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Impact of carrageenan addition on rheological characterisation of some hydrocolloid aqueous solutions during long-lasting agitating with rotational speed changes

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The paper presents the impact of carrageenan addition on rheological characterisation of some hydrocolloid aqueous solutions during stirring with rotational speed changes. Carboxymethyl cellulose, guar gum and xanthan gum were used. Measurements were conducted in a vessel equipped with an anchor stirrer under rotational speed increase and decrease conditions, equivalent to a hysteresis loop rheological test. Rheological parameters were calculated using the power-law equation. It was found that a carrageenan addition generally causes a reduction of liquid apparent viscosity and time-dependent rheological behaviour intensification, with some exceptions.

Keywords: mixing, viscoelasticity, rheology, hydrocolloids

1. INTRODUCTION

In the mass-scale chemical industry and related industries, substances in the form of liquid non-homogeneous mixtures are used, most frequently prepared by mixing processes (Stręk, 1971). The most common variation of this operation consists in mechanical stirring using various stirrers. In the food industry, various substances called food additives are used during processing and preservation of foods. They are applied in order to obtain products with defined features. Food additives are systems whose preparation is based on hydrocolloids, solutions of which exhibit rheological properties depending not only upon the shear rate, but also the shear time. Complex properties of this type are exhibited by solutions of commonly used hydrocolloids: carrageenan gums (CAR), carboxymethyl cellulose (CMC), xanthan gum (XG) or guar gum (GG).

Carrageenan is a hydrocolloid used in industrial practice, obtained from red algae (Imeson, 2010). It is used mainly as a texture-improving agent for various products of the meat industry, ice-cream, dessert products and dairy products. Aqueous solutions of this hydrocolloid form elastic gels at lower temperatures, while they take on a fluid consistency when the temperature rises (Imeson, 2010).

Carboxymethyl cellulose is a polymer obtained from cellulose (Togrul and Arslan, 2003), used as a thickener, gelling agent and stabilizer (da Silva Coutinho, 2012; Gomez-Diaz and Navaza, 2004). Typically,

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CMC solutions exhibit shear thinning (Togrul and Arslan, 2003); although, depending on the conditions of technological operations, as well as carboxymethyl cellulose concentration in the solution, dilatation or thixotropy may also occur (Imeson, 2010).

Xanthan gum is a polysaccharide included in the plant resin group. It is synthesised as a result of fermentation by microorganisms from the *Xanthomonas campestris* group (Xuewu et al., 1996). This gum has emulsifying, thickening, stabilising and dispersive properties (Xie et al., 2014). In solutions, xanthan gum alone does not form a gel but a pseudo-gel structure (Pelletier et al., 2001), and its solutions are characterised by a very high viscosity. In food processing, the addition of xanthan gum is used mostly in manufacturing of such articles as: cream, juices, dressings, as well as ice-cream and desserts (Faria et al., 2011).

Guar gum is a long-chain polysaccharide having a high polydispersion, consisting of a linear (1-4)-β-D-mannopyranose chain and individual (1-6)-α-D-galactopyranose side chains. This hydrocolloid is a galactomannan obtained from *Cyamopsis tetragonolobus L* endosperm (Casas, et al. 2000). Guar gum is applied in chemical, cosmetic and textile industries, as well as in the production of explosives and drilling fluids (Kono, et al., 2014). It has found wide application in food processing as a thickener, emulsifier, water-binding agent and structure-stabilising agent (Mannarswamy et al., 2010). GG solutions are included among fluids with non-Newtonian rheological properties – their apparent viscosity decreases with an increase in shear rate (Torres et al., 2014). On the other hand, shearing of systems containing guar gum in higher concentrations (above 0.5%) results in the occurrence of the thixotropy phenomenon.

The aim of presented work was to describe the impact of carrageenan addition on food simulant fluids based on some of the most common hydrocolloids used in food industry during agitation under conditions of stepwise rotational speed changes.

2. MATERIALS AND METHODS

Materials

In this research two groups of food simulant fluids were investigated. The first one included 1% solution of carboxymethyl cellulose (CMC, ρ = 1006.45 kg · m^{-3}), guar gum (GG, ρ = 1004.41 kg · m^{-3}) and xanthan gum (XG, ρ = 1003.08 kg · m^{-3}), and the second group included fluids based on following hydrocolloids, but with 0.8% concentration and with 0.2% addition of carrageenan (CAR, ρ = 1006.66 kg · m^{-3}). The producer of hydrocolloids is Regis Food Technology (Poland).

Apparatus

Solutions were prepared using an FCM planetary kneader (Stalgast, Poland) equipped with a beater. The so-prepared systems were left for 24 hours to degas.

The material for studies was subjected to agitation lasting for 3 hours, under conditions of stepwise increases and decreases of stirrer rotation, which corresponded to a shear rate jump test used in rheology (Dziubiński et al., 2014). Values of the rotational speed of the stirrer were imposed in the range of 9.7 min^{-1} to 44.6 min^{-1}. The change in the stirrer's rotation rate occurred every 12 minutes.

The systems were mixed in a cylindrical tank having a capacity of 12.0 dm^3, diameter D = 0.24 m and height H = 0.32 m, using an anchor stirrer (Fig. 1) at a station for tests of non-Newtonian food fluids (Kabziński and Grzesik, 2014).

Fig. 1. Anchor stirrer used for the studies

The value of the Metzner constant (k_s), equal to 26.3 for the stirrer used, was determined using glucose syrup having a Newtonian viscosity of 1.5 Pas, according to the procedure included in the paper by Wilkinson (1963).

Methodology

The data collected during the tests (instantaneous value of torque, rotational frequency of the stirrer and time) were used to calculate values characterising mixing and further rheological quantities. Values of shear stress were determined based on the measured value of torque and knowledge on the geometry of the stirrer (Cullen, 2009).

$$\tau = \frac{2M_0}{\pi d^2 h} \tag{1}$$

On the basis of the rotational frequency of the stirrer and the value of proportionality factor, called the Metzner constant, the value of shear rate was determined.

$$\dot{\gamma} = k_s N \tag{2}$$

The value of the k_s coefficient for the anchor stirrer amounted to 26.3.

The values of the apparent viscosity were calculated by following equation:

$$\eta_{app} = \frac{\tau}{\dot{\gamma}} \tag{3}$$

The obtained values of shear stress and shear rate were used to determine parameters of the Ostwald-de Waele relationship (Wilkinson, 1963), which were calculated for mixing under conditions of increasing and decreasing stirrer rotations.

$$\tau = K \cdot \dot{\gamma}^n \tag{4}$$

The above equations are valid in the laminar mixing area. To define the flow type, values of the equivalent criterion number for mixing were determined:

- Reynolds number:

$$Re_m = \frac{Nd^2\rho}{\eta_{app}} \tag{5}$$

- and Newton number:

$$Ne_m = \frac{2\pi M_0}{N^2 d^5 \rho} \tag{6}$$

The dependence between these numbers, described by the equation (7)

$$Ne_m = A\,Re_m^B \tag{7}$$

is called power characteristics and is used, among others, for determination of the flow area (character), within which the mixing is carried out (Koch and Noworyta, 2005).

The apparent viscosity changes in time were calculated as the differences between last and first apparent viscosity value for every rotational speed value, according to the following equation:

$$\Delta h = \eta_{last_{N_n}} - \eta_{first_{N_n}} \tag{8}$$

3. RESULTS AND DISCUSSION

To enable a description of rheological properties of fluids on the basis of data obtained during the mixing operation, it is necessary to maintain a laminar flow. To this end, the parameters of Eq. (7) were determined and gathered in Table 1. For each of the fluids used in the experiments, the value of the exponent of the discussed equation was −1, indicating the occurrence of laminar flow in the mixer. One should also note the evident expansion of the laminar flow range, above the arbitrary limit of $Re_m = 10$, during mixing under the reported conditions of operation and geometric parameters of the experimental system.

Table 1. Power characteristics equations and Reynolds number ranges for agitated mediums

Medium	Equation	Reynolds number range
CMC 1%	$Ne_m = 245.66 Re_m^{-1}$	1.48÷20.99
CMC 0.8% + CAR 0.2%		3.05÷34.27
GG 1%		2.69÷35.09
GG 0.8% + CAR 0.2%		0.33÷64.29
XG 1%		1.48÷37.11
XG 0.8% + CAR 0.2%		1.79÷40.47

On the basis of the obtained measurement data, flow curves of the examined system without carrageenan addition and with the addition of this hydrocolloid were then plotted and are presented in Figs. 2–4. Additionally, to better show apparent viscosity changes in time, the functions of apparent viscosity relative to time are shown in Figs. 5–7.

Analysis of the presented plots shows that the aqueous solutions of hydrocolloids used for the studies are characterised by non-Newtonian rheological properties. Moreover, the difference in the course of the curves for time periods with an increase and a decrease of the stirrer rotation is characteristic for fluids

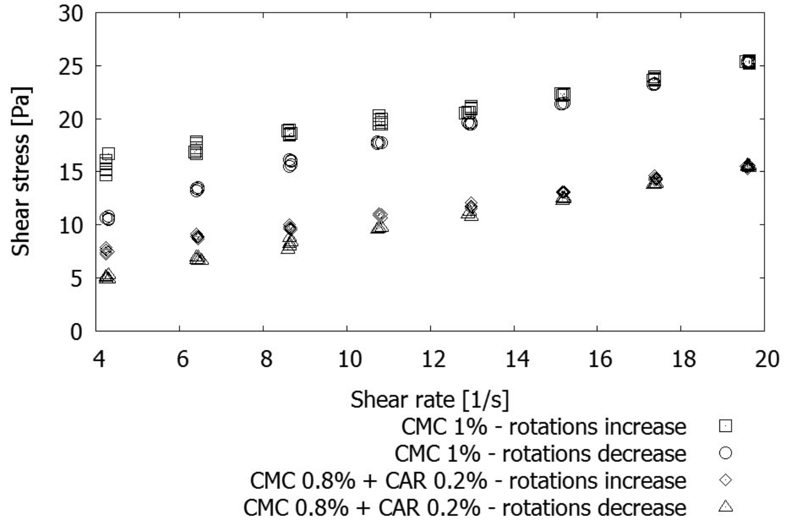

Fig. 2. Flow curves of carboxymethyl cellulose (CMC) solutions with and without a carrageenan (CAR) addition

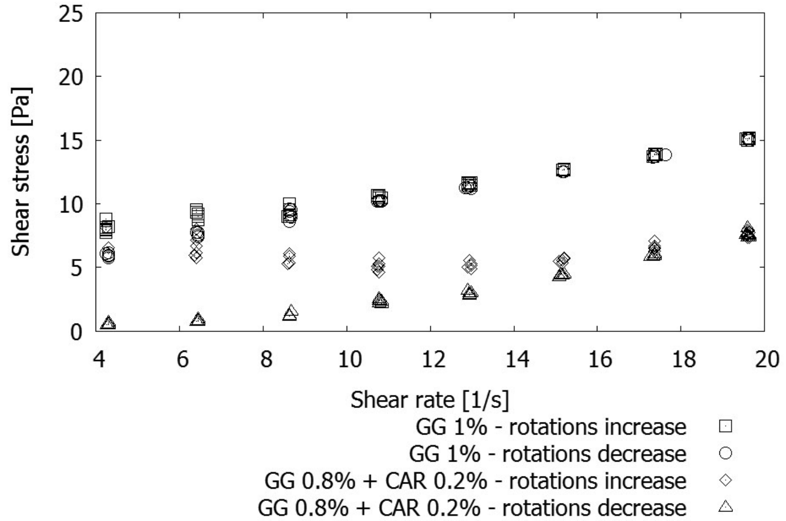

Fig. 3. Flow curves of guar gum (GG) solutions with and without a carrageenan (CAR) addition

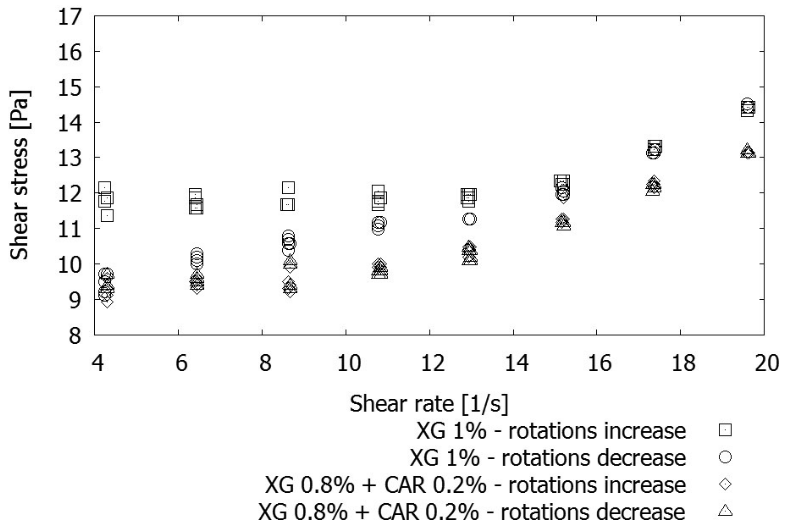

Fig. 4. Flow curves of xanthan gum (XG) solutions with and without a carrageenan (CAR) addition

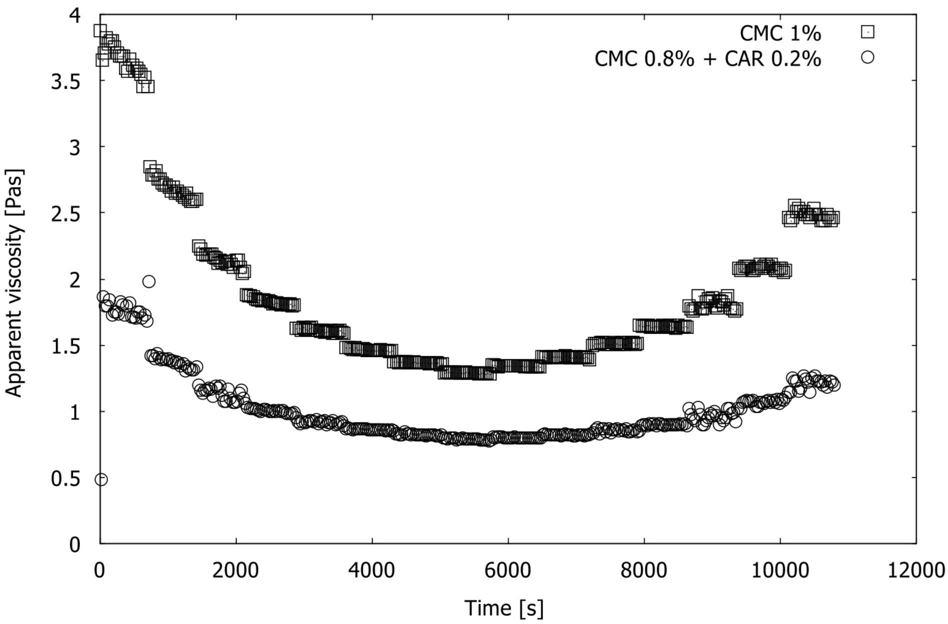

Fig. 5. Function of apparent viscosity dependences on time of carboxymethyl cellulose (CMC) solutions with and without a carrageenan (CAR) addition

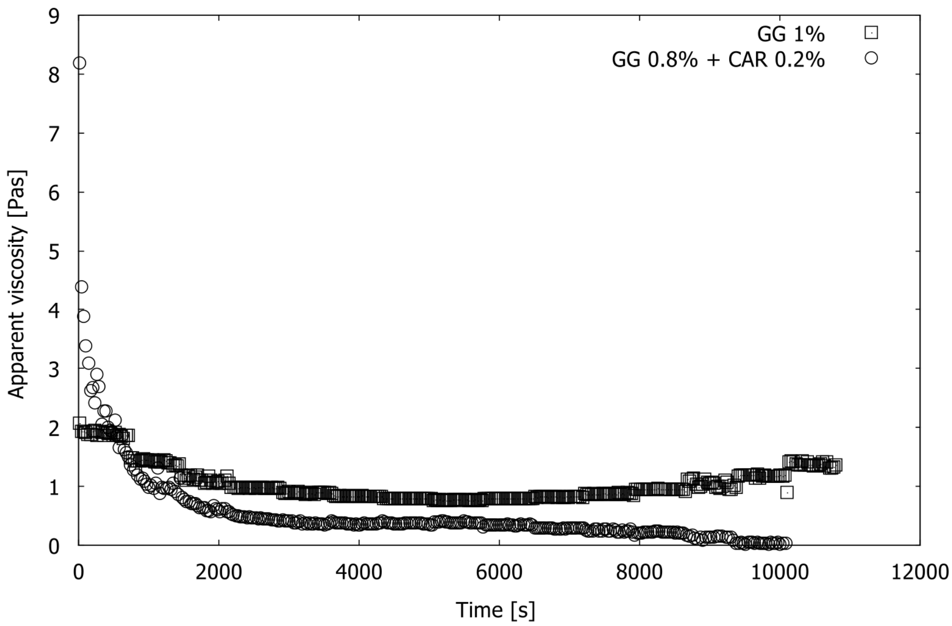

Fig. 6. Function of apparent viscosity dependences on time of guar gum (GG) solutions with and without a carrageenan (CAR) addition

which are time-dependent. A precise definition of the rheological character of mixed fluids and the impact of the carrageenan addition and the operation duration have become possible after the determination of parameters of the Ostwald-de Waele relationship for both time periods. The calculation results of the parameters mentioned above are gathered in Table 2. To better show the apparent viscosity changes in time, calculated differences between first and last values of the parameter (for every rotational speed used) are presented in Table 3.

For solutions based on carboxymethyl cellulose and xanthan gum, the addition of carrageenan caused a significant decrease in the apparent viscosity of the system, with increase while shearing was reduced,

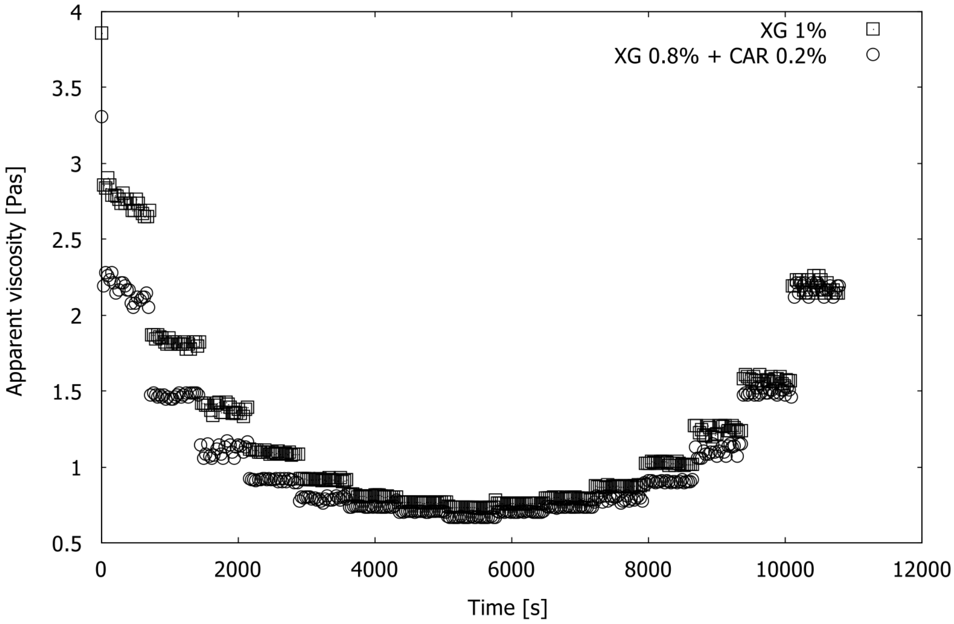

Fig. 7. Function of apparent viscosity dependences on time of xanthan gum (XG) solutions with and without a carrageenan (CAR) addition

Table 2. Power-law model parameter values and changes for agitated mediums

Medium	Rotation increase		Rotation decrease		Parameter changes	
	K [Pa · s^n]	n [–]	K [Pa · s^n]	n [–]	$\frac{K_{decrease}}{K_{increase}}$	$\frac{n_{decrease}}{n_{increase}}$
CMC 1%	9.342	0.325	4.571	0.571	0.489	1.757
CMC 0.8% + CAR 0.2%	3.464	0.494	1.714	0.734	0.495	1.486
GG 1%	3.966	0.434	2.398	0.612	0.605	1.410
GG 0.8% + CAR 0.2%	4.551	0.114	0.013	2.136	0.003	18.737
XG 1%	9.529	0.111	6.034	0.270	0.633	2.432
XG 0.8% + CAR 0.2%	5.927	0.243	6.012	0.237	1.014	0.975

providing partial reconstruction of the system structure. Another situation occurs in the case of media containing guar gum and carrageenan. For such a system, a strong decrease in the apparent viscosity was observed. Moreover, the shear reduction did not cause structure rebuilding. While analysing the values of the flow index, it may be concluded that all the systems exhibited features of strongly shear-thinned fluids, and in the case of systems containing carboxymethyl cellulose and xanthan gum, the addition of carrageenan caused a decrease in the deviation of rheological behaviour of these media from Newton's law. For the fluids based on guar gum, an opposite dependence was observed (an increase in the deviation).

Considering data presented in Table 2 and Table 3 in their variability in time, the apparent viscosity of media subjected to stirring in the experiments decreased with time of the operation, which is characteristic for the phenomenon of thixotropy. Moreover, for the majority of fluids, the values of the flow index *vs.* time exhibit an increasing tendency, indicating the reduction of deviation from Newton's law connected with the duration of agitation. These changes did not affect the rheological character of the solutions, which remained characteristic for shear-thinned fluids. Different behaviour was exhibited by the systems

Table 3. Differences between last and first apparent viscosity values for every rotational speed value

		$\Delta\eta$ [Pa · s ± 0.002 Pa · s]					
	N [rpm]	CMC 1%	CMC 0.8% + CAR 0.2%	GG 1%	GG 0.8% + CAR 0.2%	XG 1%	XG 0.8% + CAR 0.2%
Rotational speed increase	10	−0.850	−0.157	−0.157	−4.588	−0.224	−0.224
	15	−0.448	−0.119	−0.119	−0.462	−0.075	−0.060
	20	−0.313	−0.145	−0.134	−0.268	−0.089	−0.101
	25	−0.161	−0.045	−0.027	−0.125	−0.036	−0.018
	30	−0.082	−0.052	−0.037	−0.089	−0.022	−0.037
	35	−0.032	−0.019	−0.013	−0.045	−0.013	−0.013
	40	−0.022	−0.011	−0.005	−0.056	−0.011	−0.006
	45	−0.020	−0.015	−0.099	−0.040	−0.010	−0.005
Rotational speed decrease	40	−0.022	−0.011	−0.006	−0.022	−0.011	−0.006
	35	−0.019	−0.013	−0.006	−0.026	−0.019	−0.013
	30	−0.030	−0.045	−0.037	−0.067	−0.022	−0.037
	25	−0.018	−0.018	−0.018	−0.045	−0.018	−0.027
	20	−0.089	−0.123	−0.179	−0.123	−0.067	−0.101
	15	−0.045	−0.060	−0.045	−0.045	−0.075	−0.060
	10	−0.089	−0.112	−0.112	−0.202	−0.112	−0.134

containing guar gum and xanthan gum, with the addition of carrageenan. The former is characterised by thixotropy, but a change in the rheological character is also visible, from strongly shear-thinned to strongly shear-thickened.

4. CONCLUSIONS

The addition of carrageenan in the studied systems led to a decrease in the fluid apparent viscosity and a reduction of the deviation of rheological behaviour from Newton's law, without a change in the rheological character, which remained proper to strongly shear-thinned fluids. Also, the addition of this hydrocolloid caused an intensification of time-dependent-type phenomena. One exception is the guar gum solution with an addition of carrageenan, exhibiting synergistic effects between the hydrocolloids, manifesting themselves as an increase in the viscosity of the system. In this case, a change in the rheological character with the duration of the operation was also observed, from the shear-thinned to the shear-thickened. Another exception is the system containing xanthan gum and carrageenan, for which, differently as in the case of the other systems, a reduction of the deviation of rheological behaviour from Newton's law was found. It is essential to understand interactions between hydrocolloids in media and their impact on rheological properties for industrial process engineers from various industries, as they try to predict the behaviour of systems during mixing operations. Such information enables proper selection of apparatus design and operating parameters. It can also help to maintain high quality level of semi-finished products of the final products.

SYMBOLS

M_0	torque, Nm
d	stirrer diameter, m
h	stirrer height, m
k_s	Metzner constant
N	stirrer rotational speed, s^{-1}
K	consistency coefficient, $Pa \cdot s^n$
Re_m	equivalent Reynolds number for stirring
Ne_m	equivalent Newton number for stirring (power number)
A	equation parameter

Greek symbols

ρ	density, kg/m^3
π	constant
$\dot{\gamma}$	average shear rate, s^{-1}
τ	average shear stress, Pa
η	viscosity, $Pa \cdot s$

Subscripts

app	apparent

Superscripts

n	flow index
B	equation parameter

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