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SODIUM SALT OF STARCH OCTENYLSUCCINATE AS AN EMULSIFIER IN "LIGHT" TYPE MAYONNAISES

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ABSTRACT

Introduction. The E 1450 sodium salt of starch octenylsuccinate which exhibits emulsifying properties is used as food additive and is also recommended as yolk replacer in the process of mayonnaise production. Commercial E 1450 preparations reveal excellent functional properties in mayonnaise production. However, sodium salt of starch octenylsuccinate produced in the course of the suspension process (as well as the product of its hydrolysis in a membrane reactor), despite high surface activity, is unsuitable for this purpose. Therefore, a hypothesis was put forward that the cause of the unsuitability of these preparations for mayonnaise production is their improper profile of molecular mass distribution and the objective of this study was to verify the above thesis.

Material and methods. E 1450 preparations of different degree of substitution obtained alternately by means of reactive extrusion or enzymatic hydrolysis preceded by esterification in suspension were investigated. Preparations were characterised physico-chemically by determining the degree of substitution, viscosity, emulsifying activity index (EAI) and their capability to stabilise model emulsions (ME). Their molecular mass distribution profiles were determined and their suitability for the manufacture of low-fat mayonnaises was assessed. These investigations were also carried out for mixtures of preparations obtained as a result of a reactive extrusion and hydrolysis of the ester obtained during the suspension process.

Results. Despite the fact that the preparations obtained in suspension were characterised by 100% values of the ES parameter, all attempts to manufacture with their assistance of mayonnaise by way of a simple substitution in the formulation of dried egg yolk by E 1450 starch failed. Similarly, attempts to manufacture mayonnaise using any of the preparations obtained by means of reactive extrusion or enzymatic hydrolysis of the reaction product in suspension also ended in failure. The only successful solution was the application of equilibrium mixtures of E 1450 preparations obtained by way of reactive extrusion with a hydrolisate.

Conclusion. The performed investigations fully corroborated the correctness of the proposed hypothesis that the suitability of the starch octenylsuccinate sodium salt as an emulsifier for low-fat mayonnaises is associated with the appropriately high polydispersity of this polymer.

Key words: sodium salt of starch octenylsuccinate, extrusion, enzymatic hydrolysis, "light" mayonnaises

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INTRODUCTION

The E 1450 sodium salt of starch octenylsuccinate is a perfect additive used in food articles which exhibits emulsifying properties and is recommended as yolk replacer in the process of mayonnaise production. In the case of the Polish market, they are offered as preparations of modified starch E 1450 produced, primarily, by the National Starch & Chemicals Company and known under a commercial name of Purity Gum. Modified starch E 1450 can be produced either by way of esterification in water suspension or in the course of reactive extrusion [Jeon et al. 1999, Wang et al. 1997]. Further modification of this product is also possible by enzymatic hydrolysis contributing to its enhanced surface activity [Prochaska et al. 2007 a]. Despite the fact that commercial E 1450 preparations exhibit excellent functional properties in developing mayonnaises, sodium salt of starch octenylsuccinate obtained during the suspension process, as well as the product of its hydrolysis in a membrane reactor, despite high surface activity, are not suitable for this purpose and mayonnaise manufactured by means those preparations showed low interface stability [Kędziora 2008, Prochaska et al. 2007 b].

The role of modified starch in emulsion formation is exceptionally complex. Physicochemical properties significant from the point of view of emulsion development include: capabilities of reducing surface/interphase tension (it should be emphasised that it is not only thermodynamics but also kinetics of the process that is important), as well as stabilisation of the developed emulsion system preventing flocculation and coalescence phenomena [Dickonson 2009, Dłużewska et al. 2006]. These phenomena are so closely linked with each other that the terms: "emulsifier" and "stabiliser" are frequently used interchangeably [Garti 1999]. It is further believed that the higher effectiveness of protein emulsifiers than of hydrocolloids is associated with the presence in their composition of small quantities of low-molecular surface active substances [Dickinson 2009, Courthaudon et al. 1991]. Hence, a hypothesis was put forward that the cause of the unsuitability of modified E 1450 starches obtained in the course of the suspension process and possibly, additionally, hydrolysed in a membrane reactor is an improper profile of the molecular mass distribution of these preparations. The aim of this research project was the verification of the above-formulated thesis. The scope of research comprised investigations of the physicochemical properties, as well as of the distribution of molecular masses of the commercial preparation of the sodium salt starch octenylsuccinate preparations of different degrees of substitution obtained using different methods, as well as the assessment of their usefulness in the manufacturing process of low-fat mayonnaises.

MATERIAL AND METHODS

The experimental material was potato starch manufactured at Wielkopolska Enterprise of Potato Industry in Luboń. An octenylsuccinate anhydride (Dixie Chemical Company INC USA) was used during the esterification process. A commercial preparation of imported sodium salt starch octenylsuccinate E 1450, further on referred to as EH, was used as comparative material.

Manufacture of starch octenylsuccinate using the method of reactive extrusion. Reactive extrusion of potato starch with octenylsuccinate anhydride was carried out using a DN 20 laboratory, single-thread worm extruder (Brabender Company) at the temperature of 130°C against sodium carbonate used as a catalyst [Wang et al. 1997].

Manufacture of sodium salt starch octenylsuccinate in suspension. The esterification process with the assistance of the octenylsuccinate anhydride was carried out for 4 hours at room temperature in a batch reactor in a suspension of 8.5-9.0 pH. Both in the case of reactive extrusion as well as in the reaction in suspension, an appropriate quantity of octenylsuccinate anhydride was applied so as to obtain each time two preparations of two different contents of octenylsuccinate groups (approximately 0.5% and 2.5%) [Jeon et al. 1999].

Enzymatic hydrolysis. Only the sodium salt starch octenylsuccinate preparation obtained in suspension of higher degree of substitution was subjected to hydrolysis. The process was conducted for 2 hours in a batch reactor at the temperature of 85°C using 0.3 ml/kg DM of Termamyl Supra (Novozymes). The obtained hydrolisate was dried using a Mobile Miner™ 2000 (Niro A/S) spray drier.

Determination of the degree of substitution. Determination of the degree of substitution was carried out employing the method recommended by WHO/FHO [Modified... 1997] involving sample acidification and washing the contaminations with the assistance of 90% isopropanol which was followed by an acid-base titration of the content of carboxyl groups.

Viscosity determination. Investigations of rheological properties were carried out at the temperature of 20°C for gels of 10% concentration using a Haake rheometer operating at CR mode for the period of 5 minutes at $\gamma = 50\ s^{-1}$ shear rate. The following measuring system was employed in the performed experiments: system of coaxial cylinders: Z20 DIN Ti-4.200 mm. All samples were analysed in three replications and the results are presented as arithmetical means.

Determination of the emulsifying activity index (EAI). EAI identification was conducted using the Pearce and Kinsella [1978] method. For this purpose, 100 µl of the prepared emulsion was collected and diluted in 9900 µl 0.1% SDS (sodium dodecyl sulphate) solution. Absorbance was measured at $\lambda = 500$ nm wave length with the assistance of Specord 205 Analytik Jena apparatus (Germany). The emulsifying activity index was calculated from the following equation:

$$EAI = \frac{2 \cdot 2.303A}{l \cdot Ø \cdot c},\ m^2 \cdot g^{-1}$$

where:

A – absorbance
l – length of absorption cell, cm,
Ø – proportion (weight fraction) of dispergated oil phase,
C – concentration of the emulsifier at water phase (prior to emulsion formation), g/cm^3.

Determination of the emulsion stability (ES). ES was determined [Huang et al. 2001] by subjecting the obtained emulsion to a centrifugal force in a Multifuge 3 S-R, Heraeus, Kendro Ltd. centrifuge operating at the rotational speed of 5850 rpm for the period of 20 minutes at room temperature. At the termination of the centrifuging process, the column height of all the developed phases, i.e. emulsifying, oil and water was measured. The ES value was calculated from the following formula:

$$ES = \frac{H_e \cdot 100}{H_0}$$

where:

ES – emulsifying stability, %,
H_e – height of the emulsion chase,
H_0 – height of the entire emulsion.

Examination of the molecular mass distribution (GPC). GPC was carried out using a Waters Company apparatus (Alliance HPLC System 2695) equipped with a refractometric detector (RI) Waters 2414. Three UltrahydrogelTM columns arranged in a series were used. The obtained data were processed using the Empower Pro software in the GPC option. The following parameters were applied during the chromatographic analysis: temperatures of the injector – 25°C, column – 40°C, measuring cell – 35°C; and the flow rate of the solvent (deionised water) – 0.700 ml/min. Starch samples (4 mg/mL) were dissolved in distilled water during autoclaving process (121°C, 15 min). GPC molecular weight distribution calculations were performed using calibration curve that was based on standards of dextran in range M_w 11×10^4-1×10^6 (Polymer Standards Service Gmbh, Mainz Germany) and Blue Dextran (Sigma, St. Louis, MO, USA).

Mayonnaise preparation. Nine grams of dried yolk or, alternatively, starch octenylsuccinate, 12 g vinegar, 9 g sugar, 6 g mustard and 3 g salt distributed in 50 ml water were added to 150 g of oil stirring it intensely and followed by the addition of 14 g of modified starch *Adanet*. The process was terminated by the addition of 80 g water increasing the intensity of stirring. The entire mass was mixed for another 2 minutes until uniform mixture was achieved.

Analysis of the universal mayonnaise texture profile (TPA). The investigations were carried out with the assistance of a TA-XT2 texturemeter/fibremeter of Stable Micro Systems Company coupled with a computer using the Texture Expert Exceed program. Mayonnaise samples were penetrated twice with an aluminium cylindrical probe of 35 mm diameter to the depth of 20 mm at 0.5 mm/s velocity. Measurements were taken at room temperature for four separate

samples and the results were presented as an arithmetic mean.

RESULTS AND DISCUSSION

Sodium salt starch octenylsuccinate preparations obtained as suspensions have the form of unmodified potato starch, although the preparation of higher degree of substitution was slightly more powdery in comparison with both the initial raw material and the low-substitution counterpart. These starches were insoluble in cold water. All starch preparations obtained as a result of reactive extrusion had a form of expanded puffs and, after grinding and sieving analysis – of creamy powder (similarly as the commercial EH preparation). Preparations obtained as a result of reactive extrusion, as well as of the enzymatic hydrolysis of the reaction product in suspension, were soluble in cold water. Degrees of substitution of the examined preparations fell within boundaries of DS = 0.0034 – 0.018 which corresponds to the content of octenylsuccinate groups within limits ranging from 0.044 to 2.29. They differed very significantly with respect to viscosity values as illustrated by data from Table 1.

The highest (several orders of magnitude higher than of all the remaining preparations) viscosity was observed in the case of starches modified in suspension. This high viscosity value was reflected in an excellent, nearly 100%, stability of model emulsions (ES parameter). In addition, the preparations were also characterised by the highest values of the emulsifying activity index EAI. The lowest viscosity was determined: in the commercial preparation, as well as in the sodium salt starch octenylsuccinate hydrolisate obtained in the laboratory. This was also apparent in the lowest values of the ES parameter which, in all cases, correlated fairly well with viscosity values. On the other hand, EAI parameters failed to exhibit high variability.

Despite the fact that the preparations obtained in suspension were characterised by 100% values of the ES parameter, all attempts to manufacture with their assistance of mayonnaise by way of a simple substitution in the formulation of dried egg yolk by E 1450 starch failed. Similarly, attempts to manufacture mayonnaise using any of the preparations obtained by means of reactive extrusion or enzymatic hydrolysis of the reaction product in suspension also ended in failure. The only successful solution was the application of equilibrium mixtures of E 1450 preparations obtained by way of reactive extrusion with a hydrolisate. Table 2 collates texture parameters of the obtained mayonnaises.

Table 1. Physicochemical characteristics of the examined preparations

Preparation	OB content %	Viscosity mPa·s	ES %	EAI m^2/g
EN	0.44 ±0.07	1 601	74.63 ±0.51	129.96 ±1.25
EW	2.44 ±0.03	270	100 ±0.00	111.82 ±1.06
ZN	0.49 ±0.06	16 660	100 ±0.00	147.26 ±1.59
ZW	2.25 ±0.04	12 840	100 ±0.00	142.64 ±2.01
ZH	2.25 ±0.04	7	19.12 ±0.15	102.62 ±1.85
EH	1.61 ±0.03	5	25.40 ±0.67	129.13 ±1.62
EN+ZH	–	325	36.23 ±0.54	127.13 ±0.97
EW+ZH	–	67	42.03 ±0.87	119.22 ±0.57

EN – reactive extrusion product of lower degree of substitution, EW – reactive extrusion product of higher degree of substitution, ZN – suspension product of lower degree of substitution, ZW – suspension product of higher degree of substitution, ZH – hydrolisate of suspension product of higher degree of substitution, EH – commercial product, EN+ZH – equilibrium mixture of EN and ZH preparations, EW+ZH – equilibrium mixture of EW and ZH preparations, OB content – content of octenylsuccinate groups.

Table 2. Mayonnaise texture containing different emulsifying substances

Emulsifying substances	Hardness N	Adhesiveness N·s	Cohesiveness N·s	Gumminess N^2·s
Egg yolk	0.62 ±0.12	–2.45 ±0.20	0.60 ±0.22	0.37 ±0.12
EH	0.72 ±0.23	–4.99 ±0.37	0.54 ±0.26	0.39 ±0.15
EN+ZH	1.13	–13.67	0.75	0.85
EW+ZH	1.69	–19.62	0.64	1.08

EH – commercial product, EN+ZH – equilibrium mixture of EN and ZH preparations, EW+ZH – equilibrium mixture of EW and ZH preparations.

It is evident from the presented data that texture parameters of the mayonnaise obtained with the assistance of the dried egg yolk and the commercial preparation were very similar, whereas in the case of the application of mixtures of laboratory obtained preparations, the manufactured mayonnaises were harder and gummier. In addition, they were also characterised by higher adhesiveness.

The performed analysis of physicochemical parameters of the examined modified starches indicates that none of the values shown in Table 1 (degree of substitution, viscosity, stability of model emulsions and emulsifying activity index) makes it possible to draw conclusions concerning the suitability of modified starches for mayonnaise production. Therefore, it was decided to verify the thesis put forward by Courthaudon et al. [1991] regarding the key role of molecular mass of the emulsifier. Figure 1 presents GPC chromatograms of the examined modified starches, as well as of native potato starch.

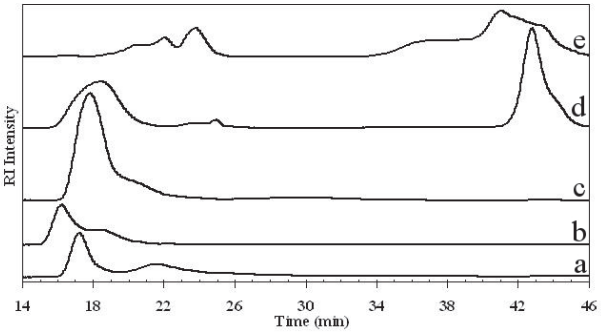

Fig. 1. GPC profiles of different starch preparations: a – native potato starch, b – modified starch ZW, c – modified starch EW, d – commercial E 1450 product, e – modified starch ZH

It is not difficult to notice, on the curve corresponding to native potato starch, two peaks at 16.7 and 21.0 retention times which can be assigned to amylopectin and amylose, respectively. Two peaks corresponding to amylopectin and amylose could also be found on the b curve, but they were observed at lower retention times: 15.0 and 18. 1 min. The identified shift towards lower retention times should not be associated with a change in molecular mass caused by the substitution with octenylsuccinate groups but by increase of the excluded volume of the starch macromolecules triggered off by the presence of modifying groups. The sodium salt starch octenylsuccinate preparation obtained by means of reactive extrusion exhibited a similar profile as its equivalent obtained in suspension, although peaks were shifted towards slightly lower retention times: 17.6 and 20.3 minutes which indicates a slight lowering of the molecular mass. These data correlate with the viscosity values given in Table 1 which were considerably lower for preparations obtained by means of reactive extrusion than in suspension. The E 1450 starch enzymatic hydrolisate revealed a bimodal molecular mass distribution (curve e; Fig. 1); the elution of the high molecular fraction occurred during 17.5 to 25.8 minutes and that of low molecular fraction – from 32.4 to 46.2 minutes. The most complicated course of the GPC curve was observed in the case of the commercial E 1450 preparation during which several wide peaks in the range of high molecular mass were found to occur at retention times from 15.3 to 26.0 as well as some peaks at low retention times – from 32.4 to 46.3 minutes. This preparation distinguished itself from the remaining ones by high polydispersity; variability of the mean weight molecular mass (M_w) was 200 times higher in comparison with the equally highly polydispersive enzymatic hydrolisate of E 1450 starch. Molecular masses of the remaining samples, which failed to reveal satisfactory stabilising properties (a, b and c curves), fluctuated around the same order of magnitude (10^6 Da). High polydispersity of the commercial starch preparation E 1450 is a probable cause of its excellent functionality in developing mayonnaise. This hypothesis is confirmed by the fact that mixtures of the E 1450 hydrolisate and E 1450 preparation obtained by way of reactive extrusion, characterised by a higher polydispersity than the components which make them up, turned out to be useful in developing mayonnaises.

CONCLUSIONS

The usefulness of the sodium salt starch octenylsuccinate as an emulsifier in low-fat mayonnaises is associated with appropriately high polydispersity of this polymer. Physicochemical parameters such as: viscosity, emulsifying activity index EAI or value of

the ES (emulsion stability) parameter cannot be treated as decisive factors affecting the usefulness of the preparation for the manufacture of mayonnaises.

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SÓL SODOWA OKTENYLOBURSZTYNIANU SKROBIOWEGO JAKO EMULGATOR W MAJONEZACH TYPU „LIGHT"

STRESZCZENIE

Wprowadzenie. Sól sodowa oktenylobursztynianu skrobiowego E 1450 jest dodatkiem do żywności wykazującym właściwości emulgujące i rekomendowanym jako zastępnik żółtka jaj w produkcji majonezów. Handlowe preparaty E 1450 wykazują doskonałe właściwości funkcjonalne w tworzeniu majonezów. Pomimo dużej aktywności powierzchniowej, nie nadaje się do tego celu sól sodowa oktenylobursztynianu skrobiowego, otrzymana w procesie zawiesinowym, jak również produkt jej hydrolizy w reaktorze membranowym. Postawiono zatem hipotezę, iż przyczyną nieprzydatności tych preparatów do wytwarzania majonezów jest ich niewłaściwy profil rozkładu mas cząsteczkowych. Celem pracy była weryfikacja postawionej tezy.

Materiał i metody. Badano preparaty E 1450 o różnym stopniu podstawienia, otrzymane alternatywnie poprzez reaktywną ekstruzję lub hydrolizę enzymatyczną poprzedzoną estryfikacją w zawiesinie. Preparaty charakteryzowano fizykochemicznie poprzez oznaczenie stopnia podstawienia, lepkości, indeksu aktywności emulgującej (EAI) i zdolności do stabilizowania modelowych emulsji (ES). Wyznaczano ich profil rozkładu mas cząsteczkowych oraz oceniano przydatność do wytwarzania majonezów niskotłuszczowych. Badania przeprowadzono również dla mieszanek preparatów otrzymanych metodą reaktywnej ekstruzji i hydrolizy estru otrzymanego w procesie zawiesinowym.

Wyniki. Mimo że preparaty otrzymane w zawiesinie charakteryzowały się 100-procentowymi wartościami parametru ES, po ich zastosowaniu nie udało się otrzymać majonezu przez proste zastąpienie w recepturze suszu żółtka skrobią E 1450. Podobnie nieudane były próby użycia któregokolwiek z preparatów

otrzymanych w drodze reaktywnej ekstruzji lub hydrolizy enzymatycznej produktu reakcji w zawiesinie. Dopiero wykorzystanie równowagowych mieszanin preparatów E 1450 otrzymanych w drodze reaktywnej ekstruzji z hydrolizatem zakończyło się sukcesem.
Wniosek. Przeprowadzone badania w pełni potwierdziły słuszność postawionej hipotezy, że przydatność soli sodowej oktenylobursztynianu skrobiowego jako emulgatora w majonezach niskotłuszczowych jest związana z odpowiednio wysoką polidyspersyjnością tego polimeru.

Słowa kluczowe: sól sodowa oktenylobursztynianu skrobi, ekstruzja, hydroliza enzymatyczna, majonezy typu „light"

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