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Rheological Properties of Some Hydrocolloid Mixtures at Low Temperatures

Reološka svojstva smjesa nekih hidrokoloida pri niskim temperaturama

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Summary

This paper deals with the rheological properties of some hydrocolloid solutions and their mixtures at low temperatures (between +5 °C and –5 °C). The aim was to determine the influence of temperature on the rheological properties of hydrocolloids and the existence of interaction among hydrocolloids examined. The rheological properties (shear stress and apparent viscosity) were measured by rotational viscosimeter with the shear rate ranging from 81 to 1312 s^{-1} and the temperature range between +5 and –5 °C. The results showed that temperature reduction had significant influence on the rheological properties of solutions of hydrocolloids as well as their mixtures. This phenomenon is especially evident with mixtures of hydrocolloids (galactomannan hydrocolloids and carrageenan) between which exists an interaction particularly at low temperatures (0 °C and lower).

Sažetak

U radu su provedena istraživanja reoloških svojstava otopina hidrokoloida i smjesa hidrokoloida, pri niskim temperaturama (od +5 °C do –5 °C), da bi se utvrdio utjecaj temperature na reološka svojstva hidrokoloida, kao i postojanje međudjelovanja među hidrokoloidima. Mjerenje reoloških svojstava (smičnog naprezanja i prividne viskoznosti) provedeno je s pomoću rotacijskog viskozimetra pri uvjetima brzine smicanja od 81 do 1312 s^{-1} i u temperaturnom intervalu od +5 do –5 °C. Rezultati istraživanja pokazali su da sniženje temperature ima znakovit utjecaj na reološka svojstva otopina pojedinačnih hidrokoloida i njihovih smjesa. Ova je pojava osobito uočljiva u smjesama hidrokoloida između kojih postoji međudjelovanje (galaktomananski hidrokoloidi i karagen), i to pri niskim temperaturama (0 °C i niže).

Introduction

It is important to have the knowledge of the rheological properties of food and to be aware of the influence of some ingredients and additives on those properties in the process of production, quality control, on stability during storage and production, as well as in defining and creating food texture *(1-5)*.

Hydrocolloids or gums *(4)* are long-chain polymers which are used in small quantities (from 0.05 to 5 %) in food production to achieve certain rheological properties, whereby nutritional values and sensory qualities of food products are not changed *(6)*. Hydrocolloids are used because of the influences they have on viscosity, also for other effects, which include stabilisation of emulsions, suspensions of particulates, control of crystallization, inhibition of syneresis etc.

Recently, hydrocolloids have been given special importance in the low-calory food production because they reduce deficiencies caused by reduction of additives or their replacement, e.g. oils, fats and sweeteners *(7-9)*. By adding hydrocolloids significant positive effects are achieved in the foods which are consumed refrigerated or which are preserved by freezing in order to reduced negative effects related to phase transitions *(2)*. Besides single hydrocolloids, hydrocolloids mixtures are also more often used to achieve these effects *(4,10-12)* because they improve thickening, forming of gels, stabilization etc.

Materials and Methods

The rheological properties of single hydrocolloids as well as their mixtures were investigated (Tables 1 and 2). Hydrocolloids were dissolved by heating in the distilled water taking into account the solubility of certain hydrocolloids *(13)*. (Hydrocolloids were manufactured in Giulini Chemie, Ludwigshafen, Germany). Rheological

Table 1. Rheological parameters of 0.2 % solutions of pure hydrocolloids at various temperatures
Tablica 1. Reološki parametri 0,2 %-tnih otopina čistih hidrokoloida pri različitim temperaturama

Solution Otopina	Temperature Temperatura t_C/°C	$\frac{k}{\text{mPa s}^n}$	Flow index Indeks strujanja n	Apparent viscosity Prividna viskoznost μ/mPa s	Flow behaviour Tip tekućine
Locust bean gum Brašno sjemenke rogača	5	109.93	0.685	11.13	pseudoplastic
	2	119.11	0.688	12.36	– " –
	0	133.31	0.678	13.02	– " –
	–3	166.57	0.655	14.04	– " –
	–5	192.10	0.642	14.77	– " –
Guar gum Guar	5	73.21	0.672	7.25	– " –
	2	108.64	0.640	8.10	– " –
	0	107.24	0.656	8.74	– " –
	–3	127.77	0.643	9.81	– " –
	–5	159.13	0.617	10.60	– " –
Carrageenan Karagen	5	87.66	0.650	7.28	– " –
	2	116.63	0.625	7.81	– " –
	0	154.26	0.595	8.19	– " –
	–3	155.59	0.601	8.82	– " –
	–5	166.09	0.595	9.27	– " –
Carboxymethylcellulose Karboksimetilceluloza	5	369.95	0.560	15.75	– " –
	2	396.75	0.557	16.44	– " –
	0	431.26	0.550	16.93	– " –
	–3	487.99	0.536	17.69	– " –
	–5	540.22	0.529	18.24	– " –
Pectin Pektin	5	13.03	0.845	4.32	– " –
	2	26.72	0.763	4.81	– " –
	0	31.33	0.750	5.17	– " –
	–3	39.40	0.731	5.77	– " –
	–5	43.80	0.728	6.21	– " –

measurements were performed by means of a rotational viscosimeter Rheotest 3 (WEB MLV), with coaxial cylinders, carryng out steady-shear tests at shear rate varying from 81 to 1312 s^{-1} at the temperature range from +5 to –5 °C. The Ultra-cryostat MK 70 was used to control the temperature.

The type of fluid was determined with regard to the interdependence of the shear stress on shear rate. Since the hydrocolloid solutions showed pseudoplastic and, in certain cases, thixotropic characteristics, power law equation was applied to calculate rheological parameters (*14*):

$\tau = k \cdot D^n$
τ = *shear stress*
k = consistency coefficient
D = shear rate
n = flow index

Calculation of apparent viscosity was done by the equation:

$\mu = k \cdot D^{n-1}$
μ = apparent viscosity

The influence of temperature on the change of apparent viscosity of hydrocolloid solutions and mixtures was monitored by applying the Arrhenius model:

$\mu = A \cdot e^{-E_a/RT}$
A = constant
E_a = activation energy
R = gas constant

Results and Discussion

The results of the rheological measurements and the values of the calculated rheological parameters are presented in the Tables 1–3 and Figs. 1–3. Based on the dependence of the shear stress on shear rate it was proved that all 0.2 % solutions of single hydrocolloids showed pseudoplastic behaviour (flow index value was lower than 1). Temperature decrease resulted in significant consistency increase. At the same time the flow index value decreased, which explains the behaviour deviation of these solutions compared to the Newtonian solutions (by Non-Newtonian solutions $n \neq 1$). Figure 1 shows that the highest value of apparent viscosity was in the carboxymethylcellulose solution while the lowest viscosity was found in the pectin solution.

Hydrocolloid combinations resulted, in certain cases, in the solutions which had significantly different characteristics from the characteristics of the solutions of single hydrocolloids. This is shown in Table 2 and Figs. 2 and 3. Significant interaction was registered, especially at lower temperatures (0 °C and lower), in the solutions of galactomannan hydrocolloids (locust bean gum and guar gum) and the carrageenan.

Interaction of galactomannan hydrocolloids and the carrageenan is the result of their structure. For example, the parts of macromolecules of the locust bean gum, which does not contain galactose molecules, can accumulate on a double helix of kappa carrageenan forming a net.

The mixtures of the locust bean gum and the carrageenan in various ratios (2:1, 1:1, 1:2) produced the solutions of high consistency which was significantly higher than the consistency of the solutions of single hydrocolloids. This phenomenon became more evident at lower temperatures when the type of fluid was also changed, assuming thixotropic behaviour. When the hydrocolloid ratio was 1:2 (with the locust bean gum and carrageenan) this feature (behaviour) became already obvious at the temperature of 5 °C but when the ratio was 1:1 thixotropy appeared at the temperature of 2 °C. When the ratio was 2:1 thixotropy occurred at the temperature of 0 °C. The appearance of thixotropy was related to gel formation. Temperature decreasing caused water releasing and its freezing on the surface of the sample measured, which prevented measurements at the temperatures lower than 0 °C. It was possible, however, to do the measurements, even at –5 °C, by the hydrocolloid mix-

Table 2. Rheological parameters of 0.2 % solutions of hydrocolloid mixtures at various temperatures
Tablica 2. Reološki parametri 0,2 %-tnih otopina smjesa hidrokoloida, pri različitim temperaturama

Solution Otopina	Temperature Temperatura t_C /°C	$\frac{k}{\text{mPa s}^n}$	Flow index Indeks strujanja n	Apparent viscosity Prividna viskoznost μ/mPa s	Flow behaviour Tip tekućine
Locust bean gum :	5	384.41	0.536	13.56	pseudoplastic
carboxymethylcelullose	2	390.84	0.539	14.28	– " –
Brašno sjemenke rogača :	0	427.09	0.535	15.16	– " –
karboksimetilceluloza	–3	444.89	0.539	16.25	– " –
2:1	–5	478.71	0.537	17.24	– " –
Locust bean gum :	5	339.22	0.555	14.00	pseudoplastic
carboxymethylcelullose	2	410.54	0.539	14.80	– " –
Brašno sjemenke rogača :	0	425.89	0.537	15.37	– " –
karboksimetilceluloza	–3	438.97	0.541	16.29	– " –
1:1	–5	459.73	0.540	16.94	– " –
Locust bean gum :	5	408.91	0.533	14.26	pseudoplastic
carboxymethylcelullose	2	418.46	0.538	15.22	– " –
Brašno sjemenke rogača :	0	418.89	0.545	15.91	– " –
karboksimetilceluloza	–3	459.20	0.540	17.03	– " –
1:2	–5	476.68	0.543	17.83	– " –
Guar gum :	5	369.89	0.526	12.31	pseudoplastic
carboxymethylcelullose	2	403.39	0.520	13.00	– " –
Guar : karboksimetilceluloza	0	428.09	0.521	13.51	– " –
2:1	–3	465.21	0.515	14.30	– " –
	–5	486.14	0.514	14.86	– " –
Guar gum :	5	346.35	0.540	12.79	pseudoplastic
carboxymethylcelullose	2	375.54	0.537	13.48	– " –
Guar : karboksimetilceluloza	0	410.47	0.530	13.79	– " –
1:1	–3	460.79	0.520	14.75	– " –
	–5	*	*	*	*
Guar gum :	5	438.99	0.525	14.57	pseudoplastic
carboxymethylcelullose	2	478.15	0.521	15.20	– " –
Guar : karboksimetilceluloza	0	495.82	0.519	15.64	– " –
1:2	–3	507.59	0.520	16.33	– " –
	–5	530.46	0.520	16.89	– " –
	5	68.28	0.695	7.50	pseudoplastic
Guar gum : pectin	2	73.65	0.689	8.08	– " –
Guar : pektin	0	91.30	0.668	8.49	– " –
2:1	–3	112.58	0.652	9.17	– " –
	–5	135.52	0.633	9.66	– " –
	5	44.00	0.738	6.77	pseudoplastic
Guar gum : pectin	2	50.53	0.733	7.34	– " –
Guar : pektin	0	64.44	0.704	7.74	– " –
1:1	–3	71.70	0.704	8.41	– " –
	–5	81.63	0.689	8.89	– " –
	5	22.14	0.804	5.54	pseudoplastic
Guar gum : pectin	2	39.31	0.744	6.12	– " –
Guar : pektin	0	46.15	0.730	6.55	– " –
1:2	–3	56.34	0.715	7.27	– " –
	–5	68.12	0.696	7.70	– " –

Table 2. (continuation)

Locust bean gum : pectin Brašno sjemenke rogača : pektin 2:1	5 2 0 –3 –5	46.03 67.44 88.99 95.79 *	0.754 0.716 0.682 0.677 *	8.03 8.67 8.96 9.58 *	pseudoplastic – " – – " – – " – *
Locust bean gum : pectin Brašno sjemenke rogača : pektin 1:1	5 2 0 –3 –5	32.68 48.98 56.83 74.81 *	0.790 0.739 0.725 0.695 *	7.19 7.60 7.89 8.35 *	pseudoplastic – " – – " – – " – *
Locust bean gum : pectin Brašno sjemenke rogača : pektin 1:2	5 2 0 –3 –5	21.25 28.23 36.01 47.60 *	0.805 0.790 0.758 0.735 *	5.40 6.20 6.44 7.18 *	pseudoplastic – " – – " – – " – *
Guar gum : carrageenan Guar : karagen 2:1	5 2 0 –3 –5	170.66 175.50 189.41 202.50 *	0.606 0.615 0.610 0.603 *	10.32 10.86 11.24 11.85 *	pseudoplastic – " – – " – – " – *
Guar gum : carrageenan Guar : karagen 1:1	5 2 0 –3 –5	161.01 165.49 166.30 167.63 173.61	0.602 0.608 0.615 0.618 0.619	9.35 9.89 10.27 10.88 11.32	pseudoplastic – " – – " – – " – – " –
Guar gum : carrageenan Guar : karagen 1:2	5 2 0 –3 –5	145.31 148.29 169.20 174.03 178.00	0.622 0.635 0.617 0.659 0.659	9.84 10.44 10.87 11.56 12.05	pseudoplastic – " – – " – – " – – " –
Locust bean gum : carrageenan Brašno sjemenke rogača : karagen 2:1	5 2 0 –3 –5	123.41 128.49 304.15 4223.90 *	0.658 0.655 0.554 0.229 *	9.86 11.68 13.10 15.61 *	pseudoplastic – " – thixotropic – " – *
Locust bean gum : carrageenan Brašno sjemenke rogača : karagen 1:1	5 2 0 –3 –5	149.36 694.61 3787.20 6733.50 1971.00	0.605 0.414 0.239 0.167 0.350	9.01 11.35 13.28 16.89 19.87	pseudoplastic thixotropic – " – – " – – " –
Locust bean gum : carrageenan Brašno sjemenke rogača : karagen 1:2	5 2 0 –3 –5	895.43 3150.90 3744.50 * *	0.390 0.297 0.291 * *	11.71 19.21 24.57 * *	thixotropic – " – – " – * *

* Measurement was not carried out because the sample started freezing
* Mjerenje nije obavljeno zbog zamrzavanja uzorka

tures whose ratio was 1:1. However, the changes in the structure of the system caused consistency reduction (Table 2).

Consistency increased also within the mixture solutions of the guar gum and carrageenan (2:1, 1:1, 1:2) compared with the solutions of pure hydrocolloids (Fig. 3). These hydrocolloid mixtures, at all measuring temperatures, had higher consistency than single hydrocolloids. It was characteristic for these solutions that the fluid type remained unchanged, i.e. the mixture solutions retained pseudoplastic behaviour.

There was no viscosity increase within the solutions of other hydrocolloids mixture compared with the pure hydrocolloids. The values of consistency coefficient of the latter solutions were of the same range as the values of the pure hydrocolloids, which implied lack of interaction between the galactomannan hydrocolloids, carboxymethylcellulose and pectin. Those solutions, which were all pseudoplastic, did not show change in the fluid type.

Table 3 presents the values of activation energy and the pertaining coefficients of the Arrhenius model. Based

Table 3. Parameters of Arrhenius model for hydrocolloid solutions and their mixtures (at 1312 s^{-1})
Tablica 3. Parametri Arrheniusova modela za otopine hidrokoloida i njihove smjese (pri 1312 s^{-1})

Solution Otopina	Temperature range Temperaturno područje °C	Activation energy Energija aktivacije E_a /kJ mol^{-1}	A /Pa s	R^2
Locust bean gum Brašno sjemenke rogača	–5 to 5	15.33	$1.53 \cdot 10^{-5}$	0.993
Guar gum Guar	–5 to 5	23.59	$2.70 \cdot 10^{-7}$	0.998
Carrageenan Karagen	–5 to 5	15.01	$1.11 \cdot 10^{-5}$	0.988
Carboxymethylcellulose Karboksimetilceluloza	–5 to 5	9.07	$3.12 \cdot 10^{-4}$	0.967
Pectin Pektin	–3 to 5	22.40	$2.69 \cdot 10^{-7}$	0.994
Locust bean gum : carrageenan, 2:1 Brašno sjemenke rogača : karagen	–3 to 5	35.90	$1.79 \cdot 10^{-9}$	0.928
Locust bean gum : carrageenan, 1:1 Brašno sjemenke rogača : karagen	–5 to 5	49.03	$5.58 \cdot 10^{-12}$	0.957
Locust bean gum : carrageenan, 1:2 Brašno sjemenke rogača : karagen	0 to 5	93.56	$3.10 \cdot 10^{-20}$	0.949
Guar gum : carrageenan, 2:1 Guar : karagen	–5 to 5	10.85	$9.46 \cdot 10^{-5}$	0.980
Guar gum : carrageenan, 1:1 Guar : karagen	–5 to 5	11.83	$5.62 \cdot 10^{-5}$	0.973
Guar gum : carrageenan, 1:2 Guar : karagen	–5 to 5	12.56	$4.31 \cdot 10^{-5}$	0.988
Locust bean gum : carboxymethylcellulose,2:1 Brašno sjemenke rogača : karboksimetilceluloza	–5 to 5	14.36	$2.72 \cdot 10^{-5}$	0.969
Locust bean gum : carboxymethylcellulose, 1:1 Brašno sjemenke rogača : karboksimetilceluloza	–5 to 5	11.80	$8.53 \cdot 10^{-5}$	0.989
Locust bean gum : carboxymethylcellulose, 1:2 Brašno sjemenke rogača : karboksimetilceluloza	–5 to 5	13.84	$3.59 \cdot 10^{-5}$	0.976
Guar gum : carboxymethylcellulose, 2:1 Guar : karboksimetilceluloza	–5 to 5	11.65	$7.98 \cdot 10^{-5}$	0.958
Guar gum : carboxymethylcellulose, 1:1 Guar : karboksimetilceluloza	–3 to 5	11.13	$1.04 \cdot 10^{-4}$	0.992
Guar gum : carboxymethylcellulose, 1:2 Guar : karboksimetilceluloza	–5 to 5	8.90	$3.11 \cdot 10^{-4}$	0.994
Locust bean gum : pectin, 2:1 Brašno sjemenke rogača : pektin	–3 to 5	13.81	$2.05 \cdot 10^{-5}$	0.972
Locust bean gum : pectin, 1:1 Brašno sjemenke rogača : pektin	–3 to 5	11.64	$4.69 \cdot 10^{-5}$	0.932
Locust bean gum : pectin, 1:2 Brašno sjemenke rogača : pektin	–3 to 5	22.23	$3.61 \cdot 10^{-7}$	0.957
Guar gum : pectin, 2:1 Guar : pektin	–5 to 5	15.69	$8.50 \cdot 10^{-6}$	0.993
Guar gum : pectin, 1:1 Guar : pektin	–5 to 5	16.85	$4.64 \cdot 10^{-6}$	0.990
Guar gum : pectin, 1:2 Guar : pektin	–5 to 5	21.12	$5.98 \cdot 10^{-7}$	0.996

R^2 = Coefficient of determination
Koeficijent determinacije

A = Coefficient of Arrhenius model
Koeficijent Arrheniusova modela

on the values of the correlation coefficient it could be concluded that there is good compatibility between the values calculated in this way and those obtained by the measurement.

Conclusion

Solutions (w = 0.2 %) of the single hydrocolloids (the locust bean gum, guar gum, carrageenan, carboxymethylcellulose and pectin) show pseudoplastic behaviour at all temperatures that were applied during the measurements (5, 2, 0, –3, –5 °C).

Hydrocolloid combinations exhibited in certain cases significantly different properties compared with single hydrocolloids. Significant interaction appeared between the galactomannan hydrocolloids (the locust bean gum and the guar gum) and the carrageenan. The mixtures of these hydrocolloids had markedly higher consistency than the single hydrocolloids. Consistency increase was more evident at lower temperatures (0 °C and below).

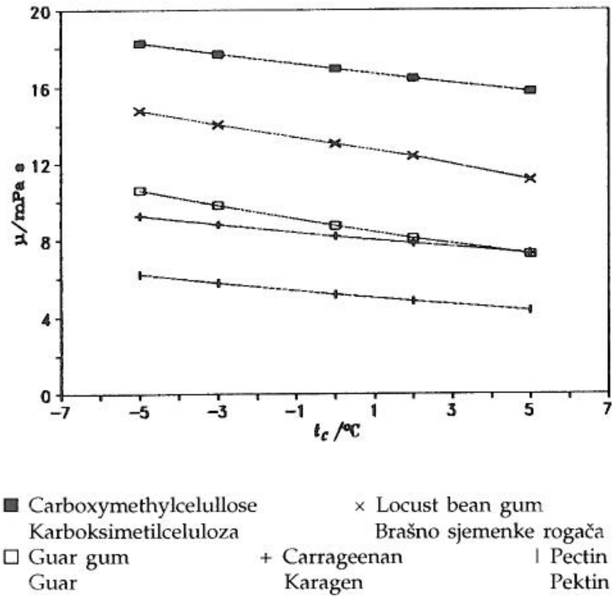

Fig. 1. Temperature dependence of apparent viscosity (at 1312 s^{-1}) of 0.2 % solutions of pure hydrocolloids

Slika 1. Ovisnost prividne viskoznosti 0,2 %-tnih otopina pojedinačnih hidrokoloida o temperaturi (pri 1312 s^{-1})

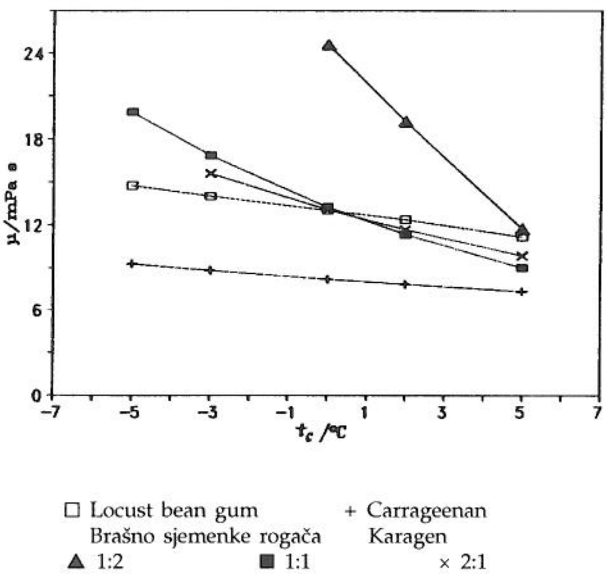

Fig. 2. Temperature dependence of apparent viscosity (at 1312 s^{-1}) of 0.2 % solutions of hydrocolloid mixtures

Slika 2. Ovisnost prividne viskoznosti 0,2 %-tnih otopina smjesa hidrokoloida o temperaturi (pri 1312 s^{-1})

Interaction was not present within the other examinated hydrocolloid mixtures, i.e. the mixture consistency had the value that was within the consistency values of the pure components (hydrocolloids).

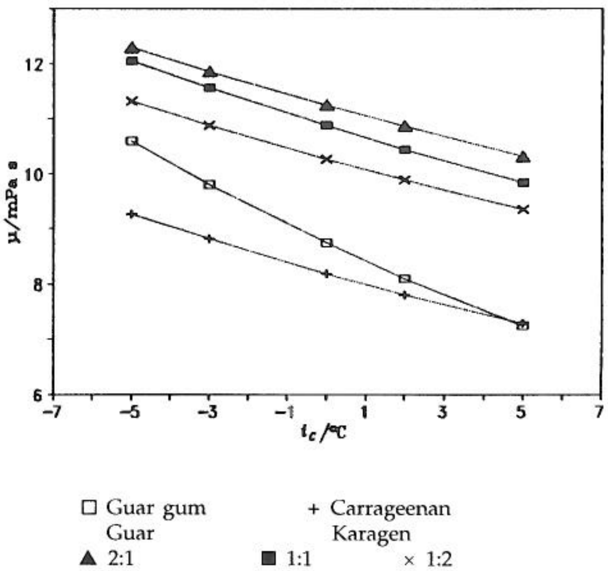

Fig. 3. Temperature dependence of apparent viscosity (at 1312 s^{-1}) of 0.2 % solutions of hydrocolloid mixtures

Slika 3. Ovisnost prividne viskoznosti 0,2 %-tnih otopina smjesa hidrokoloida o temperaturi (pri 1312 s^{-1})

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