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Effects of critical fluid lipid extraction on the gelatinization and retrogradation of normal dent cornstarch

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Abstract

Critical fluid extraction of native lipids from cornstarch using 80/20 (v/v) CO_2/ethanol and 100% ethanol was carried out in order to see what effects each solvent would have on the starch pasting profile. The results were compared with cornstarch defatted by refluxing with 75/25 (v/v) *n*-propanol/water. Pure ethanol extracted more native lipid than CO_2/ethanol, and extraction improved when the initial moisture content of the starch was increased from 10% to 19%. Granules became less swollen and less deformable with increased lipid extraction. Paste viscosity studies carried out at starch concentrations less than 8% yielded lower peak and setback viscosities of lipid-extracted cornstarch relative to native cornstarch. However, above 8% starch concentration, swollen granules were in more intimate contact, and the added rigidity caused by lipid extraction yielded much higher peak viscosities relative to the starch control. Lipid-extracted cornstarch samples at concentrations above 8% showed plateau rather than peak viscosities reflecting the limited swelling power of the granules, and the defatted samples displayed less viscosity breakdown due to their increased granule rigidity.
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Keywords: Cornstarch; Critical fluid; Lipid extraction; Gelatinization; Retrogradation

1. Introduction

The extraction of native lipids from cornstarch can alter its physical properties and thus add to the many end-use applications for this abundant agricultural commodity. Supercritical CO_2 and CO_2/ethanol blends offer a convenient and non-toxic method for carrying out these extractions. The native lipid component of cornstarch contains mainly free fatty acids along with lesser amounts of phospholipids (Morrison, 1988; Morrison, Milligan, & Azudin, 1984). Linoleic, palmitic and oleic acids are the fatty acids present in the largest amounts. The solubility of lipids in supercritical CO_2 under different experimental conditions and the use of supercritical CO_2 as an extraction medium and as a technique for separating lipid mixtures have been extensively studied (e.g., Bamberger, Erickson, Cooney, & Kumar, 1988; Brunetti, Daghetta, Fedeli, Kikic, & Zanderighi, 1989; Chrastil, 1982; Hammam, 1992). Although supercritical CO_2 is a non-polar solvent, the ability of this solvent system to dissolve polar lipids can be enhanced by adding co-solvents such as ethanol.

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There are only a few reports on the treatment of starch and flour with supercritical fluids. Braga, Moreschi, and Meireles (2006) studied supercritical fluid extraction on ginger and tumeric tuber starches and saw subtle changes in the physical arrangement of the starch molecules by X-ray diffraction, but the authors did not correlate these results as a function of the native lipid. Hubbard, Downing, Ram, and Chung (2004) used supercritical CO_2 and CO_2/ethanol to extract non-starch free lipids from wheat flour as an alternative to the traditional Soxhlet extraction with non-polar solvents such as hexane. These workers did not consider the extraction of native lipids from starch granules. Koxholt, Altieri, Marentis, and Trzasko (2003) used extraction with supercritical fluids to remove off-flavors, odors and colors from starch but did not identify the native lipids removed by this process. Francisco and Sivik (2000) examined the gelatinization of cassava, potato and wheat starches in supercritical CO_2; however, they did not determine the extent of native lipid extraction under their experimental conditions.

In this study, ethanol was used as either a solvent or co-solvent for lipid extractions at elevated temperature and pressure. The pressure and temperature used were not above the critical point for ethanol, so this procedure will be designated critical fluid extraction (CFE) rather than supercritical fluid extraction. Native lipid fractions were extracted from normal dent cornstarch at two different moisture contents using CFE with ethanol or CO_2/ethanol as solvents. X-ray diffraction patterns, microscopy, birefringence images and pasting properties were used to characterize the extracted cornstarch granules. Pasting properties of extracted cornstarch samples were compared to those of cornstarch prior to critical fluid extraction and also to cornstarch which was extracted with 75% *n*-propanol/water to remove essentially all of the native lipid component.

2. Materials and methods

2.1. Materials

Normal dent cornstarch (pure food grade) was obtained from A.E. Staley Mfg. Co., Decatur, IL. This starch had a moisture content of approximately 10% (w/w) and was used as the control. Starch with higher moisture content was prepared by placing a pan containing 130 g of the same starch in a sealed Plexiglas chamber with a pan of distilled water for 24 h at room temperature (23 °C). This starch had a moisture content of approximately 19% (w/w). A saturated starch slurry containing roughly 43% moisture content was also tested, but this sample presented difficulties during critical fluid extraction that led to non-homogeneous samples which had not been evenly extracted. Moisture content was determined either by vacuum drying weighed starch samples at 100 °C or by using an HFT 2000 moisture analyzer (Data Support Co. Inc., Encino, CA). All starch weights are given on a dry weight basis. Heptadecanoic acid and lipid reference standard GLC-68A were supplied by Nu-Chek Prep, Inc., Elysian, MN. A standard solution of heptadecanoic acid was made by diluting a weighed amount of the solid with toluene.

2.2. Lipid extraction

Lipids were extracted from 2 g (dry weight) of cornstarch using refluxing 75/25 (v/v) *n*-propanol/water as described previously (Morrison, 1988; Peterson, Fanta, Adlof, & Felker, 2005). Critical fluid/pressurized solvent extractions were carried out on an ISCO Model 3560 SFE (ISCO Corp., Lincoln, NE) apparatus. Roughly 5 g of sample was weighed and added to the extraction cell between glass-fiber filter discs on the top and bottom of the cell. Samples were extracted at 80 °C at a pressure of 8000 psi for 20 min with a solvent flow rate of 1 mL/min. Two solvent systems were used: 100% ethanol and 80/20 (v/v) CO_2/ethanol. Initially, supercritical lipid extractions using 100% CO_2 were also carried out, but the extractions did not yield any detectable lipid (<0.01 mg), apparently due to very poor lipid extraction efficiency.

2.3. Lipid analysis

Extracted lipids were analyzed by gas chromatography after esterification to form fatty acid methyl esters. Since the lipids in these samples of cornstarch are primarily mixtures of free fatty acids and monoglycerides, a dual esterification procedure utilizing diazomethane and hydrochloric acid/methanol was used in order to differentiate these two species as outlined previously (Peterson et al., 2005).

A Varian 3900 (He carrier gas, FID detector) gas chromatograph controlled by Varian Star Chromatography Workstation software version 5.52 was used with a Supelco SP2380 column (30 m × 0.32 mm × 0.2 μm). For each run, column temperature started at 100 °C and rose 3 °C/min to a final temperature of 205 °C. Retention times for the esterified lipid peaks were identified using lipid reference standard GLC-68A (Nu-Chek Prep, Inc., Elysian, MN).

2.4. Starch pasting curves

Pasting curves were obtained using a TA AR2000 rheometer (TA Instruments, New Castle, DE) utilizing a starch pasting cell attachment. Samples were prepared either at 5% or 10% starch solids; approximately 1 or 2 g (dry weight) brought to 20 g total weight with deionized water. First, an initial mixing step at 750 rpm was applied for 30 s at 25 °C. Then, a linear temperature increase of 5 °C/min was applied until the sample reached 95 °C. During this step and for the remainder of the pasting profile, the mixing head rotated at 100 rpm. At 95 °C the sample was held for 5 min, and then the temperature was decreased linearly at 5 °C/min to 25 °C. For retrogradation studies, once 25 °C was reached, the sample was immediately subjected to an oscillatory time sweep test and oscillated at 0.5% strain for a minimum of 10 h.

2.5. Microscopy

Samples were examined after the end of the pasting cycle by dispersing a small portion in a water droplet on a glass slide with a spatula and gently applying a cover slip. Samples were observed with a Zeiss Axioskop light microscope (Carl Zeiss, Inc., Thornwood, NY) using phase contrast optics. Representative fields were photographed using a Nikon D100 digital camera (Nikon Corp, Tokyo, Japan).

2.6. X-ray diffraction

X-ray powder diffraction analysis was performed with a Philips 1820 diffractometer operated at 40 kV, 30 mA with graphite filtered CuK_{α} radiation and a theta compensating slit. Data were acquired in 0.05 degree two theta, 4 s steps. Samples were equilibrated at 23 °C, 50% r.h. for 3 days prior to analysis.

3. Results and discussion

The lipid extraction efficiency of CFE as a function of initial moisture content of the starch and the composition of the solvent system is shown in Table 1. Extraction with refluxing 75/25 *n*-propanol/water is also shown. Since our extraction results for the reflux method match literature reference values for the total native lipid content of maize starch (Morrison et al., 1984), this method appears to be essentially complete in its extraction of the native lipid. Table 1 shows that CFE extraction is not as effective and only removes a portion of the total native lipid from cornstarch. The pure ethanol solvent system is more effective than CO_2/ethanol at extracting native lipid and the lipid yield increases with higher moisture content of the starch.

Table 2 shows the relative percentages of each lipid type that was extracted using CFE. Figures in parentheses represent the percentage of free fatty acids that make up the particular lipid type as opposed to monoglycerides. For the CFE extracted samples, the two starting moisture contents are displayed for comparison. Starting moisture content of the starch sample refluxed in *n*-propanol/water is irrelevant, since the reflux procedure itself uses 75% *n*-propyl alcohol/25% water (v/v) as the solvent. From Table 2 it can be seen that the composition of the extracted lipid is similar regardless of the extraction method. Thus, the CFE extraction conditions used in this work do not impart any selectivity in terms of the types of lipids extracted.

Pasting curves at 5% starch solids for CFE starches of 10% and 19% moisture contents are shown in Figs. 1 and 2, respectively. In each of these figures, CFE starch samples

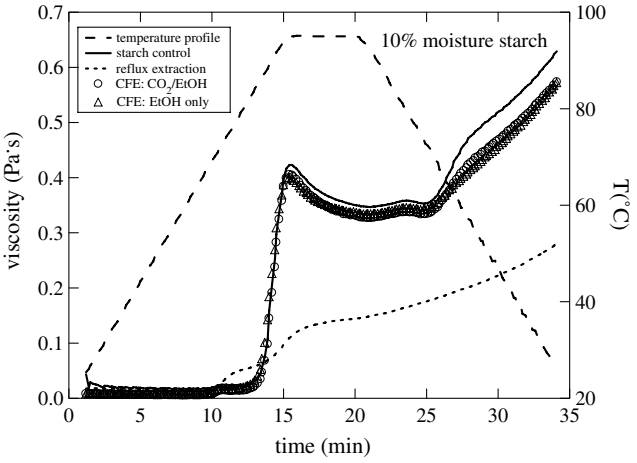

Fig. 1. Pasting profiles of cornstarch samples at 5% solids concentration and an initial moisture content of 10%.

Table 1
Lipid extraction efficiency

Initial starch moisture content (%)	Lipid extraction method	Solvent	mg Extracted lipid per g cornstarch
10	CFE	80/20 CO_2/ethanol	0.81
19	CFE	80/20 CO_2/ethanol	1.21
10	CFE	Ethanol	0.98
19	CFE	Ethanol	2.09
n/a	Reflux	75/25 *n*-Propanol/water	7.52

Table 2
Composition of extracted lipids from cornstarch samples as a function of extraction method

Extraction method	Relative percentages of lipid components[a]				
	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)
Reflux	27.2 ± 3.0 (79 ± 9)	3.1 ± 0.1 (79 ± 10)	13.5 ± 0.8 (79 ± 11)	52.7 ± 2.1 (82 ± 9)	3.4 ± 0.2 (85 ± 10)
10% moisture content					
CFE: CO_2/ethanol	24.9 (109)	3.2 (78)	12.5 (80)	48.1 (84)	3.7 (0)
CFE: ethanol	26 ± 3 (92 ± 9)	2.9 ± 0.4 (88 ± 10)	12.2 ± 0.5 (92 ± 8)	49 ± 2 (100 ± 10)	4.0 ± 0.3 (104 ± 5)
19% moisture content					
CFE: CO_2/ethanol	23 ± 2 (89 ± 9)	2.2 ± 0.2 (81 ± 7)	10 ± 1 (95 ± 8)	53 ± 3 (101 ± 8)	5.3 ± 0.5 (101 ± 6)
CFE: ethanol	25 ± 2 (71 ± 2)	2.6 ± 0.5 (71.8 ± 0.3)	12 ± 1 (77.0 ± 0.7)	53 ± 2 (87 ± 8)	4.2 ± 0.3 (93 ± 8)

[a] Values in parenthesis are the percentages of free fatty acid (as opposed to monoglyceride). Free fatty acid percentages >100% resulted from random errors in quantifying very small (<0.1 mg) lipid amounts between the diazomethane and HCl/methanol esterifications.

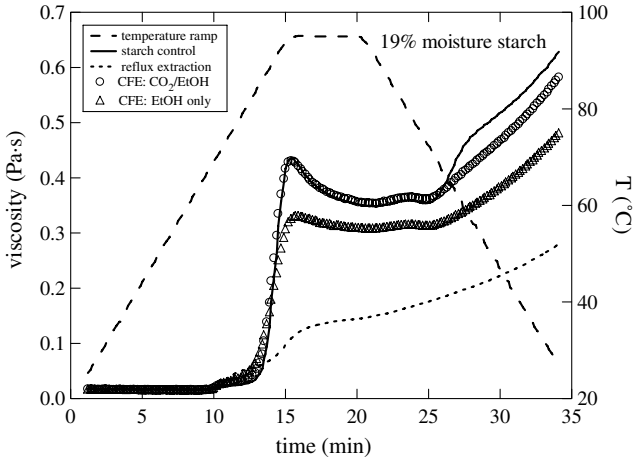

Fig. 2. Pasting profiles of cornstarch samples at 5% solids concentration and an initial moisture content of 19%.

are compared to an unextracted cornstarch control and a sample that was extracted refluxing with 75/25 *n*-propyl alcohol/water. After the lipid extraction step, all pasting profile experiments were prepared at the same dry weight to accurately compare the effects of extracted lipid on the pasting properties.

For the starch initially at 10% moisture (Fig. 1), the changes in the pasting curves (relative to the control) for the CFE starches are minimal, especially compared to the drastic change seen in the starch sample extracted with refluxing 75/25 *n*-propanol/water, which has virtually no lipid content. Removing the native lipids from starch eliminated the well known peak viscosity attributed to starch granule swelling and resulted in a significantly thinner starch slurry. The two CFE samples, on the other hand, showed little difference from the control until the setback region was reached, at an elapsed time of about 25 min. In Fig. 2, the results for the starch sample initially at 19% moisture content are shown. In addition to the changes in the setback region seen at 10% moisture content, the peak viscosity of the 100% ethanol CFE sample was reduced relative to both the control and CO_2/ethanol samples. These figures illustrate the dependence of the pasting properties on native lipid content of the cornstarch. At the two extremes are the control curve (all native lipids present) and the reflux extraction curve (virtually all lipids removed), with the 100% ethanol CFE curve in between them. Comparing this figure with Table 1, it appears that the viscosity in the setback region (25 min and after) reflects the amount of extracted lipid: the more lipid extracted, the lower the viscosity in this region. This trend also seems to be evident for the peak viscosity region (~13–17 min), although there is little change if the amount of extracted lipid is <2 mg/g starch (i.e., both CFE curves in Fig. 1 and the CO_2/ethanol curve in Fig. 2).

In general, the effects of lipid extraction on the pasting properties of various starch types are not well understood since the literature contains many examples of apparently conflicting results. Several studies have shown that removal of the native lipids from starches reduces or eliminates the peak viscosity and lowers setback viscosity as well (Goering, Jackson, & DeHaas, 1975; Kar, Jacquier, Morgan, Lyng, & McKenna, 2005; Sayar, Koksel, & Turhan, 2005; Takahashi & Seib, 1988; Vasanthan & Hoover, 1992). However, there are also cases where it appears that removal of native lipids either did not change the peak viscosity (Lorenz, 1976), or increased the peak viscosity and/or the setback region of the pasting curve (Biliaderis & Tonogai, 1991; Melvin, 1979). Biliaderis and Tonogai attributed the difference between their results and those of Takahashi and Seib to differences in starch concentration; 20–30% vs. 6.5–7.5%, respectively. Starch concentration may indeed be the key factor in understanding the effects of lipid removal on starch pasting behavior. All of the studies referenced above that indicate a decrease in the peak viscosity at lower lipid contents were done on starch samples at concentrations $\leqslant$8%. The conflicting results of Lorenz (1976), Melvin (1979) and Biliaderis and Tonogai (1991), i.e., increased paste viscosity at lower lipid content, were all obtained with starch concentrations >8%. It should also be noted that work by Lorenz (1976) did not include cornstarch so a direct comparison to this work is not totally appropriate although other A-type starches such as wheat and rice were studied.

When native lipids are extracted from cornstarch, the amylose that was bound in amylose-lipid complexes within the granule may become sufficiently mobile to crystallize to a small degree and thus form a network throughout the starch granule. Since amylose comprises only about 25% of the granule, a 10% crystallization of the amylose means that overall crystallinity would only increase about 2.5%, and probably be undetectable by X-ray diffraction. Since crystalline amylose melts at temperatures much greater than 95 °C, no melting would occur during the pasting profile, and therefore swelling would be reduced. This can be seen in Fig. 3, where starch granules extracted by refluxing with *n*-propanol/water appear to be less swollen and therefore less deformable after pasting than the swollen granules obtained from the control starch. This extra rigidity of lipid-extracted swollen starch granules becomes an important factor in the determination of pasting viscosity when the concentration becomes high enough for granules to come in close contact during the pasting process. Because of interstitial water between the swollen granules, lipid-extracted granules will exhibit a lower paste viscosity than an unextracted control sample in which the granules are more swollen. However, once a critical concentration is reached where even the smaller, less deformable, lipid-extracted granules are closely packed, a higher viscosity will result since the extracted granules are more rigid.

To determine the effect of starch concentration on paste viscosity, three of the starch samples shown in Fig. 2 were examined at 10% concentration instead of 5%. The three samples examined were a starch control, the 19% moisture content starch critical fluid extracted with ethanol only, and the starch sample extracted with refluxing 75/25 *n*-propanol/water. These samples represent three different levels of lipid extraction: no lipid-extracted (control), virtually all

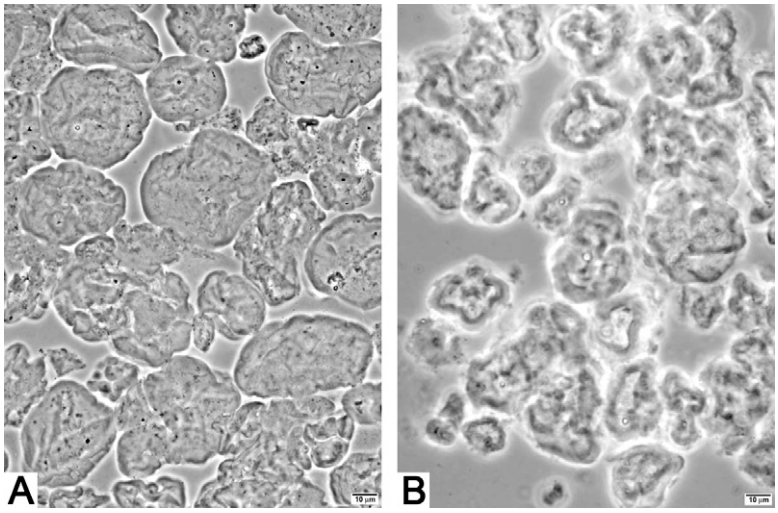

Fig. 3. Phase contrast microscopy images of cornstarch samples at 5% solids concentration at the conclusion of a pasting profile experiment: (A) control starch; (B) starch extracted by refluxing with 75/25 *n*-propanol/water.

lipid-extracted (reflux), and an intermediate sample (19% moisture, ethanol only CFE). The results are shown in Fig. 4. As a reference to illustrate the large increase in viscosity due to increased solids concentration, the control starch curve at 5% solids (corresponding to the solid line in Fig. 1) has been included. Although the control starch still has a higher peak viscosity, the effects of higher concentration coupled with the corresponding rigidity of the lipid-extracted samples can be seen. Note how the reflux-extracted sample forms a plateau rather than a peak viscosity, because the more rigid swollen granules are more resistant to shear-induced breakdown than the larger, softer, granules of the control. The CFE sample shows intermediate behavior consistent with its partial lipid extraction. Granule swelling is reduced relative to the control, resulting in a lower peak viscosity, and shear-induced breakdown (see Fig. 4, $t > 13$ min) is much larger than the refluxed sample due to lower granule rigidity.

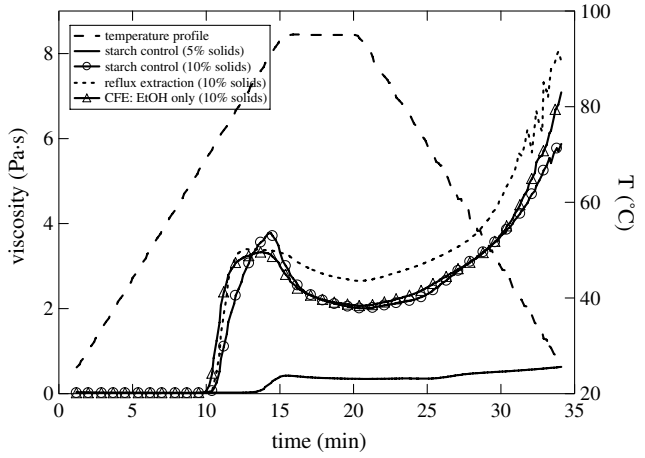

Fig. 4. Pasting profiles of cornstarch samples at 10% solids concentration. The starch control at 5% solids concentration is shown as the solid line.

In the setback region of this pasting profile ($t > \sim 20$ min), there is very little difference in the shape of the three high concentration samples. Viscosity increase in this region is due to both increased granule rigidity and to amylose that has leached out of the swollen granules and then formed an elastic gel network. At the end of the pasting profile, the relationship between the amount of lipid-extracted and the viscosity in the setback region was the opposite of what was observed at 5% starch solids. Vasanthan and Hoover (1992) showed that defatted cornstarch has increased amylose leaching relative to native cornstarch. This increased amount of leached amylose, in conjunction with the higher starch concentration and increased granule rigidity, are most likely the reasons for the trend in pasting viscosity at the conclusion of the pasting profile. The appearance of these pasted starch granules viewed by phase contrast microscopy was fully swollen for the control starch and incompletely swollen for both the CFE and reflux-extracted sample; these are shown in Fig. 5.

One of the goals of this work was to see if the changes between the samples observed in the setback region of the pasting curves (where retrogradation begins) would become more pronounced with time. During retrogradation, free amylose that has been leached from the swollen starch granules recrystallizes to form a gel network. The extent of amylose recrystallization during retrogradation can be obtained by measuring G′ (the shear storage modulus) as a function of time. Retrogradation experiments were carried out for the 5% starch samples in order to reduce the interaction effects of closely packed granules. Since the retrogradation experiments apply a very small amplitude oscillatory shear to the starch slurry, the results reveal information about the extent of free amylose recrystallization in forming a gel network and minimize the issue of granule rigidity.

Figs. 6 and 7 show the results for 5% starch samples at 10% and 19% initial moisture content, respectively. For

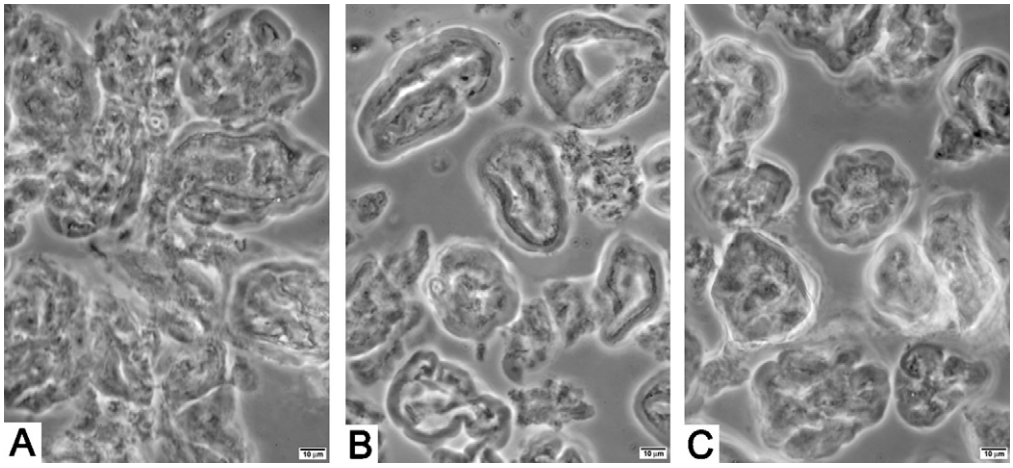

Fig. 5. Phase contrast microscopy images of pasted cornstarch samples at 10% solids concentration. (A) Control starch; (B) 10% moisture content starch CFE with 100% ethanol; (C) starch extracted by refluxing with 75/25 *n*-propanol/water. Samples were dispersed in water for photographing; therefore, spatial density of granules seen here is not representative of that during or after the pasting experiments.

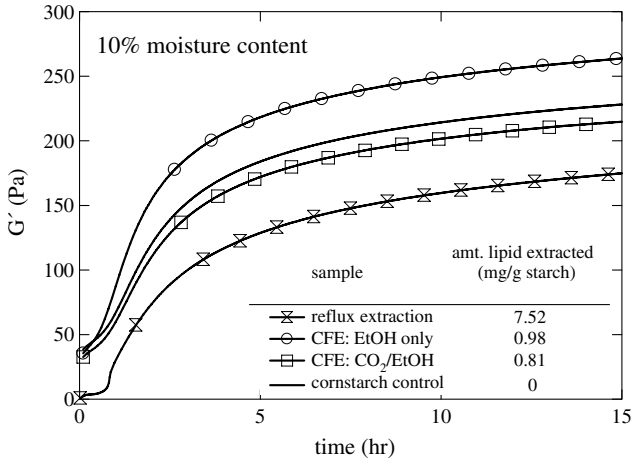

Fig. 6. G′ vs. time for cornstarch samples at 5% concentration and 10% initial moisture content.

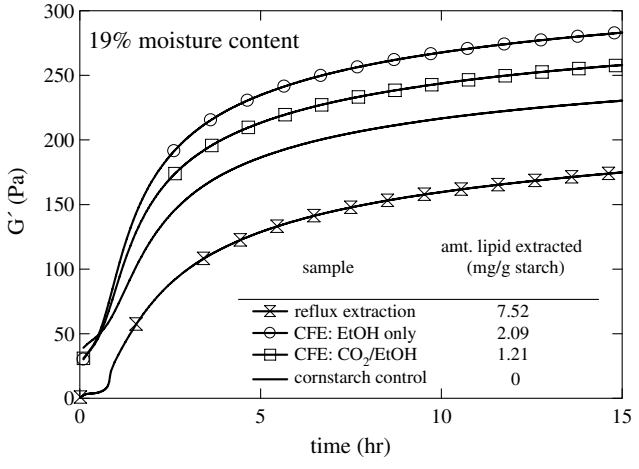

Fig. 7. G′ vs. time for cornstarch samples at 5% concentration and 19% initial moisture content.

Fig. 6, there is no clear trend relating the amount of lipid-extracted and G′. The previous discussion suggests that as the degree of lipid extraction from the starch granule increases, amylose-lipid complex formed in the granule decreases, and thus more amylose is available to be leached out of the granule and consequently recrystallize and increase G′ during retrogradation. This does not explain why the sample extracted by refluxing *n*-propanol/water, having the highest degree of lipid extraction, shows the lowest G′ value. However, the low G′ seen for the sample extracted by refluxing *n*-propanol/water can be attributed to the high temperature and available water present during the refluxing procedure allowing a more extensive degree of intragranular amylose crystallization, which both reduces swelling and restricts amylose leaching. The 19% initial moisture starch samples shown in Fig. 7 follow the predicted behavior and G′ increases with increased lipid extraction for the CFE samples.

Heat–moisture treatment is a technique used to physically modify starch without gelatinization or any other observable external change to the granule's shape, size, or birefringence; it is commonly used to form "resistant" starch for reduced caloric impact in foods (Annison & Topping, 1994). This process occurs in starches when they are held at temperatures above their gelatinization point but without sufficient water to gelatinize (<30% moisture). Typically it is detected by changes in the starch crystallinity as determined by X-ray diffraction. It also results in a more consistent paste viscosity profile and a reduction in the peak viscosity of the starch (Stute, 1992). There was some concern that heat–moisture treatment of the starch might be occurring during the CFE procedure and influencing the pasting results, since the CFE chamber was held at 80 °C (the gelatinization point of cornstarch is ~65 °C) and the moisture content of the two starch samples were 10% and 19% (insufficient water to cause gelatinization). To determine if the heat–moisture effect was occurring in our CFE

experiments, a separate experiment was carried out in which temperature and pressure conditions were set identically to those of the CFE extractions in Table 1 (80 °C and 8000 psi), and 19% moisture content starch was pressurized using CO_2 in the absence of ethanol co-solvent, so as not to alter the moisture content of the starch (Chen & Rizvi, 2005). The sample was held for 60 min instead of the usual 20, and the solvent flow was reduced to virtually zero, so that native lipid would not be extracted. As seen in Fig. 8, the pasting properties were not affected by this procedure, and thus the pasting differences seen in Figs. 1 and 2 are not caused by a heat–moisture effect and can be attributed to the extraction of native lipid from the starch. As an additional test for the heat–moisture effect, X-ray powder diffraction patterns were taken for the 19% moisture starch control and for both CFE (CO_2/EtOH and EtOH only) samples. Fig. 9 shows that the X-ray diffraction patterns were the same for all three samples, indicating the characteristic A-type pattern usually seen for normal cornstarch. Since our CFE apparatus was operating at 80 °C, this behavior is consistent with the findings of Le Bail et al. (1999), who found that structural transitions (i.e., heat–moisture treatment) in 19% moisture cornstarch only began at temperatures >100 °C.

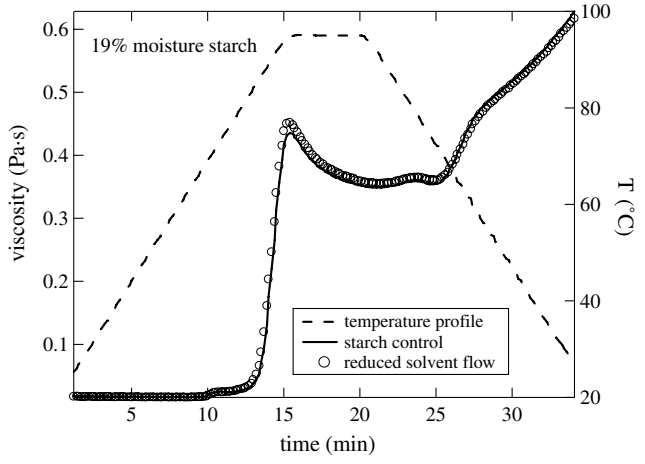

Fig. 8. Results of the heat–moisture treatment test.

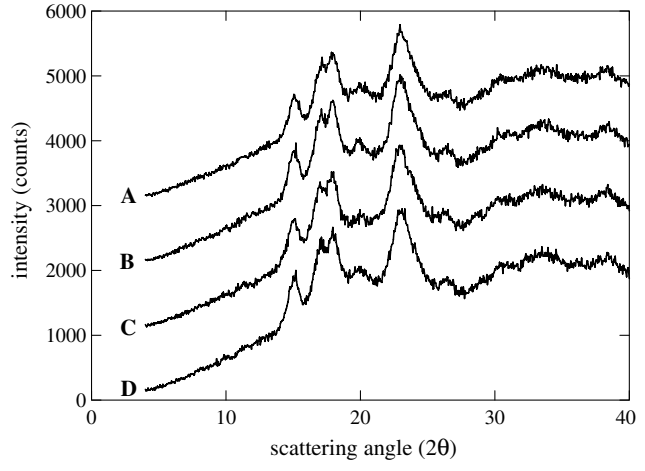

Fig. 9. X-ray diffraction results of cornstarch samples (traces have been vertically shifted for clarity): (A) CFE with 100% ethanol; (B) CFE with 80/20 CO_2/ethanol; (C) extracted by refluxing with 75/25 *n*-propanol/water; (D) starch control.

4. Conclusions

CFE of cornstarch lipids was examined and compared with refluxing 75/25 *n*-propanol/water extraction. CFE under the conditions tested resulted in incomplete lipid extraction and was not selective with respect to any particular lipid type. CFE improved when the initial moisture content of cornstarch was raised to 19% and pure ethanol was used as the solvent compared to a co-solvent system of 80/20 CO_2/ethanol.

Extracting lipids from cornstarch reduced the swelling and deformability of cornstarch granules during pasting. Two factors affected the pasting viscosity of the starch slurry for lipid-extracted starch granules: starch granule swelling size and free amylose crystallization during retrogradation. For starch slurries that had a high enough starch solids concentration (10% w/w), granule rigidity was a third factor that affected pasting viscosity. At 5% concentration where there is enough interstitial water to separate the individual swollen granules, the reduced swelling of the lipid-extracted starch granules relative to native starch caused reductions in the peak viscosity region of the pasting profile. At 10% concentration, the paste viscosity of defatted cornstarch relative to the control in the peak viscosity region was notably higher. Evidence of high granule rigidity for the completely defatted sample was shown by a plateau rather than a peak viscosity, and reduced breakdown of the swollen granules. A sample that had undergone partial lipid extraction by ethanol CFE showed an intermediate pasting profile as would be expected, i.e., a plateau-like viscosity was observed, however, breakdown of swollen granules was more pronounced than the fully extracted sample, since granules were more swollen and less rigid.

Retrogradation experiments carried out on low starch concentration samples at 19% initial moisture content show that for the CFE samples, retrogradation increased with amount of lipid-extracted. As more lipids are extracted, less amylose is contained in amylose-lipid complexes within the granule and thus more is available to be leached out. The increase in free amylose leads to more gel formation in the slurry and a higher degree of retrogradation. The fully defatted sample does not follow this trend because during refluxing with 75/25 *n*-propanol/water, high heat and available water lead to a larger amount of intragranular amylose becoming mobile enough to retrograde. This forms a network which prohibits swelling during the pasting procedure, slowing amylose diffusion out of the granule, and ultimately leading to less free amylose and reduced retrogradation.

An experiment that tested the possibility of heat–moisture effects taking place during CFE was carried out and found to be negative, so that differences in pasting viscosity in this work can be attributed to differences in lipid content

of the starch. X-ray diffraction data also confirmed that no significant changes in starch crystallinity were occurring during the heat–moisture treatment test.

The partial, nonselective removal of lipids from cornstarch by CFE with ethanol and ethanol/CO_2 provides starch granules with potentially useful pasting properties that differ from those of both native and fully lipid-extracted starch. This technique can therefore facilitate various starch studies as a function of native lipid present. For example, spherocrystal formation in jet-cooked cornstarches is an interesting phenomenon in which the native lipid plays an important but not yet fully understood role. A partially defatted cornstarch sample may lead to a better understanding of the role native lipids play in spherocrystal formation. Other solvent systems will also be explored to determine their efficacy and help extend the variability of lipid extraction available for cornstarch.

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