

Starch-Based Microcellular Foams

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ABSTRACT

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The present study was initiated to develop alternative methods of preparing microcellular starch-based foams from semirigid aqueous gels (aquagels) and to characterize the impact of the preparative method on the physical and mechanical properties of the foams. Semirigid aquagels were made from 8% solutions of wheat starch, corn starch, and high-amylose corn starch. The aquagels were freeze-dried or dehydrated in ethanol (alcogels), and either dried in air, extracted with liquid CO₂ and dried in CO₂ vapor, or critical point-dried (CPD). The wheat and corn starch foams prepared by air-drying alcogels had densities and mechanical properties similar to those that were extracted by liquid CO₂ or the CPD samples. Foams of high-amylose corn starch could only be made from alcogels by liquid CO₂ extraction and CPD. The mean densities of CPD wheat, corn, and high-amylose corn starch foams were 0.23, 0.24, and 0.10 g/cm³, respectively. The compressive strength and modulus of elas-

ticity of the foams were positively correlated with density. The wheat and corn starch foams were weaker under tension when compared to compression, due probably to the abundant voids and imperfections in the foam matrix that provided sites for cracks to propagate. Wheat and corn starch foams deformed under compressive stress also had a high range in elastic modulus (21–35 MPa) and low elastic recovery (13%) compared to freeze-dried and high-amylose corn starch samples (3–8 MPa and 27–36%, respectively). The range in thermal conductivity of the starch foams (0.024–0.043 W/m·K) was comparable to that of commercial insulation materials. The foam matrix was composed of pores (<2 μm) defined by a network of strands in which were embedded remnants of starch granules. The remnants were most abundant in wheat and corn starch samples. Freeze-dried foams had large, nonuniform pores with a continuous cell-wall structure that conferred relatively high tensile strength.

Starch is the principal constituent of wheat endosperm (64–74%) and of other cereal grains (MacMasters et al 1971), and it is a valuable source of food. The United States has depended heavily on exports for many years to market the wheat produced each year. However, some countries that were once largely dependent on U.S. exported wheat have become nearly self-reliant or have become exporters themselves. Efforts have been initiated to generate new markets for domestic wheat by developing wheat-based, nonfood products. Starch is an important resource for nonfood products because of its low cost and abundant supply. Approximately 4.5 billion pounds of starch, primarily corn starch, are already used annually in the United States for industrial applications (U.S. Congress 1991). Some current nonfood uses for starch include chemicals derived from starch fermentation, starch-containing plastics, starch adhesives, starch-based sizing products, soil conditioners, and extruded-starch packing materials (Kennedy and Fischer 1984, Mentzer 1984, Otey and Doane 1984, Mohamed 1990, U.S. Congress 1991). To further expand nonfood markets for cereal grains, new starch-based products must be developed.

One potential industrial application for starch is in the fabrication of microcellular foams. Microcellular foams are low density, solid foams composed of a solid matrix with air-filled pores a few micrometers or smaller in diameter. Microcellular foams are of commercial interest because of their unique physical and mechanical properties (Miller 1994). Polyurethane foams are commercially important microcellular foams with low thermal conductivity that can contain starch as a filler (Cunningham and Carr 1990, Cunningham et al 1991). Cunningham et al (1991) found that 10% starch, or less, in polyurethane formulations did not adversely affect the thermal and mechanical properties of the foams.

Another class of microcellular foams that has gained a renewed interest is the aerogels (Fricke 1985). Aerogels were first described in 1931 (Kistler 1931). They are produced from firm aqueous gels (aquagels) by displacing water within the gel matrix with air. Aerogels cannot be prepared by simply air-drying aquagels, because surface tension compresses the gel into a dense material

(Fricke 1985). Aerogels are typically produced by exchanging the water within the matrix of the aquagel with a solvent such as acetone or ethanol, thus forming an alcogel. The alcogel is then placed in an autoclave where the solvent is exchanged with liquid CO₂. The autoclave is finally heated beyond the critical temperature and pressure of CO₂, at which point, it can be slowly depressurized without subjecting the sample to the effects of surface tension.

Aerogels have low density, extremely small cell size, low thermal conductivity, and are often translucent or transparent (Fricke 1985). Aerogels have been produced from many different aquagels made from materials that include alumina, tungsten, ferric and stannic oxide, nickel tartrate, cellulose, cellulose nitrate, silica, egg albumin, and gelatin (Kistler 1932). Aqueous starch solutions gelatinize upon heating and form semirigid aquagels after cooling. The objective of the present study was to develop alternative methods of preparing microcellular starch-based foams from aquagels and to characterize their physical and mechanical properties.

MATERIALS AND METHODS

Unmodified wheat starch (Midsol 50, Midwest Grain Products, Inc., Atchison, KS) and unmodified regular (Melogel) and high-amylose (Hylon VII) corn starches were utilized (National Starch and Chemical Company, Bridgewater, NJ). The wheat and corn starches were composed of ~28% amylose and 72% amylopectin. The high-amylose corn starch contained ~70% amylose and 30% amylopectin.

Cylindrical Samples

Solutions of 8% starch (w/w) were made using distilled water. Wheat and corn starch solutions (500 ml) were mixed at 75 rpm in a viscoamylograph (Brabender, South Hackensack, NJ) and heated to ~95°C at a rate of 2°C min⁻¹. The temperature of the starch solution was maintained at 95°C while mixing continued until the peak viscosity was reached (~350 and 650 BU for wheat and corn starches, respectively).

The gelatinized starches were poured into cylindrical plastic molds (1.56-cm dia., 11.4-cm length), covered with aluminum foil, and refrigerated (5°C) overnight. The gelatinized starches set into semirigid aquagels that synerged sufficiently to facilitate removal of the aquagel within 24 hr. The solvent water in the aquagels was gradually displaced with ethanol by batch equilibration with

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a succession of ethanol baths. The number of baths and the ethanol concentration of each bath differed for samples of different thicknesses. Excessive shrinkage at the gel surface caused tears in the surface of slab gels, which were much thicker than the cylindrical samples. Consequently, the slab samples required more equilibration steps than did the cylindrical aquagels. Each bath contained two volumes of solvent for each volume of gel. The equilibration time for each bath was 24 hr for cylindrical samples. The sequence of baths was one time in 70% (w/w) ethanol and three times in 100% ethanol for the wheat and corn starch aquagel cylinders.

High-amylose corn starch had a much higher gelatinization temperature than wheat or regular corn starch and could not be gelatinized using the viscoamylograph. High-amylose corn starch solutions (8%, w/w) were heated at $2^{\circ}\text{C min}^{-1}$ in a 1,000-ml pressure reactor (Paar Instrument Co., Moline, IL) equipped with a mixer and controller (model 4843). The solutions were mixed at 330 rpm and heated to 140°C . The solutions were then cooled to 90°C using an internal cooling coil. The solutions were poured into cylindrical molds, covered, and refrigerated as previously described. The high-amylose corn starch aquagels did not shrink as much as the wheat and corn aquagels and could be placed directly in 100% ethanol without bending or tearing. Consequently, the high-amylose corn aquagels were successively equilibrated for 24 hr in each of four baths containing 100% ethanol.

Slab Samples

High-amylose corn starch solutions (8%, w/w) were gelatinized as described above, poured into slab molds ($38 \times 21 \times 1.9\text{-cm}$), and refrigerated (5°C) overnight. The aquagels were removed from the molds and soaked successively at least 24 hr in each of four baths of 100% ethanol.

Slab samples of gelatinized wheat and corn starch required volumes greater than could be prepared using a viscoamylograph. Consequently, large (7 L) batches of starch solution (8%, w/w) were prepared in a round-bottom flask by rigorously mixing while heating in a boiling water bath. Viscosity readings were taken intermittently with a viscometer (Brookfield, model RVT, Stoughton, MA) to determine when gelatinization was complete. The starch solutions were mixed and heated (95°C) until viscosity had peaked and begun to decrease. The starch solutions were poured into slab molds ($35 \times 43 \times 1.9\text{ cm}$) and refrigerated overnight.

The aquagels were removed from the molds and soaked 48 hr in successive baths of ethanol (40, 70, 90% and three changes of 100% ethanol).

CPD of Alcogels

Drying methods used to fabricate starch foams included freeze-drying of aquagels and air-drying, liquid CO_2 extraction, and CPD of starch alcogels. For CPD of starch alcogels, slabs and cylinders equilibrated in 100% ethanol were placed in an autoclave designed to withstand pressures in excess of 12 MPa. The autoclave was first filled with 100% ethanol and then loaded with the slabs and cylinders. The autoclave was quickly drained of ethanol and filled with liquid CO_2 . Several changes of CO_2 were made each day to displace ethanol that diffused out of the sample. The CO_2 extraction was completed over a five-day period, after which the autoclave was drained to approximately half full so that the liquid CO_2 level just covered the samples. The autoclave was then heated and further pressurized above the critical temperature (30.92°C) and pressure (7.375 MPa) of CO_2 . After reaching the critical point of CO_2 , the chamber was slowly depressurized and the dried foam samples were removed.

Freeze-Drying of Aquagels

Slabs of aquagels ($38 \times 21 \times 1.9\text{-cm}$) were removed from molds and placed in a freezer (-10°C) overnight. The aquagels were placed on trays in a freeze-drier (Virtis, Gardner, NY) equipped with heating trays that were heated to 60°C after the chamber pressure dropped below 1.33×10^{-5} MPa. Typically, the samples freeze-dried within three days. Cylinders tended to fracture during the freezing process and did not yield samples that could be tested for mechanical strength. Consequently,

mechanical tests were performed on freeze-dried slabs cut into 1-in. squares.

Air-Drying of Alcogels

Air-dried slabs and cylinders were made by placing samples equilibrated in 100% ethanol on perforated trays covered with sheets of Whatman filter paper. The trays were enclosed in a polyethylene chamber that was continuously flushed with a stream of air that had been dried by filtering through anhydrous CaSO_4 . The samples remained in the chamber for one day beyond the time that ethanol odor could be detected in either the effluent or the sample (approximately four days).

Liquid CO_2 Extraction of Alcogels

Alcogels were placed in an autoclave and equilibrated with liquid CO_2 , as described for the CPD process. After the fifth day of CO_2 equilibration, the autoclave was slowly depressurized without reaching the critical temperature and pressure of CO_2 . The samples were removed from the chamber and tested.

Physical and Mechanical Tests.

Thermal conductivity was measured at a mean temperature of 22.7°C on three sets of slab samples for each treatment according to standard methods (ASTM C 177-85) using a thermal conductivity instrument (model GP-500, Sparrell Engineering, Damarascotta, ME). Readings were taken at 1-hr intervals as the instrument approached thermal equilibrium. The mean value of at least three measurements was recorded at thermal equilibrium.

Cylindrical samples of wheat and corn starch tended to shrink while equilibrating in ethanol and often developed a curvature in their length. The dried cylindrical foams were therefore machined into cylinders on a lathe with the final length approximately twice the diameter. The cylinders were conditioned at least 48 hr in an incubator held at 23°C and 50% rh (ASTM D 1621-73). The samples were tested in compression using a universal testing machine (model 4500, Instron Corp., Canton, MA). Compressive strength was measured at 10% deformation according to ASTM methods (D 1621-73, E6-89). The modulus of elasticity (E) was measured as the ratio of stress to the corresponding strain below the proportional limit of the force-deformation curve. Mechanical tests were performed on four samples for each of four replicates made per treatment.

Density was determined from measurements of sample weight and volume. Moisture content was determined for samples equilibrated at 50% rh for more than two days according to AACC method 44-15A (AACC 1983).

SEM

Samples of expanded-bead polystyrene, explosion puffed wheat, and freeze-dried wheat foams were cut with a single-edged razor blade, using a slicing motion to avoid crushing the sample. CPD starch foams and silica aerogel samples were prepared using fragments of samples that were fractured with forceps. Alternatively, starch foam fragments were prepared from foams equilibrated in 100% ethanol before being plunged into liquid nitrogen, cryofractured (Humphreys et al 1974), and critical-point dried.

All samples were glued to aluminum specimen stubs using two-component 5-min epoxy. Samples were coated with $\sim 150\text{\AA}$ of gold in a Polaron E5100 sputter coating unit (Hatfield, PA). Polystyrene samples were viewed and photographed immediately after mounting and coating, because the sample tended to collapse with exposure to the high vacuum and the electron beam in the SEM. All other samples were stable. The samples were viewed in a Hitachi S530 scanning electron microscope (Tokyo, Japan) and photographed onto $4 \times 5\text{-in.}$ Kodak Tri-X film.

Light Microscopy

Starch foams in 100% ethanol were infiltrated and embedded in glycol methacrylate. Samples were sectioned $2\text{--}4\ \mu\text{m}$ thick using a Sorvall Porter-Blum MT-2 ultramicrotome equipped with a glass knife. Sections were stained with I_2KI (Phillips 1981), rinsed, and mounted in water. The sections were subsequently viewed and photographed in a Zeiss Universal Research microscope.

RESULTS

Sample Preparation.

The wheat and corn starch aquagels were slightly translucent when removed from the molds. As the water within the aquagel matrix was displaced with ethanol, however, the gels began to shrink and turn opaque and white. The volume of wheat and corn starch alcogels ranged from 35 to 40% of the original volume of the mold. In contrast, the high-amylose corn starch alcogels ranged from 60 to 72% of the mold volume.

Air-drying of Alcogels

Alcogels dried in air (ethanol in contact with air, Table I) were subjected to much smaller surface tension forces compared to air-dried aquagels (water in contact with air, Table I). The air-dried wheat and corn starch alcogels did not collapse into a thin film during the drying process as did the air-dried aquagels. The air-dried wheat and corn starch alcogels had a mean dry density comparable to samples dried by liquid CO₂ extraction and CPD. The high-amylose corn starch alcogels could not be air-dried without collapsing into a dense, translucent mass (Table I).

CO₂ Extraction and CPD

Starch alcogels that were dried using the CO₂ extraction or the CPD processes were similar in density and appearance. Starch alcogels dried by these processes were subjected to very low surface tension forces (Table I), and they had final volumes similar to those of their alcogels. The matrix of the high-amylose corn starch alcogels did not collapse when dried by either of these two processes. The high-amylose corn starch foams were white and opaque; their final dry density was much lower than that of wheat and corn starch foams and only slightly higher than the lowest theoretical density (Table I).

Freeze Drying

Slab aquagels frozen overnight typically formed large ice crystals that disrupted the structure of the aquagel matrix. The

freeze-dried samples of wheat and corn had large cavities where the ice crystals had been present previously and often formed cracks while drying. Samples of high-amylose corn starch were so adversely affected by the freeze-drying process that they readily collapsed into fragments and were not tested further. The wheat and corn samples were very brittle when first removed from the freeze-drier but became much more resilient when conditioned to 50% rh. The density of the freeze-dried wheat and corn starch was comparable to that of the high-amylose corn starch foams dried by CO₂ extraction or CPD (Table I).

Physical and Mechanical Tests

Samples conditioned at 50% rh had a mean moisture content of 11.5%, which largely accounted for the higher density of conditioned foams (Tables I–III). However, the density of conditioned samples may also have been affected by dimensional changes as the samples aged. The thermal conductivity for air-dried alcogels was higher than for samples prepared by CO₂ extraction or CPD (Tables II–IV). There was no significant difference in thermal conductivity for samples prepared by CO₂ extraction or CPD. The freeze-dried wheat (Table II) and corn (Table III) starch samples had among the highest thermal conductivities recorded for any of the drying techniques, even though they had the lowest conditioned densities. The high-amylose corn starch foams (Table IV) had a much lower thermal conductivity than any of the samples tested. The expanded-bead polystyrene sample (Table IV) had a thermal conductivity similar to those of the CPD wheat (Table II) and corn (Table III) starch foams, even though its density was much lower.

The mechanical properties of the starch foams appeared closely related to density. The relationship between density and compressive strength was nearly linear for starch foams consisting of a wide range in density (Fig. 1). A similar relationship was observed between modulus of elasticity and density (data not shown).

The mean compressive strengths and densities for wheat and corn starch samples were higher for air-dried samples than they were for CO₂ extracted and CPD samples, although the differences

TABLE I
Dehydrated Density of Starch Foams Dried Under Varying Conditions

Substance	Environment	Surface Tension (mN/m)	Density, g/cm ³			
			Theoretical ^a	WS ^b	CS ^c	HACS ^d
Water	Air (18°C)	73.05 ^e	0.08
Ethanol	Air (0°C)	24.05	0.08	0.24 (0.008) ^f	0.25 (0.02)	1.31 (0.010)
CO ₂	CO ₂ Vapor (20°C)	1.16	0.08	0.23 (0.01)	0.24 (0.004)	0.11 (0.002)
CPD-CO ₂ ^g		0.0	0.08	0.23 (0.008)	0.24 (0.02)	0.10 (0.002)
Frozen water	Air (freeze dry)	0.0	0.08	0.11 (0.003)	0.10 (0.002)	...

^aLowest density that can be achieved from a gel based on the original gel volume and solids content.

^bDensity of foam sample made from unmodified wheat starch.

^cDensity of foam sample made from unmodified corn starch.

^dDensity of foam sample made from high-amylose corn starch.

^eSurface tension data from Handbook of Physics and Chemistry (Lide 1992).

^fValues in parentheses are standard deviations.

^gCritical point drying.

TABLE II
Physical and Mechanical Properties of Wheat Starch^a

Sample	D (g/cm ³) ^b	S _c (MPa) ^c	E (MPa) ^d	(W/m·K) ^e	D _E (%) ^f	D _P (%) ^g	S _u (MPa) ^h
Air-dried wheat	0.27 a ⁱ	0.71 a	23 a	0.044 a
CO ₂ -extracted	0.26 a	0.57 a	21 a	0.037 c	13 a	87 a	0.17 a
CPD ^j	0.26 a	0.56 a	21 a	0.036 c
Freeze-dried	0.12 b	0.23 b	2.9 b	0.040 b	39 b	61 b	0.46 b

^aConditioned at least 48 hr at 50% rh.

^bDensity; moisture content of samples was 11.5%.

^cCompressive strength measured at 10% deformation.

^dCompressive modulus of elasticity.

^eThermal conductivity at 22.7°C mean temperature. Thermal conductivity of still air is 0.0226 W/m·K.

^fElastic deformation expressed as a percentage of the total deformation which equaled 10%.

^gPlastic deformation expressed as a percentage of the total deformation which equaled 10%.

^hTensile strength measured at breaking point.

ⁱValues within columns followed by a different letter are significantly different at the 95% confidence level (Fisher's protected least significant difference).

^jCritical point drying.

were not statistically significant ($P > 0.05$) due to sample variability (Tables II and III). The corn starch foams had greater compressive strength and density than the wheat starch and high-amylose corn starch samples. All the starch foams had much higher compressive strengths and moduli of elasticity than expanded-bead polystyrene (Table IV).

The ratio of elastic-plastic deformation resulting from a 10% compressive strain was lowest for the CO₂ extracted wheat and corn starch foams and highest for the freeze-dried starch foams (Tables II and III). The tensile stress required to break wheat and corn starch foams was much less than the compressive stress required to deform the samples 10% (compare tensile and

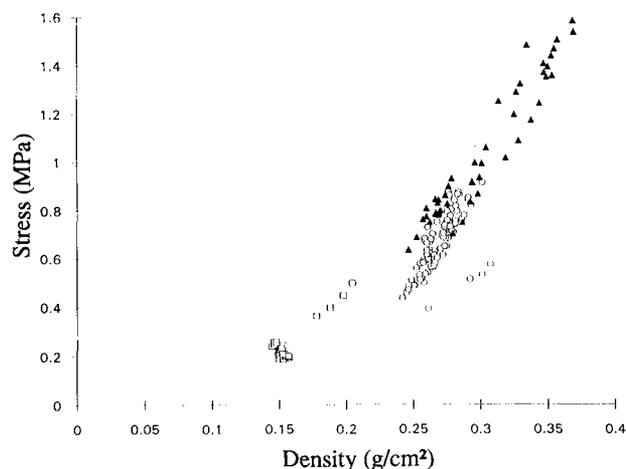


Fig. 1. Scatter plot of compressive stress and density of wheat starch (▲), corn starch (○), and high-amylose corn starch (□) foams. A positive, nearly linear relationship was observed between density and stress.

compressive strength) (Tables II and III). The high-amylose corn starch foams had tensile and compressive strengths that were similar. In contrast, the expanded-bead polystyrene and freeze-dried starch samples had greater tensile strength than compressive strength (Tables II–IV).

SEM

Expanded-bead polystyrene (Fig. 2a,d) and puffed wheat (Fig. 2b,e) both exhibited a polygonal cell type of microstructure with thin walls. The freeze-dried sample (Fig. 2c,f) of wheat starch, which was also representative of freeze-dried corn starch foams, consisted of large, thin-walled cells. Very large, nonuniform air-spaces (not shown) were apparent where large ice crystals had grown. The expanded-bead polystyrene foam had the most uniform cell size of the three samples.

The matrix of the CPD starch-based foams had much smaller pores (0.25–0.5 μm) than the expanded bead polystyrene, puffed wheat, and freeze-dried starch foams (Fig. 2g–m). The porous nature of the starch foams observed at high magnifications (Fig. 2k–m) revealed a network of small interconnecting strands within the foam matrix. The starch granule remnants interspersed throughout the matrix of the wheat starch foams interrupted the regular network of strands (Fig. 2k). The network of strands in the corn starch samples was also interrupted by starch granule remnants, but to a lesser degree than in the wheat starch samples. The fine porous nature of the high-amylose corn starch samples was less frequently disturbed by the presence of starch granule remnants (Fig. 2l,m). The upper range in pore sizes of the three starch foams was estimated to be 2 μm. The lower range in pore size was too small to determine from SEM micrographs. However, the fact that high-amylose corn starch alcogels cannot be air-dried without collapsing, whereas the other alcogels can, is indirect evidence that high-amylose corn starch foams must have a larger percentage of extremely fine pores. Although the silica aerogel appeared as a relatively smooth, solid object (Fig. 2j,n), it was

TABLE III
Physical and Mechanical Properties of Corn Starch^a

Sample	D (g/cm ³) ^b	S _c (MPa) ^c	E (MPa) ^d	(W/m·K) ^e	D _E (%) ^f	D _P (%) ^g	S _u (MPa) ^h
Air-dried	0.31 a ⁱ	1.14 a	36 a	0.037 a
CO ₂ -extracted	0.29 a	1.00 a	32 a	0.033 c	13 a	87 a	0.28 a
CPD ^j	0.29 a	0.97 a	33 a	0.033 c
Freeze-dried	0.12 b	0.19 b	2.9 b	0.040 b	36 b	64 b	0.48 b

^a Conditioned at least 48 hr at 50% rh.

^b Density; moisture content of samples was 11.5%.

^c Compressive strength measured at 10% deformation.

^d Compressive modulus of elasticity.

^e Thermal conductivity at 22.8°C mean temperature. Thermal conductivity of still air is 0.0226 W/m·K.

^f Elastic deformation expressed as a percentage of the total deformation which equaled 10%.

^g Plastic deformation expressed as a percentage of the total deformation which equaled 10%.

^h Tensile strength measured at breaking point.

ⁱ Values within columns followed by a different letter are significantly different at the 95% confidence level (Fisher's protected least significant difference).

^j Critical point drying.

TABLE IV
Physical and Mechanical Properties of High-Amylose Corn Starch and Expanded-Bead Polystyrene (PS)^a

Sample	D (g/cm ³) ^b	S _c (MPa) ^c	E (MPa) ^d	(W/m·K) ^e	D _E (%) ^f	D _P (%) ^g	S _u (Mpa) ^h
Air-dried	1.31 a ⁱ
CO ₂ -extracted	0.16 c	0.27 a	8.1 a	0.024 a	27 a	73 a	0.23 a
CPD ^j	0.15 c	0.22 a	5.1 a	0.024 a
Beaded polystyrene	0.019 b	0.098 b	3.6 a	0.036 b	25 a	75 a	0.19 a

^a Conditioned at least 48 hr at 50% rh.

^b Density; moisture content of samples was 11.5%.

^c Compressive strength measured at 10% deformation.

^d Compressive modulus of elasticity.

^e Thermal conductivity at 22.8°C mean temperature. Thermal conductivity of still air is 0.0226 W/m·K.

^f Elastic deformation expressed as a percentage of the total deformation which equaled 10%.

^g Plastic deformation expressed as a percentage of the total deformation which equaled 10%.

^h Tensile strength measured at breaking point.

ⁱ Values within columns followed by a different letter are significantly different at the 95% confidence level (Fisher's protected least significant difference).

^j Critical point drying.

less dense and more porous than the starch foams, but it consisted of a microstructure that was also too fine to study using the SEM.

All CPD foams had remnants of starch granules present in

their matrices (Fig. 2g-i, k-m) but they were most apparent in the wheat starch foams (Fig. 2g,k). The distribution of starch granule remnants was most visible in light micrographs of sections stained with I₂KI (Fig. 3a). The starch granule remnants were

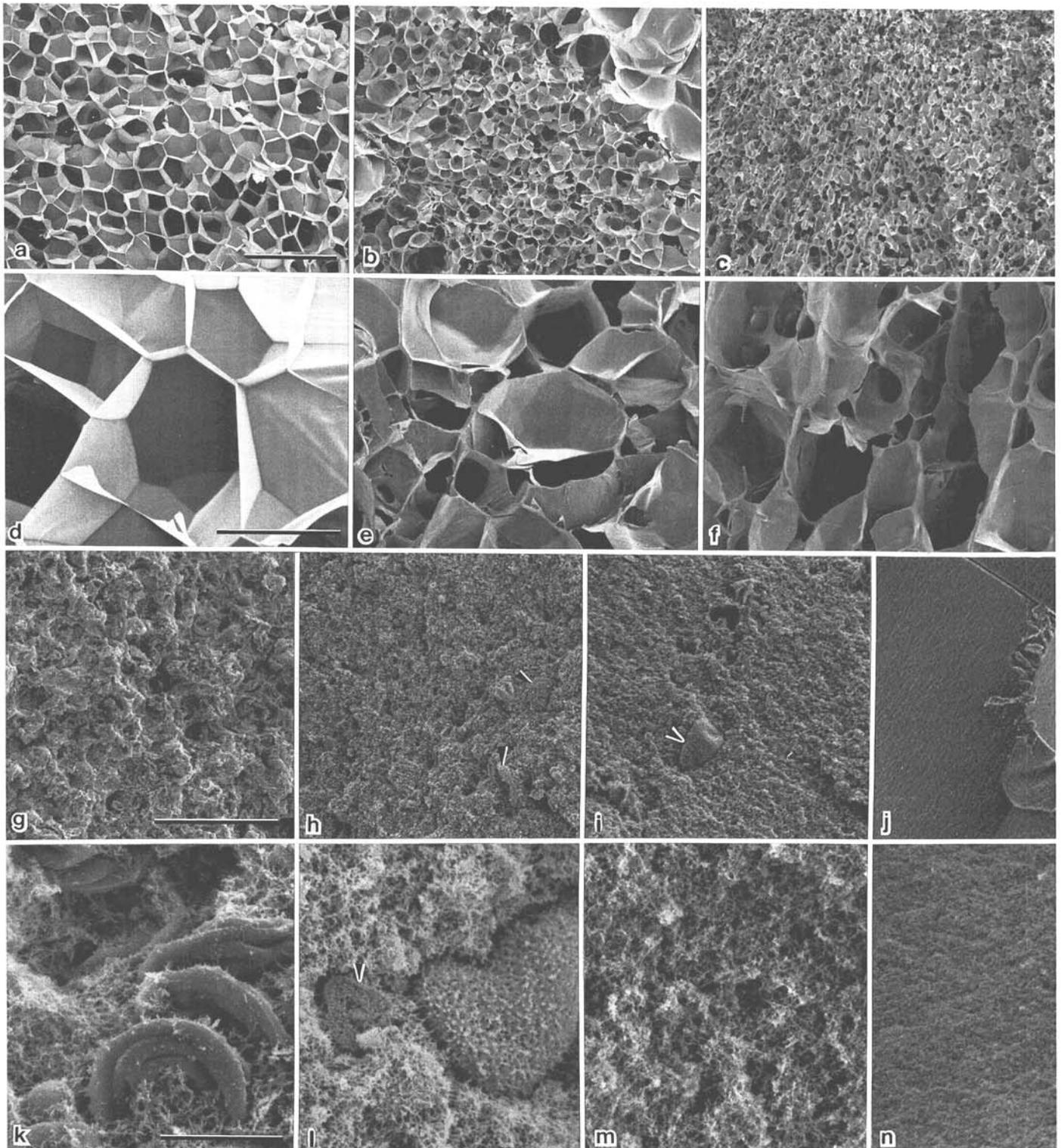


Fig. 2. Scanning electron micrographs of beaded polystyrene (a,d), puffed wheat (b,e), and freeze-dried foam made from 8% wheat starch aquagel (c,f). The foams all contained large cells with sheet-like cell walls. Note that the cells of the beaded polystyrene foam appear to be of different sizes because the cells are not cut along the same axis. Scanning electron micrographs of wheat starch foams (g,k), regular corn starch foams (h,l), high-amylose corn starch foams (i,m), and transparent silica aerogel (j,n). Note that figures g-j are the same magnification as figures d-f. The wheat starch, corn starch, and high-amylose corn starch foams had much smaller pore sizes than the samples in d-f. The pore size of the silica aerogel was much too small to discern even at high magnification (n). The wheat starch foams contained numerous starch granule remnants and some pores as large as 2 μm (g,k). The corn starch foams also contained numerous starch granule remnants (arrows) (h,l) and pores as large as 1 μm . The high-amylose corn starch foams had fewer starch granule remnants than the other starch foams (arrows) (i) and a pore size similar to that of corn starch foams. Magnification bars: a-c = 500 μm ; d-f = 100 μm ; g-j = 100 μm ; k-n = 10 μm .

densely dispersed throughout the matrix in both the wheat and corn starch samples but were sparsely distributed within the matrix of the high-amylose corn starch samples (Fig. 3a-c). The starch granule remnants prominent in the wheat starch samples were large in comparison to the starch granule remnants interspersed throughout the stained corn starch samples.

DISCUSSION

One of the limitations to wider commercialization of microcellular foams is their processing cost. This is certainly true for many of the aerogels that have been evaluated. The CPD process is a batch process requiring expensive high-pressure equipment and typically requires several days to complete. Alternative methods of processing gels were tested in the present study. The CO₂ extraction method, which requires lower processing temperatures and pressures than CPD, yielded samples that were comparable to those made by the CPD process. The air-drying process is less costly because it does not require expensive high-pressure equipment. Air-dried wheat and corn starch alcogels yielded foams that had nearly the same properties as CPD wheat and corn starch foams. The air-dried wheat and corn starch foams had higher density and thermal conductivity than did CPD high-amylose corn starch foams, yet they still have some mechanical and thermal properties comparable to commercial foams. Processing times are limited by diffusion rate during the ethanol equilibration step and during drying.

Of the three types of starches tested, CO₂ extracted and CPD high-amylose corn starch foams most closely approached the properties typical of aerogels. As with materials that form typical aerogels, the high-amylose corn starch aquagels underwent relatively little shrinkage when dehydrated in ethanol and could not be air-dried from alcogels without collapsing. The high-amylose corn starch foams also had a thermal conductivity approaching those typical for aerogels (0.0225 W/m·K) and of air (0.0226 W/m·K) (Lange 1956). The starch foams, like the aerogels, needed protection from direct exposure to liquid water, as water that penetrated the matrix resulted in surface tension forces that compressed the foam into a thin film.

The opaque property characteristic of the starch microcellular foams was in sharp contrast to the transparent nature of aerogels.

Aerogels have extremely fine particle and pore sizes (3–60 nm) that scatter light only weakly, thus rendering them translucent or transparent (Tewari et al 1985). Aqueous gels of starch that are air-dried become transparent films presumably because their pores become very small as the starch matrix collapses under the forces of surface tension. The opaque nature of all the starch foams studied was likely due to the relatively large size of the starch granule remnants and pores compared to the particle and pore size of typical aerogels. These larger size structures probably cause light scattering within the foam matrix that result in opacity.

The foam microstructure also appeared to be important in determining thermal resistance and tensile strength. The importance of microstructure in thermal resistance was apparent in comparing freeze-dried foams with CPD high-amylose corn starch foams. Both samples had similar densities but differed markedly in microstructure and thermal conductivity. The low thermal conductivity of the high-amylose corn starch foams must be largely attributable to the small pore size that reduces heat transfer by conduction and convection (Buttner et al 1985).

The mechanical properties of the starch foams appeared largely dependent upon the density of the foams. This observation confirmed other reports showing a strong correlation between foam density and compressive strength and modulus of elasticity (Nielsen 1974, Hutchinson et al 1987). The weakness of the wheat and corn starch foams under tensile stress was most likely due to imperfections in their microstructure caused by starch granule remnants and irregularities that are inherent in the pores. Nielsen (1974) found that foams have much lower tensile strength than unfoamed polymer and that cells that are larger than the average cell may act as a stress concentrator. The pores within the starch foams appeared uniform in size, except for some larger pores that formed adjacent to starch granule remnants. These imperfections could provide sites at which cracks may propagate in starch foams. This could explain why high-amylose corn starch foams, which contained relatively few starch granule remnants, had similar strength in both compression and tension. It may also explain why the freeze-dried foams, which had thin, continuous cell walls rather than interconnecting strands, had the greatest tensile strength even though they had the lowest density. The weakness of the corn and wheat starch foams and the relative

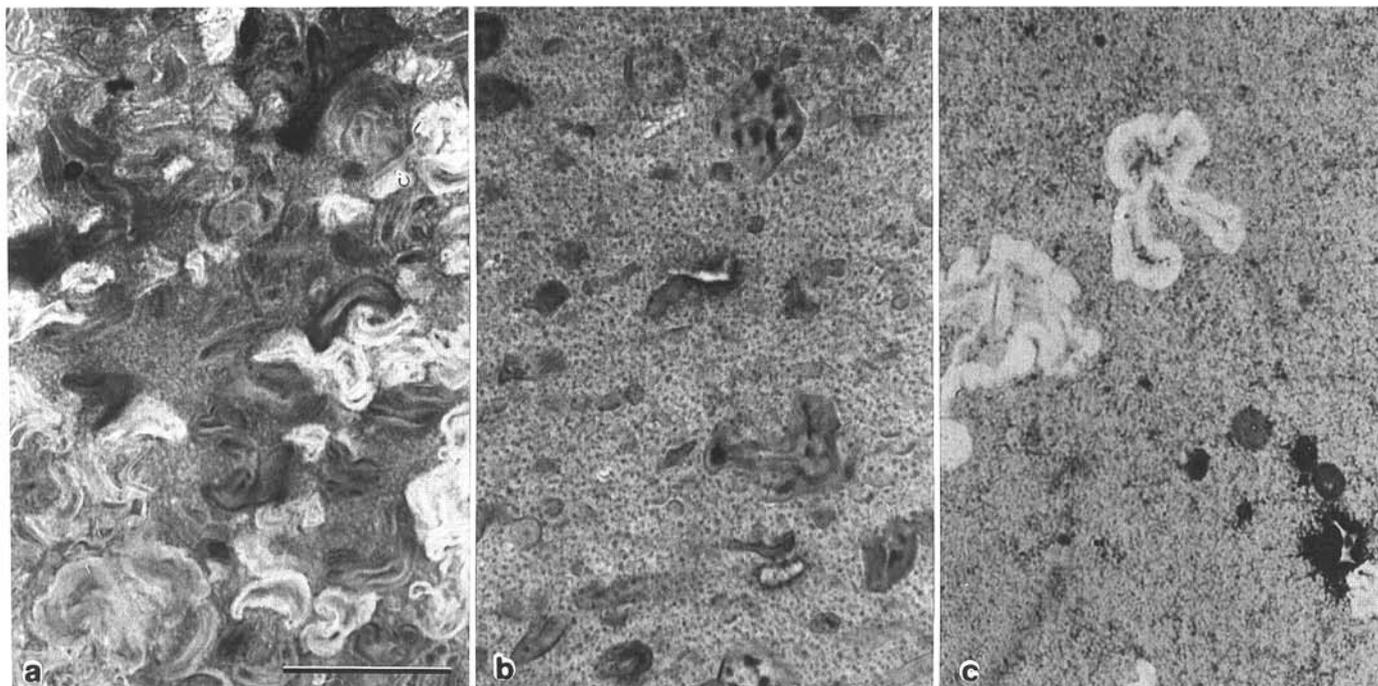


Fig. 3. Light micrographs of alcogels produced from wheat starch (a), corn starch (b), and high-amylose corn starch (c). Note the abundance of starch granule remnants in the wheat and corn starch samples and fewer starch granule remnants in the high-amylose corn starch alcogel. Magnification bar: a-c = 50 μ m.

strength of the high-amylose foams also may be attributed to differences in the molecular structures of the respective starches. The matrix of interconnecting strands seen in the SEM micrographs must form by coagulation of the starch polymers in the presence of ethanol. Other methods of dehydrating the starch aquagels that yield foams with continuous cell walls with high tensile strength should be investigated.

The shrinkage that occurred in the starch foams while dehydrating in ethanol appeared to be the most important factor in determining foam density. The cause of the shrinkage in wheat and corn starch aquagels was not clear. Shrinkage may be related to the amylopectin fraction of the starch since the wheat and corn starch had a much higher amylopectin content than did the high-amylose corn starch. Shrinkage may also be associated with the behavior of starch granule remnants found most abundantly in wheat and corn starch foams. The starch granule remnants are most likely enriched in amylopectin since amylose tends to diffuse out of hydrated starch granules faster than amylopectin (Sullivan et al 1988). Further studies using aquagels prepared by jet cooking or other high-shear starch cooking processes that completely disrupt the starch granule structure may be useful in studying the role of starch granule remnants in shrinkage.

In conclusion, the starch foams characterized in the present study had physical and mechanical properties comparable to various other microcellular foams. The starch foams were particularly strong in compression, had low density and thermal conductivity, and had very small pore sizes. These unique properties are currently being exploited in developing various possible commercial applications.

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