Fibers Made from Concentrated Viscose Solutions

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SYNOPSIS

Cellulose xanthate solutions with α-cellulose content from 9 to 14% were obtained and their properties were examined. It has been found that viscoses containing urea are more stable and possess lower viscosity as compared with conventional viscoses. Properties of fibers obtained from viscoses with increased α-cellulose content were discussed. It has also been found that such fibers show higher linear density and their tensile strength depends on the α-cellulose content in the viscose.

INTRODUCTION

The manufacture of viscose fibers from concentrated solutions is of great technical and economical importance. It is natural that research has been carried out on this subject for several years in many laboratories.[1-3] The production of fibers from such solutions could reduce the consumption of basic raw materials and increase the fiber output without deterioration of fiber properties. However, implementation of the objectives presents many difficulties from a technological point of view due to the increase in the solution viscosity, deterioration of the viscose filtrability, and prolongation of some unit operations. Despite these problems, there are many factors in favor of the production of fibers from viscose with increased content of α-cellulose in the spinning solution. There is a reduction of consumption of raw materials and energy. There is an increased efficiency of machines and equipment without new investment expenditures. Further, environmental pollution is reduced. Even an approximate analysis of the advantages resulting from the manufacture of cellulose fibers from solutions with increased polymer concentration shows that the production of fibers from viscose with increased content of α-cellulose is the most effective method of improving the economics of the viscose process.

Increasing the α-cellulose content in the viscose, one can easily maintain proper lye content in the viscose at a level of 6.0–6.5%, which is close to the thermodynamic optimum being about 7%. In such cases, the ratio of NaOH to α-cellulose in the viscose, which determines the economics of viscose, can be lowered to 0.5–0.6 without troublesome technological consequences. This leads to a reduction in the consumption of sulfuric acid during fiber spinning and a reduction of losses of the energy required for the concentration of the spinning bath.

The production of viscose with an increased content of α-cellulose results in a reduction of the volume of viscose in relation to the amount of fibers produced and also in a reduction in the amount of energy required in the transport, filtration, and deaeration of more concentrated viscose solutions. The production of viscoses with good filtrability and increased content of α-cellulose depends, first of all, on the state of molecular dispersion of the sodium xanthate in the viscose.

Our studies have shown that the addition of a small amount of urea to the NaOH solution brings about a considerable increase in the depth of steeping and results in the preparation of a viscose with better properties than those of the standard viscose.[4]

This paper describes the properties of viscose with higher than normal α-cellulose content obtained from alkalicellulose prepared in the presence of urea as a steeping activator. The properties of fibers obtained from such viscoses are also discussed.

EXPERIMENTAL

Experiments were carried out on a laboratory scale. Steeping and xanthation were performed in a 2.0

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dm³ glass reactor according to the procedure described previously.[3] A mixture of spruce cellulose with a degree of polymerization of 900 and beech cellulose with a degree of polymerization of 650 (1 : 4) was used. The steeping was carried out with a 19% aqueous NaOH solution at a temperature of 55°C for 30 min. In the case of activated steeping, the NaOH solution contained 1% of urea in relation to pure sodium hydroxide. After steeping, excess caustic was squeezed out to a pick up ratio of 2.6 to 1. The resultant alkalicellulose was disintegrated to a volume ratio of 180 g/dm³ and ripened at 55°C for 120 min. The ripened alkalicellulose was xanthated using carbon disulfide in an amount of 32% wt, relative to the weight of cellulose. The resultant sodium cellulose xanthate was dissolved in 4% aqueous NaOH solution at 4–5°C to prepare the viscose solution. Standard methods were then used to determine viscosity, ripeness, α-cellulose content, and degree of substitution γ. The viscose was then used to form fibers by means of a one-head laboratory spinning unit provided with a spinneret with 55 holes, each with a diameter of 0.09 mm. The fibers were coagulated in a spinning bath at 50°C, containing 150 g/dm³ of H₂SO₄ and 10.5 g/dm³ of ZnSO₄ with an addition of Na₂SO₄ to make up a density of 1.28 g/dm³. The obtained fibers were washed from impurities, dried, conditioned, and examined to determine their linear density, tenacity, and elongation.
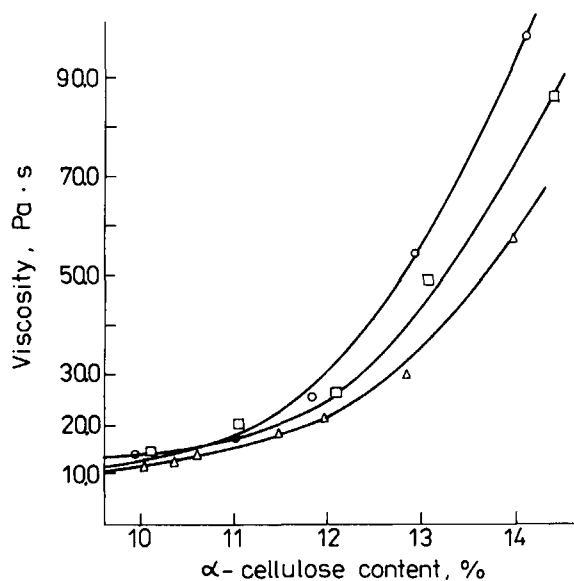

Figure 2 The effect of ripening time vs. γ value: (— ● —) standard viscose with 9% α-cellulose; (— ▲ —) standard viscose with 10% α-cellulose; (— △ —) viscose modified by urea with 10% α-cellulose.

RESULTS AND DISCUSSION

The presence of small quantities of urea as a modifier[4,5] in the caustic solution used brings about changes not only in steeping and xanthation but also in the properties of the viscose. Figure 1 shows the dependence of the viscose viscosity on the α-cellulose content in the obtained viscose. It also shows the effect of alkalization of cellulose without a modifier, with the addition of a surface-active agent, Berol Spin,† and with the addition of urea. The concentration of α-cellulose in the viscose solution varied from 10 to 14%. As seen in Figure 1, all the viscoses with α-cellulose content 10% possess viscosities about 10 Pa s. The respective viscosities increase slightly as the α-cellulose content increases to 11%. At higher α-cellulose content, however, the viscosity increases very rapidly. This is probably associated with structural changes that occur in the viscose, resulting from the isotropic molecular order of long range in cellulose xanthate macromolecules. The presence of both Berol-Spin and urea, respectively, lower the viscosity of the viscose solutions, with the latter showing a greater effect. This behavior can be explained by proposing a higher solvation of cellulose xanthate macromolecules in the viscose in which small quantities of urea are present. It seems that the system of solvated cellulose xanthate macromolecules in the presence of urea in viscose is stable under the conditions. This brings about a reduction of viscosity of the viscose at higher α-

Figure 1 The effect of α-cellulose content in viscose vs. viscosity: (— ○ —) standard viscose; (— □ —) viscose containing the modifier Berol-Spin; (— △ —) viscose with alkalicellulose containing urea.
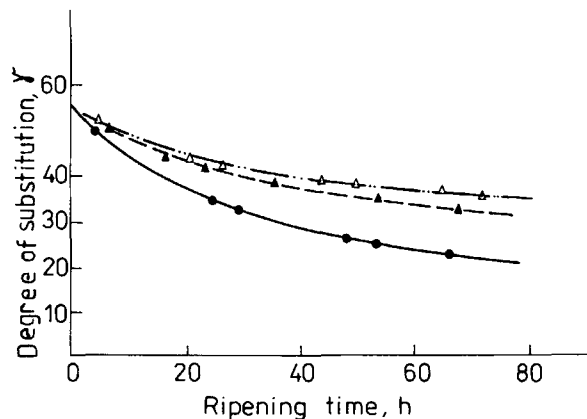
† Berol-Spin is the technical name of a surfactant produced by Berol Nobel Co. in Sweden.

cellulose concentrations. Such a conclusion is confirmed by the fact (Fig. 2) that in the viscose containing even small quantities of urea the hydrolysis of xanthate groups proceeds considerably slower.

An additional conclusion may be drawn from Figure 2, namely, that as the α-cellulose content is increased in the viscose, the degree of substitution γ, during the viscose ripening, decreases much slower than that of viscoses with lower cellulose concentrations. This phenomenon may probably be explained by a lower degree of dissociation of NaOH and smaller mobility of OH^- ions in the viscoses with higher α-cellulose content and, consequently, higher viscosity. These observations are confirmed by the fact that the ripeness of viscose expressed in Hottenrott degrees ($^\circ H$) changes considerably slower in viscoses with higher α-cellulose content (Fig. 3). The viscose containing small quantities of urea introduced with alkalicellulose is more stable and its degree of ripeness is reduced slower as compared with a standard viscose of the same α-cellulose content. This result confirms a higher degree of solvation of cellulose xanthate macromolecules in so-called urea viscoses, as compared with standard viscoses.

Viscoses with various α-cellulose content were used in our laboratory to produce fibers by the two-bath method; the second bath was only slightly acidified with sulfuric acid and maintained at a temperature of 80°C. The fiber-spinning process was carried out with a draw ratio of 30.6%, with a maximum draw ratio, and without drawing. Characteristics of the fibers prepared are shown graphically vs. the α-cellulose content in the viscose. Figure 4
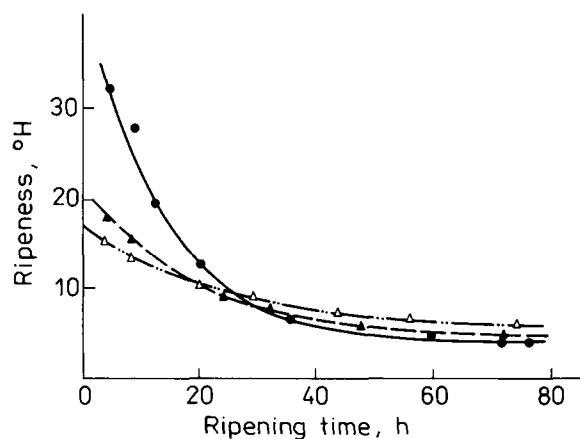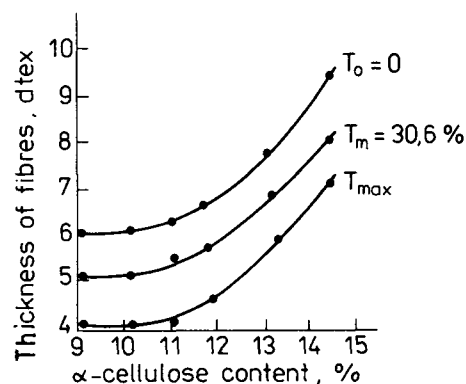

Figure 4 Concentration of α-cellulose in viscose vs. linear density of fibers: T_0, tension of fibers = 0; T_m — medium tension; T_{max} maximum tension.

shows that the fiber linear density increases with increase in the concentration of polymer in the viscose. When the α-cellulose content is increased from 9.3 to 10.3%, the fiber linear density increases slightly, but when the concentration of α-cellulose in the viscose is over 11%, a very rapid increase in fiber linear density is observed.

These changes in fiber linear density can be explained in terms of structural variations, i.e., that the structure of fibers obtained from viscose with higher α-cellulose content is less compact under the spinning conditions used. It is characteristic that the tensile strength of fibers depends not only on the α-cellulose content in viscose (Fig. 5), but also on the draw ratio of fibers during spinning. Using the maximum draw, the tensile strength of fibers is decreased as the α-cellulose content is increased from 9.3 to 14.3%. The tensile strength reduction is, in this case, about 20%. When the draw ratio is 30.6%, the tensile strength is only slightly decreased,
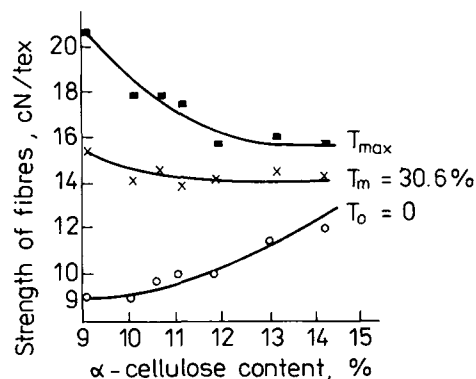

Figure 3 Viscose ripeness in Hottenroth degree vs. time: (— ● —) standard viscose with 9% α-cellulose; (— ▲ —) standard viscose with 10% α-cellulose; (— △ —) viscose modified by urea with 10% α-cellulose.

Figure 5 Concentration of α-cellulose in viscose vs. strength of fibers. See Figure 4 legend for abbreviations.
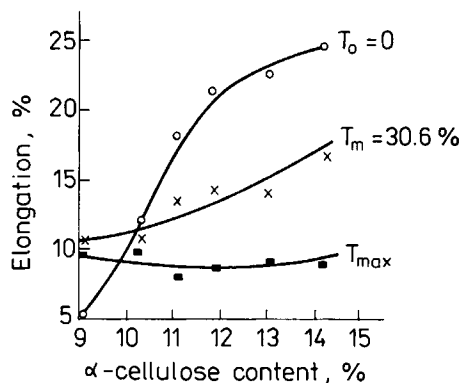
Figure 6 Concentration of α-cellulose in viscose vs. fibers elongation. See Figure 4 legend for abbreviations.

while at the draw ratio equal to 0%, the tensile strength of fibers increases with a simultaneous increase in elongation at break (Fig. 6). The elongation does not change practically when the maximum draw ratio is used on spinning.

CONCLUSIONS

The addition of urea to the steeping solution in the alkalicellulose formation results in substantial changes in the viscose obtained, namely, its viscosity is reduced, the ripening time is increased, and a higher degree of xanthate substitution, expressed as the γ value, is obtained than usually would be ob-

served without the use of the urea. Based on these experimental observations, the presumption is made that a complex of the urea with the alkalicellulose is formed, which limits side reactions occurring during xanthation. Therefore, xanthation, the reaction of carbon disulfide with alkalicellulose, occurs to a higher level. In this case, the C_6 hydroxyl group is reacted to a higher degree of substitution than in the absence of the urea. This supposition follows from our observation that the ripening time of the viscose in the presence of urea is longer than for conventional viscose solutions.

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