

EWA RUDNIK, EWA ŻUKOWSKA

Industrial Chemistry Research Institute  
ul. Rydygiera 8, 01-793 Warsaw, Poland  
e-mail: ewa.rudnik@ichp.pl

## Studies on preparation of starch succinate by reactive extrusion

### RAPID COMMUNICATION

**Summary** — Reactive extrusion was applied to obtain the starch succinate. Esterification using succinic anhydride was performed using PTW16/25D twin-screw extruder. Sodium hydroxide solution or sodium bicarbonate were used as catalysts. The influence of three kinds of starch was studied. The starch ester with degree of substitution (*DS*) higher than 0.6 was obtained from potato starch in the presence of NaOH solution.

**Key words:** starch esterification, starch succinate, reactive extrusion.

Reactive extrusion proved to be a successful and low-cost way to continuous production of materials. Twin-screw extruders are used as the reactors for bulk polymerization, graft reaction, interchain copolymer formation, coupling or branching reaction, controlled molecular weight degradation and functionalization or functional groups modification [1, 2]. In chemistry of polysaccharides reactive extrusion is usually used to the grafting or the chemical modification of starch. Examples are the reaction of polystyrene grafting onto dissolved starch in a twin screw-extruder [3] or phosphorylation of starch using reactive extrusion [4].

Various kinds of chemical modifications of starches have been attempted in order to modify their chemical and physical properties. For example an esterification with organic acids can result in thermoplastic and hydrophobic materials. Depending on the nature of substituent and the degree of substitution (*DS*), the properties of the modified starch vary significantly [5, 6]. As *DS* indicates the average number of substituents per anhydroglucose unit in starch polymers so, for starch with three hydroxyl groups per unit, the theoretical maximum of *DS* is 3. Majority of the starch derivatives, which are available commercially, have low degree of substitution (*DS* = 0.01–0.2) [6]. Starch esters of moderate to high degree of substitution (*DS* = 0.5–2.5) can show very differentiated properties such as hydrophobicity/melt processibility and a number of non-food applications such as tablet binders, hot melt adhesives, coatings, cigarette filters, biodegradable plastics and metal ion absorbants have been suggested [7].

Starch esters of low *DS* are normally prepared by adding of the desired anhydride to an aqueous starch/

water slurry along with NaOH solution. Reaction times are several hours. Starch esters of moderate to high degree of substitution (*DS* = 0.5–2.5) are prepared using fatty anhydrides and pyridine as the solvent/catalyst system. Other solvents used for the synthesis of starch esters included *N*-methylpyrrolidone, dimethylformamide and dimethylacetamide/LiCl. However, many organic solvents are expensive, toxic and difficult to remove from starch so an alternative methods have been looked for [7].

Reactive extrusion has been used to prepare the starch succinate [8, 9]. The results reported about a rather low *DS* and/or reaction efficiency (*RE*) values, *i.e.* *DS* < 0.5 and *RE* < 30 %. Those studies were concentrated on corn starch.

The aim of this work was to study the possibility to obtain the starch esters, *e.g.* starch succinates by reactive extrusion process. Various kinds of starch were studied. The effects of kind of starch, succinic anhydride concentration, and kind of catalyst on *DS* of starch succinates were evaluated.

### EXPERIMENTAL

#### Materials

Materials used were as follows:

- Starches — potato starch (POCH Gliwice), corn starch (Sigma Aldrich) and wheat starch (Sigma Aldrich).
- Succinic anhydride (analytical grade, Sigma Aldrich).
- Catalysts — NaOH and NaHCO<sub>3</sub> (analytical grade, POCH Gliwice).

## Equipment and procedures of preparation of starch esters

Esterification process was performed using the ThermoHaake PTW 16/25D twin-screw extruder. Extruder was automatically controlled by computer *via* PolyLab software, which enables the control, data acquisition and graphic presentation of the full process being run. Screw diameter was 16 mm and *L/D* ratio 25:1. The extrusion was performed with a rod die (5 mm diameter). The temperature profile of the extruder zones was set as follows: 60/80/80/80/85 °C. The rotation rate of screw was arbitrarily set at 70 rpm. The starch was premixed with succinic anhydride (SA) in various molar ratios (starch:SA from 1:0.05 to 1:0.75) before the experiments. The mixture was fed into zone 1 of the extruder using a volumetric feeder, and feed rate was 47 rpm. The 25 % NaOH solution was added in zone 2 using the ProMinent G/4B pump with 0.8 mL/min rate (starch:catalyst molar ratio = 1:0.09). In the case when the sodium bicarbonate was used as a catalyst, the procedure was different. The catalyst (starch:catalyst molar ratio = 1:0.75) was premixed with starch and succinic anhydride before the experiments (at the same molar ratios starch:SA as in a case of NaOH using) and the distilled water was added in zone 2 using the same pump and the same rate. Water added, replacing here water introduced in NaOH solution, played the same role *i.e.* dissolved the catalyst and plastified the starch.

## Methods of products analyses

FT-IR spectra were obtained from KBr pellets using a Perkin-Elmer FT-IR SPECTRUM 1000 spectrometer.

glass-filter and the residue was washed with isopropanol (100 mL). The starch was re-dispersed in deionized water (300 mL), and then dispersion was heated in a boiling water bath for 10 min. The starch solution was titrated with 0.1 N NaOH.

*DS* was calculated from the following equation:

$$DS = \frac{0.162 \cdot (A \cdot N) / W}{1 - [0.101 \cdot (A \cdot N) / W]} \quad (1)$$

where: *A* — titration volume of NaOH solution (in mL), *N* — normality of NaOH solution, *W* — dry weight of the succinylated starch (in g).

*RE* values were calculated by dividing the experimental *DS* and the theoretical *DS*.

Specific mechanical energy (*SME*) was defined as total input of mechanical energy per unit dry weight of extrudate [11]. To find *SME* value an extrudate was collected for 30 s and dried. *SME*, in Wh/kg, was calculated according to the equation:

$$SME = \frac{2\pi \left( \frac{n}{60} \right) \tau}{MFR} \quad (2)$$

where: *n* — screw speed (in rpm),  $\tau$  — average torque (in Nm), *MFR* — melt flow rate (in kg/h) determined on the basis of the weights of extrudate samples taken each 30 s.

## RESULTS AND DISCUSSION

Figure 1 represents starch and starch succinate FT-IR spectra, confirming that succinylated starch was obtained: a new peak around 1735 cm<sup>-1</sup> is appeared, attributed to ester carbonyl group stretching vibration.

The values of degree of substitution (*DS*) and reaction efficiency (*RE*) for different starch:SA ratios and dif-

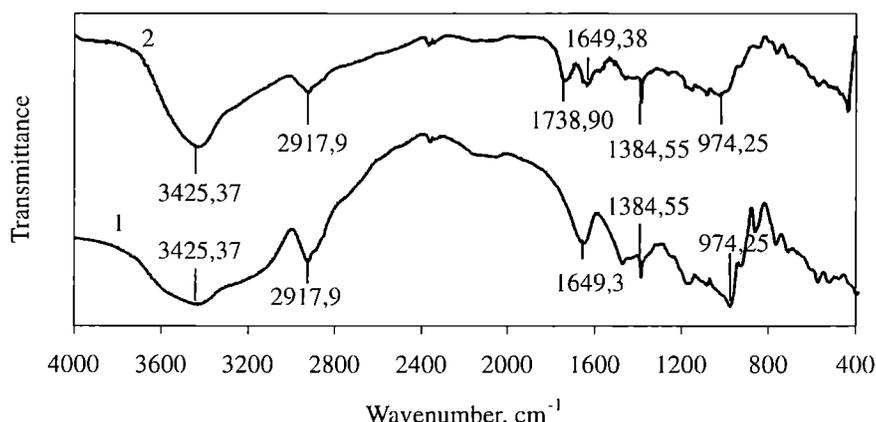


Fig. 1. FT-IR spectra of native starch (1) and starch succinate (2) (sample: PSTSA 1/3)

*DS* of succinylation was measured by alkaline titration of the carboxyl group according to the method described in [10]. The succinylated starch (1 g) was dispersed in 2.5 N HCl/isopropanol solution (25 mL) by stirring for 30 min. The dispersion was filtered through a

ferent kinds of starch are given in Table 1 and Table 2 for reactions catalysed by NaOH and NaHCO<sub>3</sub>, respectively.

*DS* values are in the range of 0.008–0.639. In all cases, an increase in the succinic anhydride concentra-

tion resulted in an increase in *DS* of starch succinates. The higher *DS* is obtained when NaOH solution is used as a catalyst for all kinds of starches.

**T a b l e 1.** Degree of substitution (*DS*) and reaction efficiency (*RE*) of starch succinates (catalyst:NaOH solution)

Symbol of the sample	Starch	Starch: succinate anhydride molar ratio	<i>SME</i> Wh/kg	<i>DS</i>	<i>RE</i> , %
PSTSA 1/1	potato	1:0.05	250.8	—	—
PSTSA 1/2	potato	1:0.1	400.7	0.008	8
PSTSA 1/3	potato	1:0.5	297.8	0.285	57
PSTSA 1/4	potato	1:0.75	338.4	0.639	85
CSTSA 2/1	corn	1:0.05	402.6	—	—
CSTSA 2/2	corn	1:0.1	344.1	—	—
CSTSA 2/3	corn	1:0.5	181.8	0.222	44.4
CSTSA 2/4	corn	1:0.75	187.1	0.401	53.5
WSTSA 1/1	wheat	1:0.05	241.1	—	—
WSTSA 1/2	wheat	1:0.1	283.2	—	—
WSTSA 1/3	wheat	1:0.5	132.4	0.247	49.4
WSTSA 1/4	wheat	1:0.75	147.2	0.381	50.8

**T a b l e 2.** Degree of substitution (*DS*) and reaction efficiency (*RE*) of starch succinates (catalyst:NaHCO<sub>3</sub>)

Symbol of the sample	Starch	Starch: succinic anhydride molar ratio	<i>SME</i> Wh/kg	<i>DS</i>	<i>RE</i> , %
PSTSA 3/1	potato	1:0.05	214.7	—	—
PSTSA 3/2	potato	1:0.1	237.0	—	—
PSTSA 3/3	potato	1:0.5	248.0	0.127	25.4
PSTSA 3/4	potato	1:0.75	245.8	0.254	33.9
CSTSA 3/1	corn	1:0.05	89.6	—	—
CSTSA 3/2	corn	1:0.1	90.5	—	—
CSTSA 3/3	corn	1:0.5	120.1	0.113	22.6
CSTSA 3/4	corn	1:0.75	106.1	0.256	34.1
WSTSA 2/1	wheat	1:0.05	121.9	—	—
WSTSA 2/2	wheat	1:0.1	119.0	—	—
WSTSA 2/3	wheat	1:0.5	123.6	0.201	40.2
WSTSA 2/4	wheat	1:0.75	123.5	0.253	33.7

*RE* is also higher for NaOH as a catalyst in comparison with NaHCO<sub>3</sub> one. Regarding the influence of kind of starch, the highest reactivity is for potato starch, *i.e.* *DS* is above 0.6 and *RE* exceeds 85 %.

*SME* varied from about 90 to about 400 Wh/kg. Compared with other starches processed under the same ex-

trusion conditions, the highest *SME* is also for potato starch regardless of kind of the catalyst used. It may be explained by the higher melt viscosity of potato starch than of other starches resulting in particularly high energy requirement [12].

## CONCLUSIONS

Reactive extrusion process was found to be rapid and simple method of preparing of starch esters. Esterification of starch using SA in twin-screw extruder resulted in chemically modified starch with substitution degree depending on the reaction conditions. The starch succinate of *DS* higher than 0.6 was obtained. The reaction efficiency was also high (>80 %). Good result could be achieved independently on the kind of a starch. However, the highest *DS* and *RE* values were obtained for succinylation of potato starch. Further studies concerning the optimization of the preparation of starch esters by reactive extrusion are under investigation.

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