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GLOBULAR PROTEIN FOR SURFACE MODIFICATION OF CELLULOSECONTAINING MATERIALS

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VA INNOVATSIYA

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GLOBULAR PROTEIN FOR SURFACE MODIFICATION OF CELLULOSE-CONTAINING MATERIALS

N.Z.SAYDALIEVA (Tashkent Institute of Textile and Light Industry, Tashkent city, Republic of Uzbekistan)*

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Abstract. *The purpose of this work is the chemical modification of cotton fabrics with natural globular protein. Modification was carried out in the process of finishing cotton fabrics, after decoction and bleaching in a continuous mode. The effect of modification on the strength, protein content and functional groups of cotton fabric has been studied. According to the results obtained using the AUTOGRAPH AGS-N machine, it was found that the modification of cotton fabrics with a solution of globular protein increases the strength of the treated fabrics, depending on the concentration of the modifier and the temperature regime. Treatment with a highly concentrated protein solution completely fills the fabric structure, which reduces strength and breathability. Due to the fixation of the structure, the elongation at break is reduced to 15.5%, shrinkage - up to 1.6 times. High-temperature treatment of the fabric with a low concentration solution increases strength and reduces shrinkage by 2 times. Apparently, the relatively high-temperature regime of impregnation promotes better dissolution of the protein and thereby increases the diffusion of the protein into the tissue structure. This is confirmed by the protein content in the modified sample determined on the Hanon K1100F automatic analyzer. According to the results of IR Fourier spectral analysis, it was found that the modification of cotton fabrics with globule protein leads to an increase in hydrogen bonds of various nature, a decrease in the number of characteristic -CH_2- and -CH_3 groups of the protein globule in the spectrum. This may be due to the addition of protein to cellulose. Due to the increase in functional groups in the structure of modified cellulose, hydrogen bonds increase, and a decrease in the –COO– ion can be the reason for the chemical interaction of the ion with the hydroxyl groups of cellulose.*

Keywords. *Modification, Cotton Fabrics, Globule Protein, Solution, Low Concentration, Cellulose, Structure, Temperature Regime.*

Annotatsiya. *Mazkur ishning maqsadi tabiiy globulyar oqsil eritmasi bilan paxta tolali matolarni kimyoviy modifikatsiya qilishdan iborat. Modifikatsiya paxta tolali matolarni pardozlashga tayyorlash jarayonida, qaynatish-oqartirishdan so‘ng uzluksiz usulda amalga oshirildi. Modifikatsiyaning paxta tolali mato mustahkamligiga, uning tarkibidagi oqsillar miqdoriga va funktsional guruhlariga ta’siri o‘rganib chiqildi. AUTOGRAPH AGS-N mashinasi yordamida olingan natijalarga ko‘ra, globulyar oqsil eritmasi bilan paxta matolarini modifikatsiya qilish modifikator kontsentratsiyasi va temperatura rejimi ta’siriga qarab ishlov berilgan namuna mustahkamligini oshiradi. Yuqori kontsentratsiyali oqsil eritmasi bilan ishlov berilganda mato sturturasidagi g‘ovaklar yuzasi to‘liq qoplanishi, mustahkamlik va havo o‘tkazuvchilikni kamaytiradi. Strukturaviy fiksatsiya hisobiga uzilishdagi cho‘ziluvchanlik 15,5% gacha, kirishish 1,6 martagacha pasayadi. Matoga past konsentratsiyali eritma bilan yuqori haroratda ishlov berish mustahkamlikni oshiradi va kirishishni kamaytiradi. Matoga past konsentratsiyali eritma bilan nisbatan yuqori haroratda ishlov berish mustahkamligini oshiradi va kirishishni 2 baravar kamaytiradi. Aytish mumkinki, nisbatan yuqori haroratli rejim oqsilning yaxshiroq erishiga sabab bo‘ladi va bu oqsilning mato strukturasiga diffuziyasini oshiradi. Hanon K1100F avtomatik analizatorida yordamida modifikatsiyalangan namunadagi miqdori aniqlandi. Fure- IQ spektral tahlili natijalariga ko‘ra, paxta tolali matoni globulyar oqsil bilan modifikatsiyalash turli tabiatli vudorod bog‘larining ko‘payishiga, spektrdagi o‘ziga xos bo‘lgan -CH_2- va -CH_3 guruhlari sonining kamayishiga olib keladi. Bu sellyuloza va oqsilning o‘zaro kimyoviy tasirlashuvi bog‘liq bo‘lishi mumkin. Modifikatsiyalangan sellyuloza strukturasida funksional guruhlar ko‘paygani sababli vodorod bog‘lar miqdori oshgan, oqsildagi –COO- ionining sellyulozaning gidroksil guruhlari bilan kimyoviy bog‘lanishi hisobiga spektorda bu ionga tegishli yutilishlarlishlarning kamayishi aniqlangan.*

Tayanch so‘zlar: *modifikatsiya, paxta tolali mato, globulyar oqsil, eritma, past konsentratsiya, sellyuloza, struktyra, harorat rejimi.*

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Аннотация. *Целью данной работы является химическая модификация хлопчатобумажных тканей природным глобулярным белком. Модификация проводилась в процессе отделки хлопчатобумажных тканей, после отварки и беления в непрерывном режиме. Изучено влияние модификации на прочность, содержание белка и на функциональные группы хлопчатобумажной ткани. По результатам, полученным с помощью машины AUTOGRAPH AGS-N, было установлено, что модификация хлопчатобумажных тканей раствором глобулярного белка повышает прочность обрабатываемых тканей в зависимости от концентрации модификатора и температурного режима. Обработка высококонцентрированным белковым раствором полностью заполняет структуру ткани, что снижает прочность и воздухопроницаемость. За счет структурной фиксации удлинение при разрыве снижается до 15,5%, усадка - до 1,6 раза. Высокотемпературная обработка ткани раствором низкой концентрации повышает прочность и уменьшает усадку. Высокотемпературная обработка ткани раствором низкой концентрации повышает прочность и уменьшает усадку в 2 раза. Очевидно, что относительно высокотемпературный режим пропитки способствует улучшению растворимости белка и тем самым увеличивает диффузию белка в структуру ткани. Это подтверждается содержанием белка в модифицированном образце, определенным на автоматическом анализаторе Hanon K1100F. По результатам ИК-Фурье -спектрального анализа было установлено, что модификация хлопчатобумажных тканей глабулярном белком приводит к увеличению водородных связей различной природы, уменьшению числа характерных -CH_2- и -CH_3 групп глобулы белка в спектре. Это может быть связано химическим взаимодействием белка в целлюлозу. Из-за увеличения функциональных групп в структуре модифицированной целлюлозы увеличиваются водородные связи, и уменьшение иона -COO- может быть причиной химического взаимодействия иона с гидроксильными группами целлюлозы.*

Ключевые слова: *модификация, хлопковые ткани, глобулярный белок, раствор, низкая концентрация, целлюлоза, структура, температурный режим.*

Introduction

Fabrics made of natural fibers have always attracted textile consumers with their hygienic properties. Cotton fiber plays a special role in this. Cotton fiber fabrics are in great demand in the production of fabrics of various types, these are fabrics for upper and lower clothing, as well as for other ranges of household use [1]. In the operation of such fabrics, consumers mainly meet the requirements for maintaining linear dimensions after washing. In addition, in the processes of finishing fabrics made of cotton fibers, properties such as reactivity, which is not mediocre related to the functionality of the fabric and affinity for the dye used, are important. In this regard, an urgent task for researchers in this field is to develop technologies for finishing textile fabrics made of cotton fiber that solve the problems of shrinkage and crease of cotton fabrics after washing, as well as to increase the affinity for active dyes in the process of dyeing them. For improving the above-mentioned properties of cotton fabrics, various methods of modification are proposed in scientific literature as a new direction [2;3;4;5;6].

Currently, there are various methods of modification of textile materials: physico-mechanical (structural), physico-chemical, chemical, and biochemical. In the production of textile materials, a special place is occupied by chemical modification, which is based on a directed change in the chemical composition and structure of cellulose fiber due to the implementation of chemical reactions [7;8;9;10].

Improving the operational properties of cotton fabrics is mainly used at the final finishing stage [11;12]. With the development of polymer chemistry, it became possible to create a huge assortment of polymers that have different functional groups in their composition and are able to give textile materials a complex of improved properties. The mechanism of modification of cotton fabrics aimed at improving shape stability and reducing shrinkage consists in fixing the structural elements of the fibrous substrate. It should be noted that the modification of fibers and their surfaces with biopolymers can make production more environmentally friendly and economical [13;14].

Scientists Xu Yunhui, Huang Chen and Wang Xiaoming to obtain multifunctional cotton fibers first oxidized the fabric with a solution of Na periodate, then subjected to crosslinking with a solution of collagen protein in aqueous acetic acid. IR and X-ray electron spectroscopy methods have shown the formation of Ca=N double bonds through an imination reaction between aldehyde groups of oxidized cotton fibers and amino groups of collagen protein. X-ray diffraction revealed an increase in the crystallinity of oxidized cotton fibers after treatment with collagen protein from 65.6 to 69.3%. Scanning electron microscopy has shown that collagen protein attaches to the surface of oxidized cotton fibers. Optimal conditions for the production of modified cotton fibers depend on the content of aldehyde groups in the oxidized fibers and the content of collagen protein. Mechanical properties of oxidized fibers do not undergo significant changes. Model experiments on the isolation of aloe extract from modified fibers have shown their suitability as a

carrier of drugs for their long-term isolation [15].

The process of surface modification of cotton fabric, which was first oxidized and then stitched with collagen, was studied. The optimal oxidation process was made using the following technology: the concentration of sodium periodate is 0.6 g/l, the oxidation time is 2.5 h, the temperature is 40 °C, the ratio of water and cotton fabric is 100:1. The method of modifying the surface of cotton fabric was determined on the basis of comparative analysis. The optimal process for surface modification of cotton fabric is proposed according to the following method: the concentration of collagen solution is 6%, the concentration of glutaraldehyde is 5%, the reaction is carried out for 40 minutes at 30 °C, the ratio of water and cotton fabric was 100:1. Compared with the original cotton fabric, the tensile strength and elongation of the cotton fabric modified with collagen decreased, and the percentage of staining with acid dyes increased, and by this the authors indicate the receipt of tissue modification [16].

The disadvantage of this method is the introduction of a modifying composition of glutaraldehyde into the composition, which undoubtedly leads to coagulation of a certain amount of protein during modification, a high concentration of protein in the composition, the use of water in large quantities and the duration of the modification reaction.

In connection with the above, it should be noted that the development of new technologies for modifying cotton fabrics based on natural protein modifiers is an urgent task for researchers in the field of chemical finishing of textile materials.

Materials and Methods

The experiments were carried out at the research laboratory of the Department of Chemical Technology of the Tashkent Institute of Textile and Light Industry. As an object for work, was chosen a calico fabric made of natural cotton with a density of 120 g/m^2. The air permeability of the object was 62.0 cm^3/cm^2*s at 20℃ atm, and the breaking load was 216 N.

The possibility of giving polyfunctionality to cotton fabrics using natural proteins is being considered in order to give cotton fabrics functionality and affinity for reactive dyes. As a protein modifying agent, water-soluble globular protein fractions obtained from leather processing waste were chosen. The process of modifying cotton fabric with aqueous protein solutions were carried out according to the following technology:

- Impregnation with a modifier;
- Spin until 90 - 100%;
- Drying at 105°C 10 min;
- Thermal fixation at 140°C 5 min.

The influence of the concentration of an aqueous solution of a globular protein and the impregnation temperature with a modifier on the physical and mechanical properties was studied. Experimental work was carried out at a concentration of the modifier from 1 to 15 g/l, and the impregnation temperatures were studied in the range of 25, 30, 35, 40℃ in an alkaline medium pH 8-9. The physical, chemical and operational properties of the original and modified samples were studied at the accredited Training and Certification Center operating in TITLI using the following devices: AUTOGRAPH AGS-N, flexible meter PT-2, MONSANT AV-6, AR-360SM Frazi. "Air permeability tester". To establish the multifunctionality of the processed samples, was used a Nicolet iS 50 Thermo Fisher Scientific Method IR-Fourier spectrometer.

Results

The dependence of the strength parameters of the samples on the impregnation temperature and the concentration of the modifier has an extreme character. When impregnating the fabric at a temperature of 25℃, the best performance is achieved with a solution containing 3 g/l of the modifier. An increase in the temperature mode of treatment from 30 to 35 ℃ with an increase in the concentration of collagen to 10 g/l, the strength of the fabric increases intensively, then with a further increase in concentration, this effect becomes insignificant.

A different nature of the dependence of the temperature mode at 40℃ and the amount of protein in the solution on strength. High strength of the samples is achieved with a protein content of 3-4 g/l. It should be noted that the high temperature mode of fabric processing contributes to a uniform increase in strength regardless of protein concentration.

Table 1

Influence of collagen concentration of tensile strength of cotton fabric

Impregnation temperature, ℃	Breaking load, N				
	Collagen concentration, g/l				
	3	4	5	10	15
Basic sample fabric	305/15,0*				
25	362,0/13,5	355, 9/13,0	350,0/13,0	346,3/10,0	346,0/9,0
30	367,0/13,0	371,4/13,6	373,0/13,7	382,0/10,0	350,0/9,0
35	372,0/13,6	370,8/13,7	376,0/13,4	383,0/11,4	356,0/10,0
40	378, 2/14,0	377,9/13,9	377,9/14,0	376,0/13,0	378,0/13,0

Note: * Numerator - tensile strength, N; denominator - elongation at break, %.

The treatment of the fabric at low temperature and the concentration of the elongation modifier at break is reduced to 24.4%. This pattern is observed with an increase in the amount of protein in the solution, regardless of the temperature regime. In contrast to low-temperature treatment in modified samples, elongation at rupture decreases slightly from the original fabric and ranges from 4.6 to 18.6%, depending on the concentration of modifier in the solution (Table 1).

As a result of the treatment of cotton fabric with a protein solution at 40°C, according to Table 1, shrinkage in samples treated with 3-5 g/l of collagen is reduced by 2 times. An increase in the protein concentration over 5 g/l in the modifying solution increases the stiffness of the fabric and negatively affects the whiteness.

Table 2

The effect of collagen concentration and impregnation temperature on the safety of the modifier in the fabric structure

Impregnation temperature, °C	Modifier concentration, g/l						
	1	2	3	4	5	10	15
25	2.4/1.0	2.4/1.0	2.7/1.4	2.7/1.6	2.6/1.6	2.6/1.8	2.7/1.8
30	2.4/1.0	2.5/1.0	2.8/1.8	2.8/1.5	2.7/1.4	2.7/1.7	2.7/1.8
35	2.6/1.3	2.7/1.4	2.8/1.7	2.9/1.9	2.7/1.4	2.6/1.5	2.5/1.8
40	2.5/0.9	2.5/0.9	2.6/0.7	2.7/0.5	2.4/1.3	2.6/1.0	2.6/1.6

Note: weight gain (%) / washability (%).

The quality of modification, the effect of the concentration of the modifier solution, the temperature of impregnation with the modifier on the gain and washability was studied and the protein content of the treated cotton fabric was determined (Table 2). The maximum gain of the modifier on the fabric is observed at its concentration in solution in the range from 3 to 4 g/l. It should be noted that with the temperature regime of impregnation equal to 40°C, the amount of weight gain on the fabric, depending on the concentration of the modifier in the impregnation bath, is from 0.1 to 0.3% less than with the temperature regime of 35°C. The washability of the modifier from the fabric surface in this mode is lower from 0.5 to 1.6%. A high gain and low washability of the modifier are achieved when its concentration in the impregnation bath is 3-4 g/l and the temperature regime is equal to 40°C (Fig.1).

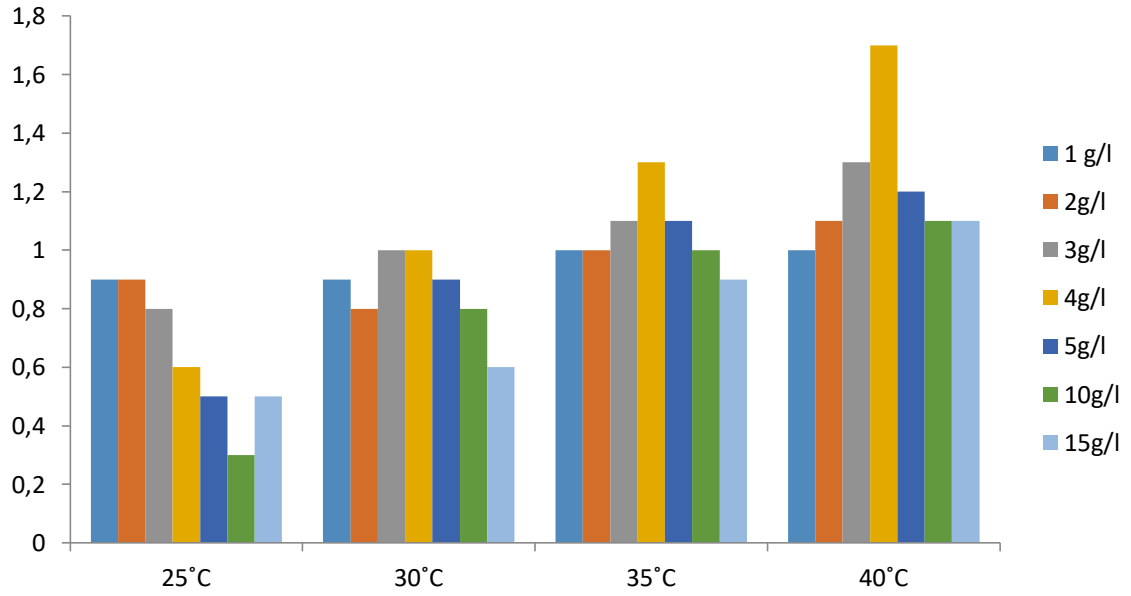

Fig.1. The effect of the concentration of the modifier solution the protein content of the treated cotton fabric was determined

Apparently, the relatively high temperature regime of impregnation contributes to better protein dissolution and thereby increases the diffusion of protein into the fabric structure. This is confirmed by the protein content in the modified sample determined by the Hanon K1100F automatic analyzer.

The IR-Fourier spectra, modifier films, samples of the original, as well as modified with protein solution were taken. Analysis of the results of infra-red spectroscopy of the original, modified cotton fabric and modifier film allowed us to draw the following conclusion: modification of cotton fabric with globular protein leads to an increase in hydrogen bonds of different nature, a decrease in the number of

characteristic groups $–CH_2–$ and $–CH_3$ modifier in the spectrum, which may be a consequence of protein attachment to cellulose.

Due to the increase in functional groups in the structure of modified cellulose, hydrogen bonds increase and a decrease in the –COO– ion can be caused by the chemical interaction of the ion with the hydroxyl groups of cellulose.

Conclusion

The study of the possibility of modifying cotton fabrics with water-soluble proteins, in this work the globular protein obtained from the waste of leather production, made it possible to improve the operational properties of both shrinkage and strength of cotton fabric, the presence of additional amino and other functional groups was also established, which is confirmed by IR- Fourier spectroscopy data .

According to the results of a series of experimental works for the modification of cotton fabrics, the following technology is proposed:

– The concentration of globular protein is 4 g/l.

– Duration of impregnation: - 60 s in a pH medium of 8÷9.

– The impregnation temperature is 40 ± 5°C.

– The degree of spin – 90%; drying – at 105°C 10 min.

– The duration of thermal fixation at 140°C is 8 minutes.

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