THE USE OF THE MODIFIED STARCH IN BIOLOGICALLY ACTIVE SYSTEM

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Abstract: *A biologically active system based on modified starch and quaternary ammonium salt has been studied. The influence of QAS on the rheological properties of CMS solutions has been investigated. Antimicrobial activity of textile materials treated with warehouse on the basis of CMS was studied. The formation of chemical bonds between functional groups of carboxymethylated starch and cationic bactericidal preparation is established by IR spectroscopy.*

Keywords: *biologically active systems, modified starch, fungicidal activity, bactericidal properties.*

1 INTRODUCTION

The concept of "biological activity" covers a wide range of the phenomena. From the point of view of chemical exposure, biologically active agents (BAA) are understood as substances that can act on the biological systems (including the human body), regulating their vital functions [1]. The use of polymeric systems allows to impart BAA absolutely new properties and to increase their efficiency considerably. Besides, high-molecular connections can have biological activity at the expense of the macromolecular nature. At the present time, the development and research of new biologically active systems (BAS) obtained on the basis of polymers and intended for the use in the medicine [2], plant growing and livestock production, biotechnology [3], the food and cosmetic industry [4] are intensively carried out in many laboratories of the world.

One of current trends of the world state in the field of the use of polymers in the BAS is a production and a consumption of textile materials with antimicrobial properties [5].

Despite the improvement quality of life, hygienic education, observance of rules of personal hygiene, the incidence caused by microorganisms remains high without visible tendency to decrease, especially at close contact between people. The quality of life and work of a large number of people in the conditions which aren't providing the appropriate level of hygiene (transport, shift work, expeditions, field conditions of the military personnel, rescue efforts) or connected with increased requirements to microbiological safety (medical institutions, pharmaceutical and food productions) can be improved considerably by the use of biocidal protection of textile materials [1, 5, 6].

One of ways of receiving such materials is the formation of the BAS. Earlier fabrics were given antimicrobial properties due to processing by their antiseptic agents however such protection was temporary, as through several washings the agent was completely washed away. Now, thanks to the formation of the BAS, there was an opportunity to create textiles with antibacterial properties, steady against numerous washings. There is a set of the ways of creation the BAS influencing microorganisms on different mechanisms.

Their biocidal activity can be connected with initial structure of polymer, is caused by its chemical modification or introduction to structure of polymer of organic or inorganic antimicrobial agents [7], for example, silver ions [8]. Now the large number of BAA is known [9]. Nevertheless, in many cases a possibility of application of the known BAA use insufficiently, quite often with the efficiency far from maximum. It is possible to carry the quaternary ammonium salts (QAS) to such BAA.

It should be noted that the use for formation of the BAS is QAS rather perspective. Quaternary ammonium salts are capable to be attached to walls of cages of bacteria and to destroy them from within. The effect of bacterial action is gained thanks to a positive charge which is born by their molecules, at the expense of it they are attracted to an external surface of the bacterial membrane loaded negatively [4]. Though the effect of substitution of quaternary ammonium salts of other positively charged ions isn't so high, it appears enough for destabilization of a microbe [8].

As it is established by researches [10], these defects can be eliminated or their role can be considerably lowered when using BAA in the form of chemical compounds with certain carriers or modifiers as most of which often use various polymers.

Authors [10] propose a method based on thiol-epoxy click chemistry to achieve durable antibacterial properties on cotton fabrics. The cotton fabric was first modified with 3-mercaptopropyltriethoxysilane (KH-580) to introduce thiol groups. Then, cotton fabric was treated with a quaternary ammonium salt by thiol-epoxy click chemistry. The results demonstrated that such treatment provides durable antibacterial properties for cotton fabric due to the chemical bonding formed between the quaternary ammonium salt and the substrate.

Proceeding from this, the purpose of the work was developing of BAS applying of carboxymethylated starch and quaternary ammonium salt as biologically active agents.

2 MATERIALS AND METHODS

As the textile carrier have been used cotton coarse calico an art. 264 and a gauze art. 033.

As a polymeric matrix for biocidal medicine was used carboxymethylated starch (Na-CMS) (TU U 6-04872 671.061-96).

BAA is a quaternary ammonium salt $[R(CH_3)_2NCH_2C_6H_5]^+Cl^-$ (CAS №: 21954-74-5).

Classical single-bath processing methods were used to give the antimicrobial activity to cotton fabrics. In the same finishing bath both film former and antibacterial substances were dissolved. Cotton fabrics were applied to that solution for 1 minute, then they were pressed to achieve 100% humidity and dried step by step.

To evaluate the rheological properties of the composition a rotating viscosimeter "Rheotest-2" was used at shifts in the range γ = 3 - 1312 s^{-1}. BAS sorption was determined by mass method.

The efficiency of antimicrobial finishing was estimated by means of a test method on the dense environment to an action of pathogenic bacteria: Escherichia coli, Bacillus subtilis and Staphylococcus aureus (received from a collection of Institute of microbiology and virology of Ukraine). Processing of results was carried out for bacteria in 2-6 days and for mushrooms in 5-7 days. It was considered bactericidal and bacteriostatic effect of substances which contain in fabric.

For our research we use IR-Fure's device spectrometer THERMO Nicolet mark AVATAR 370 FT IR (range of wavelengths 400-4000 cm^{-1}), crystal ZnSe, compressed sample from KBr.

Main objective of the work was formation of the BAS which would eliminate such lack of textiles with antimicrobial processing as low resistance of bactericidal effect to repeated washings.

Such chemical compound actually is a new biologically active polymer (I), a different chemical structure from initial polymer carrier, in the case studied by us is the scheme of formation of a new BAA.

$$Starch\ -CH_2\ -\underset{\underset{O}{||}}{C}ONa + [\![RN^+]\!]\ \ Cl^- \rightarrow$$

$$\rightarrow Starch\ -CH_2-\underset{\underset{O}{||}}{C}O^-N^+\ R + \ Na^+\ \ Cl^-$$

At the same time, it is possible to assume that ionic bond of QAS with the polymeric carrier (Na-CMS) can be steady during functioning of biologically active polymer (such polymers often call systems with the immobilized, that is "immobilized" BAA).

3 RESULTS AND DISCUSSION

A prerequisite for the formula of a composition for tissue processing is the availability of data on the nature of the dependence of the system viscosity on the concentration of the polymer. In this work, rheological research was carried out and the dependence of the initial viscosity (η_0) Na-CMS on the concentration of dry matter (C) was calculated according to the equation (1):

$$\eta_0 = K.C^{\alpha} \qquad (1)$$

where K = 19.5.10^{-4} and α = 3.35.

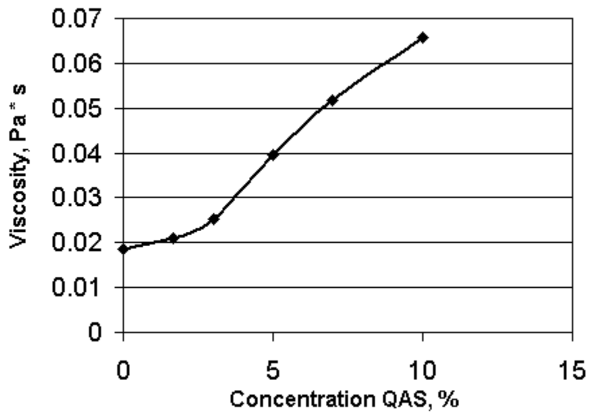

Figure 1 Influence of QAS supplements on the rheological properties of Na-CMS solutions at γ = 243 s^{-1}

The change in effective viscosity across the studied range of shift velocities has been calculated. The dependence of the effective viscosity (η_e) of the polymer composition on the shift rate (γ, s^{-1}) and the initial viscosity (η_0) can be expressed by equation (2) (correlation coefficient R = 0.918 for a concentration of 3%)

$$\eta_e = \eta_0 / [1 + 1.79(\eta_0 \cdot \gamma)^{0.47}] \quad (2)$$

During the study of Na-CMS-QAS flow curves, it was found that the addition of QAS leads to a decrease in the area of the hysteresis loop, which is presented in Figure 2).

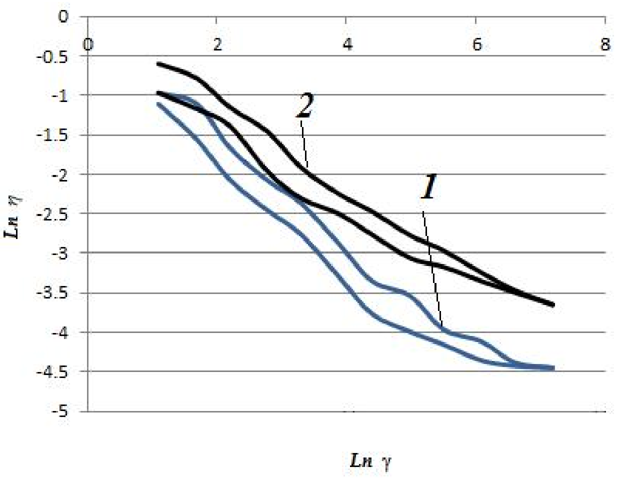

Figure 2 Rheological properties of solutions 1. Na-CMS 30 g/l; 2. Na-CMS 30 g/l, QAS 7 g/l;

The magnitude of the degree of thixotropic restoration of viscosity was calculated by the formula:

$$S = \frac{\Sigma \eta_{1i}}{\Sigma \eta_{0i}} \cdot 100\% \quad (3)$$

where S - degree of thixotropic restoration of the viscosity of solutions;

η_{1i} - is the viscosity at the i-th shift velocity, measured in the gradient mode of the decreasing rate of speed;

η_{0i} - is the viscosity at the i-th shift velocity, measured in the gradient mode of the increasing velocity;

i - speed of the shift;

n - the number of fixed values of the gradient of the rate of displacement.

The values of S for solutions of starch, Na-CMS and Na-CMC concentrations of 1-3% are presented in Table 1.

Table 1 The magnitude of the degree of thixotropic restoration of viscosity

Polysaccharide	S [%]		
	Concentration of polysaccharide		
	1%	2%	3%
Starch	87.9	83.2	74.6
Na-CMS	92.5	91.8	90.2
Na-CMS + QAS	93.8	92.6	92.3

The rheological properties of 1-3% solutions of Na-CMS and Na-CMS+QAS in the range of shift velocities from 3 to 1312 s^{-1}, the viscosity of the solutions is subject to the step-by-law and is described by the Ostwald-de-Vila equation. It has been established that the modified starch-based compositions form 1-3% of solutions, which are characterized by a sufficiently high degree of thixotropic restoration of viscosity (90.2 - 93.8%).

The kinetic dependence of an experimental additional weight of the BAS on the textile carrier depending on time of contact of phases has been defined: the influence of quaternary ammonium salt on sorption of starch and the modified starch cotton fabric. Results are presented in Figure 2.

Analyzing the sorption curves, it was established that the degree of sorption of the composition using Na-CMS and QAS is higher in mass terms by 0.0025 g/g fibers, compared with Na-CMS, and 0.0010 g/g fiber, if starch is used as a polymer carrier.

Thus, when giving an antimicrobial finish by dressing with a composition containing BAS, a sorption of the compound takes place from the coupling agent (Starch – CH_2 – CO – QAS).

The efficiency of the BAS, realized technically by the padding method has been defined. Results are represented in Table 2.

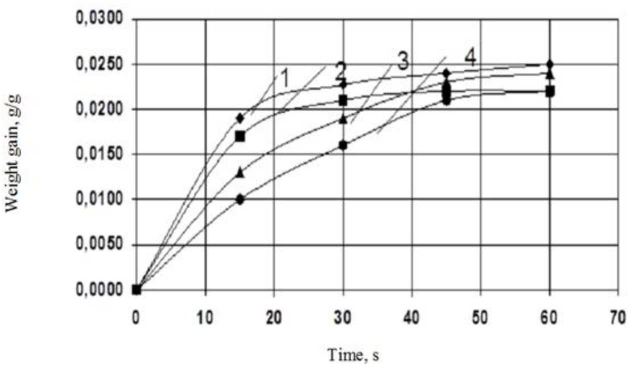

Figure 3 Kinetic dependence of an experimental additional weight of the BAS on the textile carrier depending on time of contact of phases:
1. Na-CMS 30 g/l, QAS 7 g/l; 2. Na-CMS 30 g/l; 3. starch 30 g/l, QAS 7 g/l; 4. starch 30 g/l

Testifying data of the Table 2 reveals the selective influence of the BAS on the basis of Na-CMS and QAS on gram-positive (Bacillus subtilis, Staphylococcus aureus) and gram-negative (Escherichia coli) bacteria. None of the samples gave sterile zones (bactericidal action) on the lawns of Escherichia coli. For this type of bacteria, the samples acted bacteriostatically (delayed growth of the culture).

Analyzing the received results, it is possible to draw a conclusion that despite a large number of scientific works in the field of formation of the BAS, the mechanism of their action isn't quite clear.

But probably, in the presence of a small amount of moisture there is a slow hydrolysis and continuous transition of the bactericidal reagent connected with functional groups of the polymer applied on fabric. With direct contact of the chipping-off reagent with microbes there is a suppression of their activity.

Transmittance spectrums of Na-CMS and Na-CMS + QAS are presented in Figures 4 and 5.

Characteristic bands clearly seen on spectra, indicating the existence of links -C-H (frequency of oscillations is close to 2890 cm^{-1}, the band is relatively small intensity), groups –OH (frequency of oscillations is close to 3290-3550 cm^{-1}, wide bands of sufficiently high intensity, which indicate the presence of intermolecular hydrogen bonding and is characteristic of chelate compounds), carbonyl groups (frequency of oscillation is close to 1600 cm^{-1}, the band is relatively small intensity) and carbon – carbon bonds in the corresponding compounds. Fluctuations in a simple etheric connection are not characteristic, but on an area with a frequency closed to 1000 cm^{-1} an intensive band appears due to the participation in the oscillation of the polar bond -C-O.

Table 2 Antibacterial and fungicide activity of the BAS on the basis of Na-CMS and QAS

Preparation	Concertation [g\l]	Way of processing a fabric	Escherichia coli		Bacillus subtilis		Staphylococcus aureus		Fusarium oxysporum
			BC	BS	BC	BS	BC	BS	BC
-	-	-	0	0	0	0	0	0	0
	7	impregnation, drying	0	5	1	0	3	0	1
QAS	7	impregnation, drying, washing	0	4	1	0	3	0	1
Na-CMS	30	dressing	0	3	0	0	1	0	1
Na-CMS	30	dressing, washing	0	1	0	0	0	0	0
Na-CMS QAS	30 7	dressing	0	10	3	0	1	0	1
Na-CMS QAS	30 7	dressing, washing	0	5	2	0	1	0	1
Starch	30	dressing	0	0	0	0	0	0	0
Starch QAS	30 7	dressing, washing	0	4	0	0	3	0	1

Note: BC is a bactericidal activity; BS is a bacteriostatic activity; "0" – the activity is absent; "-" – didn't defined.

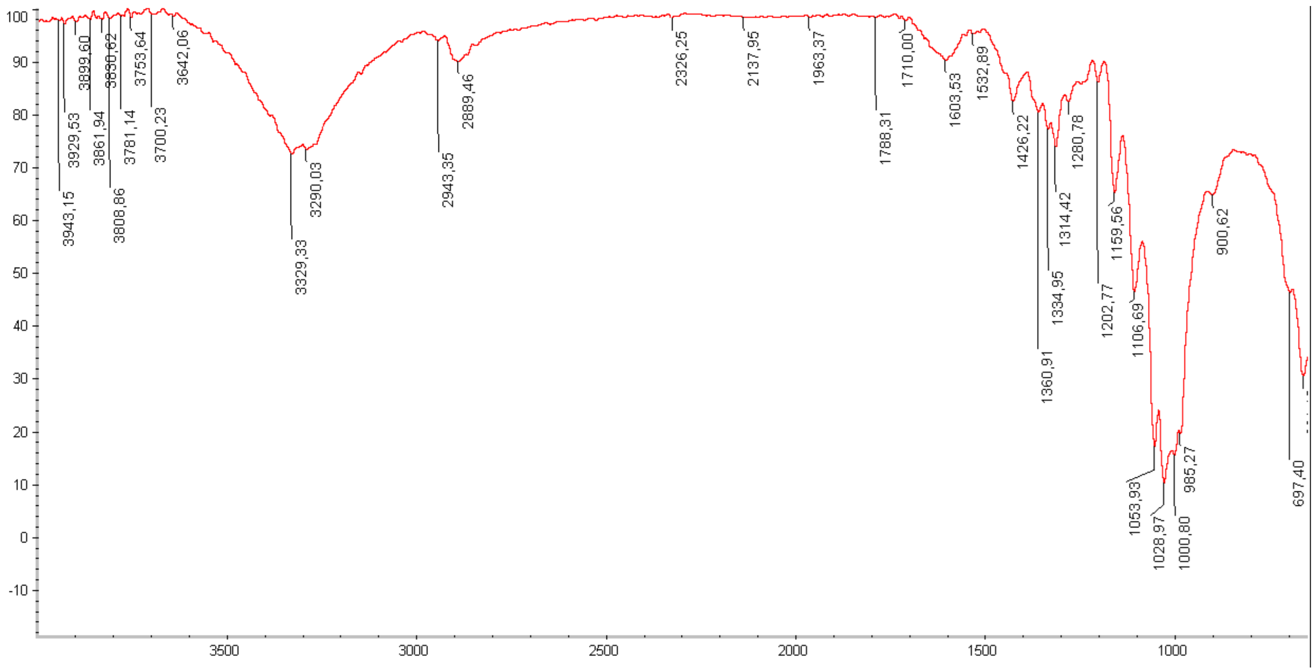

Figure 4 Transmittance spectrum of Na-CMS

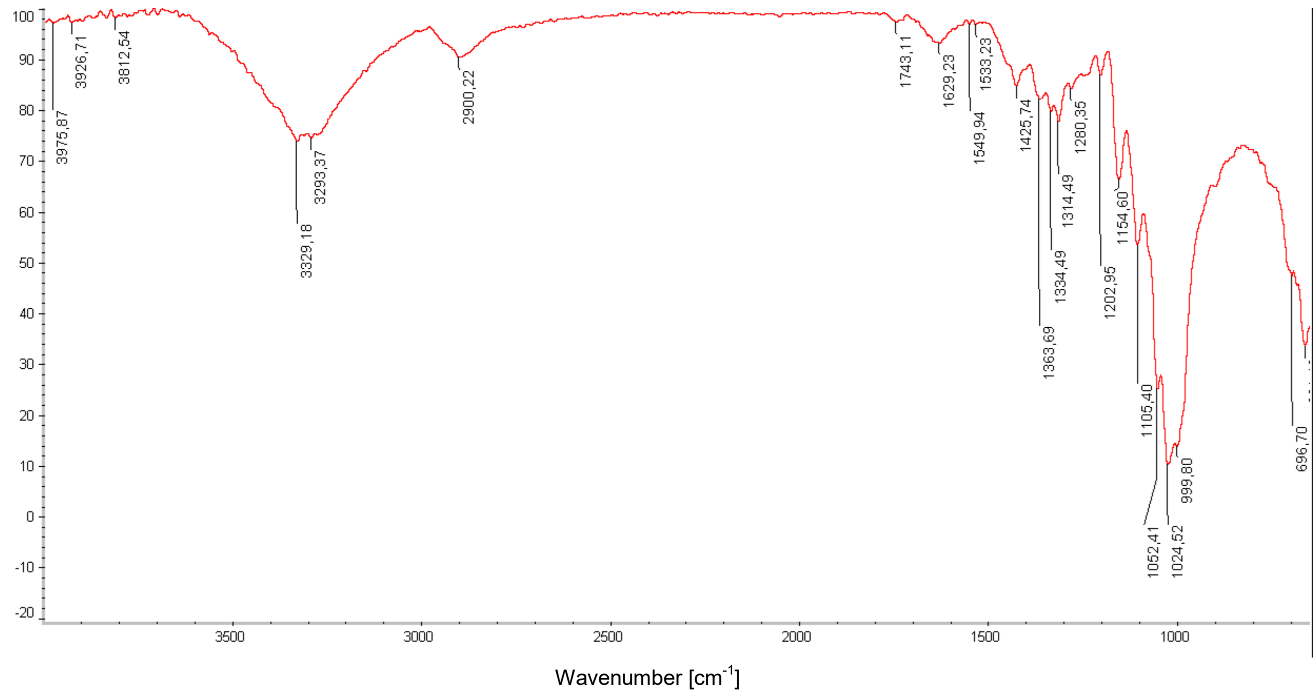

Figure 5 Transmittance spectrum of Na-CMS + QAS

However, when studying the spectrum formed during the investigation of textile material, processed with finishing solutions, it has been established that the spectrum do not have bands that are characteristic of the QAS (the connection typical for quaternary amines, the absorption band at the frequency of oscillations is close to 1440-1400 cm^{-1}). Consequently, studying the graphic material it can be concluded that new chemical bonds with the fabric are not formed. So, it can be assumed that the antimicrobial substances are contained on the textile material in a layer of the polymeric film-forming agent.

4 CONCLUSION

As a result of the research, the compound of the composition was established to provide antimicrobial properties to cotton fabrics based on carboxymethyl starch (30 g/l) and tetrachloride ammonium salt (7 g/l). It has been established that the addition of an antimicrobial agent improves the viscoelastic properties of solutions. The use of modified starch improves the sorption properties of the textile material. As far as possible, the QAS is 3 mm, as a result of the use of a polymeric modifier CMS. Another picture is observed when forming the BAS based on Na-CMS and QAS, in this case the sterile zone around the samples is much more - 10 mm.

This paper shows that the BAS on the basis of Na-CMS and QAS is rather effective. In this case it is possible to allow an explanation of the obtained data formation of new chemical compound which actually is a new biologically active polymer, a different chemical structure from initial polymer carrier and initial BAA.

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