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Effect of alkyl ketene dimer reacted starch on the properties of starch microcellular foam using a solvent exchange technique

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Abstract

The production of a hydrophobic starch microcellular foam (SMCF) through the addition of an alkyl ketene dimer (AKD) would be a bio-based material with valuable properties for many applications in which high specific surface area, low density and water resistance is important. Pigments for paper and coatings are a potential application. An emulsion of AKD and cooked corn starch was made by mixing AKD with cooked starch at 50 °C under a high rate of shear. The effects of reaction temperature, starch concentration and pH on the reaction of AKD with starch and the resulting microcellular foam structure were studied. The starch/AKD foam particles were characterized by scanning electron microscope (SEM), elemental analysis to determine extent of reaction, thermogravimetric analysis (TGA), brightness, particle size and water swellability. The apparent viscosity of the starch solution was shown to have a linear relationship with the particle size and the brightness of the particles. The particles under all conditions had a very high brightness. The AKD was able to impart a significant hydrophobicity to the particles relative to starch alone but the water resistance was not great enough to preserve the porous structure when wetted.
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Keywords: Starch; Alkyl ketene dimer; Microcellular foam; Hydrophobicity; Brightness; Viscosity; Scanning electron microscopy

1. Introduction

Starch, the principal carbohydrate storage biopolymer of higher plants, is an abundant, low cost resource. Starch is a high molecular weight polymer of anhydroglucose units ($C_6H_{10}O_5$) linked by alpha-D glycosidic bonds. Starch is synthesized in plant cells as a food reserve (Singh, 2006). Starches are comprised of two major molecules, amylose and amylopectin. Amylose is defined as a linear molecule but it is recognized that some molecules are slightly branched by (1-6)-α-linkages. Amylopectin is a branched polysaccharide constructed from hundreds of short (1-4)-α-glucan chains, which are interlinked by (1-6)-α-linkages. Amylopectin is primarily responsible for the granule structure and crystallinity in most starches (Franco & Ciacco, 1997; Xie, Liu, & Cui, 2006). The worldwide availability and low cost of starch make it a desirable raw material to use in industrial processes. Approximately 4.5 billion pounds of starch were used annually in the US for industrial applications in 1991, much of that being used in the textile, paper, and food industries (Hebeish, Abdel-Rahman, El-Hilw, & Hashem, 2005; Hong, Gu, & Li, 2005; Zhang et al., 2004). Chemical modifications of starch to change the chemical and physical properties open the way for increasing the industrial applications of starch.

The production of starch microcellular foam (SMCF), low density foams of starch based material with characteristic pores in the 1–10 micron range, is an interesting technique that has attracted several scientists in the last decade (Chiou et al., 2005; Glenn et al., 2006; Budarin et al., 2006). The SMCF can be prepared by a solvent exchange method in which water is replaced by ethanol or other lower surface tension fluid and the starch is precipitated. It was reported

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that SMCF materials could be prepared that were white, opaque, and had densities of 0.10–0.32 g/cm^3, compressive strengths of around 1 MPa, moduli of elasticity of 5–30 MPa, low thermal conductivity of 0.024–0.036 W/mK, large pore volume of 0.17–0.63 cm^3/g and large specific surface area of 50–145 m^2/g (Glenn, Miller, & Irving, 1996). SMCF has a significantly higher surface area (air–solid interfaces) relative to typical cooked starch material dried from water in air, which is not opaque. Fine particles of starch microcellular foams have an excellent ability to scatter light and be strong opacifying agents useful in applications such as coatings or fillers. The use of SMCF in the field of drug delivery and as hosting molecules for different organic materials has been explored (Tarvianen et al., 2004; Glenn et al., 2002). Recently, reports on the use of these types of materials for controlled release of biologically active microorganisms for use as fertilizers have been described (Imam et al., 2007). Porous microspheres which simulate pollen and carry active agents for controlling parasites that infect honeybees have also been described (Glenn et al., 2007). SMCF also has been used as precursors for carbonaceous materials with tunable parameters (Budarin et al., 2006).

In previous research, cooked corn starch crosslinked with glutaraldehyde (15 g/100 g starch) at 50 °C in an acidic medium was precipitated in a bath of ethanol to produce microcellular foam particles (El-Tahlway, Venditti, & Pawlak, 2007). Interesting structures with significant amounts of voids in the one micron range were observed for the concentration range of glutaraldehyde of 7.5–15 g/100 g starch. Below and above this range, the SMCF did not show the same consistency in pore volume and pore sizes. The research also showed that the foam structure is highly dependent on the starch viscosity, as modified by both crosslinking and by hydrolysis. The shear rate under which the solvent exchange occurred also improved the optical properties of the SMCF particles. Although the optical properties were promising, the foams absorbed water rapidly and thus the water resistances of the foams were lower than needed for many applications.

Alkyl ketene dimer (AKD) is a common commercial chemical that is classified as non-hazardous (under OSHA regulations). AKD is a derivative of a fatty acid that has two alkyl chains that when reacted with carbohydrates will develop hydrophobic properties in the carbohydrate (Qiao, Gu, & Cheng, 2006; Hutton, Huseman, Shen, & Parker, 2003; Champ, 2003).

To increase the hydrophobicity of such SMCF materials, efforts have been made by our group (Bolivar, Venditti, Pawlak, & El-Tahlawy, 2007) to produce starch microcellular foam followed by both blending AKD prior to particle formation and by applying AKD to the surface of the particles after particle formation. The generated particles had a porous structure and were of high brightness. The addition of the AKD to the starch particles was able to impart some amount of water resistance to the particles, resulting in contact angles of the starch with water of about 85° and 65° for the coated and blended AKD particles. However, the water resistance of the produced materials was not sufficient to maintain the porous structure upon extended immersion in water. The activity of the AKD was most effective with the coating process. It was shown with elemental analysis that the AKD was removed with a hexane extraction step, indicating that the AKD was adsorbed to the surface in the coating application or incorporated into the starch matrix in the blending application but not covalently bonded to the material. It is thus of importance to better understand the effect of reaction conditions on the extent of reaction between AKD and starch. The current work reported herein has focused on the effect of reacting alkyl ketene dimer (AKD) with cooked corn starch on the formation and properties of starch microcellular foam. The goal of this work to develop a suitable route of developing a hydrophobic starch microcellular foam. The SMCF particles were characterized using fourier transform infrared analysis, scanning electron microscope (SEM), elemental analysis to determine extent of reaction, thermogravimetric analysis (TGA), brightness, and particle size and water swellability.

2. Experimental

2.1. Material

Native corn starch was provided by Cargill, USA (Cargill Gel 03420, 25–28% amylose). Aquapel 364 wax (alkyl ketene dimer, AKD) (50% C16-50% C18 wax dimer, melting point 40–50 °C) was supplied by Hercules incorporation (Wilmington, DE 19894-0001, USA). Anhydrous ethanol, *n*-hexane and other chemicals were purchased from Fisher Co.

2.2. Preparation of starch/AKD blends

A cooked starch solution was prepared by adding a definite amount of corn starch (3–17 g) to 50 mL of deionized water in a three necked flask (100 mL) under continuous stirring (IKA-Werk, RW 16 Basic S1). The temperature was increased gradually to 95 °C over a time period of about 30 min. The cooked starch was subjected to continuous stirring for another 20 min. The cooked starch was allowed to cool to the desired temperature (30–60 °C), about 45 min to cool to temperature. Starch/AKD emulsions were prepared by adding a definite amount of AKD (10% based on weight of starch) to the cooked starch followed by increasing the mixing speed to ~4000 rpm for 30 min, forming an emulsion of the wax in the starch solution. The emulsion was allowed to stir for four hours at lower mixing speed. Adding ethanol then stopped the reaction.

2.3. SMCF formation

Starch microcellular foam was prepared using a solvent exchange technique. In this technique, solvent of higher surface tension (water) is replaced with another solvent of lower surface tension (ethanol). This was carried out by adding anhydrous ethanol (50 mL) to the starch/AKD emulsion in the presence of stirring (IKA-Werk, RW 16 Basic S1, and 4100 rpm) for 30 min, and then filtering the starch/AKD mixture. The starch/AKD material precipitates when the ethanol is introduced and the precipitate is filtered using filter paper (Fisher Scientific, P2). The precipitate is transferred to a glass beaker and ethanol is again added (100 mL) with stirring, stirred for 30 min, and then filtered again. The solvent exchange was repeated another time for 1 h to complete the removal of the water from the starch foam. Precipitated SMCF was dried on filter paper under house vacuum at ambient conditions for 24 h. The AKD is partially soluble in ethanol so that the precipitate may contain both starch-reacted and un-reacted or hydrolyzed AKD. AKD is soluble in *n*-hexane at room temperature, so in order to remove the residual unreacted AKD, the batches of SMCF particles were stirred in 100 mL of *n*-hexane using a magnetic stirring bar for 15 min and then filtered on filter paper. This was repeated twice more.

2.4. Characterization of starch/AKD MCF

Starch/AKD grafted MCF was characterized as follows:

2.4.1. Scanning electron microscope, SEM

Morphological characterization of starch microcellular foams was performed on images acquired using a scanning electron microscope (SEM), Hitachi S-3200N. The samples were coated with platinum of 10 nm thicknesses to make the samples conductive. A magnification of about 3–3.5 K was used for the samples.

2.4.2. Add-on% of AKD

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. The carbon is measured as CO_2 in an IR cell and the hydrogen is measured as water in an IR cell. The gasses are then swept over hot copper sticks to remove oxygen and reduce the NO_x to N_2. The CO_2 and H_2O are removed and the N_2 measured by a thermal conductivity cell. The add-on% of AKD on starch (for example an add-on% of 5% indicates a material with 5 g of AKD and 100 g of starch) is calculated according to the following equation.

$$\text{Add-on\%} = \frac{(C_{ms} - C_{st})}{(C_{AKD} - C_{ms})} \times 100\% \qquad (1)$$

where C_{ms} is the measured % carbon in the modified starch, C_{st} is the % carbon in the dry native starch (44.7%), and C_{AKD} is the theoretical % C of AKD (81.7%). However, several factors caused these add-on% calculations to have significant noise in their values, including the starch being an industrial product, the AKD being an industrial formulated product, the inherent noise in the elemental analysis experiment, and normal random sampling errors. A standard deviation of repeated measurements is estimated to be around ±3%. For this reason, some measured values of add-on% are greater than 10, the maximum possible value. The sample preparation steps and elemental analysis measurements were all done in the same manner and for this reason the add-on% results should be used to determine the general trend versus the independent variables investigated, rather than for absolute values.

2.4.3. Spectroscopic analysis

Starch/AKD materials were characterized using Fourier transform infrared (FTIR) spectroscopy to understand whether the AKD is reacted with the starch or not using a Perkin-Elmer FTIR spectrophotometer, Nicolet Nexus 470. The samples were ground with KBr and pressed into pellets for FTIR transmission measurements.

2.4.4. Moisture content analysis

The moisture content of the SMCF was determined using thermal gravimetric analysis (TGA, TA Instruments, G500 V6.3 Build 189) on samples equilibrated with an atmosphere of 23 °C and 50% relative humidity. In the TGA, samples were heated from room temperature to 120 °C at 5 °C/min and then held at 120 °C for 30 min.

2.4.5. Physical properties

The brightness of the SMCF (powder) was measured using a Technidyne Color Touch (model ISO) and a Brightimeter (Model S-4 brightness/color/fluorescence tester) to measure the brightness of the SMCF particles. The powders, about 6 g, were held in a glass Petri dish for brightness measurements.

Photomicrographs of the SMCF were taken using 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. Average particle sizes were determined on measurements of at least 150 particles.

2.4.6. Contact angle

The contact angle of water on the foam surfaces was measured on films of SMCF on glass slides to determine the interaction of the various starch solutions with water. Surfaces with contact angles less than 90° are considered wetting, while surfaces with contact angles greater than 90° are considered non-wetting. When the films were dried, the films were dipped and washed with hexane to remove the unreacted AKD from the surface of the films. The water droplet mass was approximately 14 mg. The contact angle was measured immediately after contact of the drop on the surface. Twenty measurements were made per sample.

2.4.7. Water retention value (WRV)

The water retention of starch/AKD foams was calculated by soaking a definite amount of foam (0.5 g) in

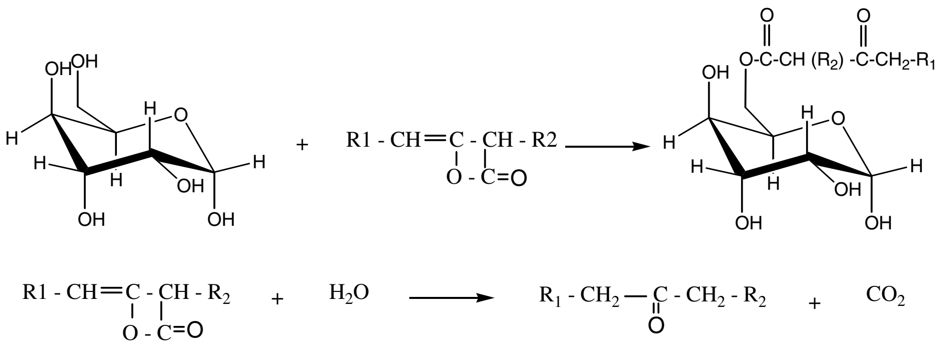
5 mL deionized water for 30 min. The unabsorbed water was removed by centrifuging the samples contained onto a water permeable support (using Centra CL3R with 958 swing horizontal motor) at 2800 rpm for 15 min. The result is reported in gram of water per gram of original starch. The percent water solubility of the starch/AKD foams was calculating using the oven dry foam material weight before and after performing the WRV test.

3. Results and discussion

When AKD wax is combined with a cooked corn starch water solution, there are two competitive routes of reaction for the AKD expected, Fig. 1. The four-membered lactone ring of AKD reacts with the starch hydroxyls to form β-keto ester linkages which serve to impart hydrophobic characteristic to the starch as desired. However, AKD can also react with water through a hydrolysis reaction forming a ketene derivative and carbon dioxide. The favorability of each route depends upon the reaction conditions.

3.1. FTIR spectra

The FTIR spectra for AKD, starch and starch grafted with AKD are shown in Figs. 2, 3 and 4, respectively. The sharp peaks in Fig. 2 located at 1731 and 1850 cm^{-1} (with a shoulder at 1870 cm^{-1}) are the C=C double bond and the C=O double bond of the carboxyl group in the lactone ring, respectively. Another sharp peak at 1467 cm^{-1} is due to the bending mode of the $-CH_2-$ bonds. The FTIR spectra of the unmodified starch show three essential bands at 1630, 2900 and around 3400 cm^{-1}. These absorption bands represent the vibrations of water molecules adsorbed in the non-crystalline region of starch, C—H stretching of alkane, and O—H stretching. The FTIR spectra of modified starch show a strong adsorption band at around 1670 cm^{-1} indicating that AKD has reacted with starch hydroxyls forming carbonyl esters. Also, a change in the shape of the absorption band around 3400 cm^{-1} between the unmodified (Fig. 3) and grafted (Fig. 4) materials indicates some interaction between the AKD and the starch



Where R_1= $C_{16}H_{32}$, and R_2= $C_{18}H_{36}$

Fig. 1. Expected chemical reactions of AKD (R1: $C_{16}H_{32}$ and R2: $C_{18}H_{36}$).

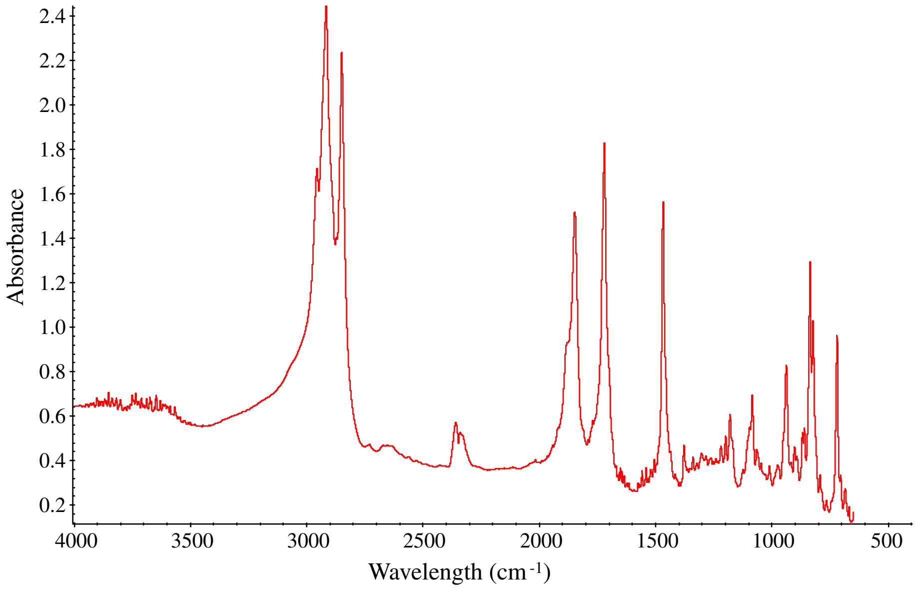


Fig. 2. FTIR spectra of the AKD.

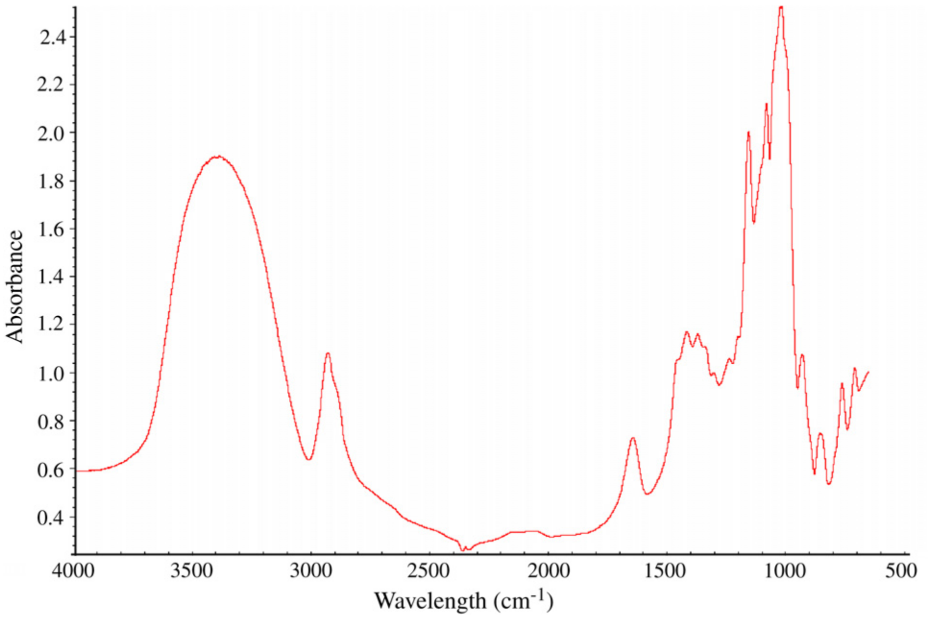


Fig. 3. FTIR spectra of the unmodified SMCF.

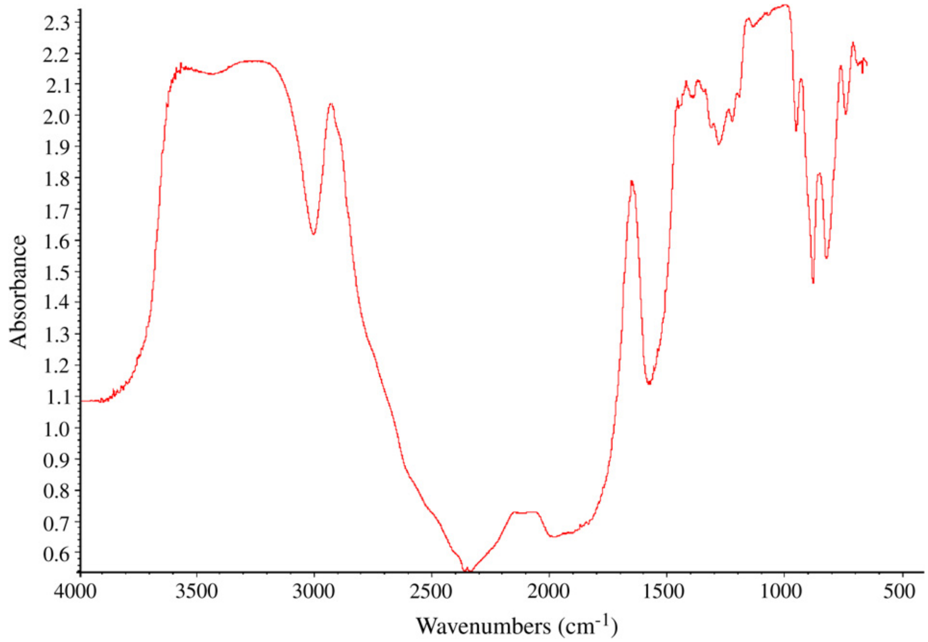


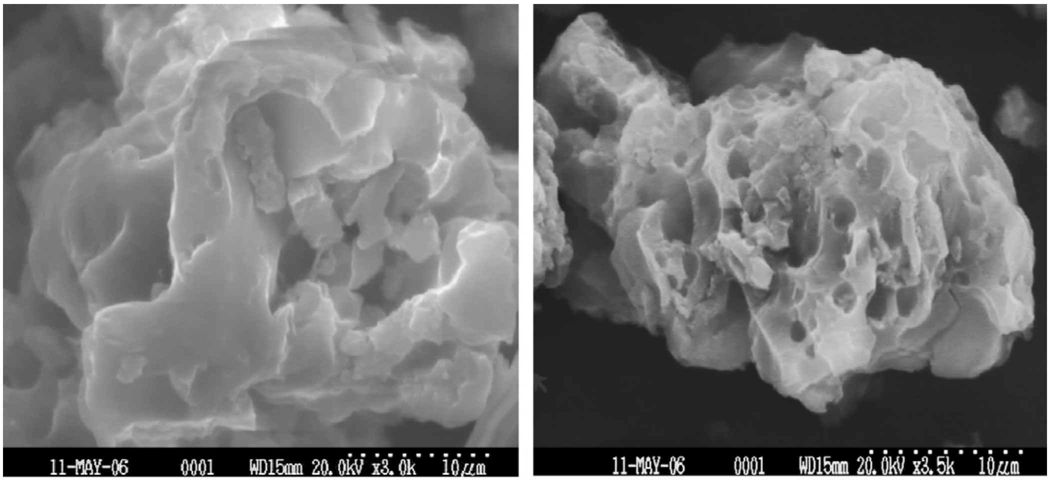
Fig. 4. FTIR spectra of the grafted AKD/starch microcellular foam.

hydroxyls. Despite this, there is still some possibility that non-covalently bonded AKD is retained in the starch matrix with strong enough interactions to starch to prevent extraction by hexane.

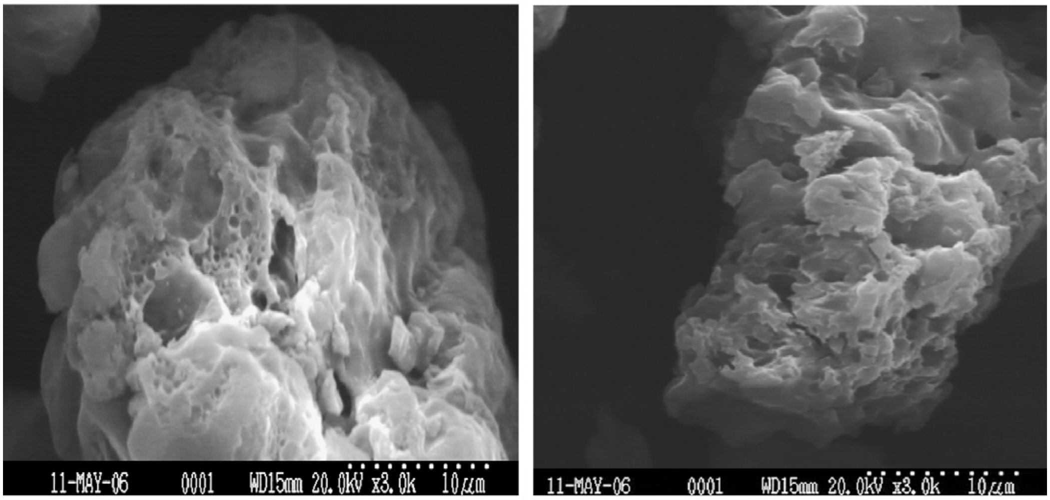
3.2. *Effect of reaction temperature*

Starch (12 g) is pre-cooked in a solution (50 mL) of pH 8 of deionized water. An emulsion was prepared by adding 1.2 g of AKD, followed by continuous stirring (4000 rpm) for 30 min. The reactions were allowed to proceed at different reaction temperatures (30–60 °C). SEM images in Fig. 5 indicate that increasing the reaction temperature from 30 to 60 °C is accompanied by a finer foam structure formation (increased concentration of pores and smaller sized pores). Such enhancement in the foam structure formation as a function of reaction temperature could be due to the following: (1) the higher kinetic energy of grafted starch chains with corresponding to higher molecular mobility, (2) differences in the solvent exchange process and (3) differences in the precipitation process.

The effect of the reaction temperature on the add-on% of the AKD onto starch is shown in Table 1. These materials were washed several times with *n*-hexane in order to



(a) 30 °C (b) 40 °C



(c) 50 °C (d) 60 °C

Fig. 5. SMCF particle surface structure for several reaction temperatures.

Table 1
Effect of reaction temperature on the properties of AKD/starch MCF (AKD charged was 10% by weight of the starch)

Reaction temperature	Physical properties						
	Add-on%	Moisture content, %	Contact angle	Water retention, g/g	% Soluble starch	Particle size, μm	ISO brightness
Uncooked[a]	–	11.1	–	0.8	12.1	–	82.5
Control[a]	–	12.6	28	1.4	11.9	11.4	94.7
30	4	11.5	89	1.2	11.1	8.6	93.2
40	6	7.2	91	1.2	10.4	14.6	93.1
50	13	6.4	91	1.2	10.0	16.6	91.9
60	6	6.7	92	1.0	8.3	20.5	92.8

[a] Uncooked and control data of Cargill Gel 0342 with no AKD from Bolivar et al. (2007). The control sample was cooked at 30% starch concentration and pH 8.0. The cooked starch was precipitated by a series of ethanol exchanges.

remove the unreacted AKD. It is well known that the reactivity of AKD to react with cellulose and carbohydrate is low, related to its structure. The add-on% increases from as the reaction temperature increases from 30 to 50 °C. In the case of 30 °C reaction only, a short heating to about 50 °C was used to disperse the AKD before reaction. Raising the reaction temperature leads to an increase in the homogeneity of the emulsion, since the melting point of the AKD wax is 40–50 °C. The fluidity of the reacting AKD near and above its melting point enhances the reaction.

The add-on% decreased significantly at 60 °C relative to 50 °C. It is well known that the AKD can hydrolyze by reacting with water and eliminating a carbon dioxide molecule (Fig. 1). It has been demonstrated that the ratio of the rate of reaction of AKD with cellulose to the rate of reaction of AKD with water decreases from 30 to 70 °C (Scott, 1996). This is a likely explanation for the decrease in add-on% at 60 °C.

At the end of the reaction time there may exist unreacted and hydrolyzed AKD which may be incorporated into the starch particles during foam formation. It is well known that the stability of an AKD emulsion is highly dependent on the following: (1) the AKD emulsion should be in a high concentration to decrease water/AKD interactions, (2) it should be kept at low temperature to avoid hydrolysis, and (3) elevated pH could affect the hydrolysis rate and (4) the presence of catalyst could increase the rates of both hydrolysis and esterification (Marton, 1990).

The moisture content, contact angle (on films), % water retention and % soluble starch measurements are related to the hydrophobicity of the foams and are shown in Table 1. The data indicate that at all reaction temperatures a significant increase in hydrophobicity with starch/AKD was realized relative to starch only foam material alone, the control. Increasing the reaction temperature up to 50 °C leads to an increase in the amount of AKD linked to the starch, and consequently increases the hydrophobicity of the starch/AKD MCF, which is reflected by a decrease in the moisture content and decreases in water retention and % soluble starch. The contact angle measurement is highly dependent on the porosity, roughness; amount of AKD linked to starch and is a surface response rather than a bulk response. For the contact angle, sufficient surface coverage of AKD is found at a reaction temperature of 30 °C. Despite the increased hydrophobicity, the particles lost their foam structure when exposed to the water in the water retention test. This was also found for the starch concentration and pH experiments, described below. This is similar to our previous findings with starch foams blended and coated with AKD (Bolivar et al., 2007).

The average particle size generally increased with increasing temperature. However, the ISO brightness of all the samples, as shown in Table 1, are all very high, indi-

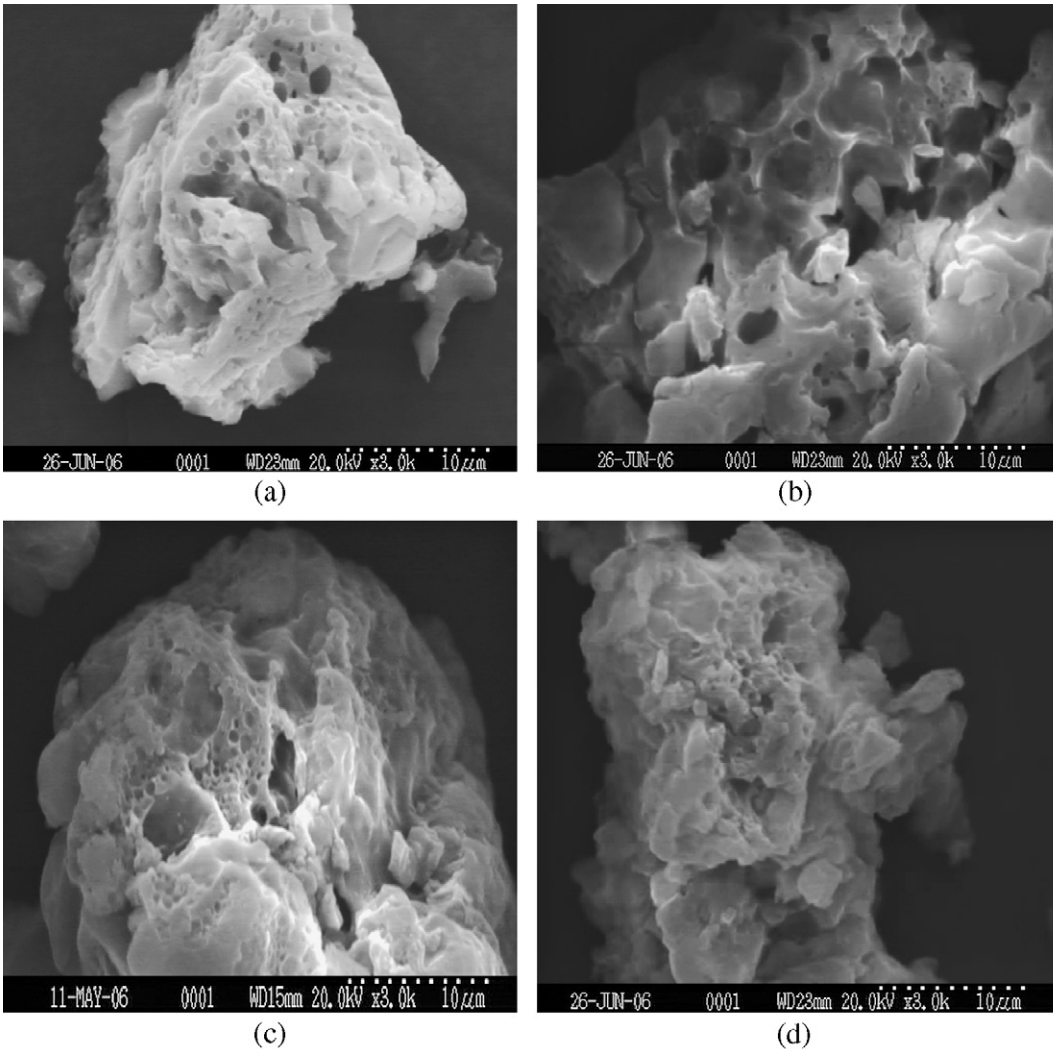


Fig. 6. SEM pictures show the effect of starch concentration on the foam structure of SMCF. Pictures a, b, c and d of starch concentrations of 6%, 12%, 24% and 34%, respectively.

cating that the particles have high specific surface areas which can scatter light and low concentrations of light absorbing components. The brightness data along with the SEM images of Fig. 1 indicate highly microporous material.

3.3. Effect of starch concentration

Starch microcellular foams were prepared by reacting starch of different concentrations (6%, 12%, 24% and 34%) with AKD wax (10% based on the weight of starch). Starch/AKD emulsions and foam particles were prepared under the same conditions as described earlier. It is noted that the starch particles showed a highly porous structure with pores in the 1 micron range for all of the starch concentrations investigated (Fig. 6). The properties of the foams reflect that at all starch concentrations a significant increase in hydrophobicity with starch/AKD was realized relative to starch only foam material alone, the control (Table 2).

The add-on% displayed a maximum versus the starch concentration in the range of 12–24% (Table 2). The concentrations of the reacting ingredients in the system play a vital role affecting the reaction efficiency. It is suggested that at the low concentration of starch the competition between starch and water to react with AKD is dominated by the ratio of water to starch and that at high starch concentration mixing and diffusion of reactants plays a role. Increasing the starch concentration generally improved the water resistance and brightness of the particles. A clear decrease in average particle size was found with increased starch concentration.

In our previous work (El-Tahlway et al., 2007) we have shown that the ISO brightness of the SMCF particles is highly dependent on the particle size of such particles, since decreasing the particle size of the foam increases the amount of light scattering light and consequently increases the ISO brightness of the foam. This is in agreement with the data in Table 2. Further, it was observed previously that the SMCF void diameter and particle size decreased and the specific surface area increased with increased starch viscosity (El-Tahlway et al., 2007). The starch viscosity in this study was measured versus shear rate for different starch concentrations, Fig. 7. The starch solutions showed a shear-thinning behavior. A linear correlation was obtained between the apparent viscosity of the starch solution prior to AKD addition and the average particle size and ISO brightness, Fig. 8. These results are in agreement with the statement that higher viscosity of the starch material enhances the foam structure of the resulting SMCF.

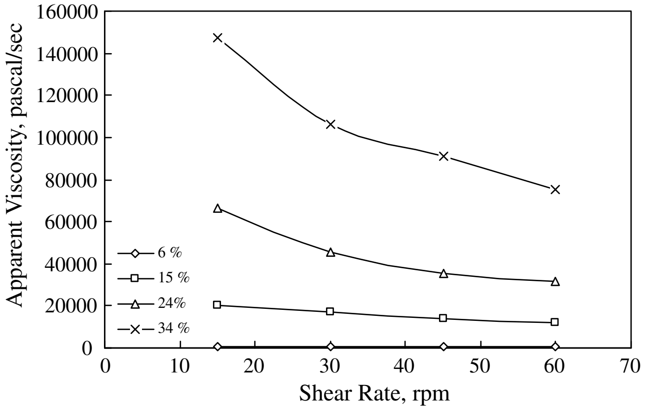


Fig. 7. Effect of shear rate on apparent viscosity for several starch concentrations.

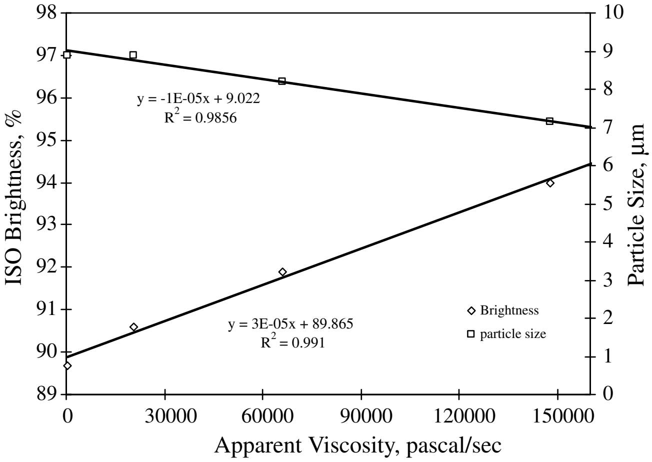


Fig. 8. Effect of the apparent viscosity of the different starch concentrations on the ISO brightness and particle size of SMCF.

Table 2
Effect of starch concentration on the properties of AKD/starch SMCF (AKD charged was 10% by weight of the starch)

Starch conc., %	Physical properties						
	Add-on%	Moisture content, %	Contact angle	Water retention, g/g	% Soluble starch	Particle size, µm	ISO brightness
Uncooked[a]	–	11.1	–	0.8	12.1	–	82.5
Control[a]	–	12.6	28	1.4	11.9	11.4	94.7
6	7	8.4	90	1.3	11.1	8.9	89.7
12	14	7.6	91	1.2	10.8	8.9	90.6
24	13	6.4	91	1.2	10.0	8.2	91.9
34	–	8.0	91	1.1	6.3	7.1	94.0

[a] Uncooked and control data of Cargill Gel 0342 with no AKD from Bolivar et al. (2007). The control sample was cooked at 30% starch concentration and pH 8.0. The cooked starch was precipitated by a series of ethanol exchanges.

3.4. Effect of pH

A series of reactions were carried out at four different pH values (5.5, 8, 8.6 and 10.5) using 24% concentration of starch and 10% AKD on the starch at 50 °C. It is noted that the starch particles showed a highly porous structure with pores in the 1 μm range for all of the starch concentrations investigated (Fig. 9). The add-on% shows a maximum at pH of around 8, Table 3. Despite this, a steady decrease in moisture content is found with increased pH in this range. The impact of pH seems to not have a consistent significant effect on the other physical properties of the starch particles. Overall, the optimum reaction conditions were determined to be 24% starch concentration, 10% wt/wt AKD/starch, and pH 8–8.6 at 50 °C. This statement is based on both the measured properties of the foam parti-

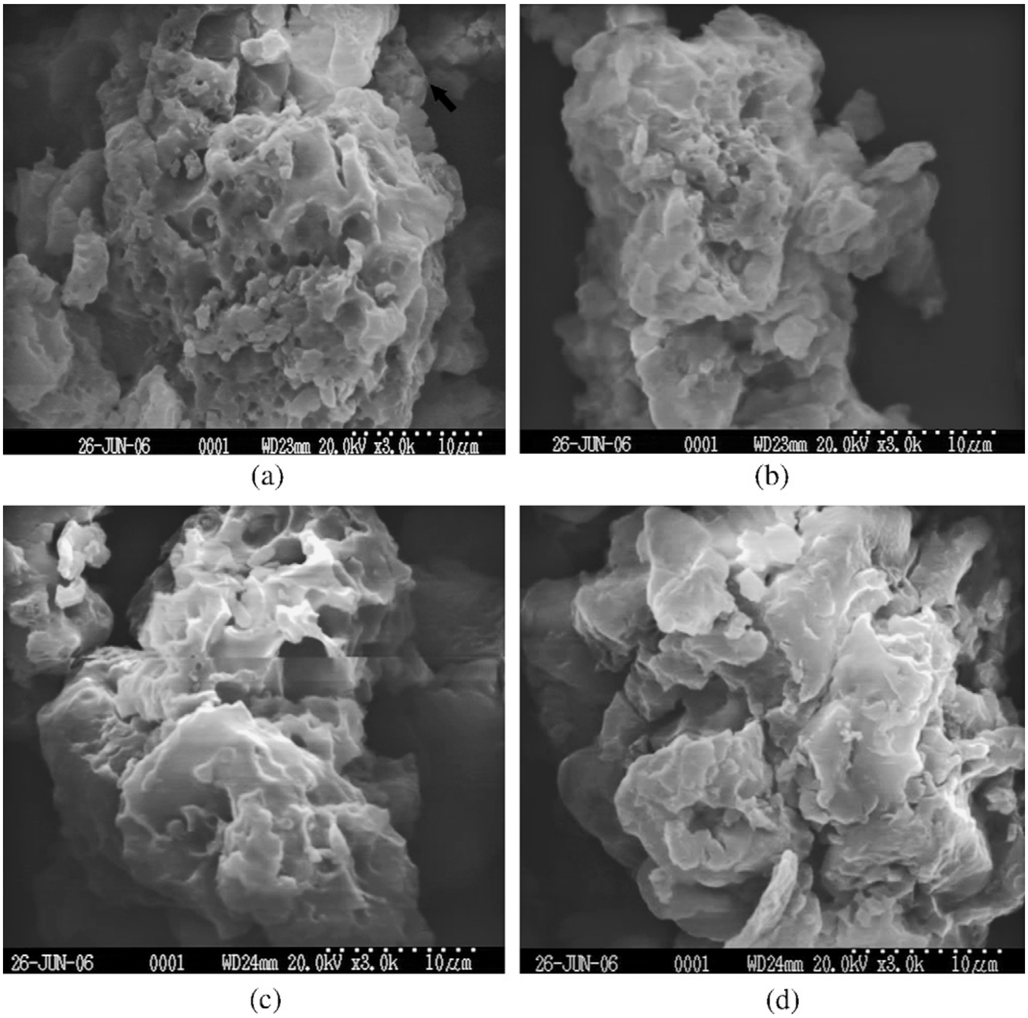


Fig. 9. The effect of pH of the reaction medium on the foam structure of SMCF. Particles in SEM images in a, b, c and d have pH values during reaction of 5.15, 8, 8.6 and 10.5, respectively.

Table 3
Effect of the pH of the reaction solution on the properties of AKD/starch MCF (AKD charged was 10% by weight of the starch)

pH	Physical properties						
	Add-on%	Moisture content, %	Contact angle	Water retention, g/g	% Soluble starch	Particle size, μm	ISO brightness
Uncooked[a]	–	11.1	–	0.8	12.1	–	82.5
Control[a]	–	12.6	28	1.4	11.9	11.4	94.7
5.15	7	10.2	89	1.2	16.4	7.0	95.0
8	13	8.0	91	1.3	11.0	7.1	94.0
8.6	9	7.3	92	0.9	5.1	7.7	92.4
10.5	7	6.3	91	1.6	21.1	9.6	93.2

[a] Uncooked and control data of Cargill Gel 0342 with no AKD from Bolivar et al. (2007). The control sample was cooked at 30% starch concentration and pH 8.0. The cooked starch was precipitated by a series of ethanol exchanges.

cles as well as the author's opinion on the processability at these conditions. For example, the 34% starch concentration was extremely difficult to mix and keep homogenous during all steps.

4. Conclusions

Starch/AKD microcellular foams were prepared by first reacting AKD (10% on starch) in an alkaline medium (pH 8–8.6) at 50 °C and then precipitated using a solvent exchange with ethanol. FTIR and elemental analysis confirmed the reaction of the AKD with the starch. The starch particles showed a significant porous foam structure for different reaction conditions, including reaction time, starch concentration and pH. The apparent viscosity of the starch solution was shown to have a linear relationship with the particle size and the brightness of the particles. The particles under all conditions had a very high brightness. The AKD was able to impart a significant hydrophobicity to the particles relative to starch alone but the water resistance was not great enough to preserve the porous structure when wetted.

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