

Aspects of the preparation of starch microcellular foam particles crosslinked with glutaraldehyde using a solvent exchange technique

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Abstract

Starch microcellular foam (SMCF) has been produced using a solvent exchange technique with a native corn starch crosslinked with glutaraldehyde. To produce a high specific surface area for the starch particles the cooked starch solution was reacted with glutaraldehyde and then precipitated under shear with ethanol. The relationship between the crosslinking density on the void structure of the SMCF has been studied. Characterization by NMR confirmed the crosslinking reaction. An increase in the glutaraldehyde concentration from 0 to 15 g glutaraldehyde/100 g starch was accompanied by a decrease in particle size and moisture content and an increase in brightness and specific surface area. Scanning electron microscope images of the SMCF particles show that the smallest average void diameter obtained was 0.182 μm at a 7.5 g glutaraldehyde/100 g starch. Four starch materials having different viscosity were prepared by hydrolysis of the native corn starch with a 1 N HCl/methanol system for different reaction durations to investigate the relationship between starch molecular weight and void structure of the SMCF. The starches were crosslinked with 15 g glutaraldehyde/100 g starch and precipitated with ethanol to form SMCF. Decreasing the starch viscosity decreased the brightness and specific surface area, and increased the particle size, void diameter and moisture content. Increases in stirring speed during the precipitation enhanced the properties of the SMCF particles. The effect of pressing the starch particles to form a pellet caused a collapse of the foam structure at pressures above about 6000 psi. The results indicate that the structure/chemistry of the starch material and the processing conditions can be controlled in order to produce particles with morphology and properties useful for light scattering applications. In particular, higher molecular weight and intermolecular crosslinking and high shear during precipitation have been found to enhance the foam formation.

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1. Introduction

Starch is considered to be the one of the most abundant biopolymers worldwide. Starch exists as semi-crystalline granules composed of amylopectin (branched polymer, ~70%, 4000 glucose units) and amylose (linear polymer, ~30%, 1000 glucose units). Both amylose and amylopectin are composed of α -glucosidic units connected to each other through a 1,4-oxygen ring atom. In addition to this, the amylopectin contains 1,6 branch points (Mauro, Abbas, & Orthoefer, 2003; Roper, 2002).

In the last decade, due to increasing environmental awareness and the environmental legislations, scientists around the world have made strong efforts to develop methods to use natural polymers as an alternative to the petroleum synthetic polymers for industrial and consumer applications. The low cost and availability of starch in the market attracts scientists for developing new functional starch derivatives for industrial applications (Cao, Xu, Feng, & Wang, 2005; Delval, Crini, Bertini, Filiatre, & Torri, 2005; Klimpl & Sonenberg, 2004). The industrial applications of starch derivatives depend on its type of functional group introduced to the main backbone of the starch, its properties (gelatinization, crystallization, retrogradation, gel formation), and amylose/amylopectin ratios

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that depend on the source of extraction (Jane, Ao, Z, & Suh, 2003). Scientists have successfully synthesized numerous products, including starch-based composites for disposable containers (Murakami & Mizuta, 2005), starch microcellular foams (SMCF) for encapsulation of volatile compounds (Buttery, Glenn, & Stern, 1999), light weight concrete (Glenn, 1997), and wood adhesives (Li, 2005). These starch-based products are not only completely biodegradable, but have physical and mechanical properties comparable to products made from synthetic polymers.

Starch microcellular foams (SMCF) are generally described as a starch based porous matrix containing pores ranging from 2 μm to sub-micrometer size (Glenn, Miller, & Irving, 1996). SMCF have very high specific areas (air–solid interfaces) that can scatter light. The fine particles of starch microcellular foams have an excellent ability to scatter light and have strong opacifying properties. Several trials have been made for increasing the industrial applications of SMCF. It has been reported that SMCF have been used to develop non-mineral starch based pigments (Saari et al., 2005), pharmaceutical (Chiou et al., 2005). Glenn and coworkers at the Western Regional USDA Research Center have studied SMCF materials extensively. They have prepared SMCF by different techniques, such as freeze drying, rapid freezing, many nucleating sites and solvent exchange. The preparation of SMCF will open new ways to utilize starch as slow release agents for dispensing chemicals, flavor encapsulation, and as a substitute for commercial plastics.

Glenn and Irving (1995) have prepared SMCF from rigid starch aquagels by an exchange of the water of the cooked starch with liquid possessing lower surface tension. The SMCF could be formed by equilibrating the aquagels of wheat and corn starch in ethanol before air drying. Since the surface tension of the air/ethanol interface was one third that of air/water weaker capillary forces exist when drying from ethanol relative to drying from water and the foams collapse to a lower extent. Also they demonstrated that if the SMCF exchanged with ethanol then had the ethanol exchanged with liquid CO_2 SMCF of very low density could be produced. This was because the drying of the SMCF from supercritical CO_2 eliminates essentially all the liquid–gas surface tension during drying.

Xu and Hanna (2005) have extruded biodegradable composite foams based on starch acetate and poly (tetraethylene adipate-co-terephthalate) (EBC). It was reported that low EBC contents in the blends favored the miscibility of the two polymers, as characterized by an increase of the glass transition temperature of starch acetate, a decrease in the melting point temperature of starch and EBC in a differential scanning calorimetry analysis and the formation of a homogeneous morphology observed with SEM. Large amounts of EBC decreased the miscibility of these two polymers.

In this research, starch based foam like particles are proposed as an effective opacifying material for use in paper and coatings due to a high specific surface area and high brightness. However, native starch SMCF is readily soluble in water, preventing its use in aqueous applications. It is pro-

posed that crosslinking the starch may limit the interaction of the starch with water. Further, the crosslinking may provide some structural integrity of the foam during exposure to pressure and/or moisture. The effect of crosslinking on SMCF materials on the processability, structure and properties of SMCF materials has not been reported previously.

Therefore, the current work has focused on the effect of crosslinking on the formation and properties of starch microcellular foam. As a complementary study, the effects of the starch viscosity (molecular weight) on the foam properties has also been investigated. The SMCF materials were characterized using nuclear magnetic resonance (NMR), scanning electron microscope (SEM), and thermo gravimetric analysis (TGA). The SMCF materials were also characterized for brightness, particle size, void diameter, and surface area. The chemical composition and processing variables had dramatic effects on the resulting properties of the SMCF.

2. Experimental

2.1. Materials

Corn starch was provided by Cargill, USA (Cargill Gel 03420). This is a native common corn starch with a 25–28% amylose content. Glutaraldehyde was purchased from Sigma–Aldrich Co. (CAS Number: 111-30-8) and anhydrous ethanol, 1 N hydrochloric acid and other chemicals were purchased from Fisher Co.

2.2. Hydrolysis of starch

An amount of 100 g of corn starch was added to a three necked flask containing 250 mL of 1 N HCl/methanol system. The flask was placed in an oil bath with head stirrer, condenser and rubber septum. The suspended solution of starch was allowed to stir for different reaction durations (30, 60, 120, and 180 min) at 50 °C. After the reaction, the hydrolyzed starches were filtered using a filter paper and washed with deionized water until complete removal of HCl had been accomplished. Finally the hydrolyzed starches were dried at 60 °C before any further characterization. The average intrinsic viscosity of the cooked hydrolyzed starches was determined as measured in an Ubbelohde viscometer (Cannone Instrument Company, 200 K3) at 25 °C by determining the flow time of the starch solution. Ten readings were taken for each sample. The viscosities of the hydrolyzed starch were found to be 210, 150, 60.45 and 21.7 cP with increased hydrolysis time.

2.3. Starch crosslinking procedure

A cooked starch solution was prepared by adding 20 g of corn starch to 100 ml of deionized water in a three necked flask under continuous stirring (IKA-Werk, RW 16 Basic S1). The temperature was increased gradually to 95 °C over a time period of about 30 min. The cooked starch was subjected to continuous stirring for another 20 min.

The cooked starch was allowed to cool to 50 °C over a period of 60 min. Different amounts of glutaraldehyde (0–30 g/100 g starch) (0–0.24 mol glutaraldehyde/repeat unit of starch) were added to the cooked starch solution at 50 °C in acidic medium (1 ml of 1 N HCl). The crosslinking reaction was allowed to proceed for 2 h under continuous stirring. The reaction was then stopped by adding ethanol.

2.4. Preparation of SMCF

SMCF was produced by a solvent exchange technique. In this process, the higher surface tension solvent (water) is replaced with a solvent of lower surface tension (ethanol). This was carried out by adding anhydrous ethanol (200 mL) to the crosslinked cooked starch (20% starch, 130 mL) in the presence of stirring (IKA-Werk, RW 16 Basic S1, speed setting of 8, 2500 rpm), and then filtering the precipitated crosslinked starch on filter paper (Fisher Scientific, P2) in a Buchner funnel with house vacuum. The precipitate is transferred to a glass beaker and ethanol is again added (200 mL) with stirring, stirred for 120 min, and then filtered again. This was repeated two more times (total ethanol batches added equaled four). The precipitated SMCF was dried on filter paper under house vacuum at ambient conditions for 24 h before any further characterization.

2.5. Characterization of SMCF

Morphological characterization of starch microcellular foams was performed on images acquired using a scanning electron microscope (SEM), Hitachi S-3200N. The samples were coated with platinum of 10 nm thickness to make the samples conductive. All the samples were performed at different magnification (2.5–3.5 K). Also the void diameters of SMCF apparent on the particle surface were determined using image J software after spatial calibration using the length scale provided with the SEM micrograph.

Fourier transform infrared spectroscopy was used to characterize native and crosslinked cooked starch (Perkin-Elmer-FTIR spectrophotometer, Nicolet Nexus 470). The samples were ground with KBr and pressed into pellets for FTIR transmission measurements. High resolution solid-state NMR was used to investigate the molecular structural changes of native and crosslinked starch using a Bruker DMX 360 Hz NMR Spectrometer. The CP/MAS experiment was run on a 4 mm MAS probe.

The moisture content of the SMCF was determined using thermal gravimetric analysis (TGA, TA Instruments G500 V6.3 Build 189) on samples exposed to ambient conditions. The samples were heated to 120 °C for 30 min at 5 °C/min.

The brightness of the SMCF (powder) and neat SMCF pellets was measured using a Technidyne Color Touch (model ISO) and a Brightimeter (Model S-4 brightness/color/fluorescence tester) to measure the brightness of the SMCF as a function of chemical modification.

The SMCF was soaked in ethanol for 2 h and photomicrograph pictures were taken using a Power HAD DXC-970 MD 3CCD color video camera connected to an Olympus BH₂-UMA microscope. Image-Pro plus software was used to measure particle sizes.

The surface area of the SMCF was determined using BET surface area analysis using 30% N₂ in He gas (Quantachrome Monosorb model MS-17, USA).

3. Results and discussion

Crosslinking of polysaccharides is one of the most common ways to reduce the solubility of polysaccharides by formation of intermolecular bridges between the polysaccharide macromolecular chains. Glutaraldehyde is a dialdehyde crosslinking agent that has been used extensively in the literature (Natarajan et al., 2005; Sung, Huang, Huang, Tsai, & Chiu, 1998; Wang & Hsieh, 2001). The crosslinking of starch macromolecules with glutaraldehyde is carried out through nucleophilic addition of a hydroxyl group to the carbonyl group to form hemi-acetal linkages, Fig. 1. The following describes the effects of crosslinking with glutaraldehyde and the starch viscosity as modified via an acidic hydrolysis reaction on the formation and physical properties of starch MCF particles.

3.1. Effect of glutaraldehyde concentration on SMCF structure

Trommsdorff, U. and Tomka, I. (Trommsdorff & Tomka, 1996) have made a model structure to visualize a molecular view of the specific interactions of the starch chains. It was reported that the atom pair distribution functions of the model structure were marked by strong correlations at distances corresponding to hydrogen bonds, and the mean number of hydrogen bonds was 7.8 per repeat unit. The mean number of hydrogen bonds per hydroxyl group was found to be 2.3 (of a maximal 3) and the ring and the glycosidic oxygen only contributed to approximately 10% of all hydrogen bonds. Of all the hydrogen bonds in the model structure, 56% were intermolecular. The hydrogen bonds occurred in a wide variety of geometries. These intermolecular hydrogen bonds provide resistance for the relative motion of starch molecular segments past one another. The amount and type of such bonds should impact foam formation. An intermolecular covalent bond is an extreme type of intermolecular interaction that also should impact foam formation and is studied here.

In this study, the precipitation of starch foam structures was induced by introducing a non-solvent, ethanol to the cooked starch solution under a single set of conditions. This resulted in precipitated particles being formed. It was of interest to determine how the glutaraldehyde concentration impacted the properties of the foam. Characteristics that were deemed important for this application were the morphology of the starch particles (Fig. 2), average particle size

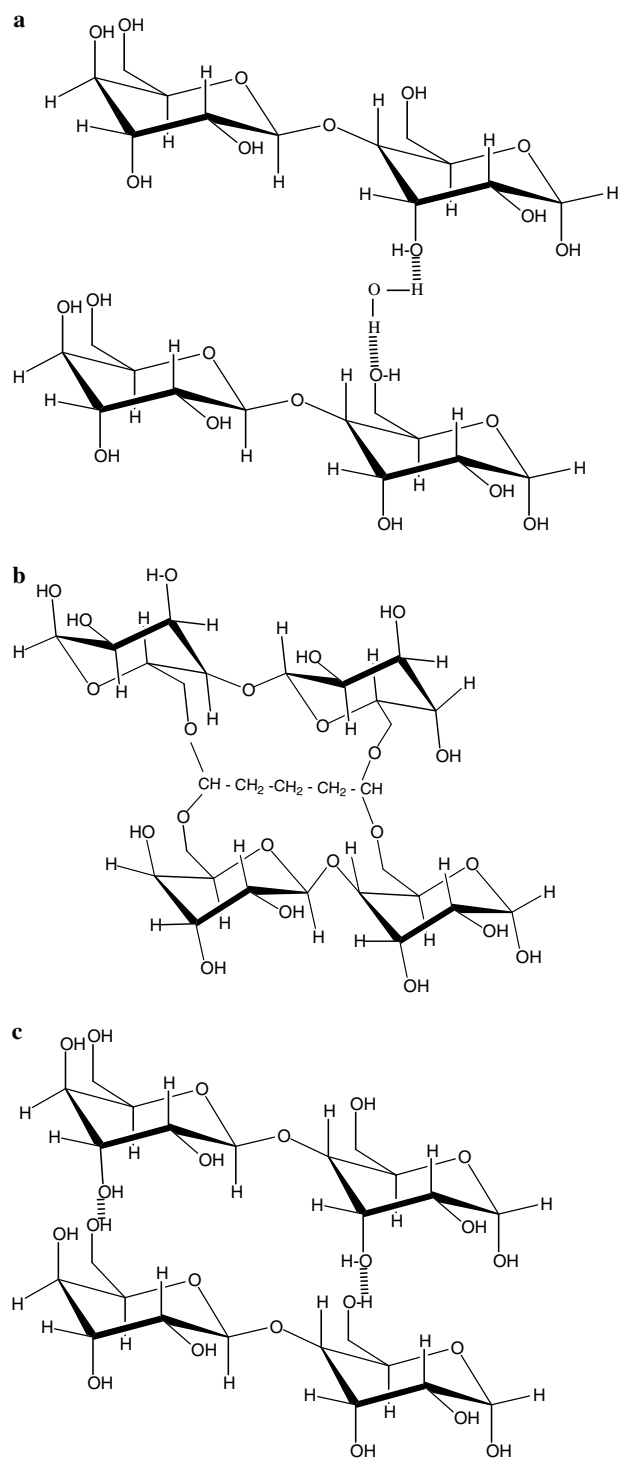


Fig. 1. Types of interactions between starch macromolecular chains (a) H-bonding of uncrosslinked SMCF with water molecules; (b) cross-linked SMCF with glutaraldehyde; and (c) inter molecular H-bonding of starch.

(Fig. 3), specific surface area (Fig. 3), moisture content (Fig. 4), brightness (Fig. 5), and void diameter (Fig. 6). The particle size and moisture uptake decreased, and the specific surface area and brightness increased with increased crosslinking.

Scanning electron microscopy (SEM) is a very important tool for analyzing the morphology of low density starch microcellular foams, foam structure and void diameter. All the SEM micrographs of the obtained foams were recorded at a magnification range of 2000–3000 X; the length scale is 20 μm for Figs. 2a–d and 10 μm for 2e–h. SEM images of the crosslinked SMCF, Fig. 2, showed that particles could be formed with a very irregular surface and considerable porosity. Interesting structures with significant amounts of voids in the 1 μm range can be clearly observed for the concentration range of glutaraldehyde of 7.5–15 g/100 g starch. Below and above this range, the SMCF does not show the same consistency in pore volume and pore sizes. Fig. 6 indicates that the smallest average size voids are produced at around 7.5/100 g starch. It is hypothesized that as the crosslink concentration increases from zero that the precipitation process is enhanced as discussed above but then as crosslink concentration increases to even higher level, the excessive crosslinking may make the starch macromolecules so rigid with low mobility that the formation of voids is resisted.

The specific surface area and particle size increase and decrease, respectively, most significantly in the 2.5–15 g/100g starch range, indicating that crosslinking levels above 15 g/100g starch are not useful with respect to developing void structures.

In the absence of glutaraldehyde, a poor foam structure is produced with the techniques used in this study, as evidenced by the lowest specific surface area, Fig. 3. There could be several mechanisms in which the intermolecular crosslinking of glutaraldehyde promotes the void formation.

- (1) Increased crosslinking increases the MW of starch decreasing the solubility of the starch in water or ethanol, enhancing the solvent exchange process.
- (2) Increased crosslinking disrupts intermolecular hydrogen bonding between starch macromolecules (Fig. 1b relative to Fig. 1c), allowing the ethanol to penetrate the starch matrix more rapidly and extensively, enhancing the solvent exchange process.
- (3) Increased crosslinking disrupts water-starch hydrogen bonding (Beery & Ladisch, 2001). (Fig. 1b relative to Fig. 1a), decreasing the affinity of the starch for the water. This will facilitate the solvent exchange, allowing the ethanol to penetrate the starch matrix more rapidly and extensively.
- (4) Crosslinking of the starch develops a stiffer structure that resists pore collapse.

It was reported by Shogren, Lawton, Doane, and Tiefenbacher (1998) that the foam formation of the starch SMCF depends on the rheological properties of the solution from which it is made. First, the starch should have an elastic strength that helps the formation of a strong foam structure, since the ungelatinized corn

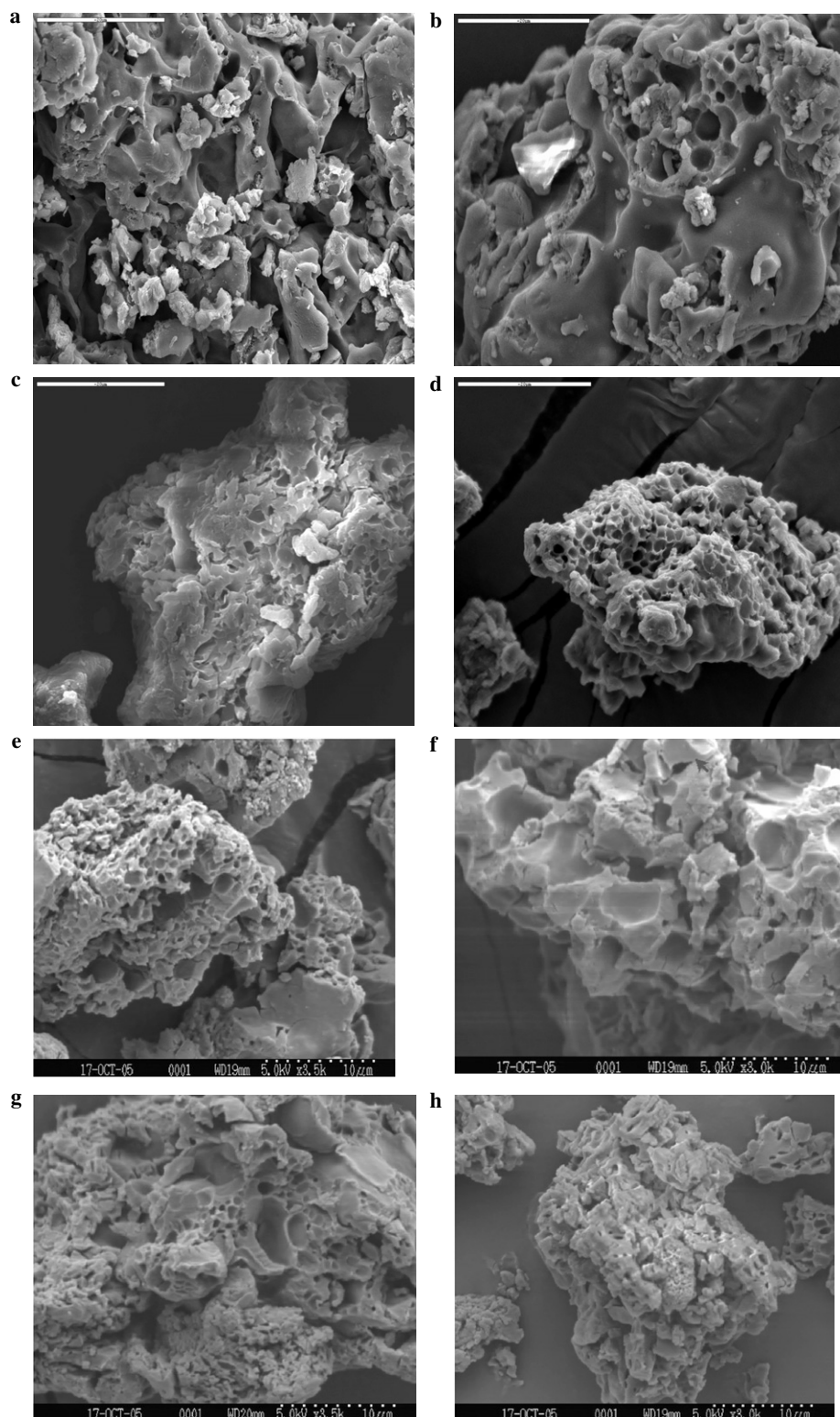


Fig. 2. SEM micrographs of SMCF at different glutaraldehyde concentrations. (a) Uncrosslinked starch; (b) 2.5 g glutaraldehyde/100 g starch; (c) 5 g glutaraldehyde/100 g starch; (d) 7.5 g glutaraldehyde/100 g starch; (e) 10 g glutaraldehyde/100 g starch; (f) 12.5 g glutaraldehyde/100 g starch; (g) 15 g glutaraldehyde/100 g starch; and (h) 30 g glutaraldehyde/100 g starch. Length scale is 20 μm for a–d and 10 μm for e–h.

starch suspension solution does not have the ability to form a foam structure. Cooking of the corn starch will disrupt the starch granules to provide the elastic solution. Second, starch of higher viscosity (molecular

weight), after cooking, is necessary to stabilize the foam structure and prevent collapse as water is removed via ethanol. Crosslinking provides the elastic strength for the foam structure to exist.

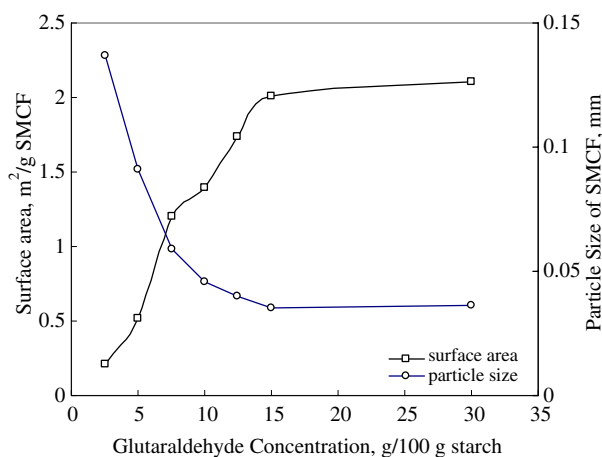


Fig. 3. The effect of glutaraldehyde concentration on the average particle size and surface area of SMCF.

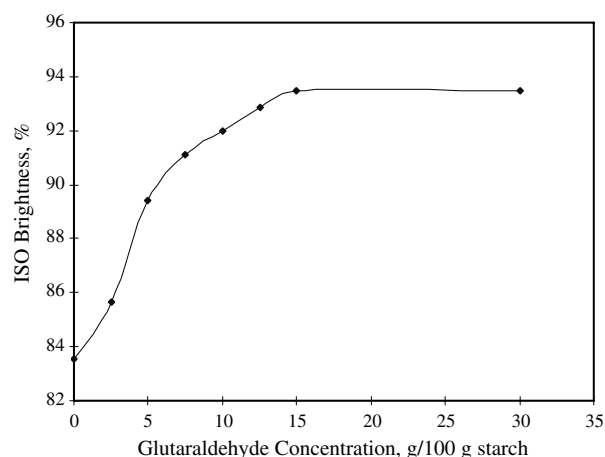


Fig. 5. Effect of glutaraldehyde concentration on the brightness of SMCF.

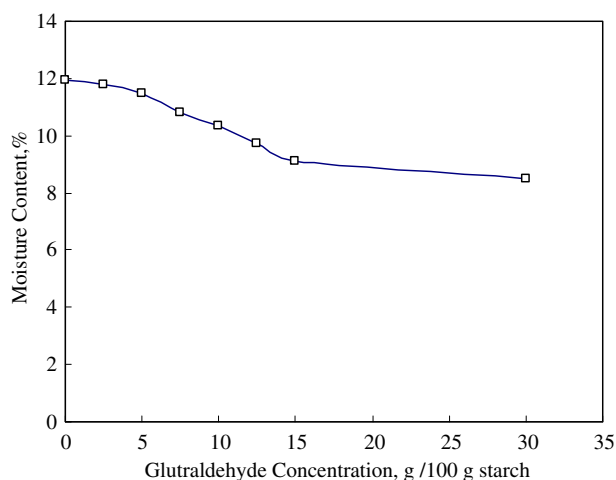


Fig. 4. Effect of glutaraldehyde concentration on the moisture content of SMCF.

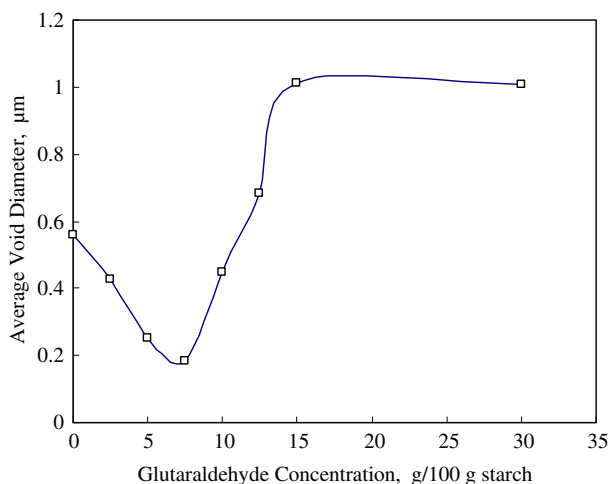


Fig. 6. Effect of glutaraldehyde concentration on the average void diameter of SMCF.

3.1.1. Effect of crosslinker on SMCF particle size and specific surface area

The effect of glutaraldehyde concentration on the particle size and surface area of the SMCF is shown in Fig. 3. The average particle size of the SMCF decreases to 0.036 μm up to a glutaraldehyde concentration of 15/100 g starch and remains constant above this concentration. It is expected that the specific surface area of the starch particles would be inversely proportional to the average particle size. This is based on the assumptions that the particles are close to spherical and that the morphology (such as pore fraction) and the surface roughness is constant. This is confirmed by a linear relationship between the inverse particle size and the specific surface area of the particles, Fig. 7. The specific surface area of the SMCF is expected to be impacted by the liquid surface tension from which it is dried. It is acknowledged that the specific surface area of the SMCF would likely increase if the ethanol was exchanged for a lower surface tension liquid, e.g.

supercritical carbon dioxide. However, the morphology of the particles formed herein with a simplified preparation may be suitable for many applications and thus further exchanges with liquids beyond ethanol may not be needed.

3.1.2. Effect of glutaraldehyde crosslinker on the water uptake of SMCF

Dry starch is extremely hydrophilic and under normal atmospheric conditions starch, like other biological materials, contains water. One characteristic that is important in the use of SMCF particles for many applications as an opacifying agent for paper, textiles and paints is that the starch be rendered hydrophobic. One question to answer in this study was if the crosslinking agent affected starch–water interactions. The moisture content of the uncrosslinked corn starch is around 12–15%. This value is due to the formation of H-bonds between two hydroxyl groups of two parallel starch macromolecules with one molecule of water (Fig. 1a) (Beery & Ladisch, 2001). Crosslinking of cooked

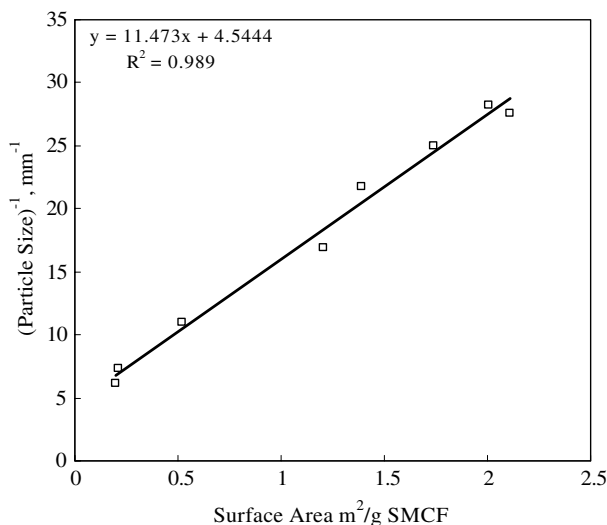


Fig. 7. Relation between the specific surface area and the reciprocal of the average particle size.

corn starch with glutaraldehyde (Fig. 4) is accompanied by a decrease in the moisture content of the crosslinked SMCF to about 9%. The decrease in the moisture content is due to an increase in the intermolecular bridges between starch macromolecules. These crosslinks decrease the concentration of hydroxyl groups per mass of material that can participate in hydrogen bonding with water. In other words, the $(\text{CH}_2)_3$ moiety of the added crosslinker is hydrophobic and decreases the effective amount of hydroxyl groups per mass of material.

3.1.3. Effect of glutaraldehyde crosslinker on the optical properties of SMCF

The brightness of SMCF is increased significantly with increased glutaraldehyde concentration, Fig. 5. The increase in the brightness is highly influenced by the particle size of the foam. The relation between the particle size and the brightness is linear ($R^2 = 0.99$) (Fig. 8). It is obvious that the brightness of SMCF is highly dependent on the particle size of SMCF. The particle size of SMCF is highly dependent on the technique of precipitating the SMCF (including the shear rate, see later), in addition to the glutaraldehyde concentration.

3.1.4. Solid state NMR

The ^{13}C CP/MAS spectra of the SMCF were used to confirm the reaction between glutaraldehyde and the starch. In the CP/MAS spectra, for the uncrosslinked and the crosslinked starch (Fig. 9) a signal at 103 exists indicative of carbon C1 for the glucose structure of starch.

A strong and wide signal from 48 to 92 appeared for both spectra which represents C4 at 82; C2, C3, C5 at 78; and C6 at 62 (Baik, Dickinson, & Chinachoti, 2003). The signal strength of crosslinked SMCF for the range of 48–92 is higher (4.59) than that the uncrosslinked one (4.43),

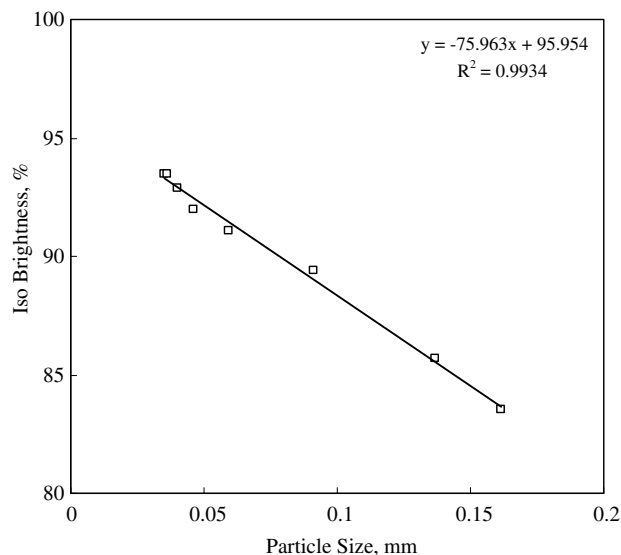


Fig. 8. Relationship between brightness and average particle size for different crosslinker concentration.

indicating that there is additional carbon atoms are added to the structure. The presence of a new signal appearing around 30 represents the aliphatic CH_2 of glutaraldehyde that confirms the crosslinking reaction of glutaraldehyde with starch.

3.2. Effect of starch hydrolysis

It is expected that higher molecular weight starch will have higher viscosity/elastic strength and when precipitated will assist in the development of an extensive foam structure (Shogren et al., 1998). To confirm this, foams with different molecular weight starch were produced and analyzed.

Hydrolysis of starch has been used for preparation of water soluble starches. It is well known that during the acidic hydrolysis of starch the following phenomena occur. The hydrolysis of the amorphous regions rapidly progresses. The hydrolysis of a crystalline region progresses more slowly (Mun & Shin, 2005; Sun, Yu, & Liu, 2004). The hydrolysis of starch is accompanied by the formation of terminal aldehyde groups. Hydrolyzed corn starches of four different viscosities (210, 150, 60.45, and 21.7 cP) were cooked at 95 °C for 20 min. Starch microcellular foams of these hydrolyzed starches were produced by the solvent exchange technique as mentioned previously using 15 g glutaraldehyde/100 starch. SEM images of crosslinked starch microcellular foam of different viscosity are shown in Fig. 10. The SEM pictures show that the hydrolysis of starch as measured by viscosity plays a vital role during the formation of starch foams, since decreasing the starch viscosity has a negative effect on the formation of SMCF when all the samples are prepared under the same conditions. At high viscosity (230 cP) the void content is higher and the average pore size is smaller (Fig. 11) than for low viscosity starch (21.7 cP). The loss

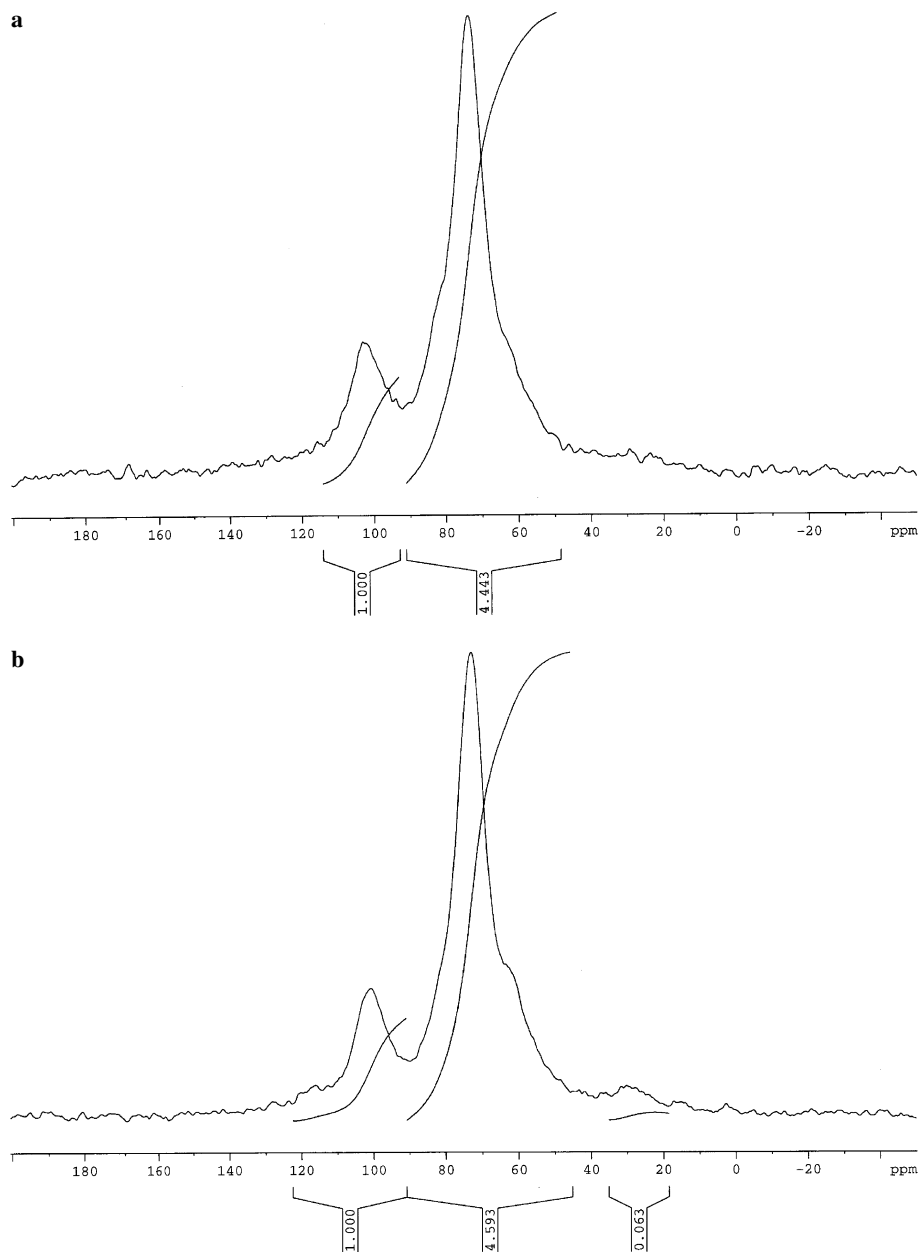


Fig. 9. NMR spectra of (a) uncrosslinked corn starch and (b) starch crosslinked with glutaraldehyde.

of the foam structure with increased hydrolysis may be due to (a) the lower viscosity starch collapses more readily than a higher viscosity starch, and (b) the decreasing starch molecular weight increases the solubility in water and consequently impacts negatively the solvent exchange process.

As the starch viscosity decreases, the particle sizes of crosslinked SMCF increase and the specific surface area decreases (Fig. 12). Increasing the hydrolysis time increases the extent of the cleavage of the 1,6 glucosidic linkages and decreases the starch molecular weight. Such a decrease in the molecular weight may facilitate the formation of aggregates of H-bonding. The hydroxyl and the aldehyde groups could participate in the formation of

a core center of hydrogen bonds that is reflected in the larger particle size of SMCF (Trommsdorff & Tomka, 1996). In addition, the aldehyde groups have the ability to form H-bonding with water molecules. As the number of aldehydes in the starch backbone increase, the ability of these groups to form H-bonds increase and consequently the moisture content of the hydrolyzed SMCF increase (Fig. 13).

The brightness of the starch MCF increases with increased viscosity (Fig. 14) and this increase in brightness is linearly related to the particle size (Fig. 15).

In summary, the effects of crosslinking via glutaraldehyde and higher molecular weight on the properties of SMCF are in agreement. Both crosslinking and higher

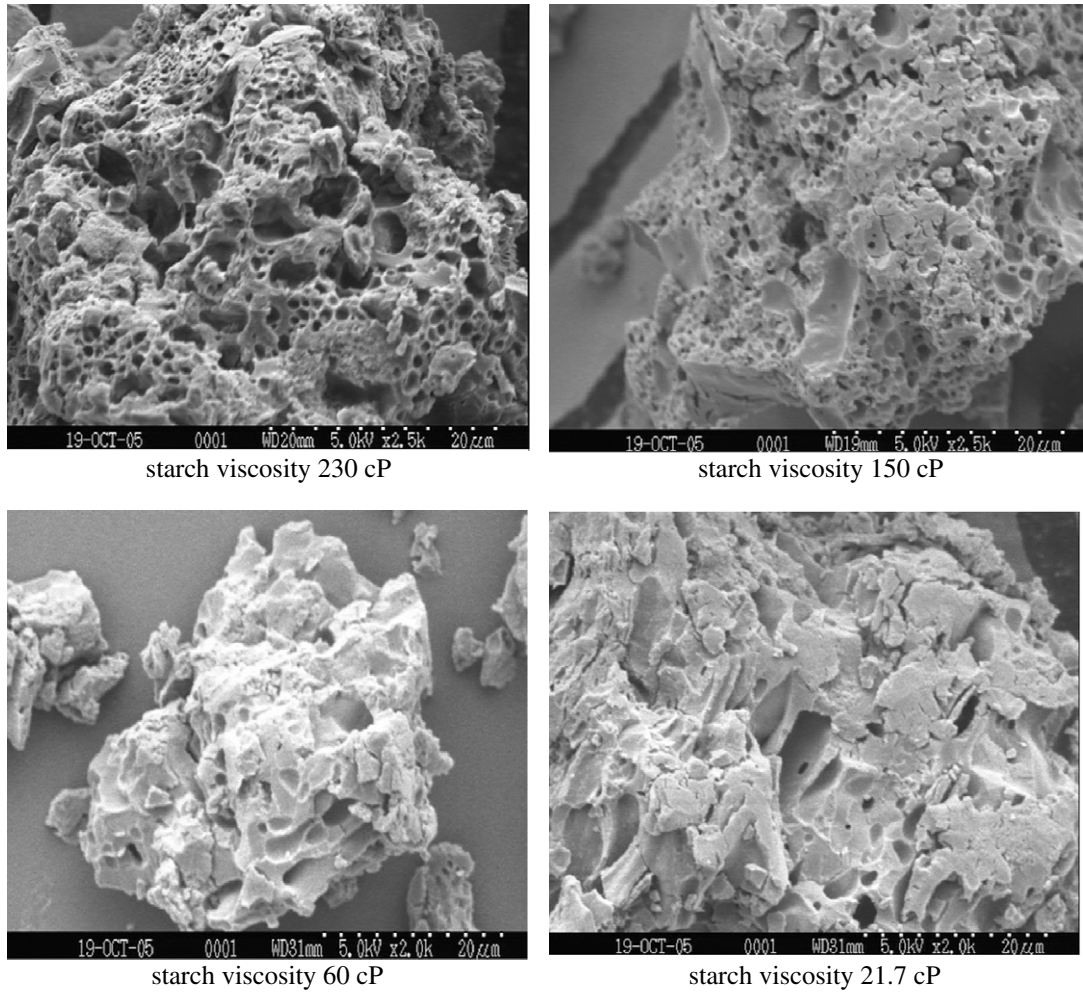


Fig. 10. SEM micrographs of SMCF made from starch of different viscosities.

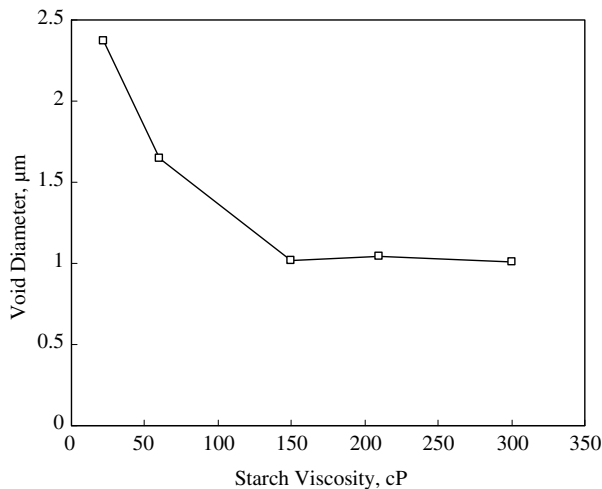


Fig. 11. Effect of starch viscosity on the void diameter of SMCF.

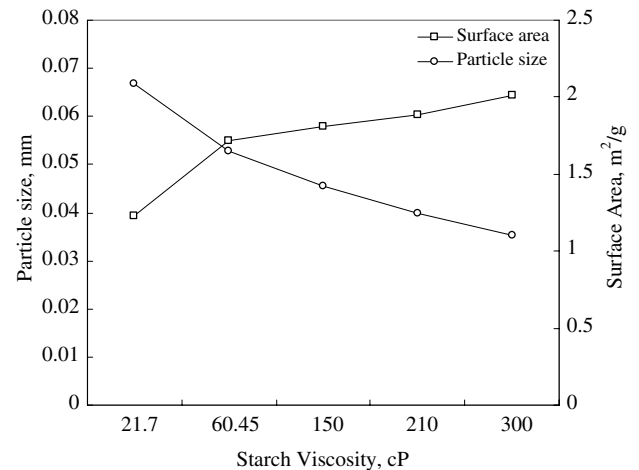


Fig. 12. Effect of starch viscosity on the brightness and average particle size of SMCF.

molecular weight develop in the starch matrix a resistance of the foam from collapsing during precipitation as the water is removed and the foam structure is developed.

3.3. Effect of pressure on the stability of void structure of SMCF

It is important for many applications to determine the effect of press loading on the structure of the starch

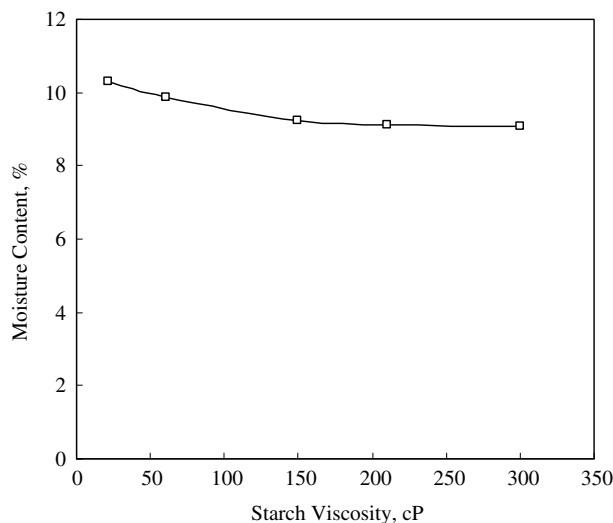


Fig. 13. Effect of starch viscosity on the moisture content.

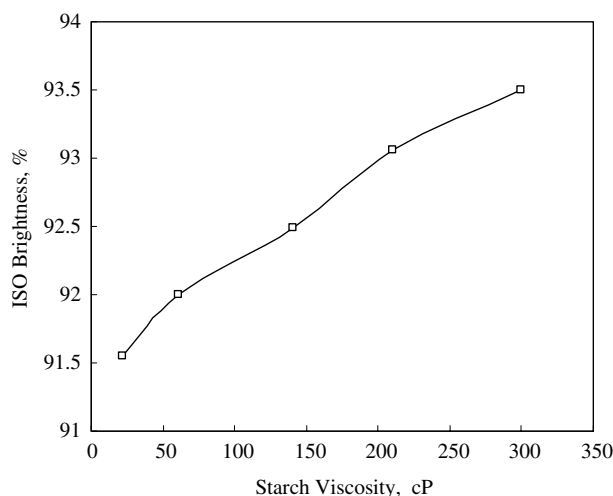


Fig. 14. Effect of starch viscosity on the brightness of SMCF powder.

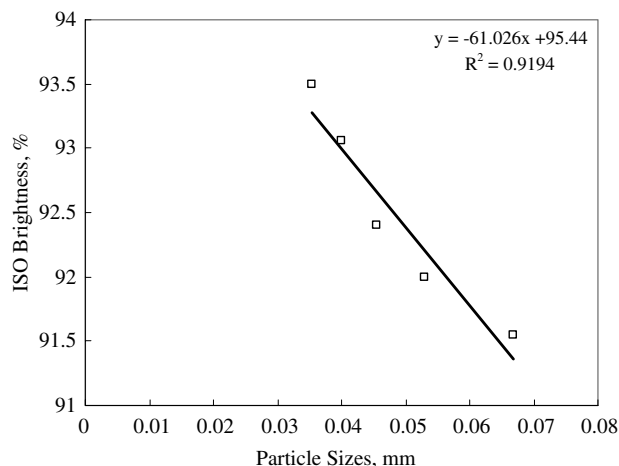


Fig. 15. Relationship between brightness and average particle sizes for different starch viscosities.

foam particles. To investigate, crosslinked starch microcellular foam particles were prepared from a 20% cooked starch crosslinked with 15 g glutaraldehyde/100 g starch, in acidic medium at 50 °C. SMCF pellets were prepared at different pressures (1400–11,200 psi). The SMCF pellets were split and the cross-sections analyzed for changes in the void structure by SEM (Fig. 16). At a pressure of 11,000 psi the foam structure is significantly compressed relative to at 1400 psi. The response of the foam structure to the loading is reflected in decreases in brightness with increased pressure (Fig. 17), presumably due to the decrease in specific surface area under loading. Crosslinking provides a resistance to foam collapse as reflected in a higher brightness relative to uncrosslinked SMCF for all loading levels (Fig. 17). The collapse of the foam is also found to be time dependent, as shown in Fig. 18. These results indicate that the crosslinking of the SMCF does contribute somewhat to the strength of the foam but that the foam structure is susceptible to mechanical crushing.

3.4. Effect of mixing speed on the particle size

SMCF was prepared from native starch using glutaraldehyde (15/100 g starch) as a crosslinking agent at 50 °C. All the samples were prepared with the same conditions except different rates of shear were applied by changing the mixer speed during the solvent exchange process. The shear was applied using an IKA-Werk, RW 16 Basic S1 stirrer with a flat mixing blade of approximately 4 cm long and 2 cm height for speeds of 1100, 1600, 2500 and 4100 rpm. The precipitation time was kept constant for all samples (6 h). The mixing speed during the solvent exchange plays an important role during the formation of starch foams, Fig. 19. The lowest mixing speed of 1100 rpm has a negative effect on the porous structure of the SMCF. Higher speeds of 2500 and 4100 rpm promote an extensive porous structure of important utility for final applications. Increases in the mixer speed cause decreases in the average particle size and increases in the brightness of the SMCF, Fig. 20. These results indicate that the formation of the porous structure is a complicated function of starting material composition and processing conditions.

3.5. Effect of solvent and drying conditions

A series of experiments were carried out to investigate the effect of the solvent exchange process and drying conditions on the foam formation. A quantity of 40 g of starch was cooked, crosslinked with glutaraldehyde (15/100 g starch) and the water exchanged with ethanol as described in the experimental section. Before drying, the sample was divided into halves. The first half was dried from the ethanol under three different conditions, (1) filtered onto filter paper with the assistance of house vacuum (ambient), (2) allowed to dry in a Petri dish in an

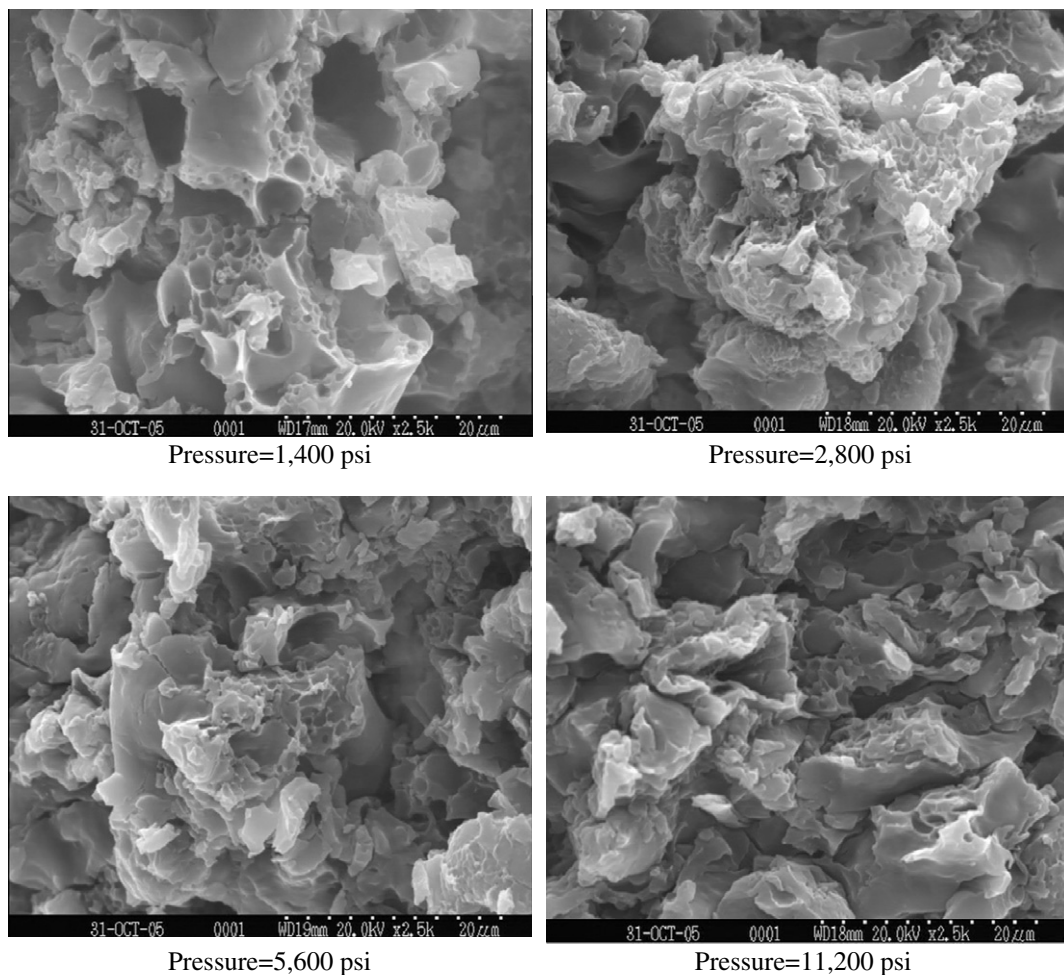


Fig. 16. SEM micrographs of SMCF pellets pressed to different pressures.

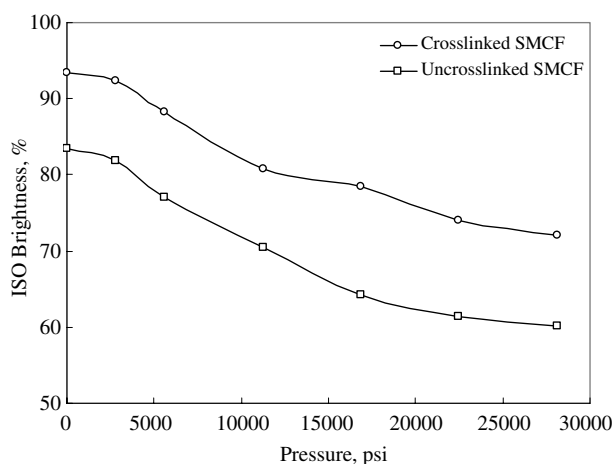


Fig. 17. Effect of the load pressure on the brightness of SMCF pellets for constant pressing time (5 min).

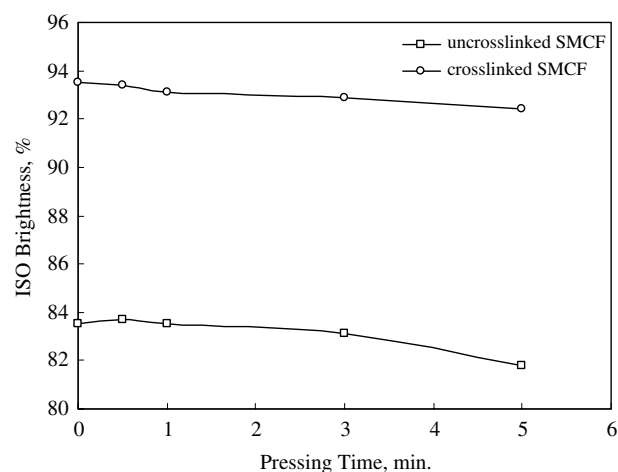


Fig. 18. Effect of the pressing time on the brightness of SMCF pellets at constant load pressure (2800 psi).

atmosphere with controlled humidity (50% RH) and temperature (23 °C), and (3) allowed to dry in a Petri dish at 105 °C in an oven. The other half of the sample was solvent exchanged with acetone two times (100 ml each,

20 min). Finally the sample was dried from acetone under the three same conditions. The brightness of the particles, indicative of the quality of the porous structure, was measured for each sample preparation method, Table 1.

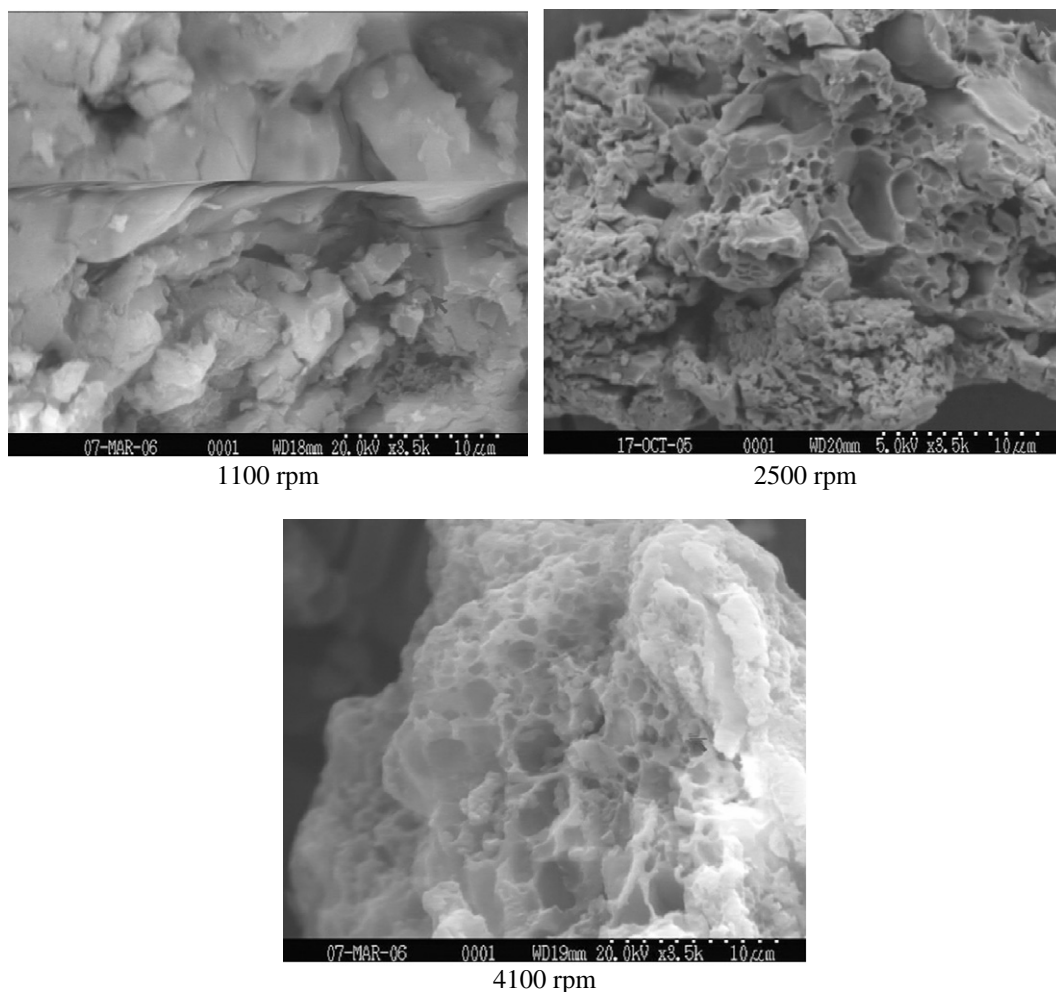


Fig. 19. SEM micrographs of SMCF at different mixing speeds during the solvent exchange process.

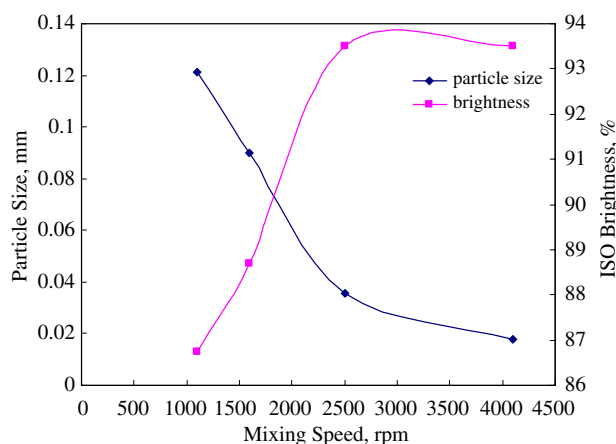


Fig. 20. Effect of mixing speed during the precipitation of SMCF on the average particle size and brightness.

The brightness data indicates that neither the liquid nor the drying conditions impacted the particle brightness significantly. This suggests that much of the morphological properties of the particles are established during the precipitation process.

Table 1

The effect of drying conditions on the brightness of starch particles

Drying conditions	ISO brightness, %	
	Acetone	Ethanol
Ambient conditions	93.3 ± 0.9	94.4 ± 0.2
50% RH and 23 °C	92.7 ± 1.2	94.0 ± 0.2
105 °C oven	94.0 ± 0.1	93.5 ± 0.7

The average brightness and range are indicated.

4. Conclusions

Starch microcellular foam was prepared by the crosslinking of cooked corn starch with glutaraldehyde (15/100 g starch) at 50 °C in acidic medium. Increased glutaraldehyde concentration from 0 to 15/100 g is accompanied by increased specific surface area, brightness and decreased particle size and moisture content. Interesting structures with significant amounts of voids in the 1 μm range can be clearly observed for the concentration range of glutaraldehyde of 7.5–15/100 g starch. Below and above this range, the SMCF does not show the same consistency in pore volume and pore

sizes. Also decreasing the starch molecular weight (as measured by viscosity) causes a decrease in the surface area and brightness and an increase in the average particle size, moisture content and void diameter. Lower starch molecular weight starting materials produce a poor void structure. Increased loading pressure and time caused a collapse of the voids within the SMCF and a subsequent decrease in brightness for both crosslinked and uncrosslinked starch. The particle size of the SMCF was greatly affected by the shear rate applied during the solvent exchange precipitation process. These results indicate that the formation of the porous structure is a complicated function of starting material composition and processing conditions.

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