RHEOLOGICAL PROPERTIES OF CONCENTRATED CELLULOSE SOLUTIONS IN N-METHYL MORPHOLINE-N-OXIDE

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The rheological properties of polymer solutions, which determine conditions for processing them into fibres, depend to a considerable extent on the concentration of polymer in the solution [1]. Increasing the polymer concentration of a spinning solution is an important factor in the technology of preparing man-made fibres, since thereupon the consumption of solvent is reduced and its facilitation is facilitated, and the productivity of the equipment is increased. Moreover, increasing the polymer concentration can lead to a considerable change in the viscoelastic characteristics of the solution and affect the stability of jet formation during spinning [2].

In the present article, we examine the rheological properties of highly concentrated solutions of cellulose and N-methylmorpholine-N-oxide (MMO) and the stability of jet outflow on varying the concentration of cellulose in the solution. We studied solutions containing from 10 to 28% by wt. of cellulose, at temperatures of 90-125°C.

The solutions were prepared from sulfite coniferous wood cellulose, which had been ground to a powdery state by use of a double-worm extruder and which had a degree of polymerization of ~600. As solvent we used hydrated forms of MMO which are solid crystalline materials at room temperature. Concentrated solutions containing 10-15% of cellulose were prepared using MMO monohydrate, which contains 13% water. The preparation of highly concentrated solutions (containing 20% cellulose or more) is possible only when one uses hydrated forms of MMO containing less than 13% water and which are characterized by a greater dissolving power and a higher melting point.

To prepare the highly concentrated solutions we used an MMO hydrate containing 6-8% H2O. The conditions for preparing the solutions for rheological studies simulated the conditions for preparing solutions in spinning, which have been described in [3]. Tablets were formed at room temperature from a powdery mixture of cellulose, MMO, and a thermostabilizer (butyl gallate), which had been homogenized by jointly grinding together. The tablets were charged to the working unit of a rheogoniometer, which had been heated to the temperature at which the experiment was performed. A 30-min heating of the tablets was sufficient for forming a solution and thermostatting. Rheological characteristics were determined on a PIRSP-1M rheogoniometer [4] under continuous shear conditions and under a regime of low-amplitude harmonic vibration. The amplitude of deformation, $\gamma_0$ was $2.82 \times 10^{-1}$. The realized region of shear stress velocities $\gamma$ and shear stresses $\tau$ was in the range $10^{-3}$ to $10^1$ sec$^{-1}$ and 1 - $10^4$ Pa, respectively. The frequency $\omega$ was varied from 1.5 - 10 to 2.8 sec$^{-1}$. From the $\tau = f(\gamma, \omega)$, we calculated the viscosity $\eta$, the elastic and loss moduli $G'$ and $G''$, and the tangent of the mechanical loss angle ($\tan \delta = G''/G'$).

In Fig. 1, we give flow curves for the investigated solutions in the form of log $\eta = f(\log \tau)$ dependences, obtained at 125°C. The temperature of 125°C was selected for reference since solutions with a concentration >25% by wt. are not formed at temperatures below 125°C. As is evident from Fig. 1, increasing the concentration of cellulose in a solution from 10-25% leads to a viscosity rise of more than 650-fold. Flow curves do not have a Newtonian region in the investigated $\tau$ range. On each curve one may discern two sections which differ in the degree of slope to the abscissa. With increase in cellulose concentration in the solution, the more gently sloping region is contracted, and the point of inflection is displaced into the region of higher $\tau$ values.

The concentration dependence of viscosity which is shown in Fig. 2 was constructed from the data of Fig. 1 for log $\tau = 2.2$. In the logarithmic coordinates, this dependence is practically linear and has a slope to the abscissa, $\tan \beta \sim 7$. This figure is comparable with that of solutions of cellulose in MMO having a concentration lower than 10% [3].
Fig. 1. Flow curves of solutions of cellulose in MMO. Numbers on curves correspond to the concentration of the solution in % by wt.; \( t = 125^\circ C \).

Fig. 2. Dependence of viscosity of solutions of cellulose in MMO on concentration in log-log coordinates; \( t = 125^\circ C \).

In Fig. 3, we give frequency dependences of the elastic modulus \( G' \) and the loss modulus \( G'' \), obtained at \( 125^\circ C \). The shape of the curves and the order of magnitude of the quantities \( G' \) and \( G'' \) are characteristic of true solutions. Increasing the cellulose concentration from 10 to 28% leads to an increase both in the elastic \( (G') \) and also in the viscous \( (G'') \) components of the viscoelastic characteristics of the solution. Here \( G' \) is increased to a greater extent than \( G'' \). The \( \tan \delta = f(C) \) given in Fig. 4 illustrates this. (The values of \( G' \) and \( G'' \) were taken at \( \log \omega = 1.38 \).) Analysis of the curve makes it possible to discern two concentration regions within whose ranges the character of this dependent is different. The value of cellulose concentration which defines these two regions is 15-18% by wt. Apparently, different supermolecular structures of the cellulose spinning solutions are realized within the range of these two regions.

Investigation of the stability of the jet-formation process was carried out by a laboratory set-up which has been described in [3], in forcing the solution through capillaries of various diameters \( d \) (from 0.3 to 1.5 mm) and of various lengths \( l \) (from 0.4 to 20 mm). The flow rate \( Q \) was varied in the range \( 5 \times 10^{-7} - 10^{-8} \) m\(^3\)/sec. In extruding 10-15% solutions and varying the spinning parameters within the indicated limits, jet formation was stable. On further increase in cellulose concentration in the solution and, correspondingly, on changing the viscoelastic properties of the solutions, a sharp impairment in the stability of outflow was observed, expressed in periodic changes in form and surface of the jet (a phenomenon of flow instability or "elastic turbulence." The concentration regions of stable and unstable flow correlate with the two characteristic regions of cellulose concentration in the spinning solution which were discovered in the rheological studies. It is considered that the onset of flow instability is connected with a build-up of highly elastic deformations in the flowing polymer solutions [5-7]. As the rheological studies showed, on transition into the region of high concentration (cellulose content of the solution 20% or more), the intensity of rise in elastic properties is increased. The highly concentrated solutions of cellulose are elastic, rubberlike masses.