Comparison of Oil-binding Ability of Different Chlorinated Starches

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ABSTRACT

Direct chlorination of isolated wheat prime starch imparted lipophilic properties to the starch. These properties nearly disappeared after treatment with 7% HCl, α-amylase, or pepsin, but were affected very little by water-saturated 1-butanol, chloroform-methanol (2:1) or sodium dodecyl sulfate solution. Rice, potato, and corn starches also became lipophilic after chlorination. Chlorinated corn starch showed the highest oil-binding capacity. However, except for pepsin treatment, response of these other starches to treatments differed only slightly from that of chlorinated wheat prime starch.

Chlorination of wheat flour improves pancake characteristics such as mouthfeel (Seguchi and Matsuki 1977a) and volume (Sollars 1968a, 1968b; Kulp 1972; Seguchi and Matsuki 1977a). These improving effects are thought to be brought about by the modification of the prime starch (Seguchi and Matsuki 1977a, Gaines 1982, Gaines and Donelson 1982) and lipid flour fractions (Kissell et al 1979; Clements and Donelson 1982a, 1982b). One characteristic of prime starch from chlorinated flour is its greater hydrophobic nature (Seguchi and Matsuki 1977a), as evidenced by granule cluster in water or by increased oil-binding capacity. The clusters were broken by the addition of sucrose fatty acid esters (Seguchi and Matsuki 1977a). The improved (dry) mouthfeel also disappeared when sucrose fatty acid esters were added to reconstituted cake batter. These results lead to the conclusion that increased hydrophobicity of chlorinated starch enhances the interaction of starch granules alone or with other components such as proteins, increasing the transfer of water to starch when swelling occurs. The resulting decrease in free water in cake crumb would affect cake crumb dryness and springiness. When sucrose fatty acid esters were added, chlorinated starch granules may have been coated with sucrose fatty acid esters and separated from other flour components. The amount of water thus transferred to swelling starch would have been decreased. The effect of the added sucrose fatty acid esters was no change in cake crumb. One may conclude that the improvement of chlorine gas on cake crumb mouthfeel is possibly due to the increased hydrophobic character of chlorinated starch (Seguchi and Matsuki 1977a). Hydrophobicity was measured by oil-binding capacity, which decreased substantially upon treatment with weak acid, amylase, or protease. Oil-binding capacity was assumed to result from alternation of a protein film on starch granules by chlorine (Seguchi 1984). It is, as yet, unknown whether the lipophilic nature of starch granules from chlorinated wheat flour is caused by a direct chlorination of prime starch or by interaction with other flour components. Prime starch fractionated from nonchlorinated wheat flour as well as starch from corn flour, rice flour, and potato were chlorinated after fractionation. This study reports comparative results on the oil-binding capacity of these chlorinated and nonchlorinated starches affected by chemical treatments, enzymatic treatments, or both.

MATERIALS AND METHODS

Materials

Wheat prime starch was prepared from nonchlorinated wheat flour as described by Seguchi and Matsuki (1977b). Rice starch and potato starch were prepared by the methods of Yamamoto et al (1973) and de Willigen (1964), respectively. Corn starch and arrowroot starch were purchased from commercial sources. Alpha-amylase type II-A with an activity of 15.7 units per milligram of protein was obtained from Sigma Chemical Co., St. Louis, MO. Pepsin (with an activity of 1,200–2,000 units per milligram of protein) and rapeseed oil were from Wako Junyaku Co., and Nissin Oil Co., Tokyo, respectively. Other materials were reagent-grade products.

Analytical Procedures

Protein (N × 6.25) and ash contents were determined by the method of Smith (1964a, 1964b). Moisture content was determined by the method of Tsutsumi and Nagahara (1961). Lipids were extracted with ethyl ether from 5.0 g of starch samples with a Soxhlet apparatus for 16 hr. The boiling range of ethyl ether was 50–70°C. Analytical values of starch samples before chlorination are given in Table I.

Chlorination of Starch Samples

Starch samples were chlorinated as previously described by Seguchi and Matsuki (1977a). Starch was treated with chlorine gas (2.5 g/kg of starch) for 10 min at room temperature. The pH of starch was 3.9.

Determination of Oil-binding Capacity

Five hundred milligrams of starch (100 mg when corn starch was used) was suspended in 5 ml of H_2O in a graduated centrifuge tube (16.5 × 105 mm) to which 1 ml of rapeseed oil was added. A minimum volume of 0.1 ml could be read. The tube was mixed at 3,200 rpm for 10 sec on a vibrio shaker with a horizontal vibration amplitude of 0.1 cm, rested a few minutes, then agitated again. This sequence was repeated 60 times. The resulting mixture was then centrifuged at 600 × *g* for 20 min at room temperature. After centrifugation, the volume (a), in milliliters of oil layer above the water, was directly measured by reading the graduated table on the centrifuge tube. Oil-binding capacity (milliliters of oil per gram of dried starch) was calculated as (1−a) × 2, or (1−a) × 10 when corn

TABLE I
Analytical Results for Starches

Starch	Moisture Content (%)	Protein (%)[a,b]	Lipid (%)[a]	Ash (%)[a]
Wheat	13.3	0.22	0.10	0.12
Potato	19.0	0.08	0.06	0.30
Corn	9.7	0.26	0.07	0.07
Rice	11.4	0.26	0.09	0.12

[a] Based on 14% moisture basis.
[b] N × 6.25.

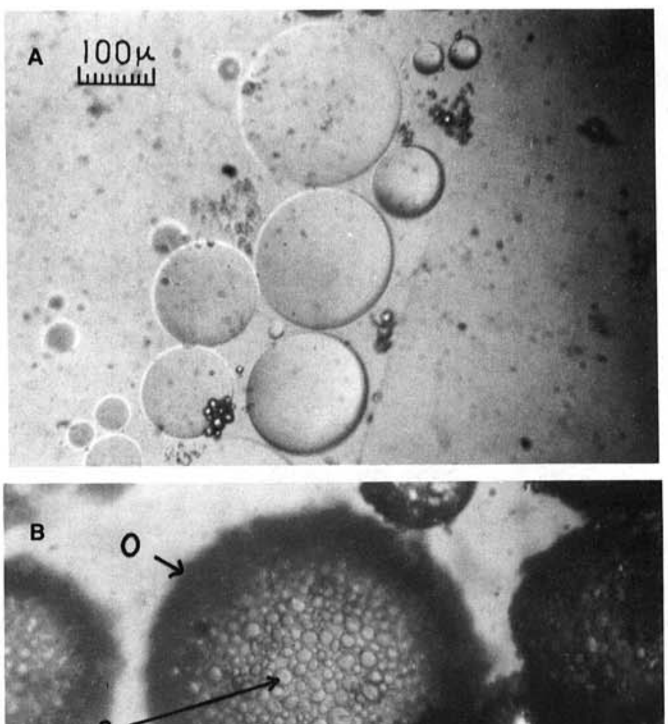

Fig. 1. Photomicrographs of oil droplets and water after mixing with **(A)** nonchlorinated wheat starch and **(B)** chlorinated wheat starch. O = oil droplet, S = starch, and W = water.

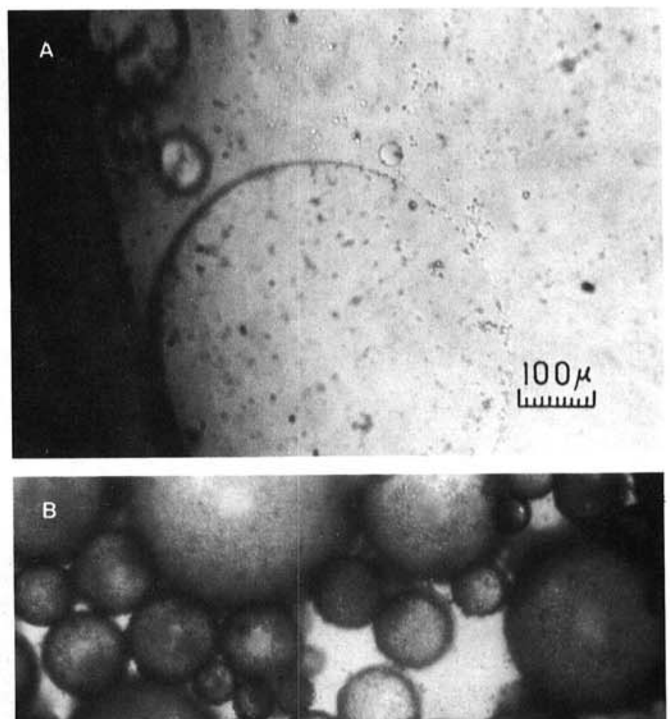

Fig. 2. Photomicrographs of oil droplets and water after mixing with **(A)** nonchlorinated rice starch and **(B)** chlorinated rice starch.

starch was used. Data in this paper were derived by means of triplicate determinations. The standard deviation was 0.06 ml with this method.

Treatment of starch samples with water-saturated 1-butanol (WSB), chloroform-methanol (2:1), sodium dodecyl sulfate (SDS), 7% HCl or various enzymes was performed as previously described by Seguchi (1984), except that solutions were dialyzed after enzyme digestion.

RESULTS AND DISCUSSION

Oil-binding Ability of Chlorinated and Nonchlorinated Starches

Photomicrographs of the nonchlorinated starches after vigorous mixing with oil in water are shown in Figs. 1A, 2A, 3A, 4A, and 5A. When these photomicrographs are paired with results presented in Table II, it is evident that these samples exhibited relatively little oil-binding capacity. The increased oil-binding capacities of chlorinated starches are shown in Table II and in Figs. 1B, 2B, 3B, 4B, and 5B. Chlorinated starch granules were observed to be evenly distributed inside and outside of oil droplets. Seguchi (1984) observed similar behavior in prime starch separated from wheat flour chlorinated at a lower concentration (1.25 g of chlorine per kilogram of wheat flour). Chlorinated rice and potato starches showed levels of oil-binding capacity similar to that of chlorinated wheat starch, whereas chlorinated corn starch showed the highest oil-binding capacity, 9 ml of oil/g of starch (Table II). Detailed data of chlorinated arrowroot starch were not estimated, but the oil-binding property was as shown in Fig. 5B. In contrast, one can see the inability of nonchlorinated arrowroot starch to bind oil (Fig. 5A). Addition of 1% SDS solution released chlorinated starch granules from oil droplets, as was found with chlorinated wheat starch (Seguchi 1984).

TABLE II
Oil-binding Capacities of Starches

Starch	Starches: Nonchlorinated[a]	Chlorinated[a]
Wheat	0.2	1.4
Potato	0.2	1.0
Corn	0.4	9.0
Rice	0.2	1.8

[a] Milliliters of oil per gram of starch.

TABLE III
Effects of Various Treatments on Oil-binding Capacity of Wheat, Potato, Corn, and Rice Starches

Treatment	Relative Oil-binding Capacity of Chlorinated Starch (%)[a]: Wheat		Potato		Corn		Rice	
None	100	1.4	100	1.0	100	9.0	100	1.8
WSB[b]	80	1.0	80	0.9	83	7.5	100	1.8
$CHCl_3$-CH_3OH	86	1.2	100	1.0	75	6.8	100	1.8
1% SDS[c]	86	1.2	20	0.8	30	2.7	22	0.4
7% HCl	14	0.2	20	0.8	15	1.4	28	0.5
α-Amylase	14	0.2	20	0.8	17	1.5	17	0.3
Pepsin	0	0.0	29	0.3	83	7.5	100	1.8
Pepsin after chloroform-methanol	ND[d]	ND[d]	ND[d]	ND[d]	17	1.5	100	1.8

[a] Milliliters of oil per gram of starch.
[b] WSB = water-saturated 1-butanol.
[c] SDS = sodium dodecyl sulfate.
[d] ND = not determined.

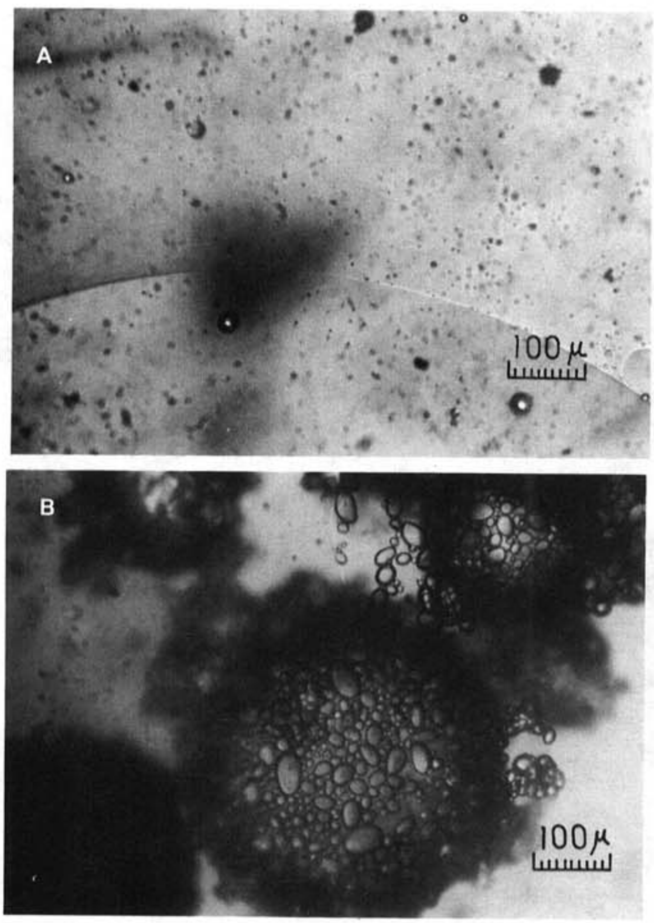

Fig. 3. Photomicrographs of oil droplets and water after mixing with **(A)** nonchlorinated potato starch and **(B)** chlorinated potato starch.

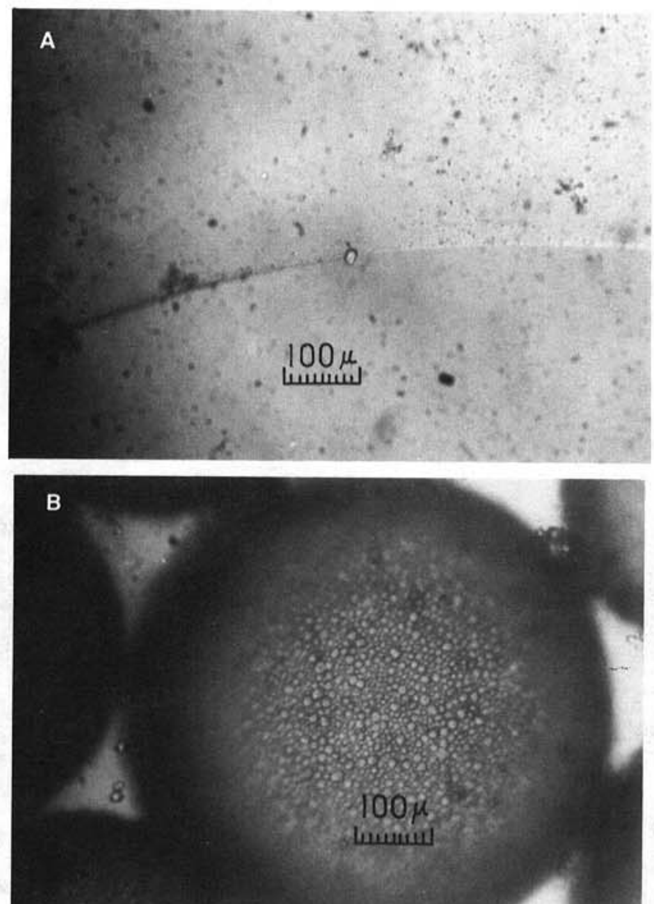

Fig. 4. Photomicrographs of oil droplets and water after mixing with **(A)** nonchlorinated corn starch and **(B)** chlorinated corn starch.

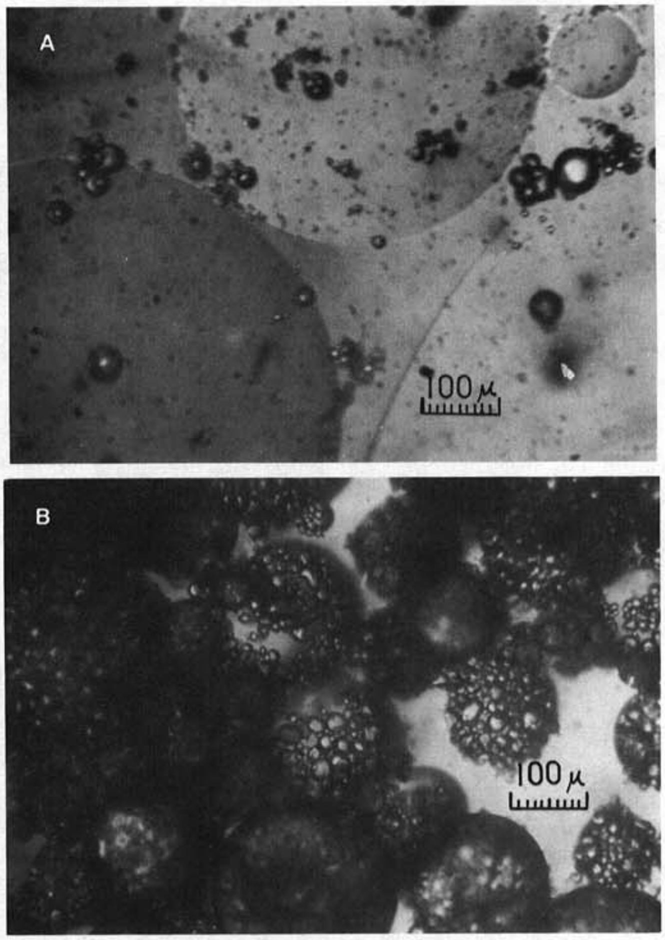

Fig. 5. Photomicrographs of oil droplets and water after mixing with **(A)** nonchlorinated arrowroot starch and **(B)** chlorinated arrow root starch.

Effects of Treatments on the Oil-binding Ability of Chlorinated Wheat Starch

Treatment of chlorinated prime starch from nonchlorinated wheat flour with WSB or chloroform-methanol, generally used as solvents for lipid extraction, had relatively little effect on decreasing oil-binding ability (Table III). This indicates that lipids have little or no relationship to this ability. The SDS treatment had little effect on the oil-binding capacity of chlorinated wheat prime starch even after extensive removal of this detergent by dialysis. Weakly binding materials such as proteins or lipids are known to be released by SDS; however, the lipophilic materials on chlorinated starch granules could not be easily released. Treatment with 7% HCl, or digestion by α-amylase or pepsin did cause chlorinated wheat prime starch to lose its binding ability. Microscopic observation, however, did not show any change in starch granules after these treatments. The loss of this ability caused by α-amylase or pepsin digestion or by treatment with 7% HCl indicates that the oil binding may be reduced when proteins are released or dissolved from the surface of starch granules. These results agree with those of starch from chlorinated wheat flour previously reported (Seguchi 1984). It is reasonable to assume that direct chlorination of prime starch imparts lipophilic properties by the change of proteins on these starch granules.

Effects of Treatments on the Oil-binding Ability of Various Other Chlorinated Starches

Lipids on the chlorinated potato, corn, and rice starches contributed little to the lipophilic character, as evidenced by the small effects with WSB or chloroform-methanol. The SDS treatment lowered the oil-binding abilities of starch from potato, corn, and rice. This effect by SDS was not the same as on chlorinated wheat starch or on starch from chlorinated wheat flour (Seguchi 1984), indicating that lipophilic sites on starch from potato, corn, and rice were more easily released by SDS than those on wheat prime starch samples.

Treatment by 7% HCl or α-amylase also effectively lowered oil-binding ability, as was observed in the samples of wheat starch. These treatments also appear to break or release lipophilic sites from these starches. Pepsin digestion of the potato starch lowered its oil-binding ability to a relatively low level, but pepsin had relatively little effect on corn and rice starch. The oil-binding ability of the corn starch was reduced by coupling of the treatment with chloroform-methanol (2:1) and with pepsin digestion, suggesting that lipids on the corn starch granule may inhibit the pepsin digestion of the proteins. The coupled treatments had no effect on rice starch. This suggests that chlorinated potato and corn starches may be lipophilized by protein films on starch granules, as in chlorinated wheat prime starch or in starch from chlorinated wheat flour.

Rice starch was the only starch to show no loss of oil-binding ability by pepsin digestion. This behavior is inexplicable, but it may be that rice proteins possess a property that binds them especially strongly to rice starch granules. These results show that starches of various sources can attain lipophilic properties by chlorination.

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