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EXAMINATION OF THE SWELLING OF HEAT PROTECTIVE HYDROCOLLOIDS BY DSC

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While the basic fermented (sour) milk products, such as yogurt and kefir can be produced only in live flora version, the post heat-treatment is preferred in their flavored variations to increase the storage time. Casein being in sour coagulum precipitates during heat-treatment; therefore protective colloids surrounding the protein should be used to prevent it. Protective colloids are plant extracts, the most known of them are pectin and amylopectin. Basic requirement of protective colloid effect is the lower swelling temperature of hydrocolloid than the temperature of precipitation of sour coagulum. In this work we have examined the precipitation of sour coagulum as a function of the type of lactic acid bacteria cultures applied during fermentation as well as the swelling of heat protective plant hydrocolloids as a function of the composition (mainly of sugar content) of medium.

To investigate the precipitation of fermented coagulum skimmed milk was fermented with mesophilic butter culture, thermophilic yogurt culture as well as with exopolysaccharide (EPS)-producing Prebiolact-2 culture. Precipitation was indicated in the increase of great extent of viscosity.

Amylopectin was dispersed into aqueous solution of pH 4.5, the saccharose concentration of which was changed during the investigation of the swelling of heat protective hydrocolloids. A definite exothermic peak was assigned to the swelling of hydrocolloids during the DSC experiments.

We could conclude that the precipitation temperature was increasing in the mesophilic-thermophilic-EPS producing microbes line, i.e. the heat stability and swelling temperature of hydrocolloids depend on the saccharose content of aqueous medium and they increase with rising the concentration of saccharose.

Keywords: *amylopectin, DSC, exopolysaccharide (EPS), protective hydrocolloids*

Introduction

Sour milk products are among the most ancient foods of mankind. They have been consumed from the time milk is available, so they are 4–8 thousand years old. They came into being spontaneously as far as the milk soured in the lack of cooling and people of the age realized soon that some of the properties of sour milk (e.g. thirst quenching effect, shelf-life) were better than that of milk. Due to the physiological investigation, by now it has been also cleared that sour milk products are more beneficial from nutrition physiological point of view only if we mention their better digestibility, or higher content of biologically active materials (vitamins, organic acids, decomposed proteins, etc.) compared to milk.

Natural sour milk products (e.g. yogurt, kefir) are made without additives and with live flora on a world scale, but at the production of flavoured versions the post heat-treatment is frequently used to guarantee a longer (several months) shelf life. However, at post heat-treatment, i.e. during the heat-treatment of sour coagulum in order to hinder the shrinking and protein precipitation protective hydrocolloids should be used. The protective colloid, e.g. pectin, enter into interaction with casein micellas [1] almost surrounding them, and thus preventing their connection with each other, i.e. the precipitation. As a protective colloid, besides pectin, in Hungary amylopectin has first of all spread as it has been produced since 1980s [2] and stabilizers were made of it for the home market [3]. Amylopectin is a component of every kind of maize starch, it can be obtained by a separation process [4]. The other possibility is to make starch from Waxy maize which contains amylopectin in amount of above 95%, which has viscosity lower than that of normal maize starch [5, 6] and its heat degradation is also smaller [7].

However, stabilizers can contain several hydrocolloids [8] the thermic properties of gel-forming and heat-protective hydrocolloids usually are not investigated combined with other hydrocolloids. Gelation of these two types is of high importance from the point of view of determination of product properties. For example κ-carrageenan does not form gel it is not

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heated up above swelling temperature which can be exactly determined by differential scanning calorimetric (DSC) method [9]. The swelling temperature and range are also of such an importance in case of native and modified starches which can also be measured by DSC-method the most effectively [10].

Swelling of maize starch depends on what type is the aqueous medium. It was determined by DSC-method that by increase of xyloglucan concentration the swelling temperature of starch also increases [11]. The increase of swelling temperature was also measured by DSC-method due to the effect of sugars and sugar-esthers, and the degree of increase depended on the kind of sugar used [12]. It was also determined by measurement of viscosity that the rheological property of water-starch dispersion is the function of glucose concentration of the aqueous solution [13]. The effect of concentration of sugar was also shown in milk protein/LBG/sugar system (LBG=locust beam gum) on protein and LBG-phase by the help of rheological and turbidimentrical methods [14].

However, we have not found any information in literature whether under what conditions the amylopectin of maize starch can be used as a heat-protective hydrocolloid.

Considering that the heat protection of proteins on the top of concentration of heat-protective hydrocolloids depends on its swelling temperature and precipitation temperature of proteins, in our experiments the precipitation temperature of proteins as a function of different properties of sour coagulum was examined on the one hand, and the amylopectin swelling temperature as a function of saccharose concentration on the other one.

Experimental

Materials and methods

Examination of precipitation of proteins

Skimmed raw milk was heat-treated accoding to the parameters listed in Table 1. The heat-treated milks were cooled down to 25, 36 and 45°C and inocculated with butter, Prebiolact-2 and yogurt culture respectively, and fermented to pH 4.5. Prebiolact-2 culture can be characterized by a great volume of exopolysaccharide (EPS)-production [15, 16]. The coagulums were cooled down to 5°C and held for 24 h then stirred. Taking into consideration that the consistency of sour coagulum changes first of all depending on the culture applied and the coagulation temperature [17] the stirred coagulum was poured into Bohlin–Visco type rotation viscometer and the change of viscosity was continuously registered in the temperature range of 20–80°C at 2°C min^{-1} heating rate. The precipitation was indicated by the quick increase of viscosity. The ratio of denaturated whey proteins (DWP) was determined by Voss–Moltzen method [18] using a spectrophotometer.

Table 1 Parameters of heat-treatment of raw milk

Heat treatments		Ratio of denaturated whey proteins/mass/mass%
T/°C	Holding time/min	
75	1	10
85	3	55
95	10	100

The examination of swelling of the heat protective hydrocolloid

To adjust the pH of the medium 1–1% NaH_2PO_4 and Na_2HPO_4 containing aqueous solution was titrated to pH 4.5 with 1 M HCl solution, and the sugar content was adjusted with saccharose to 0, 5, 10, 15, 20, 25 and 30%, respectively. 50 mg amylopectin was measured into 1 mL batch-cell, 500 mg aqueous solution of pH=4.5 was added, then dispersed for 10 s by the help of a test tube shaker. The heat flow-temperature curves were recorded in a Setaram Micro DSC-II scanning calorimeter at 0.3 K min^{-1} rate in temperature range of 20–100°C.

Results and discussion

In Fig. 1 the change of relative viscosity indicating the heat precipitation of proteins is shown in coagulums fermented with butter culture at 25°C and with yogurt

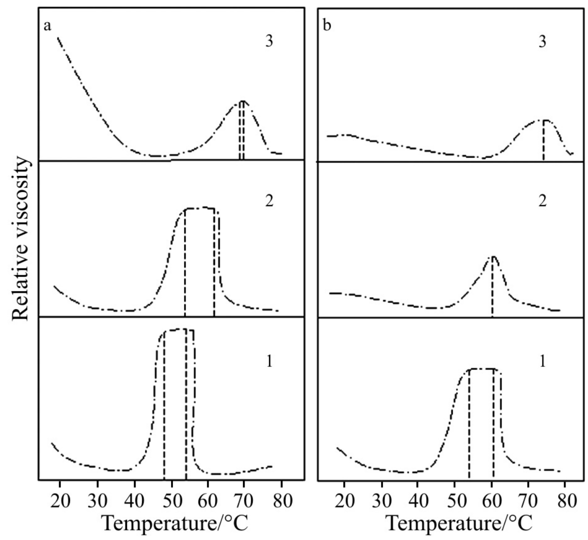

Fig. 1 Change of relative viscosity indicating the heat precipitation of proteins as a function of temperature at pH=4.5 in case of coagulums fermented at a – 25°C, b – 45°C and of DWP-value of 1 – 10%, 2 – 55% and 3 – 100%, respectively

culture at 45°C. The DWP-value of raw material at both coagulums was 10, 55 and 100%. The figure series shows if the coagulation takes place at a higher temperature, at the same DWP-value the temperature of precipitation will be higher, and in both cases simultaneously with the increase of the DWP-value the temperature of precipitation will be higher.

In Fig. 2 the precipitation temperature of coagulums made from 100% DWP-value milk with mesophilic (25°C), thermophilic (45°C) and EPS-producing (36°C) cultures is demonstrated. It is obvious that the exopolysaccharide produced by microbes exert protective colloid effect, and even in case of coagulation at a lower temperature increases the temperature of precipitation.

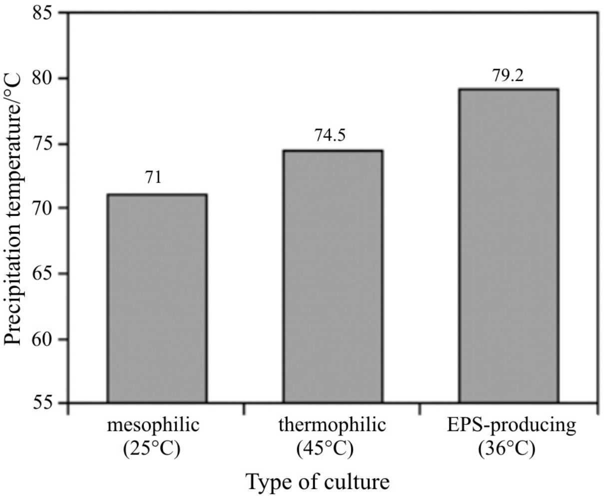

Fig. 2 Precipitation temperature of coagulums made from milk of 100% DWP-value with different cultures

Figure 3 shows the precipitation temperature of coagulums made with mesophilic butter culture, thermophilic yogurt culture and EPS-producing Prebiolact-2 culture as a function of DWP-value. Our former statements are well supported by the figure: the precipitation temperature of coagulum increases together with the rise of the coagulation temperature and DWP-value and increases to a great extent if the coagulum contains EPS of protective colloid effect.

In Fig. 4 DSC-scans of amylopectin dispersed into aqueous buffer solution of pH=4.5 containing no saccharose, 5, 10, 15, 20, 25, 30 and 40% saccharose, respectively, are shown as a function of temperature in the temperature range of 20–100°C. The peak temperatures and enthalpia-values belonging to curves are shown in Table 2.

In general we can state that together with the increase of saccharose concentration the swelling temperature and enthalpia-value of amylopectin increases.

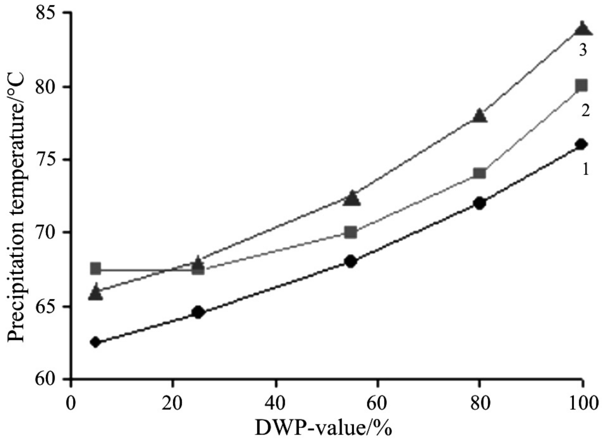

Fig. 3 Precipitation temperature of coagulums fermented with 1 – mesophilic, 2 – thermophilic and 3 – EPS-producing cultures as a function of DWP-value

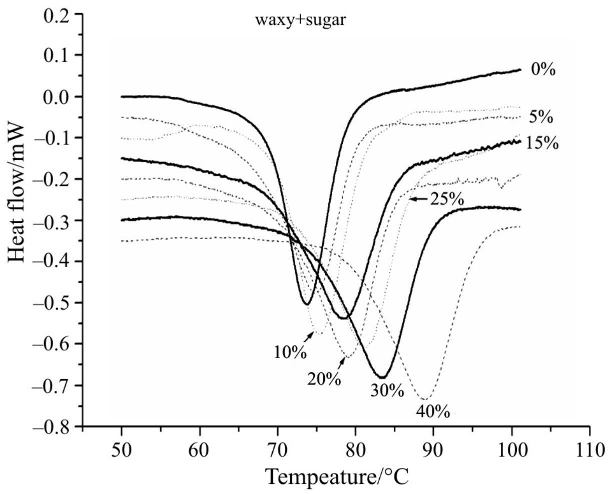

Fig. 4 Thermal denaturation of amylopectin dispersed into aqueous buffer solution of pH=4.5 containing saccharose from 0 to 40%

Table 2 Peak temperature and enthalpia-value of swelling curves of amylopectin

Saccharose concentration/ g/100 g	Swelling curves	
	peak temperature/°C	Enthalpy/J g^{-1}
0	73.8	9.80
5	74.8	14.44
10	75.3	14.94
15	78.5	15.48
20	79.1	16.48
25	81.3	17.10
30	83.4	17.10
40	88.9	17.50

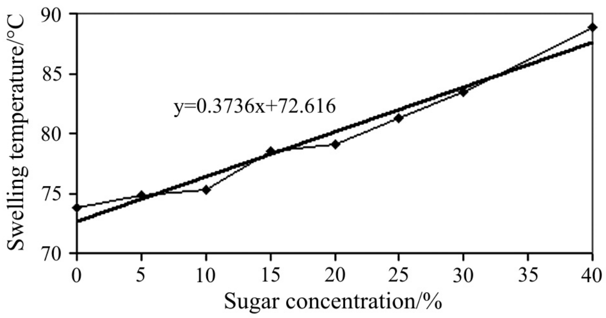

Fig. 5 Swelling temperature of amylopectin as a function of saccharose concentration of dispersion medium of pH=4.5 in a concentration range of 0–40%

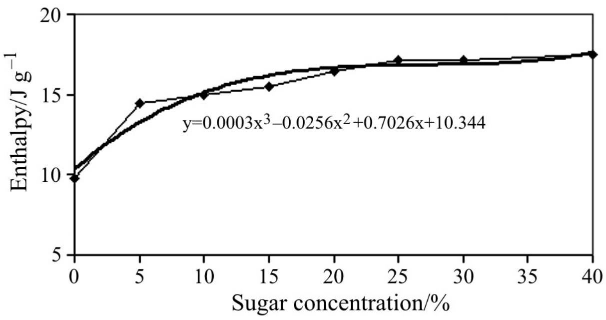

Fig. 6 Enthalpia-value of swelling curves of amylopectin as a function of saccharose concentration

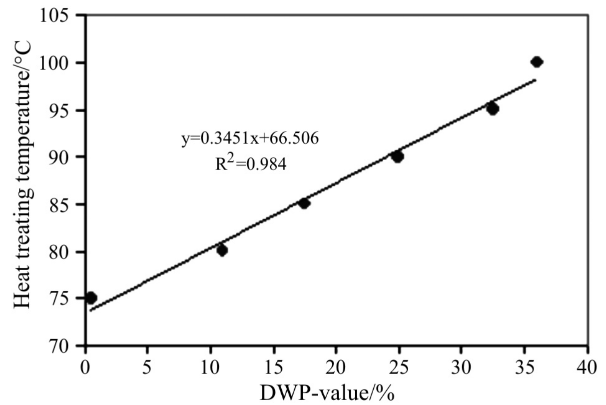

Fig. 7 The pasteurization temperature as a function of DWP-value in case of 3 min holding time

Figure 5 shows the change of swelling temperature of amylopectin as a function of saccharose concentration of dispersion medium of pH=4.5 in range of 0–40%. It is obvious that the relationship is linear and from the equation of the straight, knowing the saccharose concentration, the swelling temperature can be calculated almost exactly.

Figure 6 shows the enthalpia-value of swelling curves of amylopectin as a function of saccharose concentration. It is obvious from the figure that the enthalpia-values can be approached with a saturation curve.

Table 3 Minimum pasteurization temperatures of raw material of post heat-treated fruit-flavoured fermented milk drinks with 7 and 15% saccharose content at holding time of 3 min

Denomination of culture	Minimum pasteurization temperature/°C	
	at saccharose content of 7%	at saccharose content of 15%
yogurt culture	94	98
Prebiolact-2 culture	91	94

Conclusions

As far as a heat-protective hydrocolloid can prevent the protein precipitation in sour milk coagulum only if its swelling temperature is lower than the precipitation temperature of proteins it should be taken into consideration when technology is developed. Practical application of our results is shown in the following examples.

We plan to produce fruit-flavoured fermented milk drink with 7 and 15% saccharose content. The equation shown in Fig. 5 was applied, where x is the saccharose content in mass% and y is the swelling temperature of amylopectin in °C.

If values are substituted, the swelling temperature will be rounded 75°C at saccharose content of 7% and 77°C at saccharose content of 15%. Based on curves in Fig. 3 it can be stated that the precipitation temperature above 75°C can be attained by using all the three cultures if the DWP-value is 100% at butter culture, >80% at yogurt culture and >70% at Prebiolact-2 culture. However, the precipitation temperature above 77°C can be attained only by yogurt culture (DWP>90%) and EPS-producing culture (DWP>80%). If we have a special heat-treating equipment (pasteurizer), where the holding time for example 3 min, we should know the relationship of temperature-DWP-value belonging to 3-min-holding time, which is shown in Fig. 7.

It is obvious in Fig. 7 that at holding time of 3 min 100% DWP-value can not be attained, so only thermophilic or EPS-producing cultures can be used with temperature parameters listed in Table 3.

Acknowledgements

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