Chapter

Studies on the Property and Application of Starch Sugar Ester Dodecenylsuccinic

Liu Zhongdong, Liu Boxiang, Wei Guohua, Zhu Xin and Wang Huabin

Abstract

In this study, we have prepared starch and Brown algae sugar ester dodecenylsuccinic, and by using infrared rays, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC), we studied the structures and properties of the starch and Brown algae sugar ester dodecenylsuccinic. In addition, we studied the possibility of using this modified starch and Brown algae as emulsifier that can be used in ice cream.

Keywords: starch sugar ester dodecenylsuccinic (Brown algae sugar modified), property and application

1. Introduction

Starch sugar ester is one kind of starch derivatives and it is obtained by modifying starch via former liquefying, then esterifying or by former esterifying, then liquefying. It is an important kind of safe additive, which possessed good emulsification and dense increasing abilities, and is degradable. Starch sugar ester has been an important modified starch in food industry [1–3]. Starch sugar ester, in particular, has been used to stabilize flavor concentrates in beverages, oil in salad oil, and to encapsulate flavors, fragrances, and vitamins. Also it can be used in meat foods, cooking foods, cheese, etc. Starch sugar ester has also important application in papermaking industry, medicine industry, petroleum and chemical industry, etc. With the incorporation of alkenylsuccinates groups into normally starch molecules, starch sugar ester obtains hydrophobic and hydrophilic properties. After liquefaction, we can get starch products of different dense and mobile properties. Starch sugar ester, particularly starch sugar ester dodecenylsuccinate, has some good properties, which other products do not have, and its dense and emulsification abilities are specific [4].

2. Experimental

2.1 Materials

The materials used were as follows: wheat starch (Anyang Hei Tai Limited Liability Company of wheat starch), alkenylsuccinate

(LvShun Chemical Factory have purified by distillation), Termamyl®120L, Types (Novo, Inc.).

2.2 Reagents and instrument

Acetone, hydrochloric acid, NaOH, DMSO, LD4-2 centrifuge (Beijing Centrifuge Factory), JJ-1 Mixer (Shenzhen GUOHUA Instruments Factory), PHS-3C pH meter (Shanghai Leici Instrument Factory), Spray dried Meter (NIRO, Danman), Model 1000B Scanning electron microscopy (AMYRAY, America), Differential Scanning (Calorimetrg-2C, PE, America), PERKIN-ENMER 983G Infrared Rays Merer (PE, America).

2.3 Preparation of wheat starch sugar ester dodecenylsuccinic

2.3.1 The first method

2.3.1.1 Preparation of wheat starch dodecenylsuccinic

Starch was agitated in deionized water with vigorous stirring. The pH was maintained between 8.0 and 9.0 using a 4% NaOH solution. Dodecenylsuccinic anhydride was added slowly, the reaction was allowed to proceed for several hours, then adjusted to 7.0 using HCl, the slurry was filtered, washing with deionized water three times, then washing with acetone one time, centrifuging the isolated insoluble product was air-dried.

2.3.1.2 Liquefaction of wheat starch dodecenylsuccinic

Wheat starch dodecenylsuccinate was slurried with deionized water. The pH was regulated to 5.7; Termamyl®120L, Type S was added with stirring and made to react for some time, and then, the slurry was dried by spray.

2.3.2 The second method

Wheat starch was agitated in deionized water to consistency of 35%. The pH was regulated to 5.7; Termamyl®120L, Type S was added with stirring, and reacting it for 50 min at 85°C killed enzymes. Then, the pH was maintained between 8.0 and 9.0; dodecenylsuccinic anhydride was added slowly, reaction for several hours, then adjusted to 7.0 using HCl, the slurry was filtered, washing with deionized water three times, washing with acetone one times, centrifuging the isolated product was dried by spray.

2.4 The properties analysis of products

2.4.1 Scanning electron microscopy

Scanning electron microscopy measurements were carried out by the procedure of Shiying [5].

2.4.2 Infrared rays

The products was mixed with KBr, pressed to slice, and then determined with Perkin-Elmer 983G Infrared Rays Meter [6].

2.4.3 Different scanning calorimetry (DSC)

Samples (about 5 mg) were weighed directly into previously weighed aluminum DSC pans (**Table 1**). Water was added to obtain the starch-water ratio of 1:1, and the pans were sealed. An empty pan was used as reference. The scanning rate was 2 deg/min. The scanning range was between 320 and 470 k; Means and standard deviations were calculated.

2.4.4 The analysis of the abilities of water-holding and the stability of thawing-melting

Dry starch (1 g) was agitated in deionized water (49 g), heated to boil, cooled to room temperature, centrifuged for 10 min (3000 r/min), then the volume of upper part was determined (V_1), the lower part for 24 h (−18°C) was frozen, then thawed, centrifuged for 10 min (3000 r/min), determining the volume of upper part (V_2) [7].

$$\text{the ability of water} - \text{hoding} = \frac{50 - V_1 - V_2}{\text{weight of starch}}$$

$$\text{the resistment of thawing} - \text{melting} = \frac{1}{V_2}$$

Thawing-melting cycle and water-holding capacity are shown in **Table 2**.

2.4.5 Degree of substitution (DS) determination

A known weight of the sample was dissolved in 10 ml of DMSO by heating (70°C, 10 min) [8]. After cooling, 5–6 drops of phenolphthalein in dictator were added. This solution was titrated against 0.05 M standard NaOH solutions until a permanent pale pink color was seen. The DS was calculated by using the following equation:

$$DS = \frac{0.162A}{1 - 0.2664A}$$

where A is the millimolarity of the NaOH solution in which 1 g sample is reacted. A is calculated as follows:

$$\text{A} = \frac{V \times M}{m}$$

No	T (K)	T_p (K)	T_c (K)	T_c-T (K)	ΔH (J/g)
1	394.8	419.5	434.3	39.5	1152.67
2	365.4	387.0	403.8	38.4	345.05
3	380.2	385.8	394.3	14.1	673.33
4	372.5	386.8	400.5	28.0	549.19
5	378.5	389.8	405.9	27.4	130.63
6	394.5	396.9	412.2	16.7	706.41
7	379.7	397.7	411.9	32.2	506.07

Table 1.
DSC parameters for native and modified starches.

No.	Sample	V_1 (ml)	V_2 (ml)	The rate of water-holding	The antifreeze ability
1	Unmodified wheat starch	27.0	9.8	13.2	0.102
2	Wheat starch dodecenylsuccinate of the first method (DS = 0.0073)	27.4	5.4	17.2	0.185
3	Wheat starch dodecenylsuccinate of the first method (DS = 0.0102)	29.0	5.6	15.4	0.179
4	Wheat starch dodecenylsuccinate of the first method (DS = 0.0150)	28.9	5.8	15.3	0.172
5	Wheat starch esterdodecenylsuccinate of the first method (DE = 4.1)	47.7	0	2.3	No water separated out
6	Wheat starch ester dodecenylsuccinate of the first method (DE = 5.1)	47.5	0	2.5	No water separated out
7	Wheat starch ester dodecenylsuccinate of the first method (DE = 6.9)	48.0	0	2.0	No water separated out
8	Wheat starch ester dodecenylsuccinate of the second method (DS = 0.0099)	47.0	0	3.0	No water separated out
9	Wheat starch ester dodecenylsuccinate of the second method (DS = 0.0112)	47.1	0	2.9	No water separated out
10	Wheat starch ester dodecenylsuccinate of the second method (DS = 0.0146)	48.0	0	2.0	No water separated out

Table 2.
Thawing-melting cycle and water-holding capacity.

where V is the volume of NaOH solution used during titration, M is the molarity of the NaOH solution, and m is the weight of sample analyzed.

2.5 The preparation of ice cream in which the modified starch is used as emulsifier

2.5.1 The rate of ice-cream expanding

2.5.2 Determination of the resistance of ice-cream melting

The ice cream was cut to a block (about 100 g) at room temperature (27°C), and then it was put in the sieve and the time of the first drop dripped was recorded [9].

3. Result and discussion

3.1 Scanning electron microscopy

Figure 1 shows the wheat starch ester dodecenylsuccinate of the first method (1#: Unmodified wheat starch, 2# DS = 0.0073, 3#DS = 0.0102, 4#DS = 0.0150, 5# DE = 4.5, 6# DE = 6.9); wheat starch ester dodecenylsuccinate of the second method (7#DE = 8.2, 8# DE = 9.7, 9# DE = 11.6); and wheat starch ester dodecenylsuccinate of the second method (10# DS = 0.0099, 11# DS = 0.0112, 12# DS = 0.0146).

The unmodified starch granules have an oval or round pattern. For the DS of products, (2#) is low. We only saw individual granules surface were corroded. With the rising of DS, the number of starch granules corroded rises and forms some holes

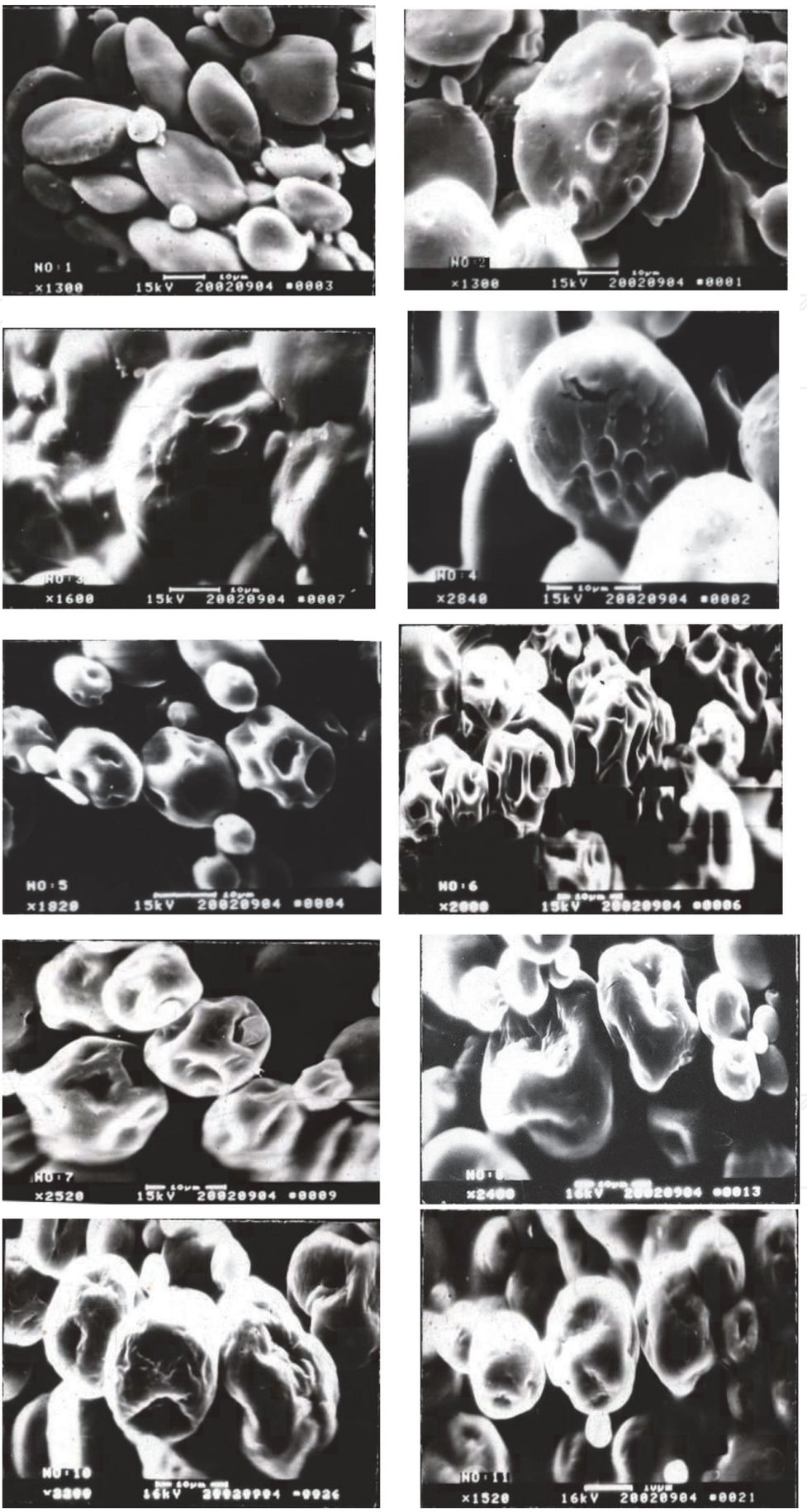

Figure 1.
SEM images of different starch.

(3# and 4#). This shows that the reaction is at the granule surface first. From the images of 5#, 6#, 7#, 8#, and 9#, we can see the obvious holes, which indicate that it is feasible and that we liquefied starch granules with α-amylase. Either liquefaction former or latter, the starch granules all maintaining granule pattern liquefaction first can increase the reaction area on starch granules surface.

3.2 The infrared ray analysis of different products

Figure 2 shows the analysis of the different products, where 1#: unmodified wheat starch; 2#: wheat starch sugar ester dodecenylsuccinate of the first method (DS = 0.0150); 3#: wheat starch sugar ester dodecenylsuccinate of the first method (DE = 6.3); and 4#: wheat starch sugar ester dodecenylsuccinate of the second method (DS = 0.0146).

In **Figure 2**, the absorptions of 1737 cm^{-1} of 2#, 1738 cm^{-1} of 3#, 1739 cm^{-1} of 4# are the absorptions $\gamma_{c=0}$—the character of ester, the absorptions of diene bond (C=C–C=C). From the analysis of the ester bond and diene bond and the comparison the spectrums unmodified wheat starch, it was proved that the products have been estered.

3.3 The differential scanning calorimetric analysis of different products

1#: unmodified wheat starch, wheat starch esterdodecenylsuccinate of the first method (2# DS = 0.0073, 3#DS = 0.0150, 4# DS = 0.0121, 5# DE = 6.3). Wheat

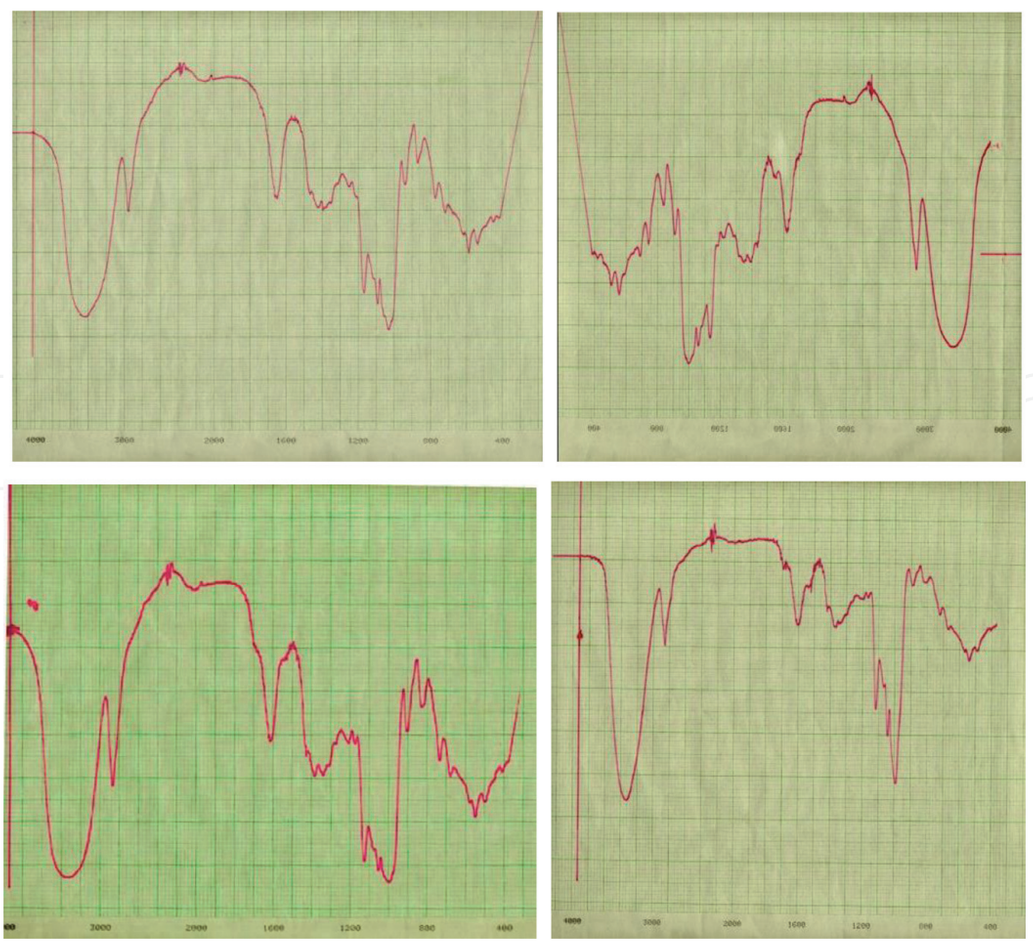

Figure 2.
Infrared rays thermograms of the different products.

starch ester dodecenylsuccinate of the second method (6# DE = 0.0107, 7# DS = 0.0146).

Compared with unmodified wheat starch, the different phases temperature of starch sugar ester descend, and they have low gelatinization enthalpy. This shows that after the alkenylsuccinate group was lead into the starch molecule, it could block hydrogen bond to form between starch chains, decreasing the bonding power away the molecule and making the structure of starch granule to become limp. Crystallized region becomes smaller, which shortens the procedure of gelatinization, and it needs less heat quantity. The reason of absorbing enthalpy of 5# may be the high DE value. The action of α-amylase was found not only in the amorphous region of starch granule but also in the region of crystallization. Also it may be eroded the molecule chain of the starch granule and easy to be melted, so the absorbing enthalpy becomes small.

3.4 Determination of the abilities of water-holding and the stability of thawing-melting

Using the first method, the starch ester dodecenylsuccinic has better water-holding ability and antifreeze capacity than the unmodified starch. From the date of 2#, 3#, and 4#, we found that the low degree of substitution of starch ester dodecenylsuccinic is better than the high one in the stability of thawing-melting. The unfrozen paste of unmodified starch separated out lots of water, the paste was white and muddy, elasticity and became fragment after stirring. We did the same action to the starch ester dodecenylsuccinic and found that the paste can hold transparent gel, in which the elasticity and the frame structure were good. The change was neglectable between after freezing and before freezing. Using the first method, the starch sugar ester dodecenylsuccinic had better water-holding ability than the unmodified wheat starch and wheat starch ester dodecenylsuccinic. The stability of thawing-melting was similar between the two methods of starch sugar ester dodecenylsuccinic.

3.5 Approachment of the application of starch sugar ester which is used as emulsifier in ice cream

3.5.1 Directions for producing ice cream and emulsifier

Directions for producing ice cream are shown in **Table 3** and directions for producing emulsifier are shown in **Table 4**.

Material	Weight (g)	Material	Weight (g)
Dried-skimmed milk	180	CMC	3.6
Maripa oil	180	Sodium alginate	0.9
Sucrose	420	Xanthan gum	1.8
Glucose syrup	150	Sodium hexameta-phosphate	3
Maltodextrin	120	Emulsifier	9
Egg	45	Water	1883.1
Guar gum	3.6		
Total weight: 3000 g.			

Table 3.
Composition of ice-cream.

No.	Emulsifier	Weight (g)
1	×	0
2	Wheat starch ester dodecenylsuccinate (DS = 0.0200)	9
3	Wheat starch ester dodecenylsuccinate of the first method (DE = 6.1)	9
4	Wheat starch ester dodecenylsuccinate of the second method (DS = 0.0146)	9
5	Glycerol monostearate	9
6	Sucrose ester	9
7	2# + 5#	4.5 + 4.5
8	2# + 6#	4.5 + 4.5

Table 4.
Types and mass of emulsifier.

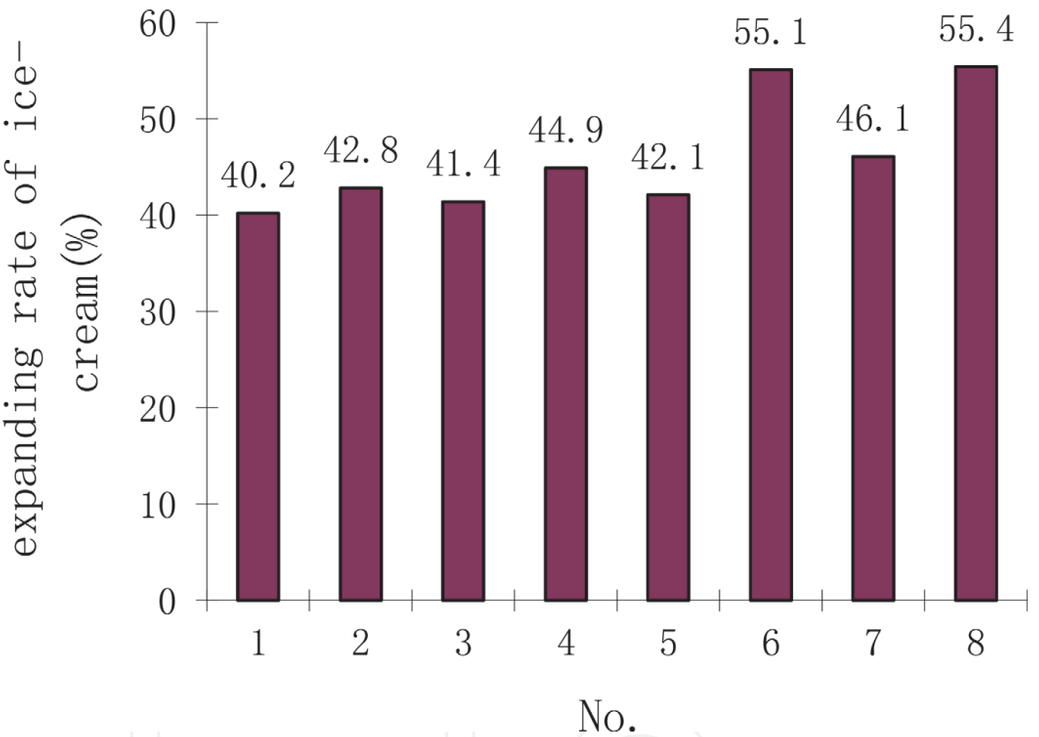

Figure 3.
The rate of ice cream expanding.

3.5.2 Determination of the expanding rate of ice cream

The results of expanding rate of ice cream are shown in **Figure 3**.

Compared with the ice cream without emulsifier, the expanding rate increased after using starch sugar ester as emulsifier. After using the mixture of starch sugar ester, glycerol monostearate and sucrose ester, the expanding rate of ice cream increased a lot. This showed that the starch sugar ester mixture, glycerol monostearate and sucrose ester, has a cooperative effect.

3.5.3 Determination of melting rate of ice cream

The results of melting rate of ice cream are shown in **Figure 4**.

From **Figure 4**, we find that using starch sugar ester as emulsifier, the melting rate of ice cream can increase 12%, compared with glycerol monostearate and

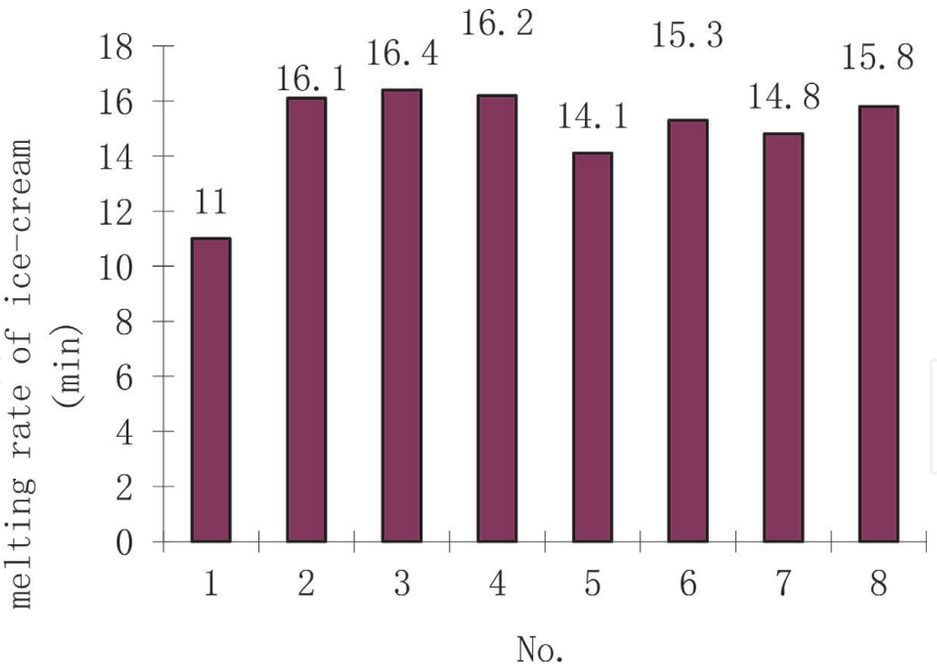

Figure 4.
Melting rate of ice cream.

sucrose ester. Also using the mixture of starch sugar ester, glycerol monostearate and sucrose ester, the melting rate of ice cream can increase 8%.

4. Conclusions

1. After analysis of infrared rays, we found that the wheat starch had been estered.

2. From SEM, we found the reaction did on the starch granule surface. Also they created some obvious holes by the α-amylase before esterification.

3. From the analysis of DSC, the different phases temperature of starch sugar ester descended, and they had a low gelatinization enthalpy.

4. The starch sugar ester can be used as emulsifier of ice cream; it has good cooperative effect with glycerol monostearate and sucrose ester.

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Author details

Liu Zhongdong, Liu Boxiang*, Wei Guohua, Zhu Xin and Wang Huabin
Henan University of Technology, Zhengzhou, P.R. China

*Address all correspondence to: jollier.liu@gmail.com

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