Rheological properties of whey proteins concentrate before and after tribomechanical micronization

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Abstract

Hydrocolloids are long-chain polymers, used in food production at small quantities (from 0,05 to 5 %) to achieve appropriate rheological properties, prevent syneresis, increase the viscosity and stability of foodstuffs and for crystallization process control.

The aim of this work was to investigate the influence of tribomechanical micronization of powdered whey protein concentrate on the rheological properties of whey proteins model systems as well as the influence of several carboxymethylcellulose hydrocolloids addition in such systems.

Measurements were done using rotational viscosimeter, Brookfield DV-III at temperature 20 ^{o}C. The rheological parameters were determined by power-law model. The results of investigation have shown that all investigated systems are non-Newtonian. Depending on the pretreatment of whey proteins and the mass fractions of hydrocolloids they exhibited pseudoplastic or dilatant properties.

Particle size analysis was performed using Fritsch – laser particle sizer "analysette 22". The operation of tribomechanical micronization caused the decreasing of particle size and incrasing specific area of whey proteins. Tribomechanical treatment of whey proteins had significant influence on the rheological parameters and the type of flowing.

Key words: rheological properties, carboxymethylcellulose, whey protein concentrate, tribomechanical micronization

Introduction

The knowledge of the rheological properties of foodstuffs and the influence of various ingredients and additives (hydrocolloids and emulsifiers) on these properties are important in defining the product′s and process quality control, predicting product stability during storage as well as creating the food texture (Hegedušić, 1992; Hegedušić et al., 1995; Herceg et al., 1999a).

Fig. 1: Shear stress and shear rate relationship of model solutions prepared with addition of YO-H hydrocolloid

Slika 1: Odnos napona smicanja i brzine smicanja modelnih otopina pripremljenih s dodatkom hidrokoloida YO-H

Hydrocolloids are mostly complex carbohydrates used to improve consistency and textural characteristics (rheological properties) of liquid and semiliquid foodstuffs. Theirs activity depend on the type and concentration of hydrocolloids, temperature and process conditions, as well as on solid matter content and chemical compositition of foodstuffs. Carboxymethylcellulose (CMC), as a typical hydrocolloid, has no direct influence on the taste and flavour of foodstuffs, while at the same time has a significant effect on gel formation, water retention, emulsifying activity and aroma retention (Hegedušić, et al., 1998; Herceg et al., 1999b; Herceg et al., 2000a).

Table 1: Composition of investigated model systems
Tablica 1: Sastav ispitivanih modelnih sustava

Model systems Modelni sustavi	Compounds Sastojci				Solid matter Suha tvar (%)
	Water Voda (g)	Hydrocolloids * Hidrokoloidi* (g)	Whey proteins Proteini sirutke (g)	Tribomechanicaly treated whey proteins Tribomehanički tretirani proteini sirutke (g)	
1**	99.90	0.1	-	-	0.1
	99.80	0.2	-	-	0.2
	99.60	0.4	-	-	0.4
2***	90.00	0.1	9.9	-	10
	90.00	0.2	9.8	-	10
	90.00	0.4	9.6	-	10
3****	90.00	0.1	-	9.9	10
	90.00	0.2	-	9.8	10
	90.00	0.4	-	9.6	10

* YO-L, YO-H, YO-M; YO-EH, DIKO, HVEP.
** - Aqueous hydrocolloids solution
*** - Whey proteins solution
**** - Tribomechanicaly treated whey proteins solution

Tribomechanics is a part of physics that is concerned with the study of phenomenon that appears during fine milling under dynamics conditions. In the year 1999 the process and activation of tribomechanical micronization as well as the appropriate equipment application are patented under the number PCT/1B 99/00757 at the International Bureau of WPO PCT Receiving Office in Geneva. (Lelas, 1998, Herceg et al., 2000b, Herceg, 2000c).

Whey proteins are comonly used in the food industry for dairy desserts production. They are also gelling agents or enhance functional properties of food. The most important functional properties of whey proteins are solubility, viscosity, water holding capacity, gelation, adhesion, emulsification and foaming (Huffman, 1996; King, 1996; Corradini, 1998). The functional role of protein as a food ingredient depends on complex's interaction of various factors, for example, heating or cooling rates, protein concentration, pH, ionic strength and interaction with other food components. (Smith, 1994; Boye et al., 1997; Alizadehfard&Wiley, 1995; Hegedušić et al., 2000; Ker&Toledo, 1992; Herceg et al., 1999c).

Fig. 2: Shear stress and shear rate relationship of model solutions prepared with addition of YO-EH hydrocolloid

Slika 2: Odnos napona smicanja i brzine smicanja modelnih ototpina pripremljenih s dodatkom hidrokoloida YO-EH

In this work, the influence of tribomechanical micronization of whey proteins and several carboxymethylcellulose hydrocolloids addition on the rheological properties of whey proteins model systems were examined.

Materials and methods

The investigation was carried out on three model solutions prepared by mixing of several ingredients shown in Table 1.

- Whey protein concentrate (WPC) (60 % proteins in solid matter) - "LURA" d.d., Zagreb
- Tribomechanicaly treated whey protein concentrate (60 % proteins in solid matter)
- Carboxymethylcelluloses (type - krisogum: YO-L, YO-H, YO-M and type - polyfibron: YO-EH, DIKO, HVEP) - Guliver-Chemie, Wiener Neudorf

Table 2:. Specific area and particle size distribution of whey proteins before and after tribomechanical treatment
Tablica 2: Specifična površina i raspodjela veličine čestica proteina sirutke prije i nakon tribomehaničkog tretiranja

Sample Uzorak	Specific area Specifična površina (m^2/g)	Particle size (µm) Veličina čestica (µm)		
		less than 10 % manje od 10 %	less than 50 % manje od 50 %	less than 90 % manje od 90 %
Whey proteins Proteini sirutke	1.6623	0.91	35.47	87.95
Tribomechanicaly treated whey proteins Tribomehanički tretirani proteini sirutke	3.1180	0.74	3.25	49.51

Powdered whey protein concentrate was treated in equipment for tribomechanical micronization and activation at 40000 rpm (Patent: PCT/1B 99/00757). Particle size analysis was performed using Fritsch – laser particle sizer “analysette 22”, using by measuring the angular dependence of the scattered laser light intensity, from a dilute suspension, and indicating the particle size distribution. The particle size distribution was calculated by computer′s program according to "Fraunhofer model” of light scattering.

Fig. 3: Particle size distribution of whey protein concentrate before and after tribomechanical treatment

Slika 3: Raspodjela veličine čestica koncentrata proteina sirutke prije i nakon tribomehaničke obrade

Carboxymethylcellulose solutions in water (0.1, 0.2 and 0.4 % by mass) were prepared by hydrating in distilled water by vigorous hand mixing at 20 °C (sample No. 1).

Model solutions of whey proteins (sample No.2) and tribomechanicaly treated whey proteins (sample No. 3) were prepared identical to sample No. 1 with proteins firstly dissolved in water and followed by hydrocolloids addition.

Measurements were performed at 20 °C using rotational viscometer, Brookfield DV-III, with concentric cylinders. Shear stress against the increasing shear rates from the lowest value of 3.9 s^{-1} to 317 s^{-1} (rising measurements), as well as, from 317 s^{-1} to the lowest shear rate values (downwards) were applyed. All measurements were carried out at the intervals of 2 minutes. Shear stress and shear rate values (rising measurements) were recalculated in flow index and consistency coefficient value according to power-law model, using Brookfield's computer program.

Table 3. Rheological characteristics of model systems with 0.1 % hydrocolloids addition

Tablica 3. Reološke karakteristike modelnih sustava pripremljenih s dodatkom 0.1 % hidrokoloida

Model solutions Modelne otopine	Hydro-colloids Hidro-koloidi	Appearent viscosity Prividna viskoznost (mPa s)	Flow index Indeks tečenja	Consistency coefficient Koeficijent konzistencije (mPa s^n)	Regression coefficient Koeficijent regresije r^2	Flow behavior
Whey proteins Proteini sirutke	YO-L	3.600	0.9733	2.0	0.995	Pseudoplastic
	YO-H	4.100	0.9166	3.5	0.993	Pseudoplastic
	YO-M	4.300	0.9342	7.8	0.991	Pseudoplastic
	HVEP	4.400	1.0990	2.0	0.990	Dilatant
	DIKO	3.800	1.0600	4.0	0.983	Dilatant
	YO-EH	3.600	1.1540	1.0	0.991	Dilatant
Tribome-chanical treatment whey proteins Tribomeha-nički treti-rani proteini sirutke	YO-L	3.400	1.1323	1.6	0.993	Dilatant
	YO-H	3.700	1.1223	1.9	0.992	Dilatant
	YO-M	3.800	1.0991	5.9	0.994	Dilatant
	HVEP	4.250	1.4066	0.4	0.989	Dilatant
	DIKO	3.600	1.1767	1.3	0.990	Dilatant
	YO-EH	4.500	1.3812	0.6	0.990	Dilatant
Aqueous solution of hydro-colloids Vodena otopina hidro-koloida	YO-L	7.400	0.9170	5.0	0.981	Pseudoplastic
	YO-H	6.950	0.8480	14.0	0.979	Pseudoplastic
	HVEP	13.100	0.8440	13.0	0.980	Pseudoplastic
	YO-M	5.200	0.8700	9.0	0.969	Pseudoplastic
	DIKO	8.450	0.7880	21.0	0.970	Pseudoplastic
	YO-EH	10.100	0.8470	19.7	0.973	Pseudoplastic

$$\tau = k\,\gamma^n \qquad /1/$$

where:

τ - shear stress (Pa) γ - shear rate (s^{-1}) n - flow index
k - consistency coefficient (Pa s^n)

Apparent viscosity at 60 s^{-1} was calculated using Newton law:

$$\tau = \mu_a \gamma \qquad /\ 2\ /$$

τ - shear stress (Pa) γ - shear rate (s^{-1}) μ_a - apparent viscosity (Pa s)

Results and discussion

Among the many factors known to affect the rheological characteristics of a compound, the solid matter and its composition have the most important role (Hegedušić, 1992.). The effect of solid matter was eliminated using model solutions with identicalsolid matter content (except aqueous hydrocolloids solution of 0.1, 0.2 and 0.4 % solid matter). Prepared aqueous hydrocolloids solution enable us to observe the interaction of the ingredients present in the solution, with hydrocolloids and to monitor the effect on the rheological characteristics of the model solutions.

From the acquired results illustrated on the figs 1 and 2 it could be seen that the aqueous hydrocolloids solution (0.1, 0.2, 0.4 % solid matter) have a higher viscosity than those prepared with whey proteins (10 % solid matter). This means that the solid matter content had a lower effect on the viscosity then the type of the solid matter used. In there figs only the viscosity of model solutions, prepared with hydrocolloids YO-EH and YO-H, are illustrated as the viscosity of the other hydrocolloids (YO-L, YO-M, DIKO, HVEP) was almost identical to the samples showned on there figs.

In order to explain this kind of the model solutions behaviour it is worth emphosising that the whey proteins are tipically compact globular proteins with relatively comparable distribution of nonpolar, polar, charged and uncharged remains of aminoacids. Intramolecular wrinkled structure of these proteins is a result of disulfide bonds between cysteine remains (S-S), which are mostly situated inside of the proteins (hydrophobic fragment of the proteins) while outer side of the proteins is made of hydrophilic remains of aminoacid (Tratnik, 1998.).

Such a behavior of the model solutions prepared with WPC addition can be explained by the interactions of positive, active groups of proteins (hydrophilic part) and negative groups of hydrocolloids that results in lowering of the solutions viscosity. This type of interaction can improve homogenity of the systems.

Table 4: Rheological characteristics of model systems with 0.2 % hydrocolloids addition

Tablica 4: Reološke karakteristike modelnih sustava pripremljenih s dodatkom 0.2 % hidrokoloida

Model solutions Modelne otopine	Hydro-colloids Hidro-koloidi	Appearent viscosity Prividna viskoznost (mPa s)	Flow index Indeks tečenja	Consistency coefficient Koeficijent konzistencije (mPa s ^{n})	Regression coefficient Koeficijent regresije r^2	Flow behavior
Whey proteins Proteini sirutke	YO-L	3.950	0.9510	5.8	0.991	Pseudoplastic
	YO-H	7.800	0.9843	6.5	0.990	Pseudoplastic
	YO-M	6.100	0.9632	13.5	0.993	Pseudoplastic
	HVEP	6.650	0.9479	3.0	0.993	Pseudoplastic
	DIKO	5.650	0.9920	5.0	0.992	Pseudoplastic
	YO-EH	8.250	0.9550	10.0	0.994	Pseudoplastic
Tribome-chanical treatment whey proteins Tribomeha-nički treti-rani proteini sirutke	YO-L	3.550	1.1160	4.6	0.994	Dilatant
	YO-H	6.500	1.2219	4.5	0.991	Dilatant
	YO-M	5.900	1.2219	11.3	0.990	Dilatant
	HVEP	5.250	1.0548	3.8	0.989	Dilatant
	DIKO	3.650	1.1092	1.9	0.973	Dilatant
	YO-EH	6.500	1.1028	6.8	0.991	Dilatant
Aqueous solution of hydro-colloids Vodena otopina hidro-koloida	YO-L	11.700	0.9560	7.0	0.960	Pseudoplastic
	YO-H	11.000	0.8460	21.0	0.971	Pseudoplastic
	YO-M	7.700	0.8840	15.0	0.969	Pseudoplastic
	HVEP	21.900	0.8540	20.0	0.968	Pseudoplastic
	DIKO	12.100	0.8070	28.0	0.969	Pseudoplastic
	YO-EH	19.500	0.8620	35.0	0.965	Pseudoplastic

But in this case the contact of ion pairs (CMC - whey proteins) has a negative effect on the rheological properties of the model solutions. This can be explained by the decreasing number of active groups of hydrocolloids that bind the water molecules.

Table 5: Rheological characteristics of model systems with 0.4 % hydrocolloids addition

Tablica 5: Reološke karakteristike modelnih sustava pripremljenih s dodatkom 0.4 % hidrokoloida

Model solutions Modelne otopine	Hydro-colloids Hidroko-loidi	Appearent viscosity Prividna viskoznost (mPa s)	Flow index Indeks tečenja	Consistency coefficient Koeficijent konzistencije (mPa s ^{n})	Regression coefficient Koeficijent regresije r^2	Flow behavior
Whey proteins Proteini sirutke	YO-L	12.400	0.8772	23.0	0.989	Pseudoplastic
	YO-H	12.050	0.8564	15.9	0.989	Pseudoplastic
	YO-M	13.600	0.8462	18.5	0.988	Pseudoplastic
	HVEP	17.300	0.7590	57.0	0.989	Pseudoplastic
	DIKO	21.300	0.7210	79.0	0.987	Pseudoplastic
	YO-EH	15.500	0.9600	17.0	0.988	Pseudoplastic
Tribomec-hanical treatment whey proteins Tribomeha-nički treti-rani proteini sirutke	YO-L	10.400	0.9128	15.0	0.990	Pseudoplastic
	YO-H	9.500	0.9834	11.3	0.992	Pseudoplastic
	YO-M	11.400	0.9834	15.0	0.989	Pseudoplastic
	HVEP	9.950	0.8717	17.4	0.988	Pseudoplastic
	DIKO	20.700	0.9241	28.1	0.87	Pseudoplastic
	YO-EH	32.900	0.9570	31.5	0.984	Pseudoplastic
Aqueous solution of hydro-colloids Vodena otopina hidro-koloida	YO-L	19.800	0.9620	28.0	0.964	Pseudoplastic
	YO-H	19.600	0.8520	36.0	0.957	Pseudoplastic
	YO-M	14.700	0.8760	25.0	0.987	Pseudoplastic
	HVEP	20.800	0.8250	44.0	0.976	Pseudoplastic
	DIKO	62.200	0.7380	98.0	0.965	Pseudoplastic
	YO-EH	45.000	0.8190	100.0	0.969	Pseudoplastic

The operation of tribomechanical micronization caused the spliting of the whey proteins macromolecules, this decreasing their particle size and increasing specific area (Fig. 3., Table 2).

Tribomechanical treatment of whey proteins accelerated the interactions between whey proteins and hydrocolloids resulting in significant changes of the rheological properties of the investigated solutions.

All model solutions prepared with tribomechanicaly treated whey proteins have a lower viscosity than the other solutions as a consequence of the spliting of the proteins during tribomechanical treatment. Therefore, there are the increased number of protein active groups available to react with hydrocolloids, lowering the water binding capacity of hydrocolloids and decreasing the viscosity of the solutions.

Rheological properties of the investigated model solutions are adequately described, according to pover law model, which is confirmed with very high regression coefficients obtained (from 0.96 to 0.99)(Tables 3.,4 and 5).

From the shape of shear stress vs. shear rate curve (figs 1 and 2) and flow behaviour index values (Tables 3,4 and 5) it is obvious that all investigated model solutions exhibit a non-Newtonian character.

All solutions prepared with tribomechanicaly treated proteins with hydrocolloids addition (0.1 and 0.2 %) exhibited dilatant properties. Tribomechanicaly treated proteins with addition of 0.4 % hidrocolloids had pseudoplastic properties. Non-treated whey proteins prepared with 0.1 % HVEP, DIKO and YO-EH addition exhibited dilatant properties. All remaining solutions prepared with non-treated whey proteins had pseudoplastic character. All hydrocolloid solutions in water had pseudoplastic properties. Increasing the hydrocolloid content in the solution made the pseudoplastic characteristics more apparent and also significantly increased the viscosity of the model solutions. Such behaviour of the solutions indicated that theirs rheological characteristics depend on the whey proteins pretreatment as well as on the content and the type of hydrocolloids.

Conclusion

Rheological properties of the examined model solutions are adequately described according to Ostwald-Reiner´s pover-law model and expressed as consistency coefficient and flow behaviour index.

CMC type and the compositions of model solutions as well as tribomechanical treatment of whey proteins have a great influence on the rheological behavior of model solutions and type of fluidity.

Model solutions, prepared with WPC (0.1 %) and WPC-tribomechanicaly treated (0.1 and 0.2 %), with the lower hydrocolloids content exhibited dilatant characteristics. By increasing the amount of hydrocolloid all the model solutions showed pseudoplastic flow.

The operation of tribomechanical micronization caused the splitting of macromolecules of whey proteins, thus decreasing the particle size and increasing their specific area.

As a result of whey protein and hydrocolloids interaction, the viscosity of model solutions, prepared with WPC and WPC-tribomechanicaly treated, was significantly lower than aqueous hydrocolloid solutions.

Tribomechanical micronization of whey proteins accelerated the interaction between whey proteins and hydrocolloids resulting in significant rheological properties change of the investigated solutions.

REOLOŠKA SVOJSTVA KONCENTRATA PROTEINA SIRUTKE PRIJE I NAKON TRIBOMEHANIČKE MIKRONIZACIJE

Sažetak

Hidrokoloidi su dugolančani polimeri, koji se upotrebljavaju u prehrambenoj industriji u malim količinama (0,05 do 5%) za postizanje odgovarajućih reoloških svojstava, sprečavanje sinereze, povećanje viskoznosti i stabilnosti prehrambenih proizvoda te kontrolu kristalizacije.

Cilj ovog rada bio je ispitati utjecaj tribomehaničke mikronizacije koncentrata proteina sirutke u prahu na reološka svojstva modelnih otopina proteina sirutke kao i utjecaj dodatka nekoliko hidrokoloida na osnovi karboksimetilceluloze u takve sustave.

Mjerenja su provedena rotacionim reometrom, Brookfield DV-III pri temperaturi od 20 ºC. Reološki parametri određeni su upotrebom zakona potencije. Rezultati ispitivanja pokazuju da su svi ispitivani sustavi ne-Newtonski. Svi sustavi ovisno o prethodnom tretmanu koncentrata proteina sirutke i udjelu hidrokoloida pokazuju pseudoplastična ili dilatantna svojstva.

Raspodjela veličine čestica određena je upotrebom Fritsch – laser particle sizer "analysette 22". Tribomehanička mikronizacija uzrokovala je *smanjenje veličine čestica i povećanje specifične površine proteina sirutke. Tribomehanička obrada proteina sirutke imala je značajan utjecaj na reološke parametre i tip tečenja ispitivanih modelnih sustava.*

Ključne riječi: reološka svojstva, karboksimetilceluloza, koncentrat proteina sirutke, tribomehanička mikronizacija

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