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PROPERTIES OF ACETYLATED STARCH OBTAINED FROM SO_2-TREATED STARCH MILK

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ABSTRACT

The number of linkages to acetyl groups decreased with the increasing contents of SO_2 in starch milk. Acetylation degree affected pasting temperatures and viscosities of the pastes obtained from acetylated starch. The changes in potato starch properties observed during acetylation by acetic anhydride at alkaline pH resulted not only from linkages to acetyl groups, but also from ion exchange.

Key words: acetylated starch, SO_2-treated starch milk, physico-chemical properties

INTRODUCTION

The process of starch acetylation has been known for over ninety years. Acetylated starch is widely used in food, textile and paper industry.

In Poland acetylated starch with a low degree of substitution, used for a variety of industrial applications, is obtained from potato starch. Starch milk collected at the section of refining is the raw material for producing acetylated starch with a low degree of substitution during starch campaign. The majority of starch processing plants make acetylated starch after the starch campaign is over, using dried starch, either stored in bulk in silos or in bags. The latter is preferred from organizational and economic points of view (prolonged employment and use of equipment and facilities). In the case of wet modified starches (e.g. acetylated starch with a low degree of substitution, starch syrups) the first stage requires starch milk production, therefore, the after-campaign manufacturing is more costly as it is more energy consuming, which is connected with some additional operations, such as starch drying, followed by storage and next mixing with water in order to obtain starch milk. The use of energy can be reduced provided that starch milk is stored instead of dried starch. The data in the literature [3, 4] show that prolonged storage of starch milk with no quantitative losses of starch is possible when starch has been pre-treated with some preserving agents. However, pre-treatment may affect the process of modification and the quality of the resultant product.

The aim of the present study was to determine the effects of SO_2-treatment on starch milk, the process of starch acetylation and properties of acetylated starch.

MATERIALS AND METHODS

The material taken for the study consisted of potato starch "Superior". Starch milk was obtained by mixing 200 g of starch (converted to dry weight) with 200 g of distilled water. Next, a solution of $NaHSO_3$ was added and the total weight of the suspension (starch + $NaHSO_3$ solution + water) was brought up to 560 g by the addition of water. The concentrations of $NaHSO_3$ expressed as mg SO_2 per 1 000 g of starch milk were as follows: 0; 37; 75; 150; 300; 600; 1 250; 2 500; 5 000 and 10 000. The mixture was blended and kept for approx. 30 min.

Production of acetylated starch with a low degree of substitution

Acetylation was carried out by the methods used in Polish starch processing plants [6].

The starch milk was blended with acetic anhydride (26.2 cm^3), at a constant rate of 1 cm^3/min, and 3% NaOH solution until the pH was adjusted to 8-9. After the whole amount of the acetic anhydride had been added, the resulting mixture was acidified with 10% HCl to adjust the pH to 5.2-5.6. The acetylated starch was separated on a funnel and washed with distilled water, so as to remove the residues of the reagents. Starch was dried at temperature lower than 30°C and screened. The analyses were made for 7-14 days after production of the acetylated starch.

Analysis

The measurements of starch milk and acetylated starch included:

- dry weight - by drying at 105°C for 3 h,
- pasting temperatures and viscosity of 4% pastes, using a Brabender viscograph [3],
- acetylation rate by titration - 10 g of the product was poured into a conical flask, filled with 65 ml of distilled water, and neutralized by adding a few drops of 0.01 M NaOH in the presence of phenolphthalein until pale pink colour was maintained for ca. 1 min. Next, 25 ml of 0.5 M NaOH was added and blended at ca. 25°C for 35 min. The resultant mixture was titrated with 0.5 M HCl.

The acetylation degree was calculated according to the method of Wurzburg [8]:

$$\text{Acetylation percent} = \frac{(25 - x)\,0.043 \cdot 0.5 \cdot 100}{a}\ [\%]$$

where
x - amount of 0.5 M HCl used for titration of a sample,
a - weight of starch (in conversion to dry weight).
The data were analyzed statistically (one-way analysis of variance, linear analysis of regression) using Statgraphics v.5.0 [2].

RESULTS AND DISCUSSION

The properties of acetylated starches depend on the kind and type of starch, pretreatment of the starch, acetylation process (amount and kind of reagents and catalysts). The present study was performed with one raw material and under standardized conditions of reactions, therefore, the properties of acetylated starch were likely to have been affected by SO_2-treatment of the starch milk.

As can be seen in Figure 1, SO_2 decreased the degree of starch acetylation. SO_2 concentrations within the range of 37-75 mg/kg reduced the acetylation rate by approx. 30% (from 3.75% to ca. 2.5%). Acetylated starch obtained from SO_2-treated starch milk (≥150 mg/kg) produced the acetylation rate lower than 2%, therefore, the concentrate did not meet the requirements of Polish starch processing plants.

The decrease in the acetylation rate due to SO_2-treatment corresponded with changes in the temperatures of starch pasting and viscosity of 4% pastes produced from acetylated starch.

Fig. 1. Acetylation degrees of starch obtained from SO_2-treated starch milk

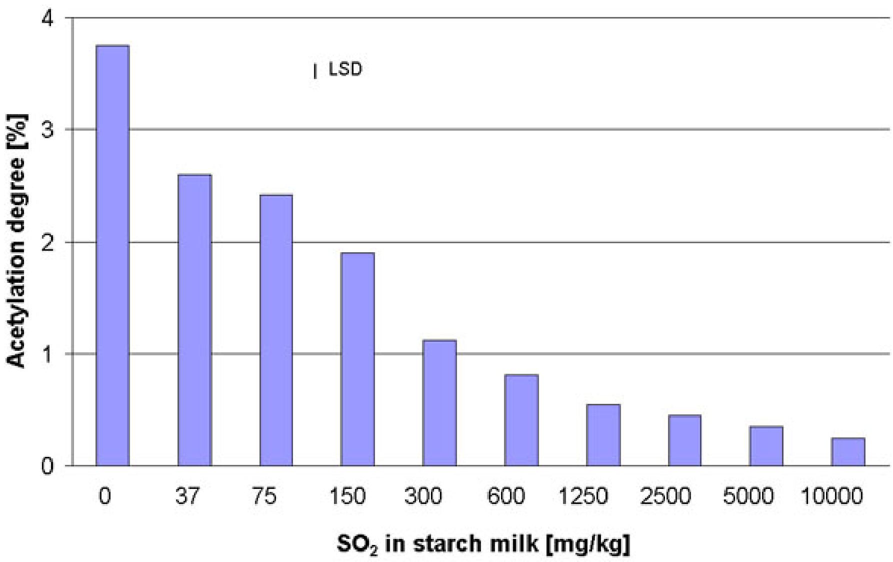


Fig. 2. Starting temperature of pasting (1) and temperature of max. viscosity (2) of acetylated

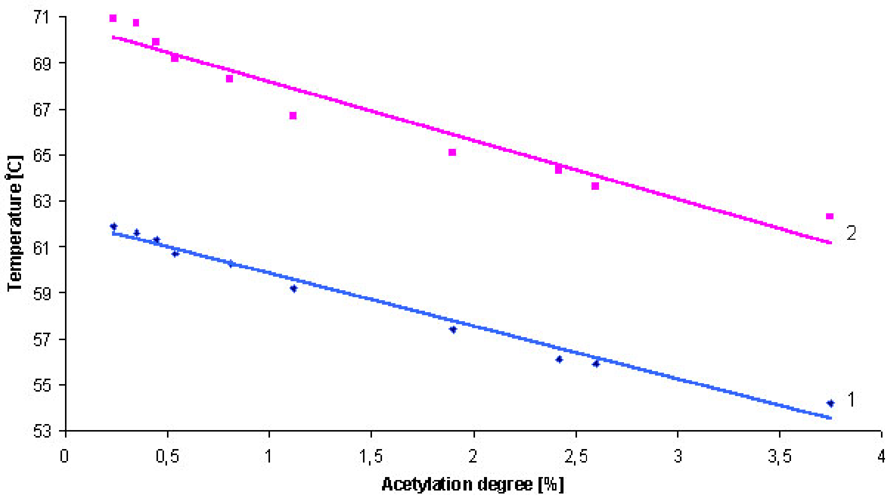


Figure 2 shows that the degree of acetylation affected the starting temperature of pasting and max. temperature of viscosity of the acetylated starch. The relationship between the degree of acetylation and pasting temperatures was strong correlated and the correlation coefficients were: r = - 0.99 (starting temp. of pasting) and r = - 0.97 (temp. of max. viscosity).

Figure 3 shows the relationship between the degree of acetylation and max. viscosity of 4% starch pastes. As can be seen in Fig. 3 the acetylation degree lower than 1% did not affect the max. viscosity of pastes; these values were correlated at higher degrees of acetylation (r = 0.98).

Fig. 3. Max. viscosity of 4% pastes obtained from acetylated starch vs. acetylation degree

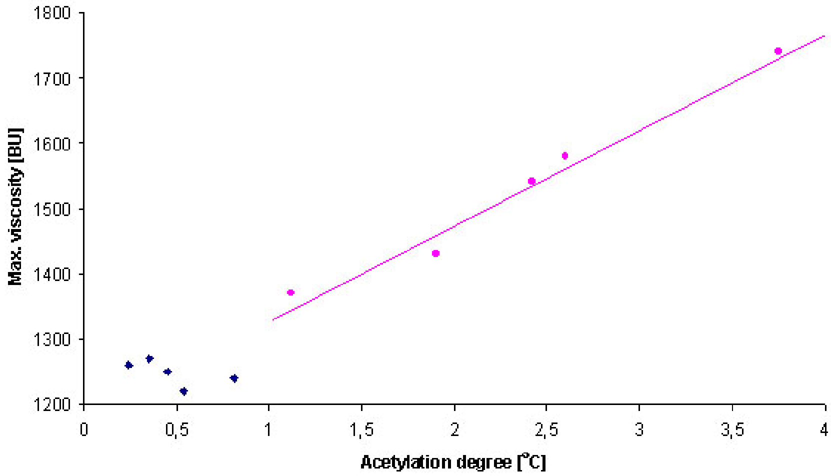
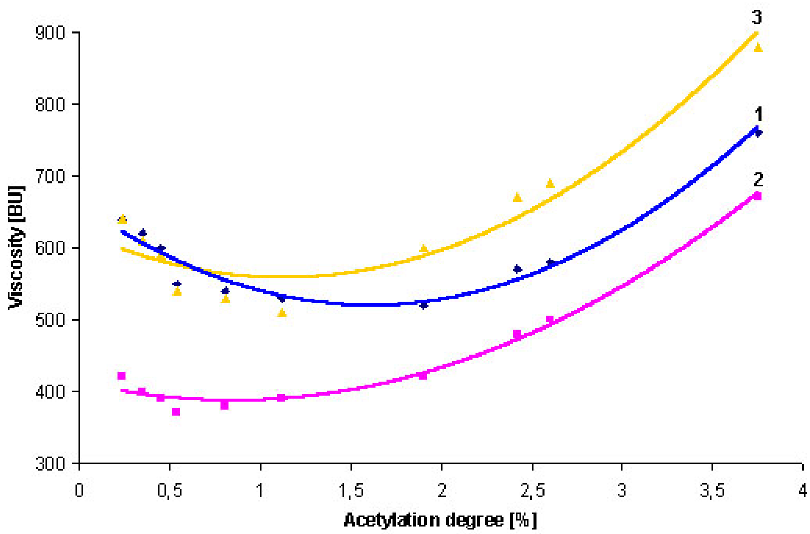


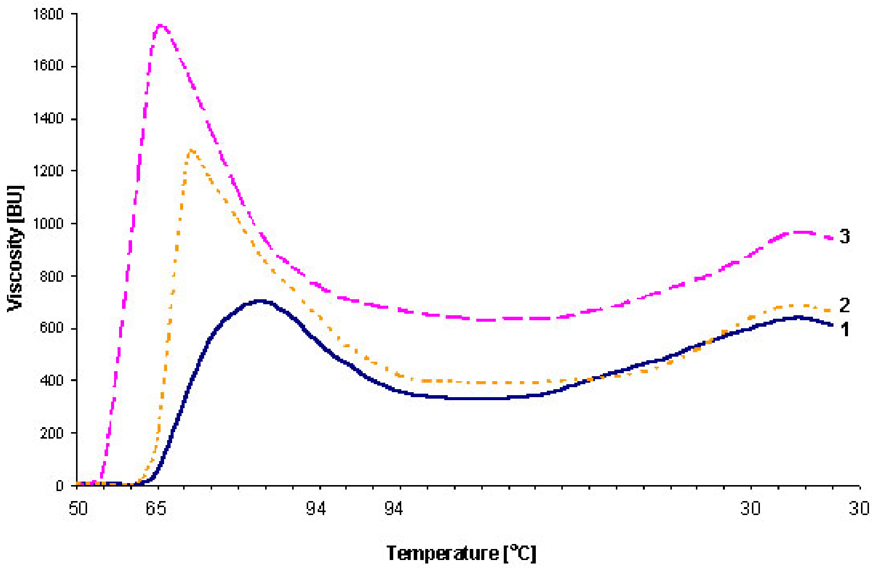
Fig. 4. The relationships between viscosity of 4% pastes and acetylation degree (1) - viscosity at 94°C; (2) - viscosity at 94°C - end holding period; (3) - viscosity at 30°C



The viscosities of 4% pastes measured at 94°C, after 10 min of storage at 94°C and 30°C were also affected by the degree of starch acetylation. As can be seen in Figure 4, the viscosities found within the range of 0.24% - 0.88% were decreasing with the increased degree of acetylation, while those within the range from 1.12% to 3.75% increased with the increasing acetylation degree. Relationships between acetylation degree and temperatures of starch pasting and paste viscosities were also reported by other authors [1, 5].

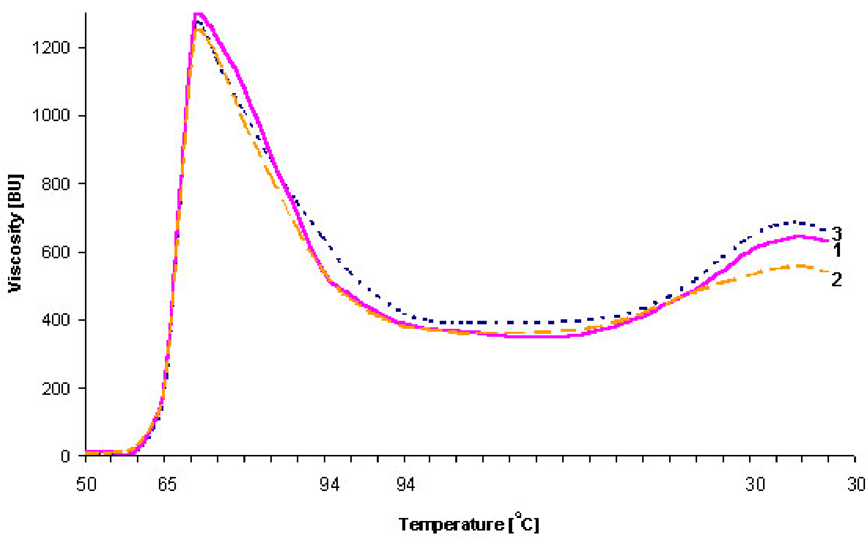
As can be seen in Figure 5, the differences in pasting temperatures and viscosities of 4% pastes between native starch and starch with a low degree of acetylation (A = 0.24%) were greater than those between starches with different degrees of acetylation (A = 0.24%; A = 3.75%). It seems unlikely that the linkage of few acetyl groups to starch (acetylation degree A = 0.24%) could have decreased the temperature of max. starch viscosity by ca. 7°C and increased max. viscosity of 4% pastes by ca. 550 BU as compared to native starch. It is quite likely that during acetylation, apart from esterification, the phosphoric acid present in starch is saturated with sodium ions present in the NaOH solution used for adjusting the pH to 8-9.

Fig. 5. Pasting characteristics of native (1), and acetylated starches: (2) - acetylation degree 0.24%; (3) - acetylation degree 3.75%



In order to determine the changes due to ion exchange, the starch was washed with NaCl solution, and next several times with distilled water, so that ”sodium” starch was obtained. The pasting temperature of this kind of starch was lower than that of native starch, whereas the viscosity of pastes was higher, typical of ”sodium” starch [7]. The curve characterizing ”sodium” starch pasting was similar to that of acetylated starch containing 0.24-0.81% acetyl (Fig. 6). It can, therefore, be concluded that the differences between native and acetylated starch were mainly due to the exchange of ions; the effect of linkage of the acetyl groups occurs at higher than 1% amounts of acetyl residues in starch.

Fig. 6. Pasting characteristics of sodium (1), and acetylated starches: (2) - acetylation degree 0.24%; (3) - acetylation degree 0.81%



In further series of the experiments, acetylated starches were made from starch milk pretreated with 10 000 mg of SO_2/kg, in which Na_2SO_3 and $Na_2S_2O_5$ were the sources of SO_2. As Table 1 shows there are no significant differences between the properties of the resultant acetylated starches (acetylation degree, pasting temperatures, viscosity of 4% pastes) and acetylated starch obtained from starch milk with the same dose of SO_2 added in the form of $NaHSO_3$. This accounts for specific impact of SO_2 on acetylation, irrespective of the compound used.

Tab. 1 Properties of acetylated starches produced with 1% addition SO_2 in the various form

Form of SO_2	Properties of acetylated starches			
	Acetylation degree [%]	starting temperature of pasting [°C]	temperature of max. Viscosity [°C]	max. viscosity [BU]
$NaHSO_3$	0.24	61.9	70.9	1 260
Na_2SO_3	0.28	61.3	70.1	1 290
$Na_2S_2O_5$	0.26	61.6	70.5	1 280

The impact of SO_2 on acetylation degree and the properties of acetylated starch should be taken into account by industrial manufacturers of acetylated starch with a low degree of substitution. SO_2 is added during technological processes of starch processing plants, therefore, it is important to know SO_2 contents of the starch milk destined for acetylation. Starch milk treated with SO_2 probably contains a relative big amount of SO_2 so it should be washed with water in order to reduce its SO_2 contents prior to acetylation.

CONCLUSIONS

1. SO_2 treatment of starch milk (irrespective of chemical compound used) decreased the acetylation degree and also affected pasting temperatures and viscosity of 4% starch pastes.
2. Changes in the properties of acetylated starches as compared to native starch (non-acetylated) were both due to the exchange of ions saturating phosphoric acid into sodium ions as well as the linkage of acetyl to hydroxy groups during acetylation.
3. Too high contents of SO_2 in starch milk destined for acetylated starch concentrate manufacturing is likely to reduce the quality of the subsequent product.

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