradable polymers can degrade in the environment by action of microorganisms in the presence of moisture. Research on the development of biodegradable polymers derived from renewable resources has gained considerable momentum in recent years and it has been estimated that worldwide demand for degradable plastics will reach 3.2 billion pounds by the year 2000 (Anonymous 1992).

Agricultural crops provide ample sources of biopolymers (starch, protein, and cellulose) which can be readily used to make biodegradable plastics. Commercially available starch foams have successfully replaced polystyrene foams. However, these foams disintegrate immediately when exposed to moisture, limiting their use in environments that are not moisture-free. Bhatnagar and Hanna (1995a,b) developed a process to make starch-based foams replacing as much as 70–80% of the plastic with starch without compromising the functional properties of the end product (Bhatnagar and Hanna 1995a,b). These foams had much better water resistance than did starch foams made from hydroxypropylated starch and polyvinyl alcohol. In this study, we made packaging foams from various starches and compared their physical and mechanical properties.

MATERIALS AND METHODS

Materials

Normal corn, wheat, potato, and rice starches were purchased from A. E. Staley, Inc., Decatur, IL. Tapioca starch was purchased from National Starch and Chemical Co., Bridgeport, NJ. Starches were granulated before extrusion as described by Bhatnagar and Hanna (1994a) to facilitate in feeding. Polystyrene was purchased

from Dow Chemical, Midland, MI. All formulations were based on a starch to polystyrene ratio of 70:30 on a dry weight basis.

Three additives were tried: 1) azodicarbonamide, 2) magnesium silicate and 3) polycarbonate (Bhatnagar and Hanna 1995a–c). Azodicarbonamide, magnesium silicate, and polycarbonate were added separately at rates of 0.5, 5, and 1%, respectively, based on dry weight of starch and polystyrene mixture. The percentages were based on earlier research (Bhatnagar and Hanna 1993; Bhatnagar and Hanna 1995a–c). Starch moisture content was adjusted to 16% dry basis and then blended with polystyrene and other additives in a Hobart mixer for 2 min. The samples were stored overnight in plastic jars to equilibrate before extrusion.

Extrusion

Extrusion was performed in a single-screw laboratory extruder (model 2803, Plasticorder, C. W. Brabender Instruments, Inc., South Hackensack, NJ) with a 1.9-cm barrel diameter, a 20:1 barrel length to diameter ratio, and a 3-mm cylindrical die nozzle. Barrel temperatures of feed, compression, metering and mixing, and die sections were maintained at 60, 140, and 140°C, respectively. The screw speed was 140 rpm. Product temperature and pressure were monitored using a transducer (model GT72HP/6JD8Z1-10K, Gentran, Fremont, CA). Process variables of pressure, barrel and melt temperatures, screw speed, and torque were recorded by a computer interface and controller unit (PL2000, C.W. Brabender) using a Programloader version 1.9.5 software (Brabender [R] OHG). The 3-mm die nozzle used gave continuous cylindrical rope-like extrudates that were cooled at room temperature and broken into finite lengths for testing purposes.

X-ray Diffraction Patterns

X-ray diffractograms were obtained from an X-ray diffractometer (model Pad [V], Scintag Inc., Sunnyvale, CA) equipped with a graphite monochromator and a scintillation detector. The X-ray source was CuK α radiation with 1.5406Å wavelength, 40 kV and 30 mA. Data were collected from $2\theta = 2-35^\circ$ with a step width of 0.02° and a step time of 0.45 sec.

Expansion Ratio and Unit Density

Radial expansion ratios of the extruded foams were calculated by dividing the mean cross-sectional area of the extrudate by the cross-sectional area of the die nozzle. Each calculated value was a mean of 20 observations.

Unit densities of the extrudates were determined using a modified glass bead displacement method originally developed for determining the volume of cookies (Bhatnagar and Hanna 1995a). Glass beads of 0.1-mm diameter were used as the displacement medium.

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Spring Index and Compressibility

Spring index refers to the ability of a material to recover its original shape after it has been deformed. The force required to initially compress the sample and the force required to recompress the same sample after 1 min of releasing the initial load were determined using an Instron universal testing machine (UTM). A 6-mm diameter cylindrical probe was used to compress a sample to achieve a deformation of 2 mm at a loading rate of 30 mm/min (Bhatnagar and Hanna 1995a). The initial gauge length of the sample was 20 mm. Recovery of the sample was determined by dividing the recompression force after 1 min by the initial compression force. An ideal elastic body has a spring index of 1. Higher percent recoveries correspond to materials that are more elastic or resilient.

Compressibility of a sample, i.e., the force necessary to achieve a deformation of 2 mm, was determined using a UTM employing the conditions noted above in measuring spring index (Bhatnagar and Hanna 1995a). A high value was attributed to a sample that was relatively hard, i.e., less compressible, while a lower value was attributed to a sample that was easily compressed.

Water Solubility Index

Water solubility index (Anderson et al 1969) was used to describe water solubility of the extrudates with some modifications. Water solubility of solid peanuts as well as crushed peanuts was determined. Sample were crushed because it was difficult to grind the extrudates to an exact size due to their plastic content. For water solubility of solid peanuts, extrudates were cut into 2.5-cm long pieces, while crushed samples were prepared by crushing the extrudates for 1 min (Powdertec, Tecator, Inc., Silver Spring,

MD). Crushed or solid extrudate (≈ 1 g of each) was dispersed in 100 ml of water in a centrifuge tube. The dispersed samples were held for 30 min with periodic stirring and were centrifuged at $5,000 \times g$ for 10 min. The supernatants were carefully decanted and solute concentrations were determined by phenol sulfuric acid (Dubois et al 1956, Bhatnagar and Hanna 1994) rather than by oven-dry method suggested by Anderson et al (1969). Water solubility indices were determined at room temperature and expressed as percent on a dry matter basis.

Statistical Analysis

All results reported here are means of three or more replicates. Extrusions were made using a randomized complete block design with three blocks representing the replicates. Results were analyzed using SAS version 6.0 statistical software (SAS Institute Inc., Cary, NC). Fisher's protected least significant differences were calculated at a 5% level for each property for comparison purposes.

RESULTS AND DISCUSSION

Five starches and three additives were used in this study. Azodicarbonamide and polycarbonate acted as blowing agents, disintegrating into CO_2 at temperatures of 160 and 170°C, respectively. Magnesium silicate, on the other hand, acted as a nucleating agent for water vapor bubbles without decomposing (Bhatnagar and Hanna 1995c). The decomposition temperature for magnesium silicate was 870°C.

X-ray Diffraction

X-ray diffractograms for native cereal starches (corn, wheat, and rice) had a typical A pattern, while tuber starches showed B pattern. These diffractograms are well documented in literature and therefore not shown here (Zobel 1988). Figure 1 shows representative X-ray diffractograms for native corn starch, extruded corn starch, ground polystyrene, and corn starch-based plastic foam. The X-ray diffraction pattern of extruded corn starch showed a trace of V pattern due to complex formation between starch and native lipids. The X-ray pattern of polystyrene showed major peaks at 9 and 19 Å. The X-ray diffraction pattern of corn starch-based polystyrene foam was intermediate compared to that of the extruded starch and polystyrene pattern. The characteristic A pattern of native corn starch and the polystyrene pattern were lost. Instead, a pattern resembling that of extruded starch was observed. Similar patterns were observed for wheat, rice, potato, and tapioca starch-based foams with all additives and hence not reported here. Loss of the characteristic polystyrene pattern confirmed that extrusion resulted in grafting of starch onto polystyrene. Chinnaswamy and Hanna (1991) also showed that grafting structures were formed between starch and polystyrene molecules during reactive extrusion processing. Gel permeation chromatography was used to confirm the presence of grafting.

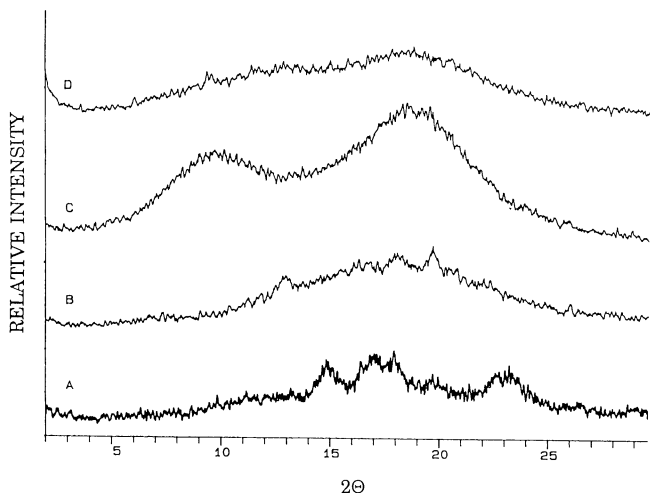


Fig. 1. X-ray diffractogram of A) native corn starch, B) extruded corn starch, C) polystyrene, and D) corn starch-based plastic foam.

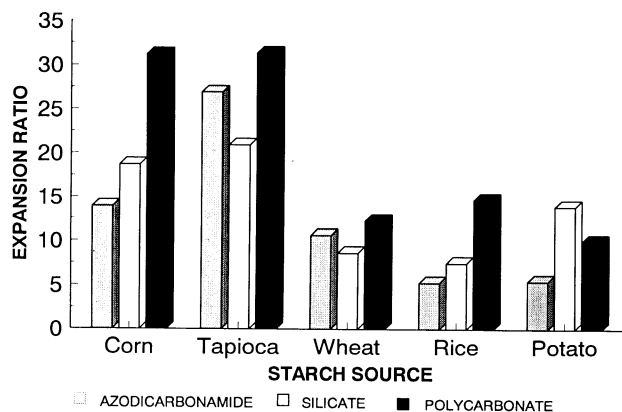


Fig. 2. Effects of source of starch and additives on expansion ratio.

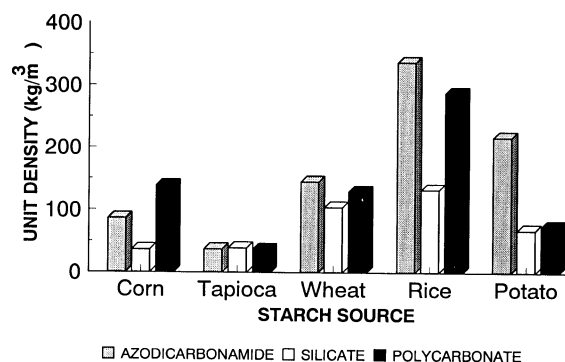


Fig. 3. Effects of source of starch and additives on unit density.

Expansion Ratio and Unit Density

Expansion ratio and unit density are generally inversely related and, therefore, when data on expansion ratio are presented, discussion on unit density becomes less important. In this article, however, both are included because these foams are to be used as packaging material, and unit density information may be useful in evaluating the shipping costs. Expansion ratio and unit density were dependent on source of starch ($P > F$ 0.0001) and type of additive ($P > F$ 0.003). These results are presented in Figures 2 and 3, which show that expansion ratios and unit densities were inversely related to each other as stated above. Polycarbonate gave the highest expansion ratios followed by magnesium silicate and azodicarbonamide for all starches. From the standpoint of higher expansion and lowest unit density, tapioca and corn starches were the best, with expansion ratios ranging from 20.9 to 31.4 and from 13.8 to 31.2, respectively, and unit densities ranging from 36 to 39 kg/m³ and from 30 to 86 kg/m³, respectively. For wheat, rice, and potato starches, the expansion ratios were not significantly different ($P > F$ much greater than 0.1). Bhatnagar and Hanna (1995a) reported unit density of 23 to 59 kg/m³ for commercial starch or starch-based plastic foams, which compares favorably with tapioca and corn starch-based foams in this study. The unit densities of all the foams including commercial starch foams were much higher than commercial polystyrene foams (8.9 kg/m³) (Bhatnagar and Hanna 1995a). One factor contributing to density was the shape of the product. The commercial polystyrene foam peanuts were S- or boomerang shaped as compared to the cylindrical shapes for starch-based foams. The shape, however, can be altered by changing the shape of the die hole. Altieri and Lacourse (1992) reported that densities of commercial starch foams were dependent on the shape of the product, with cylindrical shapes having the highest densities.

The variation in properties of different starches has also been noted by other authors (Mercier and Feillet 1975, Guidolin et al 1984). Wang et al (1995) reported lower density for wheat starch foams compared to those of corn starch extrudates while preparing a 100% starch-based cushioning material. Our results indicate that corn starch performed better than the wheat starch. Thus optimum extrusion process conditions and type of additive for each type of

starch need to be identified to get the best product. This is currently under investigation.

The three types of additives also affected the cell sizes, when viewed in a microscope. The color of the extrudates, however, depended on the additive as well as source of starch. Magnesium silicate gave white extrudates. The addition of azodicarbonamide (yellow in color) gave yellowish color to the product.

Spring Index and Compressibility

Greater spring index indicates greater degree of rebound of the product when squeezed; lower compressibility is indicative of the relative ease with which a product can be squeezed. Thus, spring index is directly related to resiliency, while compressibility is related to the relative softness or hardness of the product. Products that have high spring indexes but low compressibilities are most suitable for packaging. There is no general rule of thumb for these two values. Bhatnagar and Hanna (1995a) found spring index values of 0.97 and 0.96 and compressibility values of 97 and 136 kPa for commercial polystyrene and commercial starch foams, respectively. Comparing these values with results reported in Table I show that, for corn and tapioca starches, the spring index and compressibility values were quite comparable to that of com-

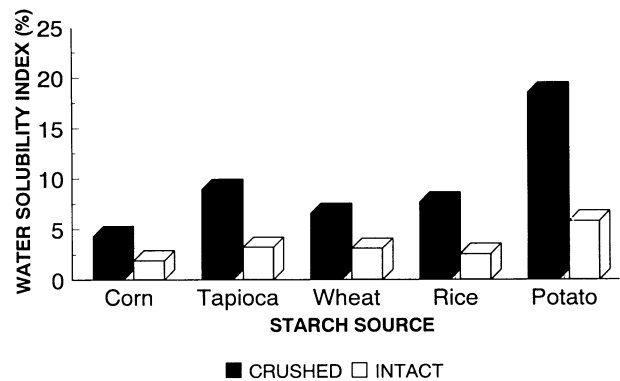


Fig. 4. Comparison of water solubilities of powdered and crushed foam peanuts made from corn starch using magnesium silicate additive.

TABLE I
Spring Indices and Compressibilities of Starch-Based Plastic Foams^a

Source	Spring Index ^b			Compressibility (kPa) ^c			Water Solubility Index (%) ^d		
	A	B	C	A	B	C	A	B	C
Corn	0.90	0.91	0.94	109	59	51	9.2	4.3	3.6
Tapioca	0.92	0.91	0.92	79	58	61	10.3	8.9	9.9
Wheat	0.85	0.85	0.72	160	161	98	8.6	6.6	8.5
Rice	0.85	0.88	0.86	760	220	246	2.1	7.6	6.9
Potato	0.91	0.90	0.92	388	147	62	6.8	15.7	18.6

^a A = azodicarbonamide, B = magnesium silicate, C = polycarbonate.

^b Least significant difference (LSD) = 0.05.

^c LSD = 126 kPa.

^d LSD = 2.4%.

TABLE II
Pressure at the Die and Torque Requirements for Starch-Based Foams^a

Source	Pressure (Mpa) ^b			Torque (Nm) ^c		
	A	B	C	A	B	C
Corn	13.33	5.87	4.92	75.2	77.3	56.4
Tapioca	6.02	5.77	5.53	68.8	63.5	61.8
Wheat	12.89	4.29	3.54	72.2	54.6	54.4
Rice	12.93	3.93	2.87	91.5	54.4	40.5
Potato	12.18	4.14	3.45	89.4	51.4	47.9

^a A = azodicarbonamide, B = magnesium silicate, C = polycarbonate.

^b Least significant difference (LSD) = 0.84 MPa.

^c LSD = 10.9 Nm.

mercial polystyrene loose-fill. Potato starch extrudates had good spring indexes with all the additives, but compressibility values were dependent on type of additive, with magnesium silicate and polycarbonate giving comparatively better products. Spring indices were significantly affected by the type of starch ($P > F$ 0.0003) but not by the type of additive ($P > F$ 0.6972). Compressibilities were, however, significantly affected both by the type of starch ($P > F$ 0.0001) and type of additive ($P > F$ 0.0004) (Table I).

Water Solubility Index

Commercial polystyrene foam was essentially insoluble; commercial starch loose-fill peanuts disintegrated immediately in water. Not all starch-based foams disintegrated when dissolved in water, but with time the water soaked through the pores and some starch leached out. Water solubility indexes for various samples (Table I) show a wide range from 2.1–18.6%. This solubility is much lower as compared to solubility of gelatinized corn starch reported in literature. The lower solubility is typically due to grafting of starch with polystyrene. The solubility of solid peanuts of starch-based foams was also determined. Fig. 3 compares the water solubility of solid peanuts with crushed peanuts for starch foams made with magnesium silicate as additive. The foam peanuts had lower water solubility compared to crushed samples (Fig. 4). The difference was due to limited surface area of the solid peanuts compared to ground peanuts. The solid peanuts typically had very thin film of polystyrene on the surface which prevented absorption of water and leaching of the soluble material. The water solubility indexes were not significantly different. As mentioned earlier, the starch was well grafted with the plastics in these foams, therefore the water solubilities were low. Thus starch-based plastic foams can be made from different starches using three additives.

Process Parameters

Torque and pressure at the die are shown in Table II. Higher torque or pressure did not necessarily result in higher expansion ratio or lower unit density. These effects were confounded by the interaction between type of additive and the source of starch with ($P > F$ 0.025) for torque and ($P > F$ 0.0001) for pressure. Tapioca and corn starches gave highly expanded products, but the pressures at the die for these foams were inversely related to expansion ratio for different type of additives. Addition of magnesium silicate and bicarbonate resulted in lower pressures than did the azodicarbonamide. All the starch-based foams extruded with ease with minimum fluctuations in pressure. The coefficient of variation ranged from 2 to 12% for pressures of 2.87–13.33 MPa.

CONCLUSIONS

One of the major conclusions of this study obviously is that starch-based foams can be prepared from different starch sources replacing 70% polystyrene with biopolymer starch. Functional starch-based plastic foams can be prepared from different starch sources depending on their availability. The properties of the resultant products depended on the additives and source of starch. In general, the polycarbonate and magnesium silicate gave the best results for all the starches.

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