

Influence of Water and Surfactants on Wheat Starch Gelatinization and Retrogradation

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수분과 계면활성제가 밀전분의 호화와 노화에 미치는 영향

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Abstract

The effects of water contents and surfactants, sodium stearyl-lactylate, sucrose ester and distilled monoglyceride(Dimodan) on wheat starch gelatinization and retrogradation were studied by differential scanning calorimetry. The endothermic peak patterns of starch varied with water content of starch. When water content was less than 30%, gelatinization did not occur. The onset temperature of gelatinization peak of native starch was 59~60°C and that of endothermal peak of retrograded starch was 50~55°C. The enthalpy value of retrograded starch were greatest in the 40~50% water content. In the presence of surfactants, gelatinization temperatures shifted slightly to higher temperatures. DSC endothermal enthalpies of the amylose-lipid complex increased. The degree of retrogradation in starch was lower with surfactant than without surfactant, but enthalpy of amylose-lipid complex did not change during storage.

Key words : starch gelatinization and retrogradation, water content, surfactant

Introduction

The gelatinization of starch granules heated in water is a well-known phenomenon, during which the granules lose their semi-crystallinity and swell. Gelatinized starch is retrograded during storage. Retrogradation is a physical change of the starch amylose and amylopectin from a swollen, gel-like state to a more crystalline state.

Donovan⁽¹⁾ suggested that starch granules had a single endotherm at high water content, but had two endothermic transitions in the presence of limited amount of water by differential scanning calorimetry. At intermediate water levels, two endothermic transitions were reported for the disorganization of starch crystallites, while a third endotherm at higher temperature was attributed to the melting of amylose-lipid complexes⁽²⁾. Enthalpy changes are unaffected by water levels above 60% and they decrease substantially at lower levels. The temperature of enthalpy changes increases as water content of the system decreases from 75 to 35%⁽³⁾. Zelezank and Hosene⁽⁴⁾ suggested that

retrogradation in wheat starch gels was controlled by the amount of water present during aging, regardless of the amount present during gelatinization.

The use of surfactants in starch-based products is increasing because of their ability to retard firming and retrogradation. Lehrman⁽⁵⁾ explained that the interaction between starch and surfactant come from an adsorption of surfactant on the surface of the starch granule. But later report showed that surfactant form insoluble inclusion compounds with amylose⁽⁶⁾. Certain surfactants form complexes with amylose and change the starch gelatinization characteristics^(6,7). Krog⁽⁸⁾ who reported on the amylose-complexing ability of several emulsifiers, found that distilled monoglyceride(MG) had the best complexing ability among nonionic surfactants and sodium stearyl lactylate(SSL) and calcium stearyl lactylate were best among the ionic ones. These differences appeared to be related to the length of the hydrocarbon chains and the number of hydrocarbon chains in the molecules, as well as to the structures of the hydrophilic moieties⁽⁶⁾. Krog and Nybo-Jensen⁽⁹⁾ showed that the ability of monoglycerides to form complexes with amylose depended on the physical form of the surfactant. Chungcharoen and Lund⁽¹⁰⁾ showed that 90% glyceryl monostearate had a slight

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effect on gelatinization temperature and no effect on enthalpy of the endothermic process.

Therefore, in this study we have attempted to use differential scanning calorimetry to investigate the gelatinization and retrogradation characteristics of wheat starch in the presence of different water contents and various surfactants.

Materials and Methods

Materials

Wheat starch was supplied by Gem of the West (Maldra Milling Corp. U.S.A.). The surfactants used were sucrose ester (SE 1170, Ryoto Co. Japan), sodium stearyl-2-lactylate (SSL, PATCO product U.S.A.) and distilled monoglyceride (Dimodan, Grinstead product U.S.A.). Surfactant-to-starch ratio was held constant at 0.35% starch basis. Pregelatinized starches were prepared by heating at boiling water bath for 20 min with different water contents and dried by absolute ethanol.

Methods

A Perkin-Elmer differential scanning calorimeter DSC-2 fitted with a 3600 thermal analysis data station (TADS) and a Perkin-Elmer plotter (Perkin-Elmer Corp. Instrument Div, Norwalk, U.S.A.) were used. Large volume capsules, LVC (No 319-0218) were used to increase sensitivity and reproducibility and to decrease sampling error. Samples for thermal analysis were prepared by weighing the required amount of starch and water. The wetted samples were allowed to equilibrate for at least 2 hrs before differential scanning calorimetry analysis. The water contents of starch were adjusted to 67, 50, 40, 30 and 20%, but the water contents of starch with surfactants were all 50%. The empty pan was used as a reference. The calorimeter was calibrated using naphthalene. The samples were heated from 27°C to 137°C at 10°C/min in the calorimeter. After the first heating run to 137°C, the sample pans were kept at room temperature for 14 days. And the second run was carried out under the same conditions after 2, 7 and 14 day storage.

Results and Discussion

Effect of water

The DSC thermograms of the wheat starch with different water contents are illustrated in Fig. 1. When the starch was heated at high water content (67%), a

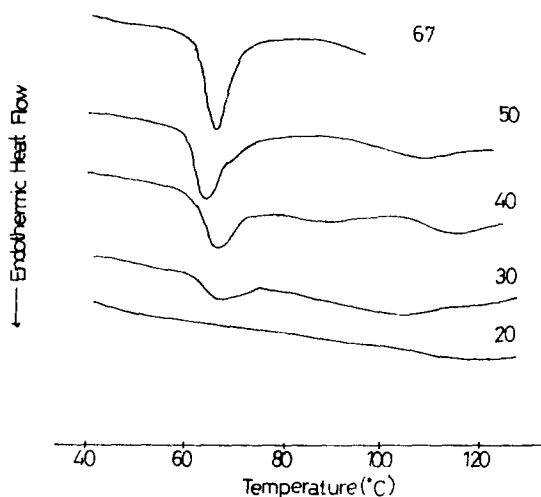


Fig. 1. Differential scanning calorimetric thermograms of wheat starch with various water contents
Numbers represent percent water content

single endothermic transition was observed at about 64°C. As the water content of starch decreased, the second endotherm started to develop at higher temperature and the amylose-lipid complex peak also appeared. Our results were similar to those reported by Ghiasi *et al.*⁽¹¹⁾. They showed that two endothermic transitions were exhibited by all native starches when heated under similar intermediated water contents (45.6~48.2% w/w). The observed biphasic endothermic transition, occurring at intermediated water levels, emerges from two discrete granule or crystallite population⁽¹²⁾. When the water content was 20%, this endothermic transition was not exhibited (Fig. 1). It is obvious that water plays an important role in the overall process by assisting the melting of the starch crystallites.

DSC characteristics of the starch with different water contents were shown in Table 1. As the water contents were varied from 67% to 30%, their gelatinization temperatures were almost same. Donovan⁽¹¹⁾ also found that the low temperature endotherm (gelatinization peak) occurred at constant temperature as the amount of water is varied. Evans and Haisman⁽¹³⁾ reported that the final gelatinization temperature starts to raise when the water content of the starch fell at 0.6~2g water/g starch, but the initial gelatinization temperature was constant at this range. When the water content increased, the enthalpy of gelatinization decreased. The enthalpy (ΔH) values are significantly affected by the

Table 1. DSC characteristics of wheat starch with various water contents

Water contents (%)	Gelatinization peak			Amylose-lipid complex peak		
	To ^{a)} (°C)	Tp ^{b)} (°C)	ΔH(cal/g)	To(°C)	Tp(°C)	ΔH(cal/g)
67	59.5	63.9	2.59	— ^{c)}	—	—
50	59.4	63.4	1.83	101.8	109.6	0.39
40	59.7	64.2	0.75	106.2	116.9	0.47
30	60.3	64.5	0.30	119.3	127.5	0.47

^{a)} To : onset temperature

^{b)} Tp : peak temperature

^{c)} — ; peaks were not detected

Table 2. DSC characteristics of raw starch and pregelatinized wheat starches which were heated with different water contents(starch : water=1 : 2)

Starch	To ^{a)} (°C)	Tp ^{b)} (°C)	ΔH(cal/g)
Raw starch	59.5	63.9	2.59
Pregelatinized starch			
Water content(%)			
20	59.9	65.9	2.06
30	58.9	65.2	0.44
40	— ^{c)}	—	—
50	—	—	—

^{a)} To : onset temperature

^{b)} Tp : peak temperature

^{c)} — ; peaks were not detected

heating rate, amount water and starch damage^(14,15). Biliaderis *et al.*⁽¹²⁾ as well as Wooton and Bamunarachchi⁽¹⁵⁾ and Donovan⁽¹⁾ indicated a pronounced decrease in the gelatinization enthalpies in the presence of limited amount of water. At high water levels, the enthalpy value mainly represents the enthalpy of melting of the starch crystallites. When the water content decreased, the amylose-lipid complex peak was shifted to the higher temperature and the enthalpy increased slightly.

Gelatinization temperature and enthalpy of pregelatinized starch was given in Table 2. When the water contents in gelatinizing system were 20 and 30%, the enthalpies were 2.06 cal/g and 0.44 cal/g, respectively. But the endothermic transition of pregelatinized starch was not obtained above 40% water content. This results showed that starch needed above 30% water content for gelatinization. No gelatinization was reported when water content was less than 30% or fewer than four water molecules per anhydro-glucose unit were present^(1,16).

DSC characteristics of starch during storage was shown in Table 3. The onset temperature of retrogradation peak was 50~55°C and peak temperature was

57~61°C regardless of water content and storage. The temperature of retrogradation peak was lower than that of gelatinization peak. And the enthalpy of retrogradation peak changed during storage. Therefore, the starch-water mixtures transformed during the retrogradation processes into a crystalline-amorphous composite different from the native structure. The enthalpies of retrograded starches with 40 and 50% increased rapidly at 2 day storage and after that increased smoothly, but that of retrograded starch with 67% water content was the lowest at 2 day storage and decreased. The differences in the enthalpy could be interpreted as resulting from variability in the gelatinization moisture or the aging-period moisture of the sample⁽¹⁾. Both annealing and recrystallization are greatly influenced by the water content. They become less prominent with increasing moisture level⁽²⁾. The enthalpy of starch with 40% water content was higher than starch with 50% water content until 7 days, but the enthalpy of both were similar after 7 days. In contrary to these results, Zeleznak and Hosoney⁽⁴⁾ reported that the enthalpy values were greater in the 50~60% starch gel than 40% starch gel. Recrystallization in starch was profound index of crystallinity in aged gels. Rongston and Legrys⁽¹⁷⁾ noted that crystallinity reached maximum development in 50% gel and disappeared in very dilute(10%) or concentrated(80%) gels.

Effect of surfactants

The effects of surfactants on gelatinization temperature and enthalpy are shown in Fig.2 and Table 4. All samples had two endothermic peaks, one, gelatinization peak and the other, amylose-lipid complex melting peak. Starch with surfactant was gelatinized at slightly higher temperature than starch without surfactant. The fatty compound was involved in the helical configuration with amylose and formed a persistent outer layer to restrict passage of water into the starch granule

Table 3. DSC characteristics of wheat starch with different water contents during storage

Storage(day)	2			7			14		
Water contents(%)	To(°C)	Tp(°C)	ΔH(cal/g)	To(°C)	Tp(°C)	ΔH(cal/g)	To(°C)	Tp(°C)	ΔH(cal/g)
40	51.2	58.5	1.13	50.3	58.8	1.22	49.3	59.4	1.24
50	49.6	58.5	0.78	50.0	58.2	1.10	53.2	61.1	1.22
67	53.6	56.7	0.43	55.0	57.9	0.12	— ^{a)}	—	—

^{a)} — : peaks were not detected

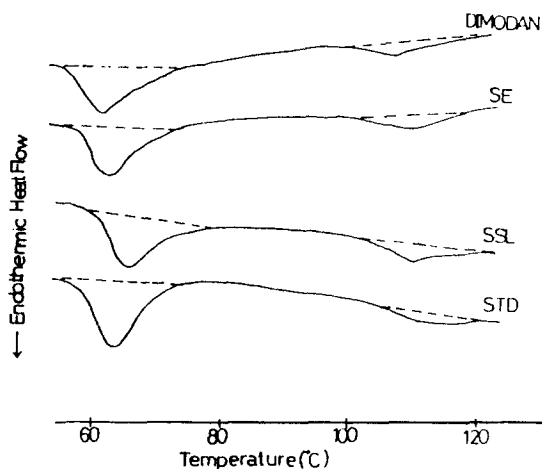
Table 4. DSC characteristics of wheat starch with 0.35% different surfactant(starch : water=1 : 1)

Surfactants ^{a)}	Gelatinization peak			Amylose-lipid complex peak		
	To ^{a)} (°C)	Tp ^{b)} (°C)	ΔH(cal/g)	To(°C)	Tp(°C)	ΔH(cal/g)
STD(not added)	59.4	63.4	1.83	101.8	109.6	0.39
SSL	61.1	65.0	1.56	104.9	111.1	0.57
SE	60.0	64.0	1.70	102.9	112.9	0.59
Dimodan	60.2	64.5	1.60	103.1	110.3	0.48

^{a)} Surfactants were used sodium stearyl lactylate(SSL), sucrose ester(SE) and monoglyceride(Dimodan)

^{b)} To : onset temperature

^{c)} Tp : peak temperature

**Fig. 2. Differential scanning calorimetric thermograms of wheat starch with 0.35% different surfactants(starch : water=1 : 1)**

STD means starch without surfactant and SSL, SE and Dimodan mean starch with sodium stearyl lactylate (SSL), sucrose ester(SE) and monoglyceride(Dimodan)

and thus decreased swell^(16,18). The onset temperature of starch without surfactant was 59.6°C and with surfactant was 60.0~61.1°C and peak temperature was 63.6°C and 64.0~65.0°C, respectively. Larsson⁽¹⁹⁾ reported the observation of an increase in temperature of the endothermic process with surfactant. Enthalpies of ge-

latinization of starch with surfactant at 50% water content were slightly lower than that of starch without surfactant(Table 4). Chungcharoen and Lund⁽¹⁰⁾ observed that the surfactant suppresses gelatinization when water is limited in system. Because the crystallization (exothermic) of amylose-lipid complexes occurs simultaneously and immediately after the onset of the thermal events⁽²⁾. But Cloke *et al.*⁽²⁰⁾ found no difference in enthalpy for gelatinization of model cake systems with or without emulsifiers.

While the enthalpy of amylose-lipid complex peak of starch without surfactant was 0.39 cal/g, the enthalpies of starch with SSL, SE and Dimodan were 0.57, 0.59 and 0.48 cal/g, respectively. The surfactants had ability to form insoluble helical complexes with amylose⁽¹⁸⁾, and inhibit the leaching of amylose effectively⁽²¹⁾. This size of the amylose-lipid complex melting endotherm varies only with the type and amount of added emulsifiers⁽¹⁹⁾. When the amount of amylose-surfactant complex increased, the enthalpy of melting of amylose-lipid complex increased. From this results, sucrose ester had the best amylose-complexing ability among them. But the possibility of some adsorption of surfactant on the surface of starch granules also was considered.

Fig. 3 shows DSC thermogram of starch with surfactants after seven days. The enthalpy of retrogradation peak of starch with surfactant was lower than that of

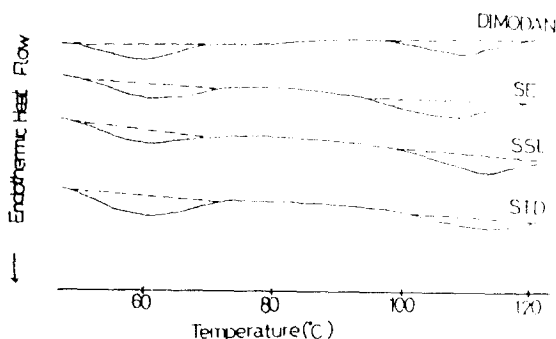


Fig. 3. Differential scanning calorimetric thermograms of wheat starch with 0.35% different surfactants after 7 day storage at room temperature

STD means starch without surfactant, and SSL, SE and Dimodan mean starch with sodium stearyl lactylate (SSL), sucrose ester(SE) and monoglyceride(Dimodan)

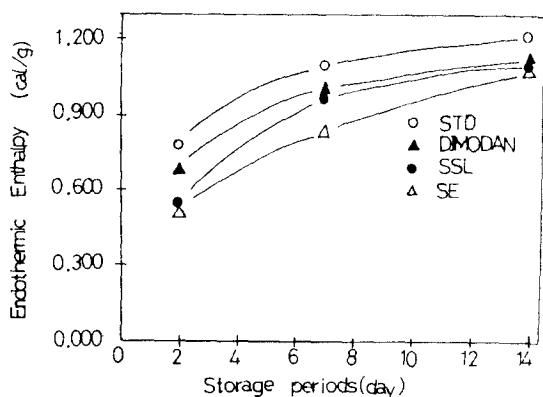


Fig. 4. Changes of endothermic enthalpies of wheat starch with 0.35% different surfactants during storage (starch : water = 1 : 1)

STD means starch without surfactant and SSL, SE and Dimodan mean starch with sodium stearyl lactylate (SSL), sucrose ester(SE) and monoglyceride(Dimodan)

starch without surfactant. The enthalpy of amylose-lipid complex remained constantly after seven days.

The change of enthalpy of retrogradation peak during storage is shown in Fig. 4. The enthalpy of retrogradation on starch without surfactant increased from 0.78 cal/g(2nd day) to 1.22 cal/g(14th day). The enthalpy of retrograded starch with surfactant during storage was lower than of starch without surfactant. The enthalpy value was the lowest in retrograded starch with SE during storage. For the case of sucrose ester, amylose-surfactant complex effectively protected amylose molecules from recrystallization process during storage. Dimodan(monoglycerides) and SSL also dec-

reased starch retrogradation. Krog *et al.*⁽²²⁾ showed that bread added monoglyceride reduced the amylopectin peak(staling endotherm). Matsunaga and Kainuma⁽²³⁾ reported that additives such as n-butyl alcohol and sucrose fatty ester in starch protected amylose molecules from retrogradation during storage. The exact manner in formation amylose-surfactant complexes and the interaction between amylopectin and surfactant are not clear. Further experiments will be reported about interaction between starch and lipid or surfactant on retrogradation process.

요 약

밀전분의 호화과 노화에 수분함량과 sodium stearyl-2-lactylate(SSL), sucrose ester(SE), monoglyceride(Dimodan) 같은 surfactant의 효과를 differential scanning calorimetry를 이용하여 조사하였다. 전분의 호화양상은 수분함량에 따라 다르고 수분함량이 30% 이하이면 호화가 일어나지 못하였다. 호화개시 온도는 59~60°C이었으며, 노화개시 온도는 50~55°C이었다. 노화된 전분의 엔탈피는 수분함량이 40~50%일 때 가장 컸다. Surfactant를 첨가하면 호화온도는 약간 높아졌고, amylose-lipid complex의 엔탈피는 증가하였다. Surfactant를 첨가한 전분은 저장에 따라 노화가 늦게 진행되었으나 amylose-lipid complex의 변화는 거의 없었다.

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