RESEARCH AND DEVELOPMENT OF COLLAGEN OF POLYMERIC COMPOSITIONS BASED ON WASTE OF RAWLEATHER

Rustamov Bobir Ismatovich
PhD bobir_rustamov@bk.ru
Shodiyeva Dilnoza Turajon qizi
Master Bukhara Engineering and Technological Institute

Abstract: *Polymer compositions were created on the basis of leather raw materials (collagen) with acrylic aldehyde, hydrolyzed polyacrylonitrile, and their properties, characteristics, texture and structure were investigated in this work.*
Keywords: *collagen, golio, hydrolysis, tanning, retanning, destruction.*

In leather and fur production, raw materials of biological origin are used, the main component of which are protein substances, or proteins - collagen of the dermis and keratin of the hair [1].Collagen is very common in the animal body: its content is 25-35% of all proteins. Therefore, it is natural that scientists of various specialties deal with the structure of collagen. Collagen as an integral part of a living organism should be of interest to medical histologists, surgeons, rheumatologists, dermatologists, etc., biologists and biochemists [2].

Recently, physicists have been paying much attention to collagen as a fibrillar protein and a high-molecular compound. Finally, collagen is also of industrial importance. The dermis of the skin of animals is the main substance for the production of a technical product - skin. Glue and gelatin are prepared from collagen. Therefore, technologists are no less interested in studying the structure and properties of collagen than other specialists. This explains the large number of studies devoted to the study of this protein [1].

Collagen is an integral part of connective tissue. In addition to the fibrous material, cells and the basic substance are also found in the connective tissue. In this regard, of course, special comprehensive studies were conducted. Proteins make up the main part of the leather fur raw materials. These proteins are read by natural polymers. When processing leather raw materials, some waste is generated.

The waste from tanneries in the form of peripheral sections of hides, mezdra, char trimmings, and substandard sawdust can be used to produce gelatin, feed flour, and protein hydrolysis.

In this regard, it was interesting for us to study the possibility of creating polymer compositions based on waste leather raw materials (collagen) with acrylic aldehyde, hydrolyzed polyacrylonitrile and to investigate their properties, structure and structure.

A characteristic analogue of the model collagen compounds is a collagen film, thread, gelatin, char powder and mezdra glue, containing not only the reactive groups characteristic of collagen, but also amino acid residues located in the same initial sequence. In this regard, we conducted a study and identified the possibility of chemical modification of collagen with acrolein. From this point of view, it is of great interest to study the interaction of collagen with acrylic aldehyde, the resulting product of collagen modification, which has a number of valuable properties.

The initial collagen for modification was obtained as follows. The salt waste was watered in a special glass container, held for 1.5-2.0 hours, then ground in a meat grinder and the pH of the crushed mass was adjusted to 10.5-11.0 with the addition of caustic soda, and the treatment solution was saturated with sodium sulfite. After that, the mass was held at 23-250C for 30 hours. The treated mass was washed in running water to remove salt. Then neutralized with 3.0% boric acid. The resulting mass was dissolved in 1 M acetic acid solution, the solution was pressed through a nylon sieve, filtered, the collagen was precipitated with acetone and dried. Acrolein (acrylic aldehyde) - CH_2=CHCHO (2-propenal) was used as another component for collagen modification.

Due to the poor solubility of acrylic aldehyde in water, the reaction was carried out in an aqueous alcohol solution of collagen (ethanol:water =2:5). The modification process of collagen with acrylic aldehyde was carried out as follows. Initiators were first introduced into the 5.0% collagen solution system (sodium sulfate - 0.3 g/ l and potassium sulfate - 0.5 g/ l), after 40-60 seconds, acrylic aldehyde was introduced in an amount of 3.0% by weight (system) of solvents.

In such a system, grafted copolymerization of acrylic aldehyde to collagen is expected. At the same time, it is impossible not to take into account the formation of a certain amount of acrolein homopolymer. Therefore, the final product of the grafted copolymerization process was carefully extracted with dimethylformamide in order to remove the homopolymer.

The turbidimetric titration method was used to study the interaction of acrylic aldehyde with collagen. Acetone, which is a selective precipitator of collagen, was chosen as the titrating agent. When acetone is added to the polyacrolein solution, turbidity does not occur. The turbidity of the solutions was determined on a turbidimeter in conventional units. Titration was carried out in 0.2 ml portions.

The addition of acetone to the dilute (collagen-acrolein) composite solution does not cause any significant change in turbidity, therefore, the precipitator used can practically be considered selective for collagen.

When comparing the titration curves (Fig. 1), it can be seen that the nature of the titration curves of the collagen-acrylic aldehyde (1, a-d) composition system varies depending on the concentration of collagen. On curves 1, a-b, a minimum is observed and its position depends on the concentration of collagen: with increasing concentration, the depth of the minimum decreases, and it itself shifts to the area of a lower content of the titrating agent acetone. The presence of a minimum is explained by an increase in protein solubility in the presence of a small amount of acetone-water solvents, with an increase in protein concentration, the minimum is smoothed and shifted to the left. The maximum value corresponding to fully titrated collagen increases in proportion to the collagen concentration, since precipitation was carried out with a selective collagen precipitator.

In order to find out whether the properties of the collagen - acrylic aldehyde composition change over time, comparative titration of freshly prepared collagen - acrylic aldehyde compositions, as well as those aged for 72 hours, was performed. The obtained curves 1, 2, and 3 (Fig. 1) do not coincide, which indicates the presence of interaction between the components of the system that occur over time.

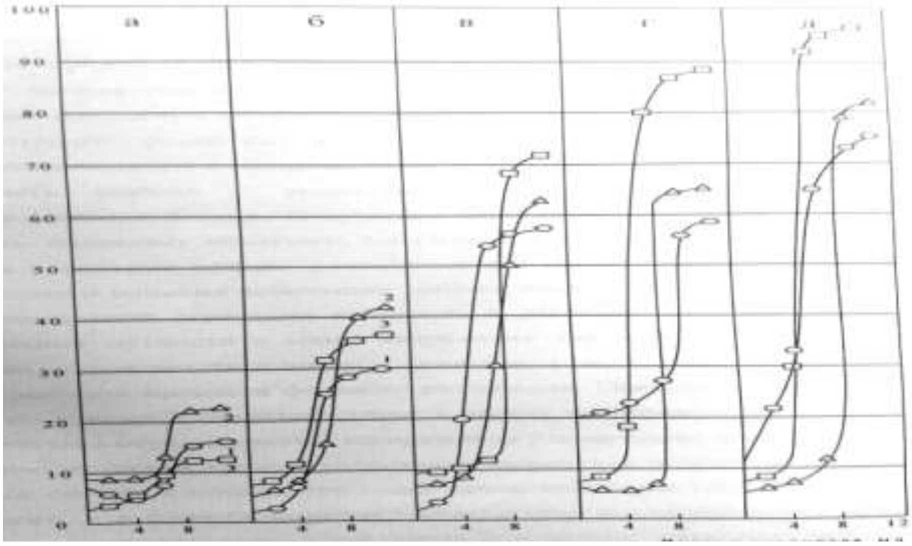

fig. 1. Turbidimetric dependences of the collagen - acrylic aldehyde system on the precipitator of the acetone titrant:

1-the collagen-water system; 2-the collagen - acrylic aldehyde system, freshly prepared; 3-the collagen - acrylic aldehyde system, aged for 72 hours. Composition ratio (collagen-water and collagen - acrylic aldehyde): a-1:9; b-3:7; s-5:5; d-7-3; e-9:1.

Some differences in the nature of the curves of the collagen - acrylic aldehyde and collagen-water compositions are expressed in a decrease in the initial values of relative turbidity in the collagen- acrylic aldehyde system (curves 1, 3, Fig.4), in the absence of an initial minimum for this system in the range of compositions 5:5, 7:3 and 9:1 (curves 3, c, d, e), in the appearance of characteristic fractures on curve 3 for the same compositions and in an increase in turbidity values corresponding to fully titrated solutions. A decrease in the initial turbidity values occurs over time, as evidenced by the different ordinates in the initial values for solutions freshly prepared and aged for 72 hours, and may be associated with an increase in the compactness of the resulting interaction products. The absence of a minimum on curves 3, c, d, and e can probably be explained by the fact that with a significant content of collagen in the system, the effect of increasing its solubility due to the polarizing effect of small salt additives will not be able to man ifest itself due to significant aggregation of collagen in solution. The large values of relative turbidity at the end of titration for curves 3, c, d, and e compared with the corresponding curves 1 and 2 indicate a more complete phase separation process. The appearance of characteristic kinks in curves 3 supports the assumption that the interaction is based on the principle of heterogeneous aggregation.

From a review of the titration curves, it can be seen that the position of curve 3 depends on the composition of the system: with a collagen content of 1:9 3:7, this curve lies lower, and in the area of high collagen content, the titration curve of the freshly prepared mixture is higher. This can be explained by the fact that with an increase in the collagen content, the interaction of the collagen-acrylic aldehyde type becomes predominant. Based on the data of the turbidimetric study, the presence of a strong interaction of collagen with acrylic aldehyde with the formation of a modified polymer product was established..

The above experimental data show that an interaction occurs between collagen and acrylic aldehyde, rather than a simple mechanical mixing of the initial components. As a result of the interaction, a physico-chemical change in the properties, in particular the rheology of the solution, occurs. In this regard, the viscosity of the resulting product was studied.

The viscosity was measured on an Ostwald viscometer with a capillary diameter of 0.5 mm at temperatures of 13, 20, 30, and 400C (since collagen macromolecules have spiral confirmation at t < 150C, tangle shape at t < 350C, and both spiral and tangle shapes of macromolecules are present at 15-350C). The data obtained are presented in Table 1.

Specific viscosity of collagen and acrolein solutions (in the ratio of 1:1) at different temperatures

System	Specific viscosity at temperature, °C			
	13	20	30	40
Collagen	0,26	0,35	0,32	0,18
Collagen + Acrylic aldehyde	0,79	1,27	1,32	1,43
Acrylic Aldehyde	0,42	0,43	0,44	0,47

It should be noted that the nonadditive increase in viscosity, indicating an interaction, is observed only at temperatures of 20 and 300C, at which the collagen macromolecule has a more elongated shape, and therefore, the interaction of acrolein with the functional groups of collagen is easier to establish. At a temperature of 400 ° C, sufficiently hydrophobic interactions occur, as a result of which the collagen macromolecule takes on a more compact shape and is in the form of a tangle, which is an obstacle to the interaction of acrylic aldehyde with the functional groups of collagen.

The conducted studies indicate that the reactive groups of collagen NH2 and NH+3 actively react with the aldehyde groups of acrylic aldehyde, and that acrylic aldehyde has a structuring effect on collagen. This will make it possible to use acrylic aldehyde in tanning and tanning leather processes as an independent tanning agent.

LIST OF LITERATURE:

1. Кодиров Т.Ж. «Средства и методы исследования коллагена», Издательство «Фан» Академии наук Респ. Узбекистан, Ташкент, 2014г. 375 с.
2. Хаитов А.А. «Создание новых эффективных коллаген - полимерных композиций из кожевенных отходов для наполнения кож и разработка их технологий». Дис. ... кан. техн. наук. Т. 2001.
3. Қодиров Т.Ж. «Наноструктура коллагена», Издательство «Фан» Академии наук Респ. Узбекистан, Ташкент, 2015г. 535 с.
4. Shamsieva M., Abduqahhorova K. Stepwise Fattening of Natural Leather and Research of Their Properties. International Journal of Advanced Research in Science, Engineering and Technology. Vol 6, Issue 9, September 2019. 10887-10890.
5. Rustamov B., Shamsieva M. Technology of fatliquoring karakul on the basis of used oils //Archive of Conferences. – 2022. – С. 26-28.
6. Shamsieva M., Rustamov B., Makhammadieva K. IR-spectroscopy of used fat substances for the process of emulsion fatliquoring of karakul //EPRA International Journal of Research and Development (IJRD) Volume. – Т. 7. – С. 1-4.