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Carbohydrate Polymers 46 (2001) 29–38

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Starch–paraffin wax compositions prepared by steam jet cooking. Examination of starch adsorbed at the paraffin–water interface ☆

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Received 30 March 2000; revised 7 July 2000; accepted 10 July 2000

Abstract

Starch–paraffin wax compositions were prepared by passing aqueous two-phase mixtures of cornstarch and paraffin wax through a steam jet cooker under excess steam conditions. Jet cooking converts the paraffin wax to micron-sized droplets that remain suspended in the aqueous dispersion and do not coalesce, due to an adsorbed layer of interfacial starch that surrounds each droplet. Solidified droplets of starch-coated paraffin wax were isolated by dilution of jet cooked dispersions with excess water followed by centrifugation. Wax droplets, having specific gravity lower than that of water, were collected from the dispersion surface, washed with water, and dried. Weight percent interfacial starch in isolated wax droplets was calculated from the weight of residual starch remaining after removal of paraffin wax by extraction with cyclohexane. Starch percentages varied from about 3–8%, depending upon whether waxy, normal, or high amylose starch was used, and whether jet cooked dispersions were diluted with hot or cold water prior to centrifugation. The effect of small amounts of lipid material (normally present in cereal starches) on weight percent interfacial starch was determined by examining products prepared from starch that was solvent-extracted to remove the lipid component (i.e. defatted). Although defatted normal cornstarch produced a product having a lower percentage of interfacial starch than a comparable product prepared from starch that still contained native lipid, defatting had little effect when waxy starch was used. The morphology of the starch layer, as observed by SEM, was affected by the presence or absence of lipid in the starting starch. Amylose was preferentially adsorbed at the paraffin–water interface when native lipid was present in the starting starch, suggesting that lipid enhances the adsorption of amylose through the formation of helical inclusion complexes. X-ray diffraction patterns of interfacial starch were consistent with this interpretation and showed the V_h-pattern commonly attributed to amylose–lipid complexes. Nitrogen analyses suggested that proteins, present in cornstarch in small amounts, may also adsorb along with starch at the paraffin–water interface.

Keywords: Starch–oil composites; Oil–water interface; Steam jet cooking

1. Introduction

Steam jet cooking is a rapid and continuous process that has been used for decades to prepare aqueous starch solutions for industrial applications (Klem & Brogly, 1981). As part of a continuing research program on starch utilization, we are studying new starch-based compositions prepared by jet cooking mixtures of starch with other materials, such as natural gums, fatty acids, polymers, oils and lipids. Compositions prepared by jet cooking two-phase mixtures of starch and lipophilic materials, such as vegatable oil, are currently under investigation. Previous work (Eskins, Fanta, Felker & Baker, 1996; Fanta & Eskins, 1995), has shown that the high temperature and intense mechanical shear of the steam jet cooking process not only dissolves starch, but also converts the lipid component into micron-sized droplets that do not phase-separate and coalesce, even after prolonged standing or drying. The preparation, properties and commercial applications of these new compositions are summarized in a recent review (Fanta & Eskins, 1998).

We have determined that the resistance of these starch–lipid compositions to droplet coalescence is caused by accumulation of starch at the lipid–water interface (Fanta, Felker, Eskins & Baker, 1999a). These interfacial starch films have been isolated as discrete entities, and their structures have been observed using both light- and scanning

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0144-8617/01/$ - see front matter
PII: S0144-8617(00)00279-4

electron microscopy (SEM) (Fanta et al., 1999a). We have suggested that starch accumulates at the interface because of the solution properties of starch in water and the known thermodynamic properties of aqueous polymer solutions at oil–water interfaces (Fanta et al., 1999a). The formation of polymer films at interfaces has been referred to in the literature as *prewetting* and is observed when the solvent for the polymer is relatively poor and when separation of a polymer from solution and its accumulation at an interface leads to a reduction in interfacial tension. Published research related to prewetting has been summarized previously (Fanta et al., 1999a).

This study addresses the formation and composition of these interfacial starch films. A low-melting paraffin wax was used as the lipophilic component in this study because droplets of melted paraffin wax solidify when cooled, thus facilitating their isolation and characterization. Specifically, we examined the amount of starch adsorbed at the paraffin–water interface with different cornstarch varieties and under different experimental conditions. The amylose content and X-ray diffraction patterns of these interfacial starch films was also examined. Since small amounts of lipid are normally present in commercial cornstarch samples, the effect of this native lipid on the formation and morphology of interfacial starch was also investigated. Finally, we have obtained preliminary evidence that protein, also present in cornstarch in small amounts, accumulates along with starch at the lipid–water interface.

2. Materials and methods

2.1. Materials

Normal, unmodified food grade cornstarch and waxy cornstarch (Waxy No. 1) were obtained from A.E. Staley Mfg. Co., Decatur, IL. High amylose cornstarch (Amylomaize VII) was a product of Cerestar, Hammond, IN. Percent moisture was determined by vacuum drying accurately weighed starch samples at 100°C, and all weights of starch are given on a dry weight basis. Paraffin wax (m.p. 61–65°C) was purchased from Aldrich Chemical Co., Inc. (catalog no. 32,720-4).

Starch samples were defatted by heating a stirred suspension of 130 g of starch in 85% methanol (1700 ml of methanol plus 300 ml of water) under reflux for 2 h. Starch was separated by filtration, and a second extracton was carried out under identical conditions. Two additional extractions were then carried out under the same conditions with refluxing 75% *n*-propanol/water (1500 ml of *n*-propanol plus 500 ml of water). The extracted starch was allowed to air dry for about 10 days and was further dried under vacuum at 55°C.

2.2. Preparation of starch–paraffin wax composites

A mixture of 40 g of paraffin wax and 1 l of water (heated to 75–80°C) was stirred at high speed in a Waring blendor for about 1 min, and 100 g of starch was added. The resulting stirred mixture was passed through a Penick and Ford Laboratory Model steam jet cooker, operating under excess steam conditions (Klem & Brogly, 1981). Cooking temperature was 140°C (back pressure: 40 psig steam), and steam line pressure was 70 psig. Pumping rate through the cooker was about 1 l/min. The cooked dispersion (solids content: about 10–11%) was collected in an insulated Dewar flask. The solids content varied because of dilution of the cooked dispersion with condensed steam. Jet cooked dispersions usually contained somewhat less than the theoretical percentage of paraffin wax, due to separation of wax from the aqueous mixture in the section of tubing leading from the pump to the hydroheater, where the jet cooking process takes place. The actual weight percent paraffin wax in these compositions was determined by freeze drying portions of the jet cooked dispersion and then heating weighed samples of dry solid in 0.5 N HCl for 1.5 h under reflux to hydrolyze the starch component. Wax was then extracted from the hydrolyzate with hexane, and the weight of wax was determined after evaporation of hexane.

2.3. Isolation of starch-coated wax droplets

Two previously used techniques (Fanta et al., 1999a) were used to prepare 20:1 dilutions of jet cooked dispersions for isolation of starch-coated wax droplets. *Hot Dilution* was carried out by adding hot, jet cooked dispersions, immediately after cooking, to water preheated to 100°C. Diluted dispersions were briefly stirred and were then allowed to stand and cool overnight to room temperature without stirring. In the *Cold Dilution* procedure, jet cooked dispersions were allowed to stand and cool overnight to room temperature without stirring. Cooled dispersions were then diluted with water at room temperature and were slowly stirred for 3 h. A third dilution method was also used to avoid the formation of gel in cooled dispersions prepared from defatted normal cornstarch. In this procedure, jet cooked dispersions were allowed to cool to about 35°C over a period of 2 h and were then diluted with room temperature water. Dispersions diluted by these three procedures were centrifuged at 5°C for 20 min at 3000 r.p.m (about $2000 \times g$) in a Beckman GS-6KR centrifuge. The upper layer of starch-coated wax droplets was separated, and this fraction was washed three times by suspending it in excess water and then centrifuging the resulting dispersion. The water-washed dispersion was then freeze dried, and the weight of dry, starch-coated wax droplets was determined.

2.4. Weight percent starch in coated wax droplets

An accurately weighed 1 g sample of the above freeze-dried solid was wet with sufficient ethanol to cover the sample. The ethanol-wet solid was allowed to stand for about 2 h and was then extracted repeatedly with cyclohexane to dissolve the paraffin wax component. A

Table 1
Characterization of starch-coated wax droplets. Comparison of cornstarch varieties and experimental conditions (N.D. = not determined)

Cornstarch type and dilution method	Replicate experiment	Fraction containing starch-coated wax droplets		
		Yield, % based on wax[a]	Starch content, weight percent	Weight percent of Amylose in interfacial starch[b]
Normal, cold dilution	1	18	7.0	34.0
	2	20	6.2	33.7
	3	13	7.7	38.9
Normal, dilution after 2 h	1	32	4.7	28.1
Normal (defatted) dilution after 2 h	1	33	3.1	15.3
Normal, hot dilution	1	53	3.1	36.4
	2	69	3.4	43.7
Waxy, cold dilution	1	63	3.8	N.D.
	2	70	3.5	N.D.
Waxy (defatted), cold dilution	1	54	3.6	N. D.
High amylose, hot dilution	1	66	5.4	N.D.
	2	76	5.4	N.D.

[a] For example, 18% yield means that 18%, by weight, of the total wax in the jet cooked product was recovered in this fraction.
[b] Normal, food grade cornstarch used for product preparation contained 21.6% amylose.

minimum of six extractions was carried out over a two-day period, and the starch solid remaining after extraction was freeze-dried from cyclohexane and weighed. The freeze-dried starch solid was allowed to air-equilibrate overnight prior to weighing, and the observed weight of starch was corrected for an assumed moisture content of 10%. Weight percent surface starch was then calculated from weight loss after cyclohexane extraction. About 1–3% paraffin wax, by weight, remained in interfacial starch samples after cyclohexane extraction, as estimated by FTIR spectroscopic analysis. To perform these analyses, we first obtained FTIR spectra of starch–paraffin wax mixtures of known composition. The starch component was subtracted from each spectrum, and a standard curve of absorbance at 2920 cm^{-1} vs. weight percent wax was constructed. This standard curve was then used to estimate the amount of paraffin wax in unknown samples. A small amount of residual wax was observed in all interfacial starch samples, and amounts did not change significantly when starches were defatted.

2.5. Nitrogen analysis and protein content of starch samples

Kjeldahl nitrogen analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN. Percent protein was estimated by multiplying %N by a factor of 6.25 (Wang & Johnson, 1992).

2.6. SEM of starch coatings

The method used for sample preparation was similar to that described previously (Fanta et al., 1999a). Water-washed dispersions of starch-coated paraffin wax droplets were added to excess absolute ethanol, and the solid was allowed to settle. The settled solid was washed with ethanol, critical point dried using supercritical CO_2, sputter-coated with gold–palladium, and examined with a JEOL 6400 V scanning electron microscope. To remove paraffin wax, a portion of the ethanolic sample was solvent exchanged, first with cyclohexane and then back into ethanol, prior to critical point drying.

2.7. X-ray diffraction of starch coatings

X-ray diffraction patterns of interfacial starch, isolated after removal of paraffin wax by cyclohexane extraction, were obtained as described previously (Fanta, Shogren & Salch, 1999b). Samples were isolated by freeze drying from cyclohexane and were equilibrated at 23°C and 45% relative humidity for 2 days prior to analysis.

2.8. Amylose content of interfacial starch

Freeze-dried samples of interfacial starch, obtained after extraction with cyclohexane to remove paraffin wax, were allowed to air equilibrate in open bottles for 1–2 days prior to analysis. Amylose was determined by measuring the absorbance of the amylose–iodine complex in 90% dimethylsulfoxide solution (Knutson, 1986). A phenol–sulfuric acid assay (Dubois, Gilles, Hamilton, Rebers & Smith, 1956; Knutson, 1997) was used to determine total carbohydrate.

3. Results and discussion

Jet cooked starch–paraffin wax compositions were prepared from commercial samples of waxy, normal, and high amylose cornstarches having amylose contents of approximately 0, 25 and 70%, respectively. A starch/paraffin wax weight ratio of 100:40 was used in all preparations. Droplets of starch-coated paraffin wax were isolated by diluting jet cooked dispersions with a 20-fold excess of water (see Section 2) to yield low-viscosity dispersions containing about 0.5% starch/paraffin wax solids, by weight. Diluted dispersions were centrifuged; and droplets of starch-coated paraffin wax were collected from the surface, washed with water to remove loosely bound starch, and then freeze dried.

Weight percent interfacial starch in these freeze-dried fractions was calculated from the loss in weight after extracting accurately weighed samples with cyclohexane to remove the paraffin wax component. Results obtained with the three cornstarch varieties under different experimental conditions are summarized in Table 1. Cold dilution of jet cooked dispersions prepared from normal cornstarch yielded starch-coated paraffin wax droplets containing about 7% interfacial starch, by weight. Somewhat higher starch percentages (about 8.5%) were observed when jet cooked dispersions were allowed to stand at room temperature for one week prior to dilution, instead of for the usual period of 20–24 h (results not shown). Apparently, starch continues to slowly accumulate over time at the wax–water interface. With normal cornstarch, weight percent interfacial starch under hot dilution conditions was about half that observed with cold dilution. Waxy cornstarch, under cold dilution conditions, yielded about half the amount of interfacial starch observed with cold-diluted normal cornstarch. We did not examine waxy cornstarch under hot dilution conditions. The cold dilution method could not be used with high amylose cornstarch due to the formation of rigid gels that could not be dispersed in excess water without high-shear mixing. In experiments carried out under hot dilution conditions, high amylose cornstarch yielded higher percentages of interfacial starch than normal cornstarch.

Cereal starches normally contain small amounts of lipid material, and these native lipids are located both at the surface and within the interior of the starch granule. Surface lipids are easily extracted with cold solvents; whereas, internal lipids are tightly bound (probably as helical inclusion complexes with amylose) and can be removed only by exhaustive extraction with hot polar solvents such as aqueous alcohols at reflux temperature. The internal lipid material in normal cornstarch is comprised of about 62% fatty acids and about 38% lysophospholipids, with the predominant species being the nitrogen-containing lysophosphatidylcholine (Galliard & Bowler, 1987). Lipid amounts increase with the amylose content of the starch; and waxy, normal and high amylose cornstarches typically contain about 0.1, 0.7, and 1% lipid, by weight, respectively (Morrison, 1988). The influence of these lipid components on the formation of interfacial starch was determined by comparing starch–paraffin wax compositions prepared from normal and waxy cornstarch with analogous compositions prepared from starch samples that were defatted by extraction with 85% aqueous methanol followed by 75% aqueous *n*-propanol at reflux temperature (Morrison, 1988; Morrison & Coventry, 1985). Although extraction of native lipid did not greatly change the viscous properties of cooled waxy starch–paraffin wax dispersions, jet cooked dispersions obtained from defatted normal cornstarch formed gels at room temperature that could not be easily diluted with excess water. These jet cooked normal cornstarch dispersions were therefore allowed to only partially cool to 35°C over a 2-h period before they were diluted. Table 1 shows that removal of lipid from waxy cornstarch resulted in little or no change in weight percent interfacial starch. With normal cornstarch, however, a lower percentage of interfacial starch (3.1 vs. 4.7%) was observed when starch was defatted.

The quantity of starch-coated wax droplets isolated from the surface of each diluted dispersion is expressed in Table 1 as percentage yield, defined as the percentage of total wax in the jet cooked product that was recovered in this fraction. Yield values varied with the dilution method and also the type of cornstarch used. These variations in yield were not unexpected; since the amount of starch adsorbed at the paraffin–water interface, and thus the specific gravity of the starch-coated droplets, depends upon the experimental method used. Yields of starch-coated droplets were lowest in experiments in which the highest percentages of interfacial starch were observed, consistent with the supposition that heavy starch coatings increase droplet density and thus inhibit their rapid rise to the surface during centrifugation. Starch coatings can also be heavy enough to cause wax droplets to precipitate, and a significant amount of wax-containing precipitate was indeed observed with normal cornstarch under cold-dilution conditions. The presence of wax in these precipitated fractions was confirmed by FTIR absorption at 2918 and 2850 cm^{-1} (C–H stretch). For example, the precipitate isolated from replicate experiment 3 of the cold diluted, normal cornstarch series (Table 1) exhibited strong C–H absorption and contained 22% wax, by weight, as determined by solvent extraction. Calculations showed that this fraction contained about 10% of the total wax in the original product. In another normal cornstarch experiment, where the dispersion was cold-diluted after one week, the precipitate contained 38% wax, and the wax component in this fraction amounted to about 23% of the total wax in the product. Little or no precipitate was observed under hot dilution conditions or when waxy cornstarch was used.

Interfacial starch fractions isolated from products prepared from normal cornstarch were analyzed for percent amylose, and these results are also shown in Table 1. When the starting cornstarch was not defatted, these amylose

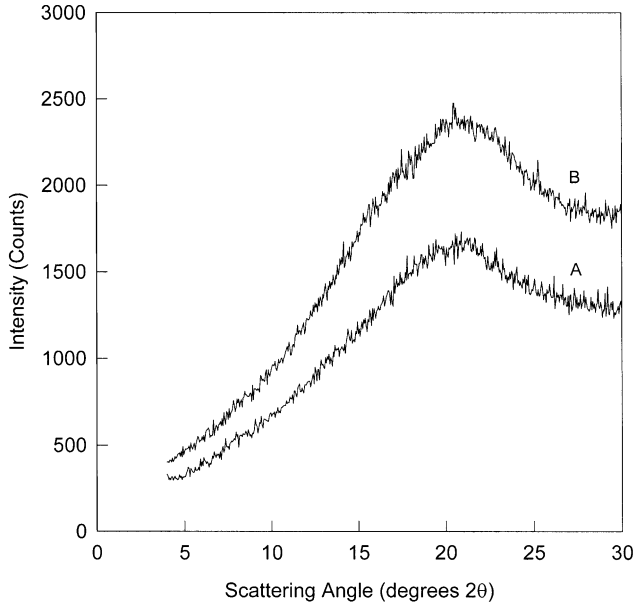

Fig. 1. X-ray diffraction patterns of waxy cornstarch samples. (A) Interfacial starch, cold dilution. Replicate experiment 2 in Table 1. (B) Control experiment. Starch jet cooked in the absence of wax and freeze dried.

percentages were higher than the value of 21.6% found for starting cornstarch, regardless of the dilution method used. When starch was defatted, however, the interfacial starch contained only 15.3% amylose. Amylose is thus preferentially adsorbed at the paraffin–water interface only when native lipid is present in the starting starch. A reasonable explanation for these findings is that polar lipids associated with the starch granule form helical inclusion complexes

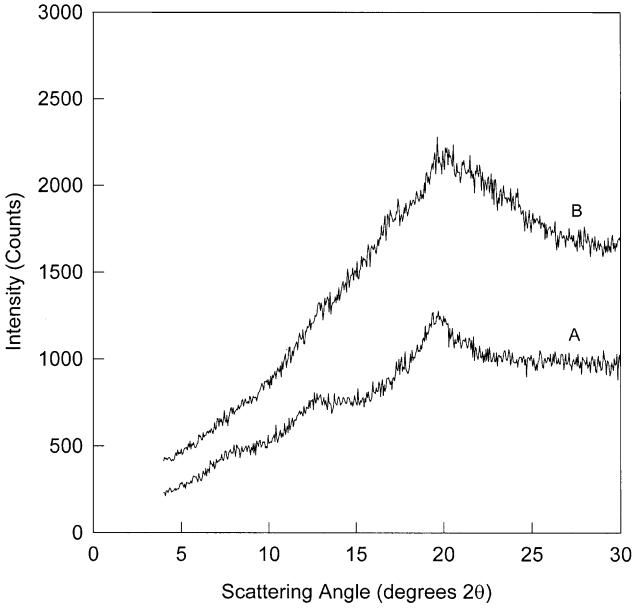

Fig. 2. X-ray diffraction patterns of normal cornstarch samples. (A) Interfacial starch, cold dilution. Replicate experiment 3 in Table 1. (B) Control experiment. Starch jet cooked in the absence of wax and freeze dried.

with amylose when starch is jet cooked. These complexes are less soluble, more hydrophobic, and possibly more surface active than amylose itself, allowing them to accumulate rapidly at the wax–water interface. These amylose–lipid complexes could well be the first species to adsorb, and uncomplexed starch could then form a secondary layer at the interface. Dickinson (1988) has suggested that hydrocolloid polymers have an increased tendency to accumulate at a lipid–water interface, when the interface is already covered with a more surface active material. The fact that lipid-containing normal cornstarch gives a higher percentage of interfacial starch than its defatted counterpart is consistent with this interpretation, as well as the fact that defatting waxy cornstarch (which complexes with lipid much less readily because of its negligible amylose content) has little effect upon weight percent interfacial starch.

X-ray diffraction patterns of interfacial starch isolated from products prepared from waxy, normal, and high amylose cornstarches are shown in Figs. 1–3, respectively, and these results are also consistent with our interpretation that amylose–lipid complexes are separating from bulk solution and are adsorbing at the wax–water interface. Also shown for comparison are X-ray patterns for these same starches jet cooked in the absence of wax and then freeze dried. Interfacial starch from the amylose-containing cornstarches showed primarily the V_h-pattern (maxima at $2\theta = 7.4$, 12.4 and 19.7°) commonly attributed to amylose–lipid complexes (Zobel, 1988), along with smaller amounts of the B-pattern (maxima at $2\theta = 16.7$, 21.9 and 23.8°) due to retrograded amylose. As expected, the interfacial starch from high amylose cornstarch showed the most intense V_h-pattern. In contrast, starch in the absence of wax showed the B-pattern characteristic of retrograded starch or amorphous scattering.

X-ray diffraction patterns of interfacial starch isolated from products prepared from normal cornstarch, before and after defatting, are shown in Fig. 4. In contrast to the V_h-pattern observed when starch was not defatted, only a weak B-type pattern was observed when defatted starch was used. This supports the conclusion that the V_h-complexes seen in samples of interfacial starch are indeed due to complexes of amylose with native lipid present already within the cornstarch granule, rather than the unlikely possibility that amylose is complexing with paraffin wax at the wax–water interface.

The presence or absence of native lipid in the starting starch also influences the morphology of the interfacial starch layer, as seen in scanning electron micrographs of starch-coated wax droplets, examined both before and after extraction with cyclohexane to remove paraffin wax. Micrographs of products obtained from defatted normal cornstarch, lipid-containing normal cornstarch, defatted waxy cornstarch and lipid-containing waxy cornstarch are shown in Figs. 5 and 6. The interfacial starch from defatted normal cornstarch appeared largely as thin filaments or webs extending from the wax droplet surface. This filament

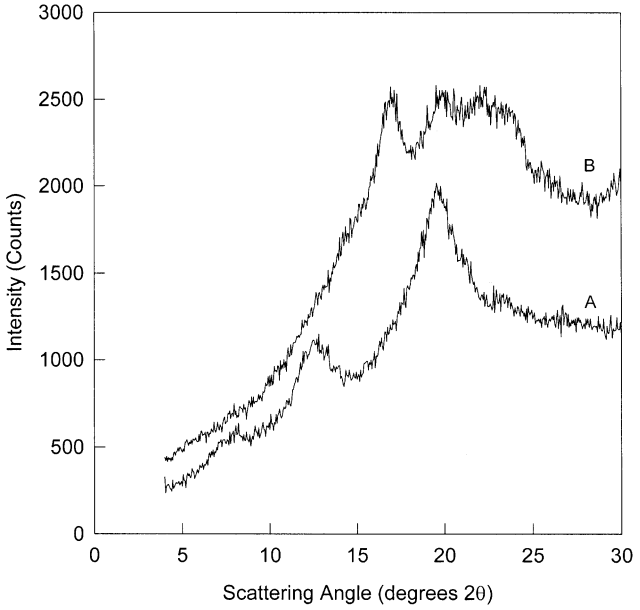

Fig. 3. X-ray diffraction of high amylose cornstarch samples. (A) Interfacial starch, hot dilution. Replicate experiment 2 in Table 1. (B) Control experiment. Starch jet cooked in the absence of wax and freeze-dried.

morphology was seen in cyclohexane-extracted samples, as well as in samples examined prior to extraction (Fig. 5A and B). In contrast, the interfacial starch from lipid-containing normal cornstarch appeared as a rough but continuous coating (Fig. 5C and D). The presence or absence of native lipid in the starting starch also affected the interfacial starch morphology of waxy cornstarch samples. When waxy starch was defatted, the interfacial starch appeared relatively smooth (Fig. 6A and B); whereas the interfacial starch had the appearance of submicron spheres when lipid was present (Fig. 6C and D). The presence or absence of lipid in waxy cornstarch thus influences the morphology of interfacial starch, even though the weight percent starch in coated droplets remains essentially the same. These findings are consistent with the theory that amylopectin can complex to some extent with lipid through interaction with the outer branches (Eliasson, 1998). Although the extent of complex formation is sufficient to affect morphology, it is not enough to significantly affect the gravimetric determination of weight percent starch in coated droplets.

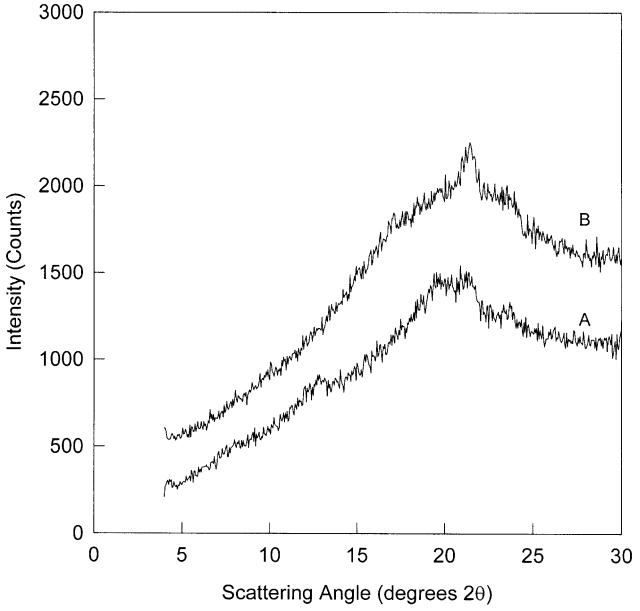

Fig. 4. X-ray diffraction patterns of interfacial starch obtained from normal cornstarch. (A) Starch not defatted, dilution after 2 h. (B) Defatted starch, dilution after 2 h.

In addition to lipid, commercial samples of cornstarch also contain small amounts of protein that are not removed by the wet-milling process. Like the amylose–lipid complexes, these proteins can adsorb at the paraffin–water interface due to their surface active properties (Dickinson, 1994). Evidence for protein adsorption was obtained from FTIR spectra of interfacial starch, which showed weak carbonyl absorption at the correct wavelength for protein (spectra not shown). Comparison of nitrogen analyses of waxy and high amylose starches with nitrogen analyses of the corresponding interfacial starches provided further evidence that protein may be adsorbed rapidly (Table 2). Protein contents in Table 2 were calculated by multiplying percent nitrogen by the commonly used conversion factor of 6.25. For both starch varieties, percent nitrogen in interfacial starch was about 20-fold higher than that in the starting starch, suggesting that most of the nitrogen containing material originally present in cornstarch is now in the interfacial starch layer. A complicating factor in these analyses, however, is the fact that cornstarch contains significant amounts of nitrogen-containing lipid material (e.g. lysophosphatidylcholine), which may also contribute to the total nitrogen in the sample. Analyses were therefore carried out on a product prepared from waxy cornstarch that was solvent extracted to remove lipid. Although extraction of lipid greatly reduced the nitrogen contents of both waxy cornstarch and the resulting interfacial starch, the nitrogen content of interfacial starch was still higher than that of the starting starch by a factor of about 40. Additional research is needed to more thoroughly resolve the question of protein adsorption. For example, it is not known whether the solvent systems used to extract lipid from starch also remove protein. Also, to conclusively determine the effect of protein on the formation and morphology of the interfacial layer, comparative experiments must be carried out with starch samples in which the protein component has been removed.

4. Summary and conclusions

Jet cooking paraffin wax with aqueous dispersions of waxy, normal, and high amylose cornstarch produced starch–wax compositions with properties similar to starch–oil compositions reported previously, i.e. paraffin

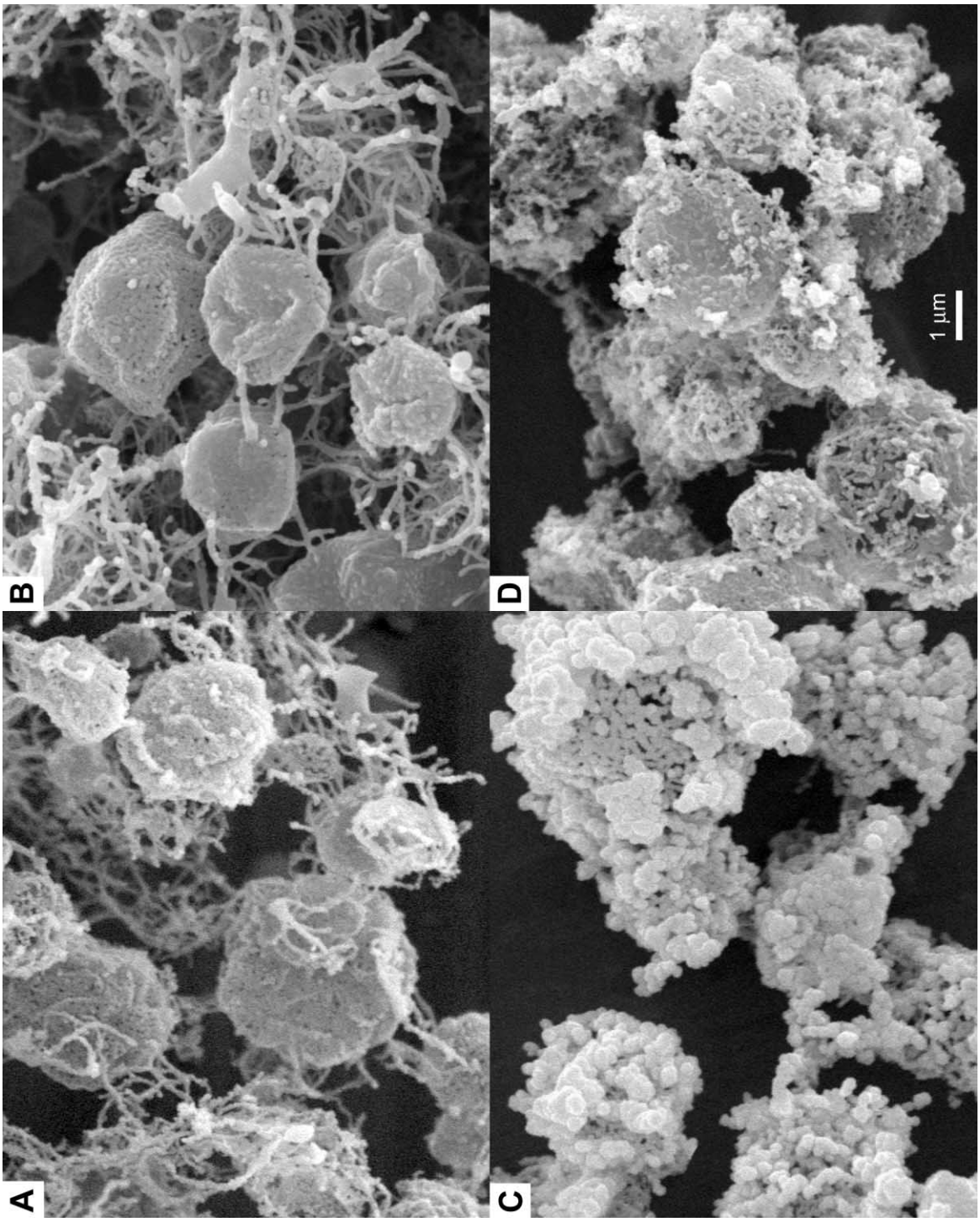

Fig. 5. SEM of starch-coated paraffin wax droplets prepared from normal cornstarch. Dilution after 2 h. (A) Starting cornstarch was defatted; droplets extracted with cyclohexane to remove paraffin wax. (B) Starting cornstarch was defatted; droplets were not extracted with cyclohexane. (C) Starting cornstarch was not defatted; droplets extracted with cyclohexane to remove paraffin wax. (D) Starting cornstarch was not defatted; droplets were not extracted with cyclohexane.

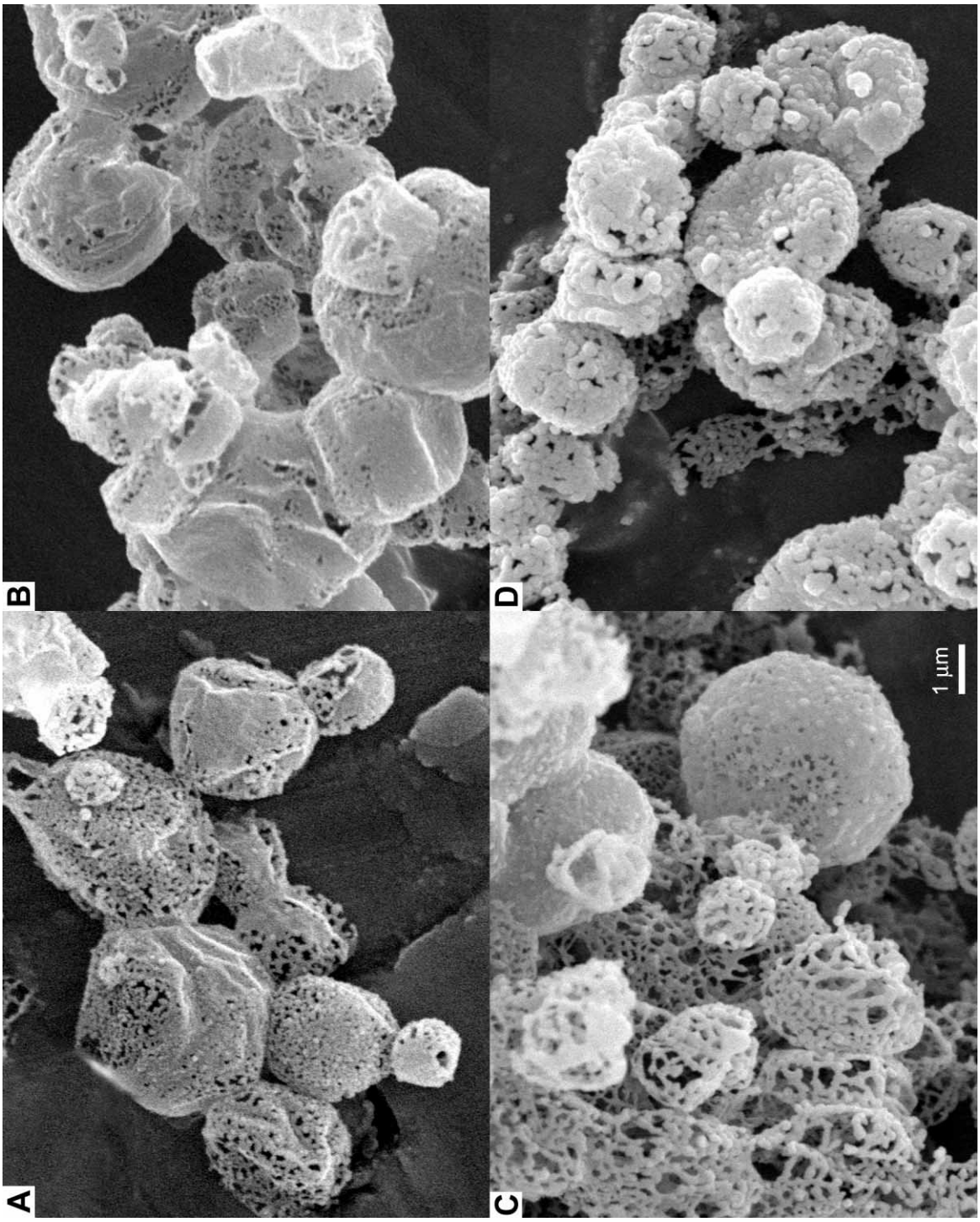

Fig. 6. SEM of starch-coated paraffin wax droplets prepared from waxy cornstarch. Cold dilution. (A) Starting cornstarch was defatted; droplets extracted with cyclohexane to remove paraffin wax. (B) Starting cornstarch was defatted; droplets were not extracted with cyclohexane. (C) Starting cornstarch was not defatted; droplets extracted with cyclohexane to remove paraffin wax. (D) Starting cornstarch was not defatted; droplets were not extracted with cyclohexane.

Table 2
Nitrogen analysis and protein content of starting starch vs. interfacial starch

Starch sample, dilution method[a]	Starting starch		Interfacial starch	
	% N[b]	% Protein[c]	% N[b]	% Protein[c]
Waxy, cold dilution, replicate 1	0.042	0.26	1.02	6.4
Waxy, cold dilution, replicate 2	0.042	0.26	0.77	4.8
Waxy (defatted), cold dilution	0.004	0.025	0.17	1.1
High amylose, hot dilution, replicate 1	0.095	0.59	2.13	13.3
High amylose, hot dilution, replicate 2	0.095	0.59	2.17	13.6

[a] Refer to Table 1.
[b] Kjeldahl analysis.
[c] Calculated by multiplying % N by the nitrogen conversion factor 6.25.

wax was reduced to micron-sized droplets by jet cooking, and droplets did not coalesce because of a thin layer of starch that surrounds each droplet at the paraffin–water interface. Starch-coated paraffin wax droplets solidified at room temperature and were separated and isolated by centrifuging diluted dispersions. Droplets rise to the surface during centrifugation because of their low specific gravity relative to water; and these droplet fractions were collected from the surface, washed with water to remove loosely-bound starch, and freeze dried. Since interfacial starch increased the specific gravity of paraffin wax droplets, a significant droplet fraction did not separate during centrifugation but remained suspended in water. Heavy layers of interfacial starch also caused droplets to precipitate.

Weight percent interfacial starch was determined by extracting starch-coated droplets with cyclohexane to remove paraffin wax and then determining the weight of residual starch. Percentages of interfacial starch varied from about 3–8%, depending upon the cornstarch variety (i.e. waxy, normal or high amylose) and the dilution method used.

The effect of lipids, normally present in small amounts in cereal starches, on weight percent interfacial starch was examined by comparing products prepared from commercial cornstarches with those prepared from starches that were defatted to remove lipid components. With waxy cornstarch, defatting caused little or no change in weight percent interfacial starch. With normal cornstarch, however, defatting resulted in a lower percentage of interfacial starch (3.1 vs. 4.7%). The presence or absence of native lipid in cornstarch also affected the morphology of interfacial starch, as observed by SEM.

The amylose/amylopectin ratio in interfacial starch also depends upon whether or not native lipid is present in the starting cornstarch. When starch was not defatted, the amylose content of interfacial starch was higher than the amylose content of the starting cornstarch. When defatted starch was used, however, the amylose content of interfacial starch was lower. Amylose is thus adsorbed preferentially at the paraffin–water interface only when native lipid is present in the starting cornstarch. These observations suggest that helical inclusion complexes, formed from amylose and the lipid components of cornstarch, accumulate rapidly at the paraffin–water interface because of their reduced water solubility and enhanced surface activity. These amylose–lipid complexes could well be the first species to adsorb at the interface, and uncomplexed starch could then adsorb as a secondary layer. X-ray diffraction patterns of interfacial starch are consistent with this interpretation and show the V_h-pattern commonly attributed to amylose–lipid complexes.

Nitrogen analyses of interfacial starch samples suggest that proteins, normally present in cornstarch in small amounts, adsorb along with starch at the paraffin–water interface.

Acknowledgements

We are grateful to Dr A.R. Thompson for scanning electron micrographs, to J.H. Salch for FTIR analyses and technical assistance, and to J. K. Lingenfelter for technical assistance.

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