

The Influence of the Stretch Ratio on the Rate of Diffusion in a Wet-Spinning Process

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Synopsis

This article describes diffusion experiments on a single filament spinning set. The aim was to find phenomena which may occur in any wet-spinning process. An alkaline poly(vinyl alcohol) solution containing an indicator was spun out into a coagulation bath containing Na_2SO_4 , after which the filament was guided into an acidic second bath. The first bath served to deswell the filament in order to avoid contamination in the diffusion study. In the second bath the diffusion of H^+ and OH^- ions was studied by measuring the distance which had to be covered by the filament in order to produce a color change of the indicator at the center of the filament. The equation for cylindrical diffusion was tested at various mechanical adjustments of the spinning set. It was found that the rate of diffusion decreases with increasing stretch ratio. Moreover, the relevant diffusion equation is qualitatively very well applicable to the phenomena considered, provided the applied stretch ratio is taken into account.

INTRODUCTION

In the rayon spinning process an alkaline cellulose xanthate solution, the viscose, is extruded into a spinning bath containing sulfuric acid and salts such as Na_2SO_4 and ZnSO_4 . The viscose is coagulated in the spinning bath by the action of the salts, while a simultaneous neutralization sets in by the diffusion of H^+ ions into the filament. (We will denote the solvated hydrogen ions simply by H^+). The H^+ ions react with the cellulose xanthate, which decomposes into the so-called regenerated cellulose. In the last two decades numerous experiments have been performed to study the diffusion process in viscose model filaments to gain more insight into the mechanism of the structure formation of the resulting cellulose product.¹⁻⁶ It is clear that the importance of the study of diffusion phenomena is not restricted to rayon spinning, since in any wet-spinning process the velocity of filament formation is determined by the rate of mass transfer of the components of the spinning solution and the spinning bath.

Booth,⁷ for instance, reported some investigations on the diffusion of ZnCl_2 into polyacrylonitrile filaments which were spun into an aqueous ZnCl_2 bath. The aim of our experiments was to study the diffusion of the components at various mechanical adjustments of the spinning apparatus. Because of the simplicity of the system, the spinning of poly(vinyl alcohol)

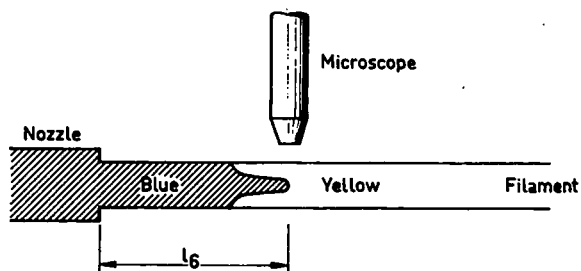


Fig. 1. Color change in filament on spinning an alkaline PVA solution to which bromocresol purple has been added into an acidic Na_2SO_4 solution; l = neutralization point distance.

filaments is very attractive for this purpose. An aqueous PVA solution can be spun by extrusion into a spinning bath consisting of an aqueous Na_2SO_4 solution. As it is not possible to determine the diffusion of Na_2SO_4 , we made a study of the transfer of H^+ and OH^- ions in a similar way as was done earlier in viscose spinning. An alkaline PVA solution to which an acid-base indicator had been added was spun into an acidic Na_2SO_4 solution. As sketched in Figure 1, the color change of the indicator in consequence of the diffusion of H^+ ions into the filament can be detected with a microscope.

The boundary between the colors in the filament indicates an equiconcentration surface of H^+ ions; in the particular case of bromocresol purple, the color change occurs at a pH of about 6.

EXPERIMENTAL

The spinning machine was the apparatus used by Vroom⁵ for his study on the viscose spinning process, with slight modifications. The PVA solution was extruded through a one-hole nozzle 100μ in diameter by means of a pump giving a solution delivery practically free from periodic fluctuations. The pump had an infinitely variable drive; the solution delivery ϕ ranged from 0.025 to 0.1 ml/min.

The cylinder and the supply lines containing the polymer solution were provided with heating jackets to keep the solution at the desired temperature of 40°C .

The composition of the spinning solution was the same for all the experiments performed. The concentrations, expressed in weight percentages, of the aqueous solution were as follows: 10% PVA; 0.99% NaOH; 0.2% bromocresol purple. In a series of preliminary experiments the purple-colored solution was spun out into an aqueous coagulant containing 30% Na_2SO_4 and 0.6% H_2SO_4 by weight. The coagulation bath was thermostated at 40°C as well, in order to avoid the possibility of interference by heat transfer phenomena. The color change from purple to yellow at the center of the filament was observed through a microscope (magnification $100\times$). The microscope assembly was mounted on a motor-driven worm

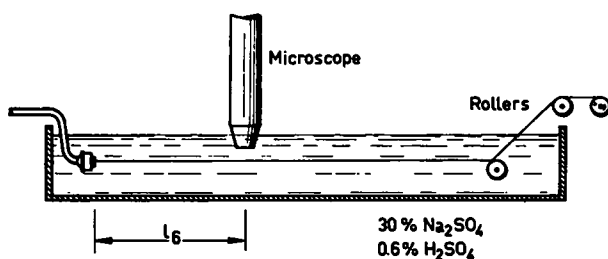


Fig. 2. Schematic sketch of one-bath spinning system.

1.15 m in length, running parallel to the spinning bath. The distance l between the nozzle hole and the point where the color change occurred was read from a ruler fixed to the worm holders. To facilitate the observations, the bottom of the bath was made of transparent glass, below which a fluorescent tube was placed. The inaccuracy of the measurement of the distance l was not greater than 2 cm. However, the one-bath spinning scheme as shown in Figure 2 did not fulfil all the requirements for our study: Within a distance of 10 cm from the nozzle, the diameter of the filament decreased by a factor of 2 as a result of osmotic deswelling of the filament. During this deswelling process the development of a water jacket around the filament was observed. The water jacket looks like a well-defined layer, which suggests a laminar flow pattern around the filament. In consequence of the difference in density with respect to the bulk of the spinning bath, the water jackets separates from the filament at a distance of about 10 cm from the nozzle. So in the first stage of the spinning process, there will be a coupling between the flow of water (deswelling) and the transfer of OH^- and H^+ ions. In order to avoid a disturbance of simple diffusion of H^+ and OH^- ions by the deswelling process, a two-stage spinning bath arrangement was preferred.

As sketched in Figure 3, the two baths were separated by a partition provided with a hole, through which the filament was guided. The first bath (30% Na_2SO_4) served to deswell the filament; in the second bath the diffusion of H^+ and OH^- ions was studied. The Na_2SO_4 concentration of the second bath was chosen somewhat lower than for the first in order to prevent further deswelling. By microscopic examination, with an ac-

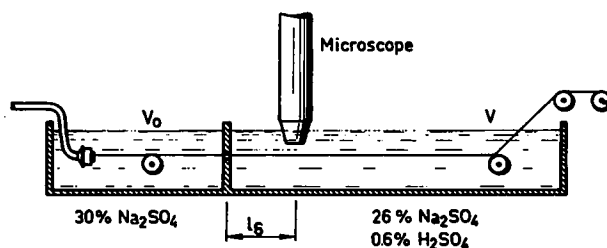


Fig. 3. Sketch of two-stage spinning bath arrangement: V_0 and V are the velocities of the respective rollers; l_6 = neutralization point distance; $\text{pH} \approx 6$.

curacy of about 10%, no change in the filament diameter could be observed after the partition. The diameter of the hole in the wall was 0.2 cm, a factor of 20 larger than the filament diameter. Now l_6 is the distance between the wall and the point where the color change occurs in the center of the filament. The index 6 refers to the fact that in our experiments the color change occurs when a pH of about 6 is reached. Due to the large volume of the spinning baths the liquid flow through the hole from one bath to the other was relatively small. Thus it was found for any specific adjustment of the spinning apparatus that l remained constant for at least 1.5 hr. Besides, the measurements of l_6 were very well reproducible for the various adjustments. As indicated in Figure 3, the circumferential speeds of the drive rollers in the first and the second bath gave the filament a linear velocity of V_0 and V , respectively. The first roller was placed at a distance of 5 cm before the partition wall to ensure a correct filament velocity V in the second bath. According to the law of conservation of mass, the following relations hold between the parameters V_0 , V , and the solution delivery ϕ :

$$\alpha\phi = \pi R_0^2 V_0 \quad (1)$$

$$\alpha\phi = \pi R^2 V \quad (2)$$

where R_0 and R are the radii of the filament, before and after the first roller, respectively. The factor α , which is smaller than 1, corrects for the fact that the diameter of the filament is decreased by deswelling. The magnitude of α could not be precisely computed, because the diameter of the filaments was not measurable with sufficient accuracy. However, as the composition of the spinning solution and the bath was the same in all the experiments described here, the correction factor α may be assumed to be equal for all cases where a definite value for V_0 was chosen. It is clear that for an arbitrarily chosen set of the parameters ϕ and V_0 , the stretch ratio V/V_0 can be adjusted to any desired value by adjustment of V . For a series of stretch ratios, the birefringence was measured with a Babinet compensator (Winkel-Zeiss, Göttingen). To this end, the compensator was mounted on the microscope and the birefringence of the filament was measured in the second bath at a distance of 30 cm from the partition wall. In these experiments the indicator in the spinning solution was omitted to facilitate the observations. The measurements on the filament tension were performed with the device used by Vroom.⁵

THEORETICAL

For a cylinder of infinite length, in which diffusion is radial everywhere, Fick's second law for diffusion reads as follows:

$$\frac{\partial c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(rD \frac{\partial c}{\partial r} \right) \quad (3)$$

where c is the concentration of the diffusing substance, t is the time, r is the distance from the axis of the cylinder, and D is the diffusion coefficient. For the relevant case the solution of eq. (3) has to satisfy the following boundary conditions for a cylinder with radius R :

$$\begin{aligned} c &= c_a & \text{for } r &= R & \text{at } t &\geq 0 \\ c &= c_b & \text{for } r &= R & \text{at } t &= 0 \end{aligned}$$

Assuming that D is independent of the concentration, the solution can be written:

$$c(r,t) = c_a + 2(c_a - c_b) \sum_{n=1}^{\infty} \frac{1}{k_n} \frac{J_0(k_n r/R)}{J_0'(k_n)} \exp - \frac{k_n^2 D t}{R^2} \quad (4)$$

where $J_0(x)$ is a Bessel function of the first kind and zero order, $J_0'(x)$ is its first derivative, and the quantities k_n are the n th roots of the equation $J_0(k_n) = 0$.

In our experiments we are dealing with diffusion of two fast-reacting ion species, viz., the H^+ and OH^- ions.

According to Hermans,¹ eq. (4) is still applicable when the diffusion coefficients of the reacting species are equal. If this is assumed to be the case, then the alkaline concentration must be regarded as a negative acid concentration. In other words, in eq. (4) one has to write $c_a + c_b$ instead of $c_a - c_b$, if the concentration parameters have the following meaning: $c(r,t)$ = acid concentration in the filament at a distance r from the axis at time t ; c_a = acid concentration at the filament surface; c_b = alkaline concentration in the filament at $t = 0$.

The problem then is relating the spinning equation, eq. (2), to the equation for cylindrical diffusion, eq. (4). We will derive this relation in a way somewhat different from that presented earlier by Vroom⁵: As mentioned before, we kept the initial concentrations c_a and c_b constant in our series of experiments. Then, $c(r,t)$ is only dependent on the dimensionless parameter Dt/R^2 . For a definite value of $c(r,t)$, the parameter Dt/R^2 also has a definite value. We have chosen an indicator which changes its color at an H^+ concentration of 10^{-6} . The color change was detected at the center of the filament. So the definite value of $c(0,t) = 10^{-6}$.

Let us say now that for $c(0,t) = 10^{-6}$, the relevant value of the dimensionless parameter

$$Dt_6/R^2 = \pi K \quad (5)$$

where t_6 is the residence time required in the second bath (see Fig. 3) to obtain an H^+ concentration of 10^{-6} at the center of the filament, $\pi = 3.14$, and K is a constant.

Experimentally, however, one measures the distance l_6 , as shown in Figure 3; t_6 and l_6 are simply related by

$$t_6 = l_6/V. \quad (6)$$

Substitution of eq. (6) in eq. (5) gives

$$l_6 = \frac{K}{D} \pi R^2 V. \quad (7)$$

Insertion of eq. (2) into eq. (7) leads to

$$l_6 = \frac{K\alpha\phi}{D}. \quad (8)$$

From eqs. (7) and (8) two statements can be derived: (I) The distance l_6 is independent of the velocity V at constant solution delivery ϕ . This is because an increase of V at constant ϕ results in a proportional decrease of R^2 according to eq. (2). (II) It must also be true that l_6 is proportional to V at constant R .

RESULTS AND DISCUSSION

To verify statement I, namely, that l_6 is independent of the circumferential velocity of the second roller V at constant solution delivery ϕ , the velocity of the first roller V_0 was kept constant (see Fig. 3). A constant V_0 in a set of experiments means that the residence times of the filaments in the first bath are equal. So one can assume that the filaments enter the second bath with the same composition of diffusing species. Figure 4 is a plot of l_6 against V : contrary to the prediction of l_6 being independent of V , it is shown that l_6 increases with an increase of V .

In a following experiment, the distance l_6 was measured as a function of V_0 at constant V and ϕ . As is shown in Figure 5, the parameter l_6 decreases with increasing V_0 . A relatively low V_0 means a longer residence in the first bath, which may affect l_6 in two ways: At longer residence times,

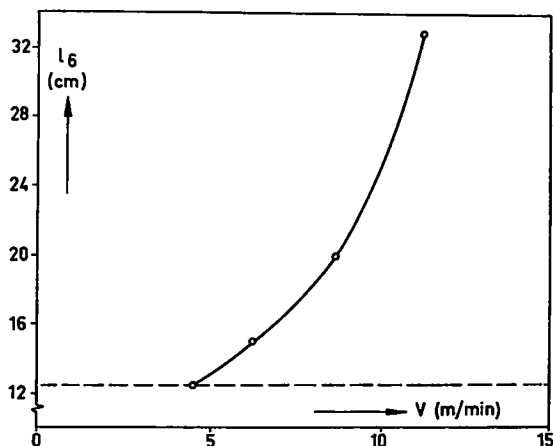


Fig. 4. Distance l_6 as a function of velocity V , with constant values of V_0 ($=2.8$ m/min) and ϕ ($=0.60$ ml/min). Horizontal broken line is the theoretical line.

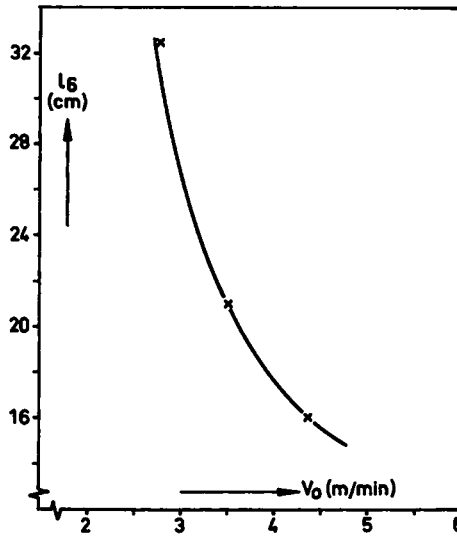


Fig. 5. Distance l_6 as a function of velocity V_0 , with constant V ($= 11.2$ m/min) and ϕ ($= 0.60$ ml/min).

in the first bath more OH^- ions will diffuse from the filament into the first bath. The filament then enters the second bath with a lower OH^- ion concentration, which should give a lower value for l_6 . On the other hand, the longer residence time in the first bath will enhance the deswelling of the filament which may result in a smaller D and consequently in a higher value of l_6 , see eq. (8).

A better insight into the phenomena described by Figure 4 and 5 is obtained when l_6 is plotted against the stretch ratio V/V_0 , as is shown in Figure 6. It is found then that the experimental data, as given in Figures 4 and 5, are represented by points belonging to one curve. So it appears

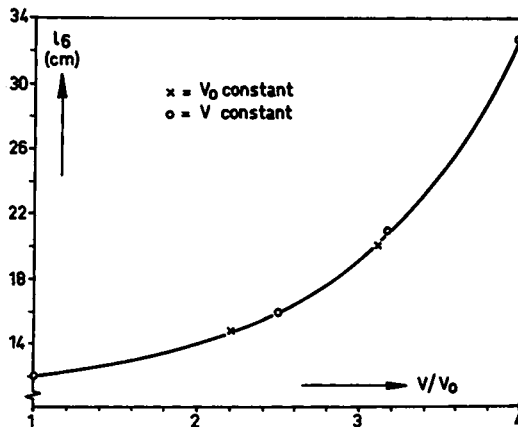


Fig. 6. Increase in l_6 with stretch ratio V/V_0 : $\phi = 0.60$ ml/min.

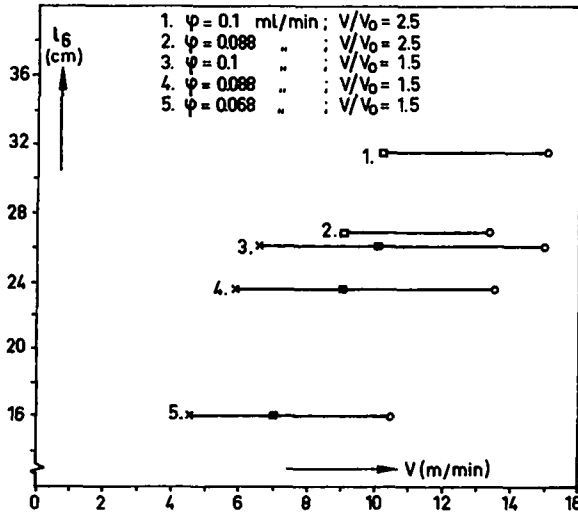


Fig. 7. Distance l_6 as a function of V at constant solution delivery ϕ and stretch ratio

that the stretch ratio has a much greater effect on the distance l_6 than the residence time in the first bath. Considering these results, it is reasonable to assume that statement I has to be modified: l_6 is independent of V at constant ϕ and constant stretch ratio.

Figure 7 shows a number of plots of l_6 against V . Each horizontal line refers to a definite solution delivery and stretch ratio. So the experimental results indeed confirm the correctness of the modified statement. If we compare the lines 1 and 3 in Figure 7, which are the results of experiments made at the same solution delivery $\phi = 0.1$ ml/min and at stretch ratios of 2.5 and 1.5, respectively, we again notice that l_6 is higher for the higher

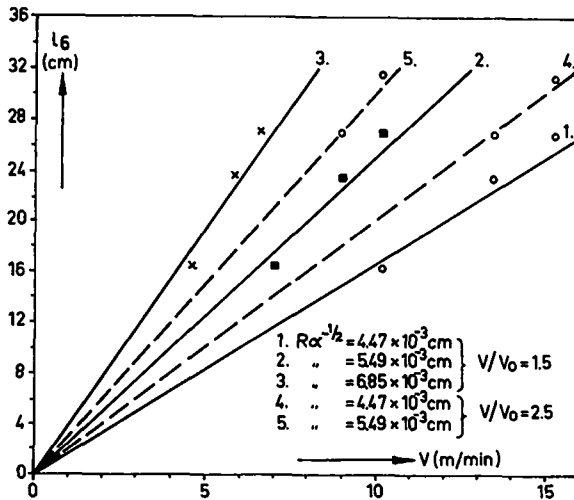


Fig. 8. Relation between l_6 and V at constant R and stretch ratio V/V_0 .

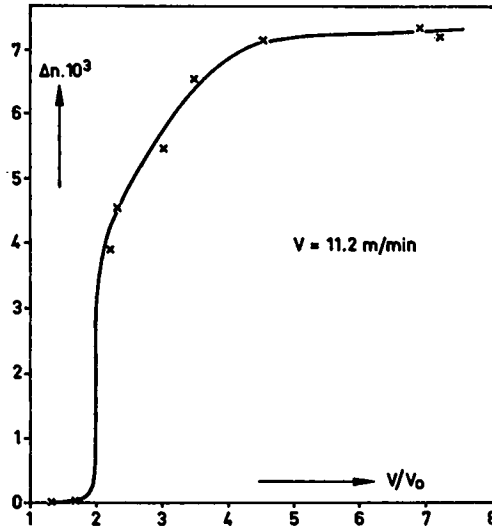


Fig. 9. Birefringence $\Delta n = n_{\parallel} - n_{\perp}$ as a function of stretch ratio.

stretch ratio. Considering eq. (8), one can conclude that the diffusion coefficient decreases with increasing stretch ratio. According to statement II, l_6 has to be proportional to V at constant R . Obviously, here, too, the additional condition of constant stretch ratio has to be fulfilled. Figure 8 gives a series of plots of l_6 against V , each line referring to a definite R and stretch ratio. Figure 8 clearly demonstrates that l_6 is proportional to V under the above-mentioned conditions.

As the diffusion presumably depends on the orientation of the polymer molecules, we also measured the birefringence of the filaments at various

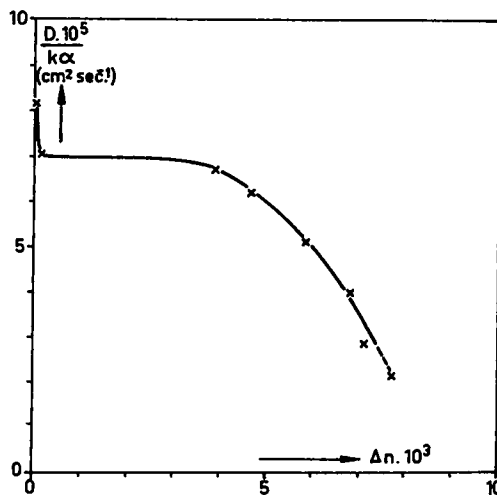


Fig. 10. Relation between diffusion constant and birefringence.

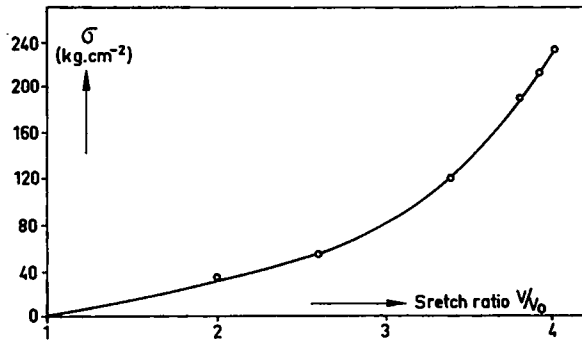


Fig. 11. Increase in tension σ with increasing stretch ratio.

stretch ratios during spinning. It is shown in Figure 9 that no measurable birefringence is found up to a stretch ratio of 2. The sudden, sharp increase of Δn at the stretch ratio of 2 may point to crystallization induced by the molecular orientation as a consequence of stretching. At ratios of V/V_0 higher than 5, Δn remains practically constant. For each stretch ratio the value of $D/K\alpha$ can be calculated by interpolation of the data given in Figure 6 and applying eq. (8). In Figure 10 the values of $D/K\alpha$ are plotted against Δn ; the relation between the two physical entities is not clear. It is peculiar that $D/K\alpha$ changes significantly at stretch ratios below 2, in the region where Δn is practically zero. Also, the tension σ was measured during spinning and plotted against the stretch ratio, as is shown in Figure 11. As could be expected, the tension increases with increasing stretch ratio. In Figure 12, finally, $\alpha K/D$ was plotted against the tension σ , and a linear relationship is found. Now, the reciprocal diffusion constant can be considered as a measure of the friction, which the ions will meet when they penetrate the filament. It must be said that the relation

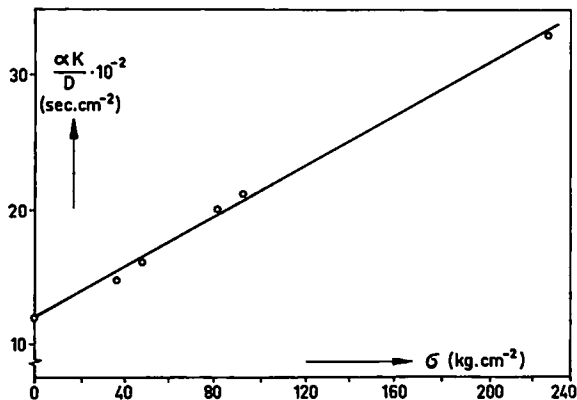


Fig. 12. Linear relationship between reciprocal diffusion constant and tension σ on the filament.

between $\alpha K/D$ and the tension σ just happens to be linear. Yet it is reasonable to conclude that the tension restricts the mobility of the polymer segment, as a consequence of which the diffusion of species is impeded.

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