Gelatinization of Wheat Starch. II. Starch-Surfactant Interaction[1]

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ABSTRACT

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X-ray diffraction patterns of the insoluble residues of wheat starch heated to 60, 70, or 80°C with monoglycerides or sodium stearoyl lactylate (SSL) showed a strong surfactant-amylose complex. This complex at a low temperature shows that surfactants enter the starch granules and complex with the amylose. At 95°C, the starch-SSL complex was no longer observed. Dissociation of the starch-SSL complex at high (95°C) temperature was shown by an increase in the starch-I_2 absorbance after a starch-SSL complex was heated to 95°C in the presence of iodine.

The use of emulsifiers in starch-based products is increasing because of their ability to retard firming and retrogradation. The mechanism by which certain surfactants retard certain changes, particularly the staling of bread, is not completely understood. The interaction between starch and surfactant was explained by earlier workers (Lehrman 1942, Whistler and Hilburt 1944) as an adsorption of surfactant on the surface of the starch granule. Later research showed, however, that surface-active agents form insoluble inclusion compounds or complexes with amylose. X-ray diffraction patterns of all surfactant amylose complexes have the so-called V-amylose pattern (Zobel 1964).

Osman et al (1961) studied the ability of certain emulsifiers to complex with the amylose fraction of starch, evaluating them by their interference with the binding of iodine by amylose. Krog and Nybo-Jensen (1970) showed that the ability of monoglycerides (MG) to form complexes with amylose depended on the physical form of the surfactant. Krog (1971), who reported on the amylose-complexing ability of several emulsifiers, found that distilled MG had the best complexing ability among nonionic surfactants and that sodium stearoyl lactylate (SSL) and calcium stearoyl lactylate were best among the ionic ones.

The purpose of our study was to investigate 1) starch-surfactant interactions and 2) the dissociation of the amylose-SSL complex at high temperatures.

MATERIALS AND METHODS

Prime starch was isolated from hard wheat flour (cultivar Cloud), milled on a Buhler experimental mill by the dough kneading procedure (Wolf 1964). SSL was obtained from C. J. Patterson Company, Kansas City, MO, and monoglycerides (MG) (Dimodan PV) from Grindsted Products, Overland Park, KS.

Dilute starch solutions (3% w/w) were heated to different temperatures with and without SSL or MG (2% w/w), as described previously (Ghiasi et al 1982). The soluble and insoluble fractions were rapidly frozen and then freeze-dried. X-ray diffraction patterns of the samples were determined as described by Dragsdorf and Varriano-Marston (1980) and iodine absorptions as described by Weintraub and French (1970).

For the study of the surfactant-amylose complex, additional samples were prepared. Starch was heated to 95°C and then stirred at 60°C for 1 hr; solubles were extracted and freeze-dried. Solubles from starch heated to 95°C with SSL were rapidly removed, stirred at 60°C for 1 hr and freeze-dried. In addition, solubles were extracted from untreated starch heated to 95°C and SSL was added to the solubles, which were stirred at 60°C for 1 hr and then freeze-dried. X-ray diffraction patterns were determined for all samples.

The effect of iodine on the complex was studied in another experiment. A dilute starch solution with and without SSL (2%) was heated to 95°C and the solubles separated by centrifugation. Five milliliters of a dilute solution of I_2 in KI (Weintraub and French 1970) was added to 20 ml of the solubles and the mixture heated in a sealed flask to 95°C. Absorbancies were measured after the solution was cooled to room temperature.

RESULTS AND DISCUSSION

Effect of MG and SSL on Starch Crystallinity

Wheat starch was heated in excess water to 75 and 95°C; then solubles were removed and the insolubles freeze-dried. X-ray diffraction patterns of the insoluble residues are presented in Fig. 1. The sample heated to 75°C (Fig. 1b) showed a low degree of crystalinity, and the sample heated to 95°C (Fig. 1a) was essentially noncrystalline. Ghiasi et al 1982 showed that at 75°C only 5.9% of the starch, mainly amylose, was soluble. Therefore, at that temperature, even though the major part of the amylose was still associated with the granules, the organization of the starch granule had changed.

Considerable controversy exists concerning which component, amylose or amylopectin, is responsible for the crystallinity of starch (Banks and Greenwood 1975, Kainuma and French 1971, Robin et al 1974, Sarko and Wu 1978). According to polymer physics, crystallites can occur whenever chain segments happen to be parallel in lattice positions. Therefore, starch crystallites can form through hydrogen bonding between linear fraction and segments of the branched fraction (Caesar and Cushing 1941).

X-ray diffraction patterns of the insoluble residue of starch obtained from heating starch to different temperatures with SSL is shown in Fig. 2. With one exception (95°C), the samples all showed the surfactant-amylose complex pattern, as indicated by the strong d-spacing at 4.4 and 6.8Å. At 95°C, the starch-SSL complex was no longer observed. Loss of the complex at 95°C helps explain why SSL did not prevent leaching of solubles from starch at high

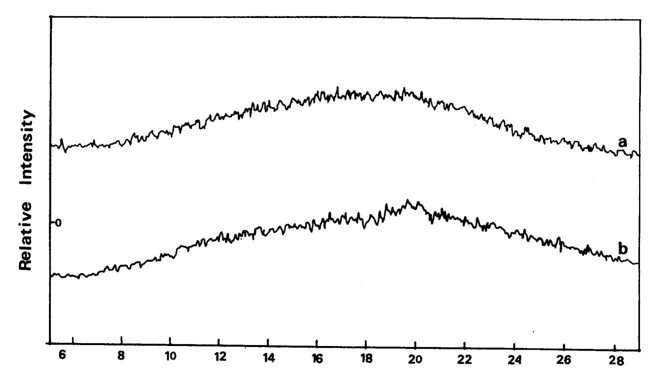

Fig. 1. X-ray diffraction patterns of the insoluble residue from wheat starch heated to: **a**, 75°C; **b**, 95°C.

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temperatures (Ghiasi et al 1982). Gray and Schoch (1962) also found that SSL was not effective in decreasing solubility of starches at temperatures of 85°C and above.

X-ray diffraction patterns of solubles isolated from starch and surfactant-treated starches heated to 95°C are shown in Fig. 3. X-ray diffraction patterns were primarily V-hydrate complex, as indicated by their d-spacings (Zobel 1964). The existence of amylose as a V-hydrate complex has been reported (Yamashita 1965). X-ray patterns of soluble starch from MG-treated samples and the control were much less crystalline than were the solubles from SSL-treated starch (Fig. 3). At 95°C, all the amylose and SSL molecules were in the soluble fraction (Ghiasi et al 1982). The insoluble residue from that sample gave a pattern with low levels of crystallinity (Fig. 2d). On the other hand, at that temperature only 4.8% of MG-treated sample was soluble (Ghiasi et al 1982). Therefore, most of the amylose and monoglyceride were still in the insoluble fraction.

Surfactant-Starch Interaction

Schoch (1965) postulated that when a surfactant enters the starch granules, it immediately complexes with amylose and forms a helix. That theory has also been reinforced by other workers (Longley and Miller 1971, Miller et al 1973), but no conclusive evidence has been presented showing that surfactants enter starch granules. X-ray diffraction patterns of starch with SSL (Fig. 2) or MG (Fig. 4) clearly showed that a strong surfactant-amylose complex formed even when the starch-surfactant mixture was heated to temperatures as low as 60°C. The only possible explanation for the existence of such complexes at 60°C is that surfactant molecules enter the starch granules. We cannot rule out the possibility that some adsorption of surfactant on the surface of starch granules also occurs (Finn and Varriano-Marston 1981).

Formation of a surfactant-amylose complex appears to delay the release of the solubles and the deformation and collapsing of starch granules (Ghiasi et al 1982). However, as the temperature increases, that complex will eventually be dissociated or released into the aqueous phase. At temperatures higher than 85°C, SSL loses its effectiveness. Other surfactants such as MG form a stronger complex than SSL, and more energy is required to dissociate them. The disappearance of the starch-SSL complex after heating to 95°C and removing the solubles (largely amylose, Ghiasi et al 1982) indicates that this complex was formed only between amylose and SSL and not between amylopectin and SSL, as has been suggested by some workers (Lonkhuysen and Blankestijn 1974, 1976).

Amylose-SSL Complex at High Temperatures

SSL has no effect on starch solubility at high temperatures, whereas monoglyceride does (Ghiasi et al 1982). Thus, we undertook to study the nature of the starch-SSL complex and to investigate the possibility of its dissociation at high temperatures.

The soluble fraction of starch heated with SSL to 95°C exhibited the typical amylose-surfactant X-ray diffraction pattern (Fig. 3b). Conversely, the insoluble fraction was essentially noncrystalline (Fig. 2), indicating that SSL was associated only with the soluble fraction.

Dissociation and Reassociation of the Complex. The existence of such a strong surfactant-amylose complex, however, does not rule out the possibility of dissociation of that complex at a higher temperature and its reformation as the temperature is lowered. Therefore, we studied the effect of temperature on the starch-SSL complex by adding SSL to the heated starch solution at different times and temperatures (Table I). X-ray diffraction patterns for all of the SSL-treated samples showed a strong surfactant-amylose complex. Relative crystallinity data (Table I) showed a higher degree of crystallinity for these samples when kept at 60°C for 1 hr. These data showed that time is required to develop more crystallinity, but they do not clarify whether or not a dissociation phenomenon has occurred at 95°C.

Iodine affinity has been used to measure the amylose-complexing ability of a number of food-grade emulsifiers.

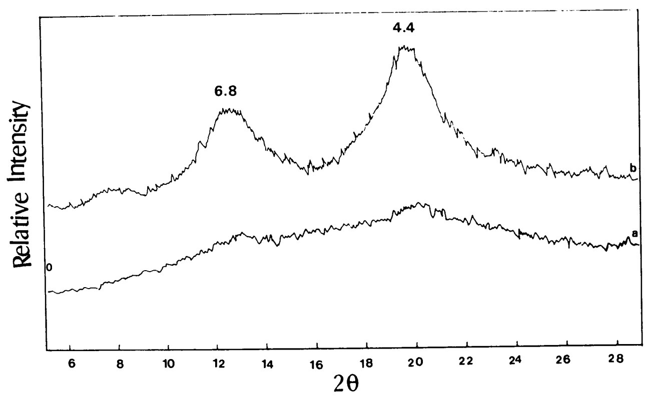

Fig. 3. X-ray diffraction patterns of solubles isolated from wheat starch heated to 95°C. **a**, control or with monoglycerides; **b**, with sodium stearoyl lactylate.

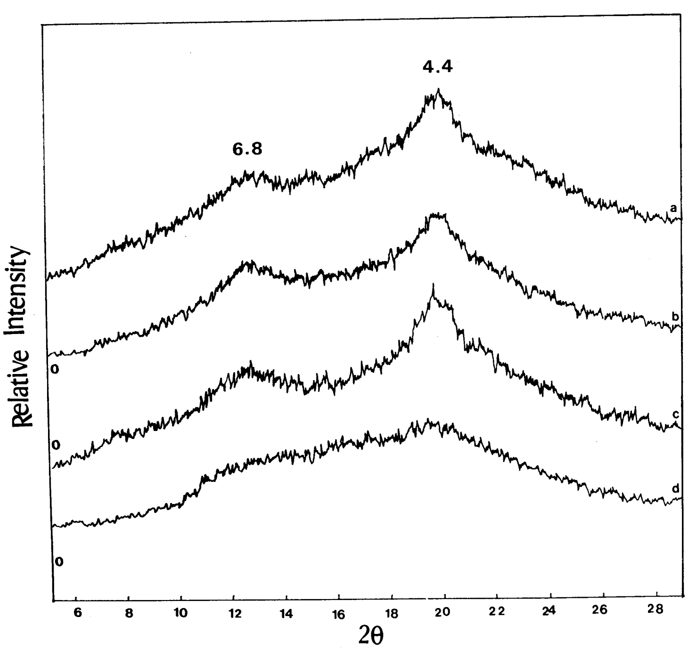

Fig. 2. X-ray diffraction patterns of the insoluble residue of wheat starch heated with sodium stearoyl lactylate to: **a**, 60°C; **b**, 70°C; **c**, 80°C; **d**, 95°C.

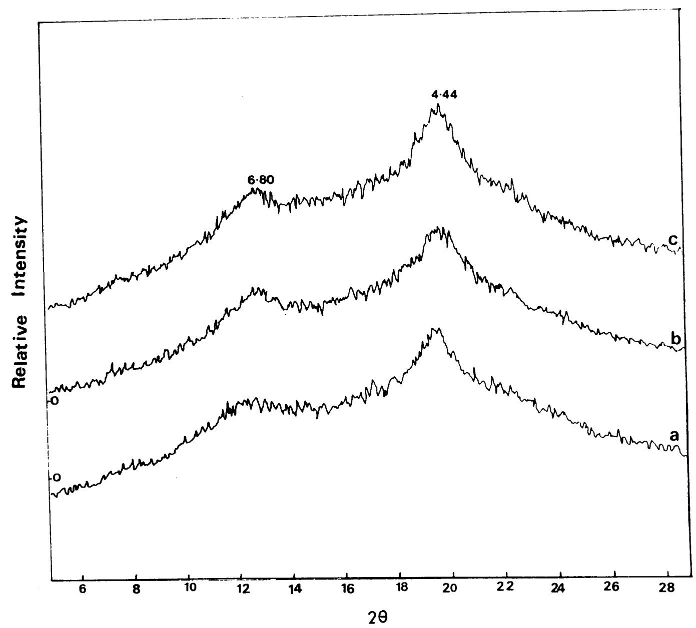

Fig. 4. X-ray diffraction patterns of the insoluble residue of wheat starch heated with monoglycerides to: **a**, 60°C; **b**, 70°C; **c**, 80°C.

TABLES I
Relative Crystallinity (RC)[a] of Solubles

Preparation of Solubles		
Starch Treated	**Solubles Treated**	**RC**
Heated to 95°C		
With no further treatment (control)	···	···
And kept at 60°C for 1 hr	···	0.59
With added SSL[b]	···	1.47
With added SSL	Kept at 60° for 1 hr.	1.93
With no further treatment	SSL added, kept at 60°C for 1 hr	1.94

[a]RC = ac/Ac, where ac is the area of the crystalline fraction and Ac is the crystalline diffraction area for 100% intact (unheated) wheat starch.
[b]Sodium stearoyl lactylate.

TABLE II
Iodine Affinity of Nondefatted Solubles

Preparation of Solubles		Iodine Affinity (%)
Starch Treated	**Solubles Treated**	
Heated to 95°C		
With no further treatment (control)	···	11
With added SSL[a]	···	0.07
With added SSL	Kept at 60°C for 1 hr	0.08
With no further treatment	SSL added, kept at 60°C for 1 hr	0.07

[a]Sodium stearoyl lactylate.

TABLE III
Effect of Temperature on Iodine Absorption of Control and SSL[a]-Treated Solubles

Sample	Absorbance at 660 nm
Soluble starch + I_2	0.60
Heated to 95 °C	0.68
With SSL added and heated to 95 °C	0.18
Soluble starch-SSL complex	
With I_2 added	0.07
With I_2 added and heated to 95°C	0.24

[a]Sodium stearoyl lactylate.

Complexes of amylose with surfactants greatly reduce iodine affinity values (Krog 1971, Osman et al 1961). Iodine affinity values for the nondefatted samples discussed above are presented in Table II. Solubles from starch had an iodine affinity of 11; the SSL-treated solubles had much lower values, presumably as a result of the amylose-SSL complex. No significant differences were observed among iodine affinity values for the different treatments. That showed that the amount of SSL complexed with the solubles was the same for all treatments. Furthermore, if the complex dissociated at higher temperatures, its reformation was rapid.

Effect of Iodine on Amylose-SSL Complex. The interaction of amylose with iodine generates a helical inclusion complex in which the iodine molecules occupy the central cavity of the molecule (Rundle 1947, Rundle et al 1944). The blue color of the amylose-iodine complex slowly disappears as the solution is heated and reappears on cooling (Peticolas 1963).

The amylose-surfactant complex resembles the complex of iodine and amylose (Mikus et al 1946). Therefore, if the amylose-SSL complex dissociates at high temperatures when iodine is added to the solution, SSL and iodine should compete for binding sites during cooling.

Table III shows the iodine absorption of control and SSL-treated solubles heated to 95°C. A significant decrease (from 0.6 to 0.18) occurred in the absorbance of a soluble starch-I_2 solution after SSL had been added and the solution heated to 95°C. In addition, absorbance of the soluble starch-SSL solution that was heated with I_2 to 95°C increased (from 0.07 before heating to 0.24 after heating). Those data clearly showed that either the amylose-I_2 complex or the amylose-SSL complex dissociates at high temperatures and that I_2 and SSL compete for the same binding site.

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