

RHEOLOGICAL PROPERTIES OF POTATO STARCH PASTES WITH THE ADDITION OF KAOLIN

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A study was undertaken to investigate rheological properties of pastes (20 g/L of starch) supplemented with kaolin at doses of 20 g/L, 40 g/L and 60 g/L, stored for various periods of time. Flow curves were plotted at a time span of 200 s, a shear rate of 0-100 s⁻¹ and a temperature of 20°C. The flow curves were described by means of Ostwald de Waele's and Casson's models. It was demonstrated that starch pastes with different addition of kaolin stored for various periods of time displayed characteristics of non-Newtonian, pseudoplastic shear-thinned fluids and that their rheological properties depended on both kaolin addition and time of storage. The pastes prepared with the addition of kaolin were characterised by higher viscosity, higher values of shearing stresses, coefficient of consistency K, plastic viscosity η_c and yield point τ_{oc} as compared to those prepared only from starch. Values of those parameters were observed to increase along with storage time in samples with the addition of kaolin, and to decrease in the case of pastes prepared only from starch.

INTRODUCTION

Rheological properties of starch pastes and gels are complex and depend on a variety of factors, including botanical origin [Abu-Jdayil *et al.*, 2004; Li & Yeh, 2001], size of starch granules [Rao & Tattiyakul, 1999], amylose-to-amylopectin ratio [Nguyen *et al.*, 1998], concentration of starch and conditions of the gelatinization process (temperature, pH, heating and stirring rate) [Nguyen *et al.*, 1998; Mali *et al.*, 2003].

Currently in scientific literature much attention is paid to rheological properties of starch mixtures heated in the presence of such substances as saccharides [Abu-Jdayil *et al.*, 2001; Acquarone & Rao, 2003; Sopade *et al.*, 2004; Yoo & Yoo, 2005], hydrocolloids [Krüger *et al.*, 2003], salts, lipids and proteins [Yoo & Yoo, 2005]. Rheological properties of starch pastes are determined not only by organic substances but also by the inorganic ones [Sajeev *et al.*, 2003; Valles-Pamies *et al.*, 1997]. Determination of those properties in starch mixtures and water-insoluble inorganic substances is especially important in the confectionery and paper industries as well as in the production of biodegradable materials.

Scientific literature provides a number of reports on interactions between starch derivatives and kaolin – silty, natural material, one of the most important filling material commonly applied in various industries. It has been proved that the adsorption capacity of starch on the surface of kaolin depends on its origin and modification [Husband, 1998b]. Adsorption of polymers on the surface of kaolin molecules is determined by a variety of factors, among others by kaolin concentration in the mixture [Golachowski *et al.*, 2005], starch modification [Husband, 1998b], pH [Herrington *et al.*, 1992; Sastry *et al.*,

1995], ionic strength [Siffert *et al.*, 1984] or polymer charge [Husband, 1998a].

Cationic and amphoteric starches have been demonstrated to form coating dispersions with kaolin characterised by very good structural properties [Bratskaya *et al.*, 2005]. Attempts of combining thermoplastic starch with silty material, including kaolin, have proved that it is possible to use those materials for the production of plastics with satisfactory mechanical properties [de Carvallo *et al.* 2001; Wilhelm *et al.*, 2003].

Despite ample papers on starch interactions with kaolin specialist literature does not provide explicit information on the rheological properties of starch mixtures containing considerable quantities of kaolin, whilst determination of those parameters seems to be indispensable in the case of their industrial application.

The research was aimed at assaying the effect of kaolin addition on rheological properties of starch pastes containing 20 g/L of starch stored for various periods of time.

MATERIALS AND METHODS

The experimental material was potato starch Superior produced by PPZ S.A. (Niechlów, Poland) in 2005 and kaolin KOWS produced by KSM Surmin-Kaolin S.A. (Nowogrodziec, Poland) with the following chemical composition: 51.3% SiO₂, 34.3% Al₂O₃, 0.5% Fe₂O₃ and <0.8% of water. Mean diameter of kaolin particles reached 11 µm.

Analyses were carried out for starch pastes (20 g/L of starch) prepared with the addition of the following doses of kaolin: 20 g/L, 40 g/L and 60 g/L. A water suspension of starch with the addition of kaolin was prepared by heating to a tem-

perature of 94°C and keeping it at that temperature for 10 min. Next, the pastes were cooled down to a room temperature. Analyses were carried out for pastes immediately after preparation and after storage. The pastes were stored at a room temperature in tightly closed containers for 24 h and 48 h. Flow curves of the prepared pastes were plotted with the use of a rotary viscometer Haake RS100 (program RheoWin) using a Z38 measuring unit. The flow curves were plotted in time of 200 s at a shear rate of 0-100 s⁻¹ and a temperature of 20°C. All determinations were carried out in triplicate. The flow curves obtained were described with the following models:

Ostwald de Waele's model

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

Casson's model

$$\tau = \tau_{oc}^{0.5} + (\eta_c \cdot \dot{\gamma})^{0.5}$$

where: $\dot{\gamma}$ - shear rate (s⁻¹), τ - shear stress (Pa), K - coefficient of consistency (Pa·sⁿ), n - flow index (-), τ_{oc} - yield point acc. to Casson (Pa), and η_c - Casson's plastic viscosity (Pa·s).

Results obtained were subjected to one-way analysis of variance with the use of Statistica 7.1 software.

RESULTS AND DISCUSSION

Analyses carried out in the reported study indicate differences in the rheological properties of the pastes examined depending on kaolin addition and storage time.

The results obtained were presented in figures (flow curves - Figures 1 and 2) and described by means of rheological models (Tables 1 and 2).

Literature data demonstrate numerous attempts of describing a flow curve of pseudoplastic fluids with the use of an appropriate rheological model. In the reported study, use was made of most often applied Ostwald de Waele power model described with two parameters: a coefficient of consistency K (Pa·sⁿ) and a flow index n. The yield point τ_{oc} (Pa) and plastic viscosity η_c (Pa) were determined using the rheological model by Casson. Parameters of the rheological models were compiled in Tables 1 and 2. The models used were found to well describe the flow curves of pastes examined, since the coefficient of fit R² was higher than 0.99 for each sample analysed.

Viscosity measurements demonstrated that both pastes prepared only from starch as well as those containing kaolin were non-Newtonian systems whose flow curves were not straight lines (Figure 1). The non-Newtonian character of the pastes is also indicated by the flow index n (Table 1), the values of which were much below 1 (from *ca.* 0.59 to *ca.* 5.4). The flow index was observed to decrease with an increasing content of kaolin and time of storage, which implies that the pastes demonstrated increasing deviations from the Newtonian fluid and confirms their pseudoplastic properties. The pastes analysed belong to shear-thinned pseudoplastic fluids, since their viscosity decreases along with an increasing shearing rate (Figure 1), and the shearing stress of those systems increases more slower than linearly. The shear-thinned character of starch pastes flow is consistent with literature data [Kapoor & Bhattacharya, 2001; Paterson *et al.*, 2001; Tako & Hizukuri, 2002; Nguyen *et al.*, 1998].

TABLE 1. Parameters of a rheological Ostwald model describing the flow curves of starch pastes with different kaolin addition, stored for different time.

Kaolin concentration (g/L)	K (Pa·s ⁿ)					n				
	Time of storage (h)									
	0	24 h	48 h	mean	LSD	0	24	48	mean	LSD
0	2.228	1.747	1.803	1.926	0.1229	0.5783	0.5944	0.5816	0.5848	0.0063
20	2.066	2.945	3.072	2.694		0.5884	0.5401	0.5491	0.5592	
40	2.751	3.145	3.217	3.038		0.5410	0.5490	0.5408	0.5436	
60	2.567	3.306	4.096	3.323		0.5466	0.5357	0.5350	0.5391	
mean	2.403	2.786	3.047	-		0.5636	0.5548	0.5516	-	
LSD	0.1064					0.0055				

TABLE 2. Parameters of a rheological Casson model describing the flow curves of starch pastes with different kaolin addition, stored for different time.

Kaolin concentration (g/L)	η_c (Pa·s)					τ_{oc} (Pa)				
	Time of storage (h)									
	0	24 h	48 h	mean	LSD	0	24	48	mean	LSD
0	0.1620	0.1401	0.1340	0.1454	0.0222	2.944	2.316	2.379	2.546	0.8809
20	0.1602	0.1667	0.1716	0.1662		2.737	4.019	3.912	3.556	
40	0.1678	0.1699	0.1768	0.1715		3.033	3.976	4.260	3.756	
60	0.1611	0.2200	0.2343	0.2051		2.719	4.417	5.593	4.243	
mean	0.1627	0.1740	0.1791	-		2.858	3.682	4.036	-	
LSD	0.0259					0.9061				

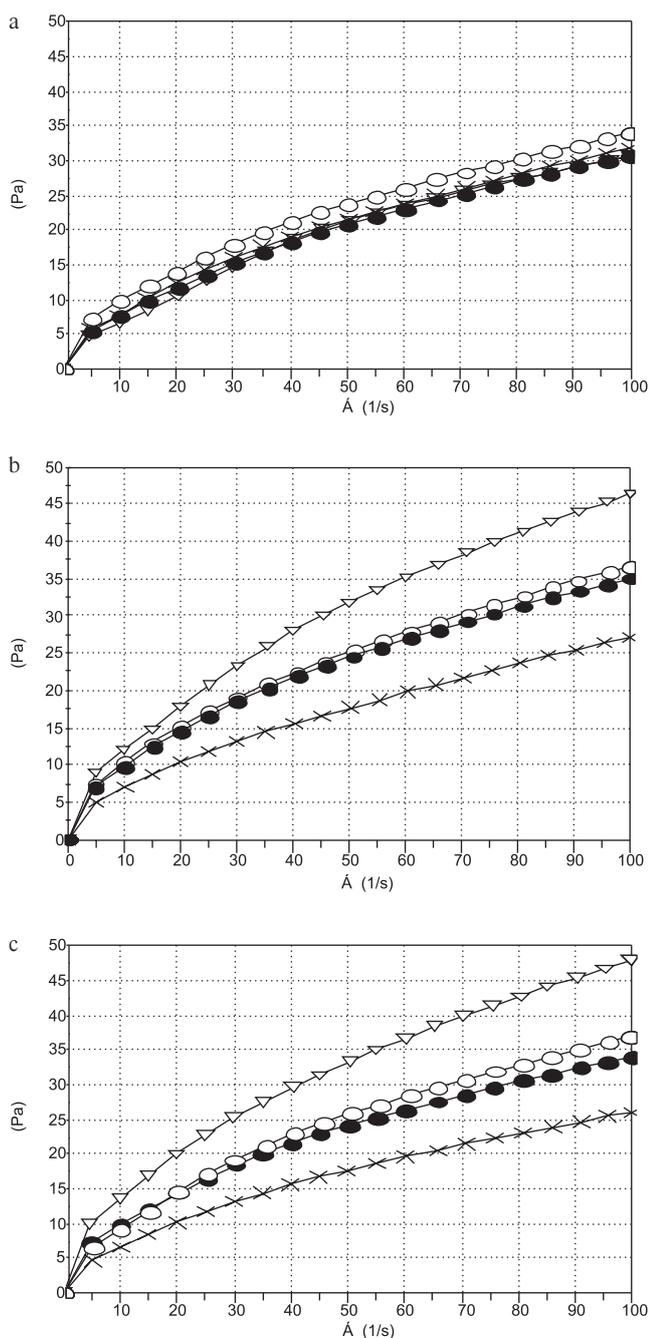


FIGURE 1. Flow curves of 20 g/L potato starch dispersions gelatinized in the presence of 20 g/L —●—, 40 g/L —○—, 60 g/L —▽— kaolin and without kaolin —×—, measured before (a) and after 24 h (b) and 48 h (c) storage.

The flow curves of starch pastes without and with the addition of kaolin stored for various periods of time were presented in Figure 1. The non-stored starch pastes were characterised by similar viscosity and values of rheological properties. A lack of distinct differences between the non-stored samples depending on kaolin addition was likely to result from the fact their structure was still unordered. During storage, differences between the sample were becoming more noticeable. Starch pastes not containing kaolin displayed decreasing viscosity along with the time of storage. Rheological parameters describing viscosity were observed to diminish – their coefficient of consistency K decreased from the initial value of $2.2 \text{ Pa}\cdot\text{s}^n$ to

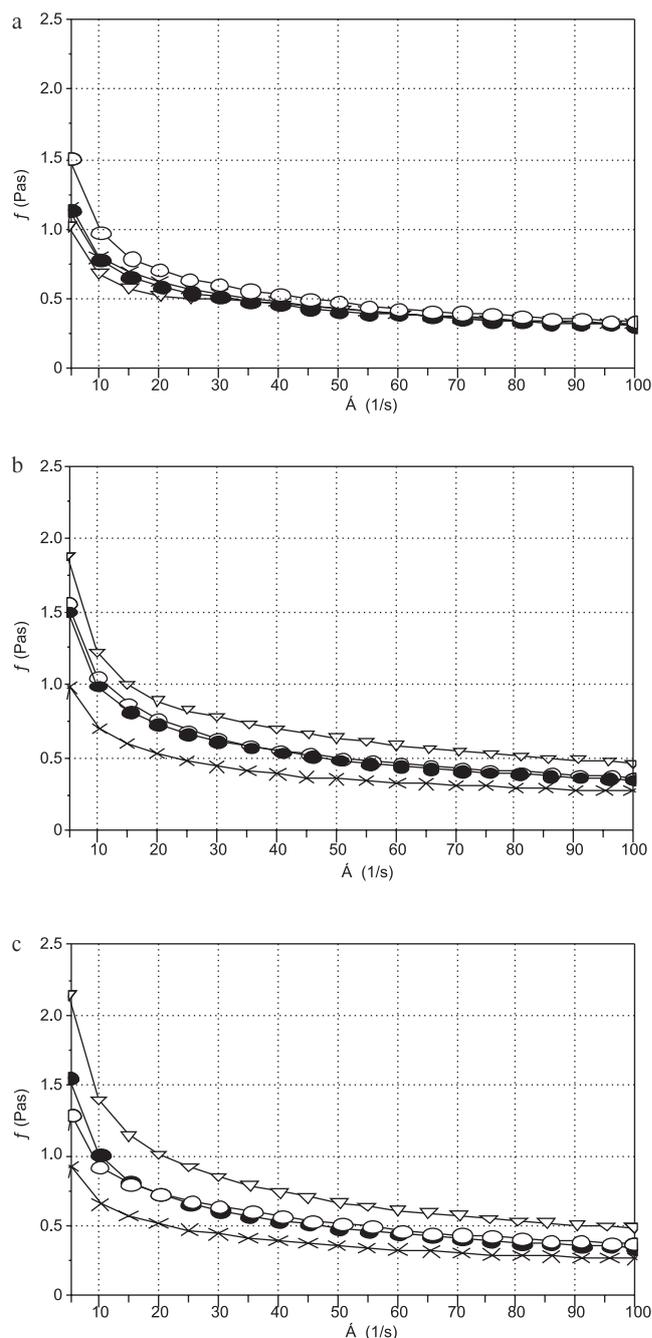


FIGURE 2. Viscosity flow curves of 20 g/L potato starch dispersions gelatinized in the presence of 20 g/L —●—, 40 g/L —○—, 60 g/L —▽— kaolin and without kaolin —×—, measured before (a) and after 24 h (b) and 48 h (c) storage.

$1.8 \text{ Pa}\cdot\text{s}^n$ after 48-h storage, whereas values of plastic viscosity η_c dropped from $0.16 \text{ Pa}\cdot\text{s}$ to $0.13 \text{ Pa}\cdot\text{s}$, respectively. The values of yield point τ_{0c} , at which the samples began to flow, were also subject to changes along with the time of storage. It means that with storage time proceeding the pastes without kaolin were observed to become less resistant to the action of shearing forces. Thus they were characterised by lower resistance to shearing forces as compared to the non-stored samples. This is linked with the retrogradation process proceeding in starch pastes during storage. After cooling down, the retrogradation process is observed in paste. The gel formed is subject to changes referred to as “ageing”. It shrinks and hardens,

and water precipitates, which indicates the phenomenon of syneresis [Bratskaya *et al.*, 2005; Rayment *et al.*, 2000]. During storage, a paste loses its stability and its viscosity diminishes. Similar reduction in the resistance of retrograded wheat starch to the action of shearing forces was also observed by other authors [Juszczak *et al.*, 2004].

All pastes containing kaolin were characterised by higher viscosity as compared to the pastes prepared only from starch. The flow curves of the first are above those of the latter (Figures 1 and 2). The increase in viscosity of the kaolin-containing pastes, as compared to those prepared from starch only, was caused by adsorption of starch chains on the surface of kaolin molecules and formation of additional hydrogen bonds between starch chains and kaolin molecules. The pastes containing 20 g/L and 40 g/L of kaolin and stored for 24 h and 48 h were characterised by a similar course of flow curves (Figures 1 and 2). The time of storage appeared not to evoke any significant changes in the course of their flow curves, whereas rheological parameters of the models applied displayed alike values, *i.e.* the coefficient of consistency K – from 2.95 Pa·sⁿ to 3.22 Pa·sⁿ, plastic viscosity η_c – from *ca.* 0.17 Pa·s to *ca.* 0.18 Pa·s, and yield point τ_{0c} – *ca.* 4 Pa. The addition of kaolin at a dose of 20 g/L and 40 g/L caused that during storage the pastes demonstrated stable structure, irrespective of storage time.

The greatest changes in rheological properties of the pastes were observed in the case of samples containing 60 g/L of kaolin. Those pastes were characterised by the highest viscosity out of all samples examined, and parameters of the rheological models applied were subjected to the greatest changes along with the time of storage. The coefficient of consistency K of the pastes containing the highest dose of kaolin and stored for 48 h was observed to increase by *ca.* 20% in respect of the samples before storage (Table 1), whereas their plastic viscosity η_c increased by *ca.* 50% and the value of yield point was almost twofold higher, respectively (Table 2). Also when compared to the pastes not containing kaolin the viscosity of pastes with kaolin addition at a dose of 60 g/L and stored for 24 h and 48 h was considerably higher, whereas values of their coefficient of consistency, plastic viscosity and yield point were 2-2.5-fold higher than those of the samples without kaolin. Values of those rheological parameters were observed to increase along with the time of storage. As a result of stronger molecular interactions in the starch pastes with a higher content of kaolin, gels obtained after their cooling were stronger and with higher viscosity. The content of kaolin exceeding three times the concentration of starch in the pastes was likely to evoke the formation of additional hydrogen bonds and further stiffening of pastes structure, thus inhibiting the process of retrogradation over the entire period of storage. The addition of kaolin could have a stabilizing effect on polymer chains, thus delaying their re-twisting during storage. It resulted in an increase of viscosity and rheological parameters linked with viscosity (K and η_c). Also the values boundary shearing stresses were observed to increase with elongated storage time of the samples. This points to a stiff structure of the pastes containing kaolin. A similar increase in viscosity and rheological parameters of the examined mixtures of various substances with kaolin was also observed in

other works [Golachowski *et al.*, 2005; Sjöberg *et al.*, 1999; Marco *et al.*, 2004].

CONCLUSIONS

Analyses carried out in the study indicated that starch pastes containing 20 g/L of starch and from 0 to 60 g/L of kaolin, stored for different periods of time, demonstrated characteristics of non-Newtonian, pseudoplastic, shear-thinned fluids, and that their rheological properties were determined by both kaolin addition and storage time. The pastes prepared with the addition of kaolin were characterised by higher viscosity, higher values of shearing stresses, coefficient of consistency K , plastic viscosity η_c and yield point τ_{0c} as compared to the pastes prepared only from starch. Values of those parameters were observed to increase along with the time of storage in the case of kaolin-containing samples and to decrease in the case of those prepared only from starch.

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WŁAŚCIWOŚCI REOLOGICZNE KLEIKÓW SPORZĄDZONYCH ZE SKROBI ZIEMNIACZANEJ Z DODATKIEM KAOLINU

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Badano właściwości reologiczne kleików o stężeniu 20 g/l skrobi z dodatkiem kaolinu w ilościach 20 g/l, 40 g/l i 60 g/l, przechowywanych przez różny okres czasu. Wyznaczono krzywe płynięcia w czasie 200 s, stosując prędkość ścinania 0-100 s⁻¹, w temperaturze 20°C. Do opisu krzywych płynięcia zastosowano model Ostwalda de Waele i Cassona. Stwierdzono, że kleiki skrobiowe z różnym dodatkiem kaolinu przechowywane przez różny okres czasu wykazywały cechy płynów nienewtonowskich, pseudoplastycznych, rozrzedzanych ścinaniem, a właściwości reologiczne tych kleików zależały od dodatku kaolinu oraz czasu przechowywania. Kleiki sporządzone z dodatkiem kaolinu charakteryzowały się wyższą lepkością, wyższymi wartościami naprężeń ścinających, współczynnika konsystencji K, lepkości plastycznej η_c oraz granicy płynięcia τ_{oc} w porównaniu do kleików z samej skrobi. Wartości tych parametrów zwiększały się wraz z czasem przechowywania prób z dodatkiem kaolinu, natomiast w przypadku kleików sporządzonych z samej skrobi ulegały zmniejszeniu.