Analysis of rheological properties of potato starch pastes as a potential binding liquid in the granulation process

Analiza właściwości reologicznych kleików skrobi ziemniaczanej jako potencjalnej cieczy wiążącej w procesie granulacji

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Abstrakt

W pracy przedstawiono ocenę właściwości reologicznych kleików komercyjnej skrobi ziemniaczanej, jako źródła stanowiącego ciecz wiążącą w procesie granulacji jedno i wieloskładnikowych materiałów sypkich poprzez zastosowanie modelu Carreau-Yasudy. Na podstawie uzyskanych wyników stwierdzono, że wysokie wartości lepkości kleików skrobiowych i znacząca sztywność ich struktury wewnętrznej nie są gwarancją odporności tej struktury na działanie sił zewnętrznych, mogą ponadto obniżać efektywność samego procesu granulacji.

Abstract

The paper presents an assessment of rheological properties of commercial potato starch pastes as a binding liquid source in the process of granulation of single and multi-component loose materials using by Carreau-Yasuda model Based on the obtained results, it was found that high viscosity values of starch pastes and significant stiffness of their internal structure are not a guarantee of resistance of this structure to external forces, and may also reduce the efficiency of the granulation process itself.

Słowa kluczowe: skrobia ziemniaczana, lepkość, granulacja, materiały sypkie

Keywords: potato starch, viscosity, granulation, loose materials

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1. Introduction

Starch is one of the most important plant polysaccharides. It is a biodegradable, non-toxic and fully biocompatible natural polymer. It is a reserve material of plants and is deposited in their tissues in the form of grains, the so-called granules, the shape and size of which depend on the botanical origin of the starch. Starch is a white solid substance, tasteless and odorless, which has found its application in many industries. In the food industry, starch has been used as a starting material for the production of hydrolysates (glucose, maltodextrin, starch syrups) and as a raw material for the production of modified starches. In baking, it is used as a bread ingredient that improves water retention and delays staleness of bread, and as an addition to pastry products. In the production of food concentrates, it is used as a thickener in powdered food (sauces, soups, puddings, jellies) and ketchups. In the textile industry, it is used for gluing yarn and starching. In the paper industry, it is needed for dyeing, satining, printing and finishing, as well as for gluing paper pulp. In the chemical industry, it has found application in the production of glues, dextrins, and even in the production of explosives. In the pharmaceutical industry, it is used for the production of baby powders, talcum powders and pills for medicines, as well as a functional additive to cosmetics. So many specialty applications of starch and its derivatives enable manufacturers to develop a range of products related to technical applications. Thanks to all these possible applications, starch as a functional material turned out to be irreplaceable in many industries. This also results in the search for new sources of its acquisition, so it should not be surprising that research on starch obtained from kiwifruit *(Actinidia deliciosa)* [1], banana *(Musa paradisiaca)* [2], common pea *(Pisum sativum)* [3], acorns *(Quercus ilex L.)* [4], or chestnuts *(Castanea sativa Mill.)* [5]. However, it is also unique because it is a hydrocolloid showing a large physicochemical diversity with an unchanged chemical structure. The starch molecule has a heterogeneous structure, composed of amorphous linear structures - amylose and branched crystalline structures - amylopectin - Fig. 1. It is the content of amylose and amylopectin in starch granules that determines its technological usefulness and physicochemical properties.

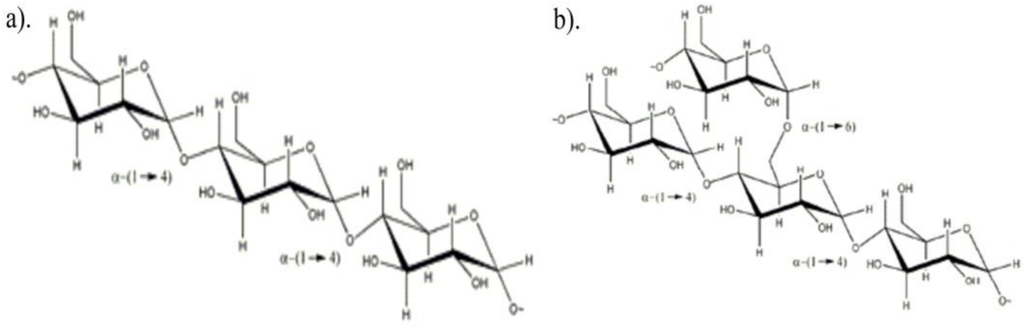

Fig. 1. Structure of molecules: a). amylose, b). amylopectin [6].

Starch, or rather a suspension of starch granules subjected to the heating process, creates the so-called paste, in which dissolved starch granules (amylose) form a continuous phase, and swollen remains of granules (amylopectin) act as fillers. It should be noted, however, that in the process of heating starch granules obtained from edible tubers (e.g. potato and tapioca starch), the primary structure of the granules is completely destroyed and a homogeneous suspension of macromolecules or their aggregates is obtained. Hence the pastes of these starches resemble opalescent solutions. It is the possibility of obtaining a homogeneous paste from potato starch that may predispose it to be used as a binding liquid in the granulation process. The granulation of powdered materials and the accompanying processes, such as mixing or grinding, depend to a large extent on the physical and rheological properties of the materials involved. Previous studies [7-10] have shown that the properties of the wetting liquid affect the nucleation and, consequently, the granulation effect, especially when it comes to the formation of agglomerates from materials that are difficult to combine, such as mixtures of biomass and mineral materials. It is the binding liquid that is responsible for producing a granular product with the desired properties. Despite the wide spectrum of research, there are no models that would take into account the impact of rheological parameters on granulation, describing both the properties related to the viscosity and elasticity of binding liquids.

Therefore, the aim of the presented work is to evaluate the rheological properties of pastes obtained from domestic, commercial potato starches in terms of their usefulness as binding liquids for the granulation process of loose materials..

2. Materials and Methods

The research material was commercial potato starch from various companies of the potato industry, operating on the domestic market and available in every grocery store. These starches were: starch Superior Standard from Trzemeszno and Grula brand starch also from Trzemeszno, Jermapol starch from Konopnica, Niechlów starch from Niechlów, and Melvit starch from Kruki.

In the tested commercial samples of potato starches, the content of amylose was determined using the spectrophotometric method with iodine according to Morrison and Laingelet [11]. Absorbance measurements were performed at a wavelength of λ=640nm using a Specord M42 spectrophotometer (Carl Zeiss, Germany).

Potato starch samples in the form of 5% aqueous suspensions were gelatinized at 95^0C for 90 minutes. After the gelatinization process was completed, the samples were cooled for 60 minutes. The gelatinized starch samples were then left at rest for a further 60 minutes at an ambient temperature of 25^0C to remove any air bubbles. After this time, the paste sample was placed in the measurement system of the rotational rheometer and left to rest for 30 minutes at a constant temperature of 25^0C to reach thermal and mechanical equilibrium. The rheological properties of the tested potato starches were determined using a Physica MCR 301 rotational rheometer by Anton Paar in a cone-plate measuring system with a cone diameter of

50 mm, an angle of inclination of 10 and a distance between the measuring elements, i.e. a cone and a plate of 0.048 mm. Rheological tests were carried out to measure the viscous properties of the tested samples of commercial potato starch in the range of shear rate from 0.001 to 100s-1, i.e. in the range of five logarithmic decades, taking 6 measurement points for each decade of shear rate.

The Carreau-Yasuda model [12-14] was used to describe the viscosity curves obtained as a result of rheometric measurements:

$$\eta(\dot{\gamma}) = [1 + (\lambda \cdot \dot{\gamma})^a]^{\frac{(n-1)}{a}} \cdot (\eta_0 - \eta_\infty) + \eta_\infty \qquad (1)$$

where the rheological parameters of this model are:

η_0 i η_∞ - the zero-shear viscosity and the infinity-shear viscosity, [Pa·s], λ - time constant, [s], n - time constant, [-], a - width of the transition region between Newtonian and power-law behavior, [-].

Determination of the rheological parameters of the Carreau-Yasuda model (especially the time constant λ) made it possible to determine the critical value of the shear rate γ_{cr} at which the transition from the behavior typical of Newtonian fluids to the behavior characteristic of non-Newtonian fluids occurs. The numerical value of this shear rate is given by the equation:

$$\gamma_{cr} = \frac{1}{\lambda} \qquad (2)$$

γ_{cr} – the critical shear rate denoting the one of shear-thinning behavior [s^{-1}]

At the same time, the knowledge of the viscosity η_0 (obtained as an independent variable, directly from rheometric measurements) and the time constant λ determined from the Carreau-Yasuda model allowed to determine the value of the shear stress τ_{cr} at which the Newtonian behavior of the fluid changes to the behavior typical for a non-Newtonian fluid:

$$\tau_{cr} = \frac{\eta_0}{\lambda} \qquad (3)$$

τ_{cr} – the critical shear stress at the transition between Newtonian and power-law regions [Pa].

Thus, thanks to the determined parameters of the Carreau-Yasuda model, two additional parameters were obtained to characterize the viscous properties of the starch pastes tested.

Mathematical analysis concerning the determination of rheological parameters of the Carreau-Yasuda model was carried out using non-linear regression methods from the Excel program. One of the tools of this program was used, namely the Solver add-on, used to solve the mathematical modeling task, i.e. to find such parameters of the mathematical model that the tested lubricants could be described in the best possible way. Using the numerical minimization procedures that the Solver tool uses, local minimization procedures were used. Therefore, for a multimodal objective function having many local minima, a solution was found that depended on the initial value of the objective function's independent variables. One of the initial values of the independent variables of the objective function was the experimentally determined value of zero viscosity η_0.

In order to assess the correctness of the description of the experimental data with the Carreau-Yasuda model equation, a statistical evaluation of the fit of the model curves to the experimental curves was carried out in relation to the value obtained directly from the rheometric measurements of the apparent viscosity η. This assessment was made by estimating the effectiveness of modeling R^2.

3. Results and Discussion

Table 1 presents the results of determining the amylose content, and thus amylopectin, in the tested samples of commercial potato starch. The data presented in Table 1 shows that commercial potato starches differ in terms of amylose and amylopectin content, and these differences can be significant - the difference between potato starch with the highest amylose content (Trzemeszno Superior Standard starch) and potato starch with the lowest amylose content (Melvit starch). This is probably due to from the starchiness of potato varieties used for the production of commercial potato starches.

Tab. 1. Content of amylose and amylopectin in the tested potato starches

Potato Starch	Amylose content [%]	Amylopectin content [%]
Trzemeszno Superior Standard	39.38	60.62
Niechlów	37.30	62.70
Jermapol	37.17	62.83
Trzemeszno brand Grula	35.95	64.05
Melvit	14.99	85.01

The graph in Fig. 2 shows the viscosity curves for all tested samples of commercial potato starch and Table 2 presents the values of rheological parameters obtained as a result of describing the viscosity curves with the Carreau-Yasuda model.

The analysis of the obtained experimental data presented in Fig. 2 allowed to conclude that for all the tested samples of potato starch, the apparent viscosity decreases with the increase of the shear rate. This indicates that the tested pastes of commercial potato starch should be treated as non-Newtonian media, shear thinned media. The shape of viscosity curves obtained from rheometric measurements, which shows zero viscosity η_0 at low shear rate values, justifies the choice of the Carreau-Yasuda model to evaluate the rheological properties of the starch pastes tested. The analysis of the data presented in Table 2 shows that:

- the highest value of viscosity η_0 at the zero shear rate is characteristic for Superior Standard potato starch from Trzemeszno, while the lowest value of zero viscosity is shown by Melvit potato starch,
- the width of the transition area between Newtonian and non-Newtonian behavior is the largest for potato starch from Trzemeszno, brand Grula, and the smallest for potato starch from Niechlów,
- the time constant λ, reflecting the susceptibility of the internal structure to

destruction by shearing, has the highest value for Superior Standard potato starch from Trzemeszno, and the lowest for Melvit potato starch from Kruki,

- Jermapol potato starch has the highest value of the characteristic flow index, whereas potato starch from Niechlów has the lowest value,

- the critical value of the shear rate at which the behavior of the pastes changes from Newtonian to non-Newtonian, i.e. when the apparent viscosity of the starch paste begins to decrease, is the highest for Melvit potato starch, and the lowest for Superior Standard potato starch from Trzemeszno,

- the values of the critical shear stress at which the starch gruel begins to show the characteristics of a non-Newtonian fluid are the highest for Superior Standard potato starch from Trzemeszno, the lowest for Melvit potato starch.

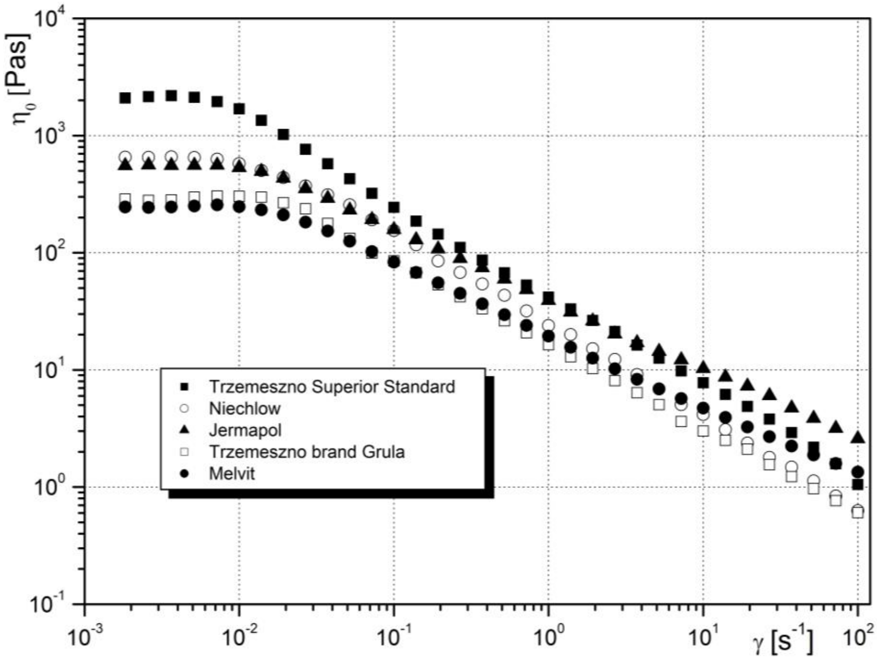

Fig. 2. Viscosity curves of the pastes of the tested potato starches.

Tab. 2. Rheological parameters of the Carreau-Yasuda model

Potato Starch	η_0 [Pa·s]	**a** [-]	λ [s]	**n** [-]	γ_{cr} [s^{-1}]	τ_{cr} [Pa]	R^2 [-]
Trzemeszno Superior Standard	2300.0	1.897	123.457	0.187	0.0081	18.630	0.999
Niechlów	675.0	1.249	99.010	0.178	0.0101	6.817	0.998
Jermapol	600.0	2.044	79.365	0.387	0.0126	7.560	0.998
Trzemeszno brand Grula	298.0	4.269	61.728	0.292	0.0162	4.828	0.998
Melvit	256.0	2.673	57.803	0.376	0.0173	4.429	0.997

For all the starch pastes tested, a very high matching efficiency was obtained, at the level of 0.997÷0.999. In order to better illustrate the nature of changes in the obtained rheological parameters of the Carreau-Yasuda model, some of them, i.e. zero viscosity η_0 and time constant λ as a function of amylose content in starch, are presented graphically in Figure 3. This graph clearly shows that with increasing amylose in potato starch, the value of zero viscosity increases η_0. At the same time, it is also accompanied by an increase in the time constant λ and the critical shear stress τ_{cr}.

The high value of the time constant for the potato starch paste Superior Standard from Trzemeszno means that this paste has a structure most susceptible to destruction by shearing. This may indicate the low mechanical stability of its structure, which is also not guaranteed by high values of the critical shear stress τ_{cr}, which here reflects the rigidity of this structure. Of all the tested potato starch pastes, it is Melvit starch, i.e. the starch with the lowest amylose content, as 14.99%, seems to be the one whose internal structure is resistant to damage caused by external force (low values of constant λ and structure stiffness in stress value τ_{cr}). The internal structure with very similar rheological properties has a paste made of starch from Trzemeszno, but of the Grula brand - its viscosity η_0 is higher by 42Pas, the time constant λ by less than 4s, and the stiffness of the internal structure by 0.4Pa.

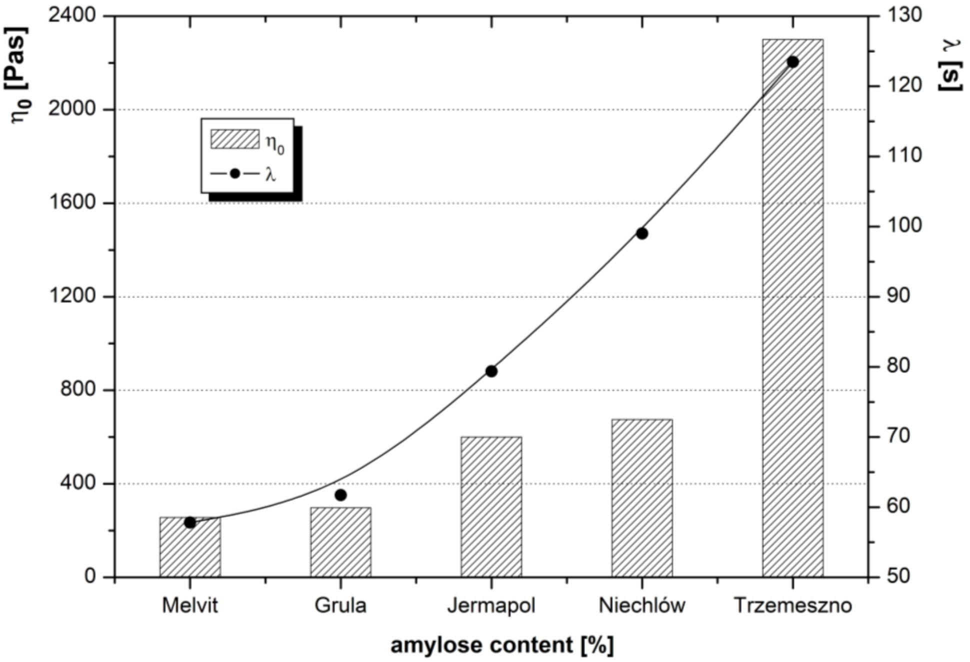

Fig. 3. Changes in some rheological parameters of the Carreau-Yasuda model.

What distinguishes Grula starch from Melvit starch is the width of the transition area between Newtonian and non-Newtonian behavior, the value of which is 1.596. This area, defined in the Carreau-Yasuda model by the parameter a, can be identified with the polydispersity of the PDI medium, which in turn may indicate that the polydispersity of potato starch Grula from Trzemeszno is greater than that of Melvit starch. Potato starches Jermapol and Niechlów have over 2 times higher zero viscosity η_0 and almost 2 times higher time constant λ with 1.5 times higher structure stiffness in the form of τ_{cr}. In addition to the susceptibility of the internal structure of the potato starch pastes to damage caused by shear forces present in the granulation process, it may also result in difficulties in uniform distribution of these pastes as binding liquids over the granulated material.

4. Conclusions

The assessment of rheological properties of pastes obtained from commercial potato starch as a material for the binding liquid in the granulation process allowed to conclude that:

- starch pastes are non-Newtonian fluids, shear thinning, the apparent viscosity of which decreases with increasing shear rate,
- high content of amylose in starch, which translates into high viscosity of the paste, does not guarantee the resistance of the structure of this paste to external forces,
- high stiffness values of the internal structure are not a guarantee of its mechanical stability,
- high values of both viscosity and stiffness of the paste may be an obstacle to the even distribution of the binding liquid over the granulated bulk material, which may consequently contribute to the low efficiency of this process.

However, commercial potato starch can be a valuable and relatively cheap source for granulating loose materials, and the characteristics of its pastes will be responsible for producing a granulated product with the desired properties.

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