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ИССЛЕДОВАНИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ СТИРОЛ-АКРИЛОВЫХ И УРЕТАНОВЫХ ПОЛИМЕРОВ, ИСПОЛЬЗУЕМЫХ В ОТДЕЛКЕ ТЕКСТИЛЬНЫХ МАТЕРИАЛОВ

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Представлены результаты исследования физико-химических свойств стирол-акриловых и уретановых полимерных пленок, а также полимерных композиций на их основе с добавлением сшивающих агентов. Для формирования пленок были использованы водные дисперсии стирол-акриловых полимеров Лакритекс 309, Лакритекс 430, Лакритекс 640 и полиуретана Аквапол 14. В качестве сшивающих агентов применялись триглицидиловые эфиры полиоксипропилентриола и триметилолпропана – Лапроксид 703 и Лапроксид ТМП. Устойчивость полимерных пленок к гидролитической деструкции была оценена после обработки при температуре 20, 40 и 100 °С, к мыльно-содовому раствору – при 40 °С. Установлено, что наиболее стойкими к гидролизу и мыльно-содовой обработке являются пленки из стирол-акрилового полимера Лакритекс 309 и композиций Лакритекс 640 / Лапроксид 703, Аквапол 14 / Лапроксид ТМП, Аквапол 14 / Лапроксид 703. Также для исследуемых полимерных пленок были определены разрывная нагрузка при растяжении, относительное удлинение при разрыве, твердость и липкость поверхности. Найдено, что наибольшей прочностью и удлинением, нетвердой и нелипкой поверхностью характеризуются полимерные пленки на основе Лакритекс 309 и композиций Лакритекс 640 / Лапроксид 703, Аквапол 14 / Лапроксид 703. Введение Лапроксид ТМП в полиуретан Аквапол 14 обеспечивает создание твердой и неэластичной пленки. Для оценки влияния полимерных покрытий на жесткость текстильного материала была использована хлопчатобумажная ткань саржевого переплетения, которая используется для спецодежды. Полимеры и их композиции наносились на ткань из раствора концентрацией 150 г/л с последующей сушкой и термофиксацией. Для аппретированной хлопчатобумажной ткани были определены показатели жесткости и разрывной нагрузки. Жесткость аппретированной хлопчатобумажной ткани определена методом консоли. Установлено, что применение полиуретана Аквапол 14 и композиции на его основе, а также стирол-акриловых дисперсий Лакритекс 309 и Лакритекс 430 приведет к получению изделий с жестким грифом. Композиция на основе Лакритекс 640 с добавлением в качестве сшивателя Лапроксид 703 обеспечивает получение эластичного и прочного текстильного материала.

Ключевые слова: стирол-акриловая дисперсия, уретановая дисперсия, полимерная пленка, гидролиз, жесткость

INVESTIGATION OF PHYSICOCHEMICAL PROPERTIES OF STYRENE-ACRYLIC AND URETHANE POLYMERS USED IN FINISHING OF TEXTILE MATERIALS

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The results of the study of the physicochemical properties of styrene-acrylic and urethane polymer films, as well as polymer compositions based on the studied polymers with the addition of crosslinking agents are presented. Aqueous dispersions of styrene-acrylic polymers Lacritex 309, Lacritex 430, Lacritex 640 and polyurethane polymer Aquapol 14 were used for the formation of films. Triglycidyl esthers of polyoxypropylene triol and trimethylolpropane — Laproxid 703 and Laproxid TMP — were used as crosslinking agents. The stability of polymer films to hydrolytic destruction was evaluated after treatment at 20, 40 and 100 °C, and to the soap-soda treatment — at 40 °C. It was found that the most resistant to hydrolysis and soap-soda treatment are films from styrene-acrylic polymer Lacritex 309 and compositions Lacritex 640 / Laproxid 703, Aquapol 14 / Laproxid TMP, Aquapol 14 / Laproxid 703. The tensile load, elongation at break, stiffness and surface tackiness were also determined for the studied polymer films. It was found that polymer films based on Lacritex 309 and compositions Lacritex 640 / Laproxid 703, Aquapol 14 / Laproxid 703 are characterized by the greatest strength and elongation, non-rigid and non-tacky surface. Adding Laproxid TMP to polyurethane Aquapol 14 provides creation of a solid and inelastic film. To assess the effect of polymer coatings on the textile material rigidity, a cotton fabric with twill weave was used, which is used for special work clothes. Polymers and their compositions were applied to the fabric from a solution with a concentration of 150 g/l, followed by drying and heat setting. For dressed cotton fabric, rigidity and breaking load were determined. The rigidity of the treated cotton fabric was determined by the method of console. It has been established that the use of polyurethane Aquapol 14 and compositions based on it, as well as styrene-acrylic dispersions Lacritex 309 and Lacritex 430 will result in hard handle of textile materials. The composition based on Lacritex 640 with the addition of Laproxid 703 as a crosslinker provides an elastic and strong textile material.

Key words: styrene-acrylic dispersion, urethane dispersion, polymer film, hydrolysis, rigidity

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INTRODUCTION

The production of fabrics that have special properties is a priority development direction of world leaders in the textile industry. The use of polymer coatings is a versatile way to give textiles a sustainable functional finish. The creations of coatings on textile materials gives to fabric the additional properties and protect it from the effects of water, oil, fire, bacteria and microorganisms, dirt [1-6]. Coatings are also known that give a textile material a complex of properties [2, 7, 8]. It is expected that in future the textile coatings market will grow steadily [9]. Despite the development of polymer chemistry and the creation of new monomers, styrene-acrylic and urethane polymers are widely used for the final finishing of cotton textile materials for clothing due to high adhesive and cohesive strength and optical properties [10-13]. Polymer coatings should not deteriorate the hygienic and strength properties of a textile material, as well as be stable throughout the life of the products. Therefore, polymers and polymer compositions, which are used to create coatings on textile materials, must meet a number of requirements to the physicochemical properties. These properties primarily include the tensile strength, resistance to hydrolysis and soap-soda treatment, as well as elongation, stiffness, and tackiness, which are depend on the parameters of the spatial network of the polymer [14, 15]. Specified parameters for polymers and polymer compositions should be examined on free films, and then the properties of textile material after the application of polymer coating should be determined.

Studies have found that the polyurethane dispersion Aquapol 14 is capable of forming films with high physical and chemical properties only in composition with crosslinking agents of the trade mark Laproxid TMP and Laproxid 703. The obtained samples are characterized by a high degree of structuring and strength and can be used as polymer matrices for immobilization of additives with various purposes on the surface of textile material [16]. In [17], it was found that styrene-acrylic individual polymers Lacritex 309 and Lacritex 430 are capable of forming strong three-dimensional spatial structures of films. This fact allows to use of specified polymers without crosslinking agents. It was found that the use of styrene-acrylic dispersion Lacritex 640, which has a low index of structuring, requires the additional introduction of a crosslinker. It was established that the triglycidyl esther of polyoxypropylene triol of the trade mark Laproxide 703 has the most effective crosslinking effect.

Thus, compositions of styrene-acrylic polymers and polyurethanes with crosslinkers were developed with the aim of forming polymer coatings on textile materials [16-18]. The use of polymer binders will allow immobilization of many functional additives that cannot be added and fixed on the surface of textile materials by other methods, as well as increase the resistance of the obtained finish to wet treatments and dry cleaning [19, 20].

The long term effective use of products is the most important task when creating polymer coatings on textile materials. Hydrolysis is one of the most common types of chemical degradation of polymers for textile products. Furthermore, protective polymer films must be non-toxic, have elasticity, mechanical strength and transparency. Also a necessary requirement for the polymer composition is high adhesion to the fiber with a reduced tackiness of the polymer coating, which contributes to low dirt retention.

The creation of polymer coatings is a universal way of obtaining special types of final finishes on textile materials that are stable under the product operating conditions. The use of polymers allows applying to the textile material substances that cannot be fixed on it in another way. In this case, the polymer plays the role of a matrix in which any functional substances can be placed, such as flame retardants, light stabilizers, antimicrobial agents, etc.

The main task in the development of polymer compositions for special finishing of textile materials is the search for a film-forming polymer. The choice of polymer matrix should be based on the chemical and physical and mechanical properties of both the polymer film and the textile material with a polymer coating.

Thus, the goal of the work was to conduct a comparative study of the stability of styrene-acrylic and urethane polymer films to hydrolysis and soap-soda treatment, tensile strength, relative elongation at break, stiffness and tackiness with a view to using polymers under study as coatings for textile materials, and also to determine the influence of the films obtained on the rigidity and breaking load of textile material.

EXPERIMENTAL TECHNIQUE

The studied polymer films were formed from compositions of polymer dispersions with crosslinking agents in the amount of 6%.

The following water dispersions of polymers produced by Polymer-Lak LLC were used:

– Lacritex 309 – thermally crosslinkable copolymer of butyl acrylate and styrene (dry residue is 50%, pH = 4-7, particle size ≈ 0.2 μm, viscosity at 25 °C is 100-1000 mPa·s);

– Lacritex 430 – copolymer of acrylic acid ester and styrene (dry residue is 50%, pH = 7.5-8.5, particle size ≈ 0.1 μm, viscosity at 25 °C is 5000-15000 mPa·s);

– Lacritex 640 – acrylic copolymer, modified by the addition of an adhesion promoter (dry residue is 55-57%, pH = 2-3, particle size ≈ 0.2 μm, viscosity at 25 °C is not less than 5000 mPa·s);

– Aquapol 14 – aliphatic polyurethane (dry residue is 35%, pH = 7.36, particle size ≈ 0.1 μm, viscosity at 25 °C is 20.1 mPa·s).

Laproxid 703 and Laproxid TMP (Scientific-Production Enterprise Macromer LLC), which are triglycidyl esthers of polyoxypropylene triol and trimethylolpropane, were used as crosslinking agents.

Polymer films were formed on glass substrates, followed by drying at 80 °C for 60 min and heat treatment at 150 °C for 3 min. The thickness of the studied composite polymer films was 0.05 mm. The films had no visible defects.

The test of film resistance to hydrolytic degradation was carried out at a temperature of 20, 40 and 100 °C for 60 min, and to soap-soda treatment at 40 °C for 60 min. The stability of polymer films to hydrolysis (S_h) and soap-soda treatment (S_{sst}) was determined by the gravimetric method.

The determination of the tensile load of the films and relative elongation at break, as well as the breaking load of cotton fabric was carried out using a RT-250M machine.

The surface stiffness of polymer film was measured by determining the time to reduce the amplitude of oscillations of the pendulum according to König.

Determination of the tackiness of polymer films was carried out according to the FINAT method (Test Method Number 9), which consists of lowering the loop from the polymer onto a rigid plate of known area and measuring the force required to detach the loop from the substrate. The measurement was performed on an LT-1000 Loop Tack Tester (ChemInstruments, USA).

Cotton fabric diagonal art. 0-166 twill weave with a surface density of 230 g/cm^2 produced by Tekstil-Kontakt LLC was used in the work, which is used for special work clothes. The polymers and polymer compositions were applied to the fabric from a solution with a concentration of 150 g/l by impregnation with double immersion and pressing to a residual moisture content of 80%. Then the treated textile material was dried at a temperature of 100 °C and was subjected to a heat setting at 150 °C for 3 min.

Determination of the bending rigidity of treated cotton fabric was performed on a PT-2 device using the console method. Rigidity of the samples was measured separately for warp and weft directions. The rigidity coefficient was determined as the ratio of warp and weft rigidity values.

RESULTS AND DISCUSSION

The tendency of polymer films to hydrolysis is determined by the nature of the functional groups and bonds that included in the polymer. During the hydrolysis of the side functional groups, the chemical composition of the polymer changes. Hydrolysis of the bonds that make up the main molecular chain leads to a decrease in the molecular weight of the polymer. The results of determining the stability of the studied polymer films to aqueous treatments at different temperatures presents in Fig. 1.

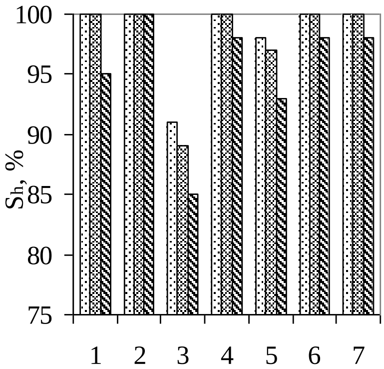

Fig. 1. Hydrolytic stability of styrene-acrylic and urethane polymer films at 20, 40 and 60 °C: 1 – Lacritex 430; 2 – Lacritex 309; 3 – Lacritex 640; 4 – Lacritex 640 / Laproxid 703; 5 – Aquapol 14; 6 – Aquapol 14 / Laproxid TMP; 7 – Aquapol 14 / Laproxid 703

Рис. 1. Гидролитическая стабильность стирол-акриловых и уретановых полимерных пленок при 20, 40 и 60 °С: 1 – Лакритекс 430; 2 – Лакритекс 309; 3 – Лакритекс 640; 4 – Лакритекс 640/Лапроксид 703; 5 – Аквапол 14; 6 – Аквапол 14/Лапроксид ТМП; 7 – Аквапол 14/Лапроксид 703

According to the data obtained, which characterize the process of dissolution of polymer films, it can be seen that the studied samples are subjected to varying degrees of hydrolytic destruction. The highest hydrolytic stability has a styrene-acrylic film Lacritex 309, which is not destroyed under the influence of water. The films of the individual polymer Lacritex 430 and compositions Lacritex 640/Laproxid 703, Aquapol 14/Laproxid TMP and Aquapol 14 Laproxid 703 are not destroyed at a temperatures of 20 and 40 °C, however, they lose some weight at a temperature of 100 °C. Individual films Lacritex 640 and Aquapol 14 have a relatively low indexes of hydrolytic stability, which decrease with increasing temperature.

A wide range of materials with a polymer finish or treated with a polymer composition cannot be washed, since this process can cause changes in the physicochemical and mechanical properties of polymers, primarily adhesive ones., The influence of standard detergents and mechanical action are added to the hydrolysis at elevated temperature during washing, which contributes to the destruction of polymers. Thus, it is important to study the stability of polymer films intended for the formation of coatings on textile materials to soap-soda treatment. The results of the study are shown in Fig. 2.

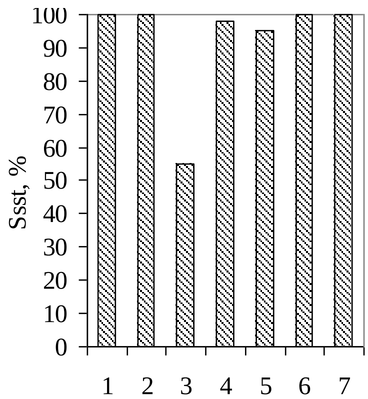

Fig. 2. Stability of styrene-acrylic and urethane polymer films to soap-soda treatment: 1 – Lacritex 430; 2 – Lacritex 309; 3 – Lacritex 640; 4 – Lacritex 640 / Laproxid 703; 5 – Aquapol 14; 6 – Aquapol 14 / Laproxid TMP; 7 – Aquapol 14 / Laproxid 703

Рис. 2. Устойчивость стирол-акриловых и уретановых полимерных пленок к мыльно-содовым обработкам: 1 – Лакритекс 430; 2 – Лакритекс 309; 3 – Лакритекс 640; 4 – Лакритекс 640/Лапроксид 703; 5 – Аквапол 14; 6 – Аквапол 14/Лапроксид ТМП; 7 – Аквапол 14/Лапроксид 703

According to the obtained results, individual films from Lacritex 430 and Lacritex 309 are not subject to destruction under the action of soap-soda treatment. The individual film Lacritex 640 is most destroyed, its stability under the action of soap-soda treatment is 55%. The addition of crosslinking agent Laproxid 703 increases this index to 98%. The individual polyurethane film Aquapol 14 has a high resistance to the action of soap-soda solution of 95%. Introduction of Laproxid TMP and Laproxid 703 crosslinkers results in 100% stability of the films obtained.

The results of the study of physical mechanical properties of styrene-acrylic and polyurethane films are given in Table 1.

Table 1

Effect of crosslinking agents on the physical mechanical properties of polymers

***Таблица 1.* Влияние сшивающих агентов на физико-механические свойства стирол-акриловых полимеров**

Composition	σ_b, MPa	ε_b, %	Kö, s	S, kPa
Lacritex 430	8	470	9	–
Lacritex 309	14	120	32	–
Lacritex 640	6	800	–	20
Lacritex 640/Laproxid 703	8	640	5	–
Aquapol 14	11	340	55	–
Aquapol 14/Laproxid TMP	12	200	80	–
Aquapol 14/Laproxid 703	12	180	91	–

Notes: σ_b, MPa – conditional tensile strength; ε_b, % – elongation at break; Kö, s – König stiffness; S, kPa – tackiness

Примечание: σ_b, МПа - условная прочность при растяжении; ε_b, % - удлинение при разрыве; Kö, s - жесткость по Кенигу; S, кПа - липкость

As shown in the Table 1, the individual styrene-acrylic films Lacritex 430 and Lacritex 309 have a high tensile strength of 8 and 14 MPa. The tackiness of both types of polymer films is absent, however, the index of stiffness and elongation at break are significantly different. For the Lacritex 430 film, the König stiffness is 9 s with an elongation at break of 470%, and for Lacritex 309 the stiffness is 32 s with an elongation at break of 120%. Also, the results obtained indicate a different effect of crosslinking agents on the change in the properties of Lacritex 640 based films. An individual styrene-acrylic polymer film has a tackiness of 20 kPa, its strength and elongation at break corresponds to 6 MPa and 800%, respectively. The use of Laproxid 703 eliminates the tackiness of the obtained composite, the stiffness of the sample is equal to 5 s. In addition, there is a decrease in elongation at break from 800 to 640% with constant tensile strength. The data in Table 1 shows the results of the study of films obtained on the basis of polyurethane dispersions Aquapol 14. The adding of Laproxid 703 and Laproxid TMP crosslinking agents increase the strength of composite films from 11 to 12 MPa and their stiffness to 80-91 s. At the same time, a decrease in elongation at break by 1.7-1.9 times compared with an individual film is also observed. It should be noted that Aquapol 14 based polymer films are not tacky.

The effect of polymer coatings on the physical and mechanical properties of cotton fabric after treatment with styrene-acrylic and urethane polymer solutions and polymer compositions with cross linkers was studied at the next stage of the work (Table 2).

Table 2

Effect of polymer coating on the physical and mechanical properties of cotton fabric

***Таблица 2.* Влияние полимерного покрытия на физико-механические свойства хлопчатобумажной ткани**

Composition	E_I, μN·cm^2		K_{EI}	Breaking load, H
	warp	weft		
No treatment	6133	3015	2.03	569
Lacritex 430	12997	3319	3.92	951
Lacritex 309	10514	3157	3.33	883
Lacritex 640	6691	3132	2.14	680
Lacritex 640/Laproxid 703	7154	3273	2.19	722
Aquapol 14	19417	4822	4.03	1012
Aquapol 14/Laproxid TMP	19854	5212	3.81	1165
Aquapol 14/Laproxid 703	20072	5414	3.71	1145

Notes: E_I, μN·cm^2 – bending rigidity; K_{EI} – rigidity coefficient

Примечание: E_I, мкН • см^2 - жесткость при изгибе; K_{EI} - коэффициент жесткости

The results found show that the studied polymer compositions increase the rigidity and strength of cotton textile material after treatment. In the process of finishing the fabric, fine-particle polymers penetrate deep into the inter fiber space and form spatially crosslinked structures after drying and heat treatment. Polymer structures impart elastic properties to the obtained polymer-fiber composite, as evidenced by the increasing rigidity of the textile material. Impregnation with polymers increases the tensile strength of textile material. Moreover, the obtained indices of the breaking load of the cotton fabric correlate with the indices of rigidity.

Among individual styrene-acrylic polymers, Lacritex 430 and Lacritex 309 impart the greatest rigidity and strength to the fabric, and Lacritex 640 affects the studied physical and mechanical properties least. Addition of Laproxid 703 crosslinker to Lacritex 640 polymer increases the rigidity and tensile strength of the textile material, however, the relevant indicators remains lower than in case of use Lacritex 430 and Lacritex 309. Coatings based on a polyurethane dispersion Aquapol 14 are characterized by high rigidity and breaking load of the treated cotton fabric. Addition of Laproxid TMP and Laproxid 703 crosslinkers to the finishing composition increases the rigidity of fabric due to the formation of structures with a high degree of crosslinking.

Based on the foregoing, we can conclude that polyurethane Aquapol 14 and compositions based on it, as well as styrene-acrylic dispersions Lacritex 309 and Lacritex 430 are not advisable to use for finishing textile materials. The use of these polymers will result in products with a hard handle. The formation of the elastic three-dimensional spatial structure of the polymer film is provided by a composition based on styrene-acrylic polymer Lacritex 640 with the addition of the glycidyl esther of the trade mark Laproxid 703 as a crosslinker.

CONCLUSIONS

A comparative analysis of the physicochemical characteristics of polymer films based on styrene-acrylic and urethane polymers was carried out, and the effect of coatings based on the studied polymers on the cotton fabric rigidity was determined.

The films based on the compositions Lacritex 640/Laproxid 703 and Aquapol 14/Laproxid TMP are characterized by the best indicators according to the results of resistance to hydrolysis and soap-soda treatment, strength, elongation, stiffness and tackiness. However, when studying the effect of the specified polymers and polymer compositions on the rigidity and breaking load of cotton fabric, it was established that the use of the composition Aquapol 14/Laproxid TMP leads to a deterioration of the elastic properties of textile material.

Thus, the composition based on styrene-acrylic polymer Lacritex 640 and crosslinker Laproxid 703 can be recommended in order to form polymer matrices for immobilization of functional additives on the surface of a cotton textile material intended for clothing. Styrene acrylic polymer Lacritex 309 and composition based on polyurethane Aquapol 14 and crosslinker Laproxid TMP can be used to create coatings on textile materials for which rigidity is not the main property.

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