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Steam jet cooking of high-amylose starch–fatty acid mixtures. An investigation of complex formation☆

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Abstract

We have investigated the formation of helical inclusion complexes when aqueous mixtures of high-amylose starch and lauric, myristic, palmitic and stearic acids are processed by steam jet cooking at 140°C. The amount of free fatty acid that complexes with amylose was compared with the amount complexed when the fatty acid was present in its water-dispersible, sodium salt form. Air-dried and finely-ground products prepared from lauric and myristic acids and their sodium salts were extracted to remove uncomplexed fatty acid. A quantitative Fourier transfrom infrared spectroscopic (FTIR) method, based upon absorption of the carboxylic acid carbonyl, was then developed to determine the amount of complexed fatty acid remaining in the product. For both of these fatty acid systems, only small differences in complex formation were observed between the free acid and the sodium salt. Although water solubility of these fatty acids is negligible at room temperature, solubility is apparently sufficient for complex formation under the high-temperature, high-shear conditions of the steam jet cooking process. Products prepared from lauric, myristic, palmitic and stearic acids and their respective sodium salts were also examined by X-ray diffraction. This technique confirmed the results obtained by FTIR and also showed that differences between free acid and sodium salt become more pronounced as the fatty acid increases in molecular weight, and water solubility is reduced. For the stearic acid system, complexation of free acid was roughly half that observed with the sodium salt.

Keywords: Starch–fatty acid mixtures; Complex formation; Steam jet cooking; Lauric acid; Myristic acid; Palmitic acid; Stearic acid

1. Introduction

Steam jet cooking has been used commercially for decades to prepare aqueous starch solutions for industrial applications (Klem and Brogly, 1981). The high temperature and intense mechanical shear of the jet cooking process completely dissolves granular starch and also reduces its molecular weight (Dintzis and Fanta, 1996; Klavons et al., 1997). The co-jet cooking of starch with non-starch materials is a relatively new area of research that is currently being investigated at our Center as a rapid and continuous method for preparing new starch-based products and derivatives. For example, we have examined the co-jet cooking of starch with salts of poly(ethylene-*co*-acrylic acid) (Christianson et al., 1992; Fanta et al., 1992) and with polycaprolactone (Shogren, 1993), and have obtained evidence that helical inclusion complexes are formed during the cooking process. We have also studied the jet cooking of aqueous mixtures of starch and lipid (e.g., vegetable oil) and have observed that the process of jet cooking converts the lipophilic component into droplets about 1–10 μm in diameter (Fanta and Eskins, 1995; Eskins et al., 1996). Although jet-cooked dispersions typically contain 20–30% lipid by weight, the lipophilic component does not separate or coalesce, even after prolonged standing or drying.

The present study was carried out to determine the nature of the product formed when a high-molecular-weight fatty acid, in its carboxylic acid form, is co-jet cooked with high-amylose starch. Although the literature contains numerous references to the formation of helical inclusion complexes when water solutions of starch, particularly amylose, interact with fatty acids in their water-dispersible, alkali metal salt forms (e.g., Karkalas and Raphaelides, 1986), the relatively water-insoluble free fatty acids have been studied to a much lesser extent. Examples of investigations using free fatty acids are those of Mercier et al. (1980) and Bhatnagar and Hanna (1994a)Bhatnagar and Hanna (1994b)Bhatnagar

☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name of USDA implies no approval of the product to the exclusion of others that may also be suitable.

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and Hanna (1996), in which starch–fatty acid complexes were prepared by extrusion cooking. Liu et al. (1997) also investigated complex formation between lauric acid and gelatinized pea starch. A major factor governing the formation of complexes is the solubility/dispersibility of the fatty acid in water; and this, in turn, depends upon variables such as temperature and fatty acid molecular weight. In this report we examine the extent of complex formation when high-molecular-weight fatty acids having only slight water solubility interact with high-amylose starch under the high-temperature, high-shear conditions encountered during steam jet cooking. Complex formation is compared with that observed for the same fatty acids in their sodium salt form.

2. Materials and methods

2.1. Materials

Starch was Amylomaize VII (amylose content about 70%) from Cerestar (formerly American Maize Products Co.), Hammond, IN. Dextran (industrial grade, average molecular weight of $5–40 \times 10^6$) was purchased from Sigma Chemical Co., St. Louis, MO. Moisture content of the polysaccharides was determined by weight loss on drying at 100°C under vacuum over P_2O_5. Lauric, myristic, palmitic and stearic acids and their sodium salts were also obtained from Sigma Chemical Co. Purities were 99% or greater.

2.2. Steam jet cooking

Mixtures were prepared from 100.0 g (dry basis) of starch, 1000 ml of deionized water and 10.0 g of lauric acid. Other fatty acids and their sodium salts were used in amounts corresponding to the molar equivalent of 10.0 g of lauric acid. Fatty acid salts were dispersed in water at room temperature. The sodium salt of lauric acid dissolved/dispersed readily. The myristic acid salt was slower to disperse, and the palmitic and stearic acid salts remained largely as discrete particles. Fatty acids in their free acid form were blended with water that was first heated to a temperature sufficient to melt the acid. Aqueous starch–fatty acid dispersions were passed through a Penick & Ford laboratory model continuous steam jet cooker (Penford Corp., Cedar Rapids, IA). The jet cooker was operated under excess steam conditions with a steam line pressure of 70 psig. Cooking was carried out at 140°C (40 psig steam within the hydroheater) with a pumping rate of about 1 l min^{-1}. Cooked dispersions were collected in a Dewar flask to maintain their temperature at about 90–95°C. Dispersions were fluid when hot but rapidly increased in viscosity as they were allowed to cool. Percentage of solids, determined by freeze drying weighed portions of each cooked dispersion, ranged from 8.5 to 9.4% and were somewhat less than theoretical due to dilution by condensed steam during the cooking process. The pH of cooled dispersions ranged from 8.6 to 9.7 when fatty acid sodium salts were used, and from 4.0 to 4.4 for dispersions prepared from the free acids. Hot, jet-cooked dispersions were poured onto polyethylene sheets and allowed to dry in air. The resulting film fragments were pulverized in a small reciprocating ball mill (Wig-L-Bug Amalgamator, model 311OB, Crescent Dental Mfg. Co., Lyons, IL) and were sieved to pass 150 mesh.

2.3. Solvent extraction

Solutions used for extraction were prepared by adding 2 ml of 1.2 N HCl to 100 ml of either methanol, ethanol, isopropanol, acetone or tetrahydrofuran (THF); and 0.5–0.6 g of pulverized starch–fatty acid product was added. The mixture was stirred slowly at room temperature for about 24 h, and the solid was separated by filtration. The solid was then extracted a second time by stirring for about 3 h with 100 ml of fresh solvent (not acidified), and about 100 mg of the twice-extracted solid was allowed to dry in air for analysis by Fourier transform infrared spectroscopy (FTIR). The remaining material was then subjected to two additional extractions with chloroform (4 h stirring with 100 ml, and then overnight stirring with 50 ml). The extracted solid was allowed to dry in air and was analyzed for fatty acid by FTIR. Extractions of free fatty acid products with chloroform only were carried out using the same sequence of steps.

2.4. Determination of fatty acids by FTIR

FTIR standards containing known amounts of lauric and myristic acid were prepared by adding accurately weighed amounts of fatty acid and corn starch (that had previously been jet-cooked and drum-dried) to hot (90–100°C) water. Normal food-grade corn starch (amylose content about 25%) was used for these preparations to minimize retrogradation and to maximize the dispersibility of jet-cooked starch in the hot aqueous mixtures. Mixtures were stirred for 2 min in a Waring blender at the highest speed, and the resulting dispersions were poured onto polyethylene sheets and allowed to dry in air to yield brittle films. Five standards were prepared for each fatty acid. Weight percentage of lauric acid in these standard mixtures, calculated from the initial dry weights of lauric acid and starch, varied from 1.02 to 9.32%. Myristic acid percentages varied from 1.05 to 9.46%.

To prepare samples for FTIR analysis, about 100 mg of sample was pulverized at liquid nitrogen temperature in a Crescent Wig-L-Bug Amalgamator; and the resulting product was allowed to warm to room temperature. About 1 mg of this product, weighed to the nearest 0.01 mg, was mixed with 300 mg of powdered KBr (item no. 0016-015, Spectra-Tech, Inc., Stamford, CT); and the mixture was pressed into a disk at 100 000 psi using a 12.5 mm die. Spectra were

obtained on a Nicolet Impact 410 Fourier Transform Infrared Spectrometer (Nicolet Instrument Corp., Madison, WI). Carbonyl absorbance in the 1705 cm^{-1} region was used to quantify weight% fatty acid. The height of the carbonyl peak was determined from a baseline established from valleys on either side of the carbonyl. For example, 1693 and 1731 cm^{-1} were the baseline points for a typical 1% starch–myristic acid spectrum. Although bands attributed to corn starch showed large variations in intensity with the particle size of the sample (Fanta and Salch, 1991), carbonyl absorbance was less sensitive to sample preparation technique. Absorbance of the fatty acid carbonyl was normalized to equal that obtained from 1.00 mg of sample, and weight% fatty acid in the sample was then calculated from standard curves generated from FTIR analyses of known starch–fatty acid mixtures. For each fatty acid, three replicate determinations were run for each of the five standard mixtures. Quadratic regression analysis gave the best data fit for starch–lauric acid standards; whereas a power series regression gave the best fit for myristic acid. For most samples, two or three replicate determinations were carried out; and the results were averaged. Sample size was not sufficient for additional replications.

Although standard deviations were not determined for each FTIR analysis, standard deviations were calculated for analyses run on the five starch–myristic acid standards. KBr pellets were prepared from these standards by three different procedures that were chosen to cause variations in both moisture content and particle size. In addition to the method of pellet preparation described in the preceding paragraph, the following methods were also used: (1) samples were ball-milled at room temperature instead of at liquid nitrogen temperature; and (2) samples were ball-milled at liquid nitrogen temperature but milling and pellet preparation were carried out under high-humidity conditions (i.e., conditions where powdered KBr absorbed enough water from the atmosphere to noticeably affect its flow properties). For each method of pellet preparation, three replicate determinations were carried out to give a total of nine determinations for each myristic acid standard. The following standard deviations were calculated for the nine determinations carried out on each of the five myristic acid (MA) standards: 9.46 ± 0.77% MA; 7.29 ± 0.74% MA; 4.98 ± 0.33% MA; 2.55 ± 0.27% MA; and 1.05 ± 0.09% MA.

2.5. X-ray diffraction

Powdered samples (pulverized to pass 150 mesh) were equilibrated at 23°C and 45% relative humidity for 2 days prior to analysis. X-ray powder diffraction analyses were performed with a Philips 1820 diffractometer operated at 40 kV, 30 mA with graphite-filtered Cu K_α radiation and a θ compensating slit. Data were acquired in $2\theta = 0.05°$, 4 s steps. Areas of the diffraction peaks were determined by cutting and weighing.

3. Results and discussion

To maximize complex formation, we used a commercially available corn starch having an amylose content of approximately 70%. The fatty acids used in this study were lauric (C_{12}), myristic (C_{14}), palmitic (C_{16}) and stearic (C_{18}). These fatty acids have water solubilities of 0.0055, 0.0020, 0.00072 and 0.00029 g/100 g at 20°C, respectively (Pryde, 1978).

Dispersions for steam jet cooking were prepared by dispersing starch and fatty acid in water at temperatures sufficient to melt the acid but not high enough to cause starch granule swelling. Melting points of lauric, myristic, palmitic and stearic acid are 44, 58, 63 and 72°C, respectively. Sodium salts of fatty acids were dispersed in water at room temperature. Although free fatty acids lowered the pH of jet-cooked dispersions to 4.0–4.4, earlier work (Dintzis and Fanta, 1996) showed that acid hydrolysis of starch during steam jet cooking is minimal at this pH. After steam jet cooking, dispersions were allowed to dry in air to yield the products as brittle films, which were then ground to pass 150 mesh. To determine the extent of complex formation in products prepared from lauric and myristic acid, selective solvent extraction was first used to remove uncomplexed fatty acid. Unextractable fatty acid remaining in the product was assumed to be complexed within the starch helix and was determined by FTIR. FTIR analysis was used instead of iodine binding capacity (Liu et al., 1997; Colburn and Schoch, 1964), because the presence of complexed fatty acid in the product could be unequivocally established by its carbonyl absorption in the 1705 cm^{-1} region.

Products examined initially were those prepared from fatty acids in their sodium salt forms, since complexation of amylose with water-dispersible fatty acid salts is known to occur readily. To facilitate the extraction of uncomplexed fatty acid salts with organic solvents, sodium salts were converted to free acids by using HCl-acidified solvents (methanol, ethanol, isopropanol, acetone or tetrahydrofuran) for the first extraction. Products were then extracted with chloroform. Extraction results for products prepared from lauric and myristic acid salts are shown in Table 1. Methanol, ethanol and tetrahydrofuran apparently dissolve complexed as well as uncomplexed fatty acid, since FTIR spectra showed that fatty acid was completely removed from the products by these acidified solvent systems, prior to chloroform extraction. Extraction of complexed lipophilic material from starch with polar solvents is well documented (e.g., Morrison and Coventry, 1989). Significant amounts of complexed fatty acid still remained in the products after extraction with acidified isopropanol and acetone, and further extraction with chloroform removed little or no additional fatty acid. In agreement with published reports (Karkalas and Raphaelides, 1986; Hahn and Hood, 1987), data in Table 1 suggest that lauric acid is more easily extracted than myristic acid.

Extraction results for products prepared from lauric and

Table 1
Solvent extraction of starch–lauric acid (Na^+) and starch–myristic acid (Na^+) products

Solvent	Lauric acid		Myristic acid	
	Amount in product after extraction (wt%)[a]	Molar ratio, FA/AGU[b]	Amount in product after extraction (wt%)[a]	Molar ratio, FA/AGU[b]
MeOH (HCl); $CHCl_3$	0	—		
EtOH (HCl); $CHCl_3$	0	—	0	—
i-PrOH (HCl); $CHCl_3$	2.6 (8.8%)	0.031	4.2 (15.8%)	0.044
Acetone (HCl); $CHCl_3$	0	—	2.6 (15.2%)	0.027
THF (HCl); $CHCl_3$	0	—	0	—

[a]Average of two determinations by FTIR (number in parentheses is the % difference between these two determinations).
[b]Moles of fatty acid per anhydroglucose unit of amylose (MW = 162), assuming that amylose comprises 70%, by weight, of the starch sample.

myristic acids in their free acid forms are shown in Table 2. It is interesting that FTIR analyses of these products prior to extraction showed that fatty acid contents were significantly less than the calculated amounts, based on initial weights of starting materials. For the lauric acid product, the weight percentages of fatty acid calculated and found were 9.09% and 5.5%, respecively. For myristic acid, these percentages were 10.23% and 6.8%. A logical explanation for these results is that some separation of the organic phase (i.e., melted fatty acid) from the aqueous starch phase occurs before the mixture reaches the hydroheater, where the cooking process takes place. Less than theoretical recovery of the lipophilic component was also observed by Knutson et al. (1996), when starch was co-jet cooked with soybean oil. Extraction of air-dried products with either isopropanol/HCl followed by chloroform, or with chloroform alone, yielded products that contained 3–5% residual fatty acid. These results are not greatly different from those reported in Table 1 for products prepared from the corresponding fatty acid sodium salts. Even though water solubilities of free fatty acids are negligible at room temperature, it thus appears that complex formation can still take place under the high-temperature, high-shear conditions of the steam jet cooking process. Complex formation is driven by the lower free energy of the fatty acid inside the hydrophobic interior of the starch V-type helix (see below) than in aqueous solution or pure melt.

The ability of solvents to extract uncomplexed fatty acid from starch/fatty acid compositions was tested by extracting an analagous series of products prepared from dextran instead of starch. Dextran, like starch, is a polyglucan; however, the alpha-1,6 linkage in dextran does not allow formation of the helical configuration that is necessary for complex formation, and fatty acids should thus be readily extractable. As expected, all solvent systems used to extract starch-based products completely removed fatty acids from the corresponding dextran-based materials.

Karkalas and Raphaelides (1986) have calculated the number of moles of fatty acid per anhydroglucose unit (AGU) that can theoretically saturate the amylose helix. Saturation molar ratios for lauric acid were either 0.077 or 0.066 moles per AGU, based upon whether the complex has six or seven glucopyanose groups per helical turn. The corresponding ratios for myristic acid were 0.067 and 0.058. In agreement with these calculations, the lauric acid/AGU mole ratio experimentally determined by Karkalas and Raphaelides was 0.068 for a complex prepared by adding the potassium salt of lauric acid to a dilute KOH solution of amylose. Molar ratios in Tables 1 and 2 are lower than these theoretical ratios and suggest that some complexed fatty acid may have been removed from our products along with uncomplexed acid by solvent extraction. This, however, should not affect the conclusions reached by comparing extractions carried out under the same experimental conditions. Molar ratios for myristic acid in these tables are closer to the theoretical values, suggesting that lauric acid is more easily removed from the complex than myristic acid.

X-ray diffraction (XRD) was also used to examine the formation of complexes in these starch–fatty acid systems. This study was carried out not only with products prepared

Table 2
Solvent extraction of starch–lauric acid (H^+)[a] and starch–myristic acid (H^+)[b] products

Solvent	Lauric acid		Myristic acid	
	Amount in product after extraction (wt%)[c]	Molar ratio, FA/AGU[d]	Amount in product after extraction (wt%)[c]	Molar ratio, FA/AGU[d]
i-PrOH (HCl); $CHCl_3$	3.7 (6.5%)	0.044	3.6 (0.8%)	0.038
$CHCl_3$ (no HCl)	3.9 (13.2%)	0.047	4.6 (15.5%)	0.049

[a]Wt% lauric acid in unextracted product = 5.5% (average of two determinations by FTIR; 14.2% difference between these two determinations).
[b]Wt% myristic acid in unextracted product = 6.8% (average of two determinations by FTIR; 5.3% difference between these two determinations.
[c]Average of two determinations by FTIR (number in parentheses is the % difference between these two determinations).
[d]Moles of fatty acid per anhydroglucose unit of amylose (MW = 162), assuming that amylose comprises 70%, by weight, of the starch sample.

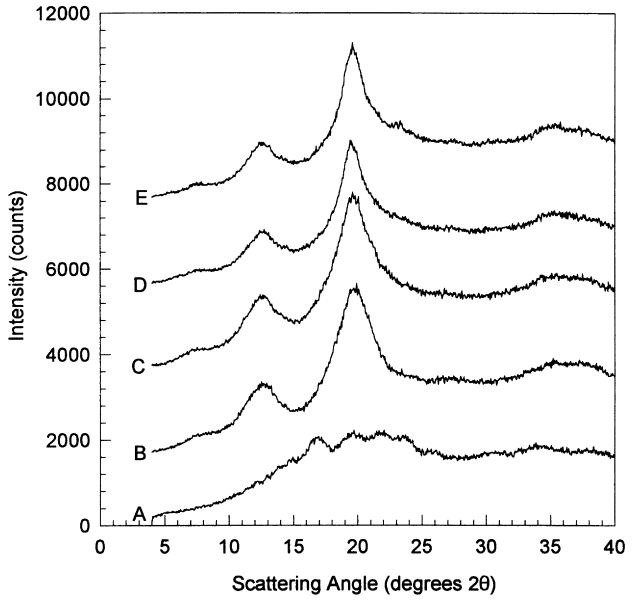

Fig. 1. X-ray diffractometer scans of jet-cooked, air-dried samples: (A) high-amylose corn starch (HACS); (B) HACS–lauric acid (Na^+); (C) HACS–myristic acid (Na^+); (D) HACS–palmitic acid (Na^+); (E) HACS–stearic acid (Na^+).

from lauric and myristic acids and their sodium salts, but also with analagous products prepared from palmitic and stearic acids. X-ray powder diffraction scans of products prepared from fatty acid salts and from free fatty acids are shown in Figs. 1 and 2, respectively. A scan of a sample of high-amylose starch, after jet cooking and air drying, is also shown in Fig. 1. This scan shows maxima at $2\theta =$ 16.7, 21.9 and 23.8°, a pattern typical of the B-type starch crystal structure (Zobel, 1988). A maximum at 19.7° is also

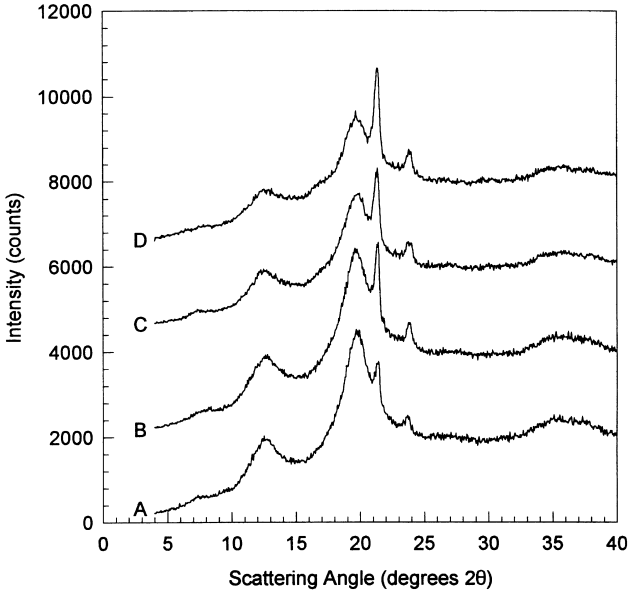

Fig. 2. X-ray diffractometer scans of jet-cooked, air-dried samples: (A) HACS–lauric acid (H^+); (B) HACS–myristic acid (H^+); (C) HACS–palmitic acid (H^+); (D) HACS–stearic acid (H^+).

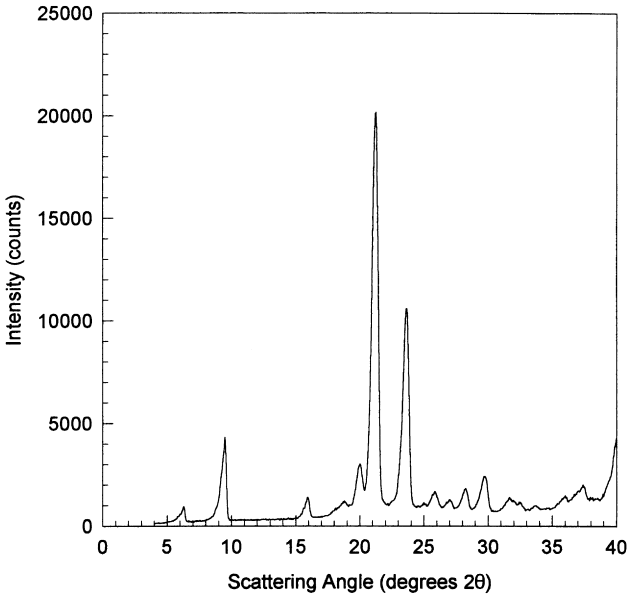

Fig. 3. X-ray diffractometer scan of lauric acid.

apparent and represents V-type inclusion complexes of amylose with naturally occurring lipid material. XRD patterns of samples prepared from sodium salts of fatty acids had maxima at 7.4, 12.4 and 19.7°. The peaks in Fig. 1 are characteristic of V-hydrate type crystals, in which the fatty acid salt has formed an inclusion complex with amylose (Zobel, 1988). With fatty acid salts, there is little change in the degree of complexing with change in fatty acid chain length, as reflected by the relative areas of the 12.4° peak (Table 3). With free fatty acids, however, Fig. 2 shows that the area of the maximum at 12.4° (and hence the amount of complex) decreases almost in half as the number of carbons in the free fatty acid increases from 12 to 18 (Table 3). This is no doubt due to the greater hydrophobicity and lower solubility in water of the longer-chain fatty acids, and hence their tendency to remain as a separate phase. This is confirmed by the sharp peaks at 21.4 and 23.8°, which increase in area as fatty acid chain length increases, and reflect the presence of pure crystalline fatty acid (see Fig. 3). Comparing intensities of the 21.4° peak in Figs. 2 and 3, it is clear that relatively little of the fatty acid has crystallized. This implies that some of the longer-chain fatty acids may be non-specifically associated with the starch.

Table 3
Effect of fatty acid chain length and ionization on complex formation: X-ray diffraction results

Fatty acid chain length	Relative areas of 12.4° peak	
	Starch–fatty acid (Na^+)	Starch–fatty acid (H^+)
12	100	100
14	103	91
16	85	72
18	92	51

Finally, it is noted that X-ray patterns of high-amylose starch with fatty acid salts and with free fatty acids (Figs. 1 and 2, respectively) are the same, indicating that both form V-hydrate complexes.

4. Conclusions

Lauric acid, myristic acid, palmitic acid and stearic acid form helical inclusion complexes with high-amylose corn starch, when aqueous two-phase mixtures of starch and fatty acid are processed by steam jet cooking at 140°C. Although the water solubility of these fatty acids is negligible at room temperature, complex formation takes place under the high-temperature, high-shear conditions encountered in the steam jet cooker.

The complexing ability of free fatty acids has been compared with that of the corresponding fatty acid sodium salts, which complex readily with amylose because of their relatively high water solubility. FTIR was used to determine the amounts of complexed lauric and myristic acids in jet-cooked products. Products prepared from each fatty acid and its sodium salt were also analyzed by X-ray diffraction. Although lauric acid and myristic acid complex with amylose to about the same extent as their respective sodium salts, differences between free acid and sodium salt become more pronounced as the fatty acid increases in molecular weight, and water solubility is reduced. For the stearic acid system, complexation of free acid is roughly half that observed with the sodium salt.

Complexed products are easily and economically prepared by the continuous process of steam jet cooking. We are currently investigating end-use applications for these materials in food products, cosmetics, adhesives and drug-delivery systems.

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