

## ABSTRACT

PATEL, SAMEERKUMAR VASANTLAL. The Effect of Processing Conditions and Composition on Starch Microcellular Foam Properties. (Under the direction of Richard A. Venditti and Joel J. Pawlak).

Starch microcellular foams (SMCF) contain pores in the micron size range and have high specific surface area and may be useful for applications such as opacifying pigments or as adsorbent materials. The objective of this research was to determine how the processing conditions and use of a sizing and crosslinking agent would affect the foam structure and properties.

Refrigerated cooked starch solutions were subjected to different solvent exchange processes involving the exchange of water for ethanol to produce SMCF materials. Exchange of water for ethanol precipitates the starch and subsequent drying from the low surface tension ethanol preserves pores on drying producing low density and high opacity microcellular foams. It was determined that the microcellular foam density passed through a minimum with respect to the solvent exchange times.

SMCF were prepared from molded aquagels and carbon dioxide assisted extruded samples. Extruded samples showed macroscopic pores whereas samples from aquagels showed a much finer micro pore structure. Aquigel based SMCF samples had lower density and higher brightness than extruded samples. Micro pores and not macro pores contributed to increased brightness and moisture content of these materials. Crosslinking with epichlorohydrin imparted significant water resistance to the extruded samples as evidenced in lower water swelling and higher contact angles.

In order to investigate the effect of adding a hydrophobicizing agent on the water sensitivity several samples of SMCF blended with alkyl ketene dimer and/or Kymene were produced and the results showed that the samples had similar brightness, higher density, and higher water contact angle than starch foams alone.

The Effect of Processing Conditions and Composition  
on Starch Microcellular Foam Properties

by  
Sameerkumar Vasantlal Patel

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APPROVED BY:

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Dr. Joel J. Pawlak  
Committee Co-Chair

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Dr. Martin Hubbe  
Committee Member

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Dr. Richard A. Venditti  
Chair of Advisory Committee

## **Dedication**

I would like to dedicate this thesis to my wife and my family. Their love, encouragement and patience have enabled me to complete this work.

## **Biography**

Sameer Patel grew up in Gujarat, India. He received his Bachelor's and Master's Degrees in Industrial Chemistry from Sardar Patel University, V. V. Nagar, Gujarat, India in 2000. After graduation he worked as a quality control chemist at SwamYog Chem for two years then he worked as a senior research fellow at ICAR (Indian Council of Agriculture Research), and as a research fellow at Department of Materials Science (Sardar Patel University). In 2005, Sameer immigrated to USA with family. In 2007, Sameer entered graduate school at North Carolina State University in the Wood and Paper Science Department. His research has focused on the use of natural polymeric materials, starch, as pigment and packaging material.

## **Acknowledgments**

I would like to thank those who have helped make this journey through graduate school possible.

I would especially like to thank my advisers Dr. Richard Venditti, and committee member Dr. Martin Hubbe for their supervision, encouragement and comments.

I would also like to express my gratitude to Dr. S. S. H. Rizvi and Dr. Ali Ayoub (Cornell University) for providing extruded starch samples. I would also like to thank you Kristin Hyden and Linda McMurray for their help for experimental setup.

Lastly, I thank my wife and family for their unconditional love and support; I could not have done this without you.

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## **List of Publications**

- (1) Patel, S., Venditti, R. A., Pawlak, J. J., Ayoub, A., and Rizvi, S. S. H., (2009). Development of cross-linked starch microcellular foam by solvent exchange and reactive supercritical fluid extrusion. *Journal of Applied Polymer Science*, 111, 2917-2929.
- (2) Rutledge, A. R., Venditti, R. A., Pawlak, J. J., Patel, S., and Cibils, J. L., (2008). Carbonized starch microcellular foam-cellulose fiber composite structures. *BioResources* 3(4), 1063-1080.

## **Chapter 1**

### **Introduction**

#### **Objective**

The objective of this research was to produce high brightness and low solubility Starch Microcellular Foam (SMCF) particles for paint, coating and paper pigment applications and to determine how the processing conditions and blending/cross-linking would affect the foam structure, physical, optical and moisture related properties of SMCF materials.

#### **Uses of Starch in Paper and Other Industries**

Starch is the third most commonly used material by weight in papermaking following cellulose fiber and mineral pigments, which makes the paper industry one of the important customer of the starch industry. Most starch used in paper industry in US derived from corn. Although corn starch is most commonly used in paper industry, potato starch is acquiring utilization, especially as a furnish additive, in the wet end of the paper machine. Current utilization of industrial corn starch for the production of paper and paperboard has reached 3.3 billion pounds annually, 70% of that is a chemically modified form of starch. Additionally, 1.2 billion pounds is used in adhesive for corrugated and laminated paper products. Starch is used for different purposes through papermaking process such as furnish preparation prior to web formation, surface sizing, coating, effluent treatment, and conversion of paperboard to packaging grades. Moreover, there are many other areas for the industrial utilization of starch such as utilization as a binder in pharmaceutical industry,

biodegradable plastics, and as a disposable packaging material in packaging industry instead of Styrofoam.

### Chemistry of Starch

Starch is a high molecular weight polymer of anhydroglucose unit ( $C_6H_{10}O_5$ ) linked by  $\alpha$ -D-glucosidic bonds, found in plant tubers and seed endosperm. Typically, starch consists primarily of two types of molecules, amylopectin and amylose. Amylopectin is the major component of most starches. It consists of very large number of short chain polymers that are bound together at their reducing end by a  $\alpha$ -1, 6 linkage, which makes this very large branched polysaccharide, Figure 1-1.

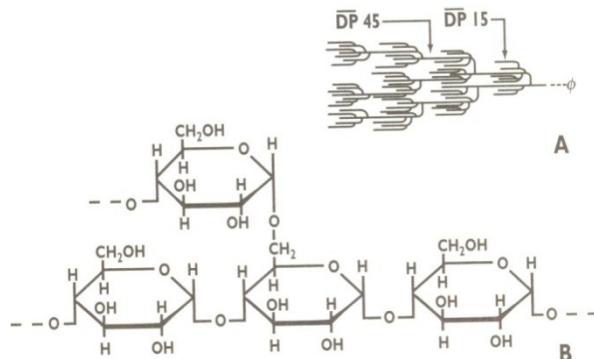


Figure 1-1: Amylopectin molecule (A) and the chemical structure of molecular segment (B). (Maurer, H. W., 2001)

Amylose is a linear chain of glucose, Figure 1-2. The stereo chemical arrangement of –CH<sub>2</sub>OH group at carbon 5 on the same or opposite sides of the carbohydrate chain, defines

the linkages as alpha or beta anomeric configurations. Amylose consists of  $\alpha$ -1,4 linked anhydroglucose units, while in cellulose the same units are linked by  $\beta$ -1,4 linkages, Figure 1-2. This linkage provides an unusual chain conformation and molecular properties for amylose that are remarkably different from cellulose.

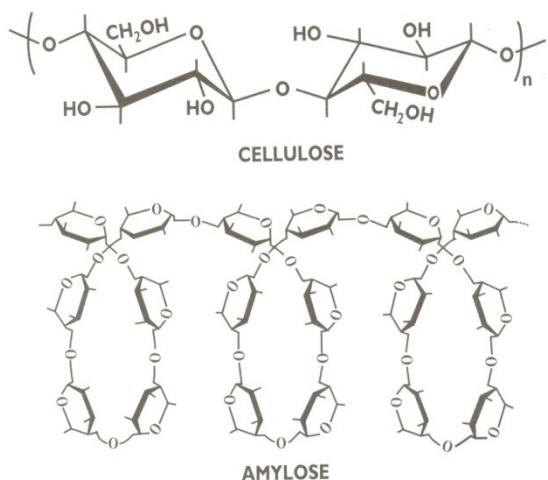


Figure 1-2: Macromolecular conformation of cellulose and amylose. (Maurer, H. W., 2001)

The  $\alpha$ -1,4 linkages result in flexible molecules with natural extended helical twist that can reorganize into a collapsed helix (retrogradation); on the other hand, the  $\beta$ -1,4 linked cellulose has rigid and flat molecule structure that accounts for the strength of cellulose fibers and the structure of plants, Figure 1-2. The  $\beta$ -linkage in cellulose provides tight packing of the polymer chains, which favors intermolecular hydrogen bonding and crystallinity between adjacent chains. The  $\alpha$ -linkage imparts a helical conformation to the glucopyranosyl chain, which prohibits extensive interchain association by hydrogen bonding, and allows easy degradation, except after retrogradation, Figure 1-2.

In carbohydrate polymers, hydroxyl orientation and hydrogen bonding between –OH groups, or between –OH groups and ring –O- atoms, affects solubility, conformation, and stability.

Intramolecular hydrogen bonding in amylose, for example between O<sub>2</sub> and O<sub>3</sub> of subsequent anhydroglucose units, gives stability to helical complexes.

### Types of Starch

Starch is available in small granules for commercial use. Granules are generated in the host plant. The size, density and shape of granules depend upon the source from which they are obtained, Figure 1-3. Normally, low moisture content tissues such as rice and wheat give small, dense, polygon-shaped granules, while high moisture content tissues such as potato and corn give large, less dense, oval-shaped granules, Figure 1-3. Moreover, moisture content of starch products depends upon the relative humidity of the atmosphere in which they are stored, and the amount of fatty substances bound as inclusion complexes with amylose.

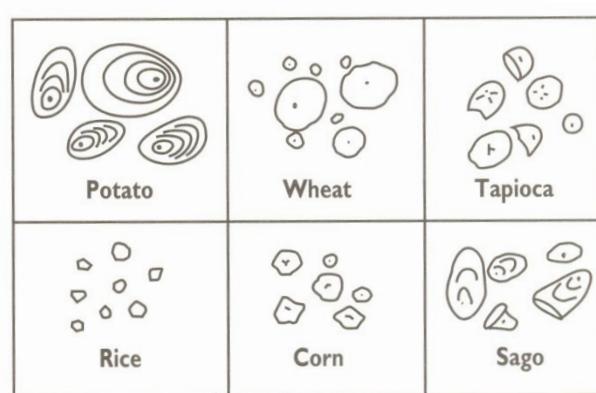


Figure 1-3: Characteristics shapes of commercially available starch granules. (Maurer, H. W., 2001)

Generally, starches are distinguished from each other by the percentage of amylose and amylopectin contained in individual starch, for example, if starch contains higher percentage of amylose than amylopectin, it would be known as high amylose starch. On the other hand, starch also named from its source, for example, if starch is derived from potato, it would be known as potato starch, Figure 1-4. Certain plants are known as waxy, because of the waxy appearance of the seed endosperm. Waxy starch has a much lower or almost negligible content of the amylose. Other types of starches have higher amylose content. The composition of amylose and amylopectin depend on the plant and the geographical locations. For example, some potato starch contains phosphate ester group. Typically one phosphate ester group may be found per 300 glucose units in its amylopectin, which makes the starch anionic in nature. Recently, genetic modification of starch crops has led to the development of starches with improved and targeted functionality. Although chemical composition of the starch component is very simple, the qualitative analysis of their structure is not.

### **Analysis of Starch**

Starch forms inclusion compounds with iodine. Most starches stain to a deep blue with an excess of iodine. The color shifts toward violet or pink when the starch is degraded. The coloration is due to the presence of amylose, since amylopectin stains violet to brown. The reaction can be used for qualitative indication of starch in paper. Quantitative analysis requires a comparative standard of the same kind of starch.

## General Properties of Unmodified Starches

The large fraction of almost all starches, amylopectin, is mainly responsible for granule structure and crystallinity. Most starches have both amylopectin and amylose, and both crystallize into joint structures, which are responsible for mixed crystal formation (Zaslow et al., 1967). Starch granules are semi-crystalline in nature due to this certain regions are highly crystalline and other regions amorphous (French et al., 1984), Figure 1-5. Moreover, both major components of starches, amylose and amylopectin, are bonded each other by hydrogen bonding. The semi-crystalline nature of starch granules is responsible for insolubility in cold water. Crystallinity is determined by X-ray diffraction. Cornstarch has 40% crystallinity, while other starches, waxy maize, high-amylase corn, rice, potato and tapioca have 40%, 22%, 38%, 28%, and 38 % crystallinity respectively.

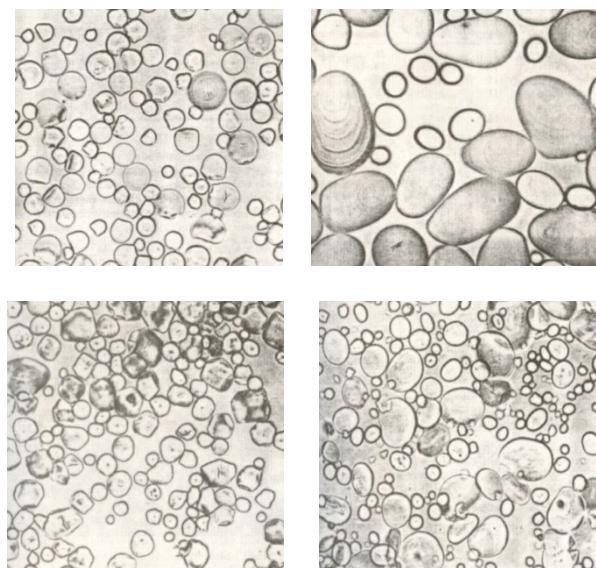


Figure 1-4: Granules of Tapioca starch (top left), Potato starch (top right), Corn starch (bottom left), and Wheat starch (bottom right) with 600X magnification. (Maurer, H. W., 2001)

Starch granules are insoluble in cold water as they have organized, hydrogen bonded, crystalline structure, which can easily observed birefringence pattern by microscope, Figure 1-5. Crystalline regions in starch granules are mainly due to tight packing of chains and interchain hydrogen bonding, while amorphous regions mainly due to branch points, chain folding, and regions where molecules are not in order(French et al., 1984).

As water is an integral part of the starch granules, it can be adsorbed and desorbed according to relative humidity of the environment. The location of water in starch granules and its affect on structure have been studied through nuclear magnetic resonance spectroscopy (Richardson et al., 1987).

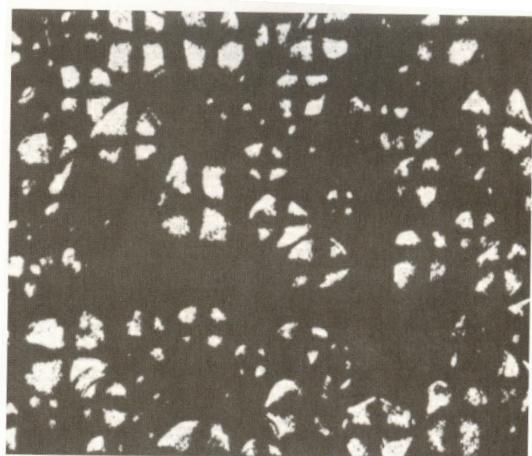


Figure 1-5: Corn starch under polarized light with 600X magnification. (Maurer, H. W., 2001)

Orientation of fibrils within starch granules is observed by electron microscopy. By looking at the cross section of starch granule a pattern, radially oriented, can be seen. These patterns

are not continuous or regular that believed to be due to alternating crystalline and amorphous regions. Crystalline regions of starch granules dissolved or destroyed when heated in water to about 72°C and higher, and starch molecules become free to hydrate and expand (Leach et al., 1967), Figure 1-6.

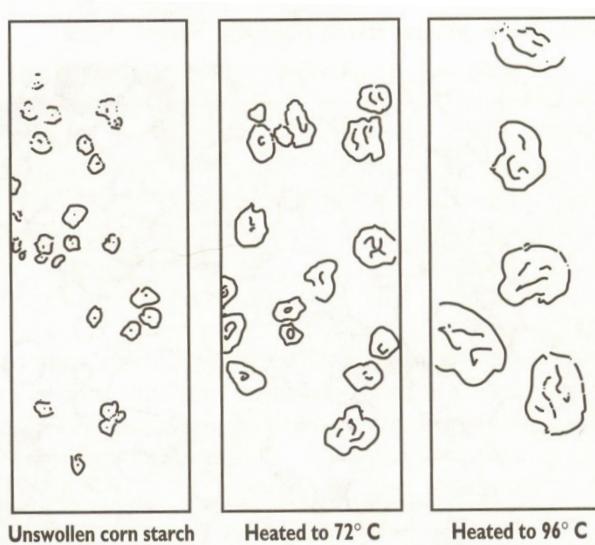


Figure 1-6: Effect of temperature on the swelling of corn starch in excess water. (Maurer, H. W., 2001)

This is irreversible breakdown of the granular structure and granule starts to swell, which is also known as first step of starch gelatinization. This can be observed by Differential Scanning Calorimetry (DSC) thermogram. Loss of birefringence is widely used to determine gelatinization temperature as it indicates molecular orientation of starch granules. On overheating, more hydrogen bonds of granules will break and the starch granules disrupt and disintegrate until a stage of partial or complete dispersion of individual starch molecules occurred. On heating starch suspensions in water, the granules expand, until the crystalline

regions ruptured, and starch molecules become available to hydrate and expand. The viscosity of solution will increase rapidly as the swollen granules take up space and increase their mutual contact. Initially, about 72°C, there is little increase in viscosity as breakage of crystalline regions just started, but at about 85-95°C it increases greatly due to the high level deterioration of crystalline regions and swelling of individual molecules at the maximum extent. Cornstarch is difficult to gelatinize than potato starch due to structural and composition differences. Moreover, cornstarch contains fatty acids, which can complex with amylose, to destroy these complexes higher temperature about 115-125°C is required.

### **Dispersion of Starch**

To disperse or “cook” starch, it is essential to induce enough energy to rupture hydrogen bonding and induce molecule of water. When solution of starch is heated, initially, the granules swell slightly and then reversible swelling observed until a critical temperature reached. This temperature is known as pasting or gelatinization temperature. At this temperature the granule structure melts and large swelling occurs, which causes a great increase in viscosity. Beyond this point, with increase of temperature the viscosity decrease due to the breakage of swollen granules. The decrease in viscosity is continuous with increase in temperature, extended cooking time and shearing of paste, until starch molecules fully dispersed. Different starches have a different pasting or gelling temperature range and properties of cooked starch pastes vary greatly due to their complex colloidal nature.

Viscosity of starch solution is greatly influenced by the type of starch, genetic variations, and environment in which it grown i.e. soil quality and weather during the growing season. These swelling and rupture processes can be observed by observing viscosity with heating, Figure 1-7. Cooking of starch involves hydrogen bonding between –OH of starch and “shell” of water during hydration. Entropy forces a confirmation that gives the interior of amylose helices hydrophobic. Removal of water from hydrated starch by competing forces, such as the presence of aluminum ions, facilitates a return to hydrogen bonding between amylose molecules, thus causing starch retrogradation.

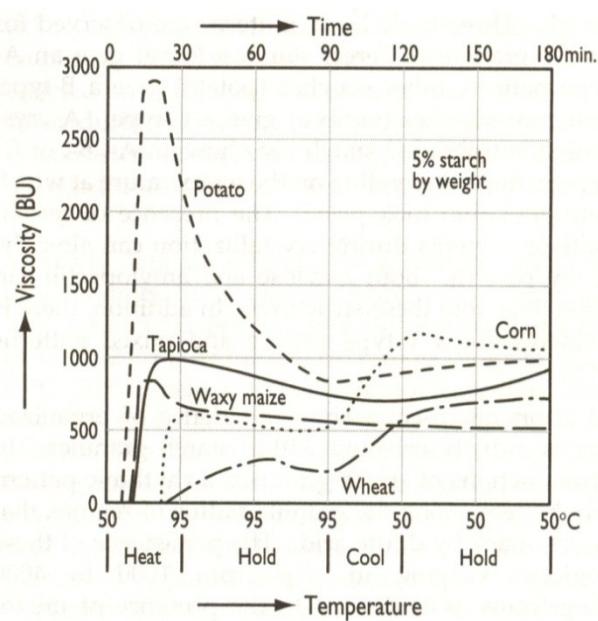


Figure 1-7: Typical Brabender traces from commercial starches (5% starch by weight). (Maurer, H. W., 2001)

The viscosity of cooked starch dispersion might be gradually decreased due to precipitation of amylose when held for an extended time in the crystalline temperature range (71-82°C), Figure 1-7. On the other hand, the viscosity of solution might increase due to gel formation when cooled below 60°C as amylose loses water of hydration, Figure 1-8. At temperature around 60°C amylose is precipitated out from the solution and forms insoluble aggregates that make a few interlocking molecules to microcrystalline regions. This phenomenon is known as a starch retrogradation and it occurs with decreasing paste temperature and with aging of starch paste.

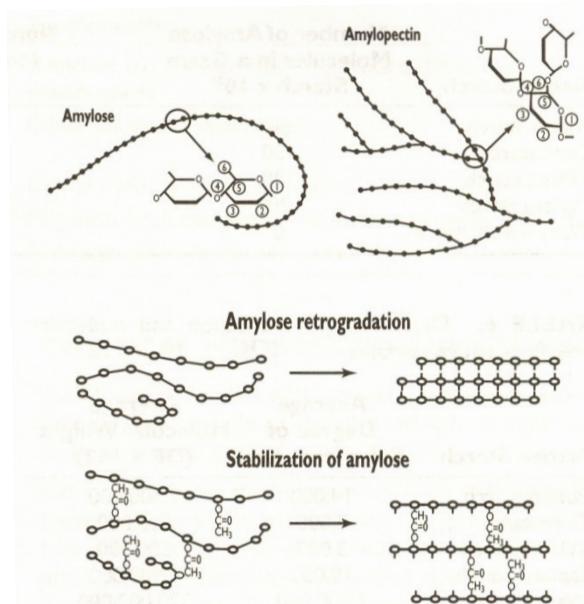


Figure 1-8: Retrogradation and stabilization of amylose. (Maurer, H. W., 2001)

By measuring viscosity of starch solution with a range of temperature various properties of starch can be studied such as the peak viscosity, the presence of blends of starches, the

gelatinizing temperature; viscosity reduction with time, temperature and shearing rate; the rate and extend of viscosity buildup on cooling, the stability of viscosity at a specified temperature, and effect of water quality and additives on paste of viscosity. Stability of viscosity is obtained by chemical substitution on the starch molecules.

### **Modification of Starches**

Unmodified starch gelatinized into high-viscosity dispersion that cannot be process easily especially on paper coating equipment. Chemical reactions to reduce the viscosity by reducing molecular size and/or by de-polymerization processes; reactions that introduced chemical groups on starch backbone are known as derivatization processes. A variety of starch derivatives are made, known as modified starch, each of them is used for specific purpose in paper industries or in other industries for certain quality requirements. Starch dispersion and viscosity depends on cooking temperature, time, and agitation. Higher temperature, longer cooking time, and application of shear lead to produce better paste. Generally, the viscosity of cooked starch will increase with cooling and will continue to increase with aging; this increase can be minimized by controlled agitation of paste over time. An unstable product will increase in viscosity to a greater extent, and its viscosity increase will be irreversible. The substituted groups present on modified starch are effective in improving both the dispersion and the stability of starch pastes. The higher degree of substitution of hydroxyethyl and cationic starch both cook into comparatively clear solutions and maintain their clarity for longer period of time.

Modification of starch can be performed by a variety of techniques. Hydroxyalkylated starch, cyanoethylated starch, cationic starch ethers, anionic starch, starch esters, starch graft, hydrophobic starches, and many more modifications can be produced by derivatization. Starch grafts combine the properties of natural and synthetic polymers. For example, biodegradability of starch graft polymer (starch-vinyl acetate graft) can be attributed to starch and mechanical properties to synthetic polymer, vinyl acetate. Various attempts have been made to produce a hydrophobic starch that would be able to give combined properties like surface sizing and adhesion. These involve grafting of hydrophobic moieties onto a hydrophilic starch backbone. They can be prepared by esterification with octenyl substituted succinic acid anhydride (Järnström et al., 2000).

Several classes of starch derivatives can be prepared but most common are ethers and esters of starch generally used in paper coating and surface sizing of paper. Specific derivatives of starch include hydroxyethyl starches, cyanoethyl starches, acetate esters, polyurethanes, cationic starches, anionic starches, and many more.

### **Hydroxyalkylated Starch**

Hydroxyethyl starch can be prepared by reacting starch with ethylene oxide in the presence of alkaline metal hydroxides. Hydroxypropyl can also be produced in same way (van Warners et al., 1986). Sometimes, neutral salts are added to the reaction to inhibit swelling and to prevent the starch from being dissolved by the alkalinity of the reaction. The changes in properties of starch depend upon the degree of substitution by hydroxyalkylation.

Although, higher degree of substitution gives lower a gelatinization temperature and greater stability of the dispersion, it would give non uniform wetting, which results in lumping. The advantage of hydroxyethylation starch for paper coating is that it has better coating capacity, better contact of binder with pigment, more uniform and stable viscosity and very good water retention as compared to unmodified starch (Lammers et al., 2001).

### **Cyanoethylated Starch**

Cyanoethylated derivatives can be prepared by reaction between starch and acrylonitrile in the presence of alkaline catalysts. The reaction must be carried out at a slow rate to get a uniform product and ease of dispersion in water. Although, cyanoethylated starches have been proposed for use in paper coating as a binder, they have not been utilized to any great extent, most likely due to the environmental concerns.

### **Cationic Starch Ethers**

Cationic starch ethers derivatives can be prepared by substituting reagents, which add cationic groups to starch molecules by forming ether linkages (Hewing et al., 1992). The reaction follows nucleophilic substitution in presence of alkali catalyst. Precautions should be required to minimize swelling of the starch granules in suspension. The temperature of reaction should be maintained below the swelling temperature and neutral salt can be used to minimize or prevent swelling during the reaction. Variety of viscosity grades of cationic starches can be prepared by subsequent de-polymerization to meet required viscosity for surface sizing and coating systems. Most widely used cationic starches are quaternary amino

derivatives, which are commonly used at the wet end of the paper machine and for surface sizing. These derivatives are inherently cationic, do not require protonation, and can be applied without regard to paper sizing. These starches gelatinize at temperature below than the parent starches.

### **Anionic Starch**

Anionic starches can be prepared by reaction of starch with phosphoric acid, with alkali metal phosphate. It can also be prepared by derivatization with carboxymethyl groups (Roushdi et al., 1982).

### **Starch Esters**

Starch esters can be prepared by reaction of starch with acetic anhydride (Khalil et al., 1992). This derivative is also used as coating binders. The introduction of acetyl groups on starch backbones improves the dispersion of starch during cooking and increase the stability of the subsequent pastes. As starch esters are de-esterified under alkaline or acidic condition, it would not be used greatly in paper industries. Although, starch esters have limited use in paper industries, they are widely used in pharmaceutical industry as a binder.

### **Starch Grafts**

Grafted starch can be prepared in granular and in colloidal dispersion forms, granular products are mainly used as a water holding agents in sanitary and horticultural applications (Hebeish et al., 1996). A variety of monomers grafted on starch by using redox catalyst

(Honig et al., 1992). The product is a mixture of starch-copolymer, homo-copolymer, and un-reacted starch, un-reacted starch should be removed from the product before utilization. Starch grafts have combination of properties of a natural polymer and synthetic polymers. Presently, several research are going on to make plastics from starch by grafting different natural or synthetic monomers on starch backbone. Urethane copolymer can be grafted on starch; this graft polymer has high degree of hydrophobicity and good mechanical properties as compared to native or other modified starches (Barikani et al., 2007).

### **Hydrophobic Starches**

Hydrophobic starches can be prepared by binding hydrophobic moieties on to starch backbone. Several attempts have been made to make a hydrophobic starch that would give combined properties like sizing and adhesion. They can be prepared by esterification with octenyl substituted succinic acid anhydride (Tomasik et al., 1995), by maleination, phthalation. Hydrophobicity can be induced to starch by grafting synthetic monomer, copolymers, and oligomers to starch backbone.

### **Starch Microcellular Foam**

Starch has gained attention of scientist due to its well known structure and biodegradability. Several researchers have conducted investigations into creating novel materials from starch. Other than derivatization, there is an interest in making new class of foam called microcellular foam, which has very small voids (<10 micrometer), and unique and useful

properties for applications like pigments, absorbents, packaging materials, and disposable plastics (Colvin et al., 1995).

Macro and micro cellular foams can be defined by cell size (Williams et al., 1989). Macrocellular foam is prepared from organic polymers and have large (100 to 1000  $\mu\text{m}$ ) closed cell with cell wall thickness ranging from 10 to 100  $\mu\text{m}$  (Williams et al., 1989). The foam structure can be classified as closed cell or open cell depending up on the cell arrangement in the matrix. Microcellular foams have cell diameter under 10  $\mu\text{m}$  and have physical and mechanical properties, which are unique and of commercial interest (Williams et al., 1989; Baldwin et al., 1969; LeMay et al., 1990).

## **Preparation of Foams**

### **Macrocellular Foams**

To produce polymeric macrocellular foam, the most commonly used system consists of simultaneously generating a gas and nucleating gas filled bubble in a liquid polymer phase. The gas bubbles expand and are stabilized as polymer gets solidify to make the resultant foam (Saunders et al., 1991). Polyurethane foams are made in the same way. In another technique, a gas can be passed throughout a polymer melt by mechanical agitation or by blowing agents. Blowing agents commonly used in the extrusion procession. The compressed gas such as CO<sub>2</sub> or N<sub>2</sub> and low boiling point liquids passed through the extruder and these agents form gases which expand as polymer melt leaves the die. A wide range of chemical

blowing agents also is available in the market that can produce gas when mixed or heated with the polymer and produce gas within the polymer matrix (Benning et al., 1969).

Starch based foams are often created during baking using leavening agents. Leavening agents create large numbers of thin walled cells by generating gases within the mixtures; these gases may be generated by fermentation or by the reaction with the chemical additives (Van Dam, H et al., 1994; Handleman et al., 1961). Starch based macrocellular foam can be made by extrusion which involves mixing, heating and conveying the starch through a heated barrel using single or twin screw configuration. This is the efficient way to make snack foods, ready to eat cereals, and some non food products.

Moisture content and extrusion temperature are the most important parameters to control starch expansion. The starting material has moisture content ranging from 10-25% and barrel temperature of 170-230°C (Rizvi et al., 1995). The moisture inside the extruder barrel becomes superheated under the conditions of high heat and pressure and when starch melts exits the barrel through the die, the pressure drops to the atmospheric pressure converts superheated moistures to vapor and cause melt to expand into the foam (Hoseney et al., 1983). Starch macrocellular foam can be made by puffing starch at 170°C; at this temperature the water inside the popcorn kernel becomes superheated and pressure reaches 135 psi. Due to high temperature and pressure the kernel ruptures, the superheated water within the kernel becomes vapor and causes the product to expand (Hoseney et al., 1983).

## Microcellular Foams

Microcellular foam have been prepared from starch by different techniques such as freeze drying, solvent exchange, super critical fluid extrusion with/without N<sub>2</sub> or CO<sub>2</sub> as a blowing agent during the extrusion, replicating removable pore former, and polymerization of inverse monomer emulsions (Glenn et al., 1995), Figure 1-9.

The freeze drying technique consists of three steps, freezing, primary, and secondary drying. The freezing is an important step and it involves freezing an aqueous system; the water will form ice crystals and separates out from the solute.

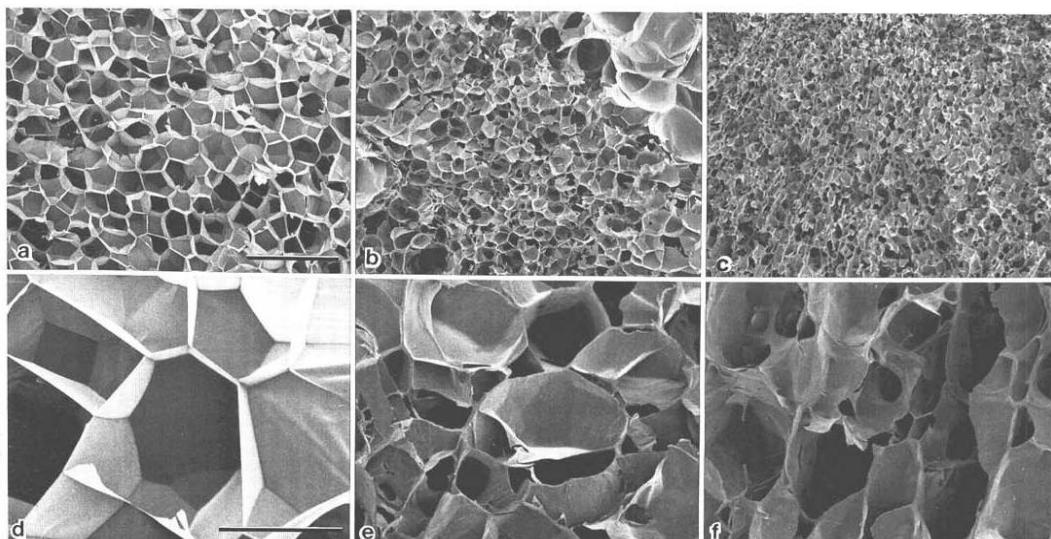


Figure 1-9: SEM of beaded polystyrene (a,d) puffed wheat (b,e) and freeze-dried foam made from 8% wheat starch aquagel (c,f). (Glenn et al., 1995).

The final pore morphology is formed as ice crystals are sublimated, a conversion of solid state to vapor state, during the primary drying step. The foam structure is therefore directly related to the size and distribution of the ice crystals in the frozen aquagel system. As a

result, a larger degree of super-cooling and higher freezing rate produce a smaller average pore size and a more homogenous pore structure. Starch microcellular foam can be prepared by preparing rigid aquagel of starch by cooling certain weight percent cooked starch solution poured in the specific mold, which can be freeze dried to produce low density starch foam by removing water phase by freeze drying from the starch matrix leaving void spaces inside the matrix (Glenn et al., 1995), Figure 1-9. Freeze drying involves phase change of water crystals from solid to vapor (skipping of liquid phase) and required a special instrument to handle entire process.

In the solvent exchange technique, water phase of a rigid aquagel is removed by a miscible liquid that is a non-solvent for starch possessing lower surface tension. The non-solvent precipitates the starch when replacing the water, forming micro-pores. Microcellular foams can be made from rigid wheat and corn starch aquagels by equilibrating the aquagels in ethanol before air-drying (Glenn et al., 1995). Since the surface tension created at the air/ethanol interface was only one third that of air/water, the gels did not collapse. High amylose corn starch aquagels possessed less compressive strength than the unmodified wheat and corn starch aquagels and collapse when exchanged in ethanol then air dried, Figure 1-10. Mesoporous carbons were prepared from starch microcellular foam without the need of templating agent (Budarin et al., 2006). This materials have wide range of applications such as use in chromatography analysis, catalyst and electro conductivity with potential applications.

Several researchers have attempted to produce microcellular foam by a newly developed low-temperature and low-shear extrusion technology, called supercritical fluid extrusion involves reactive extrusion of starch based matrices and injection of supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) as a blowing agent to produce microcellular extrudate (Rizvi et al., 2005). This SCFX process has been applied to make starch to make microcellular foam and the effect of process variation and formation of foam cell size, cell density, and mechanical properties have been studied. The super critical fluid extrusion technique is very important due to the ease of processing and suitability to use in industrial application. However, pores in this process are quite large and a well defined microcellular foam structure production method using extrusion has not been determined. In the Super Critical Fluid Extrusion (SCFX) technique, starch microcellular foam can be prepared by passing starch solution to the extruder with/without CO<sub>2</sub>/N<sub>2</sub>. It involves mixing, heating and conveying starch suspension through a heating barrel using a single or twin screw configuration (Ayoub et al., 2008). The pore size distribution was determined to be in the range of 50-250 µm with average of 129 µm.

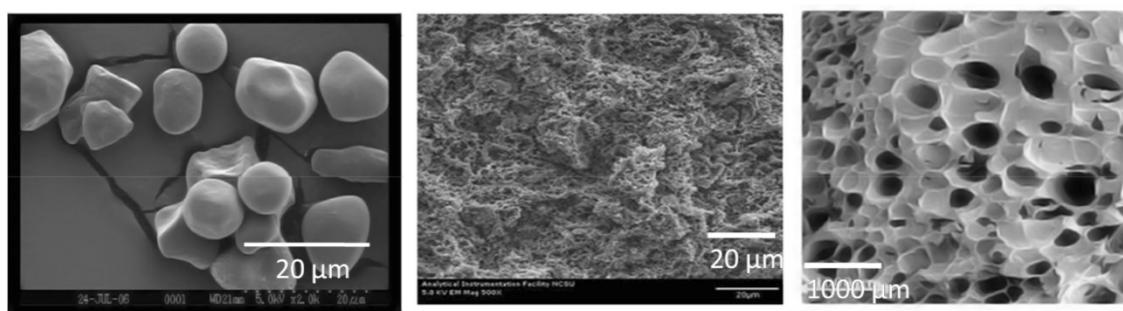


Figure 1-10. SEM images of uncooked starch (left) and SMCF by slow solvent exchange of molded starch cooked at 95°C (center) at 500× magnification. Extruded starch with 0.5 % EPI, 1% SC-CO<sub>2</sub>, 1600 psi (average cell size: 129 µm) (right).

In the replicating removable pore former technique, the microcellular foam is prepared by allowing monomer solutions to get polymerized around the small solid particles. The solid particles are then removed by dissolution, pyrolyzation or by other techniques leaving void matrix throughout the polymer matrix (LeMay et al., 1990). The other method, polymerization of inverse monomer emulsions, involves polymerizing monomers that are miscible in oil around surfactant-stabilized water droplets that are dispersed in the oil.

## References

- Ayoub, A., and Rizvi, S. S. H., (2008). Properties of Supercritical Fluid Extrusion-Based Crosslinked Starch Extrudates. *Journal of Applied Polymer Science*, 10, 3663-3671.
- Barikani, M., and Mohamaadi, M., (2007). Synthesis and characterization of starch-modified polyurethane. *Carbohydrate Polymers*, 68, 773-780.
- Benning, C. J., Akin, R. B., Mark, H. F., Scavuzzo, J. J., Stivala, S. S., Zukor, L. J., (1969). *Plastic Foams*. Wiley and Sons, 1, 117-334.
- Budarin, V., Clark, J. H., Hardy, J. J. E., Luque, R., Milkowski, K., Tavener, S. J., Wilson, A. J., (2006). Starbons: New starch derived mesoporous carbonaceous materials with tunable properties. *Angew. Chem. Int. Ed*, 45, 3782-3786.
- Colvin, R. (2000). Machine suppliers cater to growing market for wood profiles. *Modern Plastics*, 26-27.
- French, D., (1984). Organization of starch granules" in starch chemistry and Technology, 2<sup>nd</sup> edn. (R.L. Whistler, J.N. BeMiller, and E.P. Panschall Eds.). Academic Press, New York and London, Chap.7.
- Glenn, G.M., & Irving, D.W., (1995). Starch-Based Microcellular Foams. *Carbohydrate*, 72(2), 155-161.
- Humphreys, W. J., Spurlock, B. O., and Johnson, J. (1974). Critical point drying of ethanol-infiltrated, cryofractured biological specimens for electron microscopy. *Scanning Electron Microscopy*, 275-282.
- Heibeish, A. (1996). Synthesis, characterization and properties of polyacrylamide-starch composites. *Starch/Stärke*, 48(5), 175-185.
- Hellwing, G. (1992). Production of cationic starch ethers using an improved dry process. *Starch/Stärke*, 44(2), 69-81.
- Honig, D. H., and Carr, M. E., (1992). Preparation and characterization of copolymers of modified starches and polyacrylonitrile. *Starch/Stärke*, 44(7), 268-283.
- Järnström, P., (1993). Hydrophobically modified cationic starches for surface treatment. *TAPPI 200 Coating Conference Proceedings*, 99.

Lammer, G., (1993). Continuous production of hydroxypropyl starch in a static mixer reactor. *Starch/Stärke*, 45(7), 227-241.

Leach, H. W., (1967). Gelatinization of Starch. *Starch Chemistry and Technology* (R.L. Whistler and E.P. Paschall, Eds.). Academic Press, New York and London, 1, Chap.12.

LeMay, J. D., Pekala, R. W., Alviso, C. T., (1990). Organic aerogels: microstructural dependence of mechanical properties in compression. *Material Research Society Bulletin*, 194, 19-45.

Maurer, H. W., (2001). *Starch and Starch Products in Surface Sizing and Paper Coating*. Tappi Press.

Pekala, R. W.; Alviso, C. T.; Hulsey, S. S.; Kong, F. M., (1992). Starch foams by extrusion. *Cellular Polymers*, 38, 129-135.

Richardson, S.J., (1987). Mobility of water in corn starch suspensions determined by nuclear magnetic resonance. *Starch/Stärke*, 39(3), 79-91.

Rizvi, S. S. H., and Mulvaney, S., (1995). Supercritical Fluid Extrusion Process and Apparatus. United States Patent 5 417 992

Roushdi, M., (1982). Preparation of mixed derivatives of carboxymethyl starch and determination of substitution degree by a new calorimetric method. *Starch/Stärke*, 34(12), 410-423.

Saunders, J. H., (1995). *Handbook of Polymeric Foams and Foam Technology*, Oxford University Press, New York, NY, 1-25.

Tomasik, P., (1995). Facile route to anionic starches: succinylation, maleination, and phthalation of corn starch on extrusion. *Starch/Stärke*, 47(3), 96-112.

Van Dam, H. W., (1986). *Chemistry and Physics of Baking*; Blanshard, J. M. V.; Frazier, P. J.; Galliard, T., Eds.; Royal Society of Chemistry Burlington House: London, UK. 117-130.

Van Warner, A., (1994). Kinetics of the hydroxyethylation of starch in alkaline salt containing aqueous slurries. *Ind. Eng. Chem. Res*, 33, 981-1001.

Xu, Y., & Hann, M.A., (2005). Physical, Mechanical, and Morphological Characteristics. *Journal of Polymers and the Environment* , 13(3), 221-230.

Zaslow, B., (1967). Crystalline nature of starch. *Starch Chemistry and Technology* (R.L. Whistler and E.P. Paschall, Eds.), Academic Press, New York and London, 1, Chap.11.

## **Chapter 2**

### **Starch Microcellular Foam by Solvent Exchange and Super Critical Fluid Extrusion**

#### **Abstract**

Starch microcellular foams (SMCF) are prepared by pore preserving drying or formation processes and contain pores in the micron size range. SMCF have high specific surface area and are useful for applications such as opacifying pigments or as adsorbent materials. The objective of this research was to determine how the processing conditions and use of a crosslinking agent would affect the foam structure and properties. SMCF (crosslinked and uncrosslinked) were prepared from molded aquagels and carbon dioxide extrusion processes separately and then solvent exchanged. Extruded samples contained macroscopic pores whereas samples from aquagels contained a much finer micro pore structure. Aquagel based SMCF samples had lower density and higher brightness than extruded samples. The starch foams with micro pore structure had low density and high brightness. The solvent exchange process was the most important variable in generating a microcellular structure. Micro pores and not macro pores contributed to increased brightness of these materials. The brightness and density of the foams were found to be linearly related. Cross-linking with epichlorohydrin imparted significant water resistance to the extruded samples as evidenced in lower water swelling and higher contact angles. Equilibrium moisture content was correlated with the micro-porous structure.

## **Introduction**

Starch is an important agriculture product that in the United States is derived primarily from corn, potatoes, and wheat (Ellis et al., 1999). In the raw state, starch is in the form of dense granules that range in size from 2 microns in wheat to over 100 microns in potato starch (Vasanthan et al., 1996). Granular starch is utilized in many food and non-food products and is often chemically modified to further expand its uses (Fang et al., 2002 & Jobling, S., 2004). The low cost and availability of starch in the market attracts researchers to develop new functional starch derivatives for industrial applications (Ellis et al., 1999). Starch granules are generally composed primarily of two glucose polymers: amylose (linear) and amylopectin (branched), with the largest portion being amylopectin (70-85%). However, starch granules from certain plant varieties are almost entirely amylopectin (98%) while others may contain 45% to 80% amylose (Kobayashi et al., 1985). Amylose is a polymer of (1-4)-linked  $\alpha$ -D-glycopyranosyl units with a molecular weight that varies depending on the source of the starch but is generally much smaller than that of amylopectin. Amylopectin has short branches on about 4 % of the D-glycosyl residues.

Starch may be dissolved in water. When heat is applied to water and starch granule slurry, the granules initially swell. The amylose material in particular extends from the starch granules and forms a gel in the water phase (Jacobs et al., 1998 & Hoover et al., 1994). Eventually, the initial starch granules completely dissolve in the water. If the water is removed in a normal drying process, large capillary forces act on the starch and collapse the polymer into low porosity material (Glenn et al., 1995).

Starch microcellular foams (SMCF) are generally described as a starch based porous matrix containing pores ranging from 2  $\mu\text{m}$  to sub-micrometer size (Glenn et al., 1995 & 2001). Glenn and Stern (U.S. Pat. 5,958,589) have prepared SMCF from rigid starch aquagels by exchanging the water with liquids possessing lower surface tension. The SMCF can be formed by equilibrating the aquagels of wheat and corn starch with ethanol. Subsequently, the ethanol/starch mixtures are air dried to remove the ethanol. Since the surface tension of the air/ethanol interface is one third that of air/water, weaker capillary forces exist when drying from ethanol relative to drying from water. The result is that the foam structure is preserved (Tiefengacher, K., 1993; Glenn et al., 2002; El-Tahawy et al., 2007).

Recently at Cornell University a new, low-temperature, and low-shear extrusion technology, called supercritical fluid extrusion (SCFX), has been developed. The technology involves reactive extrusion of starch-based matrices and injection of supercritical carbon dioxide (SC-CO<sub>2</sub>) as a blowing agent to continuously produce microcellular extrudates (Rizvi et al., 1995). SC-CO<sub>2</sub>, is an environmentally sound replacement for toxic solvents generally used in the manufacture of plastics foams. The effects of process variables and formulation on native starch foam expansion, cell size, cell density and mechanical properties have been studied and reported (Alavi et al., 2003 & 2005). However, native starch foam is readily soluble in water, preventing its use in aqueous environments. Crosslinking by reactive extrusion and subsequent expansion by SC-CO<sub>2</sub> offers a novel approach to making expanded biodegradable products using a benign and green solvent in a continuous fashion.

A number of researchers (Albertsson et al., 1995; Alexander, R., 1996; Doane, W., 1992; Yoon et al., 2006) have explored the possibility of using dispersed and crosslinked starch granules as organic filler. These researchers demonstrated that paper with starch fillers had better strength properties relative to paper with traditional inorganic fillers. This was presumably due to the ability of the starch to hydrogen bond with cellulosic fibers, whereas the inorganic filler could not participate in hydrogen bonding (Varjos et al., 2004; Krogerus, B., 1999; Yoon et al., 2006). However, the starch fillers had inferior optical properties when compared to inorganic fillers. Recently, high brightness (93 %) and surface area starch microcellular foam particles were prepared by solvent exchange with ethanol from dissolved corn starch crosslinked with glutaraldehyde (El-Tahlawy et al., 2007 & 2008; Bolivar et al., 2007) The crosslinking was found to provide some structural integrity of the foam during exposure to pressure and/or moisture (Nabeshima et al., 2001).

The current research was undertaken to explore the production of starch microcellular foam using a combination of two technologies: (1) supercritical fluid extrusion (SCFX) and (2) solvent exchange. The first technology involves the extrusion of a starch/water mixture and the injection of supercritical carbon dioxide (SC-CO<sub>2</sub>) as a blowing agent to generate a foam. The resulting extrudates were immersed in ethanol/water solutions of varying concentration and subjected to two different protocols to successively displace the water with ethanol. For comparison, aquagel samples of starch were prepared and SMCF was generated from the aquagel using a solvent exchange technique. The brightness, particle size, void diameter, and surface area of the SMCFs was measured for all of the samples.

This research is unique in that there has been no prior research using the combination of SCFX and a post-extrusion solvent exchange process to form foams, the combination of which produces new, interesting structures. Also, this is the first report in which a direct comparison of SCFX, SCFX followed by solvent exchange, and aquagel solvent exchanged materials is reported.

## **Materials and Methods**

Corn starch used for aquagels was supplied by Cargill, USA (Cargill Gel 03420), consisting approximately of 25 % amylose and 75 % amylopectin. Anhydrous ethanol Fisher product Number A405<sup>P</sup>-4) was used for solvent exchanges. Epichlorohydrin (EPI) was purchased from Sigma (45327S).

### **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 under continuous stirring (IKA-Werk, RW 16 Basic S1) with a crescent shaped paddle, at speed setting of 10 with three different levels of cooking condition. The first two conditions involved heating the starch slurries to 90°C, and 95°C over a period of about 20 minutes. The third cooking condition consisted of heating the starch to 95°C over a period of about 20 minutes and then maintaining the temperature at 95°C for an additional 20 minutes. When solution of starch is heated, initially, the granules swell slightly and then reversible swelling observed until a critical temperature reached. At this temperature the granule structure melts and large swelling occurs, which causes a great

increase in viscosity, Appendix 2-A. The cooked starch solution was allowed to cool to room temperature over a period of 1 hr in shallow metal tray. Aquagels of cooked starch solutions were prepared by refrigerating the trays containing the gelatinized starch overnight at 5°C. This aquagel was used to make SMCF by the solvent exchange technique.

### **Supercritical fluid extrusion of crosslinked starch: processing conditions and formulation**

A Wenger TX-52 (Wenger Manufacturing, Sabetha, KS) corotating twin-screw extruder with a barrel diameter of 52 mm, and length to diameter ratio (L/D) of 27 was used for extruding starch/water mixtures. The extruder was configured to operate at a screw speed of 120 rpm and feed rate of 35 kg/hour. The moisture content of the feed starch/water mixture was maintained at 35 % w/w. The temperatures of the extrudates at the die (diameter =4.2 mm) was controlled to 70°C to prevent evaporation of epichlorohydrin and moisture in the feed by circulating water at 35°C to 60°C through the jacketed extruder barrel. The average specific mechanical energy was 65 kJ/kg. A pilot scale supercritical fluid system was used for injection SC-CO<sub>2</sub> at a constant flow rate ( $7.6 \times 10^{-5}$  kg/s) into the starch/water mixture through four valves located around the extruder barrel at a short distance from the nozzle exit. SC-CO<sub>2</sub> injection pressure was automatically maintained higher than pressure inside the barrel for a continuous SC-CO<sub>2</sub> flow into the starch/water mixture, at the desired rate (0 and 1% SC-CO<sub>2</sub>) and pressure (1100 and 1600 psi). Samples produced at Cornell University were stored in sealed plastic bags and shipped overnight in dry ice (T= 0°C) to NCSU. The moisture content of the samples was 32, 37, and 38 % for extruded starch, extruded starch

crosslinked with EPI, and extruded starch crosslinked with EPI with CO<sub>2</sub> samples respectively. Samples were then subjected to solvent exchange processes as described above. Corn starch was supplied by Cargill, USA and sodium hydroxide (1%) was used as control formulation. One level of 0.5% on dry basis of the cross-linking reagent epichlorohydrin (EPI) was added. In-barrel moisture content of the starch melt was maintained at about 45% on wet basis by injection of water in the extruder barrel.

### **SMCF preparation process**

SMCF was produced by a solvent exchange technique. In this process, the higher surface tension solvent (water) is replaced with a lower surface tension solvent (ethanol), which produces SMCF from the aquagel of starch when dried. SMCF was produced by a *slow* exchange (solvent exchange was carried out at every 48 hr with 40, 70, 90, 100, 100, and 100% ethanol) and a *fast* exchange (solvent exchange was carried out at every 48 hr with 100, 100, and 100% ethanol) technique. During each exchange, the previous solvent was decanted from the SMCF and then replaced with fresh solvent. Each solvent exchange was carried out using an amount of solvent equal to approximately three times the weight of the sample. Once the solvent exchanges were completed, the samples were allowed to air dry in a 23°C and 50% relative humidity atmosphere.

## **Characterization of SMCF**

### **Scanning Electron Microscopy Analysis**

Morphological characterization of starch microcellular foam was performed on images captured by a scanning electron microscope (SEM), Hitachi s3200-N. The samples were coated with gold-palladium of 10 nm thickness to make the samples conductive at 200 milliTorr vacuum with Denton Vacuum Desk II instrument. The digital images obtained from the SEM were characterized using image analysis software. Random areas of the samples were taken and all of the pores (more than 30 pores were measured for each sample) in the area were measured (Revolution Software, 4pi Analysis, Inc.).

### **Thermogravimetric Analysis**

SMCF conditioned at 23°C and 50% relative humidity was subjected to TGA, (TGA Q500, TA Instruments) at a heating 10°C/min under nitrogen purge 40/60 ml/min of nitrogen in balance and sample flow. Mass loss at 100°C is assumed to be moisture. Initial moisture content of extruded starch samples was measured by drying in a conventional oven at 105°C until a constant mass was reached.

### **Brightness Measurement**

SMCF was crushed with mortar and pestle and the particles passing through a 20 mesh screen (850 micron opening) were collected and formed into a tablet. A Carver press (hydraulic unit model 3912, Carver Inc, Wabash IN) was used to make a 0.5 g tablet, dimensions of about 1.3-1.6 cm diameter and 0.3-0.5 cm thickness. One ton of force was

applied for one minute to make the tablet. The tablet brightness was measured with a Brightimeter Model S-5 (Technidyne Inc, New Albany IN). For each sample tablet the brightness was measured twice on both sides and the average reported. The brightness is a measure of the sample reflectivity at 457 nm wavelength of light.

### Density Measurement

Since all samples had irregular shapes the densities of the samples were measured by weighing the sample alone and then weighing the sample immersed in uniform plastic beads (average diameter of 0.25cm) in a graduated cylinder with a known total volume. The packing density of the beads was known from a plot of the volume of beads ( $\text{cm}^3$ ) versus mass of beads (grams), which resulted in a straight line relationship between mass and volume (Volume =  $0.711 \times \text{Mass}$ ,  $R^2 = 0.99$ ). The slope is the inverse of the packing density of the beads, which was found to be 1.406 g/cc. The density of a sample was then determined by the following equation:

$$\text{Volume of sample plus beads (cc)} = \frac{\text{Mass of bead (g)}}{\text{Density of bead (g/cc)}} + \frac{\text{Mass of sample (g)}}{\text{Density of sample (g/cc)}} \quad \text{Eq ... (1)}$$

For each sample, the measurement was taken six times (repacking the sample in beads each time) and the average and standard deviation reported. Foams are three dimensional cellular solids and have single important characterizing parameter for foams is relative density of foams (relative density = density of foam/density of cell wall material). And porosity of foam material is the volume fraction of pores Porosity = 1 - relative density.

## Water swelling and Mass loss measurement

Water swelling and mass loss of the SMCF was measured. In a sealed glass beaker, a known sample mass was placed into 25 ml of de-ionized water for 24 hrs at 23°C. After 24 hrs, the sample was filtered through pre-weighed wet qualitative Whatman filter paper (Product number 1004070) under conventional house vacuum for 60 seconds. The weight of the wet filter paper and sample was determined. The wet filter paper with sample was placed into an oven at 105 °C for 1 hr and then weighed again. The water swelling and mass loss of the SMCF was calculated as:

$$\text{Water swelling of SMCF (g of water absorbed /g of sample)} = \frac{d - (b \times a) - a - x}{x} \quad \text{Eq ..... (2)}$$

Where:

a = Dry mass of filter paper (OD mass of filter paper)

b = Water retention value of filter paper (g/g)

$$= \frac{\text{Weight of wet filter paper} - \text{Weight of oven dried filter paper}}{\text{Weight of oven dried filter paper}}$$

c = Initial mass of sample

d = Wet mass of filter paper with sample

e = Dry mass of filter paper with sample (OD mass of filter paper with sample)

x = Mass of starch retained = e - a

$$\% \text{ Mass loss} = \frac{c - x}{c} \times 100\% \quad \text{Eq.....3}$$

The water contact was done in two modes, one in which the foam was allowed to float or sink (in contact with water) and a second mode in which the foam was forced to be immersed completely under the water surface (forced immersion) for all samples. Results of samples in contact and with forced immersion are reported in this chapter.

### **Contact Angle Measurement**

Contact angle measurements were performed with a NRL Contact Angle Goniometer by Rame Hart Inc. (model 100-00). A drop of deionized water (mass of approximately 35 milligram) was place on the surface of the starch rod or molded starch sample. The contact angle on two sides of the drop was measured immediately and the average reported. The contact angle was then monitored every minute for four minutes. Two tests (drops) were conducted on each sample.

The contact angle measurements also were performed with Dynamic Contact Angle measurement (Phoenix 300) instrument on selected samples. A drop of deionized water was placed on the surface of the sample and images of water droplet were taken at every 10 seconds up to 4 minutes contact time. The contact angle between the surface of sample and water droplet was measured with ImageJ software. Images of the selected samples and results are reported in Appendix 2-D.

## Results and Discussion

### SMCF morphology

The main purpose of this study was to investigate methods to create a low density SMCF with micropores less than 10 micrometer in diameter. These materials typically have excellent light scattering properties. The SMCFs were produced by taking aquagels or extruded (never-dried) samples of the starch and exchanging the water with ethanol. SEM images of the uncooked starch and an example of the SMCF produced from an aquagel clearly show the increased porosity of the solvent exchanged materials, Figure 2-1. Also included is an image of CO<sub>2</sub> extruded starch material (not solvent exchanged) for comparison. SMCFs were produced by solvent exchange of extruded starch, extruded starch cross-linked with EPI, and starch cross-linked with EPI extruded in presence of CO<sub>2</sub>. The extruded samples were solvent exchanged by a slow and a fast solvent exchange procedure,

Figure 2-2.

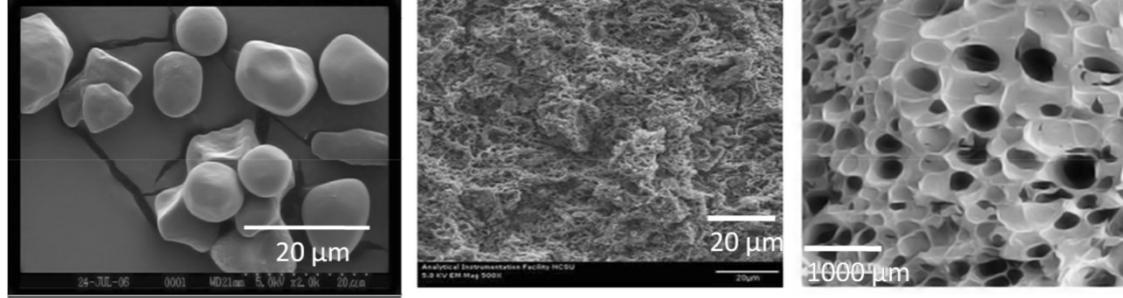


Figure 2-1: SEM images of uncooked starch (left) and SMCF by slow solvent exchange of molded starch cooked at 95°C (center) at 500× magnification. Extruded starch with 0.5 % EPI, 1% SC- CO<sub>2</sub>, 1600 psi (average cell size: 129 μm) (right).

It is observed that the porous structure is impacted by the extrusion conditions and the solvent exchange conditions. The materials in Figure 2-2 all display large macro pores. Foams can be designated as either micro or macro cellular foam according to the cell diameter or size, generally, macrocellular foams have low density, and have large (around 100 to 1000  $\mu\text{m}$ ) cells with cell wall thickness ranging from 10 to 100  $\mu\text{m}$ , whereas, microcellular foams have cell diameters or size less than 10  $\mu\text{m}$ . The pore diameter and the cell wall thickness for both the extruded and aquagel foams are listed in Table 2-1 and distribution represented in Appendix 2-B. The extruded starch has a lower pore number concentration of macro pores compared to the extruded starch cross-linked with EPI without and with  $\text{CO}_2$ . The presence of  $\text{CO}_2$  during extrusion of starch cross-linked with EPI caused an increase in the pore number concentration of the materials and also the appearance of a bimodal pore size distribution. For the  $\text{CO}_2$  assisted extrusion of starch cross-linked with EPI the larger pores were found to be mostly in the center of the extrudate whereas smaller pores tended to be towards the exterior of the extrudate.

These macro pores were not significantly altered by solvent exchange. However, the solvent exchange process produced micro pores in only the slow exchanged extruded non-crosslinked starch with an average pore diameter and cell wall thickness of about 300 nm (Figure 2-3C and Table 2-1) but not with any of the crosslinked starches, Figure 2-3(F, I) and Table 2-1. The pore size distribution is reported in Appendix 2-B. It was expected that the slow exchange process was the most effective method to preserve pores in the structure when dried and the results in this study are in agreement.

Table 2-1: Average pore diameter and cell wall thickness. Note, in some cases there is a bi-modal distribution of pores and thus the averages of both sizes of pores (labeled I and II) are listed.

Sample	Ave. pore diameter (micrometer)		Ave. cell thickness (micrometer)	
	I	II	I	II
Extruded starch – Air dry	325		153	
Extruded starch – Fast exchange	293		151	
Extruded starch – slow exchange	190	0.379	219	0.398
Extruded starch cross-linked with EPI—Air dry	132		103	
Extruded starch cross-linked with EPI—Fast exchange	85		69	
Extruded starch cross-linked with EPI—Slow exchange	77		57	
Extruded starch cross-linked with EPI with CO <sub>2</sub> —Air dry	127		66	
Extruded starch cross-linked with EPI with CO <sub>2</sub> —Fast exchange	125		41	
Extruded starch cross-linked with EPI with CO <sub>2</sub> —Slow exchange	82		3.9	
Aquagel - Starch cooked at 95°C – Fast exchange	2.7	0.172	2	0.163
Aquagel - Starch cooked at 95°C – Slow exchange	2.8	0.153	1.9	0.119
Aquagel - Starch cooked at 95°C for 20 minutes–Fast exchange	1.8	0.138	1.7	0.092
Aquagel - Starch cooked at 95°C for 20 minutes–Slow exchange	2	0.133	2	0.122

These extruded starch samples have macro pores of similar diameter but a lower pore number density to Ayoub et al., (2008) in which wheat starch samples were extruded under similar conditions but air dried. This study shows that for extruded samples, that by using an ethanol exchange prior to air drying that the pore size and cell wall thickness can be decreased. Other researchers Xu et al., (2005) have also shown that extruding in ethanol rather than water produces starch-based foams that have smaller pore and pore wall sizes and increased uniformity, in agreement with our observations on the effects of ethanol exchange on structure.

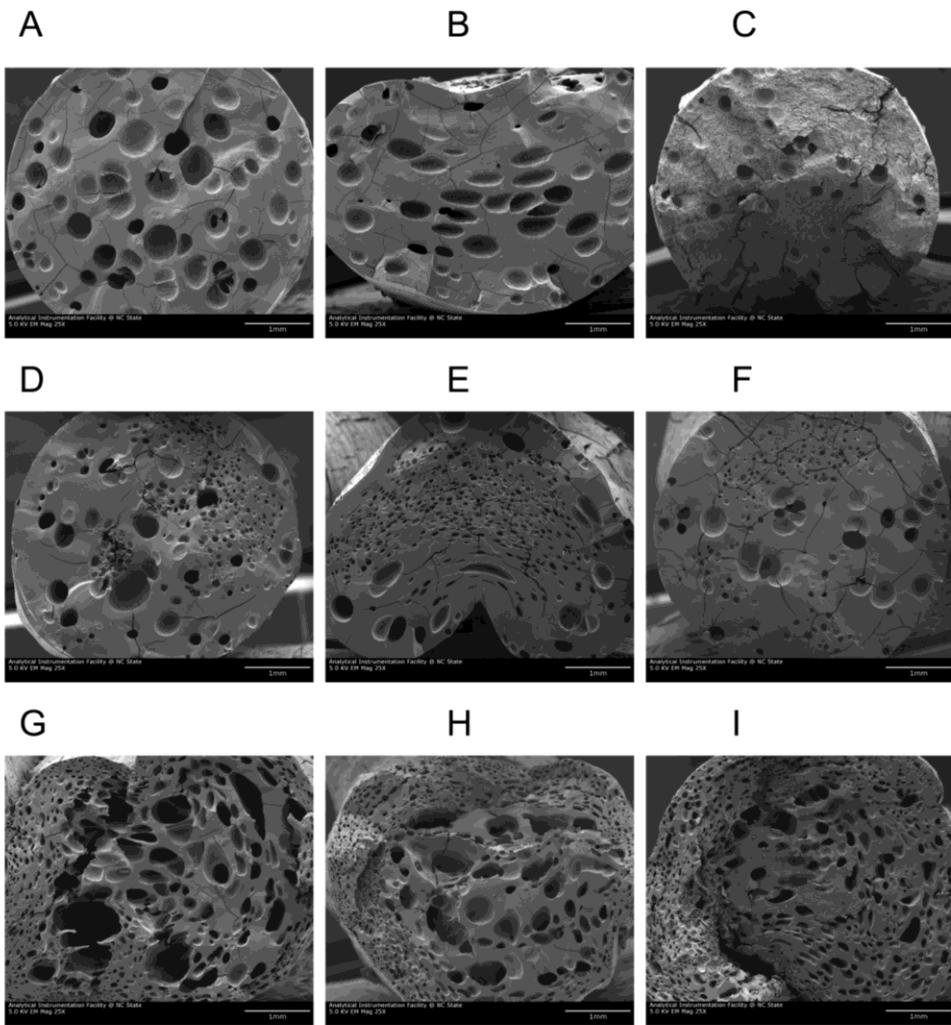


Figure 2-2: SEM images of extruded starch – air dry(A), fast exchange(B), and slow exchange(C). Extruded starch cross-linked with EPI – air dry (D), fast exchange (E), and slow exchange (F). Extruded starch cross-linked with EPI with  $\text{CO}_2$  – air dry (G), fast exchange (H), and slow exchange (I).

SMCFs formed from corn starch aquagels only exhibited a micro-pore structure, Figure 2-3 (K,L,N,O). Listed in Table 2-1 is the average pore diameters and pore wall thickness for both the fast and slow solvent exchange processes. A bi-modal pore structure was observed for these samples. The average pore diameter and cell wall thickness for the finer pores was

similar for both exchange processes, ~0.15 and ~0.12 microns respectively. The larger pore distribution of these samples was independent of exchange processes, with pores in the range of approximately 2-3 microns.

In our previous studies (El-Tahlawy et al., 2007 & 2008) SMCF particles were produced by introducing cooked starch solutions into a bath of ethanol under shear and pore sizes were determined from SEM images of the particle surfaces. Average pore diameters from 0.2 to about 1 micron were determined in that study. The pore size could be adjusted via changes in crosslink concentration and starch molecular weight. In comparison to those studies, the pore diameters generated in these aquagel molded samples were generally smaller and qualitatively more uniform, similar to SMCF molded materials generated by Glenn and coworkers (1995).

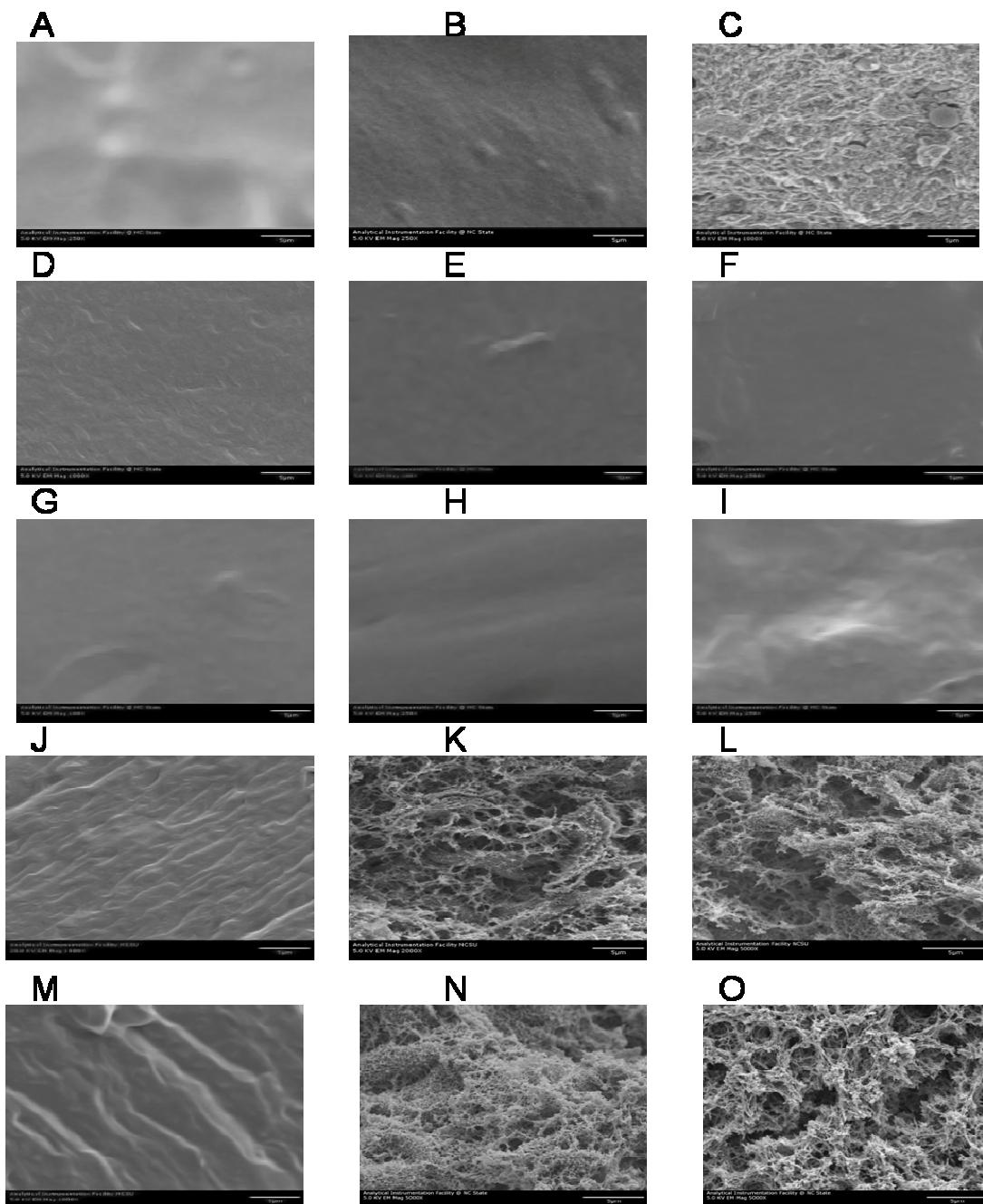


Figure 2-3: SEM images of extruded starch – air dry (A), fast exchange (B), and slow exchange (C). Extruded starch cross-linked with EPI – air dry (D), fast exchange (E), and slow exchange (F). Extruded starch cross-linked with EPI with  $\text{CO}_2$  – air dry (G), fast exchange (H), and slow exchange (I). Starch cooked at  $95^\circ\text{C}$  – air dry (J), fast exchange (K), and slow exchange (L). Starch cooked at  $95^\circ\text{C}$  for 20 minute – air dry (M), fast exchange (N), and slow exchange (O) respectively on 5 micrometer length scale

## **Density**

The density of the starch materials was measured as another way to characterize the foam materials, Table 2-2. For the extruded samples, in general, the density decreased significantly with the use of the slow solvent exchange processes relative to the air dried samples. The samples subjected to the fast solvent exchange did not show a consistent density decrease relative to the air dried samples. Visual observations also indicated a significant difference in the materials' structures. The extruded fast exchange samples had a similar clarity and yellowish-grey color as the air dried samples. In contrast, the slow exchanged samples were whiter and more opaque compared to the air dried samples, Figure 2-4a and 2-4b. The densities determined in this study are similar to those in a previous study with carbon dioxide assisted extruded wheat starches air dried (Ayoub et al., 2008). Neither crosslinking nor extrusion with carbon dioxide significantly affected the density relative to the extruded samples in this study under the extrusion conditions studied.

For the samples formed from aquagels, the air dried samples had a density of about 1 gram/cm<sup>3</sup>, Table 2-2. These samples were solid and translucent compared to the solvent dried samples. The fast and slow solvent exchange materials showed a ~40 – 60 % decrease in density relative to the air dried samples, Table 2-2. Both the fast and slow exchanged materials displayed an opaque white appearance in contrast to the yellowish, somewhat clear air dried materials, Figure 2-4a and 2-4b. The effect of the extent of cooking on the density of the resulting materials was much less important than if the samples were air dried or solvent exchanged before drying. The densities for ethanol exchanged aquagel samples were

around 0.39 g/cc which is slightly higher than those found by Glenn (1995) for ethanol exchanged corn starch aquagel samples with minimum density of 0.25 g/cc.

Table 2-2: Density and Calculated Pore Volume Fraction of Starch Samples.

Sample	Type of Exchange	Average density (g/cc)	Std . deviation	Relative density	Pore volume fraction (%)
Extruded starch	Air dry	0.71	0.02	0.66	34
Extruded starch	Fast	0.85	0.03	0.79	20
Extruded starch	Slow	0.56	0.01	0.52	48
Extruded starch cross linked with EPI	Air dry	0.93	0.04	0.87	13
Extruded starch cross linked with EPI	Fast	0.92	0.01	0.86	14
Extruded starch cross linked with EPI	Slow	0.59	0.01	0.55	45
Extruded starch cross linked with EPI in presence of CO <sub>2</sub>	Air dry	0.91	0.01	0.85	16
Extruded starch cross linked with EPI in presence of CO <sub>2</sub>	Fast	0.67	0.004	0.63	37
Extruded starch cross linked with EPI in presence of CO <sub>2</sub>	Slow	0.58	0.003	0.54	46
Aquagel - starch cooked at 90°C	Air dry	1.07	0.09	1.00	0
Aquagel - starch cooked at 90°C	Fast	0.39	0.02	0.36	64
Aquagel - starch cooked at 90°C	Slow	0.53	0.02	0.50	50
Aquagel - starch cooked at 95°C	Air dry	1.05	0.06	0.98	2
Aquagel - starch cooked at 95°C	Fast	0.45	0.02	0.42	58
Aquagel - starch cooked at 95°C	Slow	0.53	0.008	0.50	51
Aquagel - starch cooked at 95°C for 20 minutes	Air dry	1.06	0.03	0.99	2
Aquagel - starch cooked at 95°C for 20 minutes	Fast	0.59	0.02	0.55	45
Aquagel - starch cooked at 95°C for 20 minutes	Slow	0.51	0.005	0.48	52

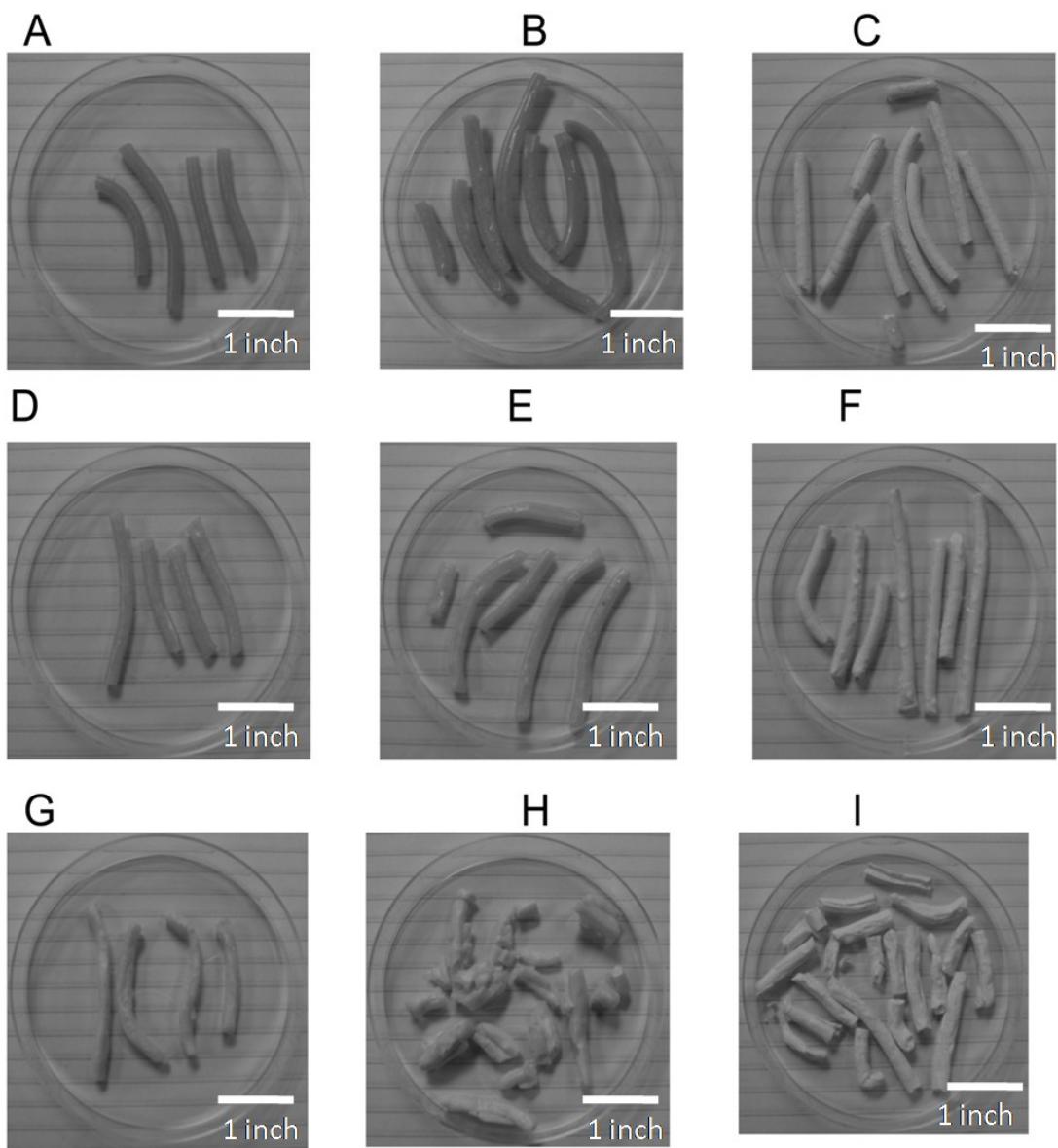


Figure 2-4(a): Extruded starch – air dry (A), fast exchange (B), and slow exchange (C). Extruded starch cross-linked with EPI – air dry (D), fast exchange (E), and slow exchange (F). Extruded starch cross-linked with CO<sub>2</sub> – air dry (G), fast exchange (H), and slow exchange (I) respectively.

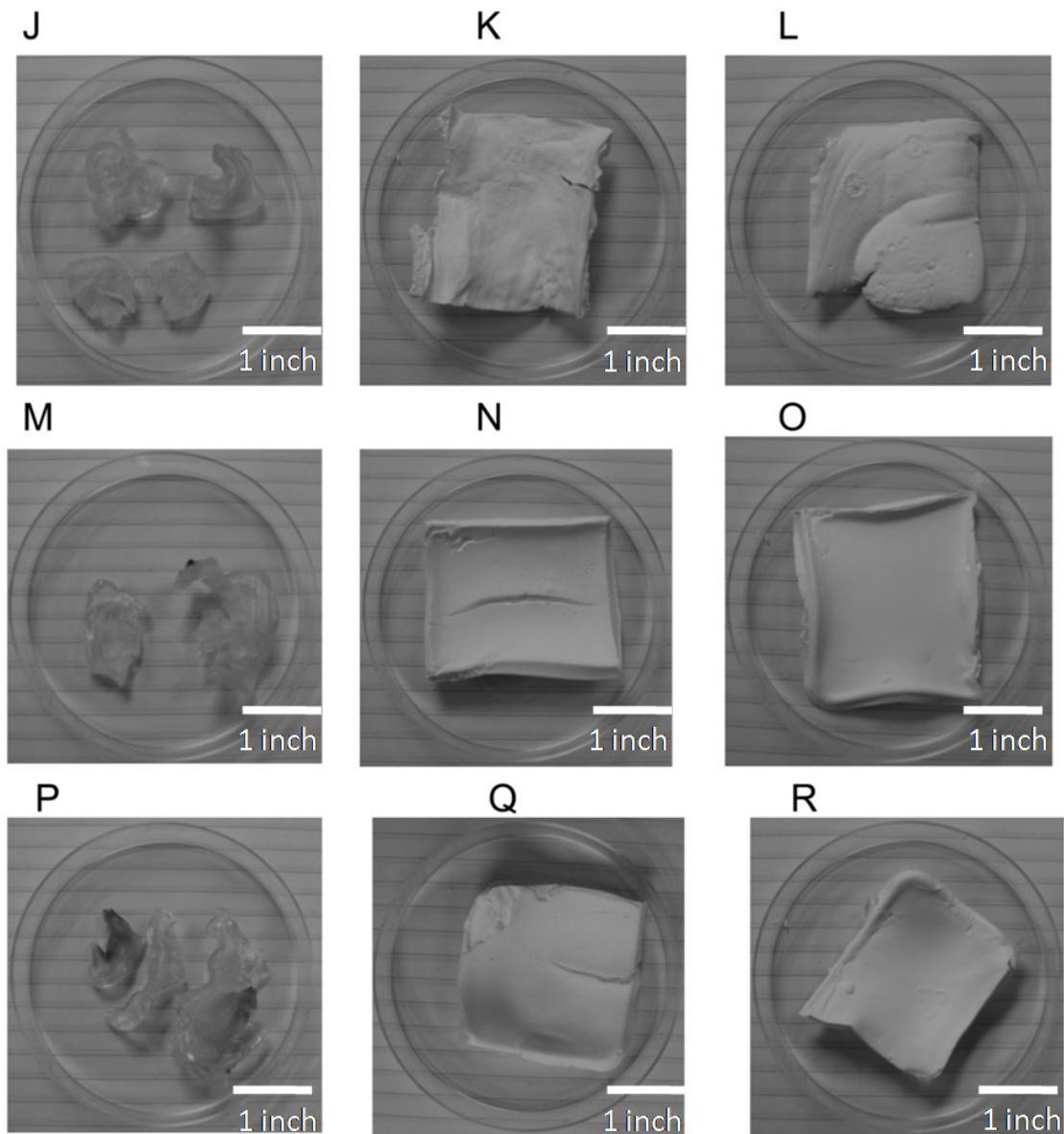


Figure 2-4(b): Starch cooked at 90°C – air dry (J), fast exchange (K), and slow exchange (L). Starch cooked at 95°C – air dry (M), fast exchange (N), and slow exchange (O). Starch cooked at 95°C for 20 minute – air dry (P), Fast exchange (Q), and slow exchange (R) respectively.

## Brightness

It was expected that the brightness of the SMCF samples will be related to the pore volume of the materials. Most specifically, there should be a strong relationship between micro-pore volume and the brightness. In general, structures with high micro pore volume visually had higher brightness, see Figures 2-3 and 2-4. The brightness measurements of particles ground from the samples and pressed into pellets are presented in Figure 2-5. The standard deviation for the brightness measurements on a single sample pellet was 0.973%. For the extruded samples, slow exchange samples had a significantly higher brightness than did fast exchange samples. For aquagel samples, fast versus slow exchange did not alter the brightness significantly. A somewhat linear correlation exists between the brightness and the density of the materials, Figure 2-6. As expected, the solvent exchanged materials that have highly porous microstructure display the highest brightness.

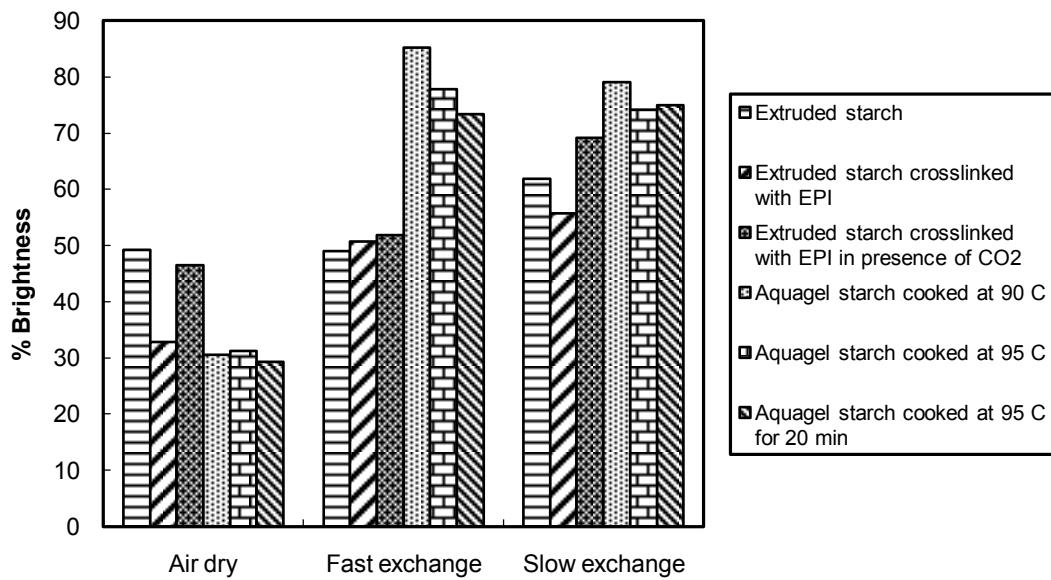


Figure 2-5: Percent brightness of starch materials. Note that in general solvent exchange samples exhibited higher brightness.

The existence of crosslinker or CO<sub>2</sub> during extrusion or the different cooking levels during preparation of aquagel samples is not as significant as the sample density. Data from both aquagel and extruded samples all fall on the same brightness versus density line in Figure 2-6, indicating the processing method is not as important as the final density in determining brightness. In previous research, a maximum brightness for fine precipitated SMCF particles of around 96% ISO was determined (El-Tahlawy et al., 2007; Bolivar et al., 2007), whereas in this study with molded aquagel samples a maximum brightness of only 86% GE was determined. This may be due to the differences in the particle diameters, as shown to be important in determining the brightness (El-Tahlawy et al., 2007). Also, differences in sample preparation for the brightness measurement could affect the measured brightness.

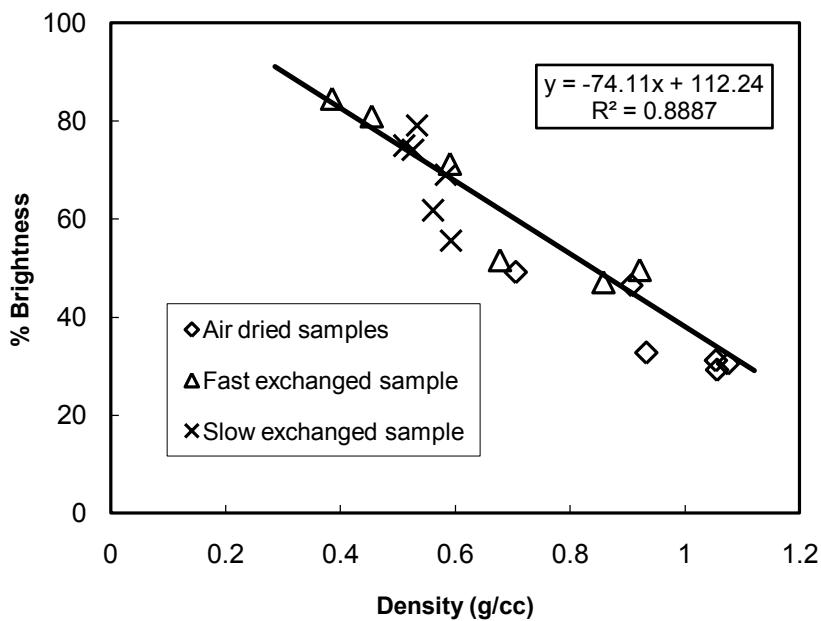


Figure 2-6: Correlation between brightness and density of starch materials. Note the near linear relation between brightness and density of starch materials.

If one assumes that starch foam is essentially air voids within a continuous matrix, a simple model can be generated for the foam structure, Figure 2-7. In this model, the air voids are considered round pores within a continuous matrix of starch. Considering the three dimensional nature of the material and assuming the density of the cell wall remains constant, then the density of the starch foam can be simply calculated by accounting for the voids within the starch matrix.

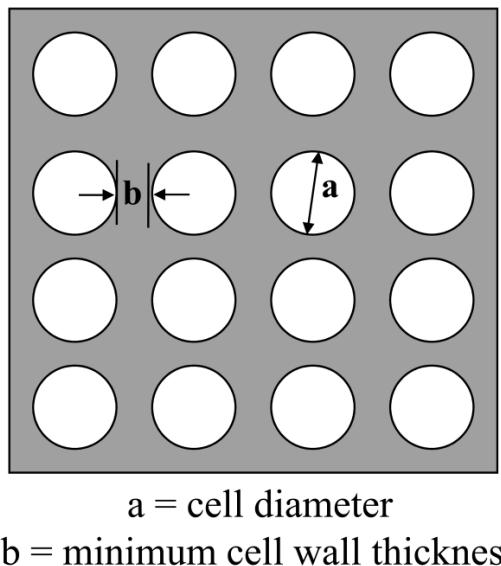


Figure 2-7: Model of the foam structure

The result is that a foam structure is specified by its cell wall thickness and void diameter. Using this model, the minimum possible density for a starch foam would be when the wall thickness goes to zero. The resulting minimum density, assuming the cell wall density is 1.3 g/cc, is 0.62 g/cc for this packing geometry. The overall minimum packing density of mono-

dispersed spherical pores in the starch matrix is 0.338 g/cc with the pores arranged in a closed packing geometry. The relationship between density and brightness can be modeled using known optical theories. Using these inputs into a Mie theory (Mie, G., 1908) computational program, the specific scattering coefficient of the Kubelka-Munk (Kubelka et al., 1931) theory can be determined. This can then be used in the Kubelka-Munk theory to determine the brightness of the material. The end result is a relationship between density and brightness as shown in Figure 2-8. It is worth noting the relationship exists for a given pore cell size, when the density is varied by changing the cell wall thickness. As the density of the material approaches the density of the cell wall material, the relationship between the density and brightness becomes non-linear. This model is in agreement with our findings that the brightness and the density are somewhat linearly related.

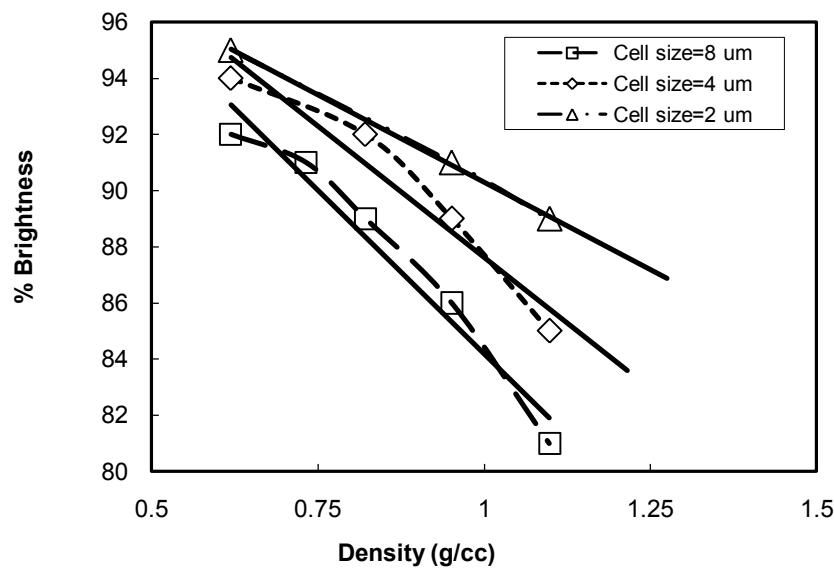


Figure 2-8: Correlation between density and brightness from Kubelka-Munk theory. Note that the existence of relationship for a given pore cell size, when the density is varied by changing the cell wall thickness. Solid lines are best-fit straight lines of the simulation results.

### **Water swelling and mass loss**

The dry structure of the starch microcellular foam is desired to be maintained when immersed in water or subjected to high humidity environments. To investigate, the foams were soaked in for 24 hours (no stirring). After this soaking, the water swelling and mass loss were measured. The solvent exchanged aquagel samples all initially floated on the surface of the water, but settled to the bottom of the container after a time period of approximately 5-6 hours. Air dried aquagel samples settled to the bottom immediately. Solvent exchanged extruded samples settled after 0-20 minutes except for the extruded starch crosslinked with EPI with CO<sub>2</sub> (fast and slow) solvent exchanged, which took almost 8 hours to settle. Air dried EPI with CO<sub>2</sub> samples took approximately 2 hours to settle, in contrast to all other air dried samples, which settled in approximately one minute. These settling times indicate that crosslinking of the starch prevented water penetration through the thick pore walls of the extruded samples. Generally, it is expected that SMCF microporous structures with higher pore volume and thinner pore walls should increase water swelling. If the starch material is soluble, then a higher specific surface area would be expected to increase the rate of mass loss.

The swelling of extruded starch was about 4.5 grams of water per gram of starch and this was not significantly affected by solvent exchange, Figure 2-9. The extruded crosslinked samples showed a significantly lower swelling than for the extruded starch alone. This is in agreement with previous work showing that increased crosslinking of starch with EPI decreases the water diffusion in the starch (Ayoub et al., 2008). The crosslinked and CO<sub>2</sub> extruded samples

were the only extruded samples that showed a significant increase in the water swelling for solvent exchanged extruded samples relative to the corresponding air dried sample.

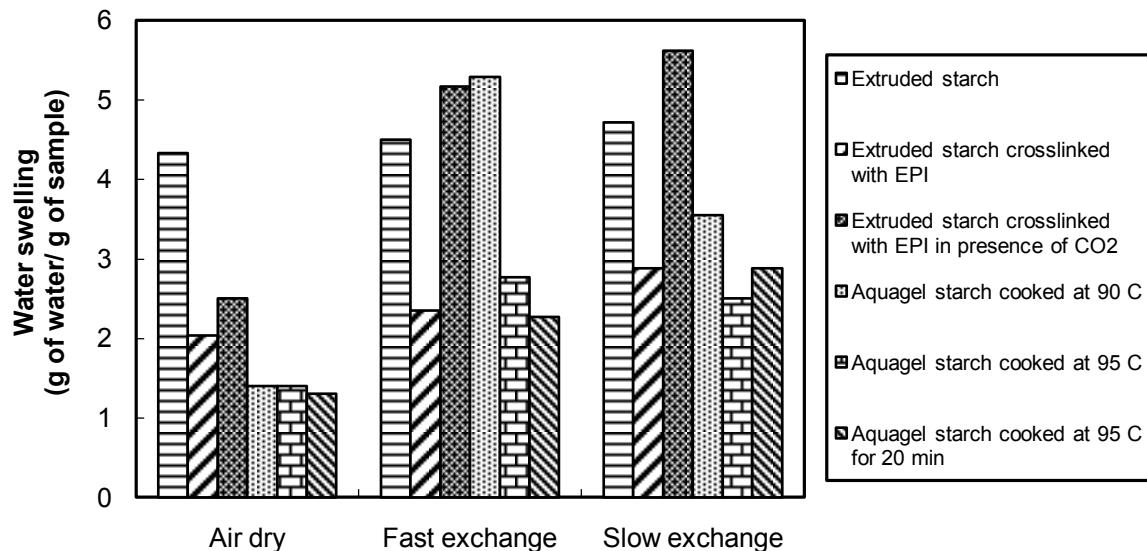


Figure 2-9: Water swelling (g of water/g of sample) of starch samples in contact with water after 24 hrs. Note in general increase in water swelling of starch materials with solvent exchange processes.

For the aquagel samples, the air dried samples showed the lowest swelling of about 1.2 g/g. The slow and fast solvent exchanged aquagel samples showed about twice the swelling as the corresponding air dried sample. There seems to be an approximate trend that increased cooking decreases the swelling, although more data is required to confirm this relationship. The swelling of the samples was plotted versus density but displayed no correlation, data not shown.

Mass loss of the crosslinked extruded samples during the swelling experiments were approximately 15%, which is much less than the over 50% mass loss for the uncrosslinked extruded samples, Figure 2-10. This indicates that the crosslinking inhibited the dissolution of the starch in extruded samples as would be expected.

Unexpectedly, for the aquagel samples, the air dried materials showed approximately 10% mass loss whereas the solvent exchanged materials showed about 1% mass loss. It was expected that higher pore volume would promote more dissolution of the starch foams, but this was not the case.

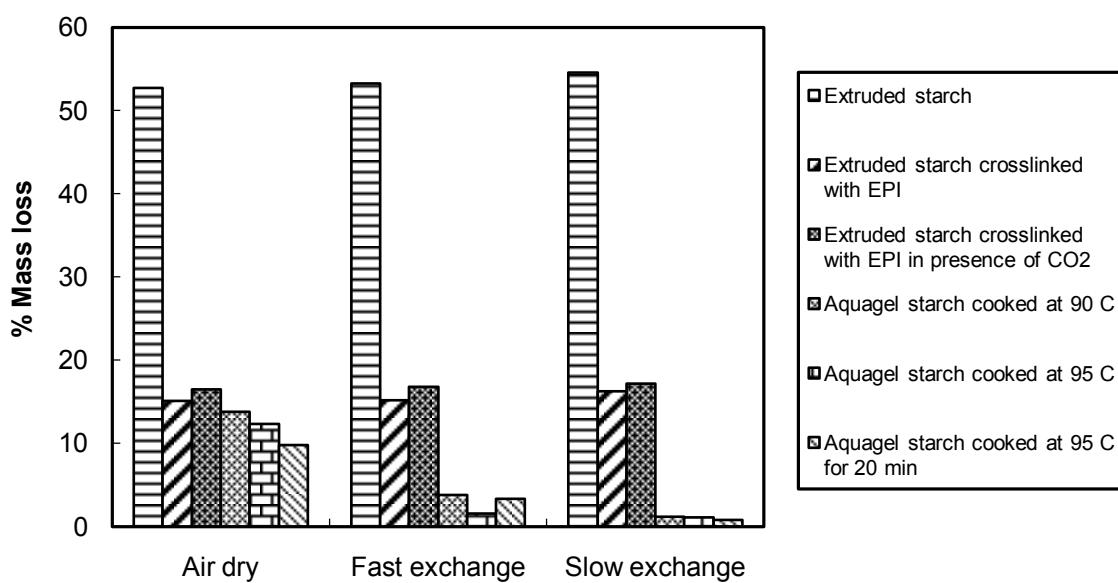


Figure 2-10: Percent mass loss of starch samples after in contact with water for 24 hours. Note that there was no significance difference in mass loss of extruded samples for solvent exchange processes, however, aquagel samples showed decrease in mass loss with solvent exchange processes.

## Water swelling and mass loss by forced immersion

The dry structure of the starch microcellular foam is desired to be maintained when immersed in water or subjected to high humidity environments. In addition to the tests in which the sample was allowed to sink or float, termed in contact with water, water swelling and mass loss after forced immersion for 24 hours in water were conducted.

For both extruded starch and aquagel samples there was observed an increase in the water swelling and mass loss for forced immersion (Figure 2-11 and 2-12) relative to in contact with water samples (Figure 2-9 and 2-10). This increase in water swelling and mass loss can be attributed to the forced immersion allowing water and starch to diffuse on all sides of the object immediately, rather than on only part of the sample surfaces for floating samples for the in contact with water test. Both test modes showed the similar trend of results,

Appendix 2-E.

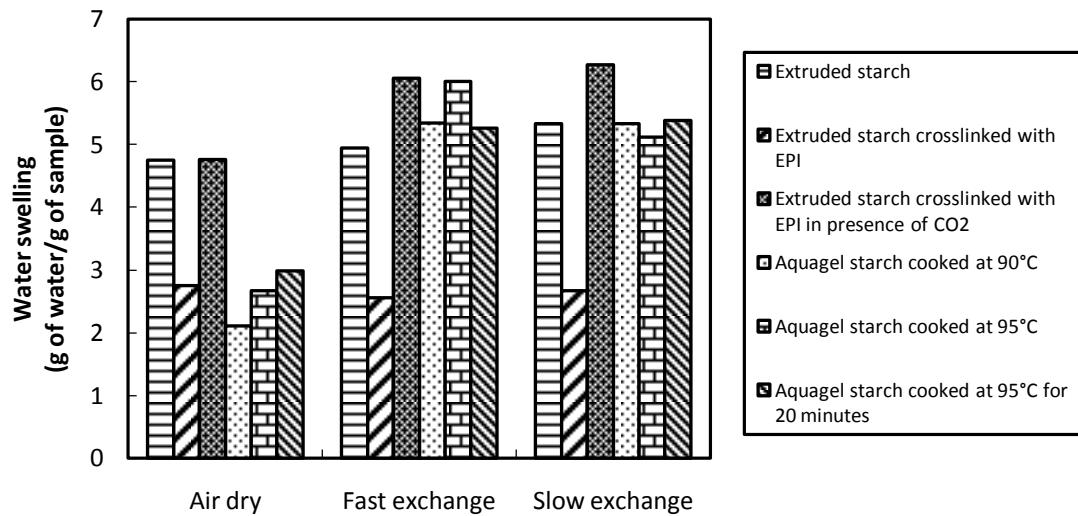


Figure 2-11: Water swelling (g of water/g of sample) of starch samples by forced immersion in water after 24 hrs. Note in general increase in water swelling of starch materials with solvent exchange processes.

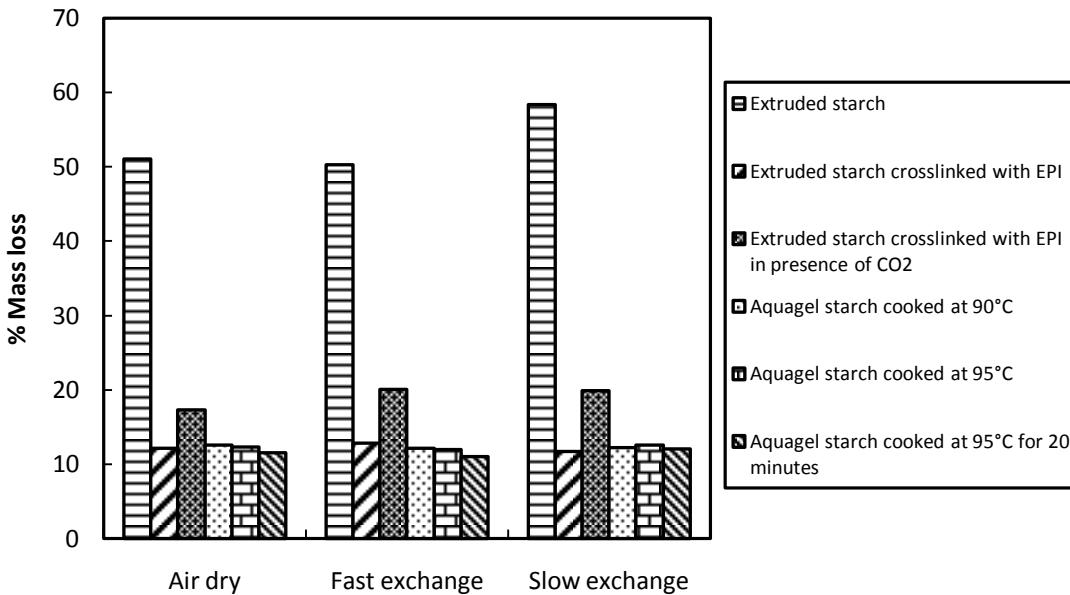


Figure 2-12: Percent mass loss of starch samples by forced immersion in water for 24 hours.

### **Moisture Content and Thermal Degradation**

Thermal degradation and adsorbed moisture were observed by TGA, on samples that were conditioned at 23 °C and 50% relative humidity. All samples showed similar trends of thermal degradation, Appendix 2-C. Maximum peak in mass loss rate occurred around 260-280°C for all samples. The indication is that the extent of crosslinking occurring in the EPI containing samples does not affect measurably the thermal degradation process.

Mass loss at 100°C was considered mainly due to the removal of water associated with the sample, which was considered as the moisture content of the sample, Figure 2-13.

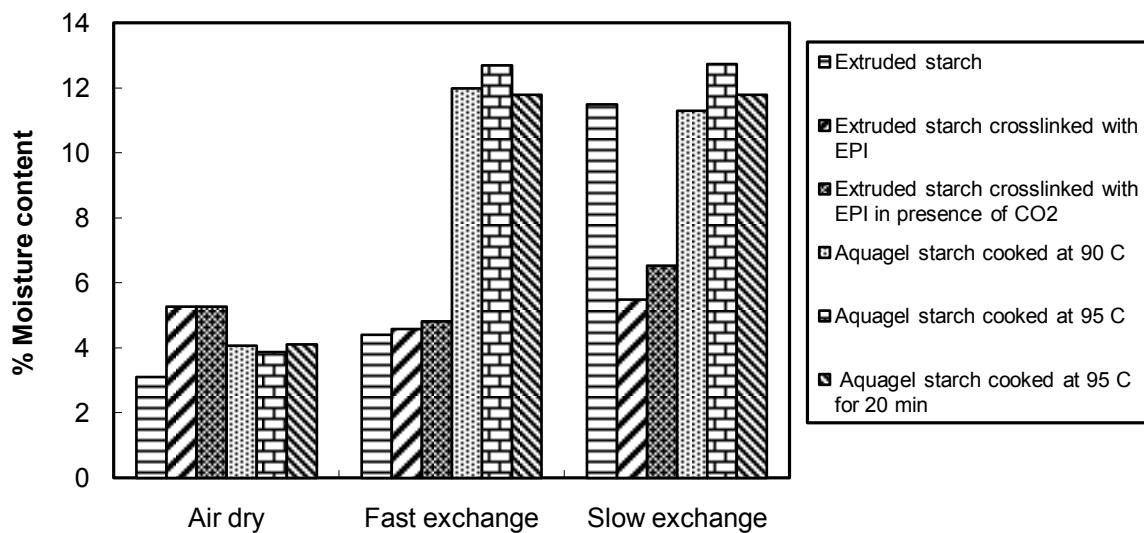


Figure 2-13: Percent moisture content of starch samples. Note in general the increase in moisture content with solvent exchange.

The solvent exchanged aquagel samples showed significantly higher moisture content compared to air dried samples, which can be attributed to the micro-porous structure of the solvent exchanged materials. The solvent exchanged aquagel samples showed a similar moisture content as SMCF particles produced with or without crosslinking in previous research (El-Tahlawy et al., 2007; Bolivar et al., 2007).

Of the extruded starch samples, the extruded slow exchanged sample showed significantly higher moisture content, 11.5%, relative to all other extruded samples. This is in agreement with the observation that this sample was the only extruded one that demonstrated a well formed microporous structure. This sample also had the lowest density and the highest

brightness among the extruded samples. These results indicate that moisture content is sensitive to the micro-porous structure of the materials.

### **Water Contact Angle**

Contact angles of water on starch samples were determined as a function of time for all extruded and aquagel samples, Table 2-3. The contact angle of extruded starch, extruded starch cross-linked with EPI with and without CO<sub>2</sub> for air dried samples were 51, 60, and 72° respectively at the beginning of measurement. For the aquagel samples the contact angle values of the air dried samples were all around 45° degrees, independent of cooking conditions. All samples, except for cross linked samples, had a decreasing contact angle with time. Crosslinking caused the water drop to not absorb into the starch; the contact angle was observed to be approximately constant with respect to time for crosslinked samples. This is in agreement with previous research showing a decrease in water diffusion with increased EPI crosslinking of starch foams (Ayoub et al., 2008). The aquagel samples showed a rapid decrease in contact angle compared to extruded samples. At four minutes of contact time, the water drop was completely absorbed into the aquagel samples.

Table 2-3: Contact angle of water on starch materials.

Sample	Contact angle (°), at start	Contact angle (°), at 1 min	Contact angle (°), at 2 min	Contact angle (°), at 3 min	Contact angle (°), at 4 min	% decrease in Contact angle
Extruded starch – Air dry	51	48	45	45	45	12
Extruded starch – Fast exchange	46	45	44	36	35	24
Extruded starch – Slow exchange	31	17	0	0	0	100
Extruded starch cross-linked with EPI – Air dry	60	58	58	57	57	5
Extruded starch cross-linked with EPI – Fast exchange	63	63	61	60	60	4
Extruded starch cross-linked with EPI – Slow exchange	82	80	80	80	80	2
Extruded starch cross-linked with EPI in presence of CO <sub>2</sub> – Air dry	72	71	71	71	71	1
Extruded starch cross-linked with EPI in presence of CO <sub>2</sub> – Fast exchange	71	70	69	69	68	4
Extruded starch cross-linked with EPI in presence of CO <sub>2</sub> – Slow exchange	72	72	70	70	69	4
Aquagel starch cooked at 90°C – Air dry	45	35	20	0	0	100
Aquagel starch cooked at 90°C – Fast exchange	26	16	0	0	0	100
Aquagel starch cooked at 90°C – Slow exchange	26	15	0	0	0	100
Aquagel starch cooked at 95°C – Air dry	47	33	23	8	0	100
Aquagel starch cooked at 95°C – Fast exchange	39	29	21	10	0	100
Aquagel starch cooked at 95°C – Slow exchange	42	30	17	10	0	100
Aquagel starch cooked at 95°C for 20 minute-Air dry	47	35	28	10	0	100
Aquagel starch cooked at 95°C for 20 minutes – Fast exchange	30	25	14	0	0	100
Aquagel starch cooked at 95°C for 20 minutes – Slow exchange	30	19	8	0	0	100

The slow exchanged extruded starch (the only extruded starch with microporous structure) also had rapid water drop absorption similar to the solvent exchanged aquagel samples, indicating that the microporous structure accelerates the absorption of water into the material.

In previous work, the addition of a reactive wax (Alkyl Ketene Dimer) with the starch demonstrated that small amounts of the wax could increase the contact angle to approximately 90 degrees (El-Tahlwy et al., 2007; Bolivar et al., 2007). This indicates that the combination of crosslinking and blending or coating with a hydrophobic component would be a strong method to improve water resistance in SMCF materials. The water contact angle measurements also were performed on selected samples with Dynamic Contact Angle measurement techniques. The similar trend of results was found. The results and correlation with Goniometer results are represented in Appendix 2-D.

## **Conclusions**

Starch based microcellular foam with porous structure were produced with a solvent exchange process. The starch foams which showed existence of micro pore structure had low density and high brightness. The solvent exchange was much more important in generating a microcellular structure than extrusion versus aquagel, existence of crosslinking, existence of CO<sub>2</sub> during extrusion, and cooking extent. Micro pores and not macro pores contributed to increased brightness of these materials. Brightness and density of the foams were found to be linearly related. The cross-linking with EPI imparted significant water resistance to the extruded samples. Moisture content was a better predictor of microporous structure than water swelling.

## References

- Alavi, S. H., Rizvi, S. S. H., and Harriott, P., (2003). Process dynamics of starch-based microcellular foams produced by supercritical fluid extrusion. I: model development. *Food Research International*, 36 (4), 309-319.
- Alavi, S., and Rizvi, S. S. H., (2005). Strategies for Enhancing Expansion in Starch Based Microcellular Foams Produced by Supercritical Fluid Extrusion. *International Journal of Food Properties*, 8 (1), 23-34.
- Albertsson, A-C., Karlsson, S., (1995). Degradable polymers of the future. *Advanced Polymers*, 46, 114-123.
- Alexander, R. J., (1996). Starch in plastics. *Cereal Foods World*, 41, 426-426.
- Ayoub, A., and Rizvi, S. S. H., (2008). Properties of Supercritical Fluid Extrusion-Based Crosslinked Starch Extrudates. *Journal of Applied Polymer Science*, 10, 3663-3671.
- Biliaderis, C. G., Maurice, T. J., and Vose, J. R., (1980). Starch Gelatinization Phenomena Studied by Differential Scanning Calorimetry. *Journal of Food Science*, 45 (6), 1669-1674.
- Bolivar, A. I., Venditti, R. A., Pawlak, J. J., & El-Tahlawy, K. (2007). Development and characterization of novel starch and alkyl ketene dimer microcellular foam particles. *Carbohydrate Polymers*, 69(2), 262–271.
- Budarin, V., Clark, J. H., Hardy, J. J. E., Luque, R., Milkowski, K., Tavener, S. J., & Wilson, A. J. (2006). Starbons: New starch-derived mesoporous carbonaceous materials with tunable properties. *Angewandte Chemie International Edition*, 45(23), 3782–3786.
- Chiou, Bor-Sen, Glenn, G. M., Imam, S. H., Inglesby, M. K., Wood, D. F., & Orts, W. J. (2005). Starch polymers: Chemistry, engineering, and novel products. *Natural Fibers, Biopolymers, and Biocomposites*, 639–669.
- Doan, W. M., (1992). USDA research on starch-based biodegradable plastics. *Starch/ Stärke*, 44, 293-295.
- Ellis, R. P., Cochrane, P. M., Dale, Duffus, C. M., Lynn, A., Morrison, I. M., Prentice, R. M., Swanston, J. S., Tiller S. A., (1999 ). Starch production and industrial use. *Journal of the Science of Food and Agriculture*, 77 (3), 289-311

El-Tahlway, K., Venditti, R. A., & Pawlak, J. J. (2007). Aspects of the preparation of starch microcellular foam particles crosslinked with glutaraldehyde using a solvent exchange technique. *Carbohydrate Polymers*, 67(3), 319–331.

El-Tahlway, K., Venditti, R. A., & Pawlak, J. J. (2008). Effect of alkyl ketene dimer reacted starch on the properties of starch microcellular foam using a solvent exchange technique. *Carbohydrate Polymers*, 73, 133-142.

Fang, J. M., Fowler, P. A., Tomkinson, J. and Hill, C. A., (2002). The preparation and characterisation of a series of chemically modified potato starches. *Carbohydrate Polymers*, 47(3), 245-252.

Franco, C. M. L., & Ciacco, C. F. (1997). Study of the structure of the normal and waxy corn starch granules. *Cienciae Tecnologia de Alimentos*, 17(3), 295–300.

Glenn, G. M., and Stern, D. J., (1999). Starch-Based Microcellular Foams. United States Patent 5 958 589

Glenn, G. M., and Orts, W. J., (2001). Properties of starch-based foam formed by compression/explosion processing. *Industrial Crops and Products*, 13 (2), 135-143.

Glenn, G. M., and Irving, D. W., (1995). Starch-based microcellular foams. *Cereal Chem*, 72, 155–161.

Glenn, G. M., Miller, R. E., & Irving, D. W. (1996). Microcellular starchbased foams. In G. Fuller, T. A. McKeon, & D. D. Bills (Eds.), *Agricultural materials as a renewable resources: Nonfood and industrial applications* (pp. 88–106) ACS Symposium Series, No. 647.

Glenn, G. M., Klamczynski, A. P., Takeoka, G., Orts, W. J., Wood, D., & Widmaier, R. (2002). Sorption and vapor transmission properties of uncompressed and compressed microcellular starch foam. *Journal of Agricultural and Food Chemistry*, 50, 7100–7104.

Glenn, G., Klamczynski, A., Chiou, B. S., Orts, W. J., Imam, S. H., & Wood, D. (2007). Preparation and applications of starch-based porous microspheres, In International symposium on polymers and the environment: Emerging technology and science, Vancouver WA: BioEnvironmental Polymer Society and the Biodegradable Products Institute, October 17–20, abstract #62.

Glenn, G. M., Klamczynski, A. P., Ludvik, C., Shey, J., Imam, S. H., Chiou, Bor-Sen, et al. (2006). Permeability of starch gel matrices and select films to solvent vapors. *Journal of Agricultural and Food Chemistry*, 54(9), 3297–3304.

Hebeish, A., Abdel-Rahman, A., El-Hilw, Z., & Hashem, M. (2005). Cationized starch derived from pre-oxidized starch for textile sizing and printing. *Starch/Staerke*, 57(12), 616–623.

Hong, Yan, Gu, Zhengbiao, & Li, Zhaofeng (2005). Property investigation and application of waxy corn starch for food processing. *Zhongguo Liangyou Xuebao*, 20(3), 30–34.

Hoover, R., and Vasanthan, T., (1994). Effect of heat-moisture treatment on the structure and physicochemical properties of cereal, legume, and tuber starches. *Carbohydrate Research*, 252 (3), 33-53.

Imam, S., Wheeler, J., Glenn, G., Woods, D., Orts, W. J., Azam, F., Lodhi, A., Arshad, R., & Arshad, M. (2007). Perspective on agricultural feedstocks for biobased products: Functionality and performance of an encapsulation matrix. In International symposium on polymers and the environment: Emerging technology and science, Vancouver, WA: BioEnvironmental Polymer Society and the Biodegradable Products Institute, October 17–20, abstract #12.

Jacobs, H., and Delcour, J. A., (1998). Hydrothermal Modifications of Granular Starch, with Retention of the Granular Structure: A Review. *J. Agric. Food Chem.*, 46 (8), 2895-2905.

Jobling, S., (2004). Improving starch for food and industrial applications. *Current Opinion in Plant Biology*, 7 (2), 210-218.

Kobayashi, S., Schwartz, S. J., Lineback, (1985). Rapid analysis of starch, amylose and amylopectin by high-performance size-exclusion chromatography. *Journal Chromatography*, 319 (2), 205-214.

Kubelka, P.; Munk, F. *Zeitschrift für technische Physik* 1931, 12(11a), 593.

Marton, J. (1990). Practical aspects of alkaline sizing. On kinetics of alkyl ketene dimer reactions: Hydrolysis of alkyl ketene dimer. *Tappi Journal*, 73(11), 139–143.

Maurer, H. W., (2001). *Starch and Starch Products in Surface Sizing and Paper Coating*. Tappi Press.

Mie, G. Beitrage zur optik truber medien, speziell kolloidaler metallosungen, *Annalen der Physik* 1908, 25, 377. An English translation is available as Mie, G. Contributions to the Optics of Turbid Media Particularly of Colloidal Metal Solutions, Royal Aircraft Establishment, Library Translation No. 1873. Her Majesty's Stationery Office, London 1976.

Nabeshima, E. H., and Grossmann, M. V. E., (2001). Functional properties of pregelatinized and cross-linked cassava starch obtained by extrusion with sodium trimetaphosphate. *Carbohydrate Polymer*, 45 (4), 347-353.

Rizvi, S. S. H., and Mulvaney, S., (1995). Supercritical Fluid Extrusion Process and Apparatus. United States Patent 5 417 992

Preechawong, D., Peesan, M., Supaphol, P., and Rujiravanit, R., (2005). Preparation and characterization of starch/poly(L-lactic acid) hybrid foams. *Carbohydrate Polymers*, 59 (3), 329-337.

Scott, W. E. (1996). Principles of wet end Chemistry, Chapter 14: Sizing with synthetic sizing materials. Tappi Press. Singh, N. (2006). Starch in food: Structure, function and applications Edited by Ann-Charlotte Eliasson. *International Journal of Food Science and Technology*, 41(1), 108–109.

Tarvianen, M., Pelton, S., Mikkonen, H., Elovaara, M., Tuunainen, M., Paronen, P., Ketolainen, J., & Sutinen, R. (2004). Aqueous starch acetate dispersion as a novel coating material for controlled drug release. *Journal of Controlled Release*, 96(1), 179–191.

Tiefenbacher, K. F., (1993). Starch-based foamed materials-use and degradation properties. *J.M.S.-Pure Appl. Chem. A*, 30 (9-10), 727–731.

Vasanthan, T., Bhatty, R. S., (1996). Physicochemical properties of small- and large-granule starches of waxy, regular, and high-amyllose barleys. *Cereal Chemistry*, 73 (2), 199-207.

Xie, Xueju, Liu, Qiang, & Cui, Steve W. (2006). Studies on the granular structure of resistant starches (type 4) from normal, high amylose and waxy corn starch citrates. *Food Research International*, 39(3), 332–341.

Xu, Y., and Hanna, M. A., (2005). Physical, Mechanical, and Morphological Characteristics of Extruded Starch Acetate Foams. *Journal of Polymers and the Environment*, 13 (3), 221-230.

Yoon, S., and Deng, Y., (2006). Starch-fatty complex modified filler for papermaking. In Proceedings of the Pan Pacific conference, Advances in Pulp and Paper Sciences and Technologies, (pp. 79–84) Vol. 1, Korea Tappi, Seoul Korea, 6–9 June 2006.

Zhang, Hongwei, Zhu, Zhijian, Tang, Aimin, Chen, Gang, Liu, Yingyao, & Xie, Guohui (2004). Synthesis of cationic starch and its reinforcing effects on paper. *Zhongguo Zaozhi*, 23(10), 21–23.

## **Chapter 3**

### **Starch Microcellular Foams from Starch Blended with AKD and/or Kymene**

#### **Abstract**

Starch microcellular foams (SMCF) are prepared by pore preserving drying or formation processes and contains pores in the micron size range. SMCF have high specific surface area and are useful for applications such as opacifying pigments or as adsorbent materials. The objective of this research was to determine how the processing conditions and use of a sizing and wet strength agents would affect the foam structure and properties. SMCF were prepared from molded aquagels by fast and slow solvent exchange processes with different solvent exchange time intervals to determine the optimum exchange times. Also, the use of alkyl ketene dimer (AKD) and/or Polyaminopolyamide-epichlorohydrin (PAE) (Kymene) as additives to starch to produce SMCF pigments that are water resistant and of high brightness were evaluated. SMCFs prepared with a solvent exchange time interval of 12, and 24 hours had well formed microcellular porous structure and lower densities relative to longer exchange time intervals. Blending with AKD imparted significant water resistance without affecting brightness. Curing of the AKD-SMCF reduced the water swelling and mass loss and increased the water contact angle of the SMCF.

## **Introduction**

Synthetic plastics have possessed an important position in the packaging industry, especially dominating applications with need of water resistance. This position is supported by an extremely well-developed and profitable petroleum industry. However, the vast use of the petroleum based plastics and packaging material have 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 a 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 starches 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 and 1995b). 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 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, H. W., 2001). Both amylose and amylopectin are composed of  $\alpha$ -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 gelatinized point by thermal mean and processed into solution form. Water sensitivity is one of the issue 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.

Recently, in our research group, starch microcellular foam (SMCF) particles from starch, starch crosslinked with glutaraldehyde and 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<sub>2</sub> and crosslinked with epichlorohydrin. 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. Improvements in the foam structure were found with increased shear rate during the ethanol solvent exchange precipitation process. Even though sizing and crosslinking increased water resistance moderately in these studies, the materials still had a high water affinity and their mechanical integrity and porous structure was compromised by contact with water.

Our research also has had as an objective to make starch microcellular foam based pigments for the paper industry. It is proposed that starch based pigments can contribute to hydrogen bonding with cellulose fibers, thus making stronger paper relative to paper made with clay or other inorganic materials (Yoon et al., 2006). However, this advantage in strength comes with the disadvantage that hydrogen bonds can be ruptured by the contact with water. SMCF pigments also have the advantage of low density, produced from bio based renewable sources, and are organic and thus biodegradable or combustible. In this study, we evaluate

the use of AKD (common paper sizing agent) and/or Kymene (a common wet strength additive for paper) as additives to starch to produce SMCF pigments that are water resistant and of high brightness.

AKD is the most commonly used surface sizing agent in paper industry, applied on paper at less than a 1 wt% of the furnished for the inkjet printing paper and for other food packaging grade it could be vary depending upon the requirement basis, and is classified as a non-hazardous (under OSHA regulations) material. AKD is derived from fatty acid that has two alkyl chains that when reacted with carbohydrates will develop hydrophobic properties in carbohydrates (Qaio et al., 2006; Hutton et al., 2003; Champ et al., 2003), cf. Figure 3-1. AKD can be cured at 50-70°C for 2 to 1 hour depending upon the requirements for paper application. For wood applications, higher temperature and longer curing time are needed depending upon the concentration of AKD (Hundhausen et al., 2009).

Kymene is a commercial name of Polyaminopolyamide-epichlorohydrin (PAE) resin and often used as a wet strength additive to the paper, Figure 3-2. Studies showed increases of approximately 0.2-1% and 0.4-1.5% in the wet and dry tensile strength of the paper, respectively, for treatment with PAE when compared to non treated paper (Devore et al., 1993). Generally, Kymene is cured at 80-105°C in 3-10 minutes depending upon the Kymene concentration. Lower curing temperatures require longer curing time. Fischer (1996) studied curing of PAE with two difference conditions, curing at 105°C for 3 minutes and 80°C for 10 minutes, and found no significant difference in wet and dry tensile strength of the prepared

materials. The reaction of Kymene with cellulose has been proposed to involve formation of ester linkage between Kymene and cellulose (Yano et al., 1991).

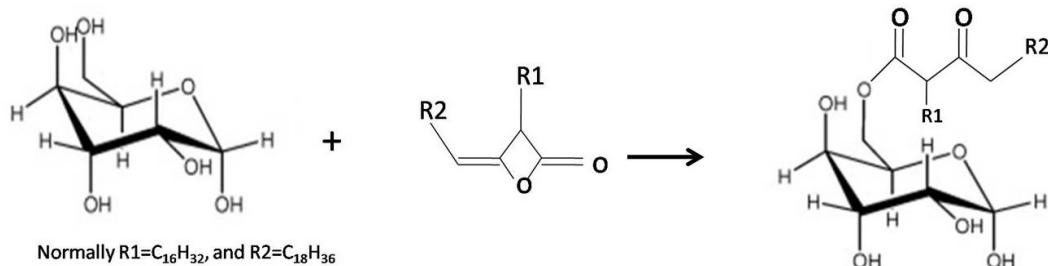


Figure 3-1: Chemical structure of AKD and expected chemical reaction with carbohydrate polymers and competing reaction with water. (El-Tahlawy et al., 2008)

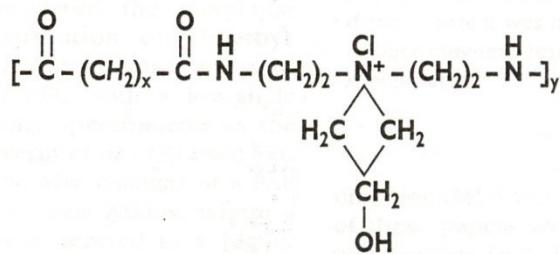


Figure 3-2: Chemical structure of Polyaminoamide-epichlorohydrin (PAE), Kymene. (Fischer et al., 1993)

As background for this research on improved water resistance of SMCF materials, we also investigate herein some processing conditions of the solvent exchange process that may impact the final structure of the material. Previous research had used (Patel et al., 2009 ) an exchange process in which the water in the starch gels were exchanged with ethanol using a 3:1 weight ratio of ethanol exchange volume to starch gel. 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 time needed to produce the materials, either 6 or 12 days, would be a significant disadvantage for commercial implementation. In order to determine the optimum exchange times, several exchange times were evaluated with respect to foam structure herein. (It should be noted that the exchange time in combination with the shortest dimension for diffusion both are important in determining the effectiveness of the solvent exchange bath.) Based on these results, an advantageous time interval was used to process the SMCF modified with the AKD and Kymene and the physical and moisture related properties were determined.

## **Experimental**

### **Materials and Methods**

Corn starch was supplied by Cargill, USA (Cargill Gel 03420), consisting approximately of 25 % amylose and 75 % amylopectin. Anhydrous ethanol Fisher product Number A405<sup>P</sup>-4) was used for solvent exchanges. Alkyl ketene dimer (AKD) and Kymene 500 were supplied from Hercules Incorporation, Wilmington, DE.

### **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 under continuous stirring (IKA-Werk, RW 16

Basic S1) with a crescent shaped paddle, at speed setting of 10. The cooking involved heating the starch slurries to 95°C in oil bath, approximately 15-20 minutes. The cooked starch solution was poured into identical glass petri (PYREX, Product no Product #3160-101) dishes and allowed to cool to room temperature over a period of 1 hr, approximate volume of petri dish was 70 cubic centimeter and initial weight of starch gel was 60-70 grams.

Aquagels of cooked starch solutions were prepared by refrigerating the starches in the petri dish containing the gelatinized starch overnight at 5°C. This aquagel was used to make SMCF by the solvent exchange technique.

### **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 water is 72 dyne/cm) is replaced with a lower surface tension solvent (ethanol, surface tension of ethanol is 22 dyne/cm), which produces SMCF from the aquagel of starch when dried. SMCF was produced by a *slow* exchange (solvent exchange was carried out at either 6, 12, 24, and 48 hr exchange times with 40, 70, 90, 100, 100, and 100% ethanol-water solutions) and an *fast* exchange (solvent exchange was carried out at either 1.5, 3, 6, 12, 24, and 48 hr exchange times with 100, 100, and 100% ethanol) technique. 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 an amount of solution equal to approximately three times the weight of the sample. Once the solvent exchanges were completed, the samples were allowed to air dry in a 23°C and 50% relative humidity atmosphere, minimum time of about 3 days.

### **Starch blended with different amount of AKD 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 under continuous stirring (IKA-Werk, RW 16 Basic S1) with a crescent shaped paddle, at speed setting of 10 with one cooking condition. pH of the starch solution was adjusted to above 8 by adding sodium hydroxide. The cooking involved heating the starch slurries to 95°C in oil bath, approximately 15-20 minutes. The cooked starch solution was allowed to cool to 50°C, about 20 minutes in the flask under ambient conditions. At this temperature addition of required amount of AKD was done with continuous stirring for 30 minutes. The solution was then poured into identical petri dishes and allowed to cool to room temperature over a period of 1 hr. For cured samples petri dishes with lid on placed into the oven at 50°C for 30 minutes and then allowed cool to room temperature.

Aquagels of cooked starch solutions were prepared by refrigerating the petri dishes containing the gelatinized starch overnight at 5°C. This aquagel was used to make SMCF by

the fast solvent exchange technique (24 hr exchange times with 100, 100, and 100% ethanol) and then air dried as described above.

### **Starch blended with AKD and/or Kymene 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 under continuous stirring (IKA-Werk, RW 16 Basic S1) with a crescent shaped paddle, at speed setting of 10 with one cooking condition. The pH of the starch solution was adjusted to just above 8 by adding sodium bicarbonate, measured by pH meter. (Some samples were pH adjusted using sodium hydroxide, the results of these are discussed in Appendix 3-A, water swelling mass loss and density.) The cooking involved heating the starch slurries to 95°C in oil bath, approximately 15-20 minutes. The cooked starch solution was allowed to cool to 50°C, about 20 minutes) in the flask under ambient conditions. At this temperature AKD (1% by weight on starch, 0.24g) and /or Kymene (1% by weight active material on starch, 8 ml of a 1% solution) was added and continuously stirred for 15 minutes. The solution was then poured into identical petri dishes and allowed to cool to room temperature over a period of 1 hr.

Aquagels of cooked starch solutions were prepared by refrigerating the petri dishes containing the gelatinized starch overnight at 5°C. This aquagel was used to make SMCF by the fast solvent exchange technique (12 hr exchange times with 100, 100, and 100% ethanol) and then air dried as described above.

### **Curing of SMCFs of starch blended with AKD and/or Kymene**

It has been reported that Kymene can be cured at 80-105°C in 3-10 minutes depending upon the Kymene concentration (Yano et al., 1991; Fischer, S., 1996) and AKD can be cured at 70-50°C for 1 to 2 hours (Qaio et al., 2006; El-Tahlawy et al., 2008). In order to use only one condition for curing, samples were cured in a convection oven at 95°C for two hours in glass petri dish with a loosely held petri dish cover.

### **Characterization of SMCF**

#### **Scanning Electron Microscopy Analysis**

Morphological characterization of starch microcellular foam was performed on images captured by a scanning electron microscope (SEM), Hitachi s3200-N. The samples were coated with gold-palladium of 10 nm thickness to make the samples conductive at 200 milliTorr vacuum with Denton Vacuum Desk II instrument. The digital images obtained from the SEM were characterized using image analysis software. Random areas of the samples were taken and all of the pores (more than 30 pores were measured for each sample) in the area were measured (Revolution Software, 4pi Analysis, Inc.).

#### **Thermogravimetric Analysis**

SMCF conditioned at 23°C and 50% relative humidity was subjected to TGA, (TGA Q500, TA Instruments) at a heating rate of 10°C/min to 500°C under nitrogen purge 40/60 ml/min of nitrogen in balance and sample flow. Mass loss at 100°C is assumed to be moisture. Initial

moisture content of extruded starch samples was measured by drying in a conventional oven at 105°C until a constant mass was reached.

### **Brightness Measurement**

SMCF was crushed with mortar and pestle and the particles passing through a 20 mesh screen (manufacture part number 850 micron opening) were collected and formed into a tablet. A Carver press (hydraulic unit model 3912, Carver Inc, Wabash IN) was used to make a 0.5 g tablet, dimensions of about 1.3-1.6 cm diameter and 0.3-0.5 cm thickness. One ton of force was applied for one minute to make the tablet. The tablet brightness was measured with a Brightimeter Model S-5 (Technidyne Inc, New Albany IN) with no backing. For each sample tablet the brightness was measured twice on both sides and the average reported. The brightness is a measure of the sample reflectivity at 457 nm wavelength of light.

### **Density Measurement**

Since all samples had irregular shapes the densities of the samples were measured by weighing the sample alone and then weighing the sample immersed in uniform plastic beads (average diameter of 0.25cm) in a graduated cylinder with a known total volume. The packing density of the beads was known from a plot of the volume of beads ( $\text{cm}^3$ ) versus mass of beads (grams), which resulted in a straight line relationship between mass and volume ( $\text{Volume} = 0.711 \times \text{Mass}$ ,  $R^2 = 0.99$ ). The slope is the inverse of the packing density of the beads, which was found to be 1.406 g/cc. The density of a sample was then determined by the following equation:

$$\text{Volume of sample plus beads (cc)} = \frac{\text{Mass of bead (g)}}{\text{Density of bead (g/cc)}} + \frac{\text{Mass of sample (g)}}{\text{Density of sample (g/cc)}} \quad \text{Eq ... (1)}$$

For each sample, the measurement was taken six times (repacking the sample in beads each time) and the average and standard deviation reported. Foams are three dimensional cellular solids and have single important characterizing parameter for foams is relative density of foams (relative density = density of foam/density of cell wall material). And porosity of foam material is the volume fraction of pores Porosity = 1- relative density. The pore wall material density is assumed to equal the density of the starch when air dried from the aquagel directly, without any solvent exchange, determined herein to be 1.06 g/cc.

### **Water swelling and Mass loss measurement**

Water swelling and mass loss of the SMCF was measured. In a sealed glass beaker, a known sample mass was placed into 25 ml of de-ionized water for 24 hrs at 23°C. After 24 hrs, the sample was filtered through pre-weighed wet qualitative Whatman filter paper (Product number 1004070) under conventional house vacuum for 60 seconds. The weight of the wet filter paper and sample was determined. The wet filter paper with sample was placed into an oven at 105 °C for 1 hr and then weighed again. The water swelling and mass loss of the SMCF was calculated as:

$$\text{Water swelling of SMCF (g of water absorbed /g of sample)} = \frac{d - (b \times a) - a - x}{x} \quad \text{Eq ..... (2)}$$

Where:

a = Dry mass of filter paper (OD mass of filter paper)

b = Water retention value of filter paper (g/g)

$$= \frac{\text{Weight of wet filter paper} - \text{Weight of oven dried filter paper}}{\text{Weight of oven dried filter paper}}$$

c = Initial mass of sample

d = Wet mass of filter paper with sample

e = Dry mass of filter paper with sample (OD mass of filter paper with sample)

x = Mass of starch retained = e – a

$$\% \text{ Mass loss} = \frac{c-x}{c} \times 100\% \quad \text{Eq. .... 3}$$

The water contact was done in two modes, one in which the foam was allowed to float or sink (in contact with water) and a second mode in which the foam was forced to be immersed completely under the water surface (forced immersion) for all samples. Results of samples in contact and with forced immersion are reported in this chapter and correlation of results represented in Appendix 3-G.

### Contact Angle Measurement

Contact angle measurements were performed with a NRL Contact Angle Goniometer by Rame Hart Inc. (model 100-00). A drop of deionized water (mass of approximately 35 milligram) was place on the surface of the molded starch sample. The contact angle on two sides of the drop was measured immediately and the average reported. The contact angle was

then monitored every minute for four minutes. Two tests (drops) were conducted on each sample. The contact angle measurements also were performed with Dynamic Contact Angle measurement (Phoenix 300) instrument. A drop of deionized water was placed on the surface of the sample and images of water droplet were taken at every 10 seconds up to 4 minutes contact time. The contact angle between the surface of sample and water droplet was measured with ImageJ software. Images of the selected samples and results are reported in Appendix 3-B.

## **Results and Discussion**

### **Effect of Solvent Exchange Time Intervals on SMCF**

The main purpose of this part of the study was to determine the minimum time interval for solvent exchanges that can produce fully developed microcellular foam structure. Once identified, this solvent exchange protocol would be used as the standard method for investigating the addition of AKD and Kymene to the starch materials. Both a slow exchange (40, 70, 90, 100, 100, and 100% ethanol) and a fast exchange (100, 100, and 100% ethanol) series of solvent baths were explored with different exchange times.

For the samples formed from aquagels using the fast solvent exchange process, at very short exchange times of 1.5 and 3 hours a glassy non porous material is formed (Figure 3-3) and the resulting density is high (Table 3-1). It is considered that the time allowed for exchanges was too short to allow full exchanges of ethanol for the water, and thus, the starch dried from significant amounts of water did not form foams. For similar starch aquagels that were

directly dried without any solvent exchange, the samples produced were hard, non-porous, translucent solids with a density of 1.06 g/cc (Patel et al., 2009).

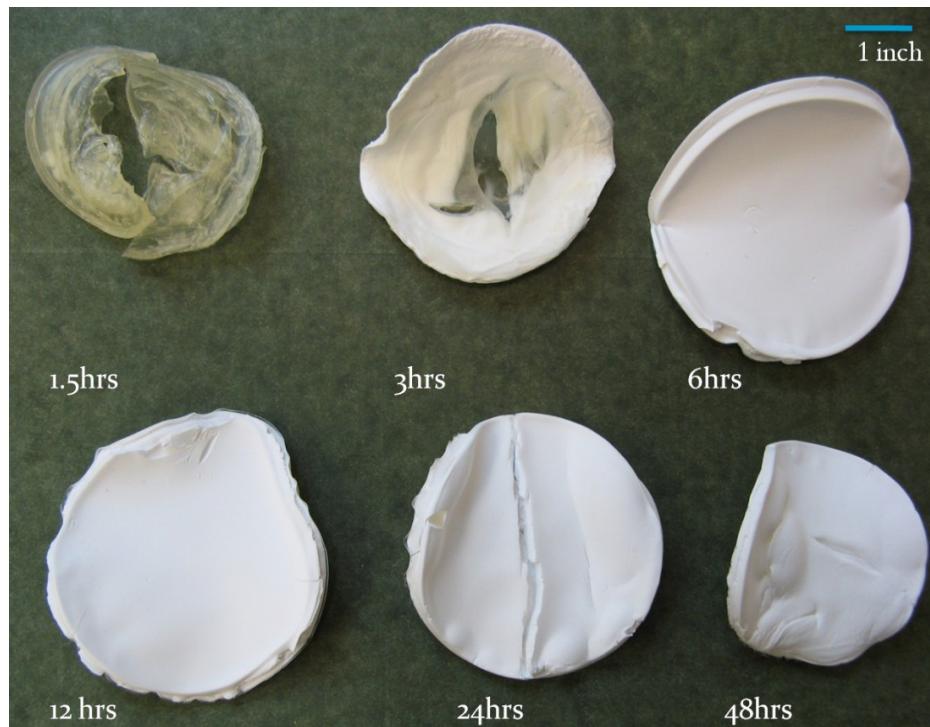


Figure 3-3: SMCFs prepared with fast exchange with 1.5, 3, 6, 12, 24, and 48 hours exchange time intervals.

For the 6 and 12 hour exchange times sufficient time is provided for exchange and a foamed structure of very high opacity is formed, Figure 3-3. For the 6 and 12 hour exchange time a very low density microcellular foam material of 0.22 g/cc and 0.24 g/cc, respectively is produced (Table 3-1). These densities are similar to those reported by Glenn (1995), who reported density of 0.25 g/cc for corn based SMCF using a exchange with ethanol. With increased exchange time the density of the SMCF increases, Table 3-1. For the foams with

48 hour exchange times, the densities are in agreement with those previously reported for the same type of starch, but with different cooking and exchange processes (Patel et al., 2009).

Table 3-1: Density of SMCFs prepared with different exchange time intervals.

Exchange type	Exchange time interval (hrs)	Density based on dimensions (g/cc)	% volume shrinkage	Density based on the packing density (g/cc)	STD DEV of density - packing density	Relative Density	Pore Volume Fraction (%)
No exchange	-	-	-	1.06	0.09	1.00	0
Fast	48	0.47	83	0.45	0.08	0.42	58
Fast	24	0.35	72	0.41	0.01	0.39	61
Fast	12	0.22	59	0.29	0.07	0.27	73
Fast	6	0.24	64	0.26	0.03	0.25	75
Fast	3	0.76	77	0.79	0.02	0.75	25
Fast	1.5	0.60	79	1.06	0.02	1.00	0
Slow	48	0.58	88	0.53	0.03	0.50	50
Slow	24	0.54	85	0.47	0.01	0.44	56
Slow	12	0.44	77	0.49	0.02	0.46	54
Slow	6	0.31	77	0.32	0.01	0.30	70

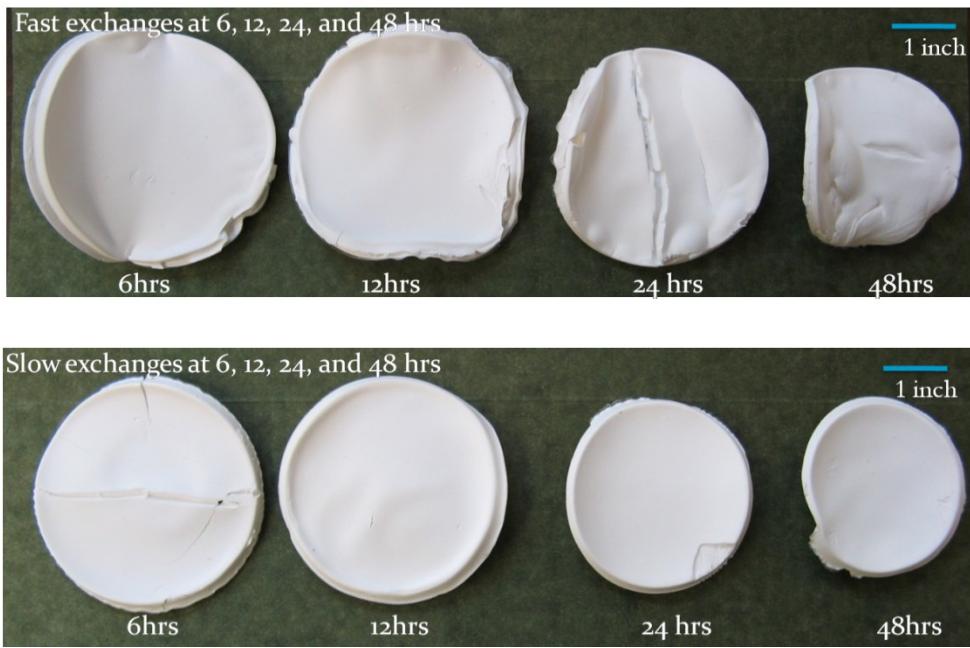


Figure 3-4: SMCFs prepared with fast and slow exchanges with 6, 12, 24, and 48 hour exchange time intervals.

For the slow exchanged samples the 6 and 12 hour exchange times produced opaque foamed materials, Figure 3-4. These samples had low density and the density increased with increased exchange time, similar to the fast exchanged materials, Table 3-1. The density is plotted versus exchange time for the fast and slow exchange processes in Figure 3-5. It is apparent that there is a minimum in density with respect to exchange time for the fast exchange. Also, the density of the SMCF from the fast exchange process is lower than for the slow exchange for all exchange times. Since the initial concentration of starch was 8% in water then if the water is removed without changing the volume of the sample the density of the remaining starch would be 0.08 g/cc, a theoretical minimum. Interestingly, if the density of SMCF for the fast exchange for the four longer exchange times is extrapolated to short times then the data approaches the theoretical minimum, Figure 3-5.

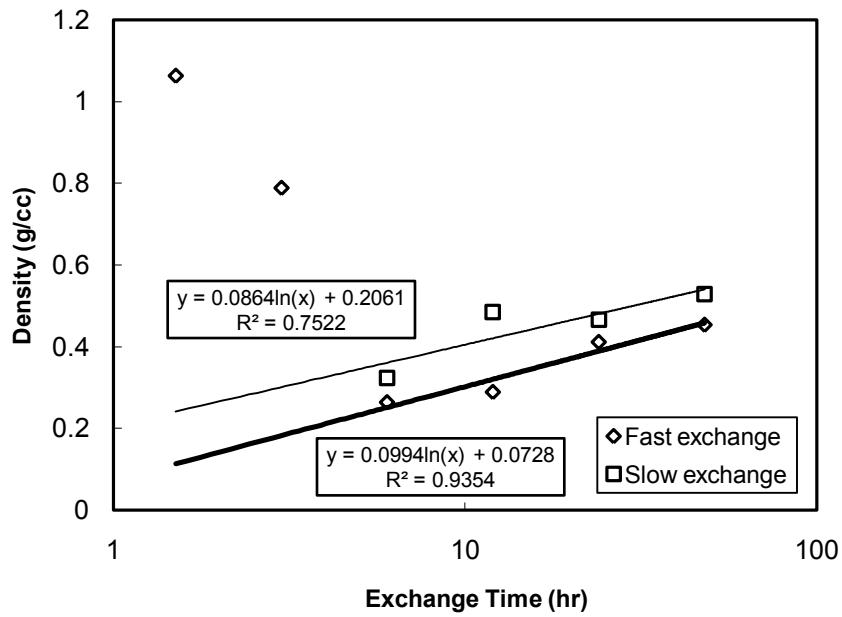


Figure 3-5: Density of SMCFs prepared with fast and slow exchanges with different exchange time intervals.

If the data is plotted on a linear scale the extrapolation of the same four points gives a y-intercept of 0.25 with a  $R^2$  value of 0.87 (plot not shown).

SEM images of starch materials show three distinct features, each of which may dominate during different processing methods, Figure 3-6. (Additional images are displayed in Appendix 3-C.) For the fast exchanged material with 1.5 hr exchange time a solid, non-porous (at the length scale of a micrometer) structure is apparent, Figure 3-6(a). It is suggested that the solvent exchange was incomplete for this process and that the water content was substantial on drying and that the drying forces from the evaporating high surface tension water-ethanol remaining in the starch collapsed the pores. It can be

reasonable to assume that when left to dry in ambient conditions, the ethanol, with a lower boiling point and higher vapor pressure will evaporate at a higher rate than the water, leaving the starch with a larger concentration of water towards the end of the drying process. This significant water concentration towards the end of the drying should collapse the pores and as apparent from the SEM image, remove any observable evidence of the starch foam structure.

Since the fast exchange process was performed with three 100% ethanol (surface tension 22 dyne/cm) exchanges and slow exchange was process performed with 40%, 70%, 90% and three 100% ethanol (surface tensions 30, 25, 23, and 22 dyne/cm respectively) exchanges, there may be some effect of surface tension on starch structure during the exchange process. For identical weighted aquagel samples, the amount of water remove from the aquagel sample should be higher and the contraction of water in the aquagel sample should be lower for the fast exchange than slow exchange process due to the lower surface tension and higher concentration of solvent in the fast exchange process and this could be a reason for higher contraction of SMCFs prepared with slow exchange process compared to fast exchange process.

Moreover, if the assumption made that the starch is no longer soluble in 50% ethanol concentration which would mean that during the slow exchange process the longer contact time with higher amount of water allow starch molecules to be mobile for longer period of time. During this the starch molecules find most suitable space to arrange themselves and forms insoluble aggregates that range from a few interlocking molecules to microcrystalline

regions, which leads to densification of dissolved starch and thus a higher foam density for slow exchanged SMCFs relative to fast exchange process, Figure 3-4. This phenomenon also is known as starch retrogradation.

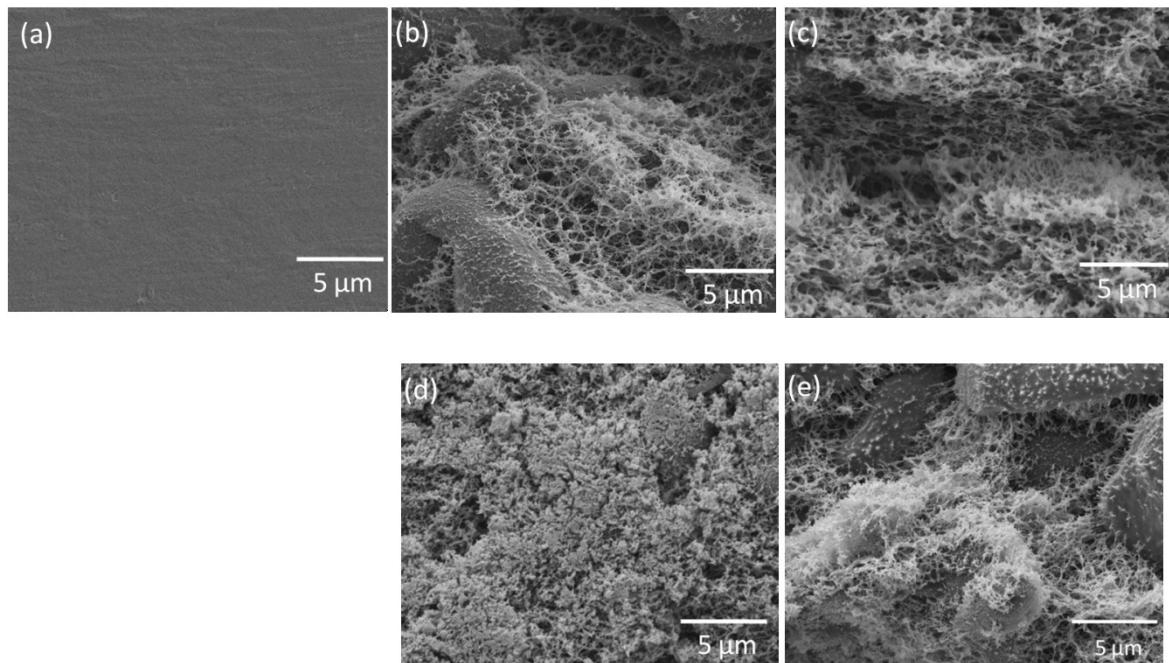


Figure 3-6: SEM images of SMCF materials with fast exchange with 1.5 hour time interval (a), 6 hour time interval (b), and 24 hour time interval (c); and slow exchanges with 6 hour time interval (d), and 24 hour time interval (e).

For the starch material with 6 hour solvent exchange times a partially developed porous structure exists, in which can be observed remnants of the initial starch granules from the plant. The uncooked starch granules have an average diameter of 20 microns (Bolivar et al., 2007) similar to the size range seen in Figure 3-6(b) for the 6 hour solvent exchange. The other prominent structural feature is a three dimensional web-like structure expanding out from the starch granules, sometimes in localized areas, Figure 3-6(b). A possible explanation

for web-like structure is that when starch granules swell in water during the cooking that amylose leaches out from the granule and extends into the water phase, leaving a amylopectin rich granule behind (Maurer, H. W., 2001) and during the solvent exchange process the amylose rich region first precipitated and make web-like structures with shorter exchange time intervals.

For the starch material with 24 hour solvent exchange times the three dimensional web-like structure dominates, with very little evidence of starch remnants, Figure 3-6(c). One possibility is that with the longer solvent exchange time that the ethanol has a better chance to exchange with water inside the remnant granules, and on drying convert the amylopectin rich portions of the granules into the web-like material.

For slow exchanged samples, 6 hour time interval sample showed only few locations with porous structure where as 24 hours time interval show partially developed porous structure with the three dimensional web-like material throughout the sample, Figure 3-6(d, e). It was observed that the formation of the three dimensional web-like structure is formed more prominently with fast exchange process at shorter solvent exchange times than for the slow exchange process.

The average pore diameters and pore wall thickness are listed in Table 3-2 and the distributions are plotted in Appendix 3-D. For these exchange processes, pore sizes of

around 400 nm and cell wall thicknesses of around 140 nm are generated, within the size range to interact with light and produced opaque materials.

Table 3-2: Average pore diameter and cell wall thickness three dimensional web-like materials of slow and fast exchanged samples with different time intervals.

Exchange Process	Time interval (hr)	Pore size range (nm)	Ave. pore size (nm)	Standard Deviation	Cell wall thickness range (nm)	Ave. cell wall thickness (nm)	Standard deviation
Slow	6	70-700	280	120	70-300	140	50
Slow	24	120-1400	360	210	50-350	140	50
Fast	6	190-1300	500	230	50-400	150	70
Fast	24	90-700	350	130	30-250	110	40

## AKD- SMCF Materials

### Density

Based on the study of solvent exchange processes, it was chosen to use a fast exchange process with exchange times of 24 hours, which was shown to produce fully developed microcellular structure. Starch-AKD materials with different concentrations of AKD blended after cooking, cured and uncured are shown in Figure 3-7. These materials did not hold the mold shape as well as those without AKD, compare Figures 3-7 with Figure 3-4. The materials were hard and strong relative to the starch samples alone, suggesting a non-foamed structure, see later and Appendix 3-E. At the 3% AKD level the material was brittle.

The density of the starch-AKD samples were higher than the starch alone samples, Figure 3-8, Table 3-3. There was no significant impact of curing of the starch-AKD samples on the

density of the starch-AKD samples relative to the experimental error, Figure 3-8, Table 2. The density increased with increasing concentration of AKD for both cured and uncured samples.

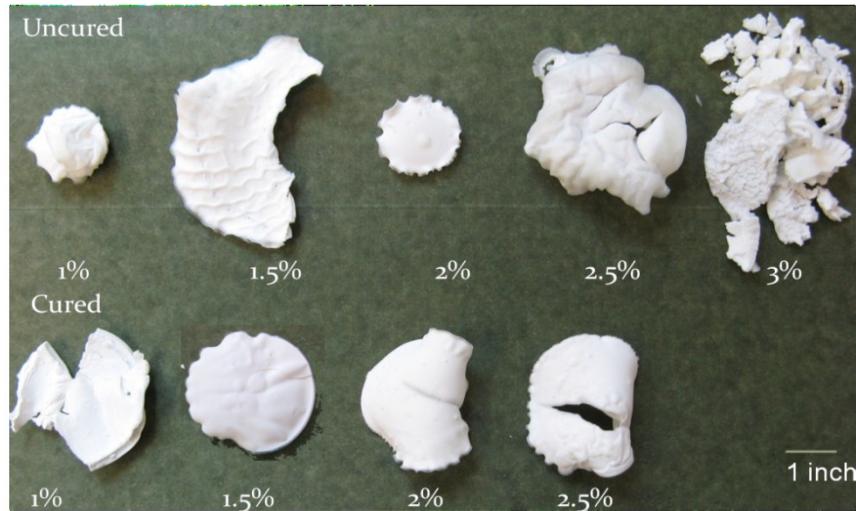


Figure 3-7: SMCFs prepared from starch blended with different level of AKD, first raw uncured SMCFs where as second raw cured.

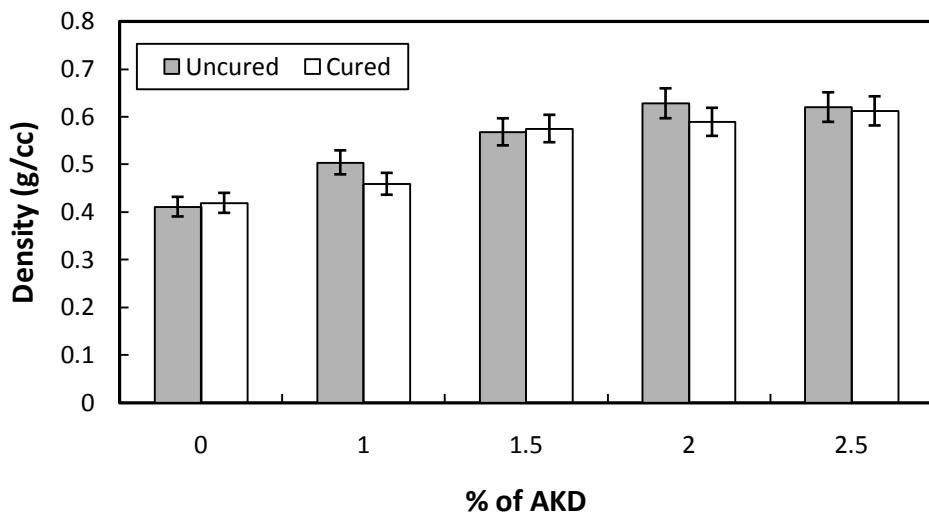


Figure 3-8: Density of SMCFs prepared from starch blended with different amount of AKD with and without curing.

Table 3-3: Density of SMCFs prepared from starch-AKD blend with 24 hour exchange time intervals.

Exchange type	Exchange time interval (hrs)	Density based on the packing density (g/cc)	Relative Density	Pore Volume Fraction (%)
No exchange- air dried	-	1.06	1.00	0
Starch-Uncured	24	0.41	0.39	61
Starch-Cured	24	0.42	0.40	60
Starch- 1% AKD-Uncured	24	0.50	0.48	52
Starch-1% AKD-Cured	24	0.46	0.43	57
Starch-1.5% AKD-Uncured	24	0.57	0.54	46
Starch-1.5% AKD-Cured	24	0.58	0.54	46
Starch-2% AKD-Uncured	24	0.63	0.59	41
Starch-2% AKD-Cured	24	0.59	0.56	44
Starch-2.5% AKD-Uncured	24	0.62	0.58	42
Starch-2.5% AKD-Cured	24	0.61	0.58	42

## Brightness

The brightness measurements of particles ground from the starch blended with AKD samples and pressed into pellets are presented in Figure 3-9. It is evident that the inclusion of AKD into the samples decreased the brightness relative to the uncured SMCF alone. This could be from a combination of the increase in density of the samples when AKD is added and also due to the slight yellow color of the AKD relative to starch.

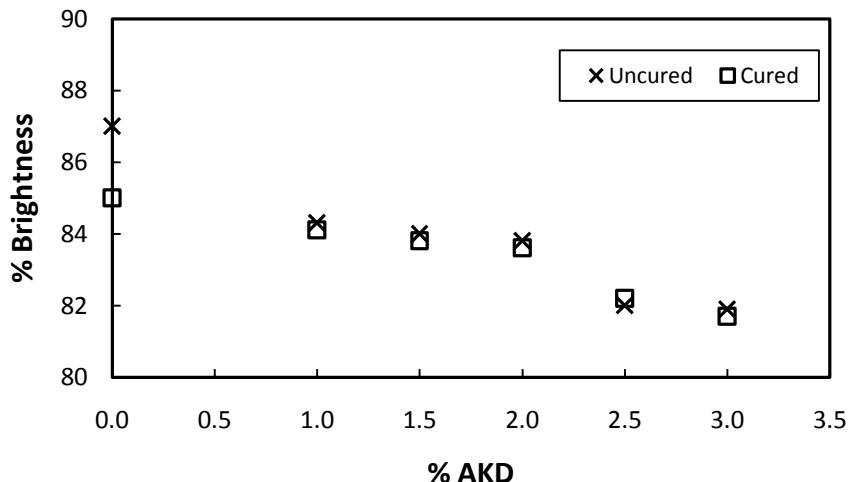


Figure 3-9: Percent brightness of starch blended with AKD SMCFs. Note that increased amounts of AKD lowered the brightness generally.

Since it was expected that the brightness of the SMCF samples will be related to the micro pore volume fraction of the materials there should be a strong relationship between micro-pore volume fraction (related to the density) and the brightness. In a previous study, SMCF materials (no AKD) with high micro pore volume fraction had higher brightness; see Figures 2-5 and (Patel et al., 2009). In previous research, a maximum brightness for fine precipitated SMCF/AKD particles with particle size 7-10  $\mu\text{m}$  (Bolivar et al., 2007) precipitated from starch solution with ethanol in the presence of shear action resulted in a 90-94% ISO, whereas in this study with molded aquagel starch/AKD blend samples a maximum brightness of 84% GE (which has an approximate 87% ISO brightness) was determined. Differences in tablet sample preparation for the brightness measurement could affect the measured brightness. These differences could be related to the particle sizes developed, in the previous study particle sizes of average diameter of 7-10  $\mu\text{m}$  were pressed into pellets and in this

study a mortar and pestle and then screening with a 20 mesh (850 micron opening) was used. In both studies, the brightness was found to decrease with increasing AKD.

### **Water swelling and mass loss**

The dry structure of the starch microcellular foam is desired to be maintained when immersed in water or subjected to high humidity environments. To investigate, the foams were soaked in for 24 hours (no stirring) by in contact with water. After this soaking, the water swelling and mass loss were measured, Figure 3-10 and 3-11. All solvent exchanged aquagel samples initially floated on the surface of the water, but settled to the bottom of the container after a time period of approximately 1-5 hours. It was important to force the complete immersion of the samples, if allowed to float; the results were impacted by the sample's different tendency to float/sink. All solvent exchanged aquagel samples initially floated on the surface of the water, but settled to the bottom of the container after a time period of approximately 1-3 hours except for the aquagel starch (0% AKD) control sample which took approximately 5 hours.

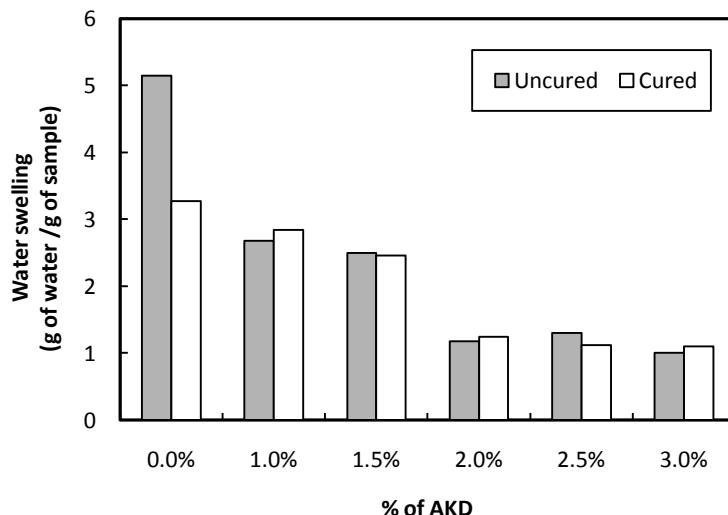


Figure 3-10: Water swelling (g of water/g of sample) of starch blended with AKD samples in contact with water after 24 hrs of immersion. Note in general decrease in water swelling of starch materials with increase of AKD concentration.

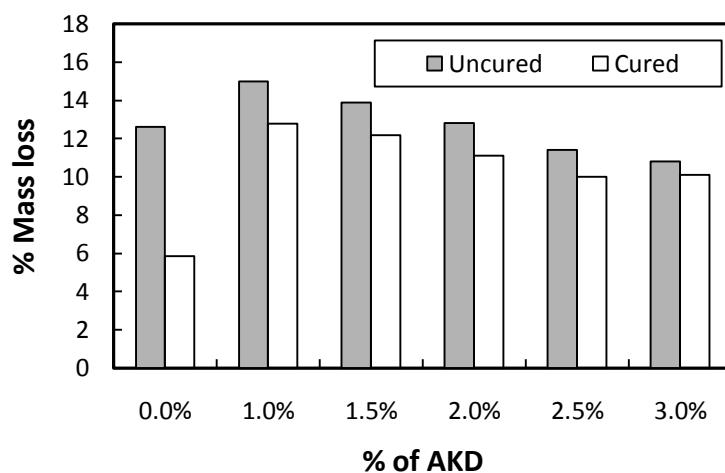


Figure 3-11: Percent mass loss of starch blended with AKD samples after in contact with water for 24 hours.

### Water swelling and mass loss by forced immersion

The dry structure of the starch microcellular foam is desired to be maintained when immersed in water or subjected to high humidity environments. In addition to the tests in which the sample was allowed to sink or float, termed in contact, water swelling and mass loss after forced immersion for 24 hours in water were conducted. To investigate, the foams were soaked for 24 hours (no stirring) by forced immersion in water at room temperature and the amount of water swelling determined, Figure 3-12. Increases in AKD concentration decreased the water swelling process of the SMCF-AKD material for both cured and uncured samples, however, even at the 3% AKD level, the material still swelled with a significant amount of water, about 1 g/gram. The samples after this process remained opaque and the size and shape intact.

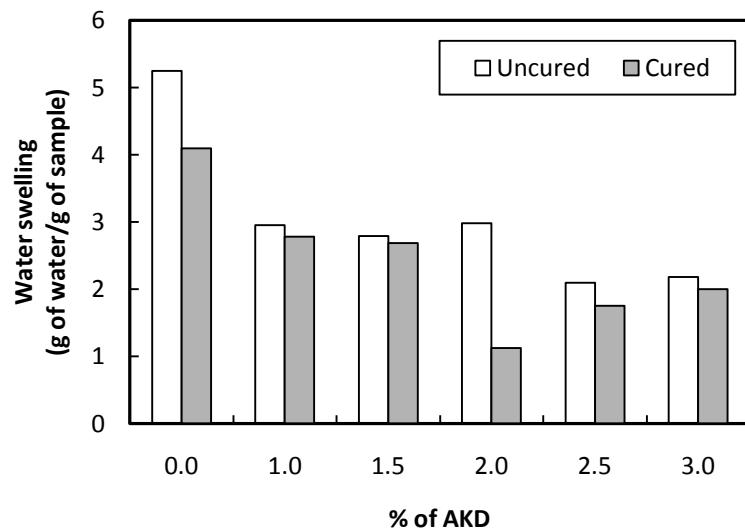


Figure 3-12: Water swelling (g of water/g of sample) of starch blended with AKD samples after 24 hrs of forced immersion. Note in general decrease in water swelling of starch materials with increase of AKD concentration.

The decrease in the water swelling is in agreement with previous work showing that increased concentrations of AKD blended with starch decreases the water swelling in the starch (El-Tahlawy et al., 2008). There was no significant difference in the water swelling between the cured and uncured samples.

Generally, it is expected that SMCF micro-porous structures with higher pore volume and thinner pore walls should increase water swelling. If the starch material is soluble, then a higher specific surface area would be expected to increase the rate of mass loss. AKD is expected to decrease the mass loss upon immersion of water by resisting water penetration, which is in agreement with the findings, Figure 3-13. There was no significant difference in the mass loss between the cured and uncured samples.

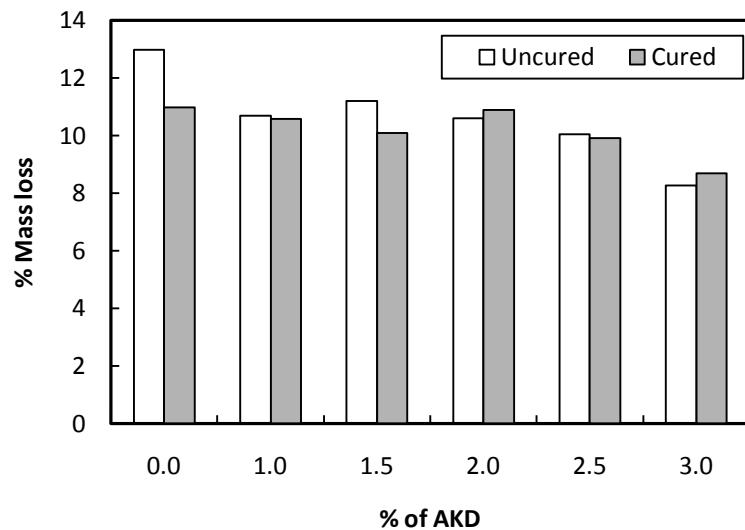


Figure 3-13: Percent mass loss of starch blended with AKD samples after forced immersion in water for 24 hours.

Somewhat higher water swelling was observed for the forced immersion samples relative to the in contact with water samples, compare Figures 3-10 and 3-12. Unexpectedly a higher mass loss for in contact with water samples relative to forced immersion samples, compare Figure 3-11 and 3-13. Plots of the forced immersion results versus the in contact with water are shown Appendix 3-G.

### **Water Contact Angle**

Contact angles of water on starch- AKD materials were determined as a function of time, Figures 3-14 and 3-15. Over a four minute period, the contact angle decreased only slightly for all AKD concentrations, Figures 3-14 and 3-15. In contrast, SMCF materials with no AKD experienced a decrease in contact angle of 44 to 14 degrees over the same 4 minute period (Patel et al., 2009). In papermaking processes, with AKD as a sizing agent used to control the rate of ink and water penetration in paper, it was reported in one study that the addition of 0.3% AKD increased the contact angle of water on the fiber surface to 80 degrees (Seo et al., 2008). In that same study, it was reported that curing for longer time may make AKD to migrate to the surface.

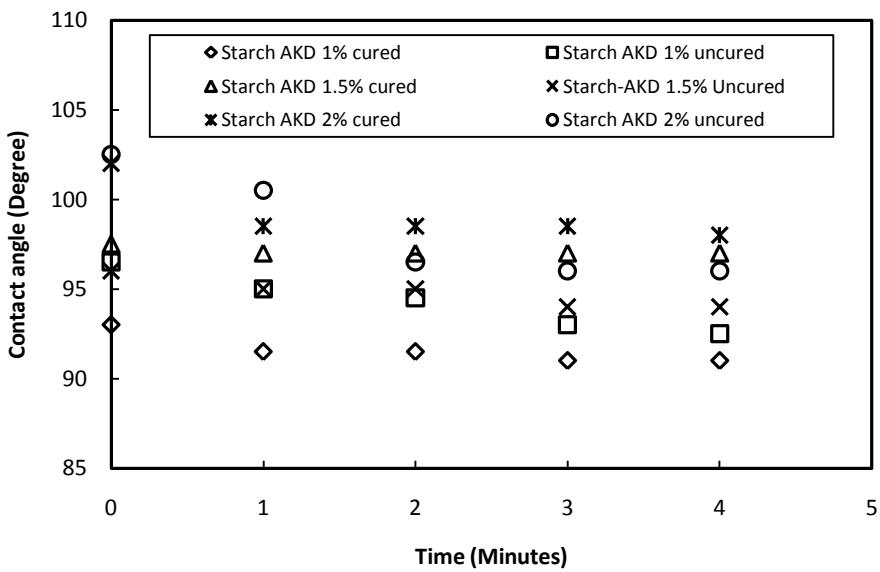


Figure 3-14: Water contact angle for starch blended with different amount of AKD over the period of 4 minutes.

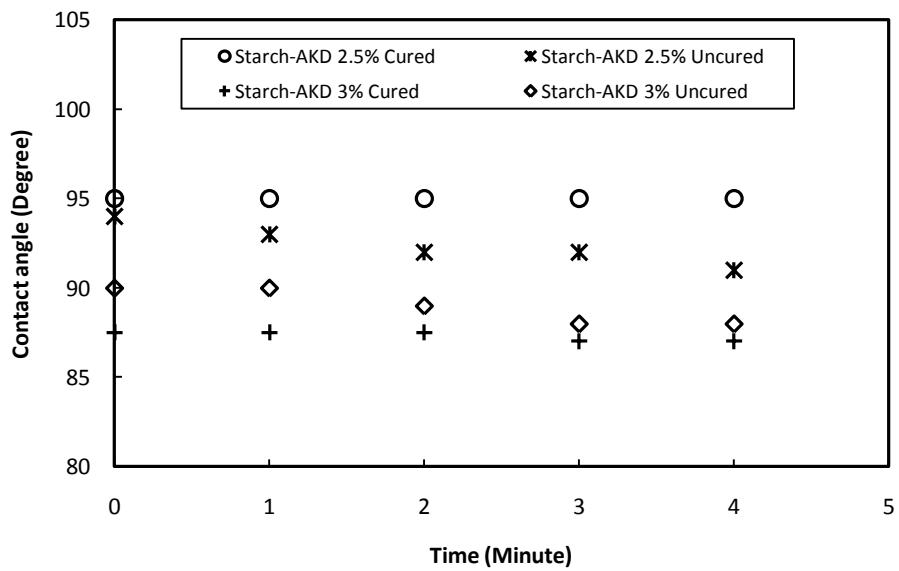


Figure 3-15: Water contact angle for starch blended with different amount of AKD over the period of 4 minutes.

Initial contact angles for starch blended with various levels of AKD are plotted in Figure 3-14. At the higher AKD levels the presence of AKD had an effect on the surface roughness/cracking which may have had an effect on the initial contact angle results herein. No systematic effect of curing on initial contact angle was observed, Figure 3-16. Based on the data in Figures 3-14 to 3-16, it appears that there is no advantage to using levels of AKD higher than 2%.

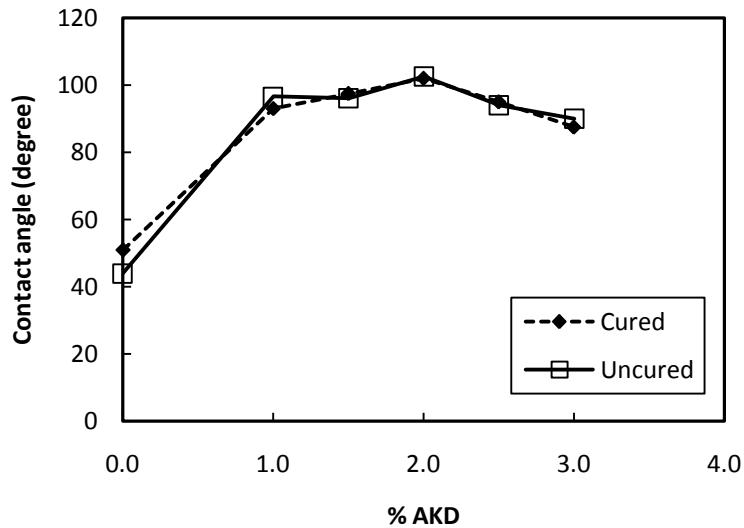


Figure 3-16: Contact angle between the water droplet and SMCFs prepared with different composition of AKD at zero minute contact time.

These results are in agreement with previous results that showed that the maximum increase in contact angle of SMCF-AKD material was achieved at 2% levels of AKD (Bolivar et al., 2007).

### **SMCF Blended with AKD and Kymene**

It was hypothesized that a combined effect of both AKD (sizing agent) and Kymene (crosslinking agent, common wet strength additive for paper) might impart significant water resistivity of the resulting SMCF. The samples were produced with the fast exchange method with 12 hours exchange time interval, Figure 3-17.

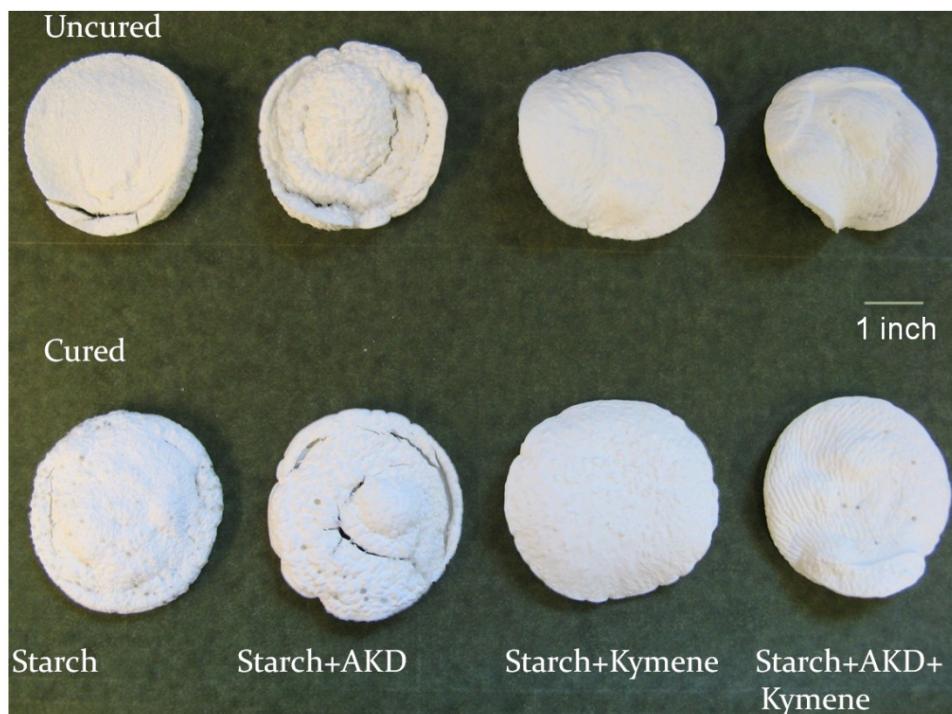


Figure 3-17: SMCFs prepared from starch, starch blended with 1% AKD and/or 1% Kymene by a fast exchange process with solvent exchange times of 12 hours.

### **SMCF Morphology**

Both AKD and Kymene decreased the porous microcellular structure relative to starch alone, Figure 3-18 (Additional images are displayed in Appendix 3-E.). Curing decreased the porous structure of the AKD and Kymene samples relative to the corresponding uncured

samples, unlike the starch alone sample which was not so affected by the curing process. Further, macroscopic voids and cracks in the AKD and Kymene samples were present, see Appendix 3-E.

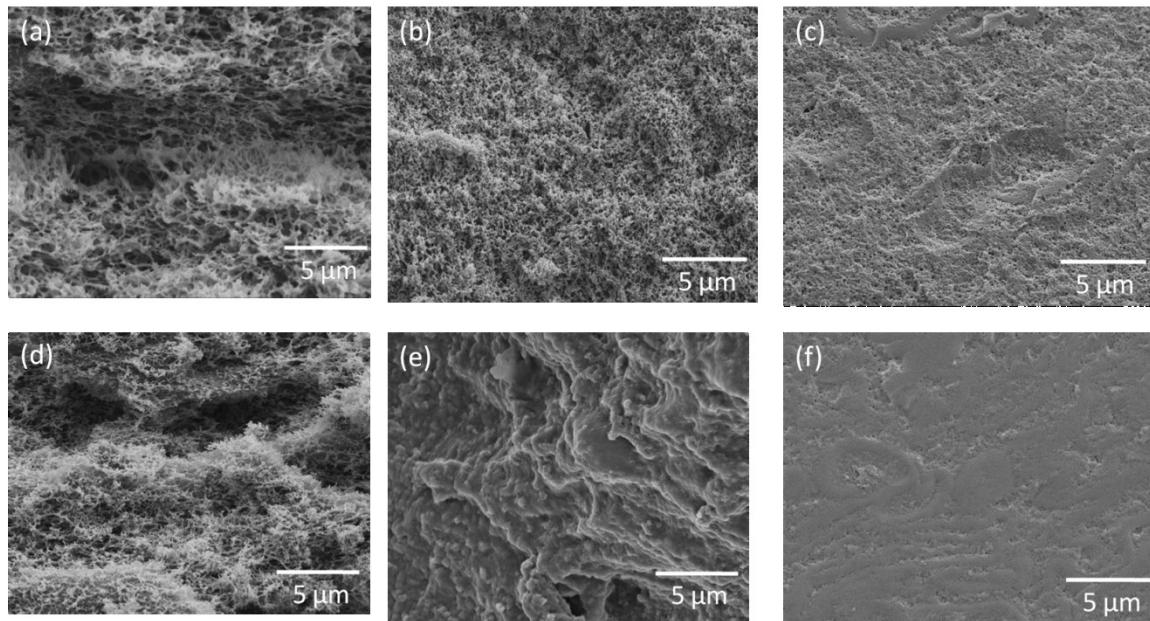


Figure 3-18: SEM images of starch – uncured (a), starch blended with 1% AKD – uncured (b), and starch blended with 1% Kymene – uncured (c), starch – cured (d), starch blended with 1% AKD – cured (e), and starch blended with 1% Kymene – cured (f). Samples were prepared by fast exchange process with 12 hour solvent exchange times.

For both, starch blended with 1% AKD and 1% Kymene, cured samples, there was a significant decrease in the pore size for starch sample compared to uncured samples, Table 3-4. Pore size and cell wall thickness distributions are represented in Appendix 3-F.

Table 3-4: Average pore diameter and cell wall thickness of cured and uncured SMCFs prepared from starch, starch blended with 1% AKD, and starch blended with 1% Kymene.

Sample	Pore size range (nm)	Ave. pore size (nm)	Standard Deviation	Cell wall thickness range (nm)	Ave. cell wall thickness (nm)	Standard deviation
Starch uncured	90-750	350	130	35-260	115	40
Starch cured	100-950	300	120	30-290	130	60
Starch+1% AKD uncured	40-400	160	85	65-230	125	35
Starch+1% Kymene uncured	30-250	130	40	60-400	190	80

## Density

The density of SMCF materials prepared with 1% AKD and/or 1% Kymene were found to be higher for the blended samples compared to the starch alone samples, Figure 3-19, in agreement with the SEM images, Figure 3-18. The increase of the density is attributed to the lower pore volume in the blended materials, Table 3-5.

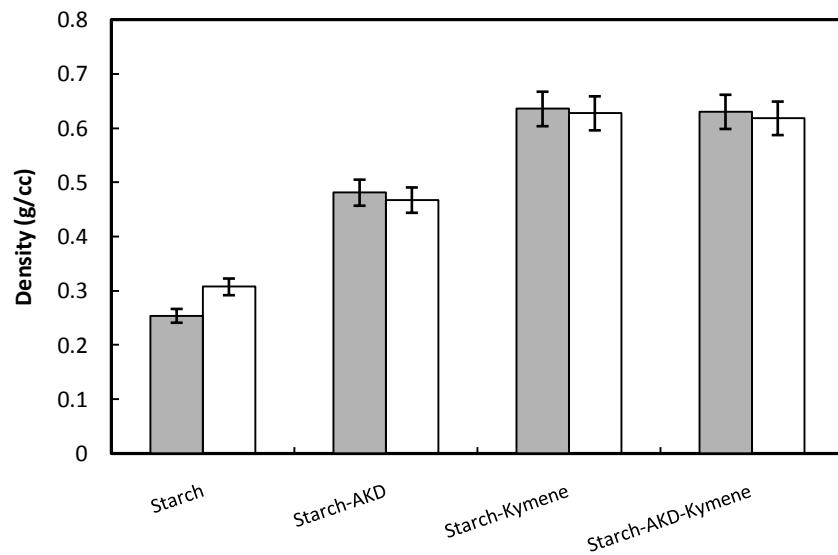


Figure 3-19: Density of SMCFs prepared from starch, and starch blended with 1% AKD and/or 1% Kymene with and without curing.

Table 3-5: Density of SMCFs prepared from starch blended with 1% AKD and/or 1% Kymene with 12 hour exchange time interval.

Exchange type	Exchange time interval (hrs)	Density based on the packing density (g/cc)	Relative Density	Pore Volume Fraction (%)
No exchange- air dried	-	1.06	1	0
Starch Uncured	12	0.25	0.24	76
Starch Cured	12	0.31	0.29	71
Starch+1% AKD Uncured	12	0.48	0.45	55
Starch+1% AKD Cured	12	0.47	0.44	56
Starch+1% Kymene Uncured	12	0.64	0.60	40
Starch+1% Kymene Cured	12	0.63	0.59	41
Starch+1% AKD+1% Kymene Uncured	12	0.63	0.59	41
Starch+1% AKD+ 1% Kymene Cured	12	0.62	0.58	42

### Water swelling and mass loss

The dry structure of the starch microcellular foam is desired to be maintained when immersed in water or subjected to high humidity environments. To investigate, the foams were soaked in for 24 hours (no stirring) by in contact with water. After this soaking, the water swelling and mass loss were measured, Figure 3-20 and 3-21. All solvent exchanged aquagel samples initially floated on the surface of the water, but settled to the bottom of the container after a time period of approximately 1-5 hours.

There was no significant difference in the water swelling of starch blended with AKD/Kymene samples between forced immersion and in contact with water, although there was higher mass loss was found for in contact with water samples, Figure 3-21 and

3-23, somewhat higher water swelling observed for the forced immersion samples relative to the in contact with water samples. Correlation of results of both techniques are represented in Appendix 3-G.

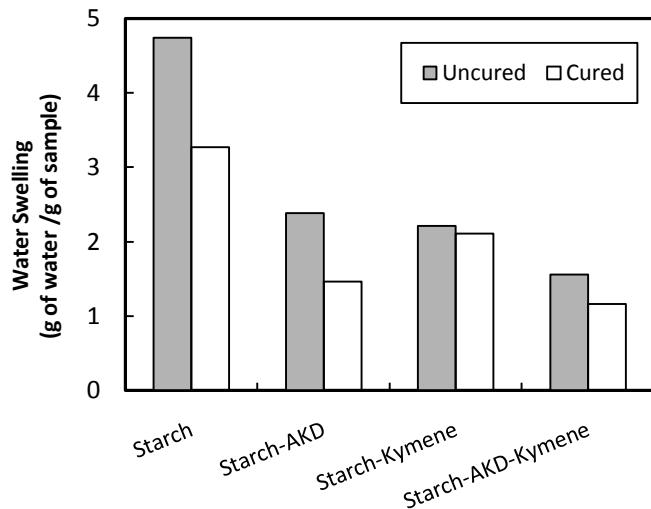


Figure 3-20: Water swelling (g of water/g of sample) of starch blended with 1% AKD and/or 1% Kymene samples after in contact with water for 24 hrs. Note in general decrease in water swelling of starch materials with increase of AKD and Kymene concentrations.

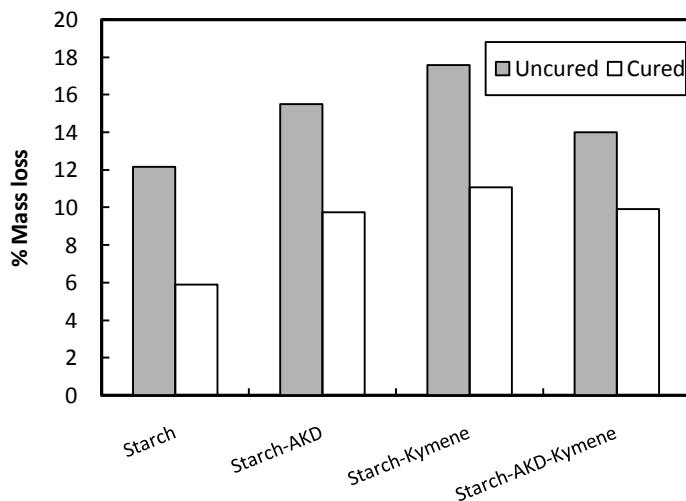


Figure 3-21: Percent mass loss of starch blended with 1% AKD and/or 1% Kymene samples after in contact with water for 24 hours. Note that there was difference in mass loss of cured and uncured samples.

### Water swelling and mass loss by forced immersion

SMCFs prepared from starch blended with 1% AKD and/or 1% Kymene show decreased water swelling relative to the control starch sample, Figure 3-22. Curing did not appear to have a significant effect on water swelling.

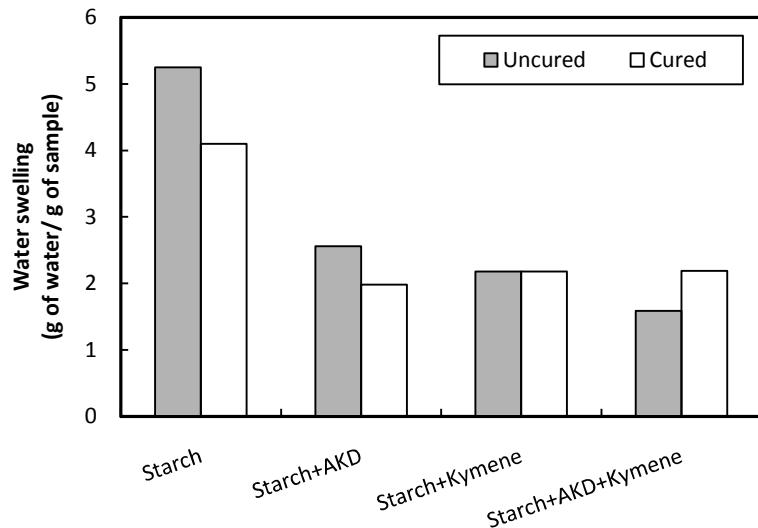


Figure 3-22: Water swelling (g of water/g of sample) of starch blended with 1% AKD and/or 1% Kymene samples by forced immersion of samples for 24 hrs. Note in general decrease in water swelling of starch materials with increase of AKD and Kymene concentrations.

Mass loss decreased for cured samples relative to uncured samples, but not enough samples were tested to confidently conclude this, Figure 3-23. From SEM images, Figure 3-18, it can be observed that curing decreased the porous structure in the AKD and Kymene blends relative to uncured samples, which would be expected to decrease both the water swelling and mass loss of cured samples.

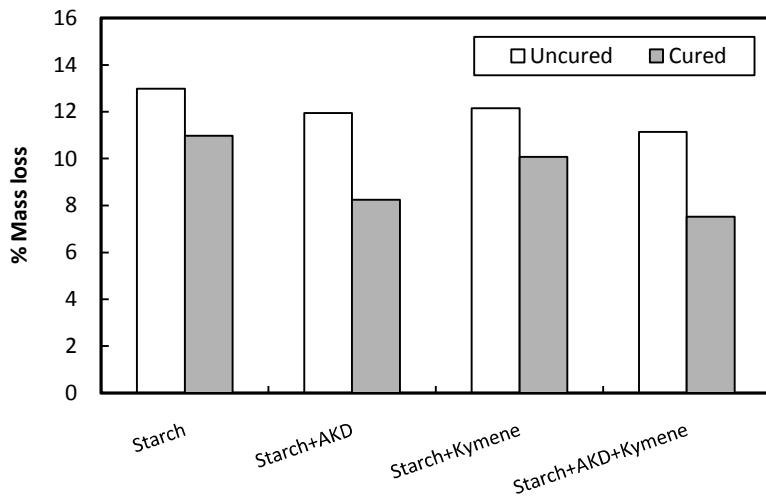


Figure 3-23: Percent mass loss of starch blended with 1% AKD and/or 1% Kymene samples by forced immersion in water for 24 hours. Note that there was difference in mass loss of cured and uncured samples.

### **Thermal Degradation and Moisture Content**

Thermal degradation and adsorbed moisture were observed by TGA on samples that were conditioned at 23 °C and 50% relative humidity. All cured samples showed higher decomposition temperature except Starch blended with Kymene samples which showed similar trend of decomposition for both cured and uncured samples, Figure 3-24 to 3-27. Additionally, all samples showed decomposition temperature around 250°C except cured starch blended with AKD sample which showed higher decomposition temperature around 280°C, Figure 3-25 and Table 3-6. SEM images also showed significant difference in the structure of cured versus uncured samples, Figure 3-18.

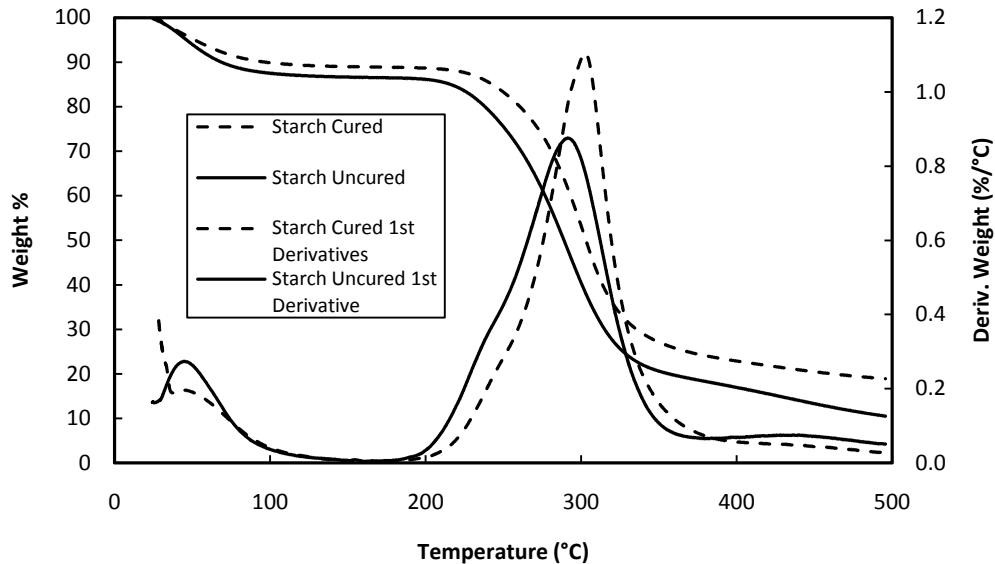


Figure 3-24: Thermogram (at a heating rate of 10°C/min) of starch cured and uncured SMCFs.

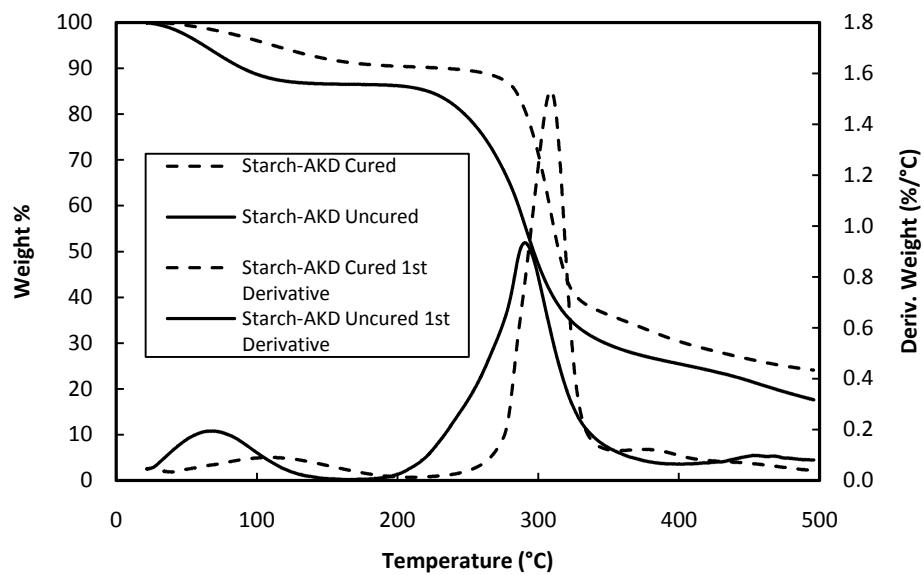


Figure 3-25: Thermogram (at a heating rate of 10°C/min) of starch blended with 1% AKD cured and uncured SMCFs.

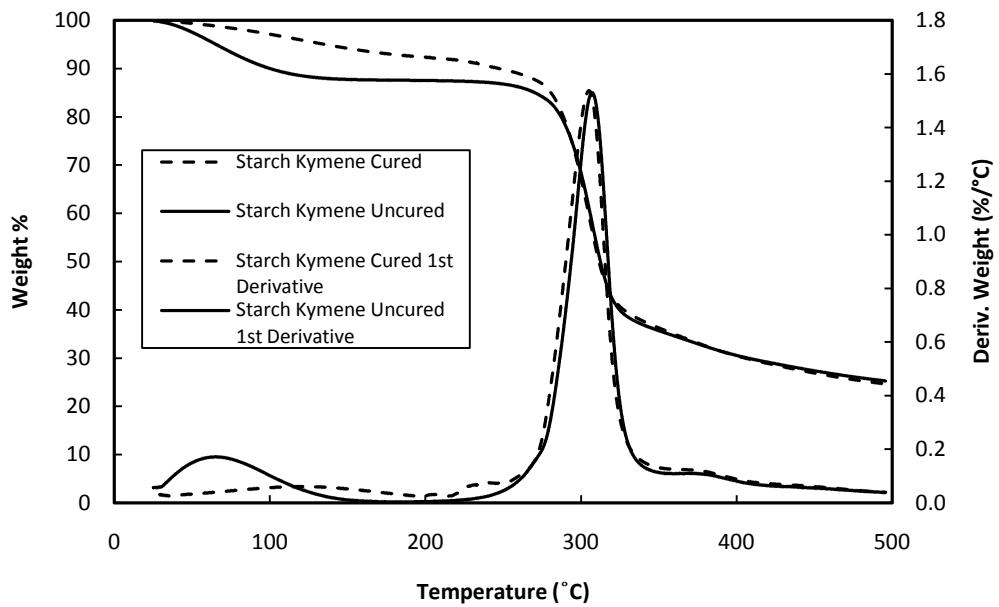


Figure 3-26: Thermogram (at a heating rate of 10°C/min) of starch blended with 1% Kymene cured and uncured SMCFs.

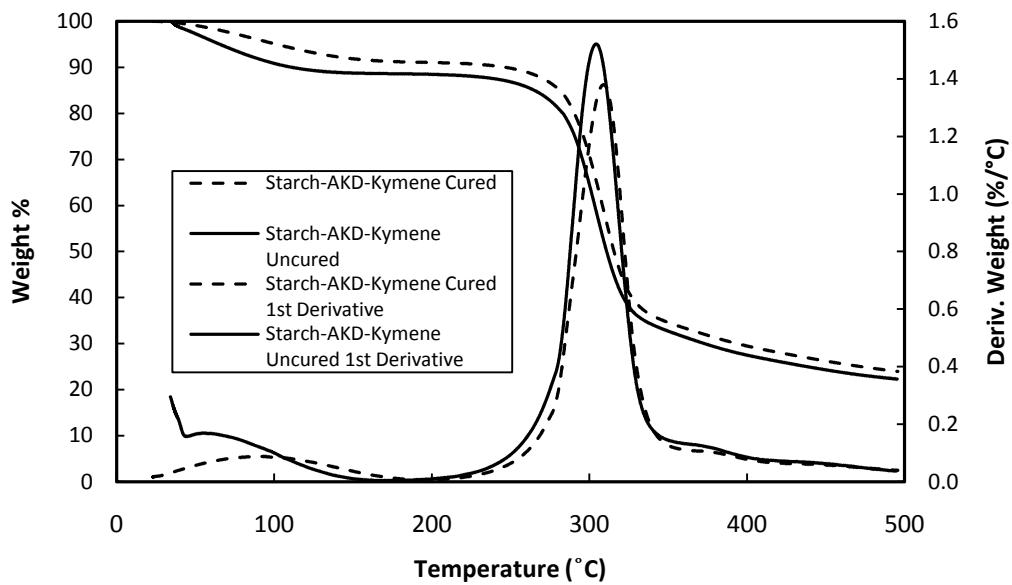


Figure 3-27: Thermogram (at a heating rate of 10°C/min) of starch blended with 1% AKD and 1% Kymene cured and uncured SMCFs.

Mass loss at 100°C was considered mainly due to the removal of water associated with the sample, which was considered as the moisture content of the sample, Table 3-6. All uncured samples showed higher moisture content compared to cured samples. There was only a small (~2%) difference in moisture content of starch cured and uncured samples compared to starch blended with AKD and/or Kymene cured uncured samples. All starch blended samples had almost ~7% decrease in the moisture content for cured samples relative to the corresponding uncured samples. Curing (95°C for 2 hours) decreased the porous structure of the blend SMCFs as seen in Figure 3-18 but the density did not change due to curing. Although the cause for the decreased moisture content for blended samples is not known, it is a possibility that the AKD or Kymene rearrange or migrate to the surface of the pores during the elevated temperature for the two hour duration.

Table 3-6: Moisture content (%) of starch and starch blended with 1% AKD and/or 1% Kymene based on TGA.

Sample	Moisture Content (%)	Decomposition Peak Temp (°C)	Total Weight Loss (%)
Starch Uncured	12	300	89
Starch Cured	10	300	81
Starch AKD Uncured	11	290	87
Starch AKD Cured	4	310	76
Starch Kymene Uncured	10	307	74
Starch Kymene Cured	3	305	75
Starch AKD Kymene Uncured	11	310	77
Starch AKD Kymene Cured	5	312	76

## Water contact angle

SMCFs prepared from starch-1% AKD by fast exchange with 12 hours exchange time interval show significant increased water contact angle compared to the starch alone control, Figure 3-28 and Figure 3-29. Blending with AKD caused the water drop not to absorb into the starch; the contact angle was observed to be approximately constant with respect to time for both starch-1% AKD and starch-1%AKD-1%Kymene cured and uncured samples, Figure 3-28 and 3-29. Almost all uncured samples showed lower contact angle compared to cured samples. Starch control and Starch-1% Kymene cured and uncured samples show rapid decrease in contact angle compared to starch-1%AKD and starch-1%AKD-1%Kymene samples, Figure 3-28, and 3-29. The water contact angle also was measured by DCA technique. The similar trend of results were observed, the results and correlation with Goniometer technique represented in Appendix 3-B.

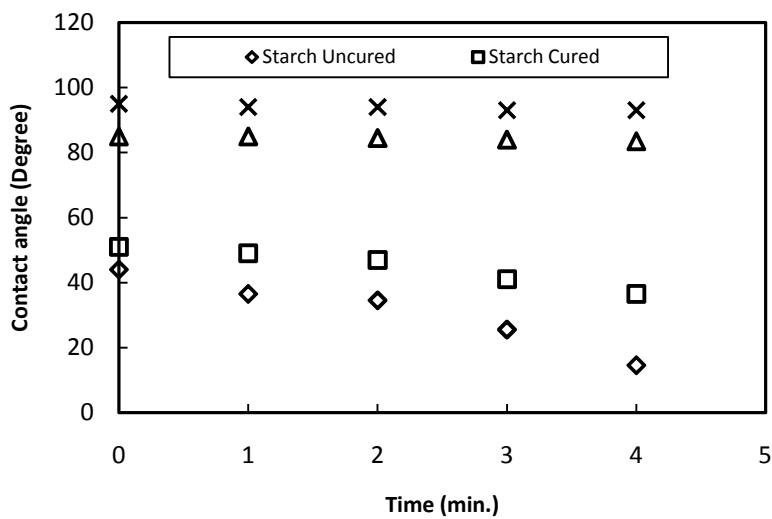


Figure 3-28: Water contact angle for starch and starch blended with 1% AKD, cured and uncured, samples over the period of 4 minutes.

In this and previous study (Patel et al., 2009) showed SMCF produced from starch alone to have a lower water resistivity compared to the SMCF prepared from starch blended with AKD. However, Kymene did not reduce water resistivity to a significant extent; the water resistivity was much more sensitive to AKD.

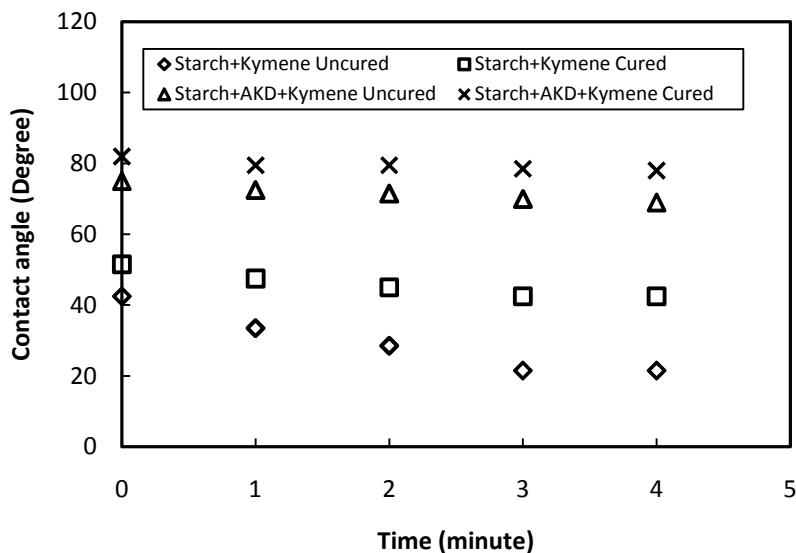


Figure 3-29: Water contact angle for starch blended with 1% AKD and 1% Kymene cured and uncured samples over the period of 4 minutes.

## Conclusions

Starch based microcellular foams with porous structure showed a minimum in density with respect to solvent exchange times, with a range of 6-24 hours producing well-developed microcellular foams. SMCFs prepared from blending starch with AKD and Kymene both reduced the porous nature of the materials. Curing these blends further reduced the porous nature of the materials relative to the uncured samples. For increasing levels of AKD, the

resulting material brightness decreased and density increased. AKD increased the water resistance of the SMCF relative to starch alone but Kymene did not.

## References

- Albertsson, A-C., Karlsson, S., (1995). Degradable polymers of the future. Advanced Polymers, 46, 114-123.
- Alexander, R. J., (1996). Starch in plastics. Cereal Foods World, 41, 426-426.
- Barikani, M., and Mohamaadi, M., (2007). Synthesis and characterization of starch-modified polyurethane. Carbohydrate Polymers, 68, 773-780.
- Biliaderis, C. G., Maurice, T. J., and Vose, J. R., (1980). Starch Gelatinization Phenomena Studied by Differential Scanning Calorimetry. Journal of Food Science, 45 (6), 1669-1674.
- Bhatnagar and Hanna, M. A., (1995a). Properties of extruded starch-based plastic foam. Industrial Crops and Products, 4, 71-77.
- Bolivar, A. I., Venditti, R. A., Pawlak, J. J., & El-Tahlawy, K. (2007). Development and characterization of novel starch and alkyl ketene dimer microcellular foam particles. Carbohydrate Polymers, 69(2), 262-271.
- Bottorff, K. J., (1994). AKD sizing mechanism a more definitive description. Tappi journal, 77, 105-116.
- Champ, S. (2003). The dynamics of alkyl ketene dimer (AKD) retention. In International Paper and Coating Chemistry Symposium, 5th (pp. 285–291). Montreal, QC, Canada, June 16–19.
- Cinelli, P., Chiellini, E., Lawton, J. W., and Iman, S. H., (2006). Foamed articles based on potato starch, corn fibers and poly(vinyl alcohol). Polymer Degradation and Stability, 91 (5), 1147-1155.
- Chiou, Bor-Sen, Glenn, G. M., Imam, S. H., Inglesby, M. K., Wood, D. F., & Orts, W. J. (2005). Starch polymers: Chemistry, engineering, and novel products. Natural Fibers, Biopolymers, and Biocomposites, 639–669.
- DEFRA, (2004). A Strategy for non-food crops and uses-creating value from renewable materials (PB10188), October, 2004, Department of food, environment and rural affairs, DEFRA Publications, Admail 6000, London ([www.defra.gov.uk](http://www.defra.gov.uk)).
- DET, 2000 DETR, (2000). Waste Strategy: A Waste Strategy for England and Wales. Department for the Environment, Transport and the Regions, HMSO, London.

Ellis, R. P., Cochrane, P. M., Dale, Duffus, C. M., Lynn, A., Morrison, I. M., Prentice, R. M., Swanston, J. S., Tiller S. A., (1999 ). Starch production and industrial use. *Journal of the Science of Food and Agriculture*, 77 (3), 289-311

El-Tahlway, K., Venditti, R. A., & Pawlak, J. J. (2007). Aspects of the preparation of starch microcellular foam particles crosslinked with glutaraldehyde using a solvent exchange technique. *Carbohydrate Polymers*, 67(3), 319–331.

El-Tahlway, K., Venditti, R. A., & Pawlak, J. J. (2008). Effect of alkyl ketene dimer reacted starch on the properties of starch microcellular foam using a solvent exchange technique. *Carbohydrate Polymers*, 73, 133-142.

Fang, J. M., Fowler, P. A., Tomkinson, J. and Hill, C. A., (2002). The preparation and characterisation of a series of chemically modified potato starches. *Carbohydrate Polymers*, 47(3), 245-252.

Fang, Q., and Hanna, M. A., (2001). Preparation and characterisation of biodegradable copolyester-starch based foams. *Bioresource Technology*, 78, 115–122.

Fang, Q., and Hanna, M. A., (2001). Characteristics of biodegradable Mater-Bi®-starch based foams as affected by ingredient formulations. *Industrial Crops and Products*, 13, 219–227.

Fischer, S. A., (1996). Structure and wet strength activity of polyaminoamide epichlorohydrin resin having azetidinium functionality. *Tappi journal*, 79 (11), 179-186.

Fischer, S. A., and Devore, D. I., (1993). Wet-Strength mechanism of polyaminoamide epichlorohydrin. *Tappi journal*, 76 (8), 121-128.

Franco, C. M. L., & Ciacco, C. F. (1997). Study of the structure of the normal and waxy corn starch granules. *Cienciae Tecnologia de Alimentos*, 17(3), 295–300.

Glenn, G. M., and Stern, D. J., (1999). Starch-Based Microcellular Foams. United States Patent 5 958 589

Glenn, G. M., and Orts, W. J., (2001). Properties of starch-based foam formed by compression/explosion processing. *Industrial Crops and Products*, 13 (2), 135-143.

Glenn, G. M., and Irving, D. W., (1995). Starch-based microcellular foams. *Cereal Chem*, 72, 155–161.

Glenn, G. M., Miller, R. E., & Irving, D. W. (1996). Microcellular starchbased foams. In G. Fuller, T. A. McKeon, & D. D. Bills (Eds.), *Agricultural materials as a renewable resources: Nonfood and industrial applications* (pp. 88–106) ACS Symposium Series, No. 647.

Glenn, G. M., Klamczynski, A. P., Takeoka, G., Orts, W. J., Wood, D., & Widmaier, R. (2002). Sorption and vapor transmission properties of uncompressed and compressed microcellular starch foam. *Journal of Agricultural and Food Chemistry*, 50, 7100–7104.

Glenn, G., Klamczynski, A., Chiou, B. S., Orts, W. J., Imam, S. H., & Wood, D. (2007). Preparation and applications of starch-based porous microspheres, In International symposium on polymers and the environment: Emerging technology and science, Vancouver WA: BioEnvironmental Polymer Society and the Biodegradable Products Institute, October 17–20, abstract #62.

Glenn, G. M., Klamczynski, A. P., Ludvik, C., Shey, J., Imam, S. H., Chiou, Bor-Sen, et al. (2006). Permeability of starch gel matrices and select films to solvent vapors. *Journal of Agricultural and Food Chemistry*, 54(9), 3297–3304.

Hebeish, A., Abdel-Rahman, A., El-Hilw, Z., & Hashem, M. (2005). Cationized starch derived from pre-oxidized starch for textile sizing and printing. *Starch/Staerke*, 57(12), 616–623.

Hong, Yan, Gu, Zhengbiao, & Li, Zhaofeng (2005). Property investigation and application of waxy corn starch for food processing. *Zhongguo Liangyou Xuebao*, 20(3), 30–34.

Hundhausen, U., Militz, H., Mai, C., (2009). Use of alkyl ketene dimer (AKD) for surface modification of particleboard chips. *Eur. J. Wood Prod.*, 67, 37–45.

Hutton, B. H., Huseman, M., Shen, W., & Parker, I. H. (2003). AKD spreading phenomena on chemically heterogeneous surfaces. In Appita annual conference and exhibition, 57th (pp. 291–298).

Imam, S., Wheeler, J., Glenn, G., Woods, D., Orts, W. J., Azam, F., Lodhi, A., Arshad, R., & Arshad, M. (2007). Perspective on agricultural feedstocks for biobased products: Functionality and performance of an encapsulation matrix. In International symposium on polymers and the environment: Emerging technology and science, Vancouver, WA: BioEnvironmental Polymer Society and the Biodegradable Products Institute, October 17–20, abstract #12.

Iman, S. H., Chiou, B., Woods, D., Shey J., Glenn, G. M., Orts, W. J., Narayan, R., Avena-Bustillos, R. J., McHugh, T. H., Pantoja, A., and Bechtel, P. J., (2008). Starch/pulp-fiber based Packaging Foams and Cast Films Containing Alaskan Fish by-products. *BioResources*, 3 (3), 758-773.

Jacobs, H., and Delcour, J. A., (1998). Hydrothermal Modifications of Granular Starch, with Retention of the Granular Structure: A Review. *J. Agric. Food Chem.*, 46 (8), 2895-2905.

Jobling, S., (2004). Improving starch for food and industrial applications. *Current Opinion in Plant Biology*, 7 (2), 210-218.

Kobayashi, S., Schwartz, S. J., Lineback, (1985). Rapid analysis of starch, amylose and amylopectin by high-performance size-exclusion chromatography. *Journal Chromatography*, 319 (2), 205-214.

Linstead and Ekins,(2001). Mass balance UK, mapping UK resource and material flows. Royal Society for Natural Conservation, p. 12.

Marton, J. (1990). Practical aspects of alkaline sizing. On kinetics of alkyl ketene dimer reactions: Hydrolysis of alkyl ketene dimer. *Tappi Journal*, 73(11), 139–143.

Maurer, H. W., (2001). Starch and Starch Products in Surface Sizing and Paper Coating. Tappi Press.

Morris, V. J., (1990). Starch gelation and retrogradation. *Trends in Food science & Technology*, 1 (1), 2-6.

Nabeshima, E. H., and Grossmann, M. V. E., (2001). Functional properties of pregelatinized and cross-linked cassava starch obtained by extrusion with sodium trimetaphosphate. *Carbohydrate Polymer*, 45 (4), 347-353.

Patel, S., Venditti, R. A., Pawlak, J. J., Ayoub, A., and Rizvi, S. S. H., (2009). Development of cross-linked starch microcellular foam by solvent exchange and reactive supercritical fluid extrusion. *Journal of Applied Polymer Science*. 111, 2917-2929.

Preechawong, D., Peesan, M., Supaphol, P., and Rujiravanit, R., (2005). Preparation and characterization of starch/poly(L-lactic acid) hybrid foams. *Carbohydrate Polymers*, 59 (3), 329-337.

Qiao, Lei, Gu, Qu-Ming, & Cheng, H. N. (2006). Enzyme-catalyzed synthesis of hydrophobically modified starch. *Carbohydrate Polymers*, 66(1), 135–140.

Rutledge, A. R., Venditti, R. A., Pawlak, J. J., Patel, S., and Cibils, J. L., (2008). Carbonized starch microcellular foam-cellulose fiber composite structures. *BioResources* 3(4), 1063-1080.

Scott, W. E. (1996). Principles of wet end Chemistry, Chapter 14: Sizing with synthetic sizing materials. Tappi Press.

Singh, N. (2006). Starch in food: Structure, function and applications Edited by Ann-Charlotte Eliasson. *International Journal of Food Science and Technology*, 41(1), 108–109.

Seo, W-S., Cho, NS., Shin, S-J., and Ohga, S., (2008). Surface Chemical States of Sizing Agents on AKD/Cellulose Blends by X-Ray Photoelectron Spectroscopy. *J. Fac. Agr., Kyushu Univ.*, 53 (2), 411–416.

Tarvianen, M., Pelton, S., Mikkonen, H., Elovaara, M., Tuunainen, M., Paronen, P., Ketolainen, J., & Sutinen, R. (2004). Aqueous starch acetate dispersion as a novel coating material for controlled drug release. *Journal of Controlled Release*, 96(1), 179–191.

Thiebaud, S., and Aburto, J., (1997). Properties of octanoated starch and its blends with polyethylene. *Carbohydrate Polymers*, 34 (1-2), 101-112.

Tiefenbacher, K. F., (1993). Starch-based foamed materials-use and degradation properties. *J.M.S.-Pure Appl. Chem. A*, 30 (9-10), 727–731.

Vasanthan, T., Bhatty, R. S., (1996). Physicochemical properties of small- and large-granule starches of waxy, regular, and high-amyllose barleys. *Cereal Chemistry*, 73 (2), 199-207.

Xie, Xueju, Liu, Qiang, & Cui, Steve W. (2006). Studies on the granular structure of resistant starches (type 4) from normal, high amylose and waxy corn starch citrates. *Food Research International*, 39(3), 332–341.

Xu, Y., and Hanna, M. A., (2005). Physical, Mechanical, and Morphological Characteristics of Extruded Starch Acetate Foams. *Journal of Polymers and the Environment*, 13 (3), 221-230.

Yoon, S., and Deng, Y., (2006). Starch-fatty complex modified filler for papermaking. In Proceedings of the Pan Pacific conference, Advances in Pulp and Paper Sciences and Technologies, (pp. 79–84) Vol. 1, Korea Tappi, Seoul Korea, 6–9 June 2006.

Yu, L., Dean, K., and Li, L., (2006). Polymer blends and composites from renewable resources. *Progress in Polymer Science*, 31, 576-602.

## **Chapter 4**

### **Conclusions, Future Work, and Practical Implications**

#### **Conclusions**

##### **Chapter 2**

- Starch based microcellular foam with porous structure were produced with a solvent exchange process.
- The starch foams which showed existence of micro pore structure had low density and high brightness.
- The solvent exchange process was much more important in generating a microcellular structure than whether the material was extruded or formed from an aquagel, the existence of crosslinking, the existence of CO<sub>2</sub> during extrusion, and the cooking extent.
- Micro pores and not macro pores contributed to increased brightness of SMCF materials. Brightness and density of the foams were found to be linearly related.
- The cross-linking with EPI imparted significant water resistance to the extruded samples.
- Moisture content was a better predictor of microporous structure than water swelling.

##### **Chapter 3**

- Starch based microcellular foams with porous structure showed a minimum in density with respect to solvent exchange times, with a range of 6-24 hours producing well-developed microcellular foams.

- SMCFs prepared from blending starch with AKD and Kymene both reduced the porous nature of the materials and curing these blends further reduced the porous nature of the materials.
- AKD increased the water resistance of the SMCF but Kymene did not.
- Curing for AKD and Kymene blends had a significant effect on moisture content as measured after conditioning at 50% relative humidity and 23°C.

### **Suggested Future Work**

- Determine mechanical properties of samples to evaluate utilization as packaging materials.
- Preparation of samples with other cross-linking materials in conjunction with sizing agents to determine the effect on water swelling and mass loss.
- Since solvent exchange process is a fundamental aspect of the research, it would be instructive to study the diffusion of ethanol into a water swollen-starch matrix and investigate how the process could be accelerated.

### **Practical Implications**

- This type of materials can be used as a pigment for paint, paper and coating applications.
- It can be used as a bio-based sustainable packaging material.
- The properties of SMCF can be altered according to the requirement. For example can be made hydrophobic or hydrophilic by blending or cross-linking.

## **Appendices**

## Appendix 2-A

Viscosity of corn starch (Cargill Gel 03420) solution (10% w/w) measured by Brookfield DV III Ultra viscometer with SC4-29 spindle. Viscosity measurement of starch solution was performed heating it to 95°C and continue heating for 20 minutes then allowed to cool with spindle speed 20 rpm and time interval for reading 1 sec.

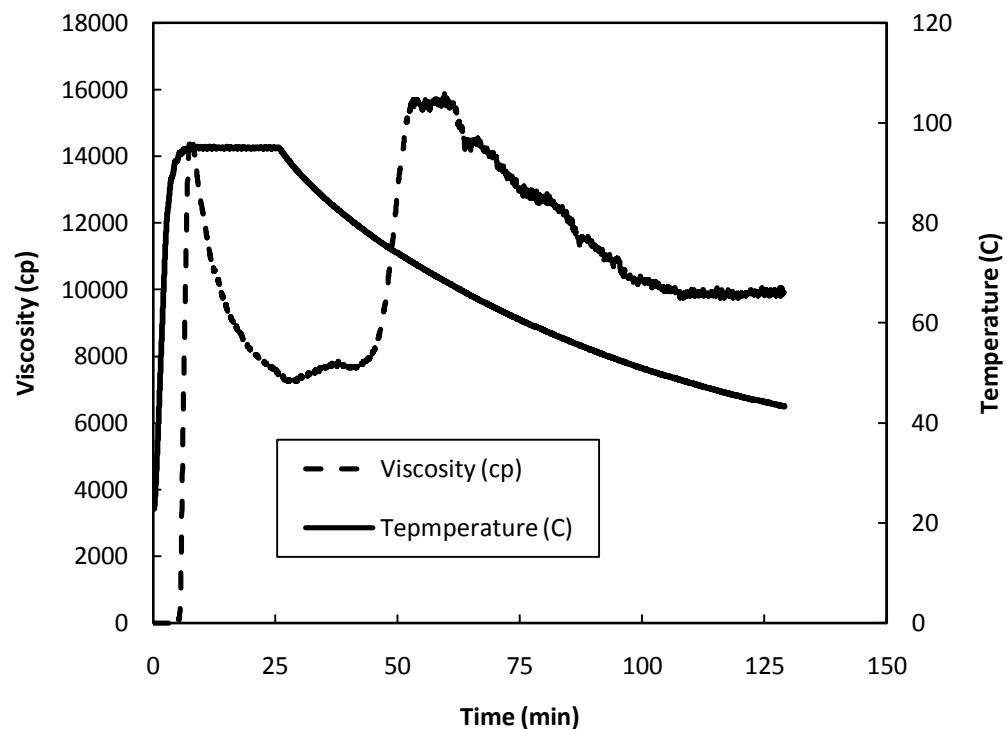


Figure 1: Viscosity of corn starch.

## Appendix 2-B

Pore size (%) and cell wall thickness (%) distribution for SMCF materials prepared from extruded starch and aquagel starch by fast and slow exchanges with 48 hours exchange time intervals. Morphological characterization of starch microcellular foam was performed on images captured by a scanning electron microscope (SEM), Hitachi s3200-N by using image analysis software (Revolution Software, 4pi Analysis, Inc.). Random areas of the samples were taken and all of the pores (more than 30 pores were measured for each sample) in the area were measured.

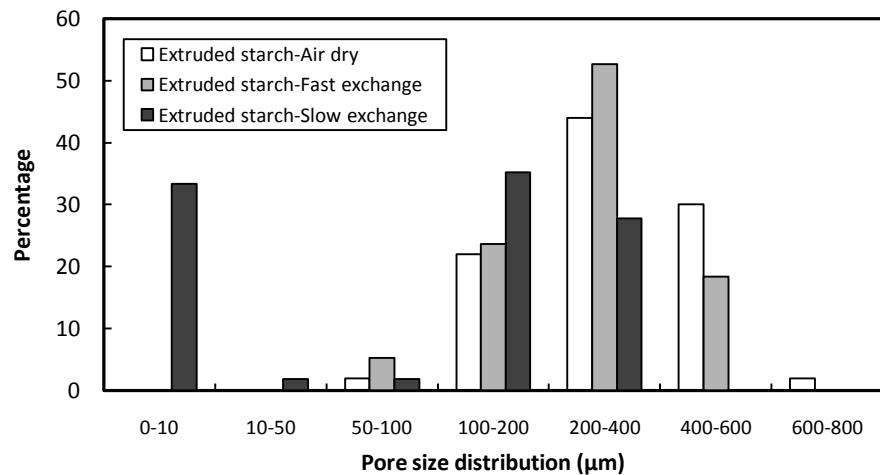


Figure 1: Percent pore distribution of extruded starch SMCF prepared by fast and slow exchange with 48 hours exchange time intervals.

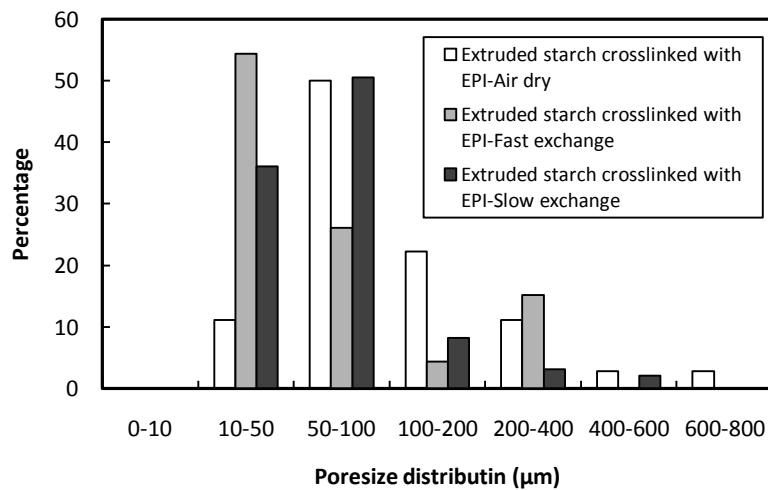


Figure 2: Percent pore distribution of extruded starch cross-linked with EPI SMCF prepared by fast and slow exchange with 48 hours exchange time intervals.

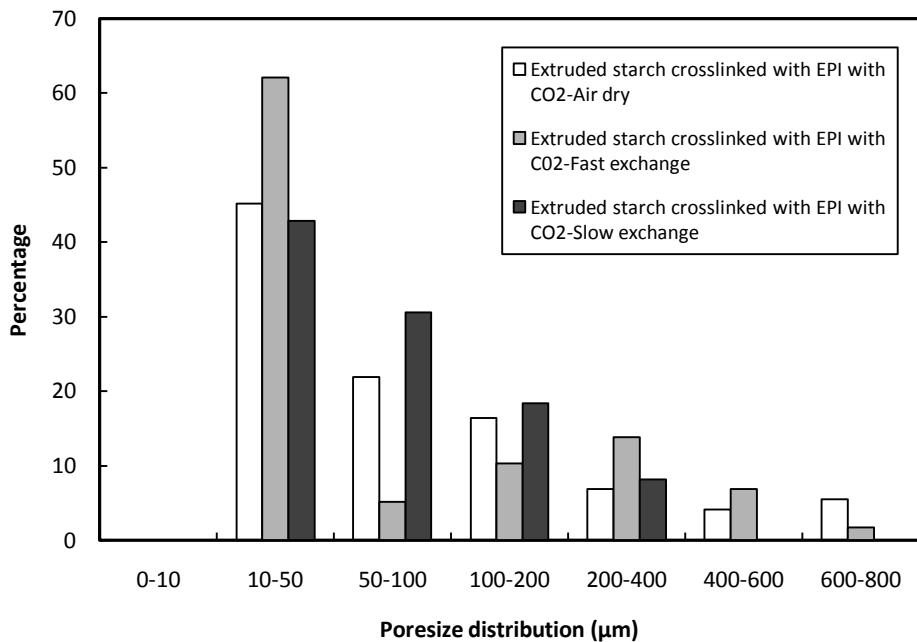


Figure 3: Percent pore distribution of extruded starch cross-linked with EPI with CO<sub>2</sub> SMCF prepared by fast and slow exchange with 48 hours exchange time intervals.

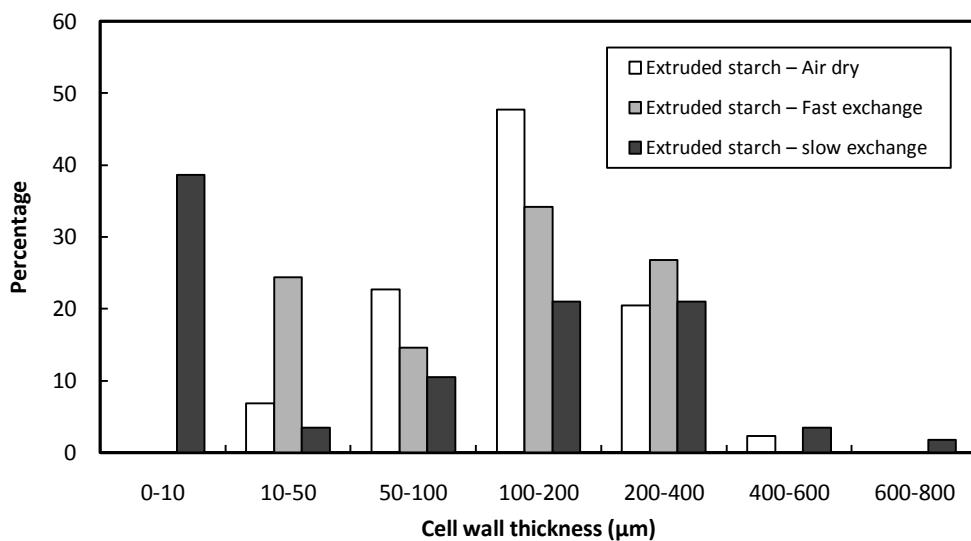


Figure 4: Percent cell wall thickness distribution of extruded SMCF prepared by fast and slow exchange with 48 hours exchange time intervals.

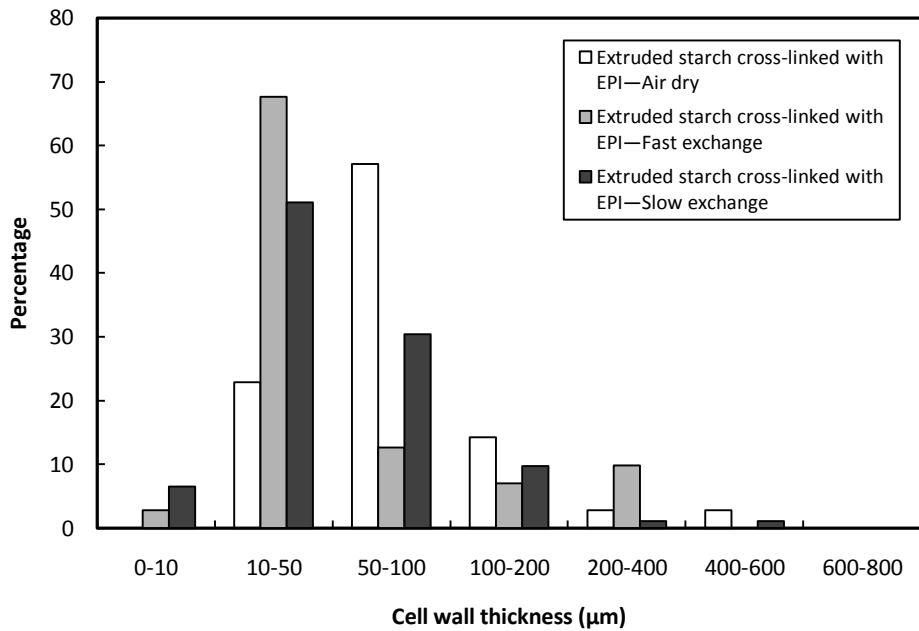


Figure 5: Percent cell wall thickness distribution of extruded cross linked with EPI SMCF prepared by fast and slow exchange with 48 hours exchange time intervals.

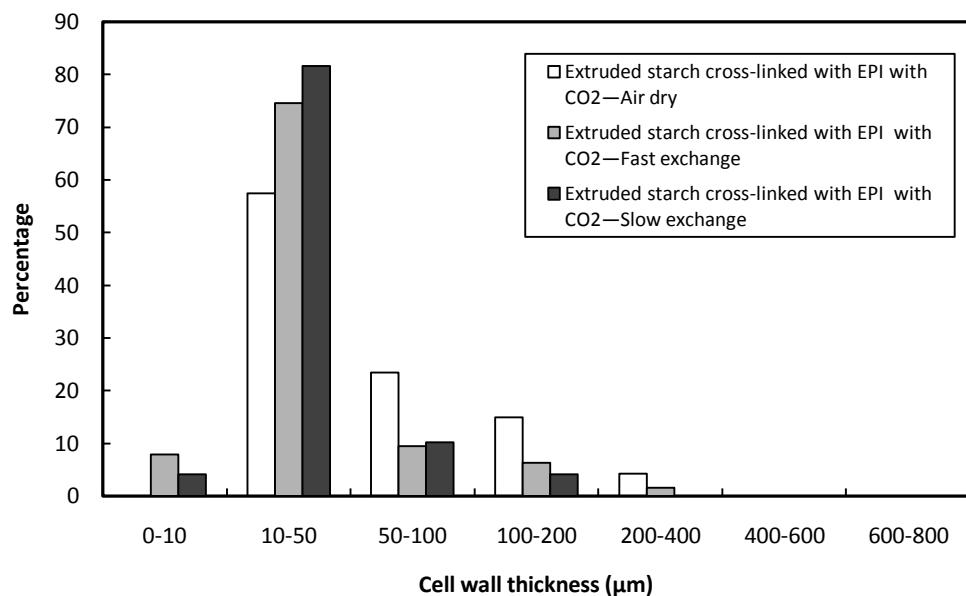


Figure 6: Percent cell wall thickness distribution of extruded cross linked with EPI with  $\text{CO}_2$  SMCF prepared by fast and slow exchange with 48 hours exchange time intervals.

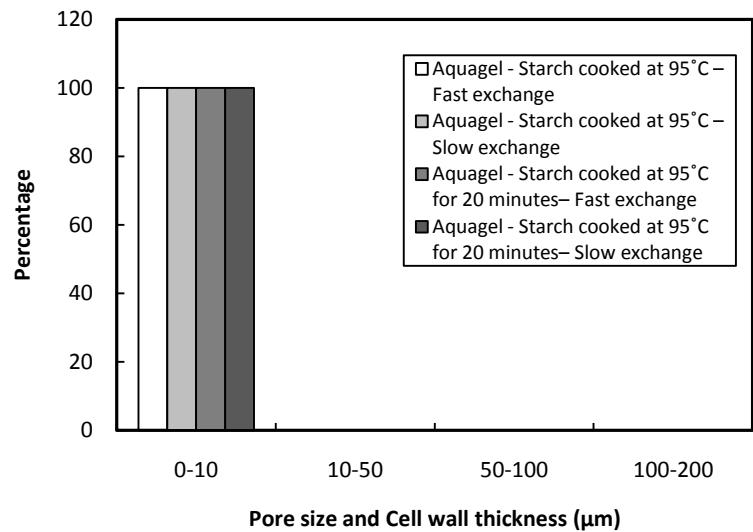


Figure 7: Percent pore size and cell wall thickness distribution of aquagel starch SMCF prepared by fast and slow exchange with 48 hours exchange time intervals.

## Appendix 2-C

SMCF conditioned at 23°C and 50% relative humidity was subjected to TGA, (TGA Q500, TA Instruments) at a heating rate of 10°C/min to 500°C under nitrogen purge 40/60 ml/min of nitrogen in balance and sample flow.

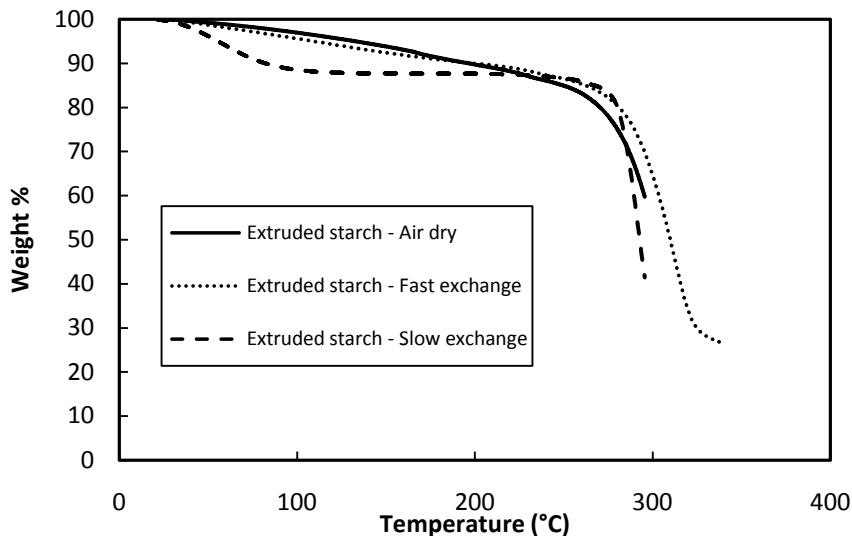


Figure 1: Thermogram (at a heating rate of 10°C/min) of extruded starch samples.

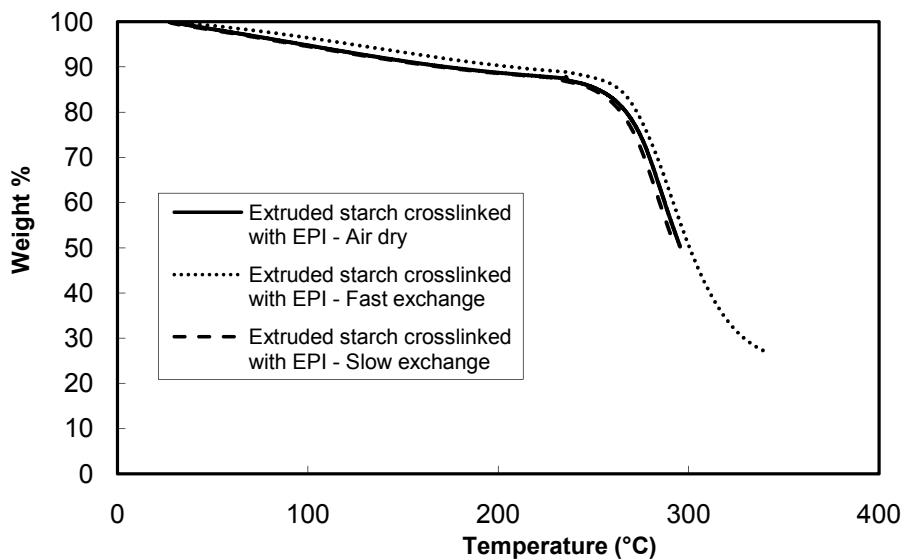


Figure 2: Thermogram (at a heating rate of 10°C/min) of extruded starch crosslinked with EPI samples.

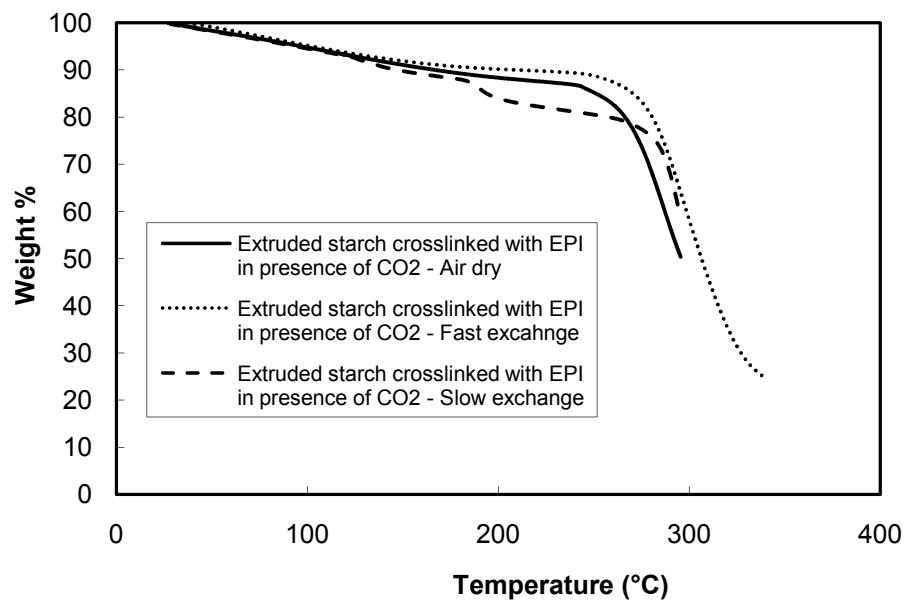


Figure 3: Thermogram (at a heating rate of 10°C/min) of extruded starch crosslinked with EPI in presence of CO<sub>2</sub> samples.

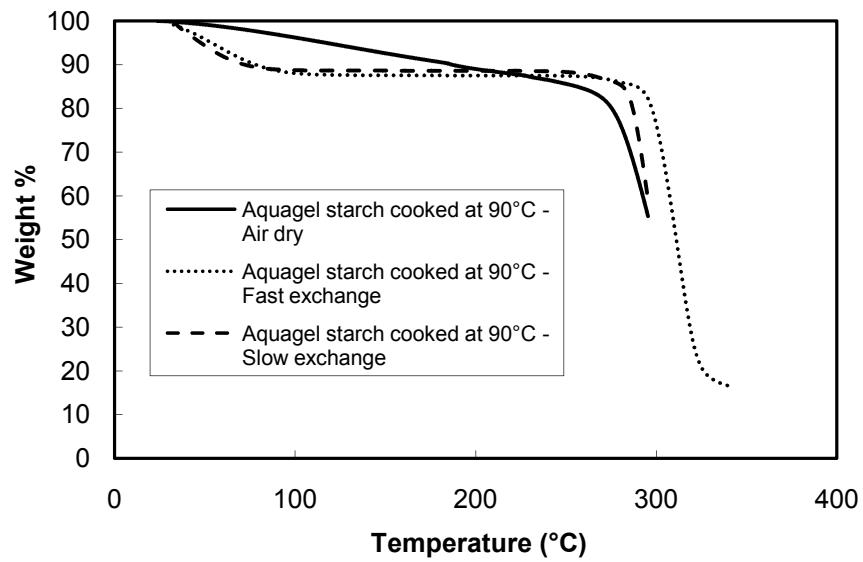


Figure 4: Thermogram (at a heating rate of 10°C/min) of Aquagel starch cooked at 90°C samples.

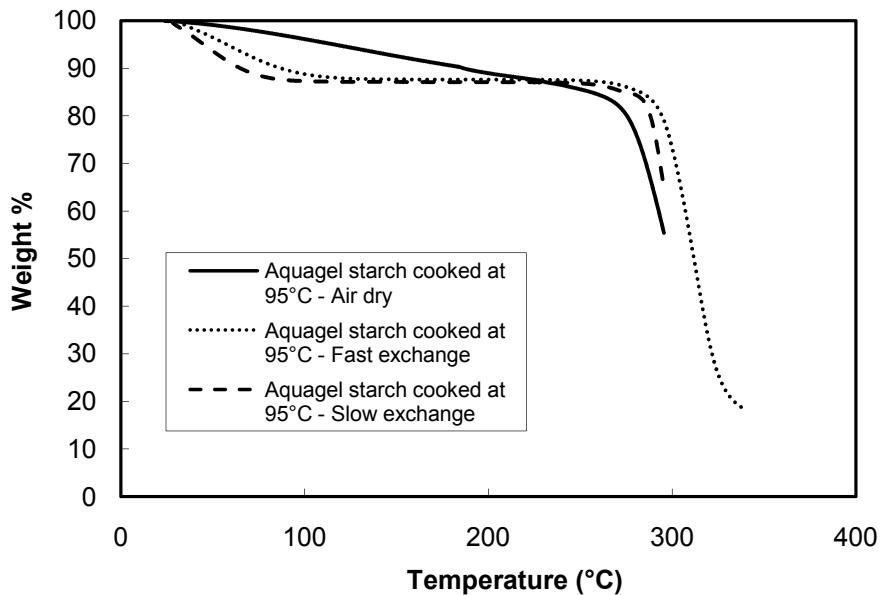


Figure 5: Thermogram (at a heating rate of 10°C/min) of Aquagel starch cooked at 95°C samples.

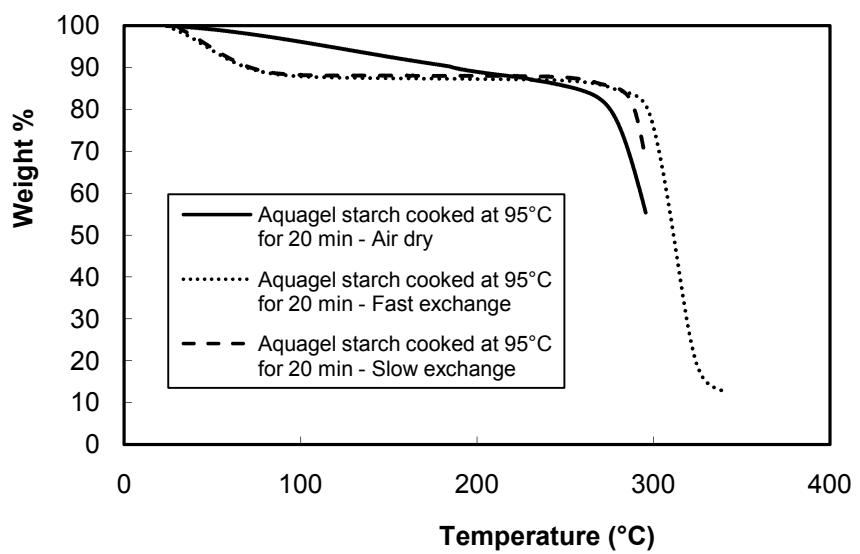


Figure 6: Thermogram (at a heating rate of 10°C/min) of Aquagel starch cooked at 95°C for 20 minutes samples.

## Appendix 2-D

Contact angle measurements were performed with a NRL Contact Angle Goniometer by Rame Hart Inc. (model 100-00) and with Dynamic Contact Angle measurement (Phoenix 300) instrument. A drop of deionized water was placed on the surface of the sample and the contact angle was then monitored every minute for four minutes.

Table 1: Contact angle between a water droplet and the surface of the sample by Dynamic Contact Angle (DCA). Note that contact angle by DCA was measured on the cross section of the extruded starch samples whereas contact angle by Goniometer was measured on the surface of the samples.

Sample	Contact angle by DCA					Contact angle by Goniometer				
	0 min	1 min	2 min	3 min	4 min	0 min	1 min	2 min	3 min	4 min
Extruded starch crosslinked with EPI + CO <sub>2</sub> - Air dry	57.5	53.5	53	52	51.5	72	71	71	71	71
Extruded starch crosslinked with EPI + CO <sub>2</sub> - Fast exchange	83.5	81.5	79	77	76	71	70	69	69	68
Extruded starch crosslinked with EPI + CO <sub>2</sub> - Slow exchange	92	87	86.5	84	73	72	72	70	70	69
Extruded starch crosslinked with EPI - Air dry	43	41	39	33	31	60	58	58	57	57
Extruded starch crosslinked with EPI - Fast exchange	55	40	34.5	32.5	30	63	63	61	60	60
Extruded starch crosslinked with EPI - Slow exchange	45	34	29.5	29	28	82	80	80	80	80
Extruded starch- Air dry	43	41	39	33	31	51	48	45	45	45
Extruded starch- Fast exchange	33	32	27.5	24	22.5	46	45	44	36	35
Extruded starch- Slow exchange	47	45.5	38.5	38.5	36.5	31	17	0	0	0

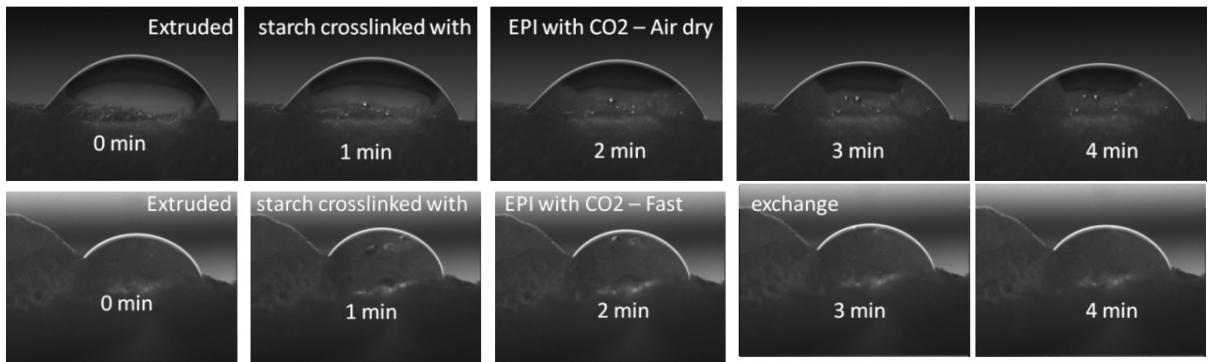


Figure 1: DCA images of extruded starch crosslinked with EPI with CO<sub>2</sub> air dried and fast exchanges samples.

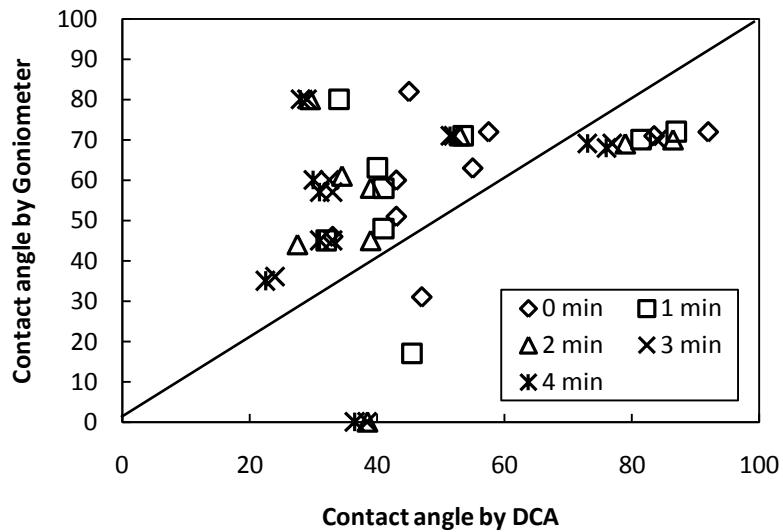


Figure 2: Correlation between the contact angle measurement by Dynamic Contact Angle (DCA) and Goniometer

## Appendix 2-E

Correlation of water swelling (g of water/g of sample) and % mass loss of extruded and aquagel starch samples by in contact with water and forced immersion of samples to water. The water contact was done in two modes, one in which the foam was allowed to float or sink (in contact with water) and a second mode in which the foam was forced to be immersed completely under the water surface (forced immersion) for all samples.

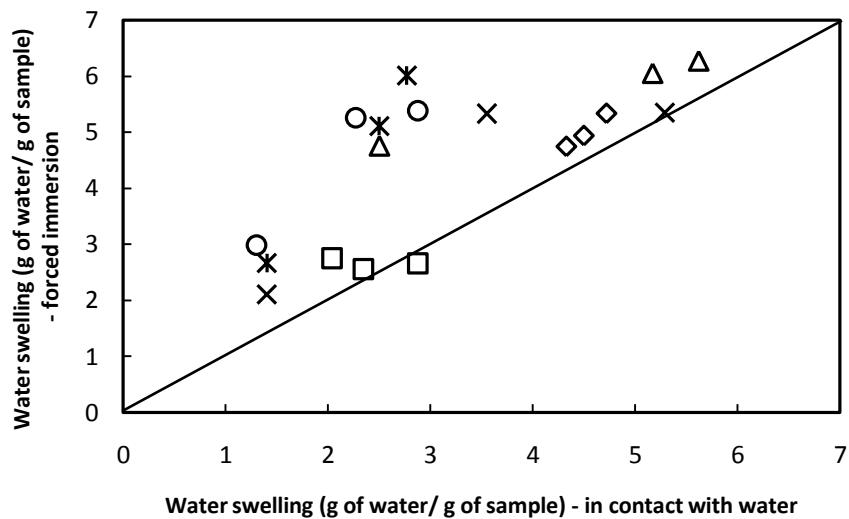


Figure 1: Correlation of water swelling by in contact with water and forced immersion of samples to water

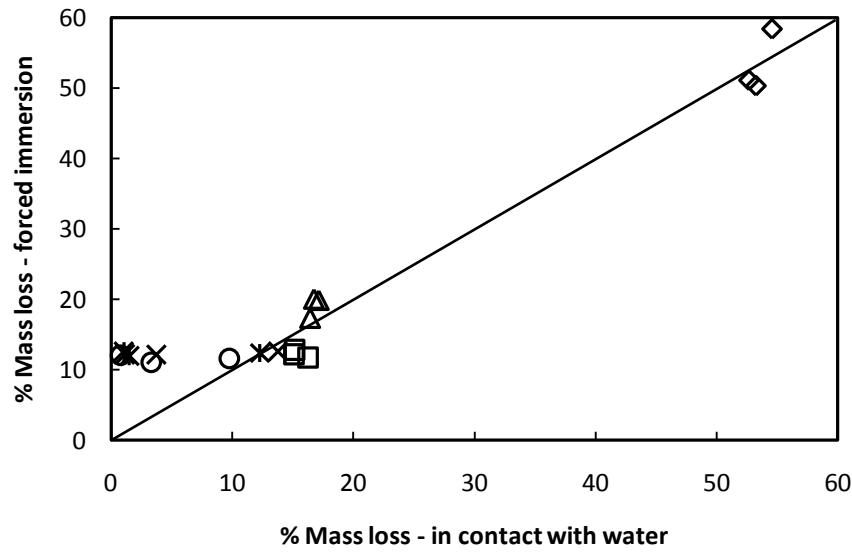


Figure 2: Correlation of % mass loss of in contact with water and forced immersion of samples to water

### Appendix 3-A

Water swelling (g of water/g of sample), mass loss (%), and density (g/cc) of starch, starch blended with 1% AKD, starch bended with 1% Kymene, and starch blended with 1% AKD and 1% Kymene cured and uncured samples prepared with NaOH to adjust pH of starch solution. Note that in Chapter 3, the pH was adjusted using sodium bicarbonate. The results are similar for the two methods of adjusting pH.

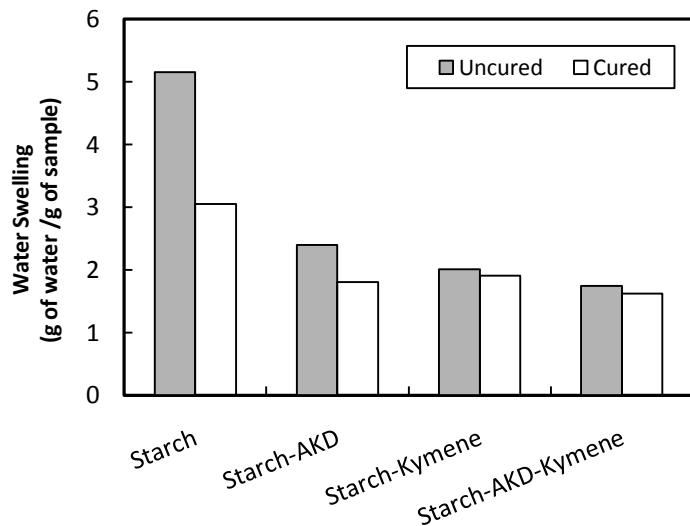


Figure 1: Water swelling (g of water/g of sample) of starch blended with 1% AKD and/or 1% Kymene samples after in contact of water for 24 hrs. Note in general decrease in water swelling of starch materials with AKD and Kymene.

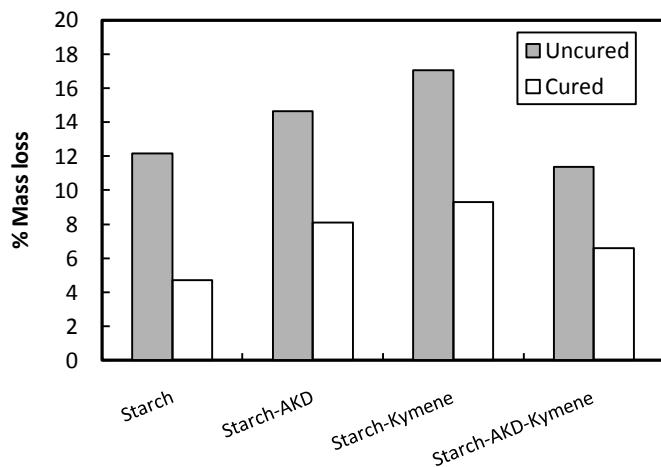


Figure 2: Percent mass loss of starch blended with 1% AKD and/or 1% Kymene samples after in contact of water for 24 hours. Note that there was difference in mass loss of cured and uncured samples. Not a forced immersion test.

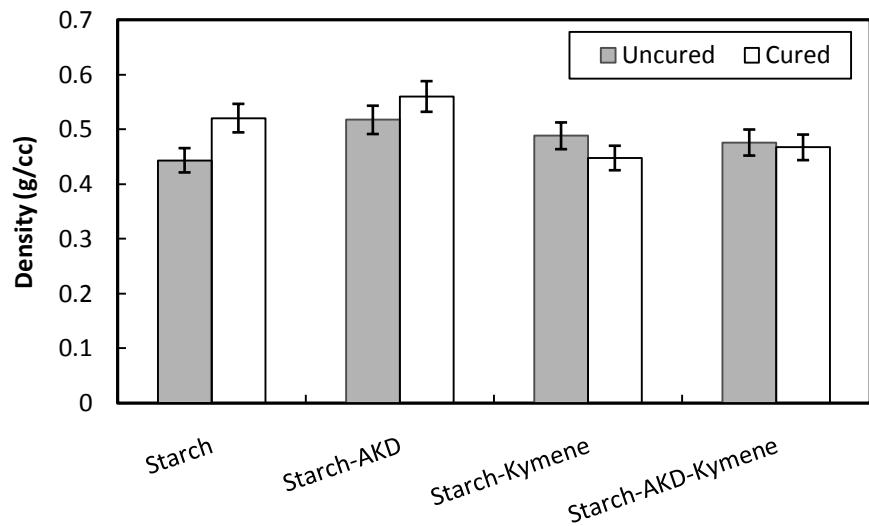


Figure 3: Density of SMCFs prepared from starch, and starch blended with 1% AKD and/ or 1% Kymene with and without curing.

## Appendix 3-B

Contact angle measurements were performed with a NRL Contact Angle Goniometer by Rame Hart Inc. (model 100-00) and with Dynamic Contact Angle measurement (Phoenix 300) instrument. A drop of deionized water was placed on the surface of the sample and the contact angle was then monitored every minute for four minutes.

Table 1: Contact angle between the water droplet and the surface of the sample by Dynamic Contact Angle (DCA).

Sample	Contact angle by DCA					Contact angle by Goniometer				
	0 min	1 min	2 min	3 min	4 min	0 min	1 min	2 min	3 min	4 min
Starch + 1% AKD Uncured	85	80.5	79.5	78	78	96.5	95	94.5	93	92.5
Starch + 1% AKD Cured	98.5	98.5	97.5	97	96.5	93	91.5	91.5	91	91
Starch + 1.5% AKD Uncured	80.5	76.5	74.5	73.5	72.5	96	95	95	94	94
Starch + 1.5% AKD Cured	82	81	80.5	79.5	79	97.5	97	97	97	97
Starch + 2% AKD Uncured	65.5	64	62	60.5	60	102.5	100.	96.5	96	96
Starch + 2% AKD Cured	90	89	88.5	88	88	102	98.5	98.5	98.5	98
Starch + 2.5% AKD Uncured	85.5	83.5	83.5	83.5	82.5	94	93	92	92	91
Starch + 2.5% AKD Cured	101	100	99.5	98.5	98.5	95	95	95	95	95
Starch + 3% AKD Uncured	73	70	68.5	67.5	67	90	90	89	88	88
Starch + 3% AKD Cured	80.5	75	75	72.5	72.5	87.5	87.5	87.5	87	87
Starch Uncured	65	59	48.5	48.5	47.5	44	36.5	34.5	25.5	14.5
Starch Cured	46.5	45.5	45	44.5	43.5	51	49	47	41	36.5
Starch + AKD Uncured	79	76.5	75.5	75	74.5	85	85	84.5	84	83.5
Starch + AKD Cured	86	84.5	84	83	83	95	94	94	93	93
Starch + Kymene Uncured	57.5	54.5	48	47.5	45	42.5	33.5	28.5	21.5	21.5
Starch + Kymene Cured	64	62	58	56.5	55	51.5	47.5	45	42.5	42.5
Starch + AKD + Kymene	65.5	64.5	63	62.5	61.5	75	72.5	71.5	70	69
Starch + AKD + Kymene Cured	76	75.5	74	73	72	82	79.5	79.5	78.5	78

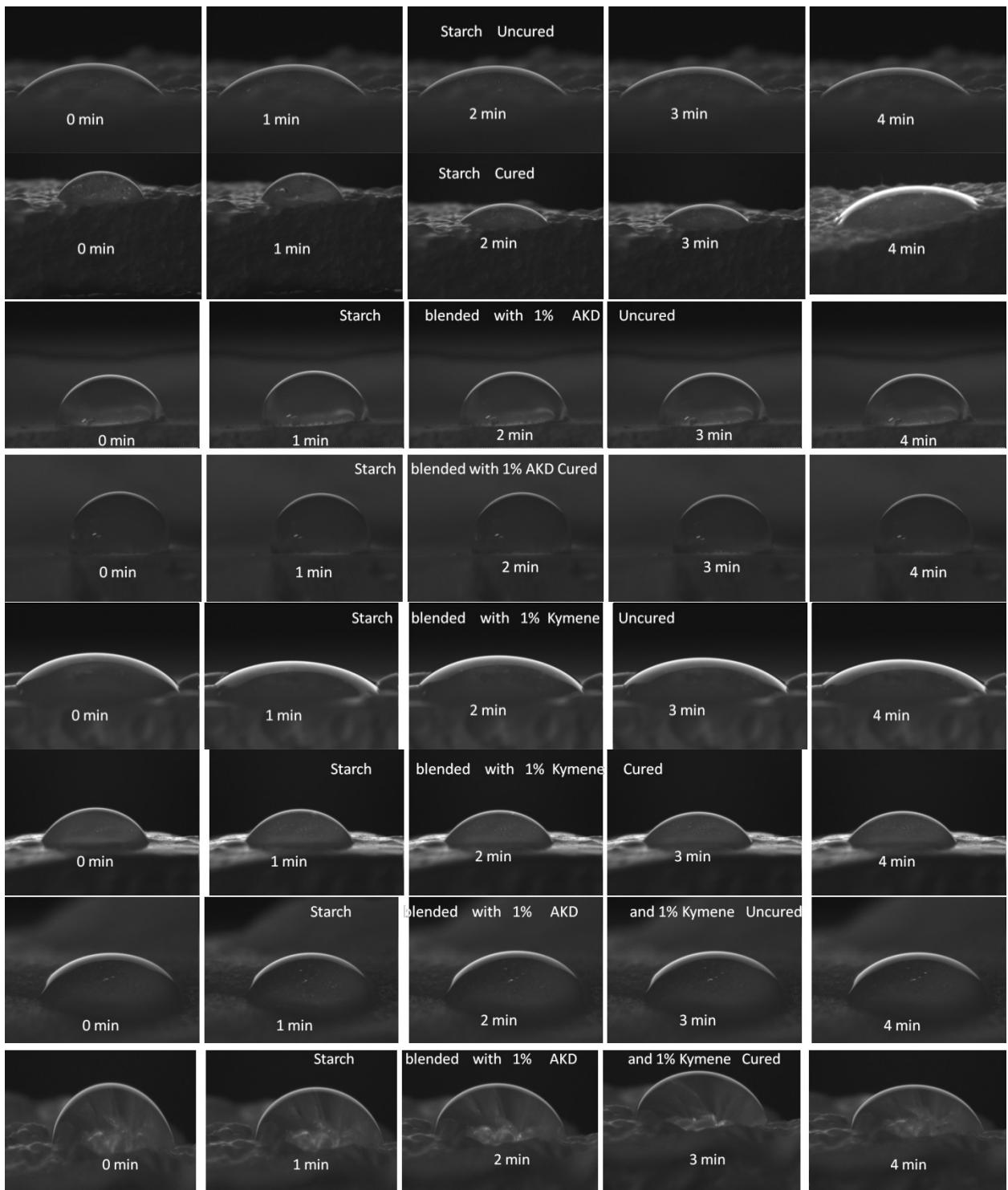


Figure 1: DCA images of Starch, Starch blended with 1% AKD, 1% Kymene and both cured uncured samples.

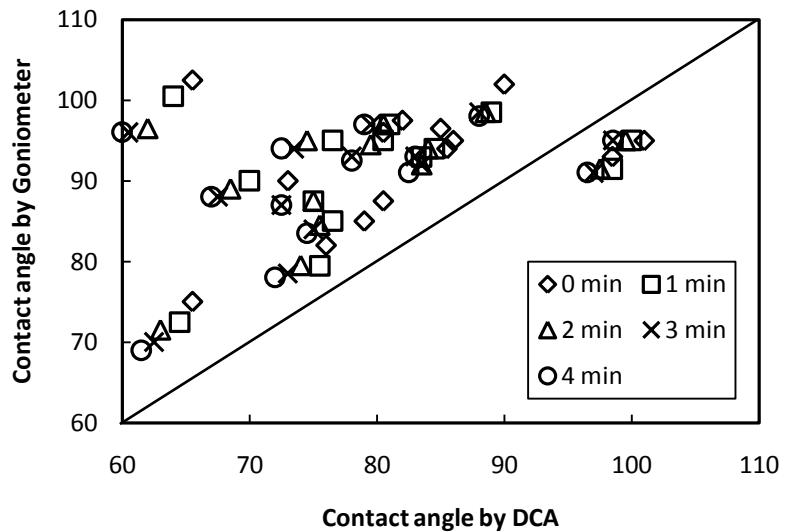


Figure 2: Correlation of contact angle measured by DCA and Goniometer on starch blended with AKD and/or Kymene samples (data shown in table 1).

### Appendix 3-C

SEM images of SMCF materials prepared with different exchange time intervals. Morphological characterization of starch microcellular foam was performed on images captured by a scanning electron microscope (SEM), Hitachi s3200-N by using image analysis software (Revolution Software, 4pi Analysis, Inc.).

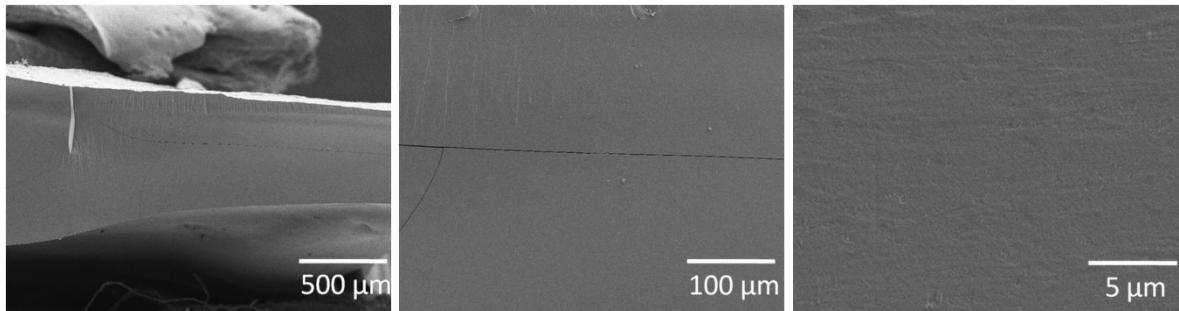


Figure 1: SEM images of SMCF material prepared by fast exchange with 1.5 hours exchange time interval.

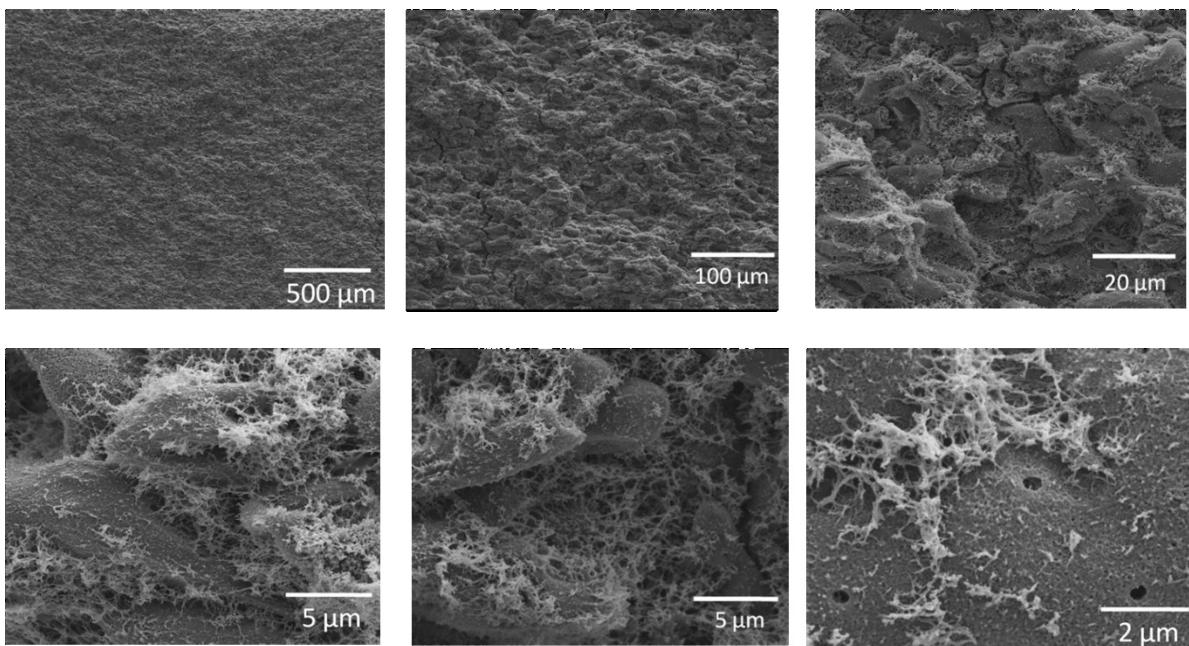


Figure 2: SEM images of SMCF material prepared by fast exchange with 6 hours exchange time interval.

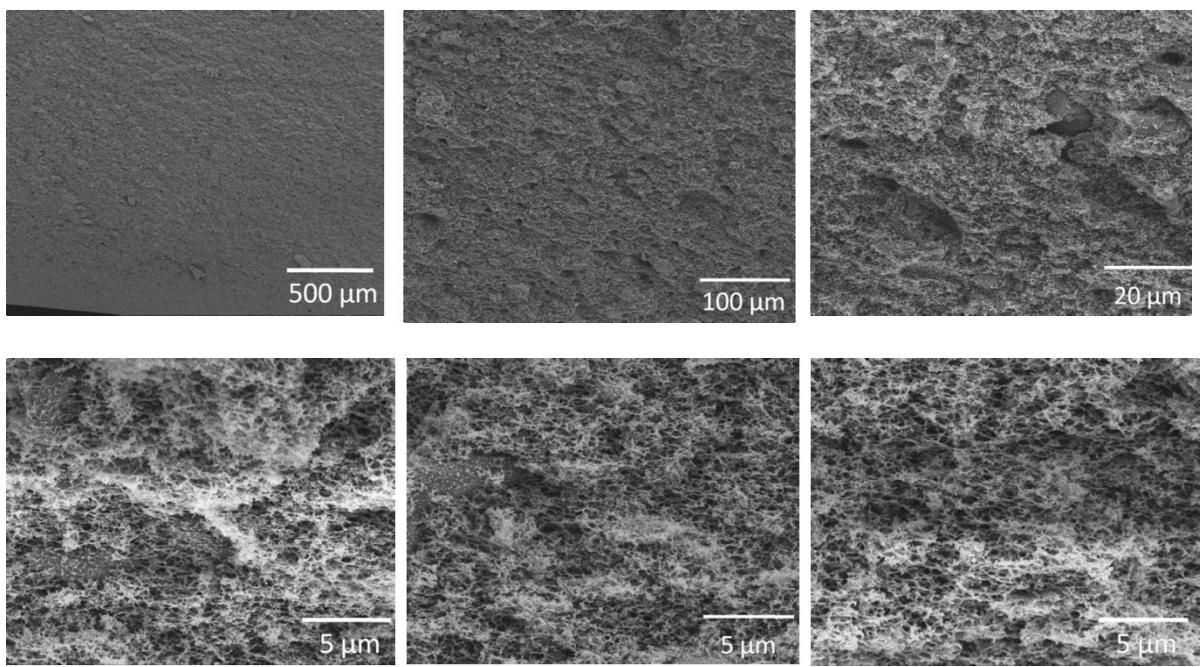


Figure 3: SEM images of SMCF material prepared by fast exchange with 24 hours exchange time interval.

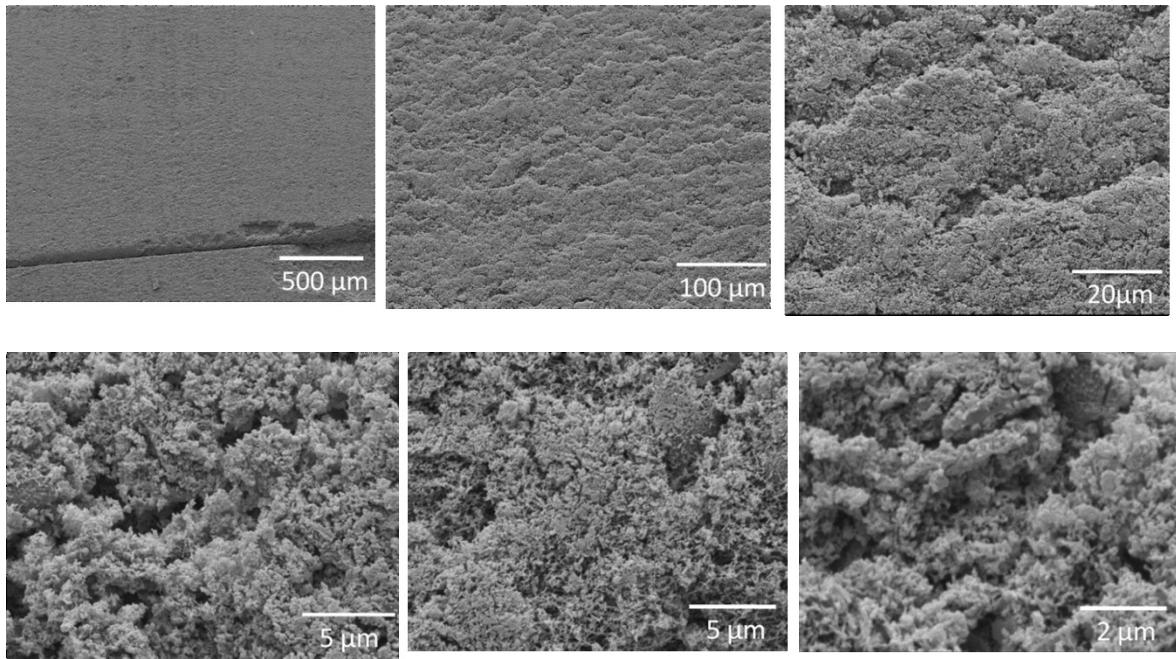


Figure 4: SEM images of SMCF material prepared by slow exchange with 6 hours exchange time interval.

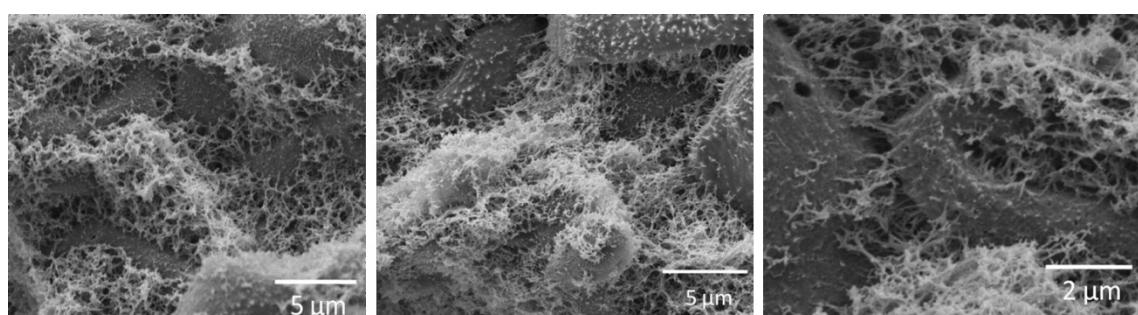
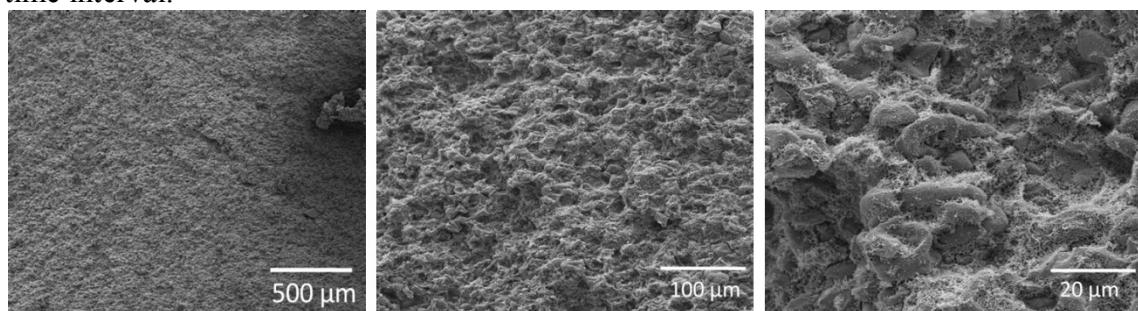


Figure 5: SEM images of SMCF material prepared by slow exchange with 24 hours exchange time interval.

### Appendix 3-D

Pore size (%) and cell wall thickness (%) distribution for SMCF materials prepared by fast and slow exchanges with different exchange time intervals. Morphological characterization of starch microcellular foam was performed on images captured by a scanning electron microscope (SEM), Hitachi s3200-N by using image analysis software (Revolution Software, 4pi Analysis, Inc.). Random areas of the samples were taken and all of the pores (more than 30 pores were measured for each sample) in the area were measured.

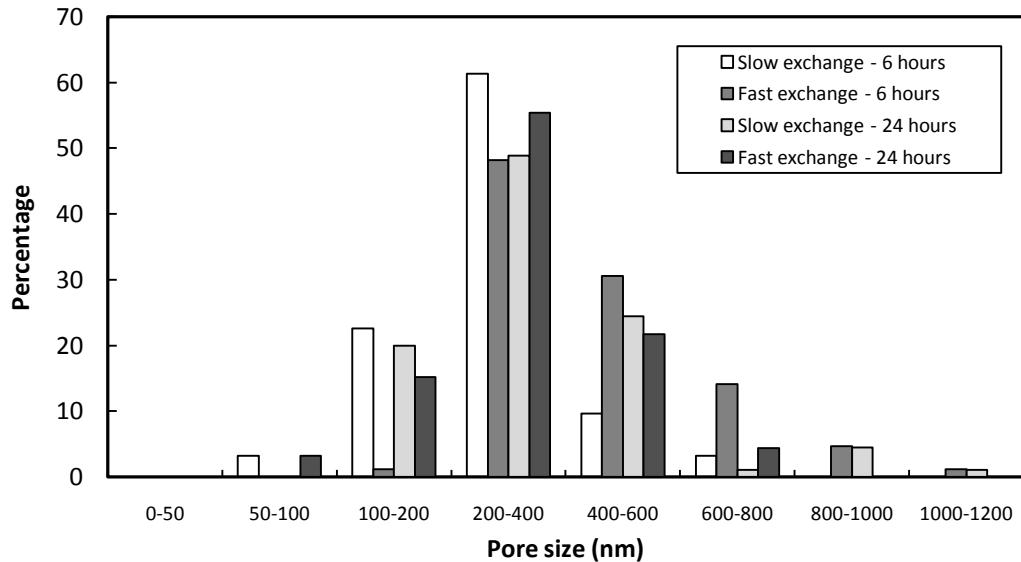


Figure 1: Percent pore distribution of SMCF prepared by fast and slow exchange with 6 and 24 hours exchange time intervals.

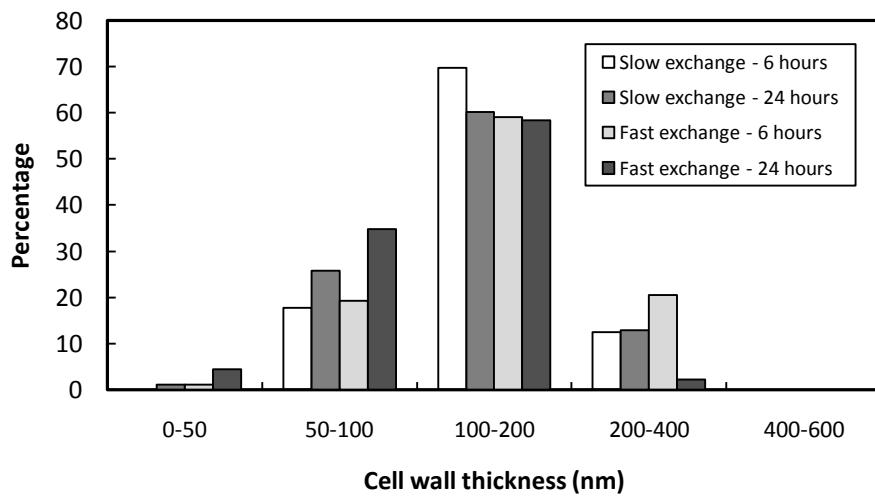


Figure 2: Percent cell wall thickness distribution of SMCF prepared by fast and slow exchange with 6 and 24 exchange time intervals.

### Appendix 3-E

SEM images of SMCF materials prepared from starch blended with 1% AKD and/or 1% Kymene with 12 hour exchange time intervals. Morphological characterization of starch microcellular foam was performed on images captured by a scanning electron microscope (SEM), Hitachi s3200-N by using image analysis software (Revolution Software, 4pi Analysis, Inc.).

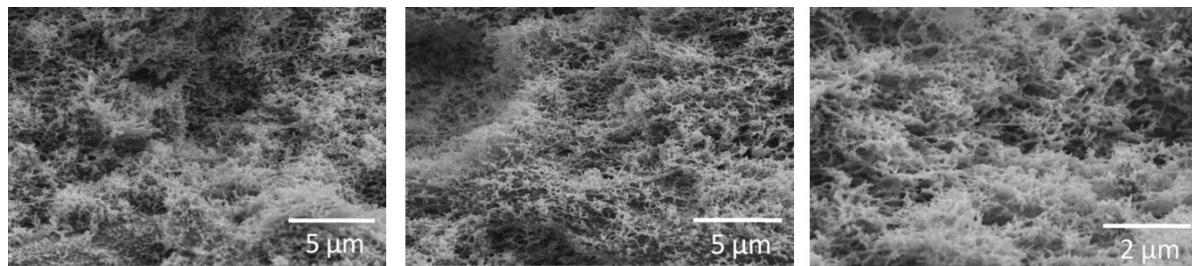


Figure 1: SEM images of starch uncured SMCF material prepared by fast exchange with 12 hours exchange time interval.

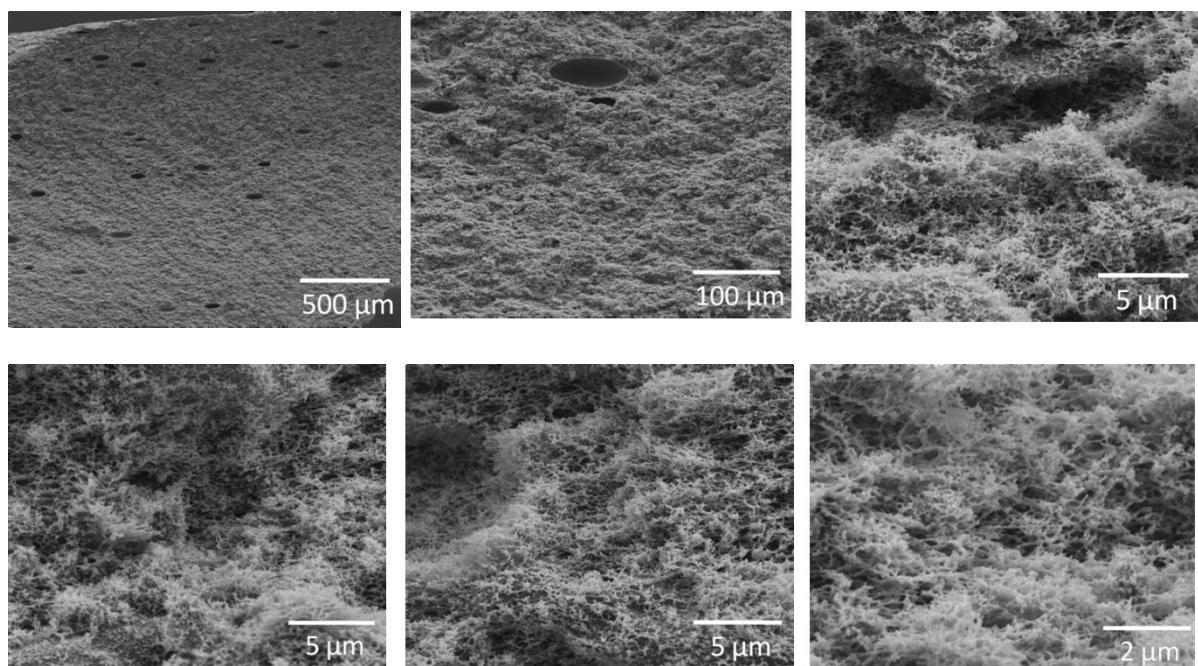


Figure 2: SEM images of starch cured SMCF material prepared by fast exchange with 12 hours exchange time interval.

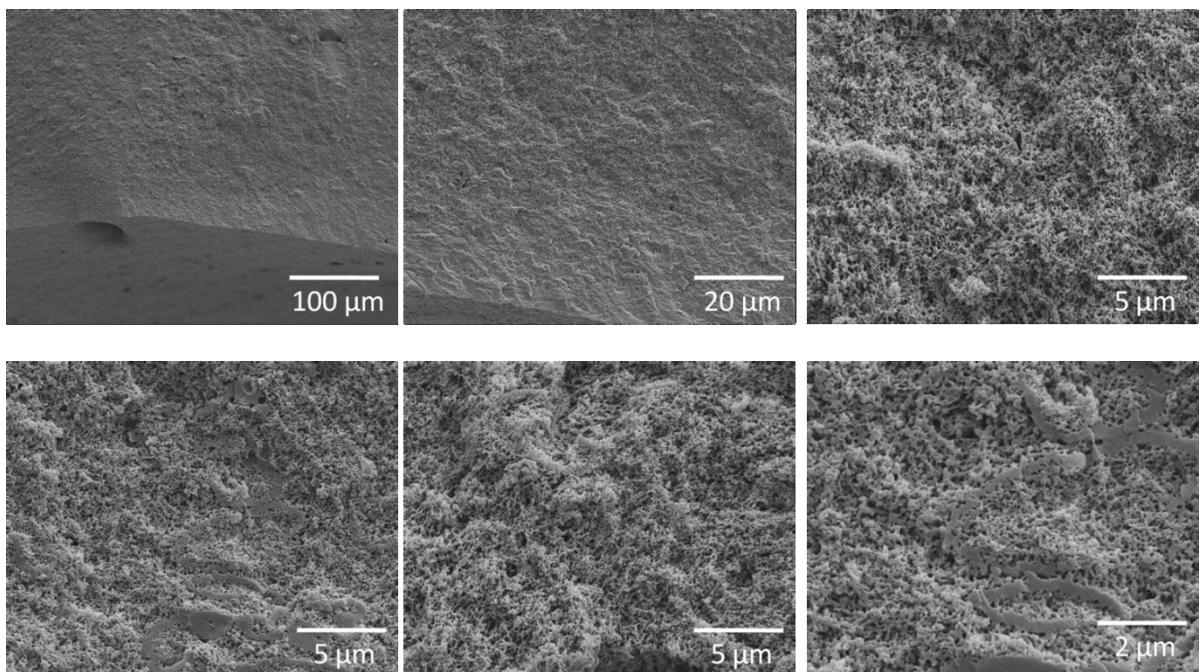


Figure 3: SEM images of starch-1%AKD uncured SMCF material prepared by fast exchange with 12 hours exchange time interval.

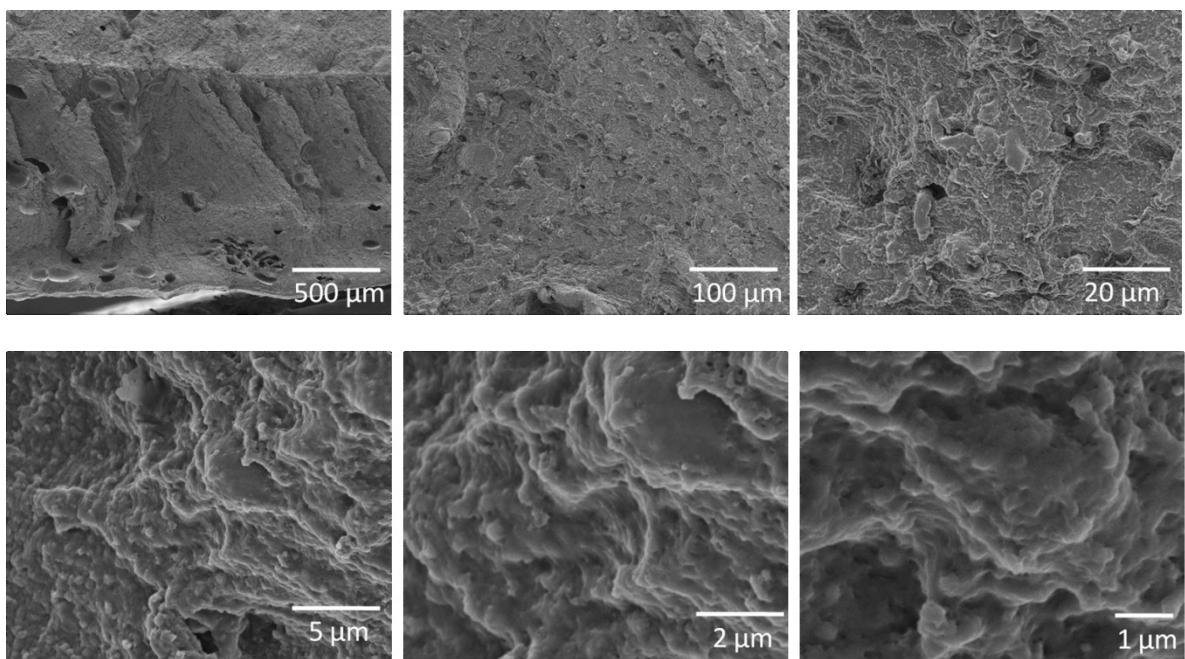


Figure 4: SEM images of starch-1%AKD cured SMCF material prepared by fast exchange with 12 hours exchange time interval.

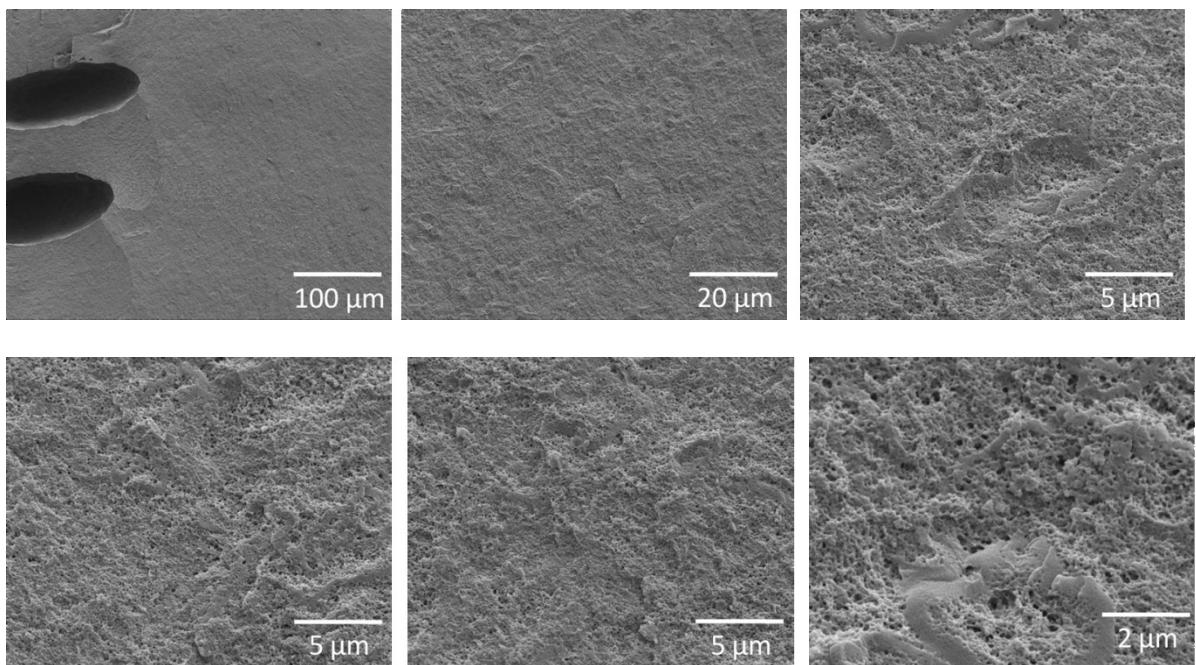


Figure 5: SEM images of starch-1% Kymene uncured SMCF material prepared by fast exchange with 12 hours exchange time interval.

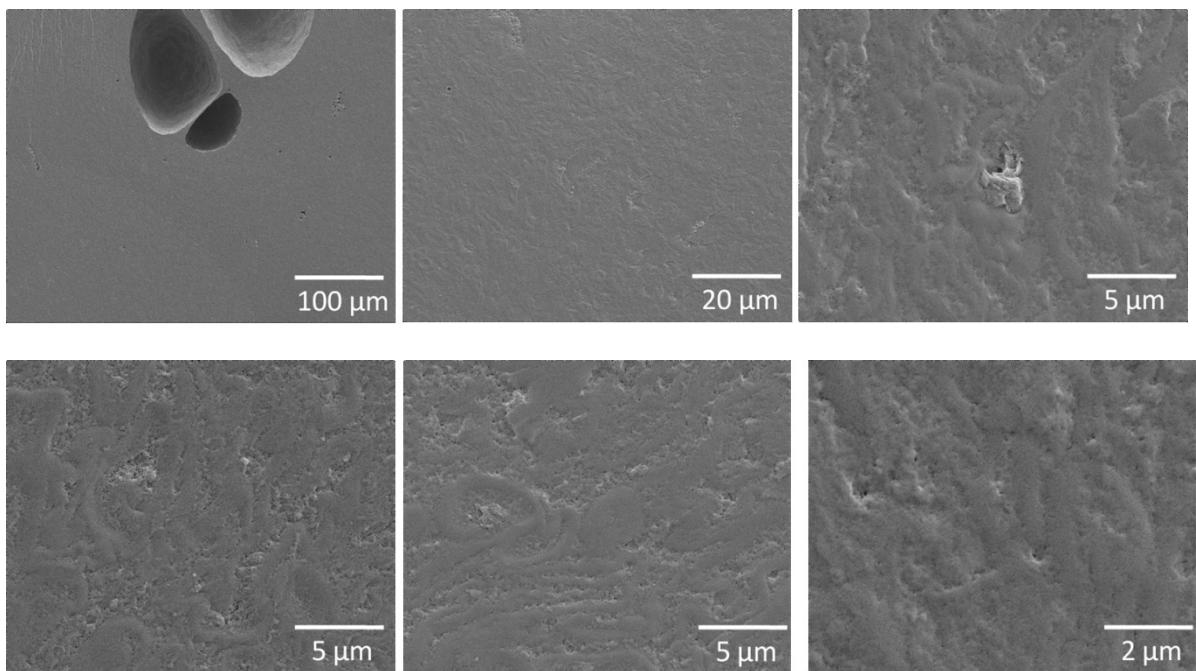


Figure 6: SEM images of starch-1% Kymene cured SMCF material prepared by fast exchange with 12 hours exchange time interval.

### Appendix 3-F

Pore size (%) and cell wall thickness (%) distribution for starch blended with 1% AKD and 1% Kymene SMCF materials prepared by fast exchanges with 12 hour exchange time intervals. Morphological characterization of starch microcellular foam was performed on images captured by a scanning electron microscope (SEM), Hitachi s3200-N by using image analysis software (Revolution Software, 4pi Analysis, Inc.). Random areas of the samples were taken and all of the pores (more than 30 pores were measured for each sample) in the area were measured.

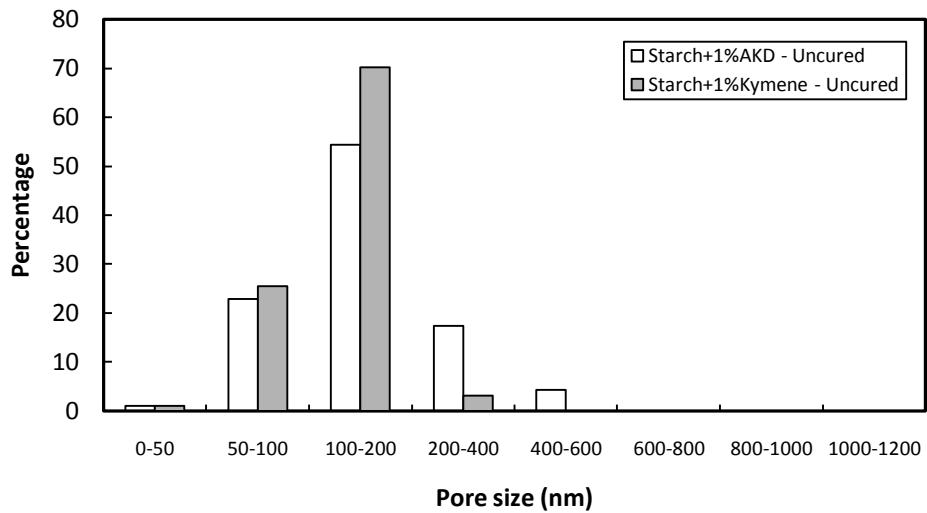


Figure 1: Percent pore distribution of starch blended with 1% AKD and 1% Kymene SMCF prepared by fast exchange with 12 hours exchange time intervals.

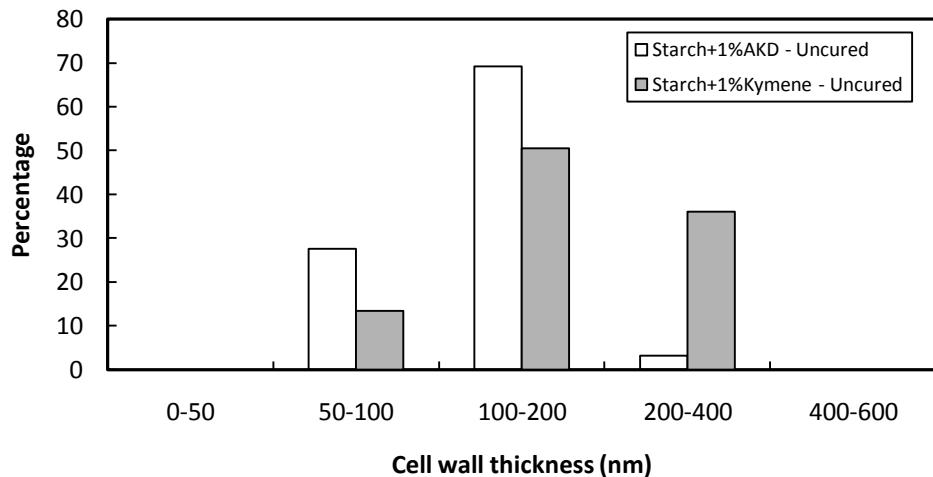


Figure 2: Percent cell wall thickness distribution of blended with 1% AKD and 1% Kymene SMCF prepared by fast 12 hour exchange time intervals.

### Appendix 3-G

Correlation of water swelling (g of water/g of sample) and % mass loss of extruded starch and aquagel starch samples of in contact with water and forced immersion of samples to water (Solid filled legends represent cured samples whereas unfilled legends represent corresponding uncured samples). The water contact was done in two modes, one in which the foam was allowed to float or sink (in contact with water) and a second mode in which the foam was forced to be immersed completely under the water surface (forced immersion) for all samples.

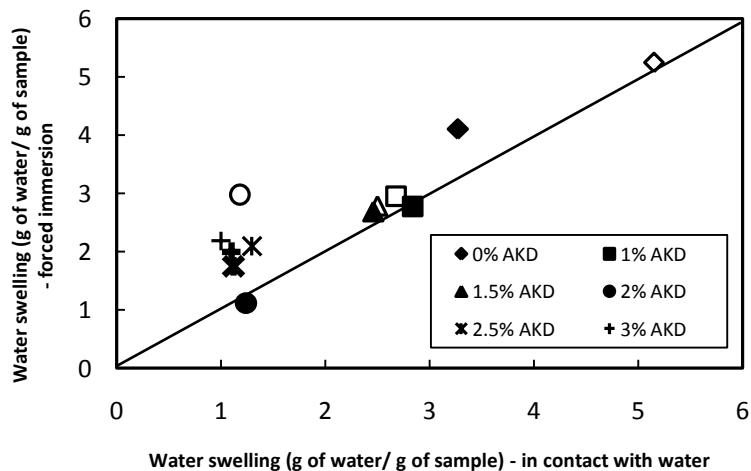


Figure 1: Correlation of water swelling by in contact with water and forced immersion of starch blended with different amount of AKD samples to water

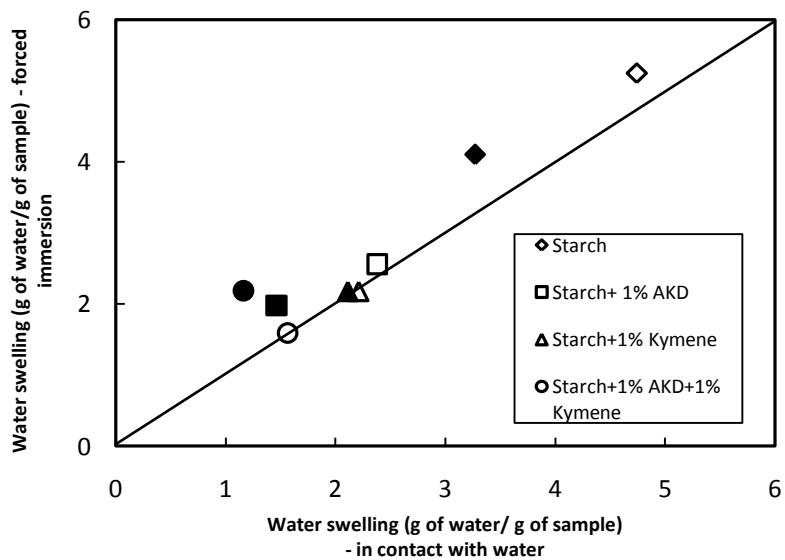


Figure 2: Correlation of water swelling by in contact with water and forced immersion of starch blended with AKD and/or Kymene samples to water

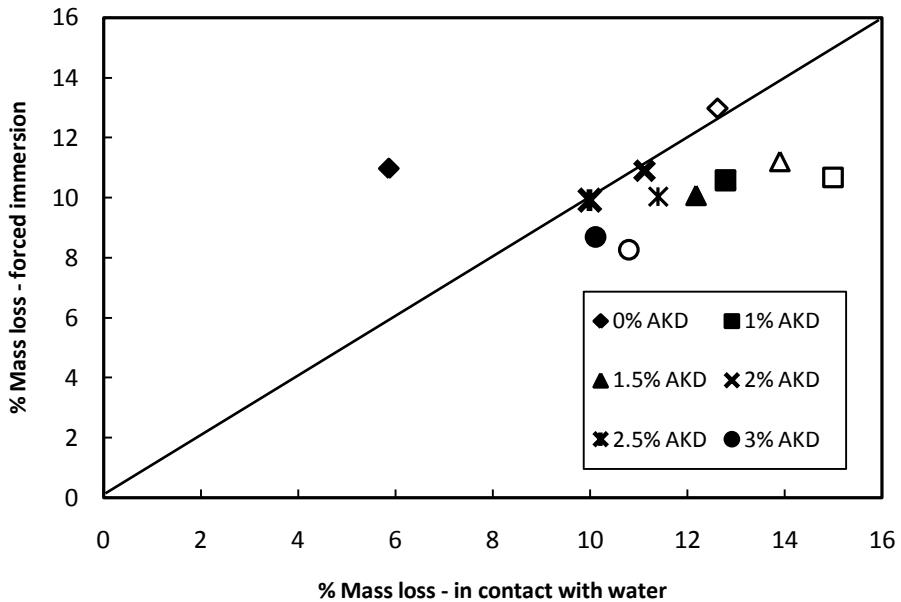


Figure 3: Correlation of % mass loss by in contact with water and forced immersion of starch blended with different amount of AKD samples to water

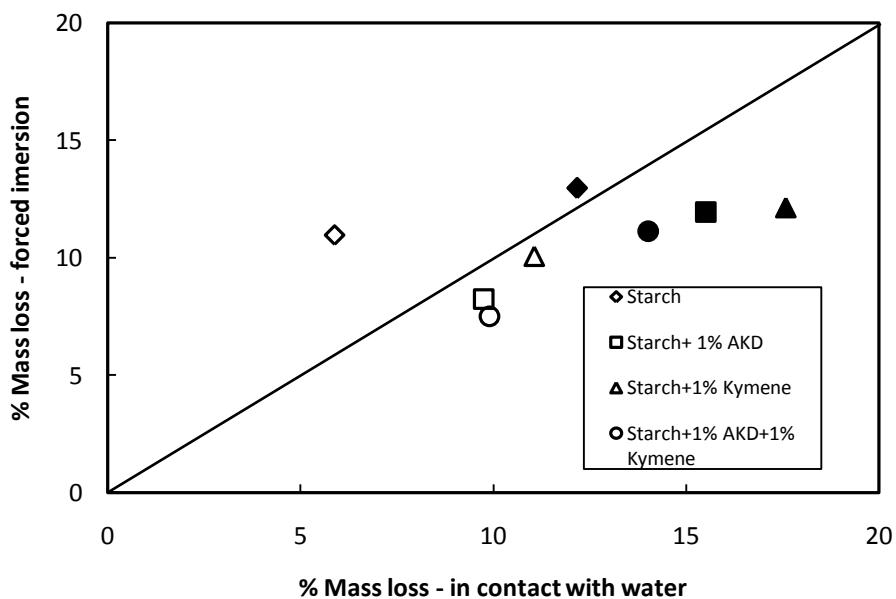


Figure 4: Correlation of % mass loss by in contact with water and forced immersion of starch blended with AKD and/or Kymene samples to water