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EFFECT OF HUMIC ACID MICROADDITIVES ON THE PROPERTIES OF STARCH HYDROGELS AND FILMS MADE FROM THEM

I. Yu. Vashurina, N. E. Kochkina, and Yu. A. Kalinnikov

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It was found that addition of small amounts of peat humic acids to starch-based sizing hydrogels increases the mass of the adhesive composition absorbed by cotton yarn during sizing and causes a technically important improvement in its physicomechanical indexes by significantly decreasing the viscosity and increasing the spreading coefficient over the cellulose surface.

Starch-based hydrogels have been used from the beginning of weaving to the present as the basic sizing agent for cotton yarn. The purpose of sizing is to give fibres greater strength by fixing pile on their surface and giving them smoothness as well as possible elasticity [1, 2].

Formation of a sufficiently strong polymer film (cohesive properties) and cohesion with the fibre (adhesion) are the basic requirements that starch hydrogels must satisfy as adhesive compounds. For adhesion, it is necessary to ensure good wetting of the yarn surface by the hydrogel and the creation of a uniformly thick adsorption layer; the latter is determined by the viscosity of the hydrogel. The viscosity is thus used as the basic criterion in evaluating the quality of starch hydrogels in sizing. Use of hydrogels of medium viscosity is recommended, where the starch is split slightly during sizing and subsequent boiling (oxidizing and hydrolyzing reagents are added for this purpose — N-chlorobenzenesulfonamide and sodium hydroxide). The low viscosity of starch sizing hydrogels is considered unacceptable due to the extreme decomposition of the polysaccharide, which causes formation of a brittle film.

In continuing the cycle of studies to substantiate the expediency of using peat humic acids (HA) in finishing of cotton yarn [3, 4], we planned to assess the effect of microadditives of these compounds on the properties of starch hydrogels and the films formed from them.

HA are natural renewable environmentally clean compounds characterized by an exceptional variety of constituent fragments and functional groups. Due to the tendency toward intermolecular interactions of a different kind, compatibility with polymers of very varied structure, high reactivity, surface-active, and other properties, HA are increasingly widely used as components of adhesive polymer compounds. They ensure obtaining several technical effects simultaneously, primarily increasing the adhesive power of glue and the working life of polymer composites [5, 6].

It was found that addition of very small amounts of HA to starch hydrogels significantly affects their relative viscosity, which initially decreases strongly as the additive content increases, then increases again. The optimum quality of sized yarn is attained on a number of indexes in the version with the least viscous starch-humic acid gels (0.08-0.12% HA, Table 1) which does not fit within the generally accepted notions.

Attention was subsequently concentrated on studying these gels — containing 0.1% humic acids (C_{HA}) of the weight of the hydrogel.

It was found that HA causes more complete oxidation of the polysaccharide by N-chlorobenzenesulfonamide (the content of carboxyl groups in the starch increases by 56-58%) and deeper splitting by a base (the degree of polymerization of the individual amylopectin branch decreases from 13.2±1.1 to 11.4±1.0) [7]. There are also important changes in the structure of the starch gels — on addition of HA, the pronounced structural branch on the flow curves almost totally disappears, indicating

Institute of Chemistry of Solutions, Russian Academy of Sciences, Ivanovo. Translated from *Khimicheskie Volokna,* No. 5, pp. 26-29, September—October, 2004.

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TABLE 1. Effect of HA Content on the Viscosity of Starch Hydrogel* and Quality Indexes of Sized Cotton Yarn**

HA content, %	Relative viscosity of sizing	Real bond, %	Breaking load, N	Elongation at break, %
0	37.75	2.31	2.25	16.10
0.016	7.87	2.95	2.38	18.75
0.048	3.75	3.89	2.51	19.75
0.08	2.12	4.39	2.55	19.25
0.12	1.75	4.84	2.56	17.80
0.16	2.25	5.22	2.54	15.10
0.32	7.18	4.44	2.47	14.00

*Composition of hydrogel: starch (5%), NaOH (0.1%), N-chlorobenzenesulfonamide (0.07%).
**Linear density of yarn: 25 tex.

TABLE 2. Effect of HA Microadditives on Adhesive and Cohesive Properties of Starch Hydrogels*

Composition of hydrogel	$\sigma_g \cdot 10^3$, J/mole	Q, deg	$W_a \cdot 10^3$, J/mole	$W_c \cdot 10^3$, J/mole	$S \cdot 10^3$, J/mole
Ordinary	90.93	47.0	152.9	181.86	–28.90
Dextrinized	85.00	30.2	158.5	170.00	–11.50
Starch-humic	81.23	19.6	157.8	162.46	–4.69

*5% polysaccharide content.

powerful decomposition of intermolecular bonds in the starch hydrogel by molecules of HA. The activation energy of viscous flow correspondingly decreases by 17-20%.

Such structural and chemical modification of starch hydrogels unconditionally causes a change in their adhesive and cohesive properties. The first are were characterized by the work of adhesion (W_a) and spreading coefficient (S) and the second are characterized by the work of cohesion (W_c) and the physicomechanical indexes of the films.

The work of adhesion is easily calculated with the Dupre—Young equation after measuring the contact angle of wetting (Q) and the surface tension of the hydrogel (σ_l) [8]:

$$W_a = (1 + \cos Q)\sigma_l. \quad (1)$$

Since by definition

$$W_a = \sigma_s + \sigma_l - \sigma_{s\text{-}l}, \quad (2)$$

the work of cohesion, i.e., the work necessary for breaking the liquid and creating two new interfaces with tension σ_l, is equal to

$$W_c = 2\,\sigma_l. \quad (3)$$

Since spreading of liquid over the surface of a solid is described by the inequality

$$\sigma_s - \sigma_l - \sigma_{s\text{-}l} \le 0 \quad (4)$$

(the left part of the inequality is the spreading coefficient S; σ_s is the surface tension of the support), it is clear that

$$S = W_a - W_c = \sigma_l(\cos Q - 1). \quad (5)$$

The experimental values of the surface tension and contact angles of wetting of three types of starch hydrogels with the same polysaccharide content (5%) and the calculated values of W_a, W_c, and S are reported in Table 2. Hydrogel dextrinized

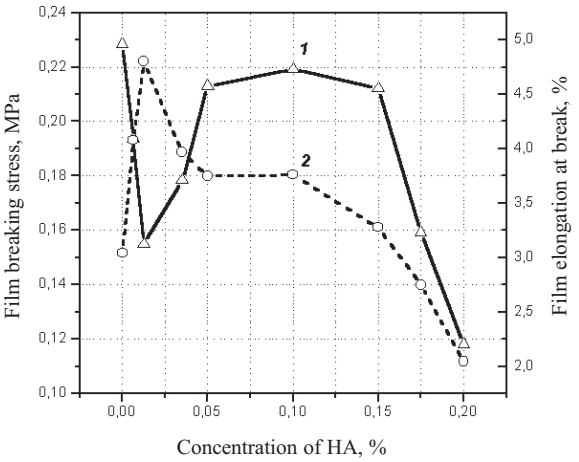

Fig. 1. Effect of the concentration of HA on the properties of films poured from sizing compounds with 5% concentration of starch: 1) breaking stress; 2) elongation at break.

TABLE 3. Relative Viscosity and Bonding of Starch Hydrogels to Yarn

Composition of hydrogel	C_{st} = 4%		C_{st} = 5%		C_{st} = 6%	
	η_{rel}	bonding, %	η_{rel}	bonding, %	η_{rel}	bonding, %
Ordinary	13.36	1.60	37.75	2.31	388.15	2.90
Dextrinized	1.31	3.25	1.75	4.42	2.06	5.00
Starch-Humic	1.31	3.66	1.75	5.00	2.06	6.14

Note: C_{st} — concentration of starch.

to the viscosity of the starch-humic hydrogel (and correspondingly with an equal degree of polymerization of amylopectin) by prolonged boiling while keeping the volume constant was also investigated together with ordinary and starch-humic hydrogel. We wanted to distinguish the contribution of the viscosity factor to the analyzed properties of starch-humic hydrogels in this way.

The surface tension was estimated by the minimum bubble pressure method in [9], and a prepared cellulose film was used as the cellulose substrate in determining the contact angle of wetting.

Addition of HA to the starch hydrogel decreases its surface tension (by 11%) and contact angle of wetting (by 59%). Dextrinization acts in the same direction, but less efficiently: the decrease in σ_l is 6.5% and the decrease in Q is 36%. As a consequence, improvement of the wetting power of the gel containing HA microadditive is not only due to splitting of the starch and a corresponding decrease in the viscosity of the adhesive but also to manifestation of the surface-active properties of HA, well known from the literature [10].

The calculated values of the work of cohesion in going from ordinary starch hydrogel to dextrinized and starch-humic hydrogel decrease uniformly.

It was interesting to analyze the effect of HA on the properties of films formed from starch-humic hydrogels in more detail. Figure 1 shows how their basic characteristics change as the peat HA content in 5% starch gel increases. At a low concentration of additive (under 0.01%), the strength of the films decreases sharply, accompanied by an almost proportional increase in their elasticity, which indicates rupture of bonds between the macromolecules of the film-forming polymer. On the macrolevel, this is manifested both by a sharp decrease in the relative viscosity of the cluster, which is totally natural. However, a further increase in the HA content corresponding to a continuous decrease in the viscosity of the gel shifts the tendencies toward changes in the examined film parameters: the breaking stress increases sharply and the elongation on the contrary decreases. At points of the extremum of curves 1 and 2 in Fig. 1, the concentration of HA attains a level where they, as macromolecular polymer compounds, are involved in formation of the mixed structure of the polymer together with the

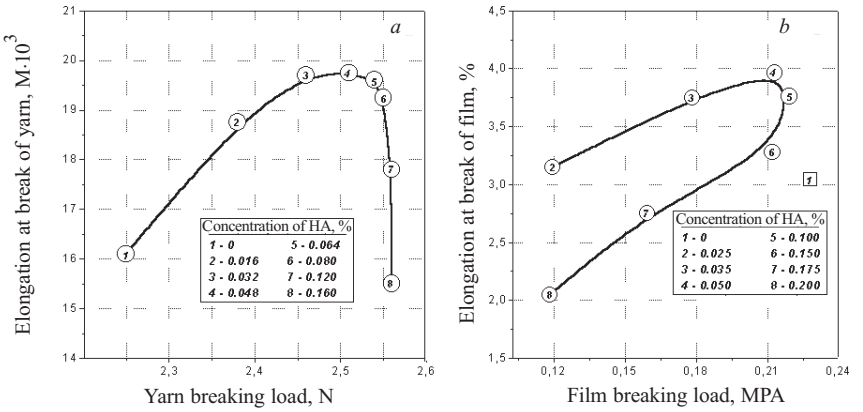

Fig. 2. Correlation between strength and elasticity of sized yarn (a) and starch film (b) at 5% concentration of starch.

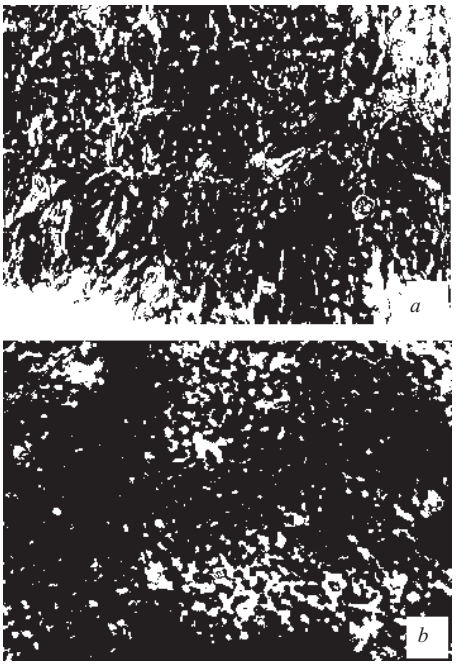

Fig. 3. Photographs (× 160) of films poured from starch (a) and starch-humic (b) sizing compounds with 5% concentration of starch.

polysaccharide. This process reaches the apogee at C_{HA} = 0.1%, i.e., where the maximum process effect is obtained. In many publications describing the conformational transformations in HA molecules, approximately this concentration is called the critical micelle concentration [11, 12]. As it is attained, the HA molecules pass from the straight-chain conformation to the coil (or helical) conformation with closing inside hydrophilic functional groups capable of forming intermolecular bonds with other compounds.

For this reason, further movement along the concentration axis to the right worsens both analyzed characteristics of starch films. The best starch-humic films (C_{HA} = 0.1%) are slightly inferior to starch films in strength (by approximately 4%), but are much better with respect to elasticity (more than 23% better).

The effect of the properties of the starch film on the target indexes of sized yarn are graphically illustrated by the curves in Fig. 2. The shape of the curves for film and yarn is almost the same. The clear correlation of the properties of the yarn and the polymer film indicate the importance of the quality of the film for attaining a high process effect in sizing. It follows from

the photographs in Fig. 3 that the starch-humic film (C_{HA} = 0.1%) is much more homogeneous than the starch film and its surface is smoother.

In generalizing the data on the effect of HA microadditives on the adhesive-cohesive properties of starch hydrogels and the quality of the films formed, it is necessary to isolate the parameter that changes most significantly. This concerns the spreading coefficient *S*. For starch-humic hydrogels, it is much higher not only in comparison to ordinary starch films (by more than 6 times) but also dextrinized films (by 2.5 times).

This indicates that together with the viscosity, wetting plays a determining role in ensuring the good quality of sizing of cotton yarn with clusterized starch compounds. The data on so-called "bonding" — the amount of polymer adhesive attached to the yarn during sizing — could be an illustration of the importance of this factor [2] (Table 3).

Actually, starch-humic compounds cause stronger bonding both with respect to ordinary starch hydrogels (due to the low viscosity and deeper penetration of the hydrogel into the structure of the yarn) and dextrinized hydrogels.

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