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Development and characterization of novel starch and alkyl ketene dimer microcellular foam particles

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Abstract

There is interest in replacing inorganic fillers in paper, coatings and plastics with renewable organic fillers to improve the economics, performance and environmental aspects of such products. Starch microcellular foam (SMCF) particles are promising materials in this regard. This research was undertaken to produce SMCF particles and characterize their morphology, optical properties and interaction with water. SMCF particles were produced using corn starch; which was solubilized in water. The foam structure was created by precipitating the starch using ethanol in a solvent exchange technique. The starch was also reacted with alkyl ketene dimer (AKD) wax at different levels in order to understand if the AKD could impart water resistance to the particles. Two methods were used to incorporate AKD: (1) the AKD was coated onto foam particles after foam formation, and (2) the AKD was blended with the starch before foam particle formation. Hexane extraction was used to purify a portion of each of the samples to determine if unreacted AKD existed with the starch matrix. Particles with porous structure and high brightness were developed for all combinations of starch and AKD. The brightness of the particles was significantly higher than that of the uncooked starch, presumably due to the development of a porous structure. For the AKD coated particles a minimum amount of AKD charged was needed to develop a high contact angle, low solubility, and low water retention value, higher levels of AKD in AKD coated particles did not further alter these properties. This indicates that the changes in properties with AKD level with coated particles is a surface phenomena. Starch AKD blends did not show any increased resistance to water relative to the particles with no AKD blended. This is due to the ethanol used in the precipitation process extracting the AKD, which was confirmed by elemental analysis. The particles, even with the 10% AKD coated or blended, lost their porous structure upon rewetting. Further work needs to be performed to more effectively hydrophobize the starch foams with AKD.

Keywords: Starch; Alkyl ketene dimer; AKD; Starch microcellular foam; SMCF; Particles; Solvent exchange; Contact angle; Particle size; Brightness; Moisture content; Solubility; Water retention; Paper; Paint; Coatings

1. Introduction

Starch is one of the most abundant biopolymers, utilized by plants as the major storage material for carbohydrates (Glenn, Miller, & Irving, 1996). Starch is a high molecular weight mixture of two glucose-based polymers, amylose (linear) and amylopectin (branched). Starch-based foams have been prepared for many decades (Shogren, Lawton, Doane, & Tiefenbacher, 1998; Shogren & Bagley, 1999). Through a combination of heat, water and shear the starch–water mixture behaves thermoplastically and can be extruded into shapes. This method has been used to produce cereals and more recently starch-based packing material (Glenn, Orts, & Nobes, 2001; Shogren & Willet, 2001). These types of foams have pore diameters on the order of 1 mm (Glenn et al., 1996) and are considered to be macrocellular foams.

When water and heat are applied to starch granules the granules swell. The amylose material in particular extends from the starch granules and forms a gel in the water phase. If the water is removed in a normal drying process,

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large capillary forces act on the starch and collapse the foam structure. In order to preserve the porous structure, several methods have been used, freeze drying and solvent exchange being prominent among these (Glenn, Gregory, & Irving, 1995, 1996, 2002). Solvent exchange involves the replacement of the water with another solvent (or sometimes a succession of solvents) of lower surface tension. Final drying from the solvent with low surface tension, e.g., liquid or critical CO_2 or ethanol, avoids the large compressive forces caused by the drying of high surface tension water and develops a microcellular foam structure. The micro-structure of the bulk region of starch microcellular foam (SMCF) sheets formed from wheat starch dried from ethanol consisted of a network of strands of amylose forming irregular pores generally less than 2 μm in diameter (Glenn et al., 2002). The surface of the sheets was observed to be not as porous as the bulk. This is very interesting for coating applications in which a smooth non-porous surface may be advantageous. The specific surface area of SMCF sheets dried from critical point CO_2 were found to be 116, 50 and 145 m^2/g for unmodified wheat starch, unmodified corn starch and high amylose corn starch (Glenn et al., 1995). This specific surface area compares favorably with the specific surface areas of common inorganic fillers used to opacify coatings: kaolin clay (5–8 m^2/g), calcinated clay (16–17), calcium carbonate (2–6), silicates (40–130), and titanium dioxide (8–25) (Eklund & Lindstrom, 1991a). The dimensions of SMCF sheets and the average pore size could be manipulated by mechanically pressing the sheets, at pressures from 1.4 to 69 MPa (Glenn et al., 2002). Extrusion of starch based foams with supercritical carbon dioxide and water has also been demonstrated to produce pores, although these pores are significantly larger than those from solvent extraction (Alavi, Gogoi, Khan, Bowman, & Rizvi, 1999; Rizvi, Mulvaney, & Sokhey, 1995).

Krogerus (1999) explored the possibly of using dispersed (unsolubilized starch) and crosslinked granular starch as an organic filler. It was 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. However, the starch fillers had inferior optical properties when compared to inorganic fillers.

A Finish research consortium (Varjos et al., 2004) has explored the use of foamed starch derivatives as paper filler and as a pigment for paper coatings. This group has used mainly starch acetate with a degree of substitution of around 2.8. To prepare particles, starch acetate was dissolved in a homogenous blend of organic solvent and water and then particles were precipitated by the addition of an excess of water or organic solvent. Several structures could be formed including spherical particles and coral-like structures. Paper coatings with these particles show potential to provide good surface properties (Saari et al., 2005). It was shown that the strength properties of paper filled within the bulk with these starch based particles is improved relative to paper filled with inorganic fillers. The same group has shown that aqueous starch acetate dispersion could be used as a novel coating material for controlled release products (Tarvainen et al., 2004). These materials are relatively expensive and their cost prohibits them from being used practically as a bulk paper filler.

Another pertinent approach to the use of insolubilized starch in paper has been to coat inorganic filler particles with a fatty acid–starch complex (Yoon & Deng, 2006). The starch-filler composite was prepared by cooking starch in water in the presence of clay particles followed by the addition of palmitic acid at a pH of 11. Decreasing the pH to 5 caused a precipitate of the fatty acid–starch complex, coating the clay. Paper filled with the clay–starch composite showed significantly improved tensile strength and brightness relative to paper with unmodified clay.

Recently, in this research group, starch microcellular foam particles from solubilized corn starch crosslinked with glutaraldehyde and precipitated with ethanol were produced with high brightness (ISO brightness of 93%) and high specific surface area using a relatively simple solvent exchange process with ethanol (El-Tahlawy, Venditti, & Pawlak, 2006). The pore structure was found to be enhanced with increased molecular weight of the starch and/or moderate amounts of crosslinking. Increased shear rate during precipitation was also found to improve the structure of the foam particles. However, the particles still had high water affinity and their porous structure was impacted by immersion in water. In this study, the impact of the incorporation of a reactive hydrophobizing agent, alkyl ketene dimer (AKD), on the structure and water interaction of the starch microcellular foam particles (SMCFP) has been determined.

2. Experimental

SMCF particles were produced using cooked corn starch and a reactive alkyl ketene dimer wax (AKD). The foam structure was created using ethanol in a solvent exchange technique. Two methods were used to incorporate AKD: (1) the AKD was coated onto foam particles after formation, and (2) the AKD was mixed with the starch before particle formation. Hexane extraction was used to purify a portion of each of the samples to determine the portion of AKD that was reacted with the starch. The different sample preparation routes are shown schematically in Fig. 1.

2.1. Materials

Corn starch was provided by Cargill, USA (Cargill Gel 03420). Alkyl ketene dimer was supplied by Hercules Inc, Aquapel 364 which is roughly 50% C16 and 50% C18 wax dimer. Ethanol used was anhydrous, Fisher Product Number A405^P-4. Hexane used was *n*-hexane anhydrous, Alfa Aesar Product Number 43263.

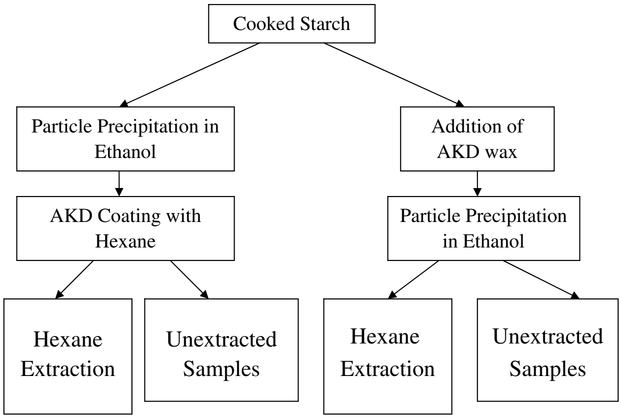

Fig. 1. Different sample preparation procedures to produce microcellular starch foam particles.

2.1.1. Starch cooking procedure

A cooked starch solution was prepared by adding 15 g of corn starch to 50 ml of deionized water adjusted to pH equal 8 with NaOH in a three necked round flask under continuous stirring (IKA-Werk, RW 16 Basic S1) with a crescent shaped paddle. The temperature was increased from room temperature gradually to 90 °C over a time period of about 15 min. The starch was subjected to continuous stirring for another 20 min. The cooked starch was allowed to cool to 50 °C over a period of 60 min.

2.1.2. Starch–AKD blending procedure

A pre-determined amount of AKD wax was added to the starch solution at 50 °C under stirring at the maximum speed (1200 rpm) and allowed to mix and react with the starch for 30 min. The melting point of the AKD is approximately 48 °C. The speed of the stirrer is then set to speed setting 3 (360 rpm) and stirring is continued for 4 h.

2.1.3. Precipitation process

SMCF was produced by a solvent exchange technique. In this process the higher surface tension solvent (water) is replaced with a compatible liquid of lower surface tension (ethanol) which precipitates the starch. The AKD is somewhat soluble in ethanol. Approximately 0.75 g of AKD was found to be soluble in 100 ml of ethanol after mixing at room temperature for 2 h.

The precipitation was carried out by rapidly adding a 50 ml batch of anhydrous ethanol to the cooked starch solution (30% starch, 50 ml of water) in the presence of stirring (IKA-Werk, RW 16 Basic S1, speed setting of 10, 1200 rpm). Upon introduction of the ethanol a cloudy phase with the starch and a clear phase without starch appear. The clear phase is discarded and a fresh 100 ml batch of ethanol is introduced. Stirring at setting 10 occurs for 30 min. The sample is then filtered using filter paper (Fisher Scientific, P2) in a Buchner funnel with house vacuum.

The precipitate is transferred back to the three necked flask and ethanol is again added (100 ml) with stirring, stirred for 60 min, and then filtered again. This was repeated one more time for 30 min. The precipitated SMCF was filtered on filter paper under house vacuum for 30 min. The SMCF is allowed to dry at ambient conditions overnight.

2.2. Starch–AKD coating procedure

Some samples of starch particles were coated with AKD after the precipitation process. In this case, 5 ml of a AKD–hexane solution were added to 2 g of the dried particles in a small glass Petri dish (60 × 15 mm, Pyrex Dish). The samples were then put in a convection oven at 105 °C for 2 h, evaporating the hexane.

2.3. Hexane extraction procedure

Both types of samples, AKD blends and AKD coated, were split in half and a portion of the sample was extracted with *n*-hexane. The AKD is soluble in *n*-hexane. The particles (2 g for coated and 6 g for blends) were placed in a 150 ml glass beaker with a magnetic stirrer and 100 ml of fresh hexane. The suspension was stirred for 10 min and the stirrer was stopped, allowing the particles to settle. The liquid portion was decanted. The hexane extraction process was repeated twice more with 100 ml of fresh hexane with 5 min stirring for each step. Finally, the particles were filtered on filter paper under house vacuum for 1 h before storing in a plastic Petri dish.

2.4. Starch films

For AKD–starch blends, a cooked solution of starch was manually spread on a glass microscope slide with a glass rod and then allowed to dry for 20 min in ambient conditions and immersed in a flask of 100 ml of ethanol for 5 min. Then the samples were allowed to dry for another 20 min under ambient conditions. For hexane extracted slides, the samples were submerged in a beaker with 100 ml of hexane for 5 min and then air dried.

For AKD–starch coated samples the cooked starch solution with no AKD was spread on the slides with a glass rod and after 20 min of air drying put in ethanol for 5 min and then allowed to air dry. A hexane–AKD solution of known AKD concentration was poured over the slide and allowed to evaporate in an oven for 5 min at 105 °C. For hexane extracted slides, the samples were submerged in a beaker with 100 ml of hexane for 5 min and then air dried.

2.5. Characterization of SMCF

Morphological characterization of starch microcellular foams was performed on images acquired using a scanning electron microscope (SEM), Hitachi S-3200 N. The samples were coated with gold–palladium of 10 nm thickness to make the samples conductive.

The moisture content of the SMCF was determined by exposing the samples to 50% relative humidity at 23 °C, weighing, and then drying in an oven at 105 °C overnight and then weighing again.

The ISO brightness of the SMCF (powder) was measured using a Technidyne Color Touch (Model ISO).

Particle sizes of the SMCF were determined by taking photomicrograph pictures with a Power HAD DXC-970 MD 3CCD color video camera connected to an Olympus BH_2-UMA microscope. Image-Pro plus software was used to measure particle sizes. Three images of random areas of a powder sample spread onto a microscope slide were taken and the average diameter of approximately 50 particles were measured in each image.

A measure of the water holding capacity of the particles was made. An approximately 0.5 g amount of particles was added to a type C glass fritted funnel that was previously washed with water and acetone, oven dried and preweighed. The funnel and starch weight was recorded. Then 5 ml of deionized water was added and allowed to soak for 30 min. Then house vacuum was applied for 1 min and the sample weighed. The sample was then dried in the oven at 105 °C for 2 h and then weighed again. The water retention value was calculated as the weight of water in the sample after the vacuum divided by the oven dried weight of the starch. The soluble portion of the starch was calculated as:

$$\%\text{Solubilized} = \left(\frac{\%K \times \text{Initial AD Starch} - \text{Final OD Starch}}{\%K \times \text{Initial AD Starch}}\right)100\%$$

where $\%K$ is the solids content in percent of the air dried starch.

Contact angle measurements on starch films were performed using a NRL Contact Angle Goniometer by Rame Hart Inc. (Model 100-00). A small drop of deionized water was placed on the surface of the coating and the contact angle on two sides of the drop measured immediately and averaged. Three drops were measured for each sample. For the AKD coated film sample, a relative weight % of AKD to starch was calculated knowing the approximate weight of the starch film and an estimate of the volume of hexane–AKD solution that was retained and dried on the surface of the starch coated slide.

Elemental analysis was performed using a Leco True-Spec CHNS elemental spectrometer. The sample was placed in a tin container, dropped in a furnace with oxygen at 950 °C, and the carbon was measured as CO_2 in an IR cell and the hydrogen was measured as water in an IR cell. The gasses were then swept over hot copper sticks to remove oxygen and reduce the NO_x to N_2. The CO_2 and H_2O was removed and the N_2 measured by a thermal conductivity cell.

3. Results and discussion

3.1. Particle morphology

The purpose of cooking the starch and then precipitating the solution in ethanol is to create a foam structure that has significant pore volume. The increased surface area of the foam should enhance the brightness and other optical properties of the particles. SEM images of the uncooked starch and the precipitated SMCF particles with no AKD are shown in Fig. 2.

In order to improve the water resistance of the starch particles AKD was either blended or coated onto the particles. These particles are shown in Fig. 3a. It is observed that a porous structure is created due to the precipitation in ethanol, independent of the AKD level. The 10% AKD coated particles display small fibrils extending from the surface, unlike the other samples (Fig. 3a and b). This is presumably due to excess AKD on the surface of the particles. It was shown using elemental analysis that the 10% AKD coated particles sample had the most retained AKD (see later).

Hexane extraction was utilized to remove excess AKD accessible to the hexane. Hexane extracted samples, both coated and blends are shown in Fig. 4. The extracted 10% AKD coated particles do not exhibit the fibrils as did the same unextracted sample in Figs. 3a and b, due to the solubilization of the external excess AKD on the

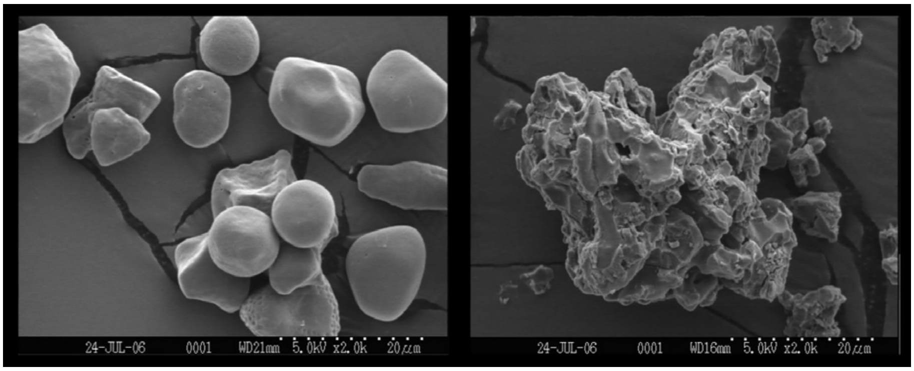

Fig. 2. SEM images of uncooked (left) and cooked and precipitated starch with 0% AKD (right) at 2000× magnification. Note the porous structure of the precipitated starch.

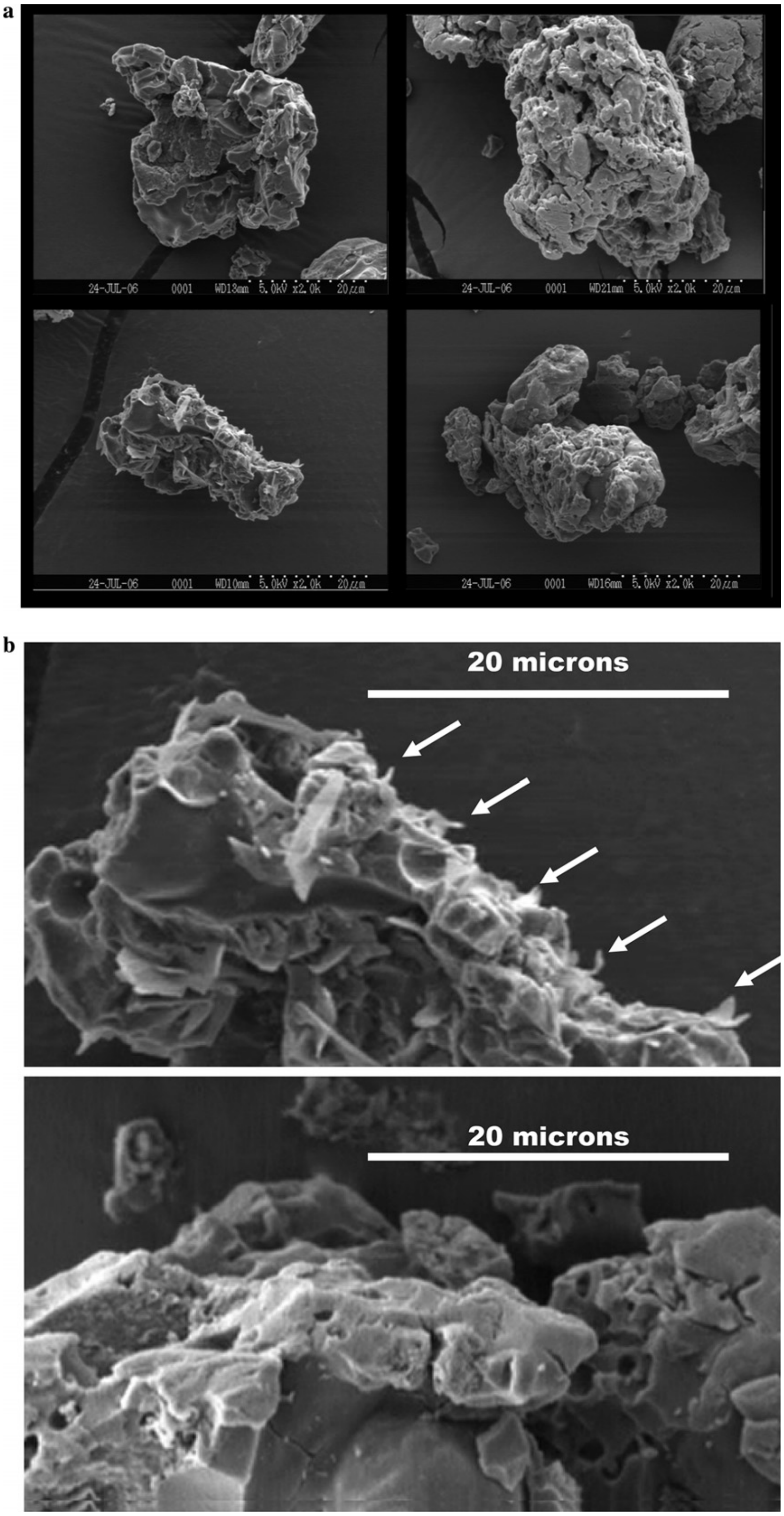

Fig. 3. (a) SMCF particles with 0.5% and 10% AKD coated and AKD blends, not extracted. (Top left: 0.5% coated, top right: 0.5% blend, bottom left: 10% coated, bottom right: 10% blended). (b) SMCF particles with 10% AKD coated and not extracted (top, expanded image from (a) and 0% AKD not extracted as a comparison (bottom). Arrows point to whiskers that were present only in samples of 10% AKD coated and not extracted samples.

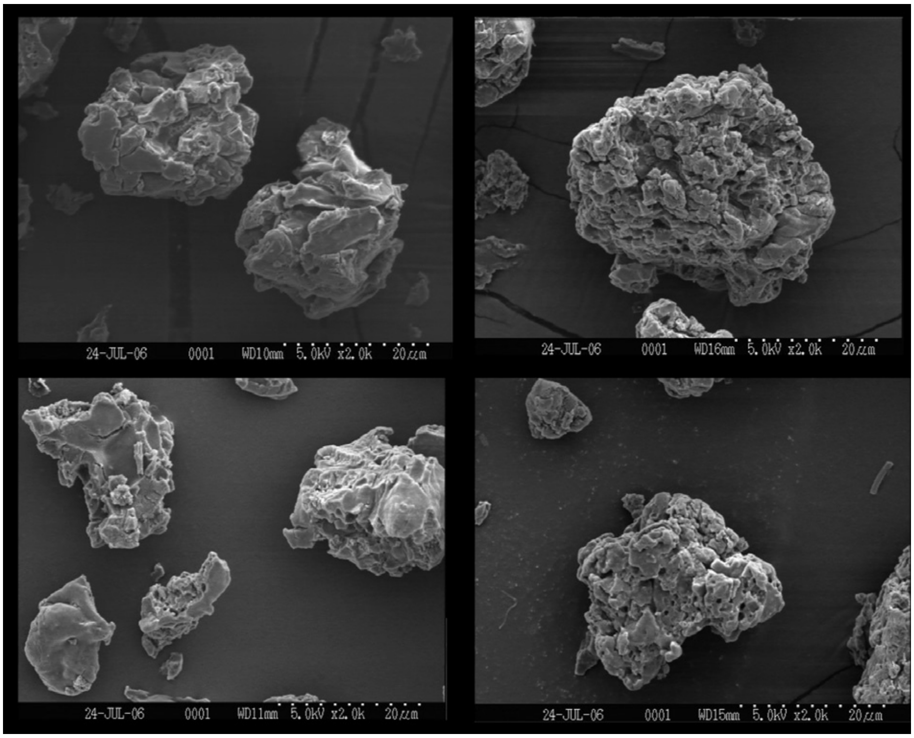

Fig. 4. SMCF particles with 0.5% and 10% AKD coated and blends, extracted with hexane. (Top left: 0.5% coated, top right: 0.5% blend, bottom left :10% coated, bottom right: 10% blend).

particle surface. For the 0.5% AKD coated and both of the levels of AKD blends, extracted and unextracted particles appear to be similar in morphology from the SEM images (Figs. 3 and 4).

The structures developed with the simple ethanol exchange display a porous structure with thicker walls with much finer and more random pores than beaded polystyrene, puffed wheat, freeze dried foam from a wheat starch aquagel (Glenn et al., 1996) or starch based supercritical carbon dioxide extruded foams (Alavi et al., 1999). However, using the simplified ethanol exchange process herein, the developed specific surface areas on the order of 1 m^2/g (El-Tahlawy et al., 2006) is significantly less than those using a more complicated, multi solvent exchange process to produce areas on the order of 100 m^2/g (Glenn et al., 1996). The structures formed in this research are qualitatively similar to "coral" like structures formed from starch derivatives precipitated in water–solvent mixtures to produce particle dispersions (Saari et al., 2005). The specific surface areas of these "coral" like structures has not been reported.

It was also of interest to determine whether the AKD concentration impacted the average particle size, Table 1. For the particles with no AKD, the average particle size was 11.4 µm, slightly larger than the uncooked starch at 10.3 µm. The AKD blends and coated particles have a smaller average particle size than the 0% AKD sample. However, the difference in particle sizes for the different samples is small relative to the standard deviation of the particle size distribution for any given sample. It was found in our previous work that the rate of shear during precipitation was an important variable affecting particle size; in this study the rate of shear was kept constant (El-Tahlawy et al., 2006).

Table 1
Average particle size (µm). The uncooked starch had an average particle size of 10.3 µm

	Coated	Standard deviation	Blend	Standard deviation
0% AKD	11.4	7.7	11.4	7.7
10% hexane extracted	8.9	9.4	9.0	8.2
5% hexane extracted	7.3		10.6	
1% hexane extracted	8.1		9.2	
0.5% hexane extracted	8.2		10.4	
0.1% hexane extracted	9.8		10.2	
Average of all extracted	8.5		9.9	
10% unextracted	6.6	8.0	8.8	8.2
5% unextracted	7.8		8.2	
1% unextracted	6.9		8.3	
0.5% unextracted	7.9		8.5	
0.1% unextracted	7.3		9.8	
Average of all unextracted	7.3		8.7	
Average of all AKD	7.9		9.3	

3.2. Brightness

It is expected that the brightness of the particles will increase relative to the uncooked starch due to the highly porous nature of the foam particles. The brightness of

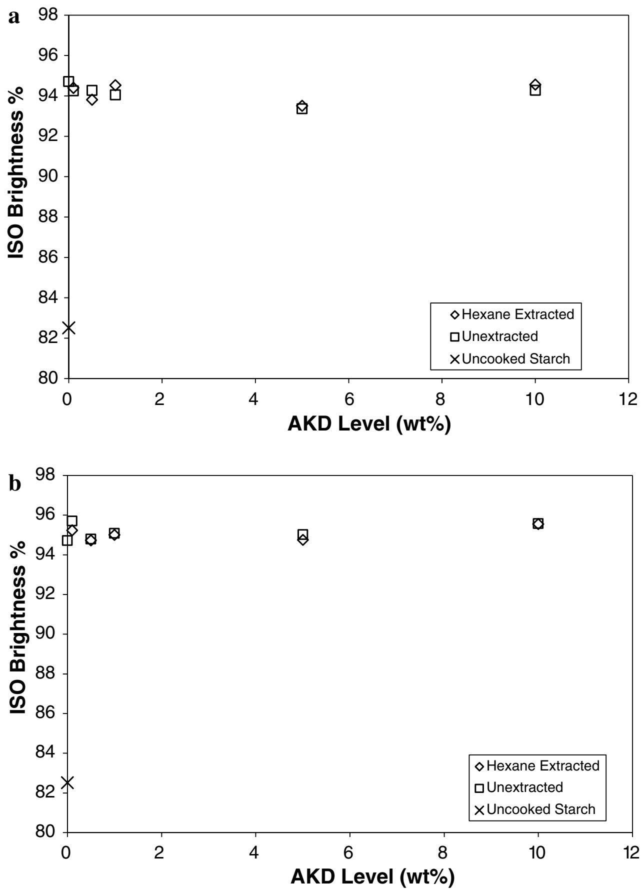

Fig. 5. (a) The brightness of the starch AKD coated and the uncooked starch. (b) The brightness of the starch AKD blends and the uncooked starch. A 95% confidence interval for each measurement is ±0.3%.

Table 2
Moisture content (g water/g sample in percent) of SMCF particles after conditioning at 50% relative humidity and 23 °C. The uncooked starch had a moisture content of 11.1%

	Coated	Blends
0% AKD	12.6	12.6
10% hexane extracted	12.3	13.7
5% hexane extracted	12.1	10.7
1% hexane extracted	12.3	13.1
0.5% hexane extracted	11.9	12.2
0.1% hexane extracted	12.8	11.6
Average of all extracted	**12.3**	**12.3**
10% unextracted	11.8	13.4
5% unextracted	10.6	12.6
1% unextracted	11.4	11.9
0.5% unextracted	10.6	12.5
0.1% unextracted	12.4	12.5
Average of all unextracted	**11.3**	**12.6**
Average of all AKD	**11.8**	**12.4**

the uncooked starch and the starch AKD coated and blended particles are shown in Figs. 5a and b, respectively. It is observed that the cooking and precipitation process increases the brightness of the particles significantly. In our previous research, it was demonstrated for these types of particles that the brightness not only depended on morphology, but also on the particle size (El-Tahlawy et al., 2006). A linear relationship between particle size and

Table 3
Water retention value (g water/g OD starch in percent) for SMCF particles. The uncooked starch had a water retention value of 78.5%

	Coated	Blends
0% AKD	143.6	143.6
10% hexane extracted	68.5	190.0
5% hexane extracted	139.1	129.5
1% hexane extracted	96.3	227.6
0.5% hexane extracted	151.4	172.5
0.1% hexane extracted	169.5	167.3
Average of all extracted	**125.0**	**177.4**
10% unextracted	57.0	143.6
5% unextracted	75.3	158.7
1% unextracted	167.4	166.1
0.5% unextracted	147.2	184.8
0.1% unextracted	148.9	258.3
Average of all unextracted	**119.1**	**182.3**
Average of all AKD	**122.0**	**179.8**

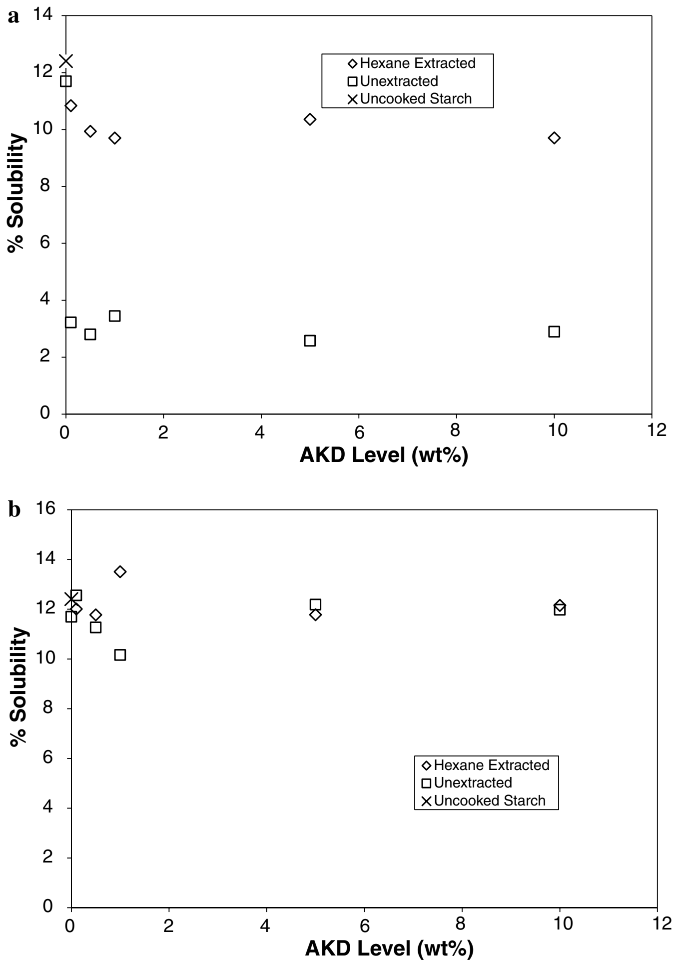

Fig. 6. (a) SMCF solubility versus AKD level for coated samples. (b) SMCF solubility versus AKD level for blend samples. A 95% confidence interval for each measurement is ±0.8%.

brightness was observed with a slope of −0.08% ISO brightness/micron particle size. Based on this slope, the difference between the uncooked starch and the SMCF particle brightness herein is not due to changes in the average particle size. It is also observed that the level of AKD or whether the AKD is blended or coated does not significantly affect the brightness values. Hexane extraction to remove excess AKD also does not impact the brightness, Figs. 5a and b. These observations about the effect of AKD on brightness is in agreement with SEM images that show that the morphology does not radically change with respect to AKD loading and hexane extraction, Figs. 3 and 4.

3.3. SMCF particle interactions with water

One of the objectives of this project was to determine if adding AKD would decrease the interaction between the starch and water, allowing the particles to be used in aqueous environments, preserving their structure and properties. The SMCF particles in general, had slightly higher equilibrium moisture contents after conditioning at 50% relative humidity and 23 °C relative to the uncooked starch, presumably due to the more extensive starch surface area, Table 2. It is observed that the moisture content of the SMCF particles with AKD blends have a similar moisture content as the SMCF particles with no AKD. The reason for this is due to the extraction of the AKD when ethanol is used in the precipitation process, see later, rendering the starch particles hydrophobic. Further, the AKD reacts both with starch and water (Eklund & Lindstrom, 1991b), thus, if much of the AKD is hydrolyzed by water and not reacted covalently with the starch, the extraction during the ethanol solvent exchange would remove the AKD not reacted with the starch. The coated AKD particles show a slightly lower moisture content relative to the SMCF particles with no AKD, due to the hydrophobic nature of the AKD that coats the particles. Note that for the coated particles, the AKD reacts with the starch in a non-aqueous environment (introduced in hexane and then dried at 105 °C for 2 h), facilitating the reaction between AKD and starch (without interference of water). Note that only a small amount of AKD can react with the surface starch, assuming that the AKD does not diffuse into the starch matrix.

Due to the close values of moisture content between the 0% AKD samples and those with AKD, it is expected that

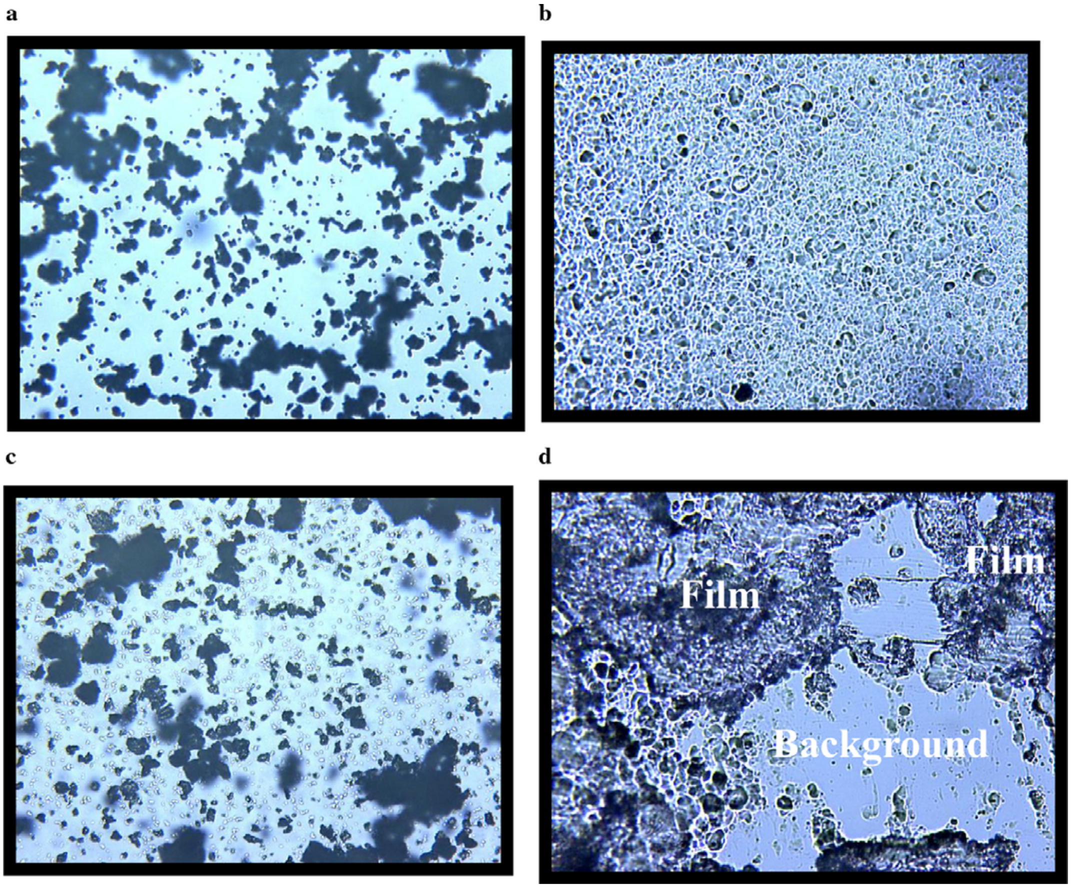

Fig. 7. (a) SMCF 10% AKD-blend dry particles (image width 0.5 mm, image height 0.4 mm). The particles appear as dark discrete objects relative to the light background. (b) SMCF 10% AKD-blend after wetting during water retention value experiment (image width 0.5 mm, image height 0.4 mm). The SMCF particles form a continuous film with a porous structure. (c) SMCF 10% AKD-coated air dry (image width 0.5 mm, image height 0.4 mm). The particles appear as dark discrete objects relative to the light background. (d) SMCF 10% AKD-coated wet after wetting during water retention value experiment (image width 0.5 mm, image height 0.4 mm). The SMCF particles do not form a continuous film. Areas of the film and background areas not covered by film are indicated.

the equilibrium moisture content is a bulk phenomena that does not mainly depend on AKD surface coverage.

Water retention values, the amount of water retained by the starch under mild vacuum, is shown in Table 3. The WRV of the SMCF with no AKD is approximately twice that of the uncooked starch, in agreement with the development of a porous surface and bulk structure. The WRV of the AKD coated and blends in general decreases with increasing AKD level, both for extracted and unextracted samples, in accordance with the AKD being more hydrophobic than the starch.

The water solubility of the particles versus AKD level for coated and blends are shown in Figs. 6a and b, respectively. For the AKD blends the water solubility is independent of the AKD value and similar to the 0% AKD and uncooked starch. Again, the reason for this is due to the extraction of the AKD when ethanol is used in the precipitation process, see later. Hexane extraction does not affect the water solubility of the blends, probably due to most of the AKD being extracted previously with ethanol.

In contrast, for the coated samples however, the unextracted samples have significantly lower solubility than the 0% AKD and uncooked starch. The solubility is constant with respect to AKD level for the unextracted samples. For the extracted samples, the solubility decreases slightly with AKD level relative to the 0% AKD and uncooked starch, with most of the decrease in solubility occurring with minimal AKD level. These results indicate that the larger amounts of AKD present on the surface of the particles is significant in resisting the solubility of the starch to water under the conditions described herein.

It was observed that the structure of the particles was largely disrupted during the water retention value soaking procedure. Fig. 7a shows SMCF AKD blend (10%) particles in the dry state before soaking in water. After soaking the particles, the particles lose most of their structure and congeal. When the congealed mass was spread onto a glass slide and dried a continuous film was formed, Fig. 7b. For the AKD coated particles, Figs. 7c and d the particles also lose their structure upon wetting. However, a qualitative observation was that these wetted particles as a total mass were more elastic or solid-like relative to the 10% AKD blended material which were more fluid-like in Figs. 7a and b. This is reflected in the fact that when the 10% coated particles were spread onto a microscope slide a continuous film was not formed Fig. 7d.

The contact angles of water on SMCF films were determined for the AKD coated and AKD blends, Figs. 8a and b, respectively. The contact angle of the SMCF without AKD is 28°. The AKD coated films have an increasing contact angle with respect to AKD level, showing a significant increasing contact angle at low AKD level with an ultimate contact angle of 85°. The AKD blends also show an increased contact angle with respect to the SMCF without AKD, however, the ultimate contact angle averages about 60°, lower than the AKD coated value, due to the extraction of AKD by ethanol. The contact angle results thus agree with the solubility results, indicating a more effective hydrophobicizing effect with the coated AKD relative to the blends.

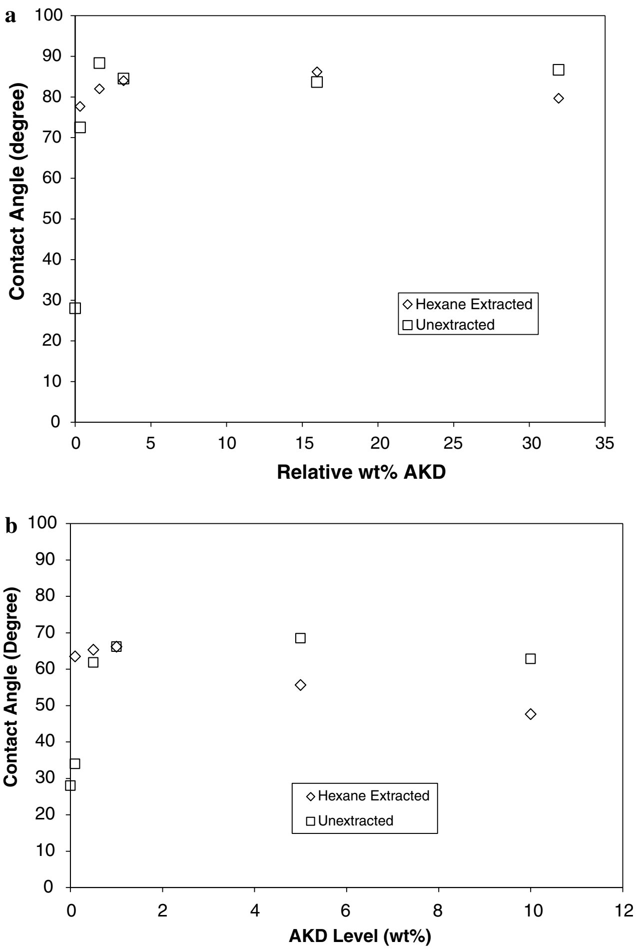

Fig. 8. (a) SMCF-water contact angle versus AKD level for coated samples. (b) SMCF-water contact angle versus AKD level for blend samples. A 95% confidence interval for each measurement is ±3.0%.

These results indicate that the procedure that develops the most hydrophobic particles is the AKD coating

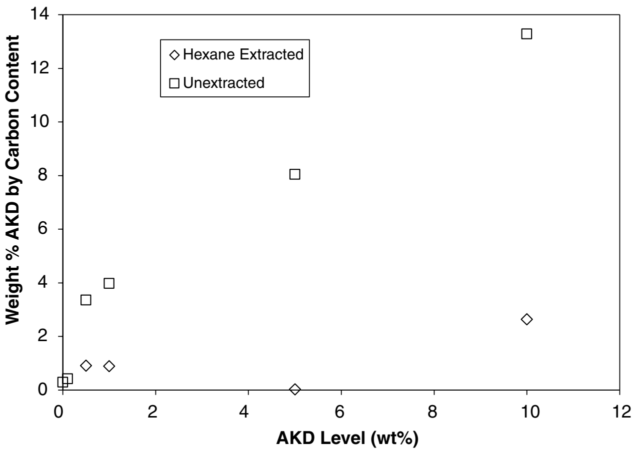

Fig. 9. Weight% of AKD on AKD-coated particles by carbon content. A 95% confidence interval for each measurement is ±0.5%.

method. Elemental analysis data confirms that the maximum amount of AKD retained with the particles is with the AKD coating that were not hexane extracted (Fig. 9). The amount of AKD in the samples increased with increased AKD initial charge. The low level of AKD in the hexane extracted samples indicates that very small amounts of the AKD are covalently bonded to the starch. The amount of AKD in the AKD blends was not detectable for both hexane extracted and non-hexane extracted samples (data not shown). The elemental analysis in combination with the contact angle data indicates that only amounts necessary for surface coverage can significantly impact the contact angle and other water interactions.

4. Conclusions

Starch based microcellular foam particles with a porous structure, high surface area and high brightness were produced with a simple precipitation process with ethanol. The addition of alkyl ketene dimer to the starch imparted some amount of water resistance to the particles. The activity of the AKD was most importantly a surface coating phenomena. Surface coating of the AKD on the particles, rather than blending the AKD and the starch, was a more effective method to increase water resistance.

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