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Перспективним способом захисту забарвлень від дії світла є застосування УФ-адсорберів, включених у склад полімерної плівки, оскільки нанесення полімеру на поверхню текстильного матеріалу є універсальним способом надання текстильним матеріалам необхідних спеціальних властивостей.

Оптичні характеристики є найважливішими показниками придатності полімерних плівок для використання в заключній обробці забарвлених текстильних матеріалів. Мета роботи полягала у спектрофотометричному дослідженні оптичних характеристик полімерних плівок на основі стирол-акрилового полімеру з додаванням зшиваючого агенту та УФ-адсорберів для використання в заключній обробці текстильних матеріалів з метою захисту забарвлень.

Полімер-матриця представляє собою водну дисперсію термозшиваючого стирол-акрилового співполімеру. У якості зшиваючого агента використано частково етерифіковану меламінову смолу, у якості УФ-адсорберів — 2,4-дигідроксібензофенон, 3,6-дигідроксіацетофенон, феніловий ефір саліцилової кислоти, п-метоксикоричну кислоту.

Оптичні характеристики полімерних плівок визначались за допомогою спектрофотометра СФ-56 шляхом побудови спектральних кривих поглинання та пропускання в діапазоні 200—800 нм.

На основі аналізу спектральних кривих поглинання полімерних плівок визначено УФ-адсорбери, що забезпечують формування безбарвних полімерних плівок. Спектральні криві пропускання досліджуваних полімерних плівок у видимій частині спектру дозволили встановити вплив УФ-адсорберів на їх прозорість, а в УФ частині спектру — на пропускну здатність по відношенню до УФ променів. Встановлені речовини, що сприяють зниженню пропускання УФ випромінювання полімерними плівками та забезпечать їх світлозахисні властивості.

На основі комплексного аналізу результатів дослідження оптичних характеристик полімерних плівок рекомендовано композиційний склад на основі стирол-акрилового полімеру, зишваючого агента та УФ-адсорбера. Знайдений композиційний склад придатний для використання в процесі заключної обробки забарвленого текстильного матеріалу з метою формування безбарвного, прозорого покриття зі світлозахисними властивостями

Ключові слова: стирол-акриловий полімер, зшиваючий агент, УФ-адсорбери, полімерна плів-ка, поглинання, пропускання, світлозахист

1. Introduction

Among the properties provided to textile materials during final processing, ensuring of lightfastness of colors is an important condition for production of high-quality fabrics, especially the summer range of fabrics.

Use of ultraviolet (UV) adsorbers is known in light stabilization of textile material colors. The mechanism of their action consists in absorbing UV radiation of the light flux  $\frac{1}{2}$ 

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# STUDYING THE INFLUENCE OF UV ADSORBERS ON OPTICAL CHARACTERISTICS OF LIGHT-PROTECTIVE POLYMER FILMS FOR TEXTILE MATERIALS

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and preventing transition of atoms in dye molecules to the excited state [1].

Derivatives of benzophenone, benzotriazole phenol, phenyl esters, substituted cinnamic acids and nickel chelates are used as UV adsorbers in technologies of manufacture of protective clothing that blocks harmful effect of UV radiation on human skin [2, 3]. These substances are applied on the textile material by plussing and spinning after dyeing. The compounds used to enhance lightfastness of textile material

colors should be non-toxic, have no effect on the initial coloration of the fabric and possess chemical bondability with the textile material.

Application of a polymeric composition on the surface of a textile material with inclusion of substances having diverse functional purposes (antibacterial, fire retardant, water repelling, etc.) in composition of substances is a universal way to provide the textile materials with required special properties [4, 5]. To this end, wide use of styrene-acrylic polymers forming the base of compositions due to high optical, physical and mechanical properties is known [6, 7].

Urgency of this study is determined by the necessity of creating light-protective polymer coatings for colored textile materials and the study of optical characteristics of polymer films obtained by adding a cross-linking agent and UV adsorbers to the polymer matrix.

### 2. Literature review and problem statement

Optical characteristics are among the most important indicators of suitability of polymer films for their use in final processing of colored textile materials. These polymer materials should be colorless and transparent. If all rays of the visible portion of spectrum completely pass through a transparent body in interaction of light with a body, then the object is perceived as colorless. In the case when the body selectively absorbs some rays of the visible portion of the spectrum and the rest pass through or are reflected from the body, it is perceived as colored [8]. Thus, transparent polymer film passes all or almost all rays visible to the eye without absorption and scatter.

Most films produced of polymers that do not have multiple links are transparent, that is, they do not absorb light in UV and visible portions of the spectrum. Energy of excitation of electron shells is high for saturated compounds which promotes absorption in the far (vacuum) UV portion of the spectrum with a wavelength  $\lambda$ <150 nm which do not affect the human visual apparatus. These include polymers in which macromolecules have tens and hundreds of thousands of saturated C-C and C-H  $\sigma$ -links. Films made of polymers containing unsaturated links of various types selectively absorb rays in the near-UV and visible spectra and appear to be colored. This absorption is determined by presence of easily exciting  $\sigma$ -electrons in unsaturated links [8].

Transparency is the main characteristic that determines suitability of polymer films for the use in final processing of textile materials after dyeing. It depends on transparency how well the textile material color will be seen through the polymer film which can have significant and low transparency [8].

The value of coefficient of total transmission cannot completely characterize the polymer film in terms of transparency which is connected with asymmetry of scatter [8]. Turbidity of a polymer film is characterized by coefficient of directed transmission or coefficient of scattered transmission. Scatter common for surface and inhomogeneities within the material is most commonly observed in polymers. When film is formed, composition turbidity often occurs because the increase in scatter is associated with the formation of microcracks. For example, polymer films based on polytetrafluoroethylene do not absorb rays in the UV and visible spectra but are visually opaque and turbid when they are thicker than ten microns [15].

The polymers that do not have structural groups capable of exhibiting significant fluctuations are most transparent. These include polyolefins [10], polyvinyl chloride [11], homo- and copolymers of fluoro-olefins [12]. At the same time, a polymer of polyethylene terephthalate with complex chromophore groups absorbs a significant portion of UV light because of presence of a complex chromophore in a macromolecule in a form of a benzene ring with carbonyl groups attached to it in a preposition [13].

Polymers of fluoro-alkyl-methacrylates have high optical characteristics and the significant interest payed to them is explained by high transparency due to low light losses. It is thanks to this property that these polymers are used as shell components in the production of optical fibers [14].

However, polymers studied in [11–20] do not have practical application in the technologies of final processing of textile materials. In addition, the procedure of conducting the study is one of shortcomings of these studies. For example, optical characteristics were established in these studies using single-wavelength instruments which is noneffective in the study of polymer compositions with absorbing components.

Polyvinyl alcohol is a quite commonly used optical material. For example, integral transmission coefficient,  $\tau$ , is 89 % and 88 % at specimen thickness of 0.1 and 2.0 mm, respectively. However, the essential disadvantage of polymer films based on polyvinyl alcohol is low atmospheric resistance of the latter. A decrease in transparency and strong yellowing of the polymer is observed under the influence of UV and radiation [15].

Acrylic polymers have some of the best optical characteristics in terms of transparency of polymer films and are characterized by translucence in a wide range including UV, visible and a part of the near-infrared spectra. Translucence of polyacrylates is 92 % in the wavelength range  $\lambda = 360-2,000$  nm and 100 % in the visible portion of the spectrum [16]. This determines the widespread use of acrylates in the processes of dyeing and final processing of colored textile materials [7, 17]. For example, a 10  $\mu m$  thick polymer film of polymethylmethacrylate passes practically all UV rays in the range 250–300 nm. Even for a 2 mm thick specimen, the short-wave transmission cut-off is about 260 nm [18].

The variety of acrylates makes it possible to select a matrix with definite optical (refractive index, transparency) and physical-mechanical (strength, hardness) characteristics. Previous studies have shown promising use of acrylates in the process of final processing [19, 20]. However, it was found in [21] that individual acrylic films have the highest transmittance of approximately 95 %. When a cross-linking agent is added, transparency of the acrylate-based films is reduced and, accordingly, transmittance decreases to 85 %. Thus, in order to develop a polymer composition based on acrylic polymers and a cross-linking agent, it is advisable to introduce additional compatibilizers to rise transmission coefficient and transparency of the polymer film.

For example, methacrylate-based polymers with addition of tetraphenyl benzidine were synthesized in [22]. The presence of chromophore groups of the latter has led to formation of polymer films with absorption bands in the range of 450–550 nm. The main disadvantage of these films was the lack of transparency.

Films of methacrylic polymer with azochromophores in the side chain were studied in [23]. The chromophore groups have enabled absorption at 470 nm which corresponded to absorption in the visible spectrum and the formed films were non-transparent.

It was found in [24] that in the spectrum of absorption of polymer films in which amino-acobenzene was used as a chromophore group, absorption band was shifted bathochromically compared to the polymer films which contained azobenzene.

Critical analysis of the performed studies has shown that the type of chromophore in the composition of acrylic polymers directly affects the absorption wavelength and, accordingly, transparency of the polymer film. Thus, the polymer films which contain esters of acrylic or carboxylic acids with a carbonyl chromophore, absorb light at the boundary of the vacuum UV region (about 200 nm). Polymer films containing components with carboxylic chromophore or benzene rings and ethers have higher transparency in the UV region (200–400 nm) [25].

Knitted wear made of various raw materials is becoming increasingly widespread. Its production exceeds production of fabrics 1.3 times this year and further production growth is expected [26, 27]. Besides, cotton knitted fabric is an indispensable material for the summer wear for which color protection against light is an issue.

Color fastness of active dyes was studied in [28] but no methods for light protection of colored textile materials were offered.

Influence of UV adsorbers on protective ability of textile made of various raw materials against harmful effects of UV radiation on human skin was studied in [29, 30]. However, influence of UV radiation on the change of color of the studied textile materials has not been studied in these works.

UV adsorbers have been found in [31] to improve light fastness of dyed fabric without affecting its original color. Studies were carried out using only protein-based textile materials dyed with natural dyes.

Water-soluble and insoluble substances were used in [32, 33] as UV adsorbers. They were applied to the textile material after dyeing [32] and printing [33] with active dyes. But it should be noted that light fastness of the light-protective treatment before washing was not tested in the above-mentioned studies.

2,4-dihydroxybenzofenone, 3,6-dihydroxyacetophenone, phenyl ether of salicylic acid and p-methoxy cinnamic acid were selected in previous studies [34] as active UV dye adsorbers for the color stabilization of the dyed knitted cotton fabric.

The selected substances were applied to the textile material by successive impregnation, spinning, drying and thermal fixation. It has been established that color of the dyed textile material was least altered by p-metoxicuric acid and phenyl ether of salicylic acid and most notably by 2,4-dihydroxybenzophenone and 3,6-dihydroxyacetophenone. It has also been found that the proposed treatments were unstable in washing since the studied preparations taken for light stabilization of paints had no functional groups to form covalent links with cellulose fibers. It was suggested that the studied UV adsorbers on cotton knitted fabric could be fixed by their adding as components of the polymer coating.

Taking into consideration continuous growth of world production of knitted fabrics and products, the technologies aimed at improvement of performance of textile materials, in particular light fastness of colors, are promising. Analysis of studies [28–33] indicates the lack of targeted and systematic

studies concerning development of technologies for providing high light fastness of textiles.

Use of UV adsorbers is a promising method for increasing light fastness of colors. In this case, the resulting light-protective effect must be resistant to repeated washing. This problem can be solved by introducing UV adsorbers into a polymer composition followed by application on the textile material. It is expedient to use styrene-acrylic dispersion as a polymer matrix which will ensure formation of a coating resistant to physical and mechanical action on the surface of the treated textile material. However, the polymer compositions for final treatment of colored textile materials should be colorless and transparent. This can be determined by studying optical properties of the obtained polymer films.

Thus, analysis of published data allows us to conclude that the problem of development of polymer compositions based on styrene-acrylic polymer with addition of UV adsorbers to provide light fastness of colors for cotton knitwear was not solved so far. In this case, study of optical properties of composite polymer films is necessary to solve the problem of producing high-quality textile materials with a high light fastness.

### 3. The aim and objectives of the study

The study objective was to establish an effective composition based on a styrene-acrylic polymer with addition of a cross-linking agent and UV adsorbers to protect color of textile materials by spectrophotometric study of optical characteristics of the formed polymer films.

To achieve the objective, the following tasks were set:

- determine color of composite polymer films by analyzing spectral curves of absorption of polymer films;
- study the effect of a cross-linking agent and UV adsorbers on transparency of polymer films using transmission spectra and establish effective UV adsorbers for protection of textile material color against photodegradation;
- based on a comprehensive analysis of optical characteristics of polymer films, establish suitability of the studied compositions for their use in the process of final light-protective treatment of colored textile materials.

# 4. Materials and methods used in the study of optical characteristics of composite polymer films

Aqueous dispersion of thermally linking styrene-acrylic copolymer (dry residue: 45 %, pH=7–9, viscosity at 20 °C:  $<\!500\,\mathrm{mPa}\cdot\!\mathrm{s}$ ) was used as a study object and a partially esterified melamine resin was used as a cross-linking agent. Structural formulas of the polymer monomer links and the cross-linking agent are shown in Fig. 1, 2.

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Fig. 1. Styrene-acrylic polymer

Fig. 2. Partially etherified melamine resin: R=-H,  $-CH_2OH$ ,  $-CH_2OCH_3$ 

Structure of the selected UV adsorbers is given in Table 1.

Table 1

# Characteristics of UV adsorbers

Name Formula 2.4-dihydroxybenzophenone (DHBP) ΟН 3.6-digidroxiacetophenone (DHAP) salicylic acid phenyl ester (SAP) ΉO H<sub>3</sub>CO p-methoxy cinnamic acid (PMCA)

The styrene-acrylic polymer composition contains 4 wt. % cross-linking agent. UV adsorbers in a form of aqueous-ethanolic solutions were introduced into polymeric composition in an amount of 2 wt. % in a ratio of 9:1.

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

Color and transparency of the polymer films were determined using SF-56 spectrophotometer and constructing spectral absorption and transmission curves within 200–800 nm. Absorption and transmission rates of polymer films have been determined relative to air.

Color of polymer films was determined by finding absorbance by the light absorption index *A*:

$$A = \ln \frac{I_0}{I},\tag{1}$$

where  $I_0$  and I are intensities of the light flux before and after passing through the film, respectively.

Transparency of investigated polymeric films was evaluated by the coefficient of transmission  $\tau$  which is related to the light absorption index A as the following ratio [11]:

$$A = \ln \frac{100}{\tau}.\tag{2}$$

Measurements were carried out with two repetitions and the data obtained were averaged.

# 5. Investigation of optical characteristics of composite polymer films

# 5. 1. Investigation of absorption spectra of composite polymer films

In order to determine effect of the cross-linking agent on optical characteristics of styrene-acrylic polymer, spectral absorption curves of a film of styrene-acrylic polymer and in a composition with the cross-linking agent were built (Fig. 3, a).

Film 1 of the initial polymer-matrix (styrene-acrylic polymer) is characterized by maximum absorption at 350 nm which corresponds to the UV spectrum portion while light absorption is 0.21. In the spectral curve of a film of styrene-acrylic polymer with a cross-linking agent (film 2), a 70 nm hypochromic displacement with a slight hyperchromic effect occurs. Maximum absorption is 0.26 at wavelength of 270 nm. Absorption for the given sample of polymer film also occurs in the near UV spectrum region. The absorption band is even and there is no vibrational structure in it. By its intensity, it can be attributed to  $n \rightarrow \pi^*$  transitions which is characteristic of complex chromophore, derivatives of six-membered heterocycles which include melamine.

Fig. 3, b shows spectral absorption curves of composite polymer films which, in addition to the styrene-acrylic polymer and the cross-linking agent, contain additives of UV adsorbers.

Multivariate analysis of spectral absorption curves (Fig. 3) shows that absorption bands are characterized by maxima in the range 290–390 nm for all films, that is, absorption occurs in the near UV and the visible spectrum portion. Presence of absorption bands in the indicated spectrum region indicates cross-linking of carboxylic groups and allows us to attribute the investigated films to related structures.

As for the film containing DHBP (film 3), the absorption band is heterogeneous and characterized by two peaks at 390 and 540 nm. In addition, in comparison with the initial sample (film 2), a shift of the maximum absorption up to a maximum wavelength of 390 nm is observed. This phenomenon, together with the presence of a second maximum at  $\lambda$ =540 nm, causes yellowing of the sample. Strips with negative values of light absorption in the curve 3 can indicate presence of areas with undistributed DHBP in the polymer film.

Thus, a significant bathochromic shift of the absorption maximum from the near-UV region occurs in the visible spectrum portion corresponding to  $\pi \rightarrow \pi^*$  electron transitions. Convergence of  $\pi$ - and  $\pi^*$ -orbital levels and appearance of n-orbital occurs as a result of introduction of a DHAP polymeric composition having a nonseparated pair of electrons. Melamine and DHBP act as chromophores with carbonyl groups which form linked complexes as a

result of cross-linking with the styrene-acrylic polymer. It also helps to shift the absorption band in the visible spectrum region which causes deepening of the polymer color. A hypochromic shift of maximum absorption is also observed. Maximum light absorption in polymer films is 0.18 at 390 nm.

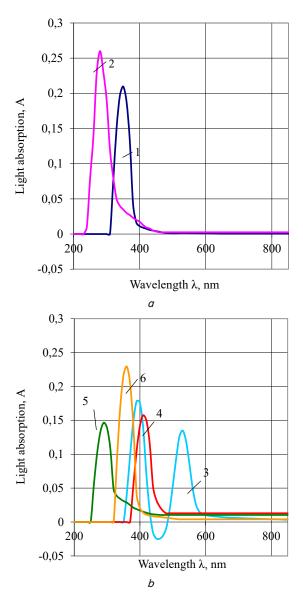


Fig. 3. Spectral absorption curves of composite polymer films: styrene-acrylic polymer (1); styrene-acrylic polymer+cross-linking agent (2); styrene-acrylic dispersion+cross-linking agent+DHBP (3); styrene-acrylic polymer+cross-linking agent+DHAP (4); styrene-acrylic polymer+cross-linking agent+SAP (5); styrene-acrylic polymer+cross-linking agent+PMCA (6)

The spectral curves of absorption in composite polymer films are characterized by clear peaks and have common features when DHAP (film 4), SAP (film 5) and PMCA (film 6) are added.

Compared to the original sample (film 2), a bathochromic displacement of maximum absorption up to 410 nm causing yellow-green coloring of the sample is observed when DHAP is added to the composition (film 4). Adding of SAP (film 5) causes a small (10 nm) shift of maximum

absorption in the polymer film and the sample is colorless. Introduction of PMCA (film 6) leads to a slightly larger displacement of absorption maximum (from 270 to 360 nm) and does not cause coloration of the polymer.

Hypochromic shift of absorption maxima is observed in polymer films with addition of UV adsorbers. Addition of SAP reduces absorption rate most of all and light absorption in the polymer decreases from 0.26 to 0.15. Introduction of PMCA slightly changes optical density index resulting in 0.23. With addition of DHBP and DHAP, absorption maxima fall to 0.18 and 0.16, respectively.

# 5. 2. Investigation of the transmission spectra of composite polymer films

Transparency of polymeric films under study was evaluated by constructing dependences of transmission coefficients  $\tau$  on wavelength  $\lambda$ . The obtained results are presented in Fig. 4.

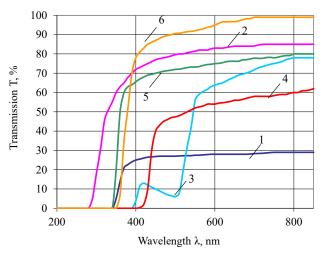


Fig. 4. Spectral curves of transmission in composite polymer films: styrene-acrylic polymer (1); styrene-acrylic polymer+cross-linking agent (2); styrene-acrylic dispersion+cross-linking agent+DHBP (3); styrene-acrylic polymer+cross-linking agent+DHAP (4); styrene-acrylic polymer+cross-linking agent+SAP (5); styrene-acrylic polymer+cross-linking agent+PMCA (6)

The spectral transmission curves of the studied composite polymer films (Fig. 4) have common features. In the section where light transmission is zero, a high-frequency boundary of the spectral region is established. Further, transmission begins to increase and reaches maximum values for each sample in the region of 800–850 nm.

The polymeric film 1 formed from the polymer matrix has the lowest light transmission (about 18 %) in the near-UV region ( $\lambda$ =200–400 nm) and 21–28 % in the visible spectrum portion ( $\lambda$ =400–760 nm). This explains the turbidity of a film of this styrene-acrylic polymer.

In film 2, transmission coefficient is 68 and 68-85% for UV and visible spectrum portion, respectively. Thus, the composite film passes radiation in the studied spectrum portion, that is, the film is transparent.

Addition of DHBP (film 3), DHAP (film 4) and SAP (film 5) to the composition reduces light transmission of polymer films to 60–80 % in the studied wave range. PMCA (film 6) raises light transmission of the formed polymer film to 99 % and accordingly its transparency.

### Discussion of the results obtained in the study of optical characteristics of composite polymer films

The styrene-acrylic polymer features presence of long flexible sections of molecules separated by carboxyl groups which contribute to a strong local interaction between chains resulting in formation of linear structures (Fig. 5). Presence of carboxyl groups of methacrylic acid in the acrylic copolymer provides formation of an elastic polymer structure.

When self-linking in styrene-acrylic polymers takes place (Fig. 5), not all carboxyl groups react. Therefore, admixtures of free acid monomers are deliberately added in industrial production of styrene-acrylic polymers to achieve maximum degree of interaction of the polymer with cross-linking agents.

In order to increase the degree of cross-linking in the styrene-acrylic polymer, a cross-linking agent (partially etherified melamine resin) was added (Fig. 3, film 2). In this case, interaction between the carboxyl groups of styrene-acrylic polymer and methylolene groups of the cross-linking agent is formed and a strong grid-type structure arises [35] (Fig. 6).

Introduction of cross-linking agents into the polymer composition results in a change of optical characteristics of the films being formed, namely, in a growth of transparency. Growth of the coefficient of light transmission of a polymer indicates formation of a three-dimensional spatially "stitched" structure. Analysis of the spectral transmission curves for films 1 and 2 (Fig. 4) allows us to conclude that introduction of a melamine derivative as a cross-linking agent to the styrene-acrylic polymer results in formation of a strong spatial polymer mesh. This ensures formation of a polymer coating resistant to action of external factors, primarily to hydrolysis.

Fig. 5. Scheme of self-linking in styrene-acrylic polymer

In addition, the results obtained (Fig. 3) show that the polymer films formed from the styrene-acrylic polymer and the styrene-acrylic polymer composition and the melamine resin derivative as a cross-linking agent are colorless. At the same time, optical density of the composite polymer (Fig. 3, film 2) is higher (0.26) than that of the polymer matrix film (0.21).

Polymer films with UV adsorbers are characterized by absorption bands with maxima in the range 290-410 nm, that is, in the near UV and visible spectrum portion which confirms their property of light absorption in this range. Addition of UV adsorbers to polymeric compositions results in a deeper color and appearance of color in the polymer films in the case of use of DHBP, DHAP and SAP. Among the UV adsorbers under study, addition of PMCA does not cause appearance of polymer

coloring. All investigated UV adsorbers help reduce the absorption maxima in polymer samples (hypochromic effect).

Fig. 6. Scheme of formation of a spatial structure of styreneacrylic polymer and cross-linking agent

Analysis of the transmission spectra of polymer films (Fig. 4) in the UV spectrum portion ( $\lambda$ =200–400 nm) makes it possible to draw a conclusion concerning protection of the formed coatings against the degrading effect of UV radiation on dyes. Analysis of these spectra in the visible spectrum portion ( $\lambda$ =400–850 nm) indicates the degree of transparency of the investigated polymer films.

For example, a polymer matrix film (Fig. 4, film 1) is characterized by light transmission in a range of  $\lambda$ =350–850 nm at a level of 28 %. This indicates the fact that this film does not interfere with the action of UV rays on the dye and is opaque. Addition of a cross-linking agent shifts the marginal minimum of the spectral curve of transmission in the film 2 into the far UV spectrum region which leads to an increase in the coefficient of light transmission in the UV region and in the visible spectrum region to 67–80 %. Thus, addition of a cross-linking agent facilitates formation of a highly transparent polymeric film.

When applied in the final processing of textile materials, polymer compositions should create a transparent coating, that is, have a high transmission in the visible spectrum region.

Light transmission of a polymer film produced solely from a polymer has the lowest values (21–28 %). Introduction of a cross-linking melamine agent (film 2) promotes a rapid increase in light transmission of the polymer both in the UV and the visible spectrum regions of radiation up to 72 % and 85 %, respectively. The best transmission of up to 99 % was demonstrated by a film with PMCA. Addition of other UV adsorbers studied allows one to obtain polymer films with light transmission of 60-80 %.

Scatter of light by supramolecular formations causes lack of transparency in composite polymer films which is brought about by their higher optical heterogeneity: when the film is formed, loose packing of macromolecules takes place. In this case, the main contribution to light scatter is made by the scatter on spheroliths the size of which is of the same order as the wavelength of the visible light. Therefore, transparency of polymer films is limited not only by absorption and transmission of light but also by its scatter from surface to the film body.

It is known that the process of photodegradation of dyes occurs under the influence of UV radiation [1]. Thus, this polymer will not be able to prevent the destructive effects of light, namely, UV radiation, in relation to dyes. The UV protection effect of UV adsorbers consists in prevention of UV radiation passage.

Films produced from a polymer matrix (Fig. 4, film 1) and a polymer composition with a cross-linking agent (Fig. 4, film 2) are characterized by high transmission coefficients in the UV region. In view of this, it can be predicted that the said polymer films will not exhibit light-protective properties in relation to the color of textile materials.

The UV adsorbers under study contribute to lowering of light transmission over entire wavelength range. The film with DHAP (Fig. 4, film 4) has the highest ability of protection against UV radiation. This film does not transmit light in the UV spectrum region and threshold bandwidth is 410 nm in this case. Besides, high light-protective properties in the UV region are also intrinsic to the polymer film with addition of DHBP (Fig. 4, film 3) with boundary transmission region of 400 nm. The use of SAP and PMCA (Fig. 4, films 5 and 6) reduces light transmission in the UV region compared to the composite film 2 but does not exclude it completely. It can be assumed that the use of DHAP and DHBP in the composition will contribute to formation of polymeric films with light-protective properties on the surface of textile materials.

The obtained indicators of light absorption and light transmission characterize optical properties of polymer films of just the studied thickness which is the main limitation of this study.

In the future, combination of a spectrophotometric method of investigating optical characteristics of polymer films with a refractometric one is promising in finding a relationship between light absorption and refractive index of polymer films for determination of the optical distortion index. In addition, it is necessary to study the effect of final treatment of cotton knitted fabric with polymeric composi-

tions based on styrene-acrylic polymer, cross-linking agent and UV adsorbers on brightness of dyed textile materials and verify the obtained lightfastness treatment to washing.

### 7. Conclusions

- 1. Analysis of absorption spectra of polymer films has shown that addition of a cross-linking agent to the polymer matrix contributes to formation of a colorless polymer film with a strong spatial structure as evidenced by growth and hypochromic shift of maximum absorption. Of all UV adsorbers studied, DHBP and DHAP contribute to formation of colored polymer films. When adding SAP and PMCA, colorless polymer films are formed as indicated by location of absorption maxima in the UV portion of the spectrum.
- 2. Spectral curves of transmission of the investigated polymer films in the visible portion of the spectrum indicate that the cross-linking agent promotes formation of a transparent polymer film with light transmission of 68–85 %. In this case, the polymer film without additives has the lowest transmission values of 21–28 %. Introduction of DHBP, DHAP and SAP to the composition reduces transmission of formed polymeric films to 60–80 %. Addition of PMCA increases light transmission of the formed polymer film to 99 % and hence its transparency.

Analysis of spectral curves of transmission in the UV spectrum region has shown that films of the polymer without additives and of a composition with cross-linking agent pass UV rays, hence will not protect color of the textile material against photodegradation. The UV adsorbers under study in compositions contribute to reduction of UV radiation transmission in polymeric films which will provide them with light protection properties. By their efficiency, UV adsorbers can be arranged as follows: DHAP>DHBP>PMCA>SAP.

3. Comprehensive analysis of the results obtained in the study of optical characteristics of polymer films shows that a composition based on styrene-acrylic polymer, cross-linking agent and PMCA can be recommended for use in final processing of textile materials. This polymeric composition will ensure formation of a colorless and transparent coating on the surface of a textile material providing it with light-protective properties.

## References

- The photofading mechanism of commercial reactive dyes on cotton / Batchelor S. N., Carr D., Coleman C. E., Fairclough L., Jarvis A. //
  Dyes and Pigments. 2003. Vol. 59, Issue 3. P. 269–275. doi: https://doi.org/10.1016/s0143-7208(03)00118-9
- 2. Das B. R. UV Radiation Protective Clothing // The Open Textile Journal. 2010. Vol. 3. P. 14–21.
- 3. Cristea D., Vilarem G. Improving light fastness of natural dyes on cotton yarn // Dyes and Pigments. 2006. Vol. 70, Issue 3. P. 238–245. doi: https://doi.org/10.1016/j.dyepig.2005.03.006
- 4. Chowdhury K. P. Effect of Special Finishes on the Functional Properties of Cotton Fabrics // Journal of Textile Science and Technology. 2018. Vol. 04, Issue 02. P. 49–66. doi: https://doi.org/10.4236/jtst.2018.42003
- 5. Vishwanathan N. Anti-Shrink/Anti-Stretch Treatment on Cellulosic Knits // Colourage. 2004. Vol. 50. P. 55-58.
- 6. Evaluating Fluorinated Acrylic Latices as Textile Water and Oil Repellent Finishes / Castelvetro V., Francini G., Ciardelli G., Ceccato M. // Textile Research Journal. 2001. Vol. 71, Issue 5. P. 399–406. doi: https://doi.org/10.1177/004051750107100506
- Water and Oil Repellent and Durable Press Finishes for Cotton Based on a Perfluoroalkyl-Containing Multi-Epoxy Compound and Citric Acid / Shao H., Sun J.-Y., Meng W.-D., Qing F.-L. // Textile Research Journal. 2004. Vol. 74, Issue 10. P. 851–855. doi: https://doi.org/10.1177/004051750407401002
- 8. Speranskaya T. A., Tarutina L. I. Opticheskie svoystva polimerov. Leningrad: Himiya, 1976. 136 p.
- 9. Tager A. A. Fiziko-himiya polimerov. Moscow: Nauchniy mir, 2007. 576 p.
- El'yashevich G. K., Kuryndin I. S., Rozova E. Y. Optical transmission of porous polyolefin films in immersion media // Journal of Optical Technology. 2017. Vol. 84, Issue 7. P. 481. doi: https://doi.org/10.1364/jot.84.000481

- 11. Mohamed A., Shaker A., Razzaq S. Optical Properties of Polyvinyl Chloride Doped with DCM dye Thin Films // World scientific news. 2016. Vol. 30. P. 45–56.
- 12. Mohammadian-Kohol M., Asgari M., Shakur H. R. Effect of gamma irradiation on the structural, mechanical and optical properties of polytetrafluoroethylene sheet // Radiation Physics and Chemistry. 2018. Vol. 145. P. 11–18. doi: https://doi.org/10.1016/j.radphyschem.2017.12.007
- 13. Krynin A. G., Hohlov Yu. A. Optical performances thermostabilised polyethyleneterephtalate film used for the functional materials of a glass cover // Aviatsionnye materialy i tekhnologii. 2013. Issue 4. P. 31–34.
- Ftorsoderzhaschie monomery i polimery so spetsial'nymi svoystvami dlya integral'noy optiki i fotoniki / Igumnov S. M., Sokolov V. I.,
   Men'shikov V. K., Mel'nik O. A., Boyko V. E., Dyachenko V. I. et. al. // Doklady akademii nauk. Himiya. 2012. Vol. 446, Issue 3. P. 288–293.
- 15. Serova V. N. Opticheskie i drugie materialy na osnove prozrachnyh polimerov: monografiya. Kazan': KGTU, 2010. 540 p.
- Study of the optical properties of poly (methyl methaacrylate) (PMMA) doped with a new diarylethen compound / Najeeb H. N.,
   Balakit A. A., Wahab G. A., Kodeary A. K. // Academic Research International. 2014. Vol. 5, Issue 1. P. 48–56.
- 17. Synthesis of a novel perfluorinated acrylate copolymer containing hydroxyethyl sulfone as crosslinking group and its application on cotton fabrics / Li Z.-R., Fu K.-J., Wang L.-J., Liu F. // Journal of Materials Processing Technology. 2008. Vol. 205, Issue 1-3. P. 243–248. doi: https://doi.org/10.1016/j.jmatprotec.2007.11.284
- 18. Optical properties and UV-curing behaviors of optically clear semi-interpenetrated structured acrylic pressure sensitive adhesives / Lee S.-W., Park J.-W., Kwon Y.-E., Kim S., Kim H.-J., Kim E.-A. et. al. // International Journal of Adhesion and Adhesives. 2012. Vol. 38. P. 5–10. doi: https://doi.org/10.1016/j.ijadhadh.2012.04.002
- Investigation of impact of crosslinking agents on characteristics of spatial net and properties of styrene-acrylic polymer films / Slepchuk I., Semeshko O. Y., Asaulyuk T. S., Saribekova Y. G. // Izvestiya Vysshikh Uchebnykh Zavedeniy Khimiya Khimicheskaya Tekhnologiya. 2018. Vol. 61, Issue 7. P. 68–76. doi: https://doi.org/10.6060/ivkkt.20186107.5670
- Development of styrene-acrylic polymeric compositions for the coating of textile materials used for packing / Saribyekova Y., Kunik A., Asaulyuk T., Semeshko O., Myasnykov S. // Eastern-European Journal of Enterprise Technologies. 2017. Vol. 5, Issue 6 (89). P. 35–41. doi: https://doi.org/10.15587/1729-4061.2017.110039
- Yong Q., Liang C. Synthesis of an Aqueous Self-Matting Acrylic Resin with Low Gloss and High Transparency via Controlling Surface Morphology // Polymers. 2019. Vol. 11, Issue 2. P. 322. doi: https://doi.org/10.3390/polym11020322
- 22. Negru O. I., Vacareanu L., Grigoras M. Electrogenerated networks from poly[4-(diphenylamino)benzyl methacrylate] and their electrochromic properties // Express Polymer Letters. 2014. Vol. 8, Issue 9. P. 647–658. doi: https://doi.org/10.3144/expresspolymlett.2014.68
- 23. The effect of chromophores concentration on the nonlinear optical activity of methacrylic copolymers with azochromophores in the side chain / Smirnov M. A., Mukhtarov A. S., Ivanova N. V., Vakhonina T. A., Semashko V. V., Balakina M. Y. // Journal of Physics: Conference Series. 2014. Vol. 560. P. 012015. doi: https://doi.org/10.1088/1742-6596/560/1/012015
- 24. Functionalized polymers with strong push-pull azo chromophores in side chain for optical application / Derkowska-Zielinska B., Skowronski L., Sypniewska M., Chomicki D., Smokal V., Kharchenko O. et. al. // Optical Materials. 2018. Vol. 85. P. 391–398. doi: https://doi.org/10.1016/j.optmat.2018.09.008
- 25. Avvakumova N. I., Budarina L. A., Divgun S. M. Praktikum po himii i fizike polimerov: ucheb. izd. / V. F. Kurenkov (Ed.). Moscow: Himiya, 1990. 304 p.
- 26. Akter A., Uddin M. M. Knit sector gains a great momentum in 2018 // TextileToday. 2019. URL: https://www.textiletoday.com.bd/knit-sector-gains-a-great-momentum-in-2018/
- 27. Looking into the Future of Global Knitting Industry. URL: https://www.fibre2fashion.com/industry-article/5398/looking-into-the-future-of-global-knitting-industry
- 28. Kissa E. Lightfastness of Reactive Dyes // Textile Research Journal. 1971. Vol. 41, Issue 9. P. 715–719. doi: https://doi.org/10.1177/004051757104100901
- 29. UV-Protecting properties of textile fabrics and their improvement / Reinert G., Fuso F., Hilfiker R., Schmidt E. // Textile Chemist & Colorist. 1997. Vol. 29, Issue 12. P. 36–43.
- 30. UV absorber aftertreatment to improve lightfastness of natural dyes on protein fibres / Lee J. J., Lee H. H., Eom S. I., Kim J. P. // Coloration Technology. 2001. Vol. 117, Issue 3. P. 134–138. doi: https://doi.org/10.1111/j.1478-4408.2001.tb00051.x
- 31. Yang Y., Naarani V. Improvement of the lightfastness of reactive inkjet printed cotton // Dyes and Pigments. 2007. Vol. 74, Issue 1. P. 154–160. doi: https://doi.org/10.1016/j.dyepig.2006.01.030
- 32. Thiagarajan P., Nalankilli G. Improving light fastness of reactive dyed cotton fabric with antioxidant and UV absorbers // Indian Journal of Fibre and Textile Research. 2013. Vol. 38, Issue 2. P. 161–164.
- 33. Semeshko O. Ya., Saribiekova Yu. H. Perspektyvy rozrobky tekhnolohiy nadannia svitlostiykosti tekstylnym materialam viyskovoho ta tsyvilnoho pryznachennia // Perspektyvy rozvytku ozbroiennia ta viyskovoi tekhniky Sukhoputnykh viysk: zb. tez dop. Mizhnar. nauk.-prakt. konf. Lviv: NASV, 2019. P. 90.
- 34. Bauer D. R., Dickie R. A. Crosslinking chemistry and network structure in organic coatings. I. Cure of melamine formaldehyde/acrylic copolymer films // Journal of Polymer Science: Polymer Physics Edition. 1980. Vol. 18, Issue 10. P. 1997–2014. doi: https://doi.org/10.1002/pol.1980.180181001