ACTIVATION OF SYNTHETIC FIBRES WITH TRANSITION METAL SALTS IN DYEING WITH ANIONIC DYES

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The results of studies of the role of transition metal salts in increasing the sorption capacity of synthetic fibres are analyzed. A possible mechanism of activation of poly(ethylene terephthalate) fibres by transition metal compounds with organic ligands in dyeing with anionic dyes is proposed.

The modifying effect of the salts of some transition metals was established on the example of increasing the sorption capacity of some synthetic fibres with respect to dyes. Giving them elevated hygroscopicity and increasing their diffusion-sorption properties with respect to anionic dyes as a result of treating them with metal salts was noted for fabrics made of polycaproamide fibre in [1]. A sufficient number of active sites capable of fixing anionic dyes based on the mechanism of formation of a salt bond and the possibility of conducting the process below the boiling point of an aqueous solution of the dye allowed investigating the characteristics of dyeing of modified fibres.

The direct dependence of the dyeability of polyamide fibres on the content of zinc and chromium cations [4] bound by them during preliminary treatment of the fibres with solutions of the salts is due to their enhancing effect in different stages of the dyeing process. An increase in the dyeability in the given case is a specific test that allows confirming changes in the properties of a fibre-forming polymer when a significant number of mobilized transition metal cations is present in its structure.

In dyeing synthetic fibres in practice, delivery of low-molecular-weight substances to the reactive groups of the substrate located not only on the surface but also in the depth of the fibre is one that determines the uniformity and strength of the color. From this point of view, poly(ethylene terephthalate) fibres are the most complex object.

In going from the general characteristics of modification of polymers with metal compounds to processes of deliberate alteration of the properties of highly oriented poly(ethylene terephthalate) in the form of fibres, it is necessary to consider both the features of the chemical nature and the specific features of its supramolecular organization. The presence of aromatic phenylene rings in the molecular chains of terephthalic acid ester and ethylene glycol is one of the most important features of the structure of this polymer. Due to the effect of conjugation of phenylene rings, the electron density and correspondingly the bond energy in adjacent ester groups increase [3]. The high glass transition temperature is due to the rigidity of the molecular chains and the weak intermolecular interaction due to the absence of polar functional groups. The low hygroscopicity of polyester fibres is determined to a great degree by the packing density of the macromolecules on the supramolecular level. The low energy of the surface reaction with water and the impossibility of dyeing with water-soluble dyes is the result of steric and kinetic hindrances to diffusion of low-molecular-weight substances into the fibre substrate.

The number of organic dyes that can be sorbed by polyester fibres can be increased and the dyeing temperature can be significantly decreased by chemical modification in the synthesis stage. Copolymers with sulfoisophthalic acid acquire affinity for dye molecules due to the formation of new polar groups, and partial substitution of ethylene glycol by 1,3-propanediol yields fibres with a diffusion-permeable structure that can be dyed at the boiling point. However, giving a fibre-forming polymer special properties in the stage of synthesis is limited by the small volume of products, and in conditions of mass production, chemists and finishers must dye articles made of polyester fibres fabricated by traditional technology.

It is necessary to solve the problem of delivering these compounds to the active sites in the polymer in order to significantly alter the sorption-diffusion properties of polyester fibres by incorporating transition metal compounds in their structure.

Of the organic compounds used in dyeing of synthetic thermoplastic fibres and playing the role of plasticizers with respect to the fibre-forming polymer, benzoic acid was selected. The joint use of a chromium salt and an organic acid made it possible to modify the fibre in conditions below the boiling point of their aqueous solutions, where the maximum positive effect is obtained. The fact that the highest number of chromium cations was fixed on the fibre only at a certain molar ratio of the components suggested the possibility of formation of a complex salt with organic ligands. The analysis of the spectra of solutions obtained at different salt and acid ratios demonstrated the formation of complex cations whose composition was determined by the ratio of the reagents [4]. Having high affinity for polyester fibre, complex particles with organic ligands are sorbed more efficiently than chromium aqua complexes. The role of benzoic acid in this case is not restricted to plasticization of the polymer, as it has an effect on the thermodynamic parameters of the system and causes transfer of metal cations from the solution to the fibre phase.

The effect on the fibre-forming polymer should increase with an increase in the number of metal cations sorbed by the fibre as a result of treating it with the salt solution. The efficiency of the treatment can be evaluated by determining the change in its sorption capacity with respect to different reagents. The change in the capillarity of textile materials made of synthetic fibres allows judging the increase in their overall hydrophilicity. The capillarity increased significantly in the samples treated with solutions of salts combined with organic acids. The maximum treatment efficiency was observed in the solution containing chromium chloride (0.1 M) and benzoic acid (0.1 M). The liquid rose 8.8 cm in 60 min. The capillarity of the washed sample decreased markedly (to 5.6 cm) due to partial desorption of the chromium salt during washing. Since capillary processes are a function of the characteristic surface layer of the fibre, these results can be considered systematic and are in good agreement with the results of determining the maximum concentration of benzoic acid in solutions of salts that guarantee the highest fixation of metal cations by polyester fibre. We can thus draw a conclusion between the number of metal cations bound by the fibre and the change in its sorption properties, characterized by an increase in the capillarity of the fabric.

The absence of functional groups capable of acting as active sites for fixation of anionic reagents, the high glass transition temperature, and the compact supramolecular structure of the thermoplastic polymer almost exclude the possibility of dyeing polyester fibre with water-soluble dyes of the anionic type. If we consider the high negative charge of this fibre and the lack of affinity of acid dyes in aqueous solutions, this possibility is excluded in ordinary conditions. Only important changes in the structure and the chemical nature of the polymer can create the necessary conditions for dyeing polyester fibre with dyes of this class, i.e., their sorption and diffusion into the structure of the fibre. Attaining the effect of dyeability of polyester fibre by acid dyes could demonstrate the high modifying effect of solutions of polyvalent metal salts in the presence of organic acids on its properties.

The results of dyeing polyester fibre previously treated with chromium salt and benzoic and salicylic acids demonstrated the change in its sorption capacity with respect to acid dyes. The chromium and benzoic acid composition is characterized by the highest rate of fixation of the dye and highest equilibrium sorption, which is 2.5 times higher than this index for the initial chromium salt. The efficacy of salicylic acid is slightly lower than the efficacy of benzoic acid. In comparing the dependences obtained with the results of determining the number of metal cations fixed by polyester fibre, we note that the highest dyeability by acid dyes is attained in conditions corresponding to maximum fixation of metal cations. The results characterizing the change in the capillarity of modified fabric confirm this mechanism [5].

Combining preliminary treatment of the fibre with dyeing, i.e., the use of a complex chromium chloride—organic acid—dye in one bath does not decrease the fibre activation effect and does not affect the stability and intensity of the color. The dyeing process conducted with this scheme is characterized by several features. The efficacy of salicylic acid decreases and the result is attained with benzoic acid when chromium salts in a lower concentration are used.

From the point of view of the basic relations of the theory of dyeing of synthetic fibres, the analysis of the results obtained suggests the following mechanism of activation of polyester fibre during dyeing with anionic dyes. The basic role of benzoic acid consists of plasticizing the fibre-forming polymer, i.e., increasing the free volume accessible to diffusion of the reagents. the chromium cations in the form of complex particles of different composition are adsorbed on the surface of the fibre, decreasing its negative charge and promoting sorption of dye anions. When a certain concentration gradient is attained, complex particles and dye anions diffuse into the structure of the fibre.

The basic role in fixation of dye particles on the functional groups of the polymer is played by chromium benzoate complexes, which have a high affinity for the fibre substrate. On contact of such particles with the active sites in the polymer,