Chemistry of Natural Compounds, Vol. 36, No. 1, 2000

MODIFICATION OF NATURAL SILK

M. Abdukarimova[1] and Yu. T. Tashpulatov[2]

UDC 677.37.027.622

The effect of ethylene chlorohydrin on the treatment of silk with active dyes is studied by chromatography. The aminoacid glycine is used as a model for silk. Active dyes can be covalently bound to silk using ethylene chlorohydrin.

Key words: fibroin, chemical modification, bifunctional compound, active dye.

Fibroin of natural silk can be modified using various compounds, including active dyes, because it has chemically active functional groups in its structure. Depending on the chemical nature of the dye, the mechanism of the fibroin reaction can be nucleophilic substitution or addition to form a covalent bond [1]. This makes the dye highly stable to moisture. In addition to the desired reaction of the active dye with fibroin, it also reacts with water and becomes deactivated and consumed uselessly up to 30%. The rate of the heterogeneous reaction of the active dye with fibroin and the rate of hydrolysis have their maximal values at pH 10.0-10.5.

If the dye is absorbed by the silk before it reacts chemically, part of the dye is situated in a sterically unfavorable orientation relative to the reactive centers of fibroin. This part of the dye, even though it is active, cannot react and should be removed from the silk at the end of the process together with the hydrolyzed dye. Therefore, the binding of sorbed dye to natural silk should be studied. Solving this problem will reduce the consumption of dye and amount of wastewater.

We studied the possibility of using several bifunctional compounds to bind covalently sorbed dye, both hydrolyzed and active. Ethylene chlorohydrin is a very common bifunctional compound for these purposes. It was found that adding 5 g/dm^3 ethylene chlorohydrin to the dye solution increases the efficiency of various active dyes from 6.4 to 50.5% [2].

Dying silk with active dyes and added ethylene chlorohydrin can cause silk—silk, silk—dye, and dye—dye cross-linking through the bifunctional compound. Differential thermal and thermogravimetric analyses and the loss of solubility for silk treated with ethylene chlorohydrin under controlled (time and temperature) conditions indicate that fibroin—ethylene-chlorohydrin—fibroin bonds are formed [3]:

$$\begin{gathered}\text{HOOC—Silk—NH}_2 + \text{Cl—CH}_2\text{—CH}_2\text{—OH} + \text{HO—CH}_2\text{—Silk—(NH}_2\text{)COOH} = \\ \text{HOOC—Silk—NH—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—Silk—(NH}_2\text{)COOH} + \text{HCl} + \text{H}_2\text{O}\end{gathered}$$

The model compound glycine was used to prove that silk—dye and dye—dye bonds form if ethylene chlorohydrin is used. TLC and HPLC were used for the analysis. Glycine was chosen as the model compound for silk because its content is high (~43%) in the fiber and mainly the amino groups of silk react under the conditions chosen by us.

Figures 1*a* and -*b* and Table 1 present the results of our TLC studies on active-dye solutions and their mixtures with ethylene chlorohydrin and glycine.

The data show that solutions of bright red 5CX contain the active dichlorotriazine species (I) and small quantities of partially hydrolyzed hydroxychlorotriazine (II) and fully hydrolyzed dihydroxytriazine (III) dye. The monochlorotriazine dye Cibacron blue F3GA consists mainly of the active species (I) and a small quantity of the hydrolyzed (II) dye.

The sharp decrease in the R_f values of the products from reaction of the dyes and ethylene chlorohydrin indicates that all species of the active dye react with the bifunctional reagent. Apparently glycine reacts mainly with the active dye species.

---

1) Tashkent Institute of Textiles and Light Industry, fax (3712)-53-36-17; 2) Institute of Polymer Chemistry and Physics, Tashkent, fax 3(7312)-44-26-61. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 66-68, January-February, 2000. Original article submitted December 21, 1998.

0009-3130/00/3601-0084$25.00

TABLE 1. R_f Values of Active Dyes and Their Reaction Products

Active bright-red 5CX	R_f	Cibacron blue F3GA	R_f
Dichlorotriazine (I)	0.694	Monochlorotriazine (I)	0.810
Hydroxychlorotriazine (II)	0.564	Hydroxychlorotriazine (II)	0.642
Dihydroxytriazine (III)	0.541	Product of reaction with glycine	0.635
Product of reaction with ethylene chlorohydrin	0.506	Product of reaction with ethylene chlorohydrin and glycine	0.567
Product of reaction with glycine	0.552	Product of reaction with ethylene chlorohydrin	0.527
Product of reaction with ethylene chlorohydrin and glycine	0.529		

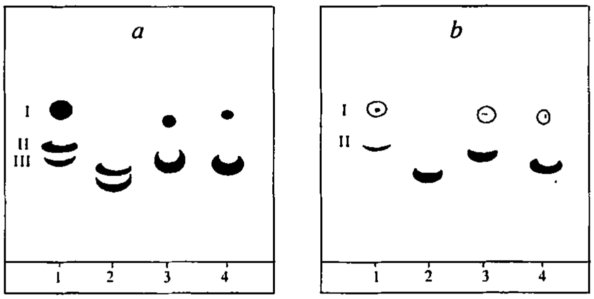


Fig. 1. Chromatograms of active dyes and their reaction products: solution of active bright red 5CX (*a*), solution of Cibacron blue F3GA (*b*); solution of starting dyes (1), solution of product from reaction of dye and ethylene chlorohydrin (2), solution of dye—glycine mixture (3), solution of dye—glycine—ethylene-chlorohydrin mixture (4); *a*: dichlorotriazine (I), hydroxytriazine (II), dihydroxytriazine (III); *b*: monochlorotriazine (I), hydroxytriazine (II).

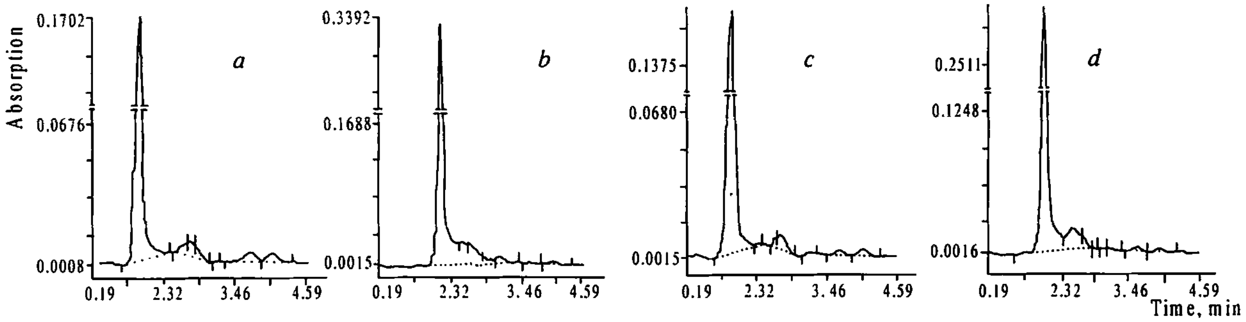


Fig. 2. Chromatograms of bright red 5CX (*a*) and the product of its reaction with ethylene chlorohydrin (*b*), glycine (*c*), and ethylene chlorohydrin and glycine (*d*).

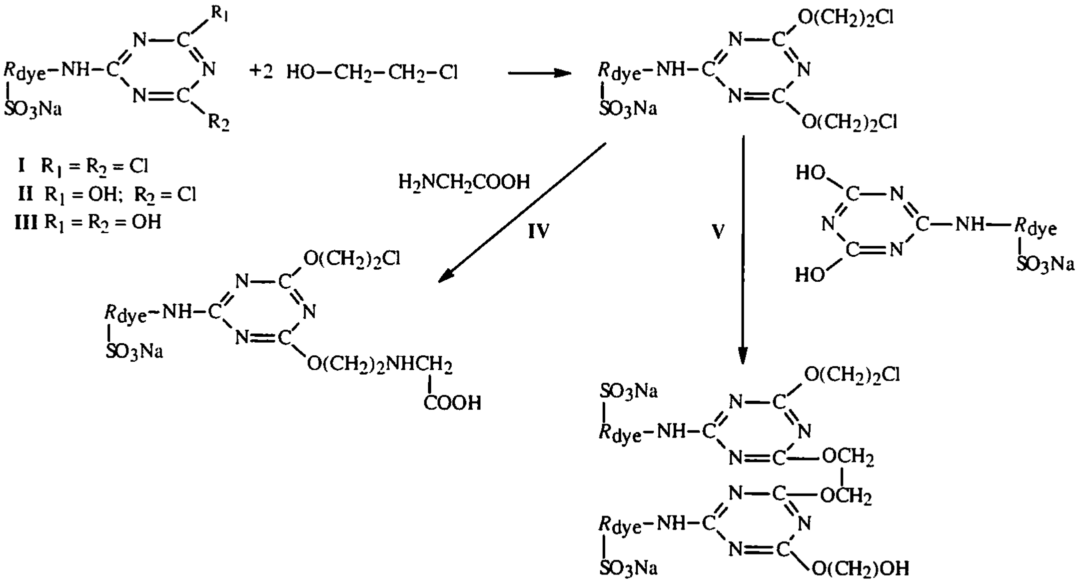
The hydrolyzed species reacts if ethylene chlorohydrin is added to the solution.

The dye—ethylene-chlorohydrin mixture does not contain active free dye with R_t = 1.78 min (85%) and partially (hydroxychlorotriazine) and fully hydrolyzed dye (dihydroxytriazine) with R_t = 2.61-2.73 and 3.65 min (Fig. 2*a*).

The peak appearing at R_t = 3.99 min is most probably due to an acidic dye used as an intermediate for synthesizing the active dye. The product from the reaction of dye and ethylene chlorohydrin gives an asymmetric peak at R_t = 2.15 and 2.23 min (Fig. 2*b*).

About 90% of the product results from the glycine—dye reaction if the reaction mixture contains an excess of glycine. Apparently the reaction product results from formation of ionic and covalent bonds between the dye and aminoacid because the peaks with R_t = 3.65 and 3.99 min disappear. These peaks are due to the fully hydrolyzed and acidic dyes. Adding ethylene chlorohydrin to the last solution changes the products. The principal product (about 89%) with R_t = 2.13 min is analogous to that from the dye—ethylene-chlorohydrin reaction with R_t = 2.15 min.

Chromatography studies are consistent with the chemical reactions involving ethylene chlorohydrin that were presented above. In these reactions, R_{dye}—SO_3Na is the dye chromophore; I is the dichlorotriazine species of the active dye; II is the hydroxychlorotriazine species; and III is the dihydroxytriazine species (fully hydrolyzed).



The products from reaction of ethylene chlorohydrin and all three dye species (IV) are more reactive toward natural silk than I because the active Cl is bonded to the more flexible (–CH_2–CH_2–) linker. The experiments showed that the physicomechanical properies of modified silk are comparable to those of natural silk upon treatment with active dyes in the presence of ethylene chlorohydrin (Table 2).

Silk treated with dye becomes less soluble in the solvent used for viscosimetric studies.

Thus, chromatographic studies using a model compound reveal the mechanism by which additional covalent bonds form between the active dye and silk if ethylene chlorohydrin is used.

TABLE 2. Effect of Conditions for Silk Modification by Ethylene Chlorohydrin on its Properties

Treatment conditions	[η]	Tear strength, cH	Stretch, %
Distilled water, T = 80°C, time = 90 min	0.97	202.0	10.3
Ethylene chlorohydrin solution, 5 g/dm^2, T = 80°C, treatment time = 90 min	0.16	211.0	11.2
Ethylene chlorohydrin solution, 5 g/dm, acetic acid, 2.5 g/dm^3, T = 80°C, time = 90 min	-	241.0	11.2

EXPERIMENTAL

We used type 310/3 textile-grade silk filaments with 2.33 mg/m linear density that was dyed using a soap-sodium method under industrial conditions. The filament moisture was 8.1%. The residual raw silk content was 3.5%. Samples were treated with ethylene chlorohydrin under temperature—time dying regimes without dye in a thermostatted bath initially at 20°C. After 20 min the temperature was raised to 80°C. The bath was held at that temperature another 90 min. The content of ethylene chlorohydrin was 5 g/dm^3; of acetic acid, 2.5 g/dm^3. Samples in ethylene chlorohydrin solution without acetic acid were prepared for the viscosimetric studies because the silk becomes less soluble under the above conditions.

The characteristic viscosity [η] of fibroin solutions was determined in order to estimate the destruction of the polymeric substrate under dying conditions. The solvent was a mixture of 62% aqueous NaSCN and glacial acetic acid (80:20 by mass). The viscosity was masured using a Ubellohde viscometer (with a hanging level) of capillary diameter 1.12 mm at 25 ± 0.05°C. The physicomechanical properties of the silk were determined according to GOST 5618-80.

The following solutions were prepared for chromatography: 1) bright red 5CX and Cibacron blue F3GA (1.5 g/dm^3) dyes that were freshly prepared and unused; 2) a mixture of dye (1.5 g/dm^3) and ethylene chlorohydrin (5 g/dm^3) used in the temperature—time regimes discussed above; 3) dye and glycine (1:10) used in the temperature—time silk-dying regimes; 4) dye, glycine, and ethylene chlorohydrin used under the same conditions as solutions 2 and 3.

TLC of solutions was performed on Merck (Germany) TLC plates. The eluent was $C_3H_7OH:NH_3:H_2O$ (7:1:2). Liquid chromatography of these solutions was performed on a Beckman System Gold (USA) chromatograph with a 275-nm detector, an Ultrasphere C-18 column, a mobile phase of 40% CH_3CN in water, and a flow rate of 1 ml/min.

REFERENCES

1. I. Ya. Kalontarov, *Properties and Applications of Active Dyes* [in Russian], Dushanbe (1990).
2. M. Z. Abdukarimova, N. G. Valeeva, A. D. Midovanov, and K. E. Ergashev, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, No. 5, 118 (1993).
3. M. R. Abdullaeva, N. G. Valeeva, and M. Z. Abdukarimova, *Shelk*, No. 4, 22 (1991).
4. GOST 5618-80, *Raw Silk.*