Influence of electrochemically activated water on the rheological indicators of starch suspensions

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Abstract

Introduction. The purpose of the work is to determine the influence of electrochemically activated water (catholith and anolyte) on the rheological indicators of corn starch suspensions under different temperature regimes.

Materials and methods. The functional and technological properties of corn starch were investigated in terms of water-absorbing, moisture-retaining, fat-absorbing and fat-retaining ability. The influence of electrochemically activated water on these parameters were determined in comparison with tap water. Rheological characteristics of starch suspensions prepared on electrochemically activated water were determined at different temperatures on a Kinexus Pro+ rheometer.

Results and discussion. Electrochemically activated water causes change in the functional and technological properties of corn starch: the water absorption and moisture retention ability of starch prepared on catholyte decreased by 26% and 10%, and when anolyte is added, it increased by 18% and 36%, compared to the sample on tap water. Starch is able to absorb more amount of water in an acidic medium (anolyte) than in an alkaline one (catholite). Electrochemically activated water also has a significant effect on the rheological parameters of starch suspensions: when the shear rate changed in the range of 0.1–100 s^{-1}, the shear stress increased linearly. At the temperature of gelatinization shear stress was 0–10.6 Pa, 0–13.6 Pa and 0–23.8 Pa for control sample, sample on anolyte and catholyte, respectively. At a temperature of 25 ºC, the change was greater – 0–19.5 Pa, 0–28.4 Pa, and 0–30.8 Pa, respectively. At zero shear rate, the initial shear viscosity of suspensions at 25 ºC and at 68 ºC on the catholyte and anolyte was higher than the control sample. When the shear stress changed at 25 ºC, the values of the shear viscosity increased, having the highest values at the final stage on the catholyte and anolyte – 1.7 and 13 Pa·s compared to the control sample – 0.6 Pa·s. At 68 ºC, the trend of change of the studied indicator is similar, but the initial values are higher than the corresponding values at 25 ºC, and the final values are lower. The angular velocity index increased linearly with a change in shear stress.

Conclusion. The conducted research show that electrochemically activated water has a significant impact on the functional and technological properties and rheological characteristics of semi-finished products, in particular corn starch suspensions, which in turn will have an impact on some indicators and structure of food products with this raw material.

Introduction

Studying the regularities of the physico-chemical and biochemical processes in the human body, first of all, attention is paid to water and food products as factors which cause the course of these processes. Water is a sensor of physical and chemical factors of influence in the environment and human body. These factors cause changes in physical and chemical properties of water and its biological activity (Ivanov et. al, 2021). The statistical conclusion of the WHO indicates that 70% of diseases in the world are associated with poor-quality drinking water (WHO, 2022).

The biological activity of water caused by increased electronic or proton activity is related to the fact that water is a quantum-mechanical system consisting of free and associated water phases (Cejka et. al., 2017; Tamaki et. al., 2016).

The association of charged dipole water molecules in clusters is carried out due to hydrogen bonds between different electric poles of neighboring water molecules. After the destruction of associates in the aqueous medium, when heated, H_2O monomolecules appear in large quantities (Iino et. al., 2009).

Saturated with molecular hydrogen water has a positive effect on the human body, but molecular hydrogen has a low solubility in water. Due to the high diffusivity of hydrogen, its concentration in water is unstable and changes rapidly, approaching zero under normal conditions. In this regard, hydrogen water involves either immediate use or special storage conditions (Kurokawa et. al., 2011).

It was established that under the influence of non-reagent factors such as electromagnetic field, light radiation, heating, cooling or freezing with subsequent thawing, a change in the kinetics of chemical and biochemical reactions in water occurs. Such changes influence on its solubility, as well as biological activity. This takes place under the condition of constancy of the elemental chemical composition of the factors associated with the consumption of external energy (Mghaiouini et. al., 2020).

One of the most effective methods of water activation is electrochemical activation. The essence of the process is the electrophysical and electrochemical action on the aqueous solution of ions and molecules in the space charge zone in the immediate vicinity of the surface of the electrodes under conditions of non-equilibrium transfer of charges through the "electrode-electrolyte" interface by electrons (Ignatov et. al., 2015). At the same time, water is saturated with oxygen, changes own energy state, accelerates the removal of metabolic waste and promotes the most complete assimilation of nutrients by the human body from the substrate prepared with its use (Ignatov et. al., 2019).

Products of the starch-molasses industry are used in many branches of the food industry. The most common is the use of corn starch as an emulsifier and thickener (Silva et al., 2021).

Native corn starch has low thermal stability, high tendency to retrograde and low resistance to shear force. To solve this problem, it needs to be modified to improve its application in food industry. Hydrothermal modification is one of the physical modifications by heating the starch above the gelatinization temperature with a limited water content (Marta et al., 2022).

The task of studying the possibilities of drinking water acquiring signs of nutritional (biological) value by optimizing the content of macro- and microelements with biogenic properties in water and the influence of this water on the structure and characteristics of semi-finished and ready products is relevant. These tasks can be solved by developing new and improving existing methods of activating water used in the food industry and ways of using it in the manufacturing of food products.

Therefore, the aim of research is to determine the influence of electrochemically activated water (catholith and anolyte) on the rheological indicators of corn starch suspensions under different temperature regimes.

Materials and methods

Materials

Electrochemically activated water obtained by the electrochemical method was used for the research. To obtain electrochemically activated water, tap water was used (supplier – JSC "Kyivvodokanal"), which was characterized by redox potential (RP) = +224, pH=6. For activation, tap water is passed through the diaphragm electrolyzer. Two experimental samples of activated water were obtained with different set parameters of PR: catholyte (RP = -542±20, pH = 10) and anolyte (RP = +767±15, pH = 3).

Corn starch suspensions were prepared in the ratio of corn starch:water – 1:10 using catholyte and anolyte at a temperature of t = 23±2 ºC (the temperature at which starch modification begins), the suspensions were kept for 2 hours to ensure starch hydration. The control was a suspension sample prepared with tap water.

Methods

Water-absorbing ability of starch

Test samples weighing 0.5 g were placed in a beaker and dispersed in 50 ml of water. Samples were placed in pre-weighed centrifuge tubes and left for 30 minutes at room temperature. After that, the suspension was centrifuged for 30 min at 3500 rpm. The upper layer with water was removed and dried in a thermostat (drying cabinet) for 25 minutes at a temperature of 50 ºC to remove the remaining excess moisture. Then it was re-weighed.

Water-absorbing ability (WAA) was expressed in ml of absorbed moisture in 1 g of dry sample or %, which was determined by the formula:

$$WAA = (W_2 - W_1) \cdot 2$$

where W_1 is the mass of the test tube with a dry weight of the test sample;

W_2 is mass of the sample with tube after centrifugation (Silva et al., 2016).

Moisture-retaining ability of starch

Test samples weighing 0.5 g were placed in a heat-resistant beaker and dispersed in 50 ml of water.Samples were left for 30 minutes at room temperature. Next, the mixture was subjected to heat treatment in a water bath for 30 minutes (with constant stirring) to a temperature of 95±2 ºC in the center. Then they were cooled to a temperature of 10±2 ºC, placed in pre-weighed centrifuge tubes and centrifuged for 30 min at 3500 rpm. The upper layer with water was removed and dried in a thermostat (drying cabinet) for 25 minutes at a temperature of 50 ºC to remove the remaining excess moisture. Then it was re-weighed.

Moisture retaining ability (MRA) was expressed in ml of retained moisture in 1 g of dry sample or %, which was determined by the formula:

$$MRA = (W_2 - W_1) \cdot 2$$

where W_1 is the mass of the test tube with a dry weight of the test sample;

W_2 is the mass of the sample with tube after centrifugation (Silva et al., 2016).

Fat-absorbing ability of starch

Test samples weighing 0.5 g were placed in a beaker and dispersed in 15 ml of refined sunflower oil for 60 seconds. Then they were placed in weighed centrifuge tubes and kept at room temperature for 10 minutes, after which they were centrifuged for 30 minutes at 3500 rpm. The upper layer of the separated oil was removed, and the test tubes were left at an angle of 45º for 10 min to drain the remaining oil and weighed.

Fat-absorbing ability (FAA) was expressed in ml of absorbed oil in 1 g of dry sample or %, which was determined by the formula:

$FAA = (W_2 – W_1)·2$

where W_1 is the mass of the test tube with a dry weight of the test sample;

W_2 is mass of the sample with tube after centrifugation (Silva et al., 2016).

Fat- retaining ability of starch

Test samples weighing 0.5 g were placed in a heat-resistant beaker and dispersed in 15 ml of refined sunflower oil for 60 seconds. Then the mixture was kept at room temperature for 10 minutes. Then it was subjected to heat treatment in a water bath for 30 minutes (with constant stirring) to a temperature of 95±2 ºC in the center, followed by cooling to a temperature of 10±2 ºC. After that, it was centrifuged for 30 minutes at 3500 rpm. The upper layer of the separated oil was removed, and the test tubes were left at an angle of 45º for 10 min to drain the remaining oil. Afret that tubes with sample were weighed.

Fat-retaining ability (FRA) was expressed in ml of retained oil in 1 g of dry sample or %, which was determined by the formula:

$FRA = (W_2 – W_1) ·2$

where W_1 is the mass of the test tube with a dry weight of the test sample;

W_2 is mass of the sample with tube after centrifugation (Silva et al., 2016).

Rheological characteristics of starch suspensions

For conducting rheological research, suspensions were analyzed at temperatures of 25 and 68 ºC. Changes in the structure and rheological characteristics of corn starch were investigated after its modification using tap water and activated water. This study not only shows the ability of starch to swell and gelatinize, but also the change in the rheological characteristics of starch suspensions, which will make it possible to expand the use of activated water for the process of starch modification. Heat treatment was applied at 68 ºC, since this value is the average value of the temperature range of gelatinization of corn starch. In the temperature range of 25 – 68 ºC, starch gradually changed from one state to another (Malumba et al., 2010).

Determination of rheological characteristics was carried out on a Kinexus Pro+ rheometer. Using the Starch Paddle Plastic 2 Blade geometry, which is a coaxial cylinder with a paddle stirrer (PC34 SL0007 SS) mounted on a vertical shaft. The prepared suspension was placed in a cylinder at a height of 70 mm, the stirrer was lowered and brought to a temperature of 25 ºC. Viscosity and flow curves were determined by changing the shear rate with its gradual increase (0.1–100 s^{-1}) and shear stress (0–200 Pa), with 10 measurement points per decade. Each step was maintained until a steady state was reached in the minimum time. Similarly, the experiment was conducted after heating the suspension to 68 ºC (Alvarez et al., 2015).

Statistical analysis

All experiments were carried out in triplicate. The results are given as mean±standard deviation (SD). Differences were considered to be significant at validity of α=0.95. Statistical analysis was performed using XLstat (2020 version) software.

Results and discussion

Before using raw materials in food technologies, it is necessary to know their characteristics, because they can affect the structure and properties of products containing them. The rheological characteristics of starch suspensions are largely influenced by the functional features of the raw materials. Studies of water-absorbing (WAA), moisture-retaining (MRA), fat-absorbing (FAA) and fat-retaining (FRA) ability showed (Table 1) that corn starch has high water-absorbing ability - it is able to retain water 6.18 times more than its own weight, in particular due to small particle sizes (from 20 to 400 μm). This indicates that when using it in the recipes of food products, it is necessary to increase the amount of water. However, the moisture- retaining ability is low – it can hold water 0.58 times more than its own weight, which indicates that this component will not contribute to the product's long-term preservation of a wet state. The ability of starch to absorb and retain fat is 1.5 and 1.3 times more compared to its own weight, respectively.

Table 1

Functional and technological properties of corn starch

Indicator	Value, %
Water-absorbing ability	618±5
Moisture-retaining ability	58±1
Fat-absorbing ability	152±3
Fat-retaining ability	136±3

It is important not only to analyze the functional and technological properties of starch, but also the influence of electrochemically activated water on the studied parameters (Table 2).

Table 2

Functional and technological properties of corn starch when using electrochemically activated water

Indicator	Value, %
Water-absorbing ability (catholite)	592±5
Moisture-retaining ability (catholite)	48±1
Water-absorbing ability (anolyte)	636±5
Moisture-retaining ability (anolyte)	94±1

When adding catholyte to dry starch water-absorbing ability and moisture-retaining ability of starch decreased by 26% and 10%, and when anolyte is added it increased by 18% and 36%. This is due to various properties of water, in particular, pH. Starch is more able to absorb water in an acidic medium (anolyte) than in an alkaline one (catholite). In addition, the salts present in the catholyte prevent its absorption by starch granules (Han et. al., 2009).

Due to the peculiarities of the chemical structure and the ability to swell and gelatinize when heated in the presence of water, starch plays a decisive role in the formation of the structure and consumer properties of many products. Studies of the dependence of the change in shear stress (σ) on the shear rate (γ) of corn starch suspensions (Figure 1) showed a linear increase in the indicator.

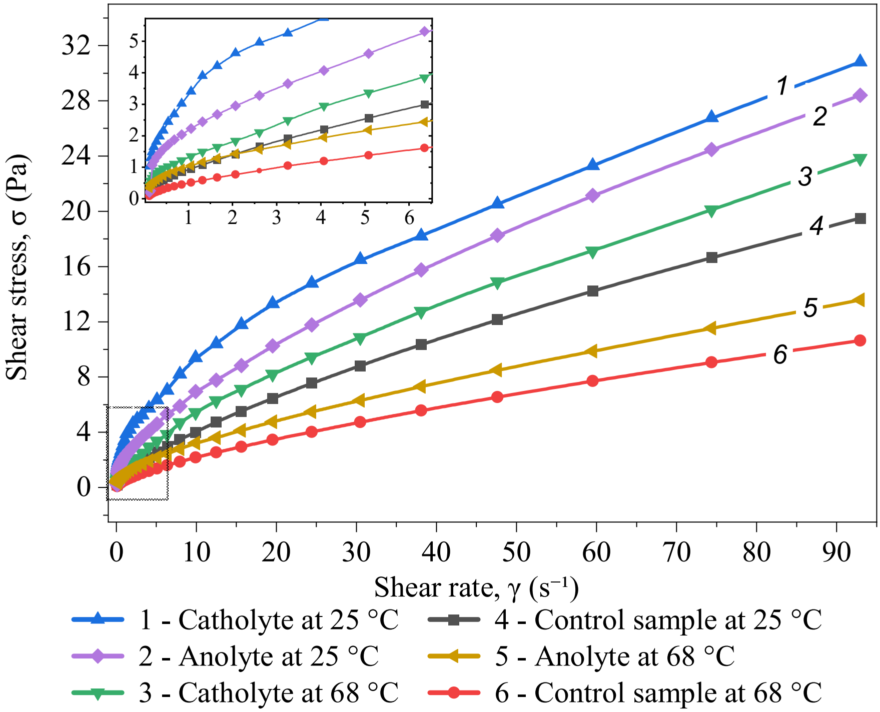

Figure 1. The dependence of the change in shear stress on the shear rate

As the shear rate increased in the entire range, the trajectory of change in shear stress of samples was similar. The samples had a lower shear stress at the gelatinization temperature: control sample, suspension on the anolyte and catholyte – 0–11 Pa, 0–14 Pa, and 0–24 Pa, respectively. At a temperature of 25 ºC the change was greater – 0–19 Pa, 0–28 Pa and 0–31 Pa, respectively. Analysis of the dependence of shear viscosity (η) on shear rate (γ) (Figure 2) showed that at zero shear rate, the initial shear viscosity of suspensions at 25 ºC and at 68 ºC on catholyte and anolyte was higher than for the control sample. At 25 ºC it was 8.6 Pa, 5.9 Pa and 1.6 Pa, respectively. At 68 ºC it was 3.8 Pa, 2.9 Pa and 0.8 Pa, respectively. This is explained by the fact that the increase in viscosity at zero shear rate partially corresponds to a higher degree of flocculation, since the formation of non-permanent loose aggregates from starch particles is more active when activated water is used (Fall et. al., 2017).

As the shear rate increases and the hydrodynamic forces become large enough to deform and break the flocs, a rapid decrease in viscosity occurs (McClements, 2005).

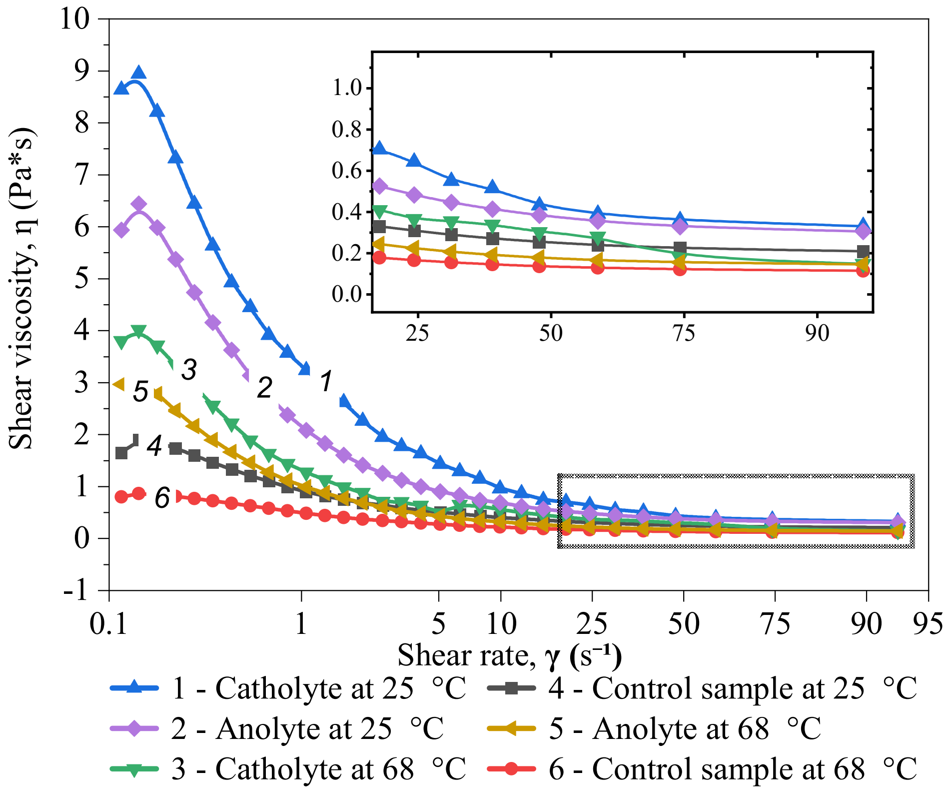

Figure 2. The dependence of the change in shear viscosity on the shear rate

When the shear rate increased to 50 s^{-1}, the shear viscosity of the samples gradually decreased: for the control sample it was slower, and for the samples of suspensions on activated water it was more rapid.

However, when the shear rate was more than 50 s^{-1}, all samples acquired almost the same shear viscosity. The nature of the change was hyperbolic and typical for all samples. However, the degree of change of the investigated parameter was not the same: for the sample on the catholyte at 25 ºC the indicator decreased by 8.3 Pa·s, at 68 ºC – by 3.7 Pa·s; for sample on anolyte – by 5.6 and 2.8 Pa·s; for sample on tap water – by 1.4 and 0.7 Pa·s.

Studies of the dependence of the change in angular velocity (θ′) on the shear stress (σ) for corn starch suspensions (Figure 3) showed an almost linear increase of the indicator.

The angular velocity when analyzing samples of suspensions prepared on activated water at a temperature of 25 ºC was lower over the entire range of shear rate change than at a temperature of 68 ºC. The same trend was observed for the control samples, but the values for them were quantitatively higher.

The values for samples at a temperature of 25 ºC changed to a lesser extent: on catholyte – 0–0.2 rad/s, on anolyte – 0–0.3 rad/s, on tap water – 0–0.7 rad/s. At a temperature of 68 ºC, the increase of the studied indicator was more rapid, but the dependence was clearly observed: on catholyte, anolyte and tap water – 0–0.6 rad/s, 0–0.8 rad/s and 0–1.3 rad/s in accordance.

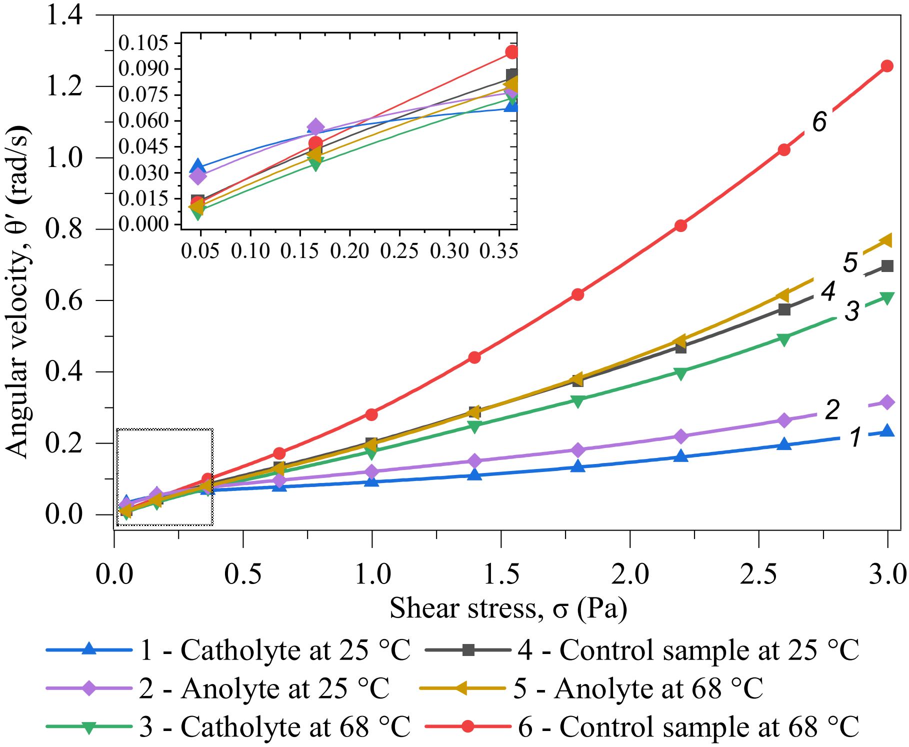

Figure 3. Dependence of the change in angular velocity on the shear stress

The flow curves of starch suspensions are shown in Figure 4. The analysis of the curves allows to make a conclusion about the strength of structural bonds in starch systems.

The initial shear viscosity (η) of suspensions at 25 ºC on the catholyte and anolyte at zero shear stress (σ) was lower than of the control sample, which is explained by the fact that the initial viscosity is the result of hydration of amorphous starch. Hydrophilic groups cannot migrate to the interfacial area in the continuous phase (Taherian et al., 2008).

However, as the shear stress increased, its values change along the trajectory of the parabola, having the highest values at the final stage (1.7 and 1.3 Pa·s compared to the control sample – 0.6 Pa·s). This is facilitated by molecular rearrangements that accelerated the mobility between starch molecules when interacting with activated water and led to greater flexibility of the starch chain, which increased their ability to bind water molecules (Donmez et al., 2021).

At a temperature 68 ºC the trend of change of the studied indicator is similar, but the initial values are higher than the corresponding values at 25 ºC: 0.5 Pa·s and 0.4 Pa·s for control sample, 0.8 Pa·s and 0.2 Pa·s for sample on catholyte, 0.6 Pa·s and 0.2 Pa·s for sample on anolyte. On the contrary, the final values were lower: 0.3 Pa·s and 0.5 Pa·s for control sample, 0.6 Pa·s and 1.7 Pa·s for sample on catholyte, 0.5 Pa·s and 1.3 Pa·s for sample on anolyte. This is explained by the fact that high temperature and external force contributed to the entry of water molecules into starch granules (Shi et al., 2021).

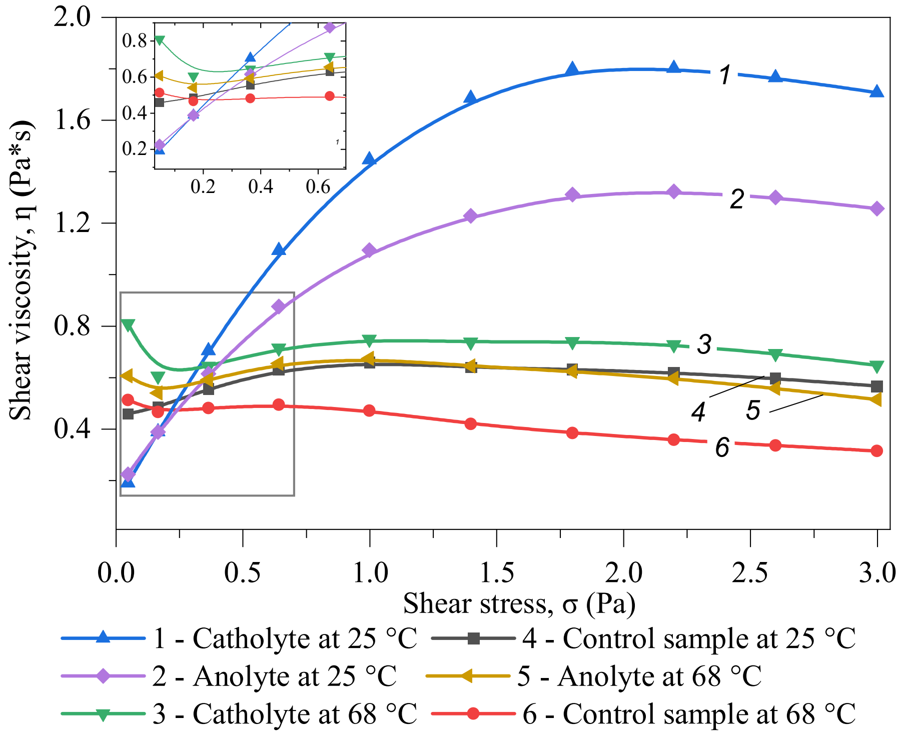

Figure 4. Dependence of shear viscosity on shear stress

Thus, on the basis of the conducted research, it was established that the electrochemical activation of water modifies its chemical composition and properties, contributes to changing the functional and technological properties of raw materials with its content, in particular corn starch. Electrochemical activation of water also has a significant effect on the rheological parameters of starch suspensions. This, in turn, will be reflected in the structural and mechanical properties of food products with the content of this semi-finished product in its composition and will form the structure of the product.

Conclusion

1. The functional and technological properties of food products are significantly influenced by the properties of raw materials. Corn starch has a high water absorption ability – it can hold water 6.18 times more than its own weight. The moisture-retaining ability is low – it can hold water 0.58 times more than its own weight. The ability to absorb and retain fat with starch is 1.5 and 1.3 times more than its own weight, respectively.
2. When adding catholyte water-absorbing ability and moisture-retaining ability of starch decreased by 26% and 10%, and when anolyte is added, it increased by 18% and 36%.

Starch is able to absorb more water in an acidic medium (anolyte) than in an alkaline one (catholite).

3. When the shear rate changes, the shear stress of starch suspensions also changes, namely, in the shear rate range of 0.1–100 s^{-1}, the shear stress increased linearly. At the temperature of gelatinization shear stress was 0–10.6 Pa, 0–13.6 Pa and 0–23.8 Pa for control sample, sample on the anolyte and catholyte, respectively. At a temperature of 25 ºC, the change was greater – 0–19.5 Pa, 0–28.4 Pa, and 0–30.8 Pa, respectively.
4. At zero shear rate, the initial shear viscosity of suspensions at 25 ºC and at 68 ºC on the catholyte and anolyte was higher than of the control sample. When the shear rate increased above 50 s^{-1}, all samples acquired almost the same shear viscosity. The degree of change of the studied parameter was not the same: for the sample on the catholyte at 25 ºC – by 8.3 Pa·s, at 68 ºC – by 3.7 Pa·s; on anolyte – by 5.6 and 2.8 Pa·s; on tap water – by 1.4 and 0.7 Pa·s.
5. When the shear stress changed at 25 ºC, the shear viscosity values increased, having the highest values at the final stage on the catholyte and anolyte – 1.7 and 13 Pa·s compared to the control sample – 0.6 Pa·s. At 68 ºC, the trend of change of the studied indicator was similar, but the initial values were higher than the corresponding values at 25 ºC, and the final values were lower.
6. The angular velocity indicator increased linearly with a change in shear stress. For samples at a temperature of 25 ºC, changes were in the range of 0–0.2 rad/s on catholyte, 0–0.3 rad/s on anolyte, 0–0.7 rad/s on tap water. At a temperature of 68 ºC: on catholyte, anolyte and tap water – 0–0.6 rad/s, 0–0.8 rad/s and 0–1.3 rad/s, respectively.
7. It was established that the electrochemical activation of water modifies its chemical composition and properties, contributes to changing the functional and technological properties of raw materials with its content, in particular corn starch. Electrochemical activation of water also has a significant effect on the rheological parameters of starch suspensions. This, in turn, will be reflected in the structural and mechanical properties of food products with the content of this semi-finished product in its composition and will form the structure of the product.

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