Rheological Properties of Viscose

T. E. HOPKINS and J. W. WHATLEY

Film Department, Cellophane Research and Development Laboratory, E. I. du Pont de Nemours & Company, Inc., Richmond, Virginia

Introduction

The steady-state flow of polymers and suspensions and solutions of solids in liquids through cylindrical passages has been the subject of a number of investigations.[1-5] Since these types of fluids frequently exhibit non-Newtonian behavior, the relationship between shear stress and shear rate is not linear, and, consequently, the "viscosity" of these fluids varies as a function of shear rate.

In the manufacture of sponges, rayon, and cellophane, soluble cellulose is obtained through treatment with caustic soda, carbon disulfide, and water the result being a viscous solution known as viscose. Inskeep and Van Horn[6] have published a description of the commercial manufacture of this fluid as it pertains to the cellophane process. This study was undertaken to determine the rheological properties of viscose and to investigate the effect of cellulose concentration and molecular weight on these properties. A secondary purpose of this investigation was to show the effect of these rheological properties on the steady-state velocity profile of viscose in a round pipe.

Rheological Relationships for Pseudoplastic Fluids

The empirical power law for shear stress τ may be written

$$\tau = K(du/dr)^n \qquad (1)$$

for fluids whose properties are time-independent. Here, K is a fluid consistency index (lb. sec.^{n}/in.^{2}), du/dr is the shear rate (sec.$^{-1}$), and n is a dimensionless flow behavior index. A similar and more useful equation from an engineering standpoint is that developed by Metzner and Reed,[7]

$$D\Delta P/4L = K'(8V/D)^{n'} \qquad (2)$$

which represents the pressure drop–flow rate relationship for flow of a Newtonian as well as non-Newtonian fluid in a round pipe or tube, where D is the inside diameter of tube (in.), ΔP is the pressure drop (lb./in.^{2}), L is the length of pipe (in.), V is the average velocity (in./sec.).

The parameters n and n' are termed flow behavior indices, and their deviation from unity is a measure of the degree of non-Newtonian behavior. Metzner[8] states that few fluids have been found for which n and n' differ greatly, and therefore the two are used interchangeably. K and K' are defined as fluid consistency indices and are related by

$$K' = K[(3n + 1)/4n]^n \qquad (3)$$

The apparent viscosity μ_a is defined as the ratio of shear stress to shear rate and for power-law fluids is given by

$$\mu_a = K/(du/dr)^{1-n} \qquad (4)$$

The results reported here include numerical values for the rheological constants K, K', and n for viscose as functions of cellulose concentration and molecular weight.

Viscose Preparation

The viscoses used in this study were prepared from Southern Chemical Company's cotton linters pulp. The preparation was as follows. The pulp was steeped at 27°C. in 18% NaOH for 22 min. and shredded at 36°C. for 1 hr. The alkali cellulose thus obtained was aged for a given period of time before xanthation. Xanthation was performed in a laboratory baratte at a 45% CS_2 level (based on cellulose) at 30°C. for 2 hr. Mixing was accomplished in a laboratory-size Baker-Perkins shredder for 4 hr. at 10°C.

The viscoses used for study at varying cellulose content and constant degree of polymerization ($\overline{DP}$) were xanthated within $^1/_2$ hr. after removal from the shredder. The viscose at varying $\overline{DP}$ and constant cellulose content were made from

TABLE I
Viscose Compositions

	Viscose sample no.[a]					
	1–1	1–2	1–3	1–4	1–5	1–6
Cellulose, %	9.58	11.97	13.23	15.94	9.03	8.85
NaOH, %	5.54	6.99	8.3	10.61	5.38	5.33
Alkali cellulose aging time, hr.	0	0	0	0	16	32
$\overline{DP}$ of alkali cellulose	725	725	725	725	480	250

[a] 45% CS_2 based on cellulose and Southern Chemical Company cotton linters pulp used in preparation of all samples.

alkali cellulose aged 0, 16, and 32 hr. to give a progressively lower $\overline{DP}$. The compositions of these viscoses can be found in Table I.

Apparatus and Procedure

A capillary-tube viscometer of the type suggested by several previous investigators[1,8,9] was used for all experimental work reported in this paper. This viscometer, its support and related equipment are shown in Figure 1. The body of the viscometer was constructed from a 12-in. length of 1-in. diameter, schedule 40, stainless steel pipe. A cooling jacket concentric with the viscometer body was formed by welding a sheet metal liner around the periphery of the flanges attached to the ends of the pipe. O-ring seals were used at all flanged joints. The viscometer assembly was connected to a nitrogen pressure system consisting of a pressure gage, regulating valve, and a nitrogen cylinder by a high pressure, flexible hose.
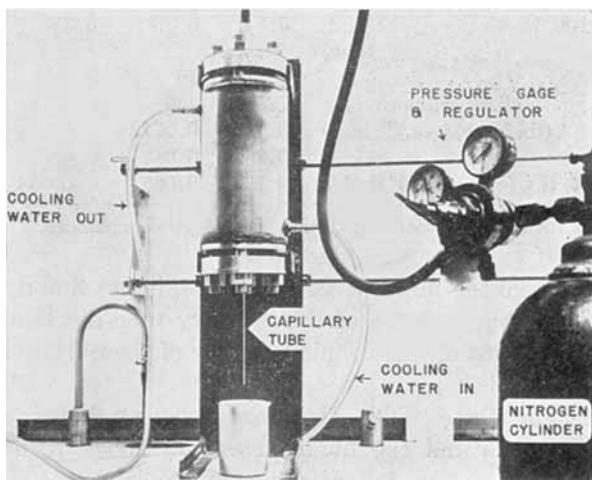

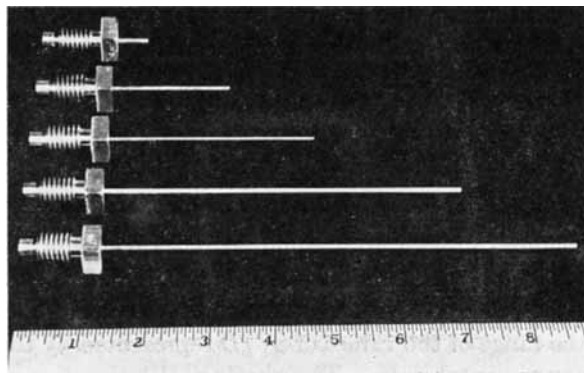Fig. 1. Capillary tube viscometer.

Fig. 2. Capillary tubes.

A 304 stainless steel, hypodermic needle tubing was used for the capillary tubes. After being cut to length, these tubes were shrunk into holes drilled into the center of $^3/_8$-in. diameter bolts. This arrangement permitted the tubes to be interchanged conveniently. Several of these tubes are shown in Figure 2, and the length and length diameter ratios for all tubes used in this study are given in Table II. All tubes had an included entrance angle of 180°.

TABLE II
Capillary Tube Length/Diameter Ratios

Tube no.	Diameter $\times$ 10^2, in.	Length/diameter
1	9.28	37.9
2	6.33	49.1
3	9.28	49.9
4	7.17	97.8
5	6.33	137.9

The procedure for a typical experiment consisted of extruding a sample of viscose through a given capillary tube at a fixed pressure and weighing a timed sample of the extrudate to determine the mean flow rate. Water was circulated continuously through the annulus surrounding the viscometer body at a temperature of 20°C. throughout the duration of the experiment. The shear rate was varied by changing both the length/diameter ratio of the capillary tube and the pressure drop across the tube.

The data from these experiments was used to calculate the shear stress at the tube wall τ_w and the quantity $8V/D$. These results were then plotted in the conventional manner. The rheological constants (flow consistency index and flow behavior index) were determined by using the method of least squares to fit straight lines to the

logarithmic plot of τ_w versus $8V/D$ for each fluid. This was done with the aid of a Bendix G-15 digital computer using the Intercom 1000 interpretive system.

Steady-State Flow Properties

The steady-state flow curves for constant $\overline{DP}$ cellulose viscose at varying cellulose contents are shown in the conventional manner in Figure 3. These curves can be considered parallel within the range of the values of $8V/D$ represented by the experimental data. The rheological properties of the fluids are summarized in Table III. The dimensionless flow behavior index n, which represents the slope of the curves of Figure 3, varies a maximum of only 0.009 for these four fluids. The flow consistency indices K' and K increase progressively as the cellulose concentration is increased from 9.58 to 15.94%.
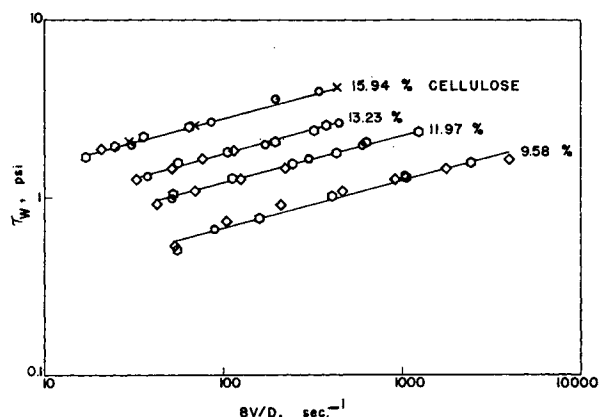

Fig. 3. Flow curves for constant $\overline{DP}$ cellulose viscose at varying cellulose contents: (O) tube 1; (×) tube 2; (□) tube 3; (○) tube 4; (◇) tube 5. Tube numbers refer to those given in Table II.

The consistency of the data is excellent for the 11.97%, 13.23% and 15.94% cellulose viscose, with every experimental data point touching the

TABLE III
Rheological Properties of Constant $\overline{DP}$ Cellulose Viscose at Varying Cellulose Contents

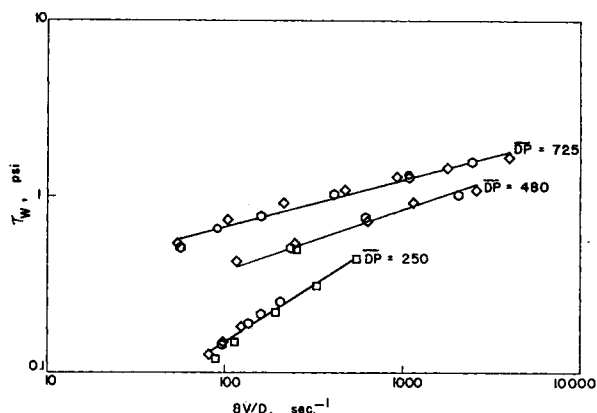|	Viscose sample no.[a]			
	1–1	1–2	1–3	1–4
Cellulose, %	9.58	11.97	13.23	15.94
NaOH, %	5.54	6.99	8.3	10.61
K', (lb. force) (sec.)$^{n'}$/in.^{2}	0.198	0.335	0.495	0.792
n	0.267	0.276	0.273	0.272
K, (lb. force) (sec.)^n/in.^{2}	0.172	0.292	0.431	0.689

[a] All samples contained 45% CS_2 based on cellulose.

Fig. 4. Flow curves for constant cellulose content viscose at varing $\overline{DP}$. Symbols as in Fig. 3.

least squares line. Several data points do not touch the least squares line for the 9.58% cellulose viscose, and the use of a polynomial would probably improve the fit of the curve to these data. It does not appear that this would modify the value of the slope of the curve at any given value of $8V/D$ enough to justify its use, however.

The flow curves for constant cellulose content viscose at varying $\overline{DP}$ are shown in Figure 4, and their rheological properties are tabulated in Table IV. Here the data are less consistent than those obtained for the curves of Figure 3, but the trend of each curve is well defined.

TABLE IV
Rheological Properties of Constant Cellulose Content Viscose at Varying $\overline{DP}$

	Viscose sample no.[a]		
	1–1	1–5	1–6
Cellulose, %	9.58	9.03	8.85
NaOH, %	5.54	5.38	5.33
Alkali cellulose aging time, hr.	0	16	32
$\overline{DP}$ of alkali cellulose	725	480	250
K', (lb. force) (sec.)$^{n'}$/in.^{2}	0.198	0.0778	0.00686
n'	0.267	0.343	0.666
K, (lb. force) (sec.)^n/in.^{2}	0.172	0.068	0.00634

[a] All samples contained 45% CS_2 based on cellulose.

Since the flow curves shown in Figures 3 and 4 are not a function of the capillary tube diameter, the extent of thixotropic behavior of these fluids is negligible.

For these fluids the flow behavior index, n increases and the fluid consistency index K decreases as the $\overline{DP}$ of the cellulose is decreased. This would indicate that the fluid becomes more
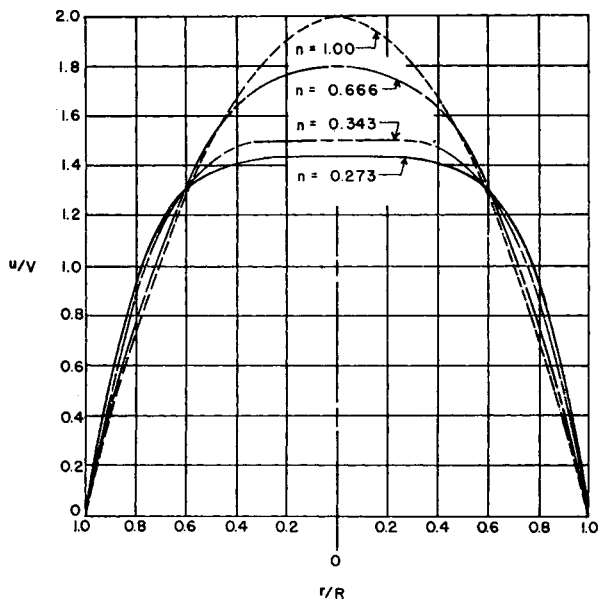
Fig. 5. Steady-state velocity profiles for viscose as a function of flow behavior index.
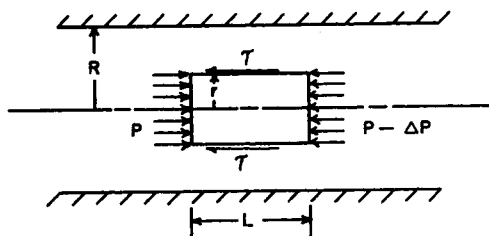

Fig. 6. Fluid element under steady-state laminar flow conditions.

non-Newtonian in behavior as the molecular weight of the cellulose molecule is increased. An explanation can be formulated for this behavior on the basis that as the cellulose molecule becomes more asymmetric the tendency for random entanglement in one another is increased.

Applications of Rheological Properties

The most obvious use of the rheological data described above would be for predicting pressure drop and throughput requirements for pipe line design. In some applications, it may be of interest to determine the velocity profile within a round pipe or tube in terms of its rheological properties. The method of determining the analytical relationship between the rheological properties of the fluid and resulting velocity profile has been published for Newtonian, dilatant, pseudoplastic fluids[8,9] and for Bingham plastics.[9]

The relationship between local and average velocities for pseudoplastics is derived in the Appendix, the final result being

$$u/V = [(3n + 1)/(n + 1)] [1 - (r/R)^{(n+1)/n}] \quad (5)$$

Velocity profiles for viscoses with flow behavior indices of 0.666, 0.343, and 0.273 are shown in Figure 5 with the velocity profile for a Newtonian fluid ($n = 1$) shown as a reference. The tendency toward plug flow as the flow behavior index decreases is easily visualized by the flat velocity profiles shown in this plot.

Conclusions

On the basis of the experimental data presented here, it may be concluded that the flow behavior index for viscose is not changed appreciably by varying the cellulose concentration from 9.58% to 15.94% if the $\overline{DP}$ of the viscose is held constant. The fluid consistency index increases, however, as the cellulose content is increased at constant $\overline{DP}$.

Both the flow behavior index and fluid consistency index for viscose vary with increasing $\overline{DP}$ at constant cellulose content. The flow behavior index decreases with increasing $\overline{DP}$, indicating a tendency away from Newtonian behavior as the cellulose molecule becomes increasingly more asymmetric.

APPENDIX

Derivation of the Velocity Profile for Pseudoplastic Laminar Flow

A force balance on the fluid element shown in Figure 6 under steady state conditions yields

$$\sum F = \pi r^2 \Delta P - 2\pi r L \tau = 0 \quad (A1)$$

$$\therefore \quad \tau = r\Delta P/2L \quad (A2)$$

For a pseudoplastic, the functional relationship between shear stress and shear rate is

$$\tau = -K(du/dr)^n \quad (A3)$$

By substituting eq. (A3) in eq. (A2) and separating the variables, the following integral equation is obtained:

$$\int du = -(\Delta P/2LK)^{1/n} \int r^{1/n} \, dr \quad (A4)$$

which yields on integration

$$u = - \left[\frac{\Delta P}{2LK}\right]^{1/n} \left[\frac{r^{(n+1)/n}}{(n+1)/n}\right] + C \quad (A5)$$

If no slip at the tube wall is assumed, the constant C can be eliminated by the condition that the local velocity u is zero at a radial distance r equal to the pipe radius R. The final form of eq. (A5) becomes

$$u = \left(\frac{n}{n+1}\right)\left(\frac{\Delta P}{2LK}\right)^{1/n} (R)^{(n+1)/n}$$
$$\times \left[1 - \left(\frac{r}{R}\right)^{(n+1)/n}\right] \quad (A6)$$

The average velocity V within the tube is given by

$$V\pi R^2 = \int_0^R 2\pi r u\, dr \quad (A7)$$

Substituting eq. (A6) in eq. (A7) yields

$$V = \frac{2}{R^2}\left(\frac{n}{n+1}\right)\left(\frac{\Delta P}{2LK}\right)^{1/n} (R)^{(n+1)/n}$$
$$\times \int_0^R \left[1 - \left(\frac{r}{R}\right)^{n+1/n}\right] r\, dr \quad (A8)$$

which results in eq. (A9) upon integration and rearrangement

$$V = [n/(3n+1)](\Delta P/2LK)^{1/n} (R)^{(n+1)/n} \quad (A9)$$

Equation (A9) is substituted into eq. (A6) to determine the dimensionless velocity u/V as a function of the dimensionless radius r/R:

$$u/V = [(3n+1)/(n+1)][1 - (r/R)^{(n+1)/n}] \quad (A10)$$

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Synopsis

The steady-state flow of viscose in a capillary tube viscometer was investigated to determine the rheological properties of this fluid as a function of cellulose concentration and molecular weight. It was found that the flow consistency index increased with increasing cellulose content at constant molecular weight. The flow behavior index was not affected under these conditions. At constant cellulose content, the flow behavior index was found to decrease as the molecular weight of the cellulose molecule was increased. Steady-state velocity profiles for viscose flowing in a round tube under laminar conditions are also presented as a function of the flow behavior index.

Résumé

L'écoulement à l'état stationnaire de la viscose dans un viscosimètre à tube capillaire a été étudié en vue de déterminer les propriétés rhéologiques de ce fluide en fonction de la concentration en cellulose et du poids moléculaire. On a trouvé que l'indice de la constance d'écoulement augmente avec une augmentation de la teneur en cellulose à poids moléculaire constant. L'indice du comportement à l'écoulement n'était pas affecté dans ces conditions. Pour une teneur en cellulose constante, l'indice du comportement à l'écoulement décroit si le poids moléculaire de la cellulose augmente. La vitesse à l'état stationnaire pour une viscose s'écoulant dans un tube circulaire dans des conditions laminaires est également présentée comme une fonction de l'indice du comportement à l'écoulement.

Zusammenfassung

Das stationäre Fliessen von Viskose in einem Kapillarviskosimeter wurde zur Bestimmung der rheologischen Eigenschaften dieser Flüssigkeit als Funktion von Cellulosekonzentration und Molekulargewicht untersucht. Es wurde gefunden, dass der Fliesskonsistenzindex bei konstantem Molekulargewicht mit zunehmendem Cellulosegehalt ansteigt. Der Fliessverhaltensindex wurde unter diesen Bedingungen nicht beeinflusst. Bei konstantem Cellulosegehalt nahm der Fliessverhaltensindex mit zunehmendem Molekulargewicht der Cellulosemoleküle ab. Geschwindigkeitsprofile für das stationäre Fliessen von Viskoselösungen in einer runden Röhre unter laminaren Bedingungen werden als Funktion des Fliessverhaltensindex angegeben.