Rheological Properties of Cellulose Solution in Paraformaldehyde/Dimethyl Sulfoxide System (1)

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ABSTRACT

The rheological properties of three cellulose samples are investigated, including the dependence of the non-Newtonian Index, structural viscosity and zero shear viscosity on temperature and the concentration of their paraformaldehyde/dimethyl sulfoxide solutions; the values of viscous flow activation energy of them are higher than that of the viscose solution. With the increase of molecular weight, solution concentration and the decrease of temperature, the rheological properties become worse. The rheological properties of cotton linters Cotton 1 are better than those of wood pulp Wood 2 despite a similar degree of polymerization. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: cellulose; paraformaldehyde/dimethyl sulfoxide solution; rheology

INTRODUCTION

It is predicted that petroleum resources on earth will run out in the middle of the 21st century. This turns attention to using cellulose instead, since it is renewable. However, cellulose cannot dissolve in ordinary solvents because of its complex structure and the traditional viscose process is tediously long with high energy and material consumption and leads to pollution[1]. Thus much work has taken place on the development of new solvents of cellulose since the middle of the 20th century[2–8]. Of all these solvents, a paraformaldehyde/dimethyl sulfoxide (PF/DMSO)[9–12] system seems to be a favorable solvent. Pulp is usually made from cotton in China; wood pulp is used mainly in other countries. Since the chemical ingredients and fiber structure of wood fiber and cotton fiber are quite different, their reaction properties are also different, and it is necessary to have some investigation on the two kinds of pulp. Since there are few reports on the comparative study of the rheological properties of the two kinds of pulp before, the effects of the types of cellulose, solution concentration and solution temperature on rheological parameters of cellulose solution in PF/DMSO are discussed below.

EXPERIMENTAL

Materials and Reagents

Three cellulose samples were used in this study. One was cotton linters Cotton 1 with a degree of polymerization (DP) of 495 and an α-cellulose content of 94.4%; the other two were wood pulps, Wood 1 and Wood 2, with a DP of 837 and 532 respectively and an α-cellulose content of 90.8% for both.

The cellulose samples were heated at 105°C to a constant mass, then dried over phosphorus pentoxide in a desiccator. Reagent-grade PF and DMSO were supplied by Shanghai Feida Chemical Co.,

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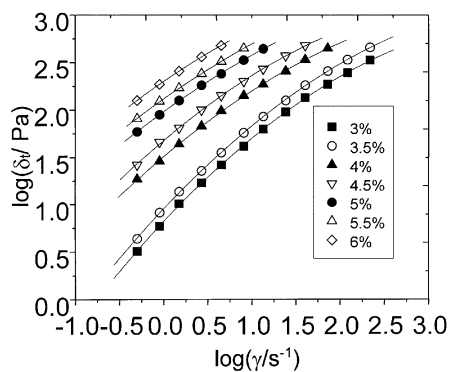
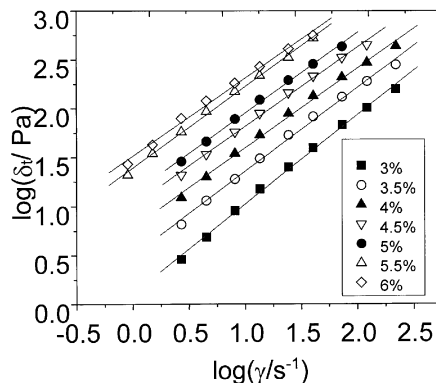**FIGURE 1.** Dependence of shear stress on shear rate of Wood 1 of different concentrations

FIGURE 2. Dependence of shear stress on shear rate of Wood 2 of different concentrations

China. PF was ground into powers and dried in a desiccator over phosphorus pentoxide before use.

Preparation of Cellulose Solution

The mixture of cellulose, PF and DMSO was heated at 60°C under mechanical stirring for 30 min, at 85°C for 1 hr, and then at 115°C for further 30 min. A transparent and stable solution was obtained, which was kept under vacuum for 10 min to remove the remaining PF from the solution. A series of solutions in the concentration range of 3–6% was prepared.

Rheological Measurement

The rheological properties of the solutions were measured on a RV-II Rotation Viscometer. The realized region of shear rate γ was 0.5–437.4 s^{-1}.

RESULTS AND DISCUSSION

Effects of Solution Concentration on Rheological Properties

Dependence of Non-Newtonian Index on Solution Concentration. Flow curves for the investigated solutions at 40°C are given in Figs 1–3 in the form of log δ_t = f(log γ). It is evident that the shear stress δ_t increases with the shear rate γ, but the velocity of increase decreases with γ, which means that the apparent viscosity η_a decreases with γ. This may be because the cellulose macromolecules show curved states in the solution and there exist hydrogen bonds through hydroxyl groups between cellulose macromolecules. Thus, the macromolecular chain entanglement can form easily, which makes the relative motion of cellulose macromolecules difficult. The entanglement crosslinks in the solution will be destroyed and rebuilt consistently and a dynamic equilibrium will be obtained under a certain condition; each entanglement only acts as a temporary crosslink. When γ increases, part of the entanglement crosslinks are destroyed, showing a decrease of η_a. At the same time, the chain segment stress among entanglement crosslinks cannot relax and may orientate along the flow field, which
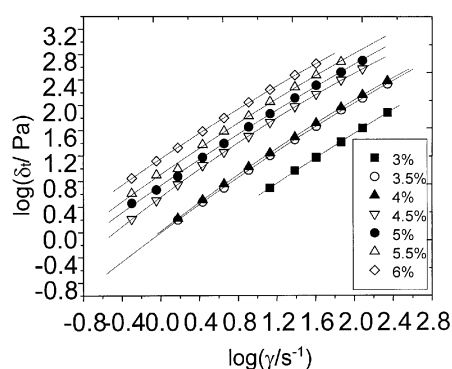

FIGURE 3. Dependence of shear stress on shear rate of Cotton 1 of different concentrations
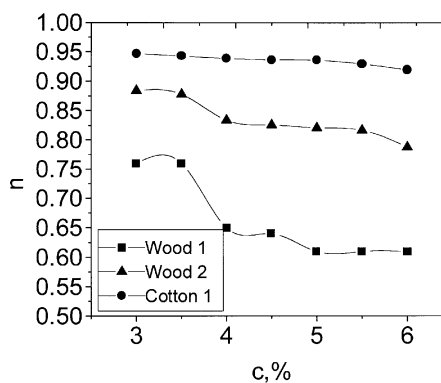

FIGURE 4. Dependence of non-Newtonian Index on concentration

makes it less able to transport energy among flow layers. Thereafter, the drag force among flow fields decreases, which also could lead to the decrease of η_a. Figure 4 gives the non-Newtonian Index n in the form of n = f(c), where n is smaller than 1 and decreases with both concentration and DP. For Wood 1, n decreases sharply with concentration until 4% and thereafter it decreases slowly. For Wood 2, n remains almost a platform in the concentration range of 4.0–5.5%. For Cotton 1, n

decreases linearly but slowly, remaining between 0.95 and 0.90 something like Newtonian fluid. The spinnability of Cotton 1 and Wood 2 is better than that of Wood 1 which possesses a higher DP, since a higher DP leads to the increase of inner-molecular resistance, intermolecular action, the crosslink and the extent of fleeing from Newtonian fluid. The spinnability of Cotton 1 is better than that of Wood 2 despite of their DP similarity. This seems to be different from previous opinion, according to which the reactive property of wood pulp is better than that of cotton linters owing to their difference in growth process and their supermolecular structure. For example, the crystallinity of cotton linters is higher than that of wood pulp, the dimension of the crystal of cotton linters is smaller than that of wood pulp and the stacking density of cotton linters fibre is denser than wood pulp, so the solvent is easier to enter into wood pulp and react with the pulp than it does with cotton linters. The reason for the spinnability behavior described here may be because of the improvement of the process of cotton linters on one hand and with that wood pulp may have more ingredients than cotton linters do on the other hand. Thereafter, we can take a higher concentration for Cotton 1 on the basis of its better spinnability and for higher production profit.

Dependence of Structural Viscosity on the Concentration. The structural viscosity index $\Delta\eta$ indicates the extent of solution structuralization, $\Delta\eta = (-\mathrm{dlg}\eta_a/\mathrm{d}\gamma^{1/2}) \times 10^2$. A large amount of polymers belong to shear-thinning fluid, where $\Delta\eta$ is larger than 0. The higher the $\Delta\eta$, the worse the spinnability for the cellulose solution, and the more difficult for the fibre formation and then the lower mechanical property for the fibre. The $\mathrm{lg}\eta_a = f(\gamma^{1/2})$ curves (Figs 5–7) show that η_a decreases with γ, which means that $\Delta\eta$ is larger than 0. It is because that the shear stress partly destroys the crosslinks among molecules, orients chain segments and desolvates cellulose. Figure 8 indicates the dependence of $\Delta\eta$ on concentration, from which it can be found that for Wood 1, $\Delta\eta$ increases sharply with concentration. For Wood 2, $\Delta\eta$ increases slowly until the concentration reaches 5.5%, where $\Delta\eta$ increases sharply. For Cotton 1, $\Delta\eta$ remains a low value. The tendency of the dependence of $\Delta\eta$ on concentration is in accordance with the dependence of n on concentration.

Dependence of Zero Shear Viscosity on Concentration. The solutions of different concentrations for the three cellulose samples were prepared and their zero shear viscosity η_0 was tested at 40°C. Curves are obtained in the form of $\mathrm{lg}\eta_0 = f(\mathrm{lg}c)$ (Fig. 9). For Wood 1, $\mathrm{lg}\eta_0 = -2.18803 + 6.05732\mathrm{lg}c$; for Wood 2, $\mathrm{lg}\eta_0 = -2.21641 + 4.78294\mathrm{lg}c$; for Cotton 1, $\mathrm{lg}\eta_0 = -2.650719 + 4.925031\mathrm{g}c$.

It seems that as the concentration increases, the number of molecules per unit volume, the macromolecular interaction, the hydrogen bonds and the entanglement crosslinks increase, which
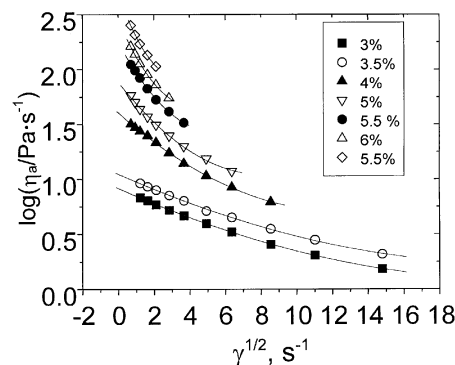

FIGURE 5. Dependence of apparent viscosity on shear rate of Wood 1 of different concentrations
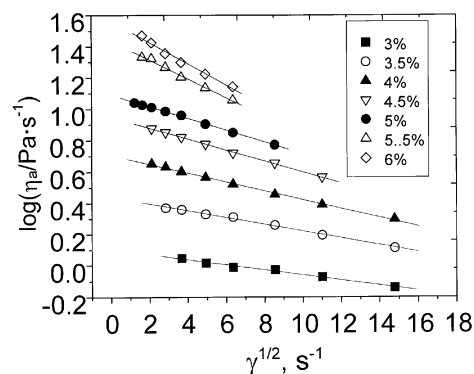

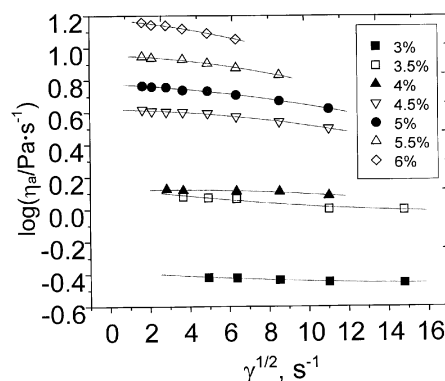**FIGURE 6.** Dependence of apparent viscosity on shear rate of Wood 2 of different concentrations

FIGURE 7. Dependence of apparent viscosity on shear rate of Cotton 1 of different concentrations

may appear as an increase of η_a macroscopically. At the same time, as the DP increases, the amount of chain segments per macromolecular chain and chain entanglement increase, the flow unit becomes bigger, which leads to the increase of flow resistance and η_0.

Influences of Solution Temperature on Rheological Properties

Dependence of Non-Newtonian Index on Temperature. Flow curves obtained at 40–70°C for the solution of 3% (wt) are given in Figs 10–12 in the form of
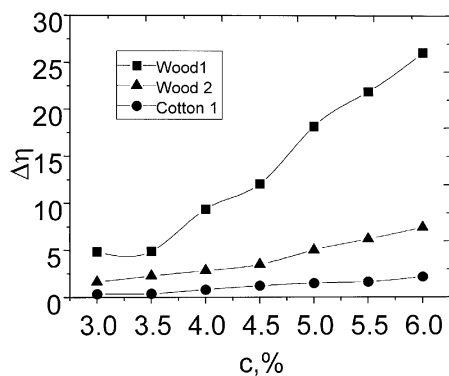
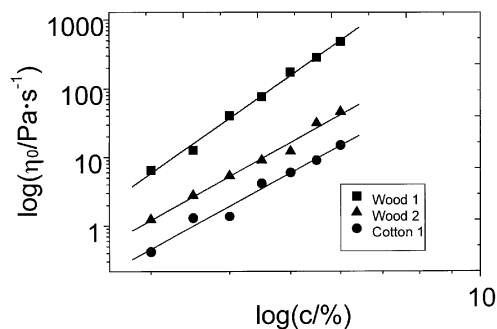**FIGURE 8.** Dependence of structural viscosity on concentration

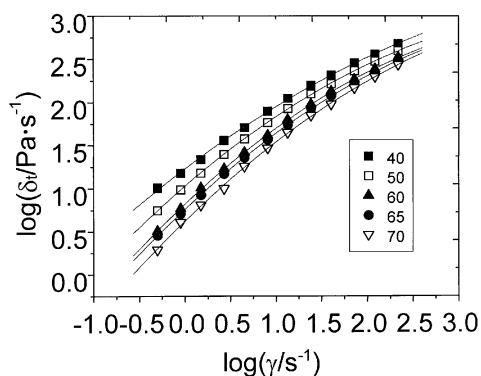**FIGURE 9.** Dependence of zero shear viscosity on concentration

FIGURE 10. Dependence of shear stress on shear rate of Wood 1 at different temperatures
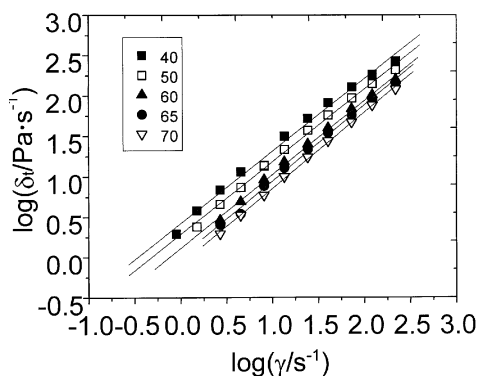

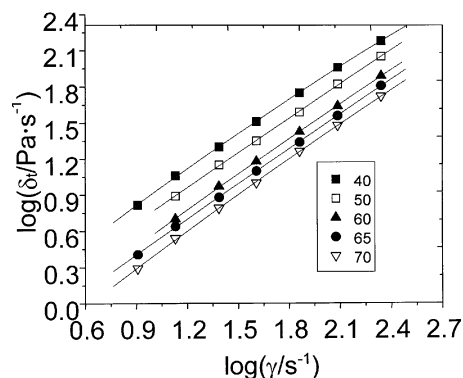**FIGURE 11.** Dependence of shear stress on shear rate of Wood 2 at different temperatures

FIGURE 12. Dependence of shear stress on shear rate of Cotton 1 at different temperatures
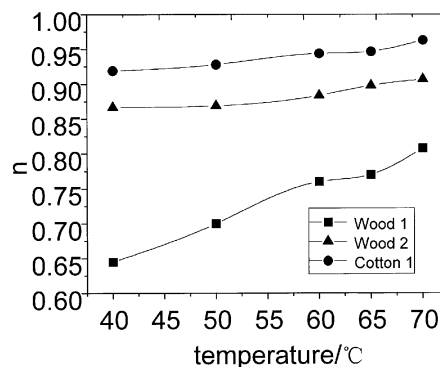

FIGURE 13. Dependence of non-Newtonian Index on temperature

$\log \delta_t = f(\log \gamma)$; the curves for n are given in Fig. 13. It can be found that for a certain sample, n increases with the temperature. This may be because the macromolecular movement resistance, the cross-links and the extent of deviating from Newtonian fluid decrease with temperature. n decreases in the order of Cotton 1, Wood 2 and Wood 1, which suggests that the interaction among molecules and crosslinks aggravates an increase with DP; the spinnability of Cotton linters is better than that of Wood 2. For Wood 1, n increases quickly at 40–50°C, but later on it increases slowly. For Wood 2 and Cotton 1, n slightly increases during the investigated temperature range. The favorite temperature range of the three samples may vary, but if 70°C is exceeded a pungent smell is released which is harmful to humans.

Dependence of Structural Viscosity and Zero Shear Viscosity on the Temperature. Figures 14–16 show the flow curves in the form of $\log \eta_a = f(\gamma^{1/2})$ at different temperatures. The curves of $\Delta\eta$ decreasing with the increasing temperature can be found in Fig. 17. This may be concerned with some kind of network being destroyed at higher temperature. It is well known
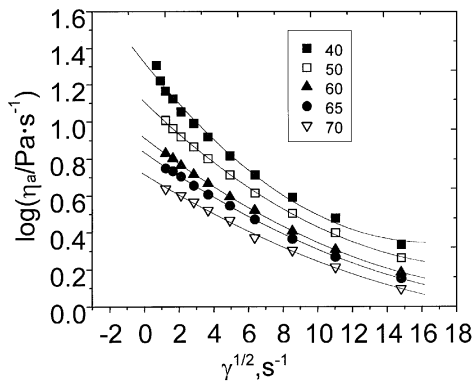
FIGURE 14. Dependence of apparent viscosity on shear rate of Wood 1 at different temperatures
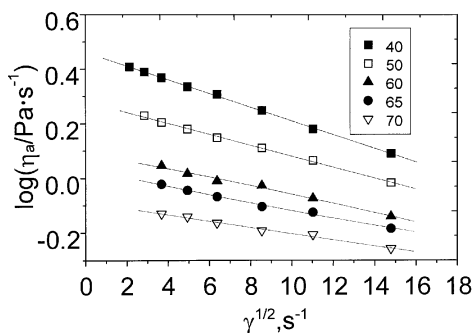

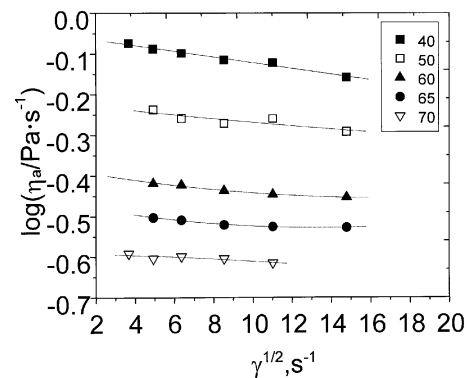**FIGURE 15.** Dependence of apparent viscosity on shear rate of Wood 2 at different temperatures

FIGURE 16. Dependence of apparent viscosity on shear rate of Cotton 1 at different temperatures

FIGURE 17. Dependence of structural viscosity on temperature
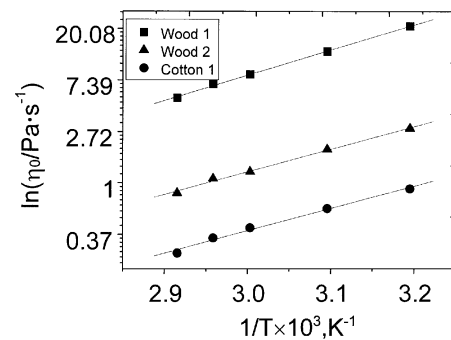
FIGURE 18. Dependence of zero shear viscosity on temperature

The Viscose Flow Activation Energy $E\eta$ of Solutions

The viscosity of the three cellulose sample solutions of 3.5% concentration at different temperatures was measured. According to Arrhenius equation, temperature and viscosity have the following relationship:

$$\eta_0 = A \exp(E\eta/RT)$$

or

$$\ln \eta_0 = \ln A + E\eta/RT$$

where $E\eta$ is a measurement of the dependence of viscosity on temperature. The bigger the value of $E\eta$, the stronger the influence of temperature on η_0, from which we may find out the possibility of changing fluid ability by temperature. The increase of temperature aids the motion of macromolecules and the expansion of solution space, so the space among macromolecules becomes exaggerated and the fluid ability of solution increases, which leads to the decrease of η_0.

It can be derived from Fig. 18 that for Wood 1

$$E\eta = 5.47171 \times 8.314 \times 10^3 = 45.492\,\text{kJ/mol},$$

for Wood 2

$$E\eta = 4.37242 \times 8.314 \times 10^3 = 36.35\,\text{kJ/mol}$$

that η_0 decreases with the increase of temperature as shown in Fig. 18.

For Wood 1

$$\ln \eta_0 = -14.47019 + 5.47171 \times (1/T \times 10^3)$$

for Wood 2

$$\ln \eta_0 = -12.97572 + 4.37242 \times (1/T \times 10^3)$$

for Cotton 1

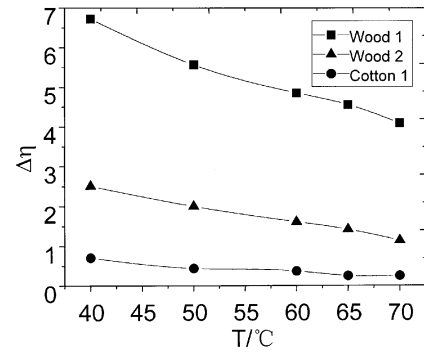$$\ln \eta_0 = -13.39287 + 4.15458 \times (1/T \times 10^3)$$

and for Cotton 1

$$E\eta = 4.15428 \times 8.314 \times 10^3 = 35.54\,\text{kJ/mol}$$

The values of $E\eta$ of the samples are all bigger than that of viscose solution ($E\eta = 29.4\,\text{kJ/mol}^{-1}$). This may be because the hydrogen bonds are not destroyed as much as in the case of the viscose solution, so there may exist more hydrogen bonds in these solutions. The $E\eta$ also increases with DP, for a higher DP may lead to the increase of molecule jump energy.

CONCLUSION

The values of non-Newtonian Index n of the three cellulose samples in PF/DMSO solution are smaller than 1 and the values of their apparent viscosity decrease with shear rate. For Cotton 1, it seems that we may choose a rather high concentration, e.g. 6% or higher at larger temperature range, e.g. 40–70°C. For Wood 2, the favorable concentration may reach 5.5% at higher temperature. For Wood 1, it may be favorable to be kept at a lower concentration at 60–70°C. The spinnability of Cotton 1 is better than Wood 2 in spite of their DP similarity. The change of cellulose content, solution temperature and molecular weight has different influences on n, structural viscosity and zero shear viscosity. The zero shear viscosity decreases in an exponential manner with temperature increase and the viscous flow activation energy increases with molecular weight.

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