RHEOLOGICAL PROPERTIES OF CELLULOSE-NaOH COMPLEX SOLUTIONS: FROM DILUTE TO CONCENTRATED STATES

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Steady-state shear flow of cotton cellulose dissolved in a NaOH complex solution (8% NaOH/6.5% thiourea/8% urea aqueous solution) was studied over a large range of concentrations (0-6.2%) and temperatures (0-20 ºC), to guide the spinning conditions. The formation of cellulose aggregates was favored when either the cellulose content or temperature was increased. The solution flow curves exhibited a Newtonian zero-shear viscosity (η_o) region and a two-shear rate dependent apparent viscosity (η_{app}) region. The rheological properties of the cellulose solution, especially at a high shear rate (according to the actual spinning process), were investigated systematically, including the dependence of zero-shear viscosity, activation energy, non-Newtonian index and structural viscosity index on cellulose concentration and temperature. On the basis of steady-shear flow test data, two critical overlaps (C^* and C^{**}) of the cellulose solution were determined, respectively, of 2.1 and 5.0%. The critical concentrations C^* and C^{**} delimitate three different states of the cellulose solution: semi-diluted entangled network, semi-diluted tangled network and concentrated solutions. The results are favorable for predicting the spinnability of the cellulose-NaOH complex spinning solution, being particularly important before using this effective solvent system in the spinning process.

Keywords: cellulose dissolution, viscosity, rheological properties, spinnability

INTRODUCTION

Cellulose, as an environmentally friendly and renewable biomaterial, represents around 1.5×10^{12} tons of the total annual biomass production. Due to its fundamental and technological importance, the dissolution and processing of cellulose attracted an enormous amount of work in the past, still remaining an active field of research nowadays. Several solvents in which cellulose can swell and dissolve were found, such as LiCl/N,N-dimethylacetamide (DMAc),[1-3] N-methyl-morpholine-N-oxide (NMMO),[4-6] ammonia/ammonium thiocyanate (NH_3/NH_4SCN),[7-10] NaOH,[11-14] NaOH/urea, NaOH/thiourea[15-17] and NaOH/thiourea/urea,[18] most of them used to directly dissolve cellulose without involving a chemical derivative.

To make an effective use of cellulose as a resource of polymer materials, extensive and profound knowledge is necessary on the molecular properties of cellulose. To this end, many researchers have investigated the solution properties of cellulose. Wang *et al*.[19] reported that a cellulose LiCl/DMAc solution is characterized as a power-law fluid. Navard and Petrovan,[20,21] who studied the shear rheology of a diluted solution of cellulose dissolved in NMMO, by steady-state and dynamical rheological methods, found out that steady-state viscosity and the first normal stress difference had a power law dependence on shear rate. Roy[22] studied the shear rheology of microcrystalline cellulose dissolved in a 9% NaOH aqueous solution by steady and oscillatory modes, his results indicating that the formation of cellulose aggregates was favored when temperature was increased. Zhang *et al*.,[23,24] who

investigated the rheological properties and behavior of cellulose in 7 wt% NaOH/12 wt% urea by dynamic viscoelastic measurements, revealed an irreversible gelation in the cellulose solution system.

A novel NaOH complex solution, that is, the NaOH/thiourea/urea aqueous solution, has been used to directly dissolve the untreated cellulose.[18] This novel solvent system has many advantages, among which low toxicity and cost and no derivative production in dissolution and regeneration process. In addition, the solvent is more powerful in dissolving cellulose, and can be used to prepare more stable spinning solutions, containing higher concentrations of cellulose than the other NaOH aqueous solvent systems. The novel technology is promising for replacing the century-old proven but environmentally destructive viscose process.

Basic understanding of the rheological and viscosity properties is essential for a successful research and application of the cellulose films and fibers from the cellulose solution. The spinnability of a spinning fluid can be determined from the values of apparent viscosity (η), zero-shear viscosity (η_o), non-Newtonian index (n) and structure viscosity index ($\Delta\eta$). These parameters were studied here for predicting the spinnability of the cellulose-NaOH/thiourea/urea H$_2$O spinning fluid. The objective of the present paper is to provide a complete and comprehensive rheological investigation of the cellulose-NaOH complex solutions, in particular to investigate the presence of a critical shear rate, which occurs at real spinning, and the relationship between the critical cellulose concentrations and the rheological behavior of the polymer solutions.

EXPERIMENTAL
Materials
The cotton linter cellulose pulp sheets were supplied by Shanghai Cellulose Pulp Factory, China. All cellulose samples were shredded into powder, and dried in a vacuum oven at 70 ºC for 24 h before use. No activation treatment was required. All other chemicals were of analytical grade and used as received. At first, the molecular weight of the polymer used in the study was determined. To characterize the polymer, the viscosity-average molecular weight ($\overline{M}_\eta$) was calculated. Cellulose was dissolved in cadoxen, and the intrinsic viscosity of a dilute

solution was measured on an Ubbelodhe capillary viscometer, and $\overline{M}_\eta$ was determined with the corresponding Mark-Houwink equation: [25]

$$[\eta] = 3.85 \times 10^{-2} \times \overline{M}_\eta^{0.76} \qquad (1)$$

The degree of polymerization (*DP*) of cellulose can be obtained from the equation:

$$\overline{M}_\eta = DP \times M \qquad (2)$$

where *M* is the molecular weight of the glucopyranosyl unit of cellulose. The *DP* of the cotton linter cellulose pulp sheets was determined as 620.

Preparation of a cellulose solution
Various weights of cellulose were dispersed into 100 g of solvent pre-cooled to -10 ºC, followed by vigorous stirring for 3 min at room temperature. After 3 min, the temperature of the solution was controlled from -2 to 0 ºC using a salt-ice bath, and the mixture was vigorously stirred for 7 min. Before the test, the so-prepared solutions (with cellulose concentrations of 0, 0.2, 2, 3.5, 5.8 and 6.2%, respectively) were degassed by centrifugation at 4800 rpm for 5 min at room temperature.

Characterization
The rheology experiment was carried out on an ARES-RFS rheometer (TA Instruments, U.S.A.). The test temperature was set to 0, 5, 10 and 20 ºC, respectively. Degassed cellulose solutions were heated or cooled to the required temperature directly in the sample chamber. Temperature was controlled within ±0.3 ºC, using a circulating thermobath with a cooling liquid (mixture of water and propylene glycol). Steady-state shear flow experiments were performed in a classical way. Solutions of different cellulose concentrations (from 0 to 6.2%) in 8% NaOH/6.5% thiourea/8% urea aqueous solution were prepared, and the viscosity–shear rate dependencies were measured at several temperatures.

RESULTS AND DISSCUSION
Dependence of zero-shear viscosity on temperature and cellulose concentration
Zero-shear viscosity has been frequently employed to study the structure–function relation of the bio-polymeric systems, as the magnitude of zero-shear viscosity is a macroscopic representation of the micro-structural nature of biopolymers. Figure 2 shows the evolution of zero-shear rate viscosity as a function of cellulose concentration and temperature. Zero-shear viscosity can be directly obtained from the viscosity in the Newtonian regime. Three regions on each viscosity–concentration dependency can be seen: a linear region in

dilute regime and two power law regions with $\eta_0 \sim C^\lambda$ above the overlap concentration c* and c**. Exponent λ was calculated for all cellulose-NaOH complex solutions; in the first power law region, the values ranged from about 2.6 at 0 ºC to 1.7 at 20 ºC, and from about 3.5 at 0 ºC to 2.4 at 20 ºC in the second power law region.

Comparable values were reported for cellulose-LiCl/DMAc (λ = 3 for bacterial cellulose and λ = 4 for cotton linters and dissolving pulp),[26] and for cellulose/ionic liquid solutions (λ = 4 for wood pulp).[27] A slightly higher value (λ = 4.6) was reported for cellulose-NMMO solutions.[28]
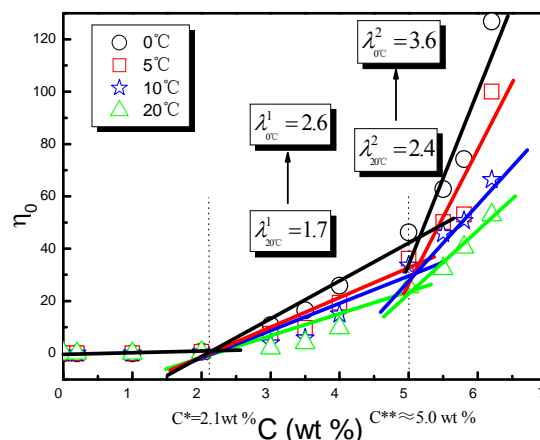

Figure 1: Dependence of zero-shear rate viscosity, η_0, as a function of cellulose concentration at different concentrations of cellulose solutions and different solution temperatures

The cellulose solution could be divided into four regions, according to the two critical overlap concentrations (c* and c**):

(1) The cellulose solution with c<0.2% was not examined here, however, it was believed that the cellulose solution was a totally dilute one, only weak interactions being found in the solution;[29]

(2) In the region from 0.2% to c* (2.1%), the cellulose molecular chains begin to overlap each other, leading to increased interactions between the molecules; it was a semidilute particle solution;

(3) In the range from c* (2.1%) to c** (5.0%), an entangled network was formed, as a result of an increased association between the cellulose chains.[30] The exponent of η_0 to c in this concentrated regime was 3.6, similar to the result for aeromonas gum in aqueous solutions, regarded as consisting of individual coils overlapping to form an entangled network;[31]

(4) Spinning dope – a concentrated solution was formed when concentration was beyond 5.0%.

Dependence of apparent viscosity on shear rate, temperature and cellulose concentration

Shear rate dependence of viscosity is demonstrated in Figure 3 over concentration ranges of 0.2-6.2%. As shown in Figure 2, viscosity decreases when temperature increases, and increases when concentration increases. As expected, an increase in temperature decreased viscosity, and this inverse relationship has been assimilated with the incidence of a freer molecule to molecule interaction at elevated temperatures. Since apparent viscosity is an indication of resistance to flow, such a freer interaction is expected to minimize resistance. When cellulose concentration increases, viscosity increases, too, because of the increase in hydrogen bonding with hydroxyl groups and distortion in the velocity pattern of the liquid by hydrated molecules of the solute. The intermolecular distance, which also affects viscosity, is inversely proportional to it, due to the changing temperature.

In addition, all solutions containing different concentrations of cellulose were non-Newtonian fluids, showing a viscosity decreasing with the shear rate. It is accepted that this shear-thinning behavior is caused by disentanglement of the polymer coils in solution or by an increased orientation of the polymer coils in flow direction.[32,33]

Furthermore, it is obvious that these curves are nonlinear, which indicates that the

power law model of Ostwald-de Waele, generally used to fit flow curves of cellulose solutions, is not suitable. At first, two distinct viscosity regions were observed: the Newtonian flow region, showing constant zero-shear viscosity (η_0) at low shear rate, and the power-law flow region, showing shear rate dependent apparent viscosity (η_{app}) at a relatively higher shear rate. At a low shear rate, a constant zero-shear viscosity can be maintained, since the rate of

intermolecular disentanglements brought about by the shear force exerted was nearly the same as that of the newly formed entanglements.[34,35] In contrast, viscosity decreased with increasing shear rates in the power-law region, since the rate of disentanglements was higher than that of entanglements. The apparent viscosity determined in the power-law region conferred practical information for process optimization.[36]
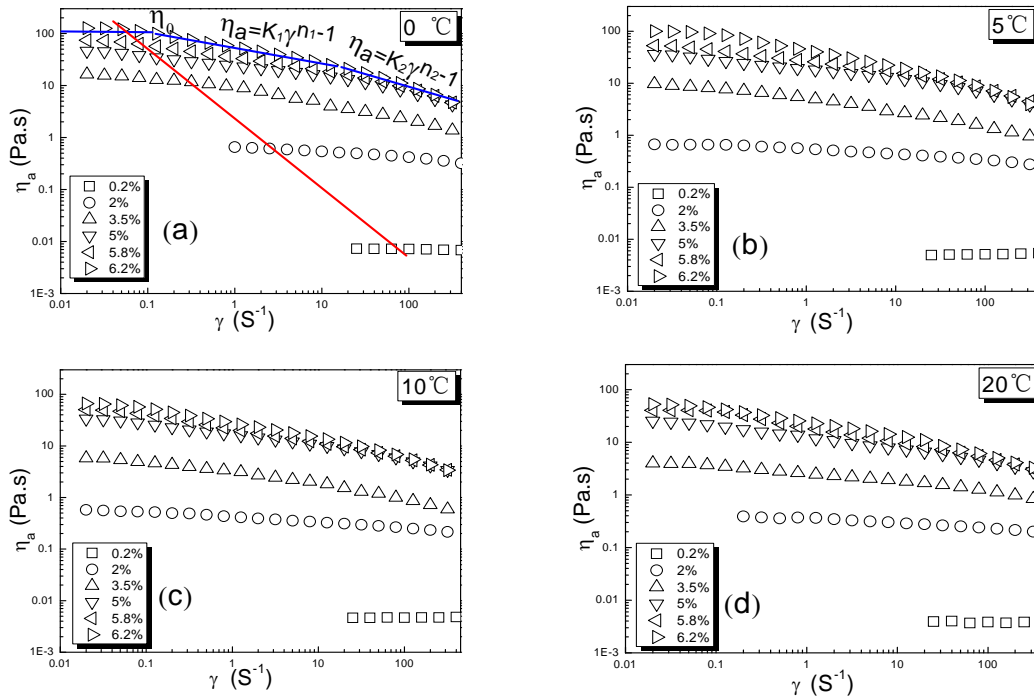

Figure 2: Effect of concentration on shear viscosity at (a) 0 °C, (b) 5 °C, (c) 10 °C, (d) 20 °C

Figure 2 shows that apparent viscosity *versus* shear rate, *i.e.* more pseudoplastic, was observed with increasing cellulose concentration. At the same shear rate, the dilute solutions experience a rheological behavior quite different from those of the higher concentrations, *i.e.*, a Newtonian plateau at low shear rates, corresponding to that of zero-shear viscosity and transition to the shear-thinning region at higher shear rates (the red straight line in Fig. 2). This could be explained in terms of the degree of chain entanglements. As polymer concentration was increased, the freedom of movement in the individual chains became restricted, due to the correspondingly increased number of entanglements,[34] which gave rise to a longer time required to form new entanglements, for replacing those

disrupted by the externally imposed deformation. Thus, with increasing polymer concentrations, the shear rate at which the Newtonian behavior was progressively lost moves towards lower values, which was consistent with the report of Morris.[36]

The shear-thinning region η_{app} *versus* γ curve could be expressed by the following Ostwald-de Waele or power-law equation:[37]

$$\eta_{app} = k\gamma^{n-1} \qquad (3)$$

where η_{app} is apparent viscosity, K is the consistency index, and n is the non-Newtonian index.

As demonstrated in Figure 2a, a transition flow region was clearly observed between the initial Newtonian region, at low shear rates, and the final power law region, at

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higher shear rates. In most cases, the intermediate transition flow region has been neglected for detailed characterization. However, it is thought that the quantification of the transition region is also of rheological significance, since polymers can provide distinct mechanisms in the early disentanglement stage, as depending on their molecular structure and interaction properties.[38]

Combined effect of temperature and concentration on viscosity

Another common way to analyze the effect of temperature and concentration on the viscosity of cellulose solutions is to use the Arrhenius equation:

$$\eta_0 = A \times \exp(E_\eta / RT) \qquad (4)$$

where E_η is the activation energy, η_0 is zero-shear viscosity, A is a constant, and T is absolute temperature. This equation can be used for predicting cellulose viscosity at any temperature valuable for processing. The activation energy is usually deduced from the slope of $\ln\eta_0$ *versus* inverse temperature, if this dependence is linear. The Arrhenius plots for cellulose-NaOH complex solutions at various concentrations are exemplified in Figure 3. Generally, it is possible to approximate each set of experimental data with a linear dependence, as shown with a solid line for each cellulose solution, at adequate accuracy ($R^2 > 0.98$). E_η measures the dependence of viscosity on temperature. The higher the value of E_η, the stronger the influence of temperature on η_0, from which one may find out the possibility of changing fluid ability by temperature. When analyzing the value of E_η in a cellulose-NaOH complex solution, the entanglement of the cellulose molecule chains caused by increased solution concentration and temperature was considered.

The value of E_η can be regarded as almost constant (ca. 20 kJ/mol), independent of the concentration of the cellulose solutions, being almost the same as the one for microcrystalline cellulose in a NaOH aqueous solution (21 ± 4 kJ/M).[22] However, E_η would increase with the degree of polymerization (DP); considering that the DP of microcrystalline cellulose dissolved in NaOH is of only ~230, it may lead to the jump of activation energy for a cellulose pulp with higher DP dissolved in NaOH aqueous solution. Moreover, for the cotton pulp with

almost the same DP, all E_η values of the cellulose pulp in NaOH/thiourea/urea aqueous solutions are lower than those in NaOH/thiourea solutions (31-32 kJ/mol).[39] This may be explained by the fact that the hydrogen bonds of the cellulose-NaOH/thiourea aqueous solution are not destroyed as much as in the cellulose-NaOH/thiourea/urea aqueous solution, so that more hydrogen bonds are formed in the cellulose-NaOH/thiourea system, causing a higher E_η. To sum up, it can be indirectly proved that the NaOH/thiourea/urea aqueous solution is a much better solvent for cellulose than other NaOH aqueous systems.

Relationship between viscosity parameters and spinnability

During the real spinning process, for semi-dilute concentrations (spinning concentration >5%), if the shear rate is too low, apparent viscosity shows a significant sensitivity when changing the shear rate, which may result in fluctuation of fiber quality. When the shear rate is too high, much more energy will be consumed, so that, one should select the stable stage of the apparent viscosity platform to spin. As a matter of fact, the shear rate required during real spinning is always higher than 100 s^{-1}, the improved understanding of apparent viscosity at high shear rate ($\eta_{app} = k_2 \gamma^{n_2-1}$ in Fig. 2a) being much more important and effective for gaining fundamental knowledge on the spinnability and structure–property relationships for the spinning solution. Special attention was paid to apparent viscosity (n_{eff}) at a high shear rate.

The effective non-Newtonian index (n_{eff}) values of cellulose obtained from the power region of apparent viscosity at a high shear rate are presented in Figure 4 as a function of concentration and solution temperature. The experimental results show that the solutions have a more pronounced Newtonian behavior (n_{eff} increase) when temperature is higher, with a linear trend. The polymer concentration of the solution has no influence on the slope of the fit.

The value of n_{eff} is less than 1 for all concentrations under investigation, indicating the pseudoplastic nature of the cellulose solution at this concentration value. With the increase of concentration, the non-Newtonian index n_{eff} decreased, which

indicates that the deviation from the Newtonian behavior increases and also that the non-Newtonian behavior of the cellulose solution became stronger. This is reasonable as, with the rise in concentration, cellulose molecular mobility decreased because of the increase in intermolecular action, of crosslinking and of the extent of deviation from the Newtonian fluid. The relative motion of cellulose molecules became difficult, and the viscoelastic behavior was intensified.

The effective structure viscosity index (coded as $\Delta\eta_{eff}$), defined as:

$$\Delta\eta \equiv \frac{-d\lg\eta_{app}}{d\dot{\gamma}^{1/2}}\times10^2 \qquad (5)$$

can be used to characterize the structuralization of a spinning solution.[20] A small $\Delta\eta_{eff}$ implies low structuralization. It has been proven that the lower structuralization of a spinning solution, the better spinnability and fiber quality are achieved. Intermolecular force and molecule entanglement led to a great number of instant physical-crosslinking sites in the cellulose solution. These crosslinking sites may counteract the orientation of the cellulose molecules during spinning and thus affect fiber quality. Reducing the structural viscosity index can weaken the structuralizing tendency of the spinning solution and, therefore, improve spinnability.

Because all tested solutions were shear-thinning fluids, their $\Delta\eta_{eff}$ were always greater than 0. Along with the increase in cellulose concentration, structure viscosity $\Delta\eta_{eff}$ rose, while spinnability got worse and fiber formation became more difficult.

A possible explanation might be that the increment of cellulose concentration led to increasing the collision chance of the cellulose molecules, promoting the formation of aggregates of the cellulose chains. $\Delta\eta_{eff}$ was also affected by temperature (Figs. 5, 6).

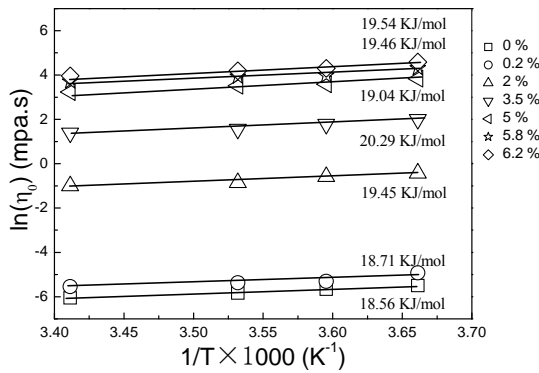

Figure 3: Dependence of apparent viscosity on temperature of cellulose solutions

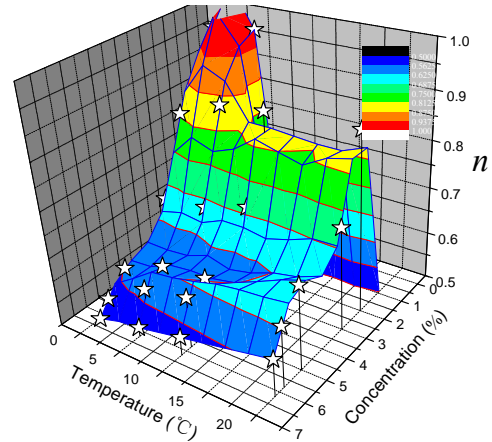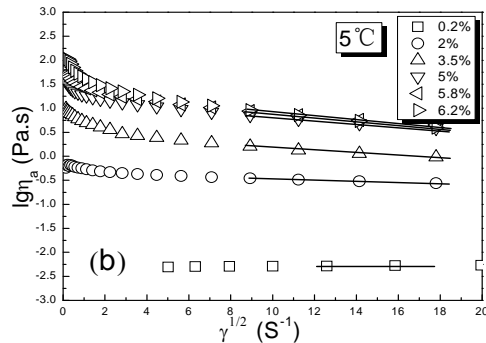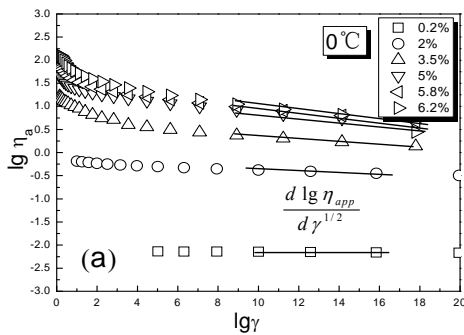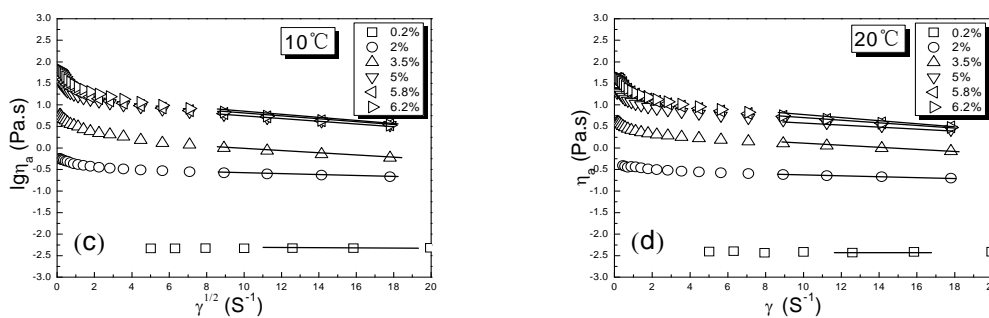Figure 4: Dependence of n_{eff} on cellulose concentration and solution temperature

Figure 5: $\lg\eta_{app}/\gamma^{\frac{1}{2}}$ dependence on cellulose concentration at (a) 0 °C, (b) 5 °C,(c) 10 °C, (d) 20 °C
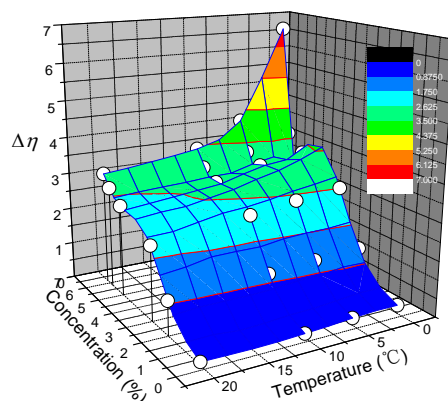

Figure 6: Dependence of $\Delta\eta_{eff}$ on cellulose concentration and solution temperature

For the cellulose solution, $\Delta\eta_{eff}$ decreased slightly with the increase in temperature, while spinnability was improved, because an elevated temperature led to an increased distance between the cellulose molecules, reducing the entanglement of cellulose polymer chains; accordingly, the structure viscosity index occurred at a slightly lower level. There results from here that increasing the spinning temperature of the cellulose solution is favorable for improving solution spinnability in the spinning process. However, a higher temperature would lead to a higher collision chance of the cellulose molecules, that is, a too high solution temperature would cause instability – such as gel formation – in the spinning process. In the actual spinning process, for a 5-6% cellulose solution, a temperature of 10 °C is determined as optimal for continuous spinning.

CONCLUSIONS

Steady rheology measurements were carried out to assess, in a reproducible and quantitative manner, the rheological behavior of a cellulose-NaOH complex solution. The results allowed the characterization of the rheological behavior of aqueous cellulose solutions. Zero-shear viscosity and the structural viscosity index of the solution decreased, along with an enhanced temperature and increased cellulose concentration, while the non-Newtonian index behaved reversely. All these can be explained by the notion of cluster formation of cellulose molecular chains at high temperature and concentration. It is worth noticing the abrupt slope change in zero-shear viscosity η_0 vs cellulose weight concentration curves at the same cellulose concentrations, around 2.1 and 5.0%. This change could be clearly related to the inner structure of the cellulose solutions, corresponding to: (1) critical overlap concentration c*, at c < c* (2.1%) – the solution systems are in dilute solution state and the intermolecular interactions can be neglected; at c* (2.1%) < c < c** (5.0%), the systems are in semi-dilute solution state and the intermolecular interactions become predominant, and (2) to the second critical concentration, c** (5.0%), which will be confirmed as the signal of concentrated solution formation. As a conclusion, for the cellulose-NaOH complex spinning solution (cellulose concentration >5%), a temperature around 10 °C should be considered for continuous spinning.

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