CHEMISTRY AND TECHNOLOGY OF NATURAL POLYMER FIBRES

THE TEMPERATURE DEPENDENCE OF THE VISCOSITY OF THE RIPENING VISCOSE

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The ripening process is still the longest and least efficient stage in viscose fibre production and its control consists mainly of bringing the ripeness index to the point required for producing a given fibre type. Process regulation is largely time-based since the quite low temperature (16 - 19°C) is constant.

However, in connection with the recently adopted continuous process of viscose deaeration the production process is now being accelerated by the short-term heating of the solution to 25 - 40°C. It is being assumed that this heating represents an intermediate stage in a change-over to ripening at a higher temperature than at present. This brings to the fore the problem of the influence of the conditions of ripening at varied temperatures on the physical and mechanical properties of the viscose.

An elucidation of the problem was sought by the writers in an investigation of the variation of the viscose viscosity which is one of the principal indices in the complex of the physical and mechanical properties of fluid polymeric systems and in the chemical composition of the cellulose xanthate and is characterized by the degree of esterification and the distribution of the xanthate groups in the glucose residues during ripening.

Fig. 1. The viscosity, degree of viscosity anomaly, and activation energy of viscous flow vs. the ripening time of the viscose at 20°C.

Fig. 2. The temperature dependence of the viscosity (in Arrhenius co-ordinates) for various viscose ripening times (h): 1) 0, 2) 24, 3) 48, 4) 72, 5) 96, 6) 114.
Fig. 3. The variation of the chemical composition of the cellulose xanthate in the viscose in the ripening process at 20°C (a) and with a stepwise increase in the temperature from 40 to 60°C, each temperature being thermostatically controlled for 15 - 20 min (b).

Fig. 4. The ripening time to minimal viscosity as a function of the ripening temperature.

Fig. 5. The effective viscosity vs. the concentration of xanthate groups at the 6th carbon atom of the glucose radical at \( \tau = 9.8 \times 10^3 \) dyn/cm\(^2\) and a ripening temperature of 20 (1), 30 (2), 40 (3) and 60 (4) °C; O denotes a decrease and A an increase in the viscosity.

The experiments were carried out with viscose of an initial degree of esterification \( \gamma_1 = 45 - 55 \). The viscosity was measured on a Heppler viscometer over a shear stress range from \( 9.8 \times 10^3 \) to \( 3.67 \times 10^5 \) dyn/cm\(^2\) at a temperature of 13 - 80°C. Each temperature was controlled thermostatically for 15 - 20 min. The relative concentration of xanthate groups \( \gamma_{2,3} \) and \( \gamma_6 \) (at the 2nd, 3rd and 6th atoms of the glucose radical) was determined by a spectrophotometric method /1/. The ripeness of the viscose was determined by the standard procedure on a 20% solution of NaCl.

The basic experimental data of viscometric measurements is represented by the relation between the viscosity \( \eta \) and the shear stress \( \tau \) at different temperatures and degrees of ripeness of the viscose. In the initial ripening stage the viscosity decreases over the entire shear stress range investigated, especially at low stress values. The result is that up to a certain ripening time, which varies with the temperature, the degree of viscosity anomaly decreases. This quantity is assessed from the ratio of the effective viscosities for \( \tau = 3.6 \times 10^5 \) and \( 9.8 \times 10^3 \) dyn/cm\(^2\). When ripening proceeds at 20°C, the viscosity (at \( \tau = 9.8 \times 10^3 \) dyn/cm\(^2\)) and the degree of viscosity anomaly are at a minimum 50 - 55 h after the end of the dissolution process (Fig.1) while subsequently both quantities increase until the viscose coagulates.

An important parameter for characterizing the viscosity of the viscose is the energy \( E \) of viscous flow activation which defines the temperature dependence of the viscosity. However, the measurement of \( E \) for a viscose is a highly complex task since the chemical processes resulting in a change in the composition of the viscose depend essentially on the temperature. In the viscosity measurements the thermostatic control time was, therefore, maintained constant for all temperatures while the chemical composition was monitored from the quantities \( \gamma_1, \gamma_6 \) and \( \gamma_{2,3} \).

The temperature dependence of the viscosity for \( \tau = 9.8 \times 10^3 \) dyn/cm\(^2\) (Fig.2) shows that for "young" as well as for "ripe" viscoses the relation between \( \ln \eta \) and \( 1/T \) can be divided into two sections corresponding to flow at dissimilar activation energies, viz. \( E_{f1} \) at 13 - 50°C and \( E_{f2} \) at 50 - 80°C.

The temperature at which the character of \( \ln \eta \) as a function of \( 1/T \) changes decreases with an increase in the ripening time and thus can serve as an indirect index of ripeness. In the ripening process \( E_{f1} \) first decreases from 9 to 6.5 kcal/mole, then increases to 8.5 - 9 kcal mole (after ripening for \( \gamma_4 \) h at 20°C). The activation energy \( E_{f1} \) is at a minimum at a ripening time of about 50 h which corresponds to minimal viscosity as Fig.1 shows. The symbatic variation of the activation energy with the viscosity was discussed elsewhere /2/.