

Viscosity characteristics compositions based on PAA, PVS and NA-CMS

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Abstract. The influence of the composition and method of preparation of gelatinized starch compositions on their relative viscosity is studied. The activation energy of the viscous flow of gelatinized starch and developed formulations was determined. The change in the viscosity of starch and developed polymer dressing compositions from time to time is studied.

Keywords: viscosity, activation energy, dressing, starch, PVS, PAA, composition, glue, sericin, concentration

1 Introduction

Currently, in the world, in order to create effective technologies in the textile industry, including at the stage of dressing cotton yarn, special attention is paid to research and development of technology that provides for the most complete and rational use of each country's own raw materials. At the same time, more attention is paid to the development of methods based on the use of cheap, affordable water-soluble polymers.

For dressing compositions with a constant starch content (4,0; 4,5; 5,0; 5,5%) and variables – PVS (0-0.5%), HYPAN (0-0.3%) measured the main target parameters: the relative viscosity of the composition and the finished dressing, its adhesion to cotton yarn, breaking load and breaking elongation of the coated thread.

Preliminary experiments have shown that at a concentration of PVS over 0.3%, even with a low starch content (5.0%) in the adhesive composition, the formation of viscous adhesives sufficient for the dressing of cotton yarn occurs. In this regard, the studies adopted an optimal concentration of PVS equal to 0.3%. In order to ensure the elasticity and flexibility of the dressing film formed on the surface of the yarn, as well as its deeper penetration into the yarn, in addition to starch and PVS, hydrolyzed polyacrylonitrile (HYPAN) in an amount of 0.1-0.2% was introduced into the composition of the dressing composition. The starch content varied in the range from 4 to 6%, which is characteristic of compositions for dressing cotton yarn with a linear density of 29.4 text [1-3].

2 Result and discussion

A series of starch hydrogels were prepared with a constant starch content (4.5%, 5.0% and 5.5%) and variable – PVS and HYPAN. The step in changing the concentration in both

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polymers was no more than 0.1%, which ensured the reliability of the study of the entire concentration range.

In order to identify the differences between existing and developed dressing compositions, we compared the relative viscosity of starch gelatinized compositions with different component composition and method of management of PVS, sericin and PAA.

The component composition of the dressing compositions varied in such a way that it was possible to distinguish the effect of the recommended components both on each individual component and on their various combinations and ratios [4].

PVS, sericin and PAA were found in freshly prepared starch gels cooled to 70 ° C (1st method) or to 30 ° C (2nd method).

The choice of starch concentration was dictated by two circumstances. Firstly, it was desirable to minimize the effect of swelling of starch grains on viscosity, which implied the use of the lowest possible starch content in the hydrogel. Secondly, it was necessary that the differences in the viscosity of the studied gels remain significant. The specified conditions are satisfied by the starch concentration in gels equal to 4%. The content of PVS, sericin and PAA in all cases corresponded to the optimal technological aspect and amounted to 0.2 and 0.5% of the starch mass, respectively.

The results of measuring the relative viscosity of gelatinized starch compositions are presented in Table.1. The presence of PVS, sericin and PAA in these compositions, the temperature at which the viscosity was measured, and the method of administration of the above components are reflected in the corresponding indexes in the tables.

The experimental data obtained turned out to be very informative. Thus, the introduction of PVS, PAA and sericin into gels formed only by starch causes a decrease in their viscosity by 1.5 -2.5 times. At the same time, the viscosity at 30 ° C does not depend on whether the additive modifiers were introduced into heated formulations (in which chemical splitting of starch is possible) or cooled (in which splitting does not occur). Consequently, in this case, the drop in viscosity is caused by a single factor - the destruction of the starch paste structure under the action of PVS, PAA and sericin.

Table 1. Influence of the composition and method of preparation of gelatinized starch compositions on their relative viscosity.

Composition	The composition was introduced into the gelatinized composition at 70 °C (1-method)		The composition was introduced into the gelatinized composition at 30 °C (2- method)	
	$\eta_{70kp} / \eta_{70kom}$	$\eta_{30kp-1} / \eta_{30kom-1}$	$\eta_{30kp-2} / \eta_{30kom-2}$	$\eta_{30kp-1} / \eta_{30kp-2}$
Starch (1%)	7.6 / 4.6 \approx 1.6	15.4/5.3 \approx 2.9	15.5/5.0 \approx 3.1	$\eta_{30kom-1} / \eta_{30kom-2}$ 0.99
Starch (1%) NaOH (0.025%)	7.2/2.5 \approx 2.9	12.5/3.4 \approx 3.7	15.0/7.3 \approx 2.0	0.83
Starch (1%) PVS (0.4%) NaOH (0.025%)	3.7/2.7 \approx 1.2	7.2/3.5 \approx 2.0	7.4/4.1 \approx 1.8	0.97
Starch (1%) PVS(0.4%) PAA(0.5%) NaOH (0.025%)	5.2/1.5 \approx 3.5	7.0 / 1.9 \approx 3.7	8.5 / 3.1 \approx 2.7	0.82
Starch (1%) PVS (0.4%) PAA(0.5%) Sericin(0.2%) NaOH (0.025%)	4.1/1.2 \approx 3.4	5.0 / 1.3 \approx 3.8	6.4/ 3.8 \approx 1.7	0.78

In the case of dressing formulations containing starch and sodium hydroxide, unlike those just discussed, the relative viscosity at 30 ° C strongly depends on whether PVA was added to hot paste or cooled. The lower viscosity of the paste prepared by the "hot" method, compared to what was prepared under normal working conditions, means that the PVS intensify the process of alkaline hydrolysis of starch, leading to a decrease in its molecular weight and, accordingly, viscosity.

In cases where starch, PVS, PAA, sericin and NaOH are included in the dressing, low values of p , generally known for modified starches, are characteristic. In [1], this fact is explained by the breakdown of starch associates into individual macromolecules as a result of dissociation of carboxyl groups formed during modification, which causes electrostatic repulsion of starch macromolecules. On the other hand, for theoretical reasons, the connection between macromolecules in starch gels is carried out not only due to intermolecular hydrogen bonds, but also due to the interaction of hydrophobic sites, then the presence of an electrolyte in the solvent, regardless of what the modifier is, should be accompanied by a weakening of interactions of this type. The reason for the decrease in the viscosity of starch hydrogels during its modification is the degradation of starch molecules due to the weakening of glucoside bonds to hydrolytic cleavage.

The viscosity of the gels under consideration at 30 ° C is almost the same when PVS is introduced into them by the first and second methods. So, in this case, as well as in this variant of starch dressing, the introduction of only PVS does not enhance the destruction of starch in the gel, but destroys the structure of the latter.

It should be noted that when PVS and PAA modifiers and alkali are present in the starch composition, the additional inclusion of sericin in it causes a significant decrease in viscosity among all the dressing options considered (Table 1). And this significantly depends on the method of introducing modifiers into the composition.

In turn, sericin in the used concentration enhances the chemical effect of the splitting reagents and at the same time contributes to the destruction of the starch hydrogel structure.

In connection with the above, it seemed advisable to separately consider the effect of sericin on the chemical processes in starch gels and on their structure with a constant content of other PVS and PAA modifiers.

Despite the low relative viscosity and degree of polymerization of starch, dextrinized paste (as well as ordinary starch) is highly structured in comparison with the developed one. The established phenomenon of high structuring of starch hydrogels is well known from the literature [2,3]. As is known, the structure of starch paste consists of supramolecular formations (globules, colloidal particles, conglomerates) in which starch macromolecules are involved in intra- and intermolecular hydrogen bonds. When the gel is passed through the capillaries of the viscometer, these structural units are moved in a solvent medium without their destruction, whereas at high shear rates achieved in rheological measurements, destruction also affects individual globules.

The absence of a stable structure in the developed composite hydrogels indicates that sericin is destroyed by colloidal starch particles, penetrating into them and breaking hydrogen bonds between polymer chains. In this case, most likely, a spatial fluctuation grid is created, which is easily destroyed under the influence of shear.

The tendency of the transition of polymer molecules from one equilibrium position to another, which is associated with overcoming the forces of intermolecular interaction, is explained by a change in the free activation energy of the viscous flow AGM3K. It is calculated based on the temperature dependence of the viscosity measured during the flow during deformation, in accordance with the activation theory of Frenkel-Eyring. The results of such a calculation for three comparable systems at a shear rate close to that realized in practice in the dressing are reflected in the dependencies in Fig. 1.

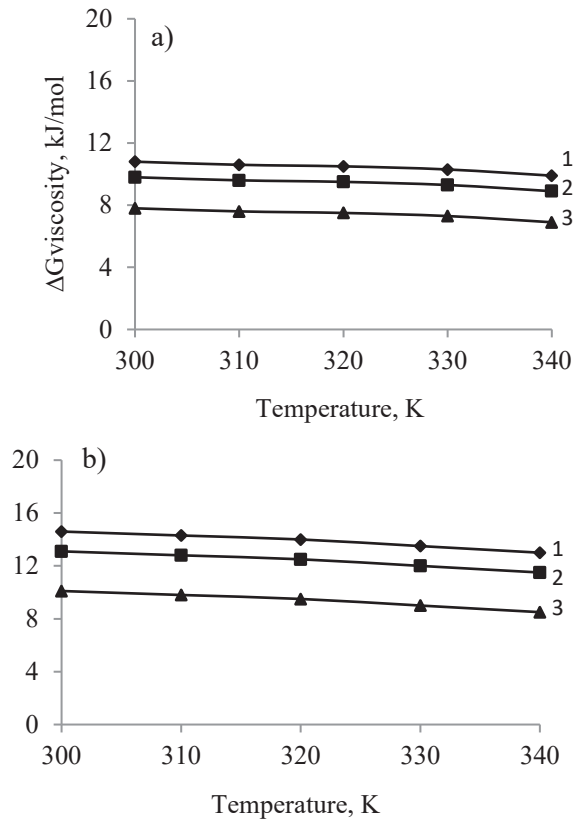


Fig. 1. Dependence of the change in the activation energy of the viscous flow of gelatinized starch compositions.

The composition of the dressing: 1 - starch, 2 - starch dextrinized, 3- composite based on PVS, PAA and sericin. Concentration of components: starch — (a) - 4%, (b) - 5%, sodium hydroxide — 0.1%, PVS-0.4%, PAA-0.5% and sericin-0.2%

From the data obtained (Fig. 1) it follows that the activation energy of the viscous flow of polymer dressing compositions is 15-20% lower than conventional starch. And this proves in favor of the assumption about the fluctuation nature of the structure of starch hydrogels containing PVA, PAA and sericin modifiers. At the same time, dextrinization does not have such a significant effect. For example, for 5% starch compositions, the decrease in the activation energy during dextrinization is only 7%.

The high solubility and weak structuring of starch in dressing compositions containing modifiers should probably lead to an increase in the stability of gels and a decrease in such an undesirable effect for the technology as starch retrogradation. As we know, the phenomenon of retrogradation is the cause of the "aging" of gelatinized formulations and is expressed in an increase in the viscosity (hardening) of gels and in their gradual delamination during storage of cooled dressing. This process is irreversible, and subsequent heating and boiling do not restore the properties of starch paste. Retrogradation is based on the replacement of hydrogen bonds between hydroxyl groups of starch mediated by water, by direct ones, that is, the displacement of water molecules from the supramolecular structure of the polymer.

To assess the effect of sericin on the stability of the finished dressing, the relative viscosity of 4% and 5% starch and dressing polymer compositions was measured during their storage for 48-72 hours, the results of which are shown in Fig. 2.

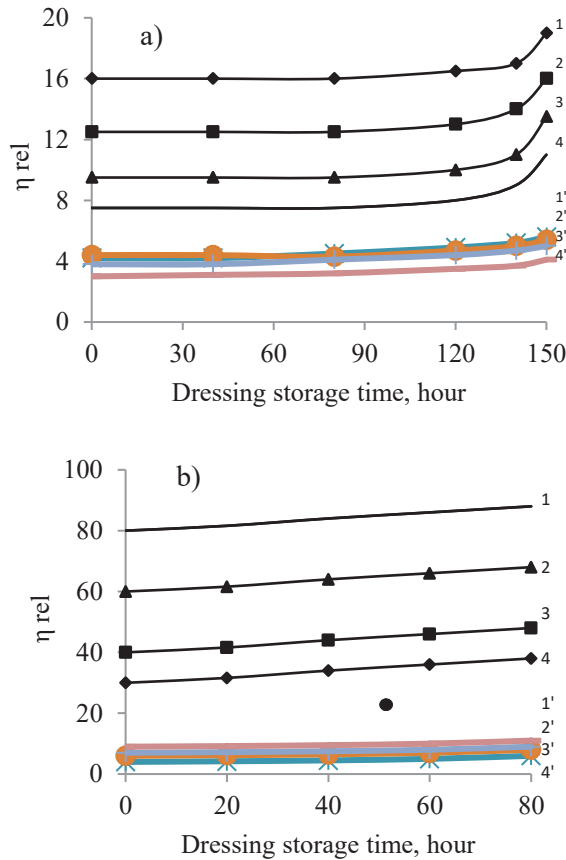


Fig.2. The dependence of the change in the viscosity of starch (1-4) and developed (1'-4') compositions on the time of dressing storage.

Starch concentration: (a) - 4%, (b) - 5%, Temperature: 1, 1'-20°C; 2, 2'-40°C; 3, 3'-60°C; 4, 4'-80°C.

From the data obtained (Fig. 2) it can be seen that the viscosity of starch gels increases with time, while the developed compositions either remain unchanged (at a starch concentration of 4%), or the observed increase is very insignificant (at a starch concentration of 5%).

It should be noted that the possibility of long-term storage of starch dressing without changing its technological properties, achieved by introducing a small addition of PVS, PAA and sericin into the dressing, is of practical importance. In case of forced shutdowns of sizing equipment, the remnants of unused sizing (and at least 35-40 liters of sizing agent remain in each sizing trough) are drained into wastewater from spinning and weaving production, which are contaminated with modified starch, which creates favorable conditions for the development of pathogenic microflora in water bodies, and chemical reagents (lye, PVS, cottonseed oil).

The experience of using the developed compositions for sizing cotton yarn at the Naksh

Oydin factory, as confirmed by the test and implementation certificates, indicates an increase in the stability of the developed sizing composition, due to which it becomes possible to store the dressing for a long time without water flaking. As a result, dressing losses in the form of unused residues are excluded.

It was of interest to analyze in more detail the effect of sericin on the properties of films formed from sizing polymer compositions. Figure 3 shows how the main characteristics of the films change as the concentration of sericin in the 4% starch gel increases.

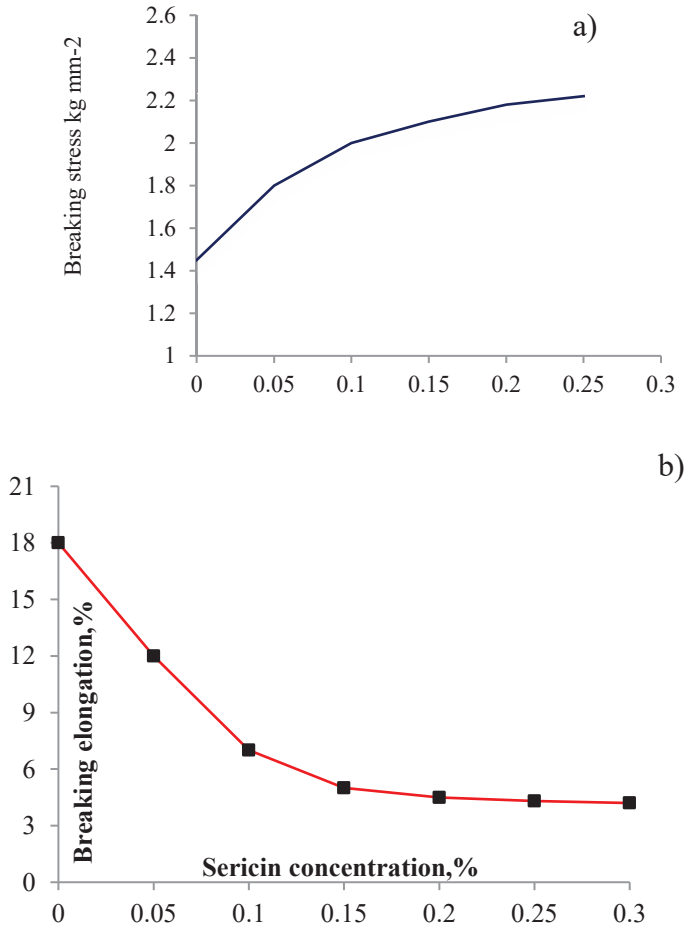


Fig. 3. Dependence of the effect of sericin concentration in sizing compositions on breaking stress (a) and breaking elongation (b) of films cast from them. Starch concentration - 4%.

At low concentrations of sericin (up to 0.1%), an increase in the strength of the films is observed, accompanied by an almost proportional increase in their elasticity, and this indicates the destruction of bonds between the macromolecules of the film-forming polymer. At the macrolevel, this manifests itself as a sharp drop in the relative viscosity of the paste, which is quite natural. However, a further increase in the content of sericin, which corresponds to a continuing decrease in the viscosity of the gel, leads to a change in the trends in the changes in the parameters of the films under consideration, namely, the breaking stress begins to increase sharply, and the elongation, on the contrary, decreases. Obviously, at the extremum points of both curves in Fig. 3. the concentration of sericin reaches the level when

they themselves, together with starch, are included in the formation of a mixed polymer structure. This process reaches its maximum at a sericin content of 0.2%, that is, one that provides the maximum technological effect. In a number of works, it was noted that approximately at these concentrations, a conformational rearrangement of sericin molecules occurs from the conformation of the straightened chain, they pass into the conformation of a coil (or helix) with the closure of hydrophilic functional groups inward, capable of forming intermolecular bonds with other compounds. Therefore, further movement to the right along the concentration axis leads to a deterioration in both analyzed characteristics of starch films. The best starch-sericin films ($C_m = 0.2\%$) are slightly higher than starch ones in strength (by about 10-15%), but more, they significantly exceed elasticity (by more than 25-30%).

Table 2. Relative viscosity and adhesion of the sizing composition to the yarn.

Sizing composition	Starch concentratione					
	3%		4%		5%	
	η_{rel}	Glue. %	η_{rel}	Glue. %	η_{rel}	Glue. %
Ordinary	11.26	2.3	46.35	2.8	176.15	3.26
Starch. dextrinized	2.45	3.6	14.8	4.4	21.43	5.10
Developed dressing composition	1.96	5.2	2.64	5.7	3.74	6.17

An illustration of the importance of the wetting factor in ensuring a good quality of sizing with starch gelatinized compositions of cotton yarn can be data on the so-called "glue" - the amount of polymer glue fixed on the yarn during the sizing process is presented in Table 2.

As expected, indeed, the developed composition based on starch, PVS, PAA and sericin makes it possible to obtain a higher adhesion both in relation to conventional starch and dextrinized ones. This is achieved due to the low viscosity and deeper penetration of the hydrogel into the yarn structure.

3 Conclusion

Thus, as a result of the study, a complex positive effect of modifiers was established: PVA, PAA and sericin introduced into sizing compositions based on starch, on their relative viscosity and film-forming ability, which ultimately makes it possible to obtain sized cotton yarn with improved physical, mechanical and operational characteristics.

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