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Research Article

VISCOSITY PROPERTIES OF AQUEOUS SOLUTIONS OF NATURAL SILK WASTE COMPOSITIONS

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ABSTRACT

The paper presents the results of a study of the rheological properties of concentrated aqueous solutions of the composition of natural silk waste (fibroin), intended for the formation of artificial fibroin fiber in the modes of stationary shear flow and dynamic tests. Calculation from rheological data of values of initial viscosities of solutions, their temperature dependences being in various phase states is carried out. The concentration dependences of the viscous flow are constructed.

KEYWORDS

Natural silk, natural silk fibroin, fibrous waste, rheological properties of solutions.

INTRODUCTION

Waste textile fibers available at various stages of production are valuable secondary raw materials that can be rationally used. In the textile industry, certain measures are being taken to use secondary material resources, but the level of use of important types of waste at the present time cannot yet be considered satisfactory [1-5].

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Fibrillar proteins isolated from non-textile waste of natural silk production are of interest as fiber-forming polymers for the formation of artificial fibroin fibers, as well as for modifying polyacrylonitrile fibers formed by the salt method. This modification of polyacrylonitrile fiber with natural silk waste improves its physical-mechanical and especially fatigue characteristics of the resulting fibers [6-7]. Thus, the technological parameters of the process of obtaining fibrous materials and their properties significantly depend on the structural features and properties of the original fibers, including its chemical composition. For example, the presence and chemical nature of fibroin in the primary structure with polyacrylonitrile is important [8-9].

THE MAIN RESULTS AND FINDINGS

The aim of our work is to study the rheological properties of concentrated aqueous solutions of the natural silk waste composition intended for the formation of artificial fibroin fiber, in the presence of 6.0 to 33.3 wt.% fibroin, a wide temperature range - from 20 to 90°C (with an interval of 5° C)

We have studied compositions of natural silk wastes consisting of fibrillar protein - fibroin, sodium thiocyanate and water in the ratio: 1.0:1.6:0.4. Fibrillar protein was isolated according to known technology by boiling natural silk waste in a 3% soda solution for 3 hours. The residual content of sericin did not exceed 2-3%. The compositions were obtained by mixing these components in a rotary disperser according to known methods [10-13].

The effective viscosity of aqueous solutions of the composition was measured on a Reotest-2 device in a system of coaxial cylinders at speeds from 0.31 to 2.08 s-1, shear stresses from 0.75 to 2.74 Pa, a wide temperature range (20-90°C between 5°C).

The figure shows the rheograms of aqueous solutions of silk fibroin from shear voltage at a fibroin concentration in solution of 15; 19.4; 23.7; 30.3 wt%.

The shape of the flow curves of the rheogram depends on the shear stress. At lower (6-10%) solution concentrations, the rheograms show a minimum and maximum viscosity in different shear stress ranges. The trend towards a scatter of experimental points indicates the presence of various structural formations of associates based on fibroin polypeptide chains, as well as the residual content of sericin, which differ both in geometry and in the strength of bonds that break in different areas of the applied shear stress (figure 1).

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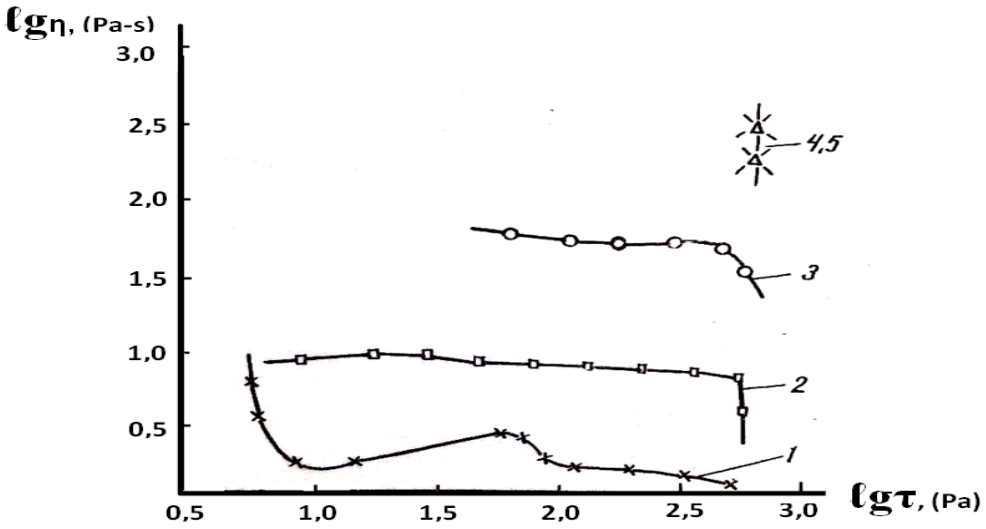

Figure 1. The dependence of the viscosity of aqueous solutions of silk fibroin on the shear stress at the concentration of fibroin in solution (%);
1-15; 2-19.4; 3-23.7; 4-27.1; 5-30.3

At a concentration of 15% (curve 1), the character and shape of the flow curve are rather complex. The decrease in viscosity occurs at a shear stress of 0.92 Pa and reaches a minimum at 1.0 Pa, then at 1.78 Pa the viscosity increases and then decreases.

An increase in the concentration of fibroin in an aqueous solution to 19.4% (curve 2) significantly stabilizes the dependence on shear stress. At ℓgτ= 0.90-1.40, a Newtonian flow is observed, i.e. viscosity does not depend on ℓgτ. A further increase in shear stress weakens the dependence and leads to a decrease in viscosity, and at ℓg=2.74, a yield point appears.

At a fibroin concentration of 23.7% in solution (curve 3), a different shape of the flow curve is observed than at a concentration of 19.4%. The effective viscosity at ℓgτ=1.70-2.10 passes in a small area to the Newtonian flow, then it noticeably decreases, which indicates the predominance of pre-orientation processes in the solution.

An increase in the concentration of fibroin in the solution from 27.1 to 30.3% (curve 4.5) leads to an increase in viscosity up to 2.74. A yield point is observed, i.e. separation of the solution flow in the measuring cylinder.

Previously [6-9], the dynamics of swelling and dissolution of fibroin in an aqueous solution of sodium thiocyanate was studied. A complex dependence of these processes on the concentration of sodium thiocyanate, which significantly affects the structure of fibroin as a result of the weakening of intermolecular and interstructural contacts, is shown. Sodium thiocyanate, by binding to fibrillar protein, increases the mobility of polypeptide chains and water molecules in the pores and voids of the fiber. This entails the appearance of volumetric (contractive) effects during swelling. A significant change in the density of fibroin was established when interacting with solutions of sodium thiocyanate. The concentration effect obtained in an aqueous solution somewhat "weights" the protein macromolecules. A

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decrease in the proportion of the crystalline phase of the fibrillar protein is accompanied by disordering of the system, which, in turn, leads to structural changes. Therefore, at relatively low concentrations of aqueous solutions of natural silk waste, the existence of various structural formations (associates) is observed, which are destroyed in different areas of the applied shear stress.

Using the example of poly-γ-benzyl-ι-glutamate, the presence of associates in pure solutions at low concentrations is shown. As a rule, in solvents with a high dielectric constant, macromolecules are joined in the longitudinal direction according to the head-to-tail principle, while in solvents with a low dielectric constant, lateral attachment occurs.

CONCLUSION

Thus, the study of the viscosity properties of concentrated aqueous solutions of the natural silk waste composition, depending on the concentration, shear stress and temperature, makes it possible to attribute solutions with a concentration of 23.7 wt. % and higher to systems that form an anisotropic system as a result of a simultaneous "coil-helix" transition.

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