Rheological investigation of aqueous solutions of poly(vinyl alcohol) during aging II. Influence of experimental conditions on dissolution and aging

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Abstract: The influence of the temperature and time of heating during dissolution on the aging of concentrated aqueous solutions of poly(vinyl alcohol) and aging at different temperatures are described. Changes occurring during aging are interpreted on the basis of non-Newtonian viscosity and normal stress measurements.

Key words: Polyvinylalcohol, aging, non-Newtonian viscosity, normal stress.

It is known that the way of preparation of poly(vinyl alcohol) (PVA) solutions, and particularly the temperature of dissolution, affects their properties connected with the relative contents of the amorphous and crystalline part in the original polymer. Properties of solutions arising under different experimental conditions have been investigated by various methods, e.g. by measurements of viscosity and light scattering [1, 2], flow birefringence [3] and turbidity [2, 4–6]. As has been reported in our earlier communication [7], during the aging of concentrated aqueous PVA solutions aggregated supermolecular structures are formed which according to the existing views [8] contain the amorphous and crystalline phase. We believed that their formation might be affected by the amount of undissolved crystallites in a freshly prepared solution, and that, consequently, the rate of aging might depend on the temperature and time of dissolution and on the temperature of aging.

This paper reports the results of a systematic study of such effects on the process of aging of concentrated aqueous PVA solutions prepared in the temperature range below 90°C. The study is based on measurements of the shear dependence of viscosity and the first normal stress difference.

Experimental

Polymer

The same polymer as in the preceding paper [7] was used, manufactured by BDH Chemicals Ltd (England). The PVA sample (Mw = 22 300) was atactic and contained less than 1% of residual acetate groups.

Sample preparation

The PVA concentration of all solutions under study was 16 wt. %; it may be assumed [7] that macromolecules in these solutions were entangled.

The polymer was dissolved at Ts = 80°C for ts = 5 h (sample A1) and ts = 6 days (sample A2), at Ts = 85°C, ts = 5 h (sample B1) and ts = 6 days (sample B2), and at Ts = 90°C, ts = 5 h (sample C1) and ts = 6 days (sample C2). The dissolution took place in a water thermostat in conical vessels. All mixtures of polymer samples with water were stirred during the dissolution with an electromagnetic stirrer for 5 h, when the dissolution was complete. Further heating proceeded without stirring. After removal from the thermostat the vessels containing the polymer solution were quickly cooled to the temperature of aging.

Aging

Samples A-C prepared at various temperatures Ts and during various times ts were subjected to aging at 23°C. The effect of the temperature of aging Ta was followed only for solutions A1, at tem-
temperatures \( T_s = 10, 13, 15, 18, 30 \text{ and } 50 \, ^\circ\text{C} \). The aging took place in a thermostat, in the same vessels as dissolution, without stirring.

**Measurement**

Rheological characteristics of the solutions under investigation, i.e., viscosity and the first normal stress difference, were measured depending on the velocity gradient at a standard temperature 23 \( ^\circ\text{C} \), during the aging within the time interval starting from one day after the dissolution of the sample till the time when the values could still be reliably measured. A Weissenberg rheogoniometer (model R-18) with cone-plate system was used in the measurement. The diameter of the cone was 5 cm, the cone angle was 2 \( ^\circ\).

**Results and discussion**

Results of the experiments which hold for all the temperatures of aging used in the range 10–50 \( ^\circ\text{C} \) may be summarized in several points.

(1) The dependences of viscosity on the velocity gradient of all fresh solutions were almost Newtonian; at \( \dot{\gamma} \to 0 \), their viscosity was virtually the same, irrespective of the temperature and time of dissolution.

(2) During the aging the dependence of viscosity on the velocity gradient became non-Newtonian, the more so the older the solutions. For various times and temperatures of heating used in the dissolution this behaviour is characterized by the normalization time constant \( \tau_o \) \([7]\) (relaxation time) (Fig. 1). The dependences of \( \tau_o \) on the time of aging of solutions \( t_o \) observed for solutions after a longer time of dissolution, \( t_o = 6 \) days (curves A2, B2, C2), are closer to each other at all temperatures \( T_s \) (80–90 \( ^\circ\text{C} \)) than the dependences for \( t_o = 5 \) h (curves A1, B1, C1). At the highest temperature of dissolution (curves C1, C2) the time of dissolution has a much weaker effect on \( \tau_o \) than at 80 \( ^\circ\text{C} \) (curves A1, A2). It seems that at a certain limiting temperature the effect of extended time of heating disappears.

(3) Viscosity at a given velocity gradient measured at 23 \( ^\circ\text{C} \) increased during the aging in all solutions (Fig. 2), until at last a gel was formed. The gels thus formed were thermoreversible, i.e., they dissolved again at the solution temperature.

(4) The first normal stress difference value increased during the aging (Figs. 3–5), and after a certain time of aging a maximum appeared on the \( N_1 \) vs. \( \dot{\gamma} \) curves. Its height \( N_{1,m} \) and position \( (\dot{\gamma})_m \) depended on the time and temperature of dissolution and on the time of aging. The longer the time and the higher the temperature of dissolution, the lower the \( (\dot{\gamma})_m \) values in solutions of the same age, and the faster the rise in \( N_{1,m} \) with time (Fig. 5). Figures 2 and 3 show the plots of \( \eta \) and \( N_1 \) on the time of aging at \( \dot{\gamma} = 71.2 \, s^{-1} \) when there is still no change in the supermolecular structure caused by flow, as indicated by the presence of the maximum. In the range of higher velocity gradients, when the supermolecular structure has already been irreversibly changed by flow (at \( \dot{\gamma} = 355 \, s^{-1} \)), the \( N_1 \) values were more poorly reproducible; nevertheless, however, the dependences in Figure 4 show a similar relative shift with the temperature \( T_s \) and the time \( t_o \) as those at \( \dot{\gamma} = 71.2 \, s^{-1} \).

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**Fig. 1.** Dependence of the relaxation time \( \tau_o \) on the time of aging \( t_o \) for various temperatures and times of dissolution temperature and time of dissolution: A1 80 \( ^\circ\text{C} \), 5 hours; A2 80 \( ^\circ\text{C} \), 6 days; B1 85 \( ^\circ\text{C} \), 5 hours; B2 85 \( ^\circ\text{C} \), 6 days; C1 90 \( ^\circ\text{C} \), 5 hours; C2 90 \( ^\circ\text{C} \), 6 days

**Fig. 2.** Dependence of viscosity \( \eta \) at \( \dot{\gamma} = 71.2 \, s^{-1} \) on the time of aging \( t_o \) for various temperatures and times of dissolution. Points and curves denoted as in Figure 1