DIMENSIONAL CHANGES OF STARCH MICROCELLULAR FOAM DURING THE EXCHANGE OF WATER WITH ETHANOL AND SUBSEQUENT DRYING

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Starch microcellular foams (SMCF) containing pores in the micron size range may be prepared by pore-preserving drying processes, developing highly porous, high specific surface area materials useful for applications such as opacifying pigments or as adsorbent materials. The objective of this research was to understand how the exchange of water with ethanol, used as a pore preserving step, affected the dimensional properties of the starch material during and after processing. SMCF were prepared from molded aquagels of cooked corn starch that were subjected to ethanol exchanges with different time intervals (6, 12, or 48 hrs) and number of exchanges (1, 2, or 3) and then air dried. To study the transformation of water-swollen starch into precipitated starch foam in ethanol, the volume of the starch material was measured in the wet state after each exchange and after final air drying. As water is replaced by ethanol, the starch material contracts, with the greatest contraction during the first ethanol exchange. The amount of contraction during air drying decreased with decreased starch water content just before air drying, presumably due to less pore collapse of the stiffer cell walls on drying. Interestingly, the minimum density of 0.37 g/cc SMCF was for the 12 hour exchange time, not the longest exchange time. Evidence of a skin-core morphology included SEM images as well as dimensional instability data on dried samples. The results indicate that SMCF of low density with fewer tendencies to deform during drying does not necessarily require extremely long exchange times.

INTRODUCTION

Foams used as engineered packaging materials can reduce packaging weight, add functionality, and help to create a package that is appealing to the customer. Synthetic plastics have held an important position in the packaging industry, especially dominating applications requiring water resistance. This position is supported by an extremely well-developed and profitable petroleum industry. However, the vast use of petroleum-based plastics and packaging materials has created environmental problems associated with their disposal and lack of biodegradability. Development of biodegradable packaging materials has been given priority in government strategic policies (e.g., DETR 2000 & DEFRA 2004) since packaging waste was identified as a critical item in the efforts to

reduce wastes to landfills (Linstead et al. 2001). Due to this, in the past two decades, interest has grown in the use of biodegradable material for packaging and disposable products. Biopolymers and bio-based products emit the same amount of carbon dioxide as was used during the plant growing period and thus can be considered as carbon dioxide neutral. In contrast, the production, use, and disposal of petroleum-based materials cause a net positive emission of carbon dioxide to the atmosphere and contribute to an imbalanced carbon cycle of the earth (Thiebaud et al. 1997).

Due to availability, cost, and functionality starch has gained interest as a raw material for bio-based products. In recent years, the United States has produced starch at the rate of more than 16 billion pounds per year. Out of this, more than 50% of the starch was produced from corn. Several studies have been conducted to develop extruded and molded starch foam to replace synthetic foam (Fang et al. 2002; Bhatnagar et al. 1995a,b). Researchers have successfully produced numerous products from starch, such as composites for disposable containers (Murakami et al. 2005), starch microcellular foam (Iman et al. 2008; Yu et al. 2006; El-Tahlawy et al. 2007; Glenn et al. 1995), light weight concrete (Glenn et al. 1997), starch modified polyurethane (Barikani et al. 2007), and many more. These starch based products are not only biodegradable and bio-based, but also have physical and mechanical properties comparable to products made from petroleum-based materials.

Starch granules from plants are generally semi-crystalline, composed of amylopectin (branched polymer, ~70%) and amylose (linear helical polymer, ~30%) (Maurer 2001). Both amylose and amylopectin are composed of α-D-glucosidic units connected to each other through a 1,4-oxygen ring atom, where amylopectin contains 1, 6 branch points. For most applications, the granules are cooked to the point of gelatinization by thermal means and processed in solution form.

Water sensitivity is one of the issues when using starch as a packaging material. There have been several approaches to induce water resistance in starches. Xu et al. (2005) extruded starch-based biodegradable foam from starch acetate to investigate the interaction between degree of substitution and blowing agent type. These researchers evaluated physical, mechanical, and morphological properties for use as a loose fill packaging. Imam et al. (2008) produced foam packaging material from composites of starch, pulp fibers, and waste from fish processing. These materials show increased mechanical properties and slower initial water absorption due to the protein from the fish waste relative to a control starch sample. Cinelli and coworkers (2008) prepared foam plates of potato starch blended with corn fibers and polyvinyl alcohol. These materials were determined to have similar mechanical and water resistance properties to the expanded polystyrene foam.

Starch microcellular foams are foam materials with a multitude of pores in the micron range, which can be produced by swelling starch in water, exchanging the water with a low surface tension liquid, and then drying, as an example. The exchange of water with a non-solvent in starch solutions generates a microcellular structure. Subsequent drying of this structure from a low surface tension solvent preserves this structure, which creates a microcellular foam.

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In our research group, starch microcellular foam (SMCF) particles from starch, starch crosslinked with glutaraldehyde, and starch blended with alkyl ketene dimer (AKD) have been produced with a simple ethanol solvent exchange process (El-Tahlawy et al. 2007, 2008; Bolivar et al. 2007). Starch foams have also been produced from extrusion via CO_2 and crosslinked with epichlorohydrin (Patel 2009; Patel et al. 2009). These particles have high brightness and high specific surface area. Enhanced pore structure with increased starch molecular weight was found with a moderate amount of crosslinking (El-Tahlawy et al. 2007). Improvements in the foam structure were found with increased shear rate during the ethanol solvent exchange precipitation process. The incorporation of AKD into SMCF was shown to increase the initial water contact angle from 28 to 91° (El-Tahlawy et al. 2008) and this contact angle persisted for greater than 4 minutes (Patel et al. 2009). Water swelling of SMCF after immersion in water for 24 hours was decreased from around 4.5 g of water per g of sample to 2.5 g of water per g of sample for SMCF blended with 2% AKD (Patel et al. 2009). The use of these modified SMCF materials with water resistance is still limited to short contact times with water; these materials cannot be used as water barriers for prolonged water exposure times.

Previous research with producing SMCF had used an exchange process in which the water in the starch gels was exchanged with ethanol using a 3:1 weight ratio of ethanol to starch gel (Patel 2009; Patel et al. 2009). One exchange method utilized three successive 100% ethanol baths for 48 hours each (total time 144 hrs). A second method utilized exchange baths of 40% ethanol, then 70% ethanol, then 90% ethanol, then three exchanges of 100% ethanol, each for 48 hours (total time 288 hrs). Both methods were suitable to produce well-developed microcellular foam structure; however, the prolonged times used would be a significant disadvantage for commercial implementation. Longer exchange times are used in order to allow the slow diffusion of water out and of the ethanol into the starch aquagel. Presumably, the complete and slow exchange will improve homogeneity of foam structure and minimize internal stresses in the material leading to less defects and more dimensional stability.

During the exchange process it has been observed that the samples contract significantly in volume, impacting the structure and the final density of the dried SMCF. Glenn and coworkers (1995) also reported significant contraction between initial starch aquagel and final dried SMCF of about 60-65% for corn starch and significantly less, about 30-40 percent for high amylose starch. They also studied larger volume samples and determined that they required longer equilibration time to remove water from the aquagel and avoid excessive shrinkage. It was also found that the exchange process had an effect on surface cracking of the samples (Patel et al. 2009).

It is very important to understand how the exchange of water with ethanol alters the dimensional properties of the starch material during exchanges and subsequent drying. This research evaluates the dimensional changes that occur as water is exchanged by ethanol during several exchange pathways. Correlations are made regarding water content and shrinkage, and it is shown that the longest exchange times are not always required to develop SMCF structures.

EXPERIMENTAL

Materials

Corn starch was supplied by Cargill, USA (Cargill Gel 03420), consisting approximately of 25% amylose and 75% amylopectin. Anhydrous ethanol (Fisher product Number A405^P-4) was used for solvent exchanges.

Starch Cooking Procedure for Aquagel Samples

A cooked starch solution was prepared by adding 24 g of corn starch to 276 g of deionized water in a three-necked round-bottom flask (500 ml) under continuous stirring (IKA-Werk, RW 16 Basic S1) with a crescent shaped paddle at a speed setting of 10. The cooking involved heating the starch slurries to 95˚C in an oil bath for approximately 15 to 20 minutes. The cooked starch solution was poured into identical glass petri dishes (PYREX, Product #3160-101, inside diameter of 9 cm, approximate volume of 90 cc) and allowed to cool to room temperature over a period of 1 hr. The initial weight of the poured starch gel samples was 70-80 grams, and the initial thickness was approximately 0.75 cm.

Aquagels of cooked starch solutions were prepared by refrigerating the starches in the petri dish containing the starch overnight at 5˚C.

SMCF Preparation Process with Different Time Intervals between the Exchanges

SMCF was produced by a solvent exchange technique. In this process, the higher surface tension solvent (water, surface tension of 72 dyne/cm) is replaced with a lower surface tension solvent (ethanol, surface tension of 22 dyne/cm), which produces a SMCF structure that is preserved upon drying. Ethanol exchange times evaluated were either 6, 12, or 48 hrs. The number of exchanges was either one, two, or three. In the first exchange the starch sample residing in the petri dish was submerged in the exchange bath. During this exchange, the starch material would detach from the dish. Subsequent exchanges involved the starch material without the petri dish. During each exchange, the previous solvent was decanted from the SMCF and then replaced with fresh exchange solution. Each exchange was carried out using approximately 300 ml of 100% ethanol *or* approximately three times the weight of the initial starch and water solution. The dimensions of the aquagels were determined using a digital caliper by measuring the diameter and height of the aquagel before and after each exchange. The amount of water that was removed from the starch aquagel was determined by measuring the density of the exchange bath solution and knowing the relationship between the density and the water content of a water-ethanol solution,

$$\% \text{ Water} = 471.7\,\rho - 371.0 \tag{1}$$

where ρ is the density of the ethanol-water solution in g/cc (R^2=0.994). Densities were measured by determining the mass of 10 ml of the solution. Once the solvent exchanges were completed, the samples were allowed to air dry in a 23˚C and 50% relative humidity

atmosphere, for a minimum time of three days, and the dimensions were determined. For samples that had curvature, the curved length dimensions were measured by measuring the contoured surface with a flexible ruler.

SMCF Preparation Process with Different Concentration of Ethanol with One Exchange

Another procedure was utilized to study the dynamic amount of water removed from starch aquagels. In this case, a single exchange was carried out on individual aquagel starch samples separately with a bath of either 20, 40, 70, 90, or 100% ethanol (300 ml) for 48 hr. The amount of water in the exchange bath was determined at 1, 3, 6, 12, 24, and 48 hours using the density method. Once the 48 hr exchange time was completed, the samples were allowed to air dry in a 23°C and 50% relative humidity atmosphere.

RESULTS AND DISCUSSION

As stated in the Introduction, the behavior of the expanded starch in the presence of water and ethanol is of significant importance in the production of the SMCF structures. In particular, it is important to understand the starch gel dimensional changes that occur as water is replaced by ethanol during the liquid exchange process. In order to investigate, the dimensions of the starch in the presence of water and ethanol were determined as a function of exchange history.

The amount of water in the starch materials changed with the ethanol-water exchange time (6, 12, and 48 hours) as well as for the number of exchanges (1, 2, and 3 exchanges). In an exchange the starch aquagel was immersed in a 100% ethanol bath that was around three times the initial starch aquagel weight. Images of the air dried starch gels after different exchange times and exchange numbers show that very opaque foams are formed with long exchange times and that the opacity increased with number of exchanges (Fig. 1).   In contrast, starch materials with short exchange time and one exchange were clear, glassy, and non-porous.

The water contents of the initial swollen starch and after several exchanges are shown in Fig. 2 as a function of the number of exchanges and exchange time.   It is evident that longer exchange times were more effective at removing water from the starch matrix, as expected. This process is governed by the diffusion rate of ethanol into the starch matrix and the diffusion rate of the water out of the starch matrix. The process is complicated by changes in starch structure that are occurring as the water (a starch solvent) is replaced by the ethanol (a starch non-solvent).   It was determined by measuring the water in the exchange bath that nearly complete replacement of the water with ethanol occurred with a single 48 hr exchange time. In contrast, only 80 and 50% of the water in the starch aquagel was removed for the 12 hour and 6 hour exchange time during the first exchange. With increased number of exchanges for the 12 and 6 hour exchange time, the water in the starch can be reduced to near zero (Fig. 2).

Fig. 1. Air dried starch samples produced from different exchange times and numbers
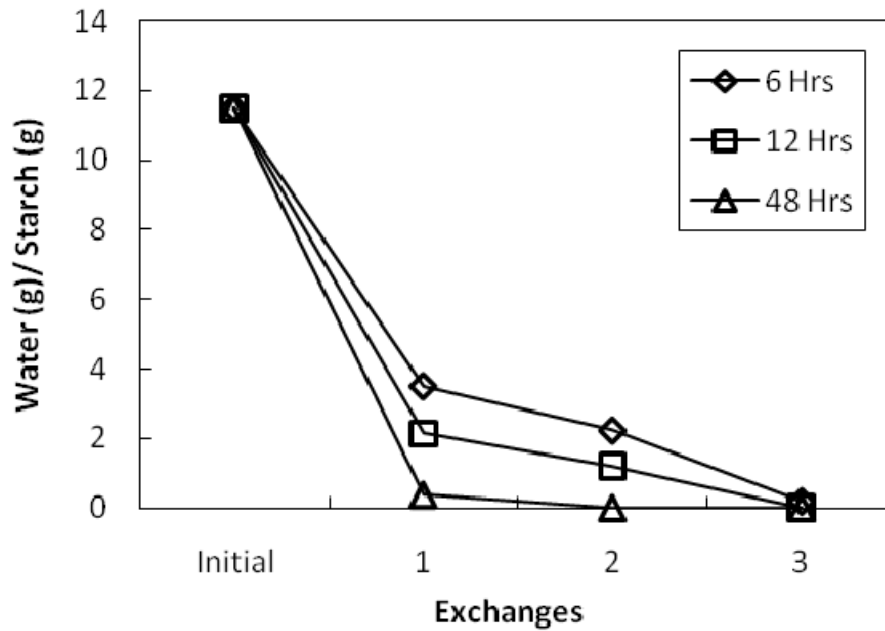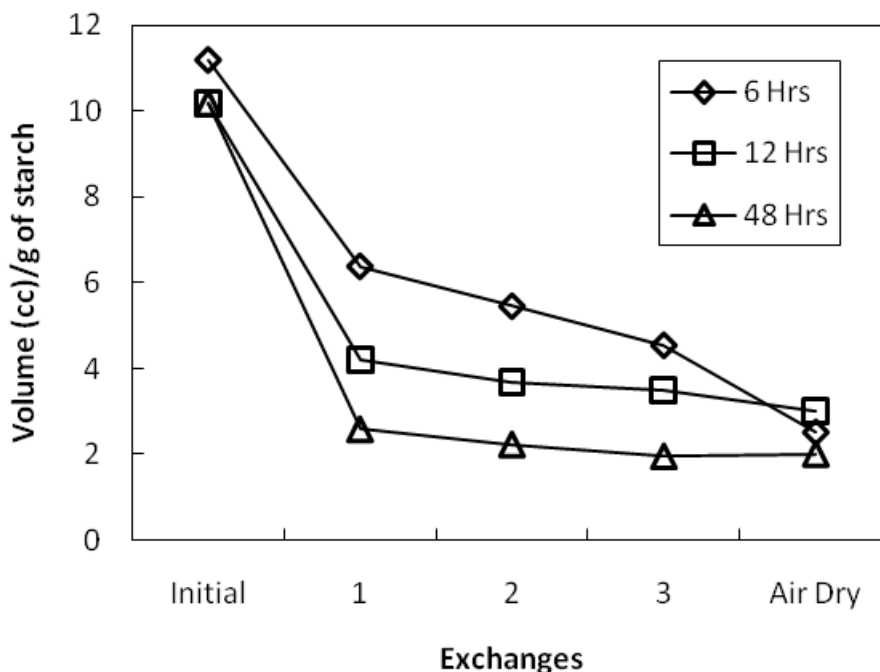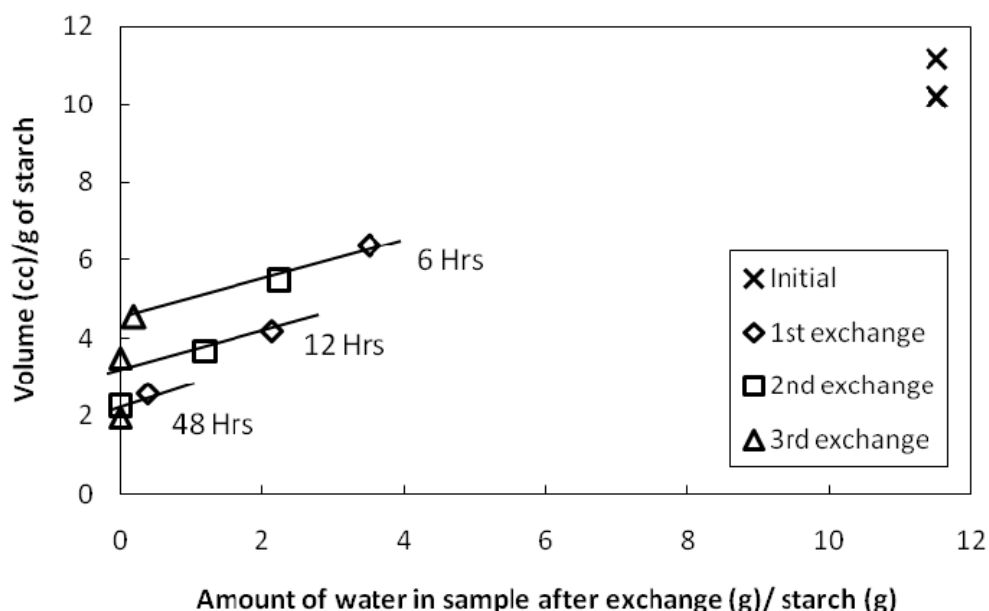

Fig. 2. Water content of the starch material after each exchange

The precipitation of the starch that occurs during dehydration resulted in a contraction of the starch material (Fig. 3). The precipitation could be observed visually, as the samples changed from a cloudy material to a brighter, white opaque material in the exchange bath. This phenomenon is similar to retrogradation, the recrystallization of starch during cooling. For the 48 hour exchange time, the majority of the contraction occured in the first exchange, followed by much smaller contractions for the second and third exchanges.   Similar results occured with the 6 and 12 hr exchange times. With the complete removal of water from the starch, the contraction occurring during air drying was very small, as in the 48 hr exchange sample. The contraction on air drying for the 6 and 12 hour exchange samples was larger, presumably due to the higher amounts of water in the starch matrix on drying. The residual water during drying may increase the contraction by a combination of the following phenomena: (1) the water plasticizes the starch foam cell wall material, lowering its modulus allowing more contraction, and (2) the water forms capillary forces that collapse the pore structure on drying. It is of interest to note that the final specific volume of the 6 and 12 hour sample was greater than that for the 48 hour sample. Thus, in the production of these types of materials, if minimizing the density is an objective, an optimum time should be identifiable that minimizes processing time but still provides a fully developed microcellular foam structure.

Fig. 3. Specific volume of starch material after each exchange

In fact, the processing pathway is important. For instance, the structure as reflected by the specific volume of the starch material depends not only on the concentration of water in the sample but also on the water and ethanol concentration history of the samples (Fig. 4). Samples with the same level of water can have different specific volumes depending on the exchange history.

Fig. 4. Specific volume of starch material versus the water content of the sample. Duplicate measures for the initial material are indicated.

The relative density of a foam is defined as the foam density divided by the pore wall material density. The pore volume fraction is then equal to one minus the relative density, one of the important characterizing features of cellular solids. The relative density can be used to indicate material transitions from a solid with isolated pores (relative density greater than 0.3) to a fully developed cellular solid (relative density less than 0.3) (Gibson and Ashby 1997). The structure of cellular solids depends on the materials, as well as the processing conditions, and can range from nearly perfect order of cells to a completely random nature of the size, shape, and location of cells. In this study, the pore wall solid material density was assumed to be 1.06 g/cc (Patel 2009). The relative density of the air-dried starch materials that had been subjected to one, two, or three solvent exchanges, is shown in Fig. 5.

In this case, the relative density of the materials after air drying is the cumulative effect of the material contraction during solvent exchange and contraction during air drying. For the 6, 12, and 48 hour exchange times, the relative density of the material decreased with increasing numbers of exchanges (Fig. 5). Materials that were about 0.4 relative density were samples that had experienced three exchanges for the 6 and 12 hour exchange times and either two or three exchanges for the 48 hour exchange time. The minimum theoretical relative density for these samples is 0.075 and would only be realizable if there were no shrinkage during exchanges or drying. These samples do not approach this minimum value. It is of practical interest to note that the 12 hour exchange for three exchanges resulted in the minimum density and also appeared to have less curl and cracking (Fig. 1). Thus, the samples with the longest total exchange times did not have the best properties.
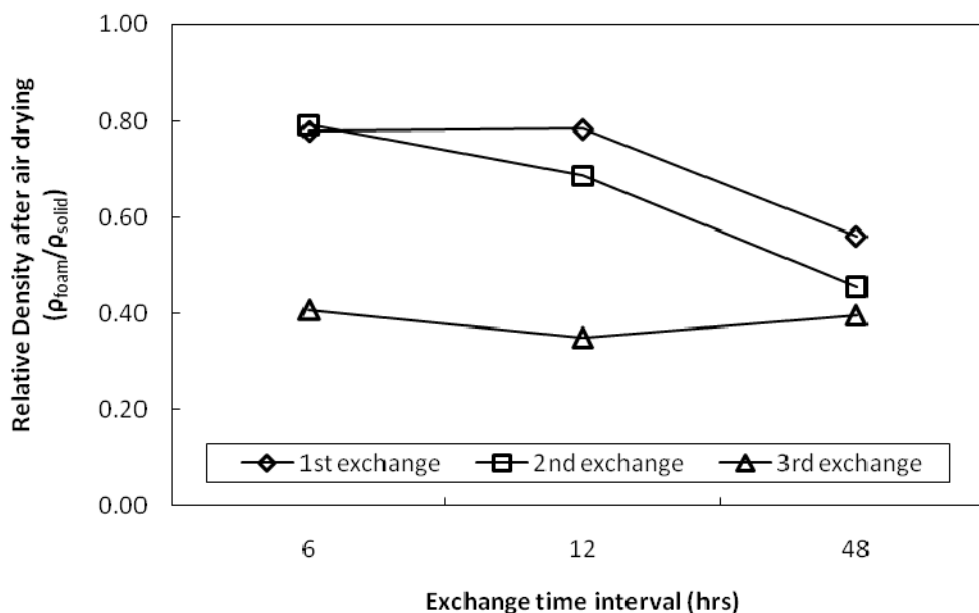
Fig. 5. Relative density of air dried samples prepared with different exchange time intervals

Scanning electron microscopy (SEM) images of a freeze-fractured cross section of an air-dried starch aquagel without any exchange (relative density equal 1) and of a starch after three 48 hr ethanol exchanges and air drying are shown in Fig. 6 (Patel et al. 2009). For the starch after three 48 hr ethanol exchanges and air drying, a very fine porous structure is observed. However, some remnants of starch granules can be observed, which is perhaps the reason for the well-developed highly porous microcellular foam structured materials having relative densities somewhat higher than 0.3. Pore size ranges for SMCF materials have been reported (Patel 2009; Patel et al., 2009).
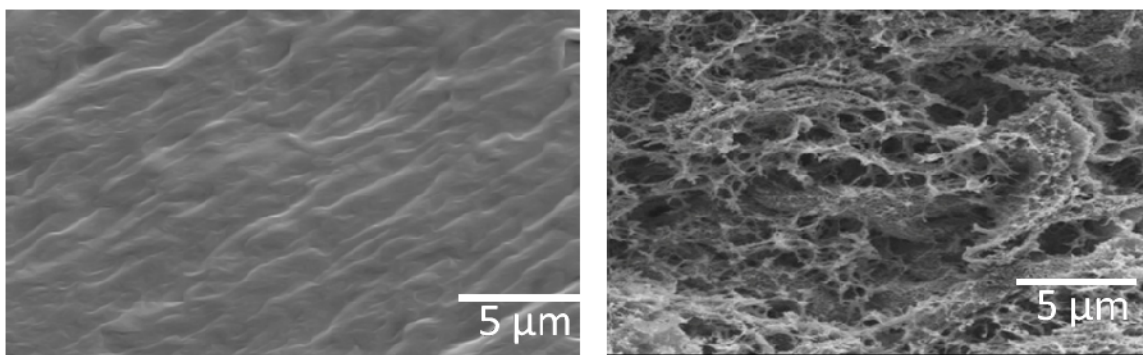
Fig. 6. SEM of air dried sample without solvent exchange (left) and with solvent exchange (right)

There was a correlation between volume contraction on drying and the moisture content of the starch just before drying, as shown in Fig. 7. The volume contraction on drying is defined as the gel volume before minus after air drying (ΔV) divided by the grams of starch. The data are in agreement with the concept that the contraction during

drying is related to the pore collapse from water-induced capillary forces and water induced plasticization. The data in Fig. 7 combined with the data from Figs. 1 and 6 indicate that one criteria for a well-developed foam structure is a very low water content prior to final drying; in this case less than 0.4 g moisture/g starch was identified.
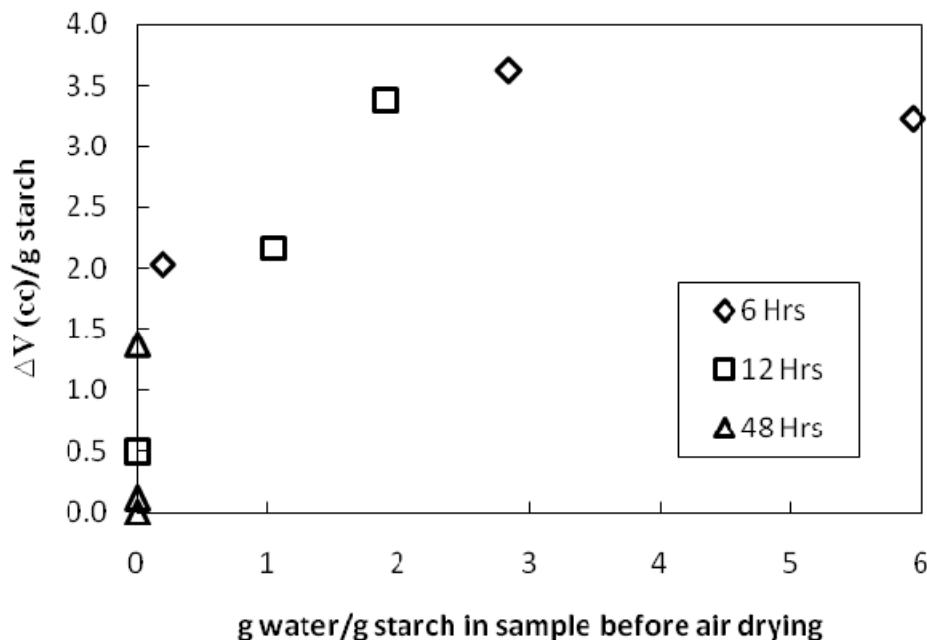
Fig. 7. Change in volume of sample due to air drying versus the initial water content during air drying

In the above studies the starch aquagels were subjected to 100% ethanol baths. It is postulated that the immediate contacting of the starch aquagels with 100% ethanol would cause immediate changes in the external surfaces of the aquagels due to a rapid decrease in water content at the surface and that internal stresses would arise due to the differences in surface and bulk properties. To investigate, starch aquagels were separately immersed in a single exchange with either 20, 40, 70, 90, or 100% ethanol for 48 hours.

By sampling the exchange bath liquid to determine the density of the liquid, the amount of water released from the starch into the exchange bath was determined (Fig. 8). Note that despite a smaller initial concentration gradient of water between gel and bath, the total amount of water diffusing out of the starch aquagel at short times was greater for 20 (data not shown) and 40% ethanol baths (Fig. 8) relative to the 100% ethanol bath. This might be explained by a structural change in the surface of the starch for the 100% ethanol bath that decreases the diffusion of water out of the starch material. The greater concentration gradients for the high % ethanol baths cause the overall percentage of water removed to be higher at long times when dynamic issues involved in diffusion are not as important. It is of interest that the data at long time are within experimental error for 70-100% ethanol baths.
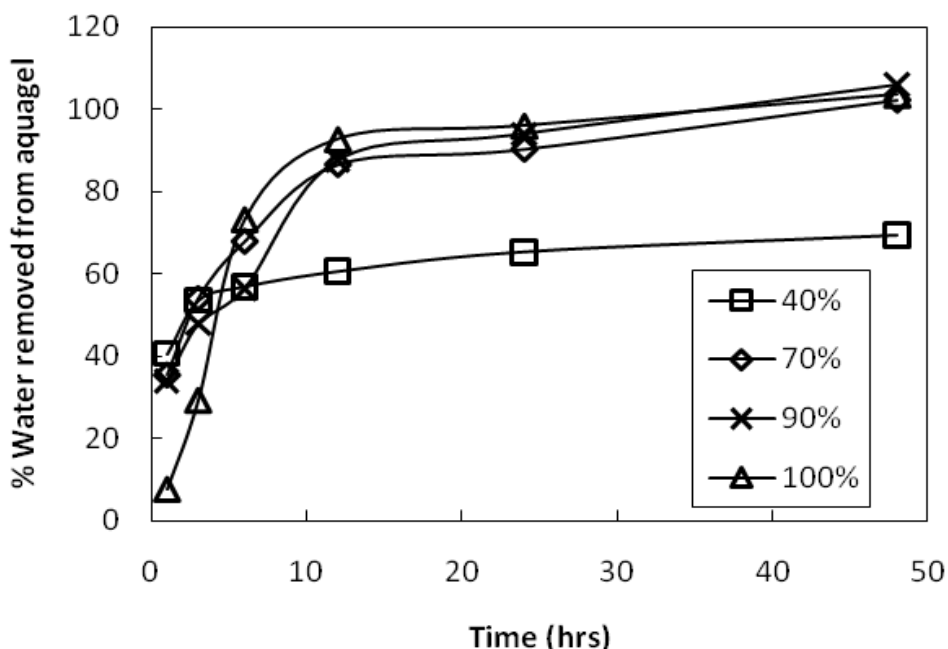
Fig. 8. Percent water removed from an aquagel over time for baths of different ethanol percent

The amount of water removed from the aquagel at one hour and at 48 hours is plotted versus initial % ethanol in the exchange bath in Fig. 9. At one hour, the baths with 20-90% ethanol all provided a greater water removal than the 100% ethanol bath. At longer times, when the diffusion rate is less important, the 100% ethanol bath had a similar water removal as the 90% and 70% baths and greater water removal than the 40 and 20% baths.
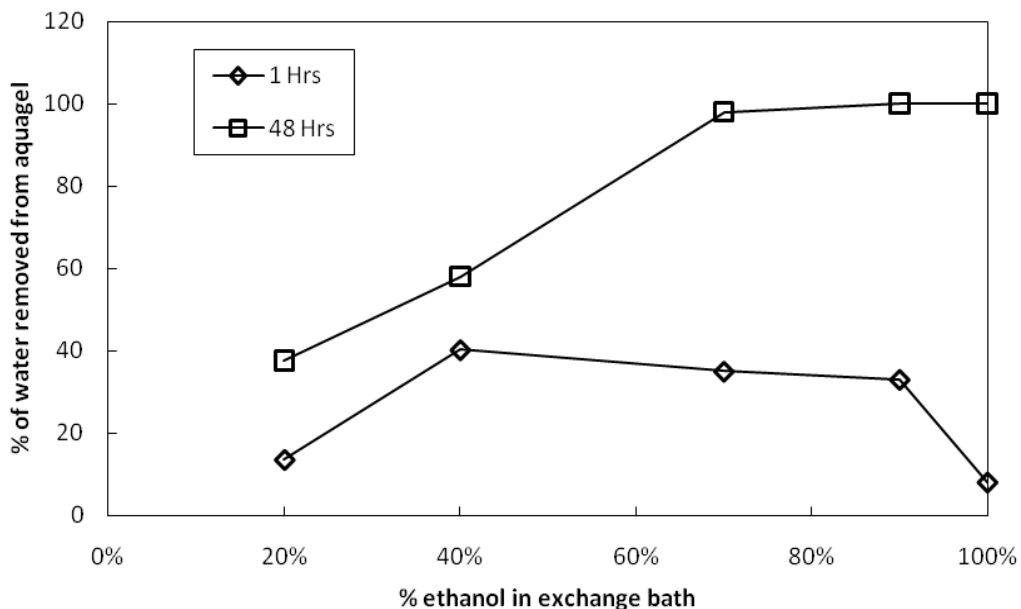

Fig. 9. Percent of water removed from an aquagel versus percent ethanol in initial exchange bath after 1 hour and after 48 hours

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Inspection of the starch materials during the exchange process and after air drying indicated that the samples with exchange baths of higher ethanol content had higher dimensional instability. Dimensional instability was observed as a curving of the initially flat disk shaped starch gel into a saddle-back shape after being air dried. The radius of curvature of these samples decreased (increased deformation) with increased initial ethanol content in the exchange bath, Fig. 10. The results suggest that internal stresses between the surface and the bulk of the starch materials increased with increasing initial % ethanol in the bath.
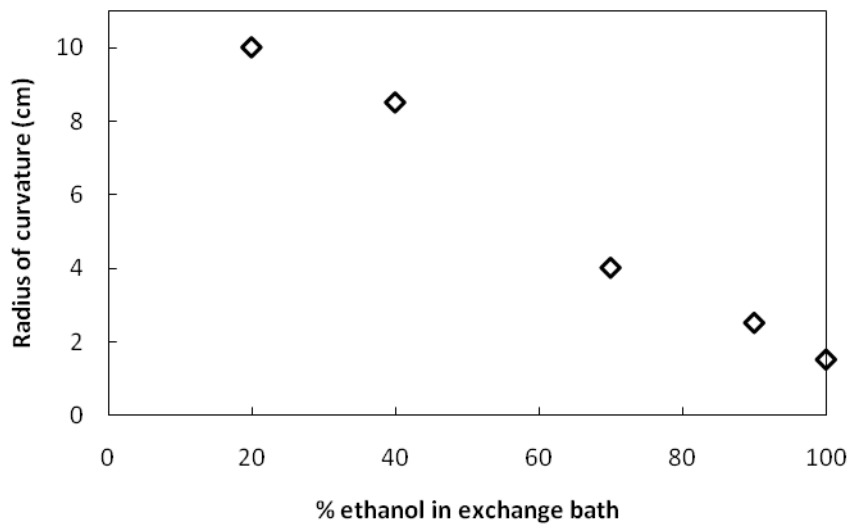
Fig. 10. Radius of curvature of the air-dried starch vs. initial % ethanol content of exchange bath

SEM inspection of starch microcellular foams indicated that there was a difference between the bulk and the surface of such materials (Fig. 11). In fact, some areas of the surface of the SMCF resemble the glassy non-porous material generated when air drying non-exchanged starch aquagels, as in Fig. 6.
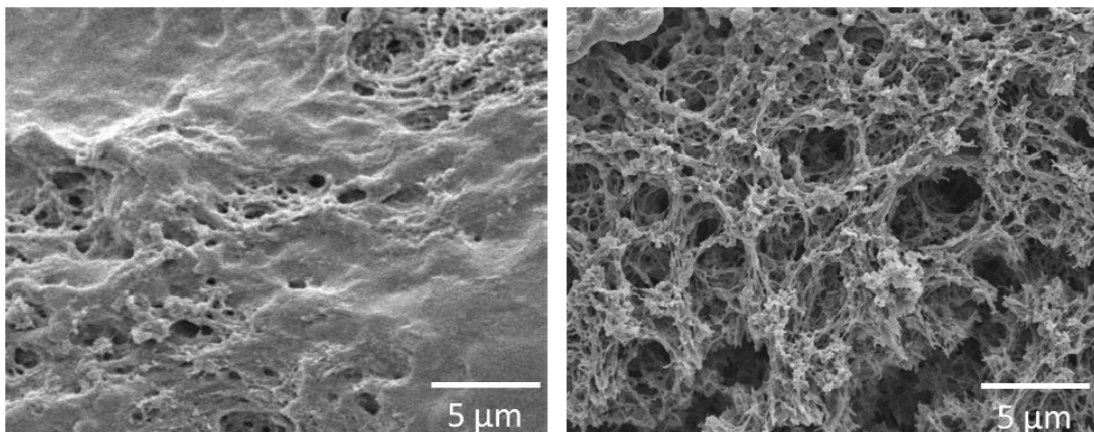
Fig. 11. Image of the surface of a SMCF (left) and a freeze fractured surface of the bulk (right) of same sample. The sample was formed from starch cooked at 95°C and held for 20 minutes followed by three 48-hour 100% ethanol exchanges.

CONCLUSIONS

As the water in a starch gel is replaced by ethanol, the starch material precipitates and contracts. The greatest volume contraction and water removal was with the first ethanol exchange. It was also observed that longer exchange times (12 and 48 hours) resulted in larger contraction in the sample volume during the first exchange when compared to shorter exchange intervals. This implies that starch precipitates during ethanol exchange as long as water is being removed from the system. This phenomenon is similar to starch retrogradation. The contraction of the starch material during air drying increases with increased moisture content present in the starch/water/ethanol material just before air drying. This increase in contraction was presumably due to more pore collapse on drying and the water-induced plasticization of starch. Interestingly, the minimum air-dry SMCF density of 0.37 g/cc was achieved with a 12 hour exchange time, not the longest exchange time. Evidence that the samples developed a skin-core morphology included SEM images as well as dimensional instability data on dried samples. The dense skin structure was responsible for an initially slow water removal rate for ethanol baths of high % ethanol. The results indicate that there may be an intermediate optimum exchange time to produce SMCF of low density with low tendency to curl during drying.

ACKNOWLEDGEMENTS

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