KINETICS OF CELLULOSE REGENERATION FROM CELLULOSE-NaOH/THIOUREA/UREA/H_2O SYSTEM

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The coagulation properties of cellulose-NaOH/thiourea/urea/H_2O solutions under various coagulation conditions have been investigated, to determine the kinetics of this special coagulation process (known as including diffusion on the contact surfaces of the polymer solution with the precipitant and the chemical reaction between acid and alkali). The observation was made that, at the beginning of the coagulation process, thickness of the coagulated layer, $\xi(t)$, is proportional to the square root of time, $\sqrt{t}$, which agrees with Fick's law. By building a coagulation model, the influence of precipitant composition and concentration, of coagulation time, bath temperature and cellulose concentration on the coagulation rate has been demonstrated. The process of cellulose shaping from NaOH/thiourea/urea/H_2O solutions can be characterized by examining the thickness and surface morphology of the coagulated layer, which is a reliable and direct method for understanding and controlling the cellulose regeneration behavior. It was found out that the coagulation rate enhanced with the increase in coagulation temperature, and decreased with increasing cellulose concentration. The activation energy of coagulation was calculated to be of 10.808 KJ/mol. The kinetics of diffusion-controlled chemical reactions has been viewed as the mechanism of coagulation.

Keywords: NaOH/thiourea/urea, direct dissolution, coagulation rate, activation energy, coagulation mechanism

INTRODUCTION

Cellulose, the most abundant renewable biopolymer in the world, has attracted much attention due to its outstanding properties. For many decades, commercial regeneration of cotton or wood celluloses in the form of fibers and films has been based on solvent systems, such as those used in xanthate and cuprammonia processes. Recently, however, with stricter governmental regulations in industry, the need to implement 'green' processes to prevent pollution and waste production and to utilize renewable resources has become imperative. There has been an intensive search for the commercial regeneration of cellulose because of the environmental problems associated with the xanthate process. Kamide and his coworkers[1-4] have already succeeded in preparing cellulose samples (soft wood pulp), with crystal forms of either cellulose I or cellulose II, completely soluble in a 1-10% NaOH solution, at low temperatures, however, the alkali soluble cellulose needs to be pretreated by steam explosion. More recently, Zhang[5-7] obtained NaOH/thiourea and NaOH/urea aqueous solutions, which can dissolve cellulose directly and quickly. Both systems represent simple and low-cost processing routes, and cellulose fibers can be prepared using a simple technology without pollution. However, the dissolving ability of these solvents is still not very strong and the prepared cellulose solutions easily gel. Gu[8] further proved that cellulose could be directly and quickly dissolved in a NaOH/thiourea/urea aqueous solvent. This

new quaternary solvent system was proved to be more powerful in dissolving cellulose, and could be used to prepare more stable spinning solutions containing higher concentration of cellulose, as compared to the NaOH, NaOH/urea (or NaOH/thiourea) aqueous solvent system.

Fibers and membranes from cellulose-NaOH/thiourea/urea solutions can be obtained by the so-called regeneration or coagulation techniques, the main principle being that the regenerating liquid must be miscible with the aqueous NaOH/thiourea/urea solution and be a precipitant for cellulose. Solidification of the spinning line in the bath is the result of phase separation, gelation and often of chemical reactions, as well. When a polymer solution is brought into contact with a coagulation bath, two processes for solvent removal and solidification of the dissolved polymer may be involved: either a chemical reaction between solvent and precipitant, or a physical exchange of solvent and non-solvent, resulting in polymer precipitation.[9] An example of a well-studied system is that of viscose fibers, as their spinning involves transformation of alkaline sodium cellulose xanthate into free xanthogenic acid and then into cellulose hydrate (regenerated cellulose), as well as a complicated chemical reaction between cellulose xanthate and various mobile ions, such as H^+, OH^-, and Zn^{2+} in the coagulation baths. The diffusion processes in rayon spinning have been investigated by numerous researchers,[10-18] however the work related to the kinetics of polymer precipitation from a solution, including viscose, is relatively limited, in spite of the obvious importance of the problem,[10,19] the apparent reason being the difficulty of studying the primary phase transitions, which usually proceed at a very fast rate in the fiber being spun. The cellulose cuprammonium system also contains chemical reactions in a coagulation sodium hydroxide solution and regeneration in an acid solution.[20]

To be different, the celluloses dissolved in NMMO, NH_3/NH_4SCN and NaOH aqueous systems were always coagulated from alcohols or water baths, the procedure of fiber or film precipitated in these coagulation baths being considered as a typical diffusion process.[9,21]

As early as in 1947, it was shown by Hermans[10] and later on by Paul,[22] in 1968, and by Liu *et al*.[9] in 1989, that a sharp boundary line is associated with the phenomenon of diffusion of various substances into polymer solutions. In 1976, Ziabicki detailed the theory related to such boundary motion and some experimental results.[23] It was deemed of considerable interest to investigate the polymer precipitation kinetics in the initial stage of the spinning process. However, the study of the coagulation processes in wet spinning fibers is attained with appreciable experimental difficulties, associated with the rapid occurrence of the chemical and physical structure-formation processes and the small cross-sectional dimensions of the fibers. Moreover, the measurements should be made on the moving elementary fibers, which undergo considerable shrinkage during spinning under the action of the precipitating bath, and often the form of the fiber section is greatly changed.[9,24-25]

The goal of this work is to obtain an insight into the regeneration kinetics of cellulose-NaOH/thiourea/urea/H_2O in the coagulation bath. The coagulation process for this complex solution (as many as 4 components occur in the aqueous solution) is too complicated (there appear chemical interactions of the precipitant with the solvent, mutual diffusion of precipitant into the cellulose solution and of the solvent from the solution) for permitting an exact examination of the coagulation behavior of each solvent components. By modeling the process of fiber-hardening through the interaction of a drop of cellulose solution with the precipitant, one can obtain useful information on the kinetics of diffusion by using direct observation of the optical moving boundary, the influence of precipitant compositions and concentration, coagulation time and temperature, and cellulose contents on coagulation rate having been demonstrated. The activation energy during coagulation, as well as the regeneration kinetics of cellulose-NaOH/thiourea/urea/H_2O samples, are also investigated. The result of this work will help to gain better understanding of the cellulose-NaOH/thiourea/urea/H_2O coagulation process.

EXPERIMENTAL

Materials

The cellulose (cotton linter pulp) was supplied by Shanghai Cellulose Pulp Factory, China. The viscosity average molecular weight ($\bar{M}_\eta$) of cellulose, determined by viscometry in cadoxen, was of 10.2×10^4. The cellulose samples were shredded into a powder and dried in a vacuum oven at 70 °C for 24 h before use. All chemicals employed were of analytical grade and were purchased from commercial sources in China.

Preparation of cellulose solution

The cellulose solution was prepared according to previously reported methods.[8] Various weights of cellulose were dispersed into 1000 g of solvent pre-cooled to 8 °C, followed by vigorous stirring for 3 min at room temperature. After 3 min, the temperature of the solution was controlled (-2 to 0 °C) using a salt-ice bath and the mixture was vigorously stirred for 7 min to obtain a transparent cellulose dope containing 3.5-6.5 wt% cellulose. The cellulose dope was subjected to centrifugation at 10000 rpm for 20 min at 5-10 °C, to exclude the slightly remaining undissolved part and to carry out degasification.

Coagulation rate measurements

Diffusion plays a very important role in wet spinning as a rate-controlling factor for many kinetic processes (diffusion transitions, chemical reactions, etc.). When a cross-section of a solution-spun fiber was taken in the initial stages of the coagulation process, two concentric circles were observed: the outer or "skin" being hard, solid and made of almost 100% polymer, and the inner circle or "core", occurring as a viscous solution of polymer dissolved in the acidic solvent. Essentially, the rate of coagulation can be determined by measuring the speed of the moving boundary. However, during real fiber spinning, these measurements are very difficult to achieve because of the fineness of the as-spun fibers. Therefore, a spinning model was used in the present study for measuring the coagulation rate.

The cellulose solutions were first poured into a glass beaker and then placed under vacuum at 40 °C for 60 h. After heating, the solutions became gels. The gelled rods could be obtained by pushing a cork borer (1.2 cm in diameter, 4 cm long) into the gelled solutions, which provided the specimens to be studied in a convenient and fixed geometrical form. The prepared gelled rods were individually immersed into a glass flume containing 5000 mL coagulating liquids. The precipitants and their concentration, coagulation time and temperature were sequentially varied. The parameters of the coagulation bath are listed in Table 1.

Table 1
Parameters of coagulation bath

Parameters	Aqueous H_2SO_4	Aqueous NH_4Cl	H_2O	Ethanol	n-Propanol
Concentration (mol/L)	0.5/1.0 2.5/4.5	2.0	-	-	-
Molecular volume $V\times10^3$ (mm^3/mol)[1]	17.65/18.26 18.58/18.98	17.91	18	58.4	74.79
Temperature (°C)	12/22/34	22	22	22	22
Coagulation time (s)	25/100/225/400/625/900/1600/2500				

[1]Defined as the value occupied by 1 mol, numerically equal to molecular weight divided by density determined at 22 °C

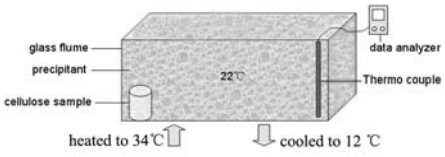

Figure 1: Experimental set-up for coagulation kinetics study

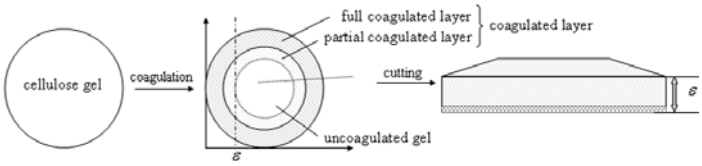

Figure 2: Schematic illustration of boundary motion with time in the cross-section of a cylindrically shaped polymer during the coagulation step

At the prescribed time, the specimen was removed from the bath, and a distinct boundary between the fully coagulated "skin" and the uncoagulated polymer was readily apparent.

Immediately thereafter, both ends of the samples were cut out, the cylindric samples were split manually with a razor blade, after which the uncoagulated gel samples (which were not rigid and maintained their initial soft gel form) were cleared, and the left coagulated layer (including the fully coagulated layer and the partially coagulated layer, the latter being more rigid than the uncoagulated gel but less than the former, which is an observation seldom mentioned in literature, the inconspicuous and soft layer generated by the cellulose coagulated from H_2O, ethanol, n-propanol, through counter-diffusion, occurring under the partially coagulated layer) was spread into a rectangle shape, which would make the measurement of the depth of coagulated skin more convenient (Fig. 2).

The depth, $\xi(t)$, that the coagulated skin had reached towards the center was measured with a vernier caliper. We have reasons to believe that this novel measuring method would be more accurate and simpler than the direct measurement of $\xi(t)$ on the cylindric samples, as mentioned in literature.[23-25] Moreover, the partially coagulated layer cannot be easily examined through direct microscopic measurements, as it evidences no distinct difference in color, comparatively with the uncoagulated gel, but it has a higher rigidity than the gel.

During the measurement of $\xi(t)$, the samples were brought at room temperature and constant humidity (20±1 °C, 60±3%).

Scanning electron micrographs (SEM) were performed on a JSM-5600LV microscope (Japan). The rectangularly shaped coagulated layers were dried at ambient temperature. The free surface (contacting the coagulant) of the sample was sputtered with gold for SEM measurements. SEM was obtained at 10 kV, which was considered suitable, as a higher voltage could burn the samples.

RESULTS AND DISCUSSION

Effect of precipitant concentration and coagulation time on boundary movement

The model experiments were performed on a solution of 5.5 wt% cellulose in a NaOH/thiourea/urea aqueous solution. The experimental data were approximated with a straight line, at a 10% experimental error. The boundary movement, as it relates to coagulation time, has been observed for several different precipitants. Typical curves and data are shown in Figure 3 and Table 2.

All samples that coagulated from H_2O, ethanol and n-propanol, allowing the application of the Fick approach, that is, the boundary position in H_2O, ethanol and n-propanol, $\xi(t)$, are proportional to the square root of time over the whole test period of coagulation, the slope, $\xi/\sqrt{t}$, providing a reliable measure of the coagulation rate.[23,24] The specific rate of this process can be characterized by parameter Ξ, defined in equation (1):

$$\Xi = \frac{1}{4}\lim_{t\to 0}(d\xi^2/dt) = \text{Const} \quad (1)$$

then

$$\xi^2/\text{t} = \text{Const and } \xi/\sqrt{t} = \text{Const} \quad (2)$$

In series of H_2SO_4 and NH_4Cl aqueous solutions, the actual numerical values ($\xi(t)$) are slightly higher than the values on the straight lines in the first 25-225 seconds. The generated coagulated "skin" is much more rigid than those coagulated from H_2O and alcohols, which is obviously caused by the rapid chemical neutralization between OH^- in the cellulose solvent and H^+ in the precipitant. However, the linear dependence between $\xi(t)$ and $\sqrt{t}$ is still to be found in both acid solutions. More precisely, when the cellulose solutions coagulated from H_2SO_4 and NH_4Cl aqueous solutions, the counter diffusion of solvents and precipitants still represented the main power in the coagulation process, in spite of the neutralization reaction between solvents and non-solvents.

Liu[25] found out that the linear relationship between $\xi(t)$ and $\sqrt{t}$ was not valid after the boundary moved to one third of the radius of the model filament.[25] As far as the cellulose-NaOH/thiourea/urea system was concerned, it was valid until 50% of sample penetration was reached by precipitants. Liu also revealed that the curve of the boundary position, $\xi(t)$, against $\sqrt{t}$ coincided with that of a linear case during initial diffusion, after which it showed a subsequent upward curvature. This increase in slope ($\xi/\sqrt{t}$) was also found after the same initial diffusion stage, when cellulose-NaOH/thiourea/urea/H_2O was coagulated from different precipitants. This is probably another consequence of the cylindrical geometry of the sample.

Further, it was found out that cellulose samples prepared by dissolving cellulose in a NaOH/thiourea/urea aqueous solution suffered only a slight contraction, even when they were coagulated from H_2SO_4 and NH_4Cl aqueous solutions. While cellulose

was dissolved in a NaOH/H_2O solution, the cellulose-NaOH/H_2O gels were contracting more than twice as when coagulated in methanol baths.[21] Due to the fact that samples were strongly contracting each other, the application of Fick's law was impossible. On the contrary, the slight contraction of the cellulose-NaOH/thiourea/urea/H_2O samples even in an acid precipitant can be explained by the fact that the concentration of the cellulose solution is higher and that the solution is prepared by cotton pulp with a high polymerization degree, which would constrain the contraction of the sample. As a result, the samples could maintain their original size (about 1.0-1.1 mm). The sizes of the samples were hardly changed when they were coagulated from H_2O, ethanol and n-propanol, because of their relatively low coagulation capability.

As generally known, the molecular volume of the precipitants plays an important role in determining the diffusion coefficient. Generally, the diffusion coefficients decrease with increasing molecular size, due to lowering of molecular mobility. Our experiments show that: $\xi/\sqrt{t}$ [H_2O] > $\xi/\sqrt{t}$ [Ethanol]> $\xi/\sqrt{t}$ [n-Propanol]

Table 2
Experimental value of $\xi/\sqrt{t}$ of 5.5 wt% cellulose gel samples coagulated from various precipitants at 22 °C

Precipitant	1 mol/L H_2SO_4	2 mol/L NH_4Cl	H_2O	Ethanol	n-Propanol
$\xi/\sqrt{t}\times10^5$ (m/s$^{1/2}$)	6.55	5.355	4.593	2.065	1.692
Regression values[1]	0.99668	0.99883	0.99671	0.99541	0.99719
Standard deviations[1]	0.09143	0.03527	0.0611	0.03937	0.03611

[1]Values obtained from the range of linearity of the curves

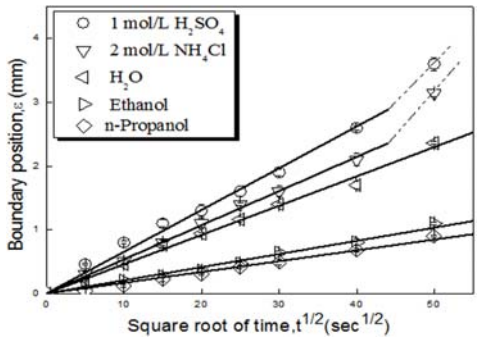

Figure 3: Curve of the boundary position of various coagulants in time during the coagulation step at 22 °C

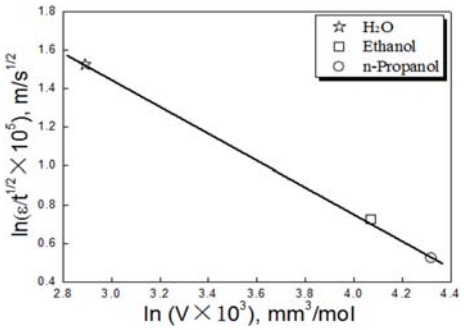

Figure 4: Dependence of diffusion rate at 400 s on the molecular volume of 3 kinds of coagulants at 22 °C

Figure 4 illustrates the plot of $\ln(\xi/\sqrt{t})$ *versus* ln V for cellulose samples in different precipitants, after 400 s at 22 °C. A straight line relationship is seen for the 3 coagulants, which suggests that Stoke's law is valid for them. The regression analysis of the line gives a value of 0.9915.

However, the situation is different when the samples were coagulated from acid solutions, that is: $\xi/\sqrt{t}$ [1 mol/L H_2SO_4] > $\xi/\sqrt{t}$ [2 mol/L NH_4Cl]

Considering the counter diffusion and the chemical reactions occurring continuously during the coagulation process, we tentatively put forward that not only the molecular volume of the precipitant, but also the affinity between solvent (NaOH, thiourea and urea) and precipitant would affect the coagulation rate, with the latter acting as a more dominant factor determining the coagulation rate. Therefore, it is easy to observe that H_2SO_4 is more inclined to react with the solvent than NH_4Cl.

Effect of precipitant type on the morphology of regenerated cellulose

Figure 5 provides digital images displaying the boundary motion in time (the ends of the sample have been cut). The difference in the coagulation rate can be

easily figured out from the various boundary positions of the cellulose samples coagulated from different precipitants.

Figure 6 shows the free surfaces of the cellulose samples coagulated with different precipitants. The acidic coagulants tend to form a surface with smaller pore size and a relatively uniform structure, due to the fast phase separation controlled by the spinodal decomposition mechanism, whereas the NH_4Cl as a coagulant could more easily form surfaces with slightly larger pore size and asymmetrical structure. A possible mechanism for coagulation and pore formation may originate from the following chemical reaction:

$$NH_4Cl+NaOH \rightarrow NaCl+NH_3.H_2O \quad (3)$$

The hydrogen ions then react with hydroxide in the solution, and the reaction proceeds in the right direction, ammonia coming out from the samples as a pore former.

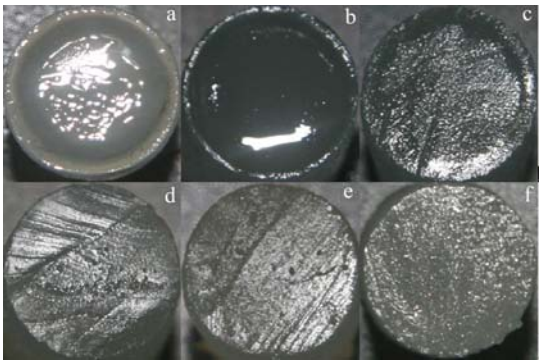

Figure 5: Cross-section of cellulose samples after 400 s of submersion in (a) 1 mol/L H_2SO_4; (b) 2 mol/L NH_4Cl; (c) H_2O; (d) Ethanol and (e) n-Propanol at 22 °C; (f) cross-section of uncoagulated cellulose sample

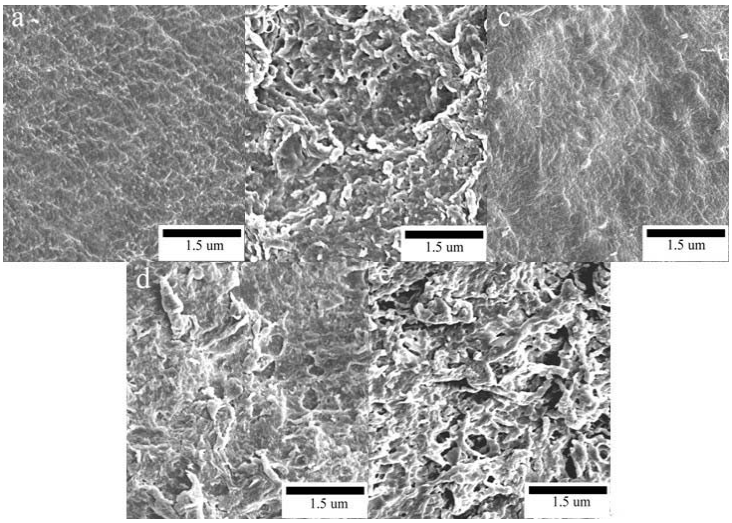

Figure 6: Free surface of cellulose samples after 400 s of submersion in (a) 1 mol/L H_2SO_4; (b) 2 mol/L NH_4Cl; (c) H_2O; (d) Ethanol and (e) n-Propanol at 22 °C

Unlike the samples coagulated from weaker precipitants – alcohols, interestingly, the cellulose sample prepared by coagulation with pure water exhibits an inconspicuous "skin" structure (Fig. 5 c), showing the smallest pore size, comparatively with any other alcohol precipitants. Water as a small molecule can penetrate the samples and coagulate them quickly, the samples not having sufficient time to form large poor phase and pores.

On the basis of the formation process of

pores,[26] when the cast cellulose solution was immersed into alcohols, the components of both cellulose solution and coagulation bath were exchanged to each other by diffusion, concomitantly with liquid–liquid demixing. This relatively slow diffusion could result in nucleation and growth of the cellulose poor phase, which was responsible for the formation of a porous structure.

To sum up, despite this complexity, the experimental value of $\xi/\sqrt{t}$ can still be considered as a parameter faithfully reflecting the effect of the coagulation variables,[27,28] whichever the conditions under which the experiment was conducted.

Effect of precipitant concentration on the coagulation process

The influence of precipitant concentration on the kinetics of cellulose regeneration was also studied. A change in precipitation bath concentration occurs only in the position of the kinetic curves (Fig. 7). With increasing the sulfuric acid content of the precipitation bath from 0.5 to 2.5 mol/L, the rate of counter-diffusion and neutralization increases. However, instead of a further increase, the coagulation rate of the cellulose sample in 4.5 mol/L H_2SO_4 decreases, as due to the factor of density (of 1.813 g/mL for 4.5 mol/L H_2SO_4 and of 1.173 g/mL for the 5.5 wt% cellulose sample measured in solution). As a result, the cellulose sample may float on the surface of the precipitant, the coagulation process being undoubtedly disturbed.

Effect of precipitant concentration on the morphology of regenerated cellulose

In fiber spinning, a precipitant with a too high concentration could be not only capable of facilitating cellulose decomposition, but also mainly responsible for serious condensing and frailness of fibers, as shown by the SEM images of the cellulose samples coagulated from 4.5 mol/L H_2SO_4 at 22 °C, the sample surface being partially decomposed by the concentrated sulphuric acid (Fig. 8 d). On the other hand, however, when the concentration of the precipitant is too low, the small concentration difference between precipitant and the cellulose-NaOH/thiourea/urea solution restrains their counter-diffusion rate, creating difficulties in the cellulose regeneration process from the coagulation bath, as regeneration occurs only on the surface of fibers, their internal part being still a semisolid cellulose gel (Fig. 8 a), which consequently leads to a drop in the tensile strength of fibers. 1-2.5 mol/L H_2SO_4 is found to be the most effective precipitant in the practical wet spinning process.[23] In our experiments, 1 mol/L H_2SO_4 was selected as the precipitant to be further studied.

Effect of coagulation bath temperature on the coagulation process

It is generally accepted that the coagulation of a dissolved polymer in a solvent/precipitant exchange bath is a rate process. In many systems, the mobility of molecules and ions increases with increasing temperature. To evaluate the effect of bath temperature on the coagulation rate of the cellulose-NaOH/thiourea/urea aqueous solution, the respective coagulation boundary movement of the cellulose solution coagulated from 1 mol/L H_2SO_4 at 12~34 °C was measured.

The results are presented in Figure 9. As expected, the higher the bath temperature, the quicker the NaOH/thiourea/urea/H_2O release from the cellulose samples, and thus the quicker the cellulose regeneration. The same holds true for the regeneration of cellulose/NaOH solutions in water baths of different temperatures.[21] For all precipitants, the coagulation rates increase with increasing bath temperatures, as due to the fact that the mobility of a precipitant molecule increases with increasing temperature.

However, in the actual wet spinning process, a too fast precipitation allows the cellulose molecular chains less time to organize themselves into an ordered structure, so that the tensile strength of the fibers drops.[29,30]

Effect of coagulation bath temperature on the morphology of regenerated cellulose

In addition, data for temperatures above 35 °C were unavailable, since the 5.5 wt% cellulose solution underwent an appreciable thermal expansion and gelation in the actual fiber spinning process; the coagulation experiments also showed that the gel samples suffered a more intense contraction when coagulated from 1 mol/L H_2SO_4 aqueous solutions at 34 °C (Fig. 10 c). When the

coagulation temperature was below 25 °C, the surface of the coagulated cellulose samples became denser.

Table 3
Experimental value of $\xi/\sqrt{t}$ of 5.5 wt% cellulose gel samples coagulated at various concentrations of H_2SO_4 at 22 °C

Precipitant	4.5 mol/L H_2SO_4	2.5 mol/L H_2SO_4	1 mol/L H_2SO_4	0.5 mol/L H_2SO_4
Density (g/mL)	1.813	1.154	1.077	1.06
$\xi/\sqrt{t}\times10^5$ (m/s$^{1/2}$)	8.057	8.964	6.55	6.134
Regression values	0.99956	0.99519	0.99668	0.99987
Standard deviations	0.03655	0.13989	0.09143	0.017

Table 4
Experimental value of $\xi/\sqrt{t}$ of 5.5 wt% cellulose gel samples coagulated from 1 mol/L H_2SO_4 at various temperatures

Temperature of precipitant (°C)	12	22	34
$\xi/\sqrt{t}\times10^5$ (m/s$^{1/2}$)	6.003	6.55	8.297
Regression values	0.99845	0.99668	0.99518
Standard deviations	0.05127	0.09143	0.14922

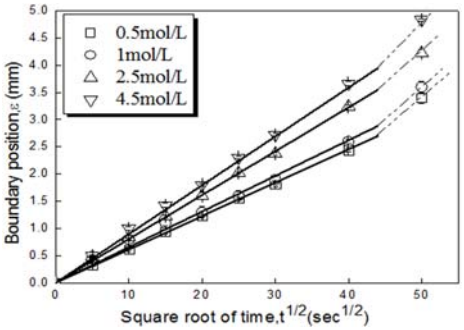

Figure 7: Adherence to Fick's Law when boundary motion is compared with the square root of time for 5.5 wt% cellulose gel samples in various concentrations of H_2SO_4, at 22 °C

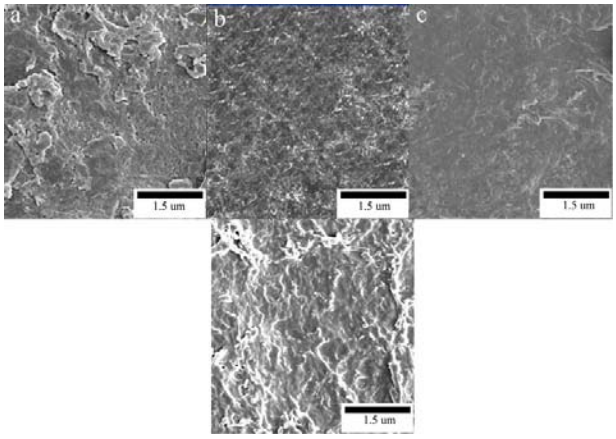

Figure 8: Free surface of cellulose samples after 400 s of submersion in (a) 0.5 mol/L H_2SO_4; (b) 1 mol/L H_2SO_4; (c) 2.5 mol/l H_2SO_4; (d) 4.5 mol/L H_2SO_4 at 22 °C

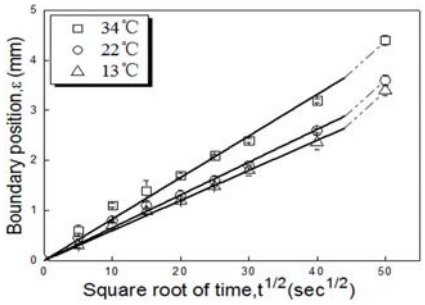

Figure 9: Adherence to Fick's Law when boundary motion is compared with the square root of time for 5.5 wt% cellulose gel samples coagulated from 1 mol/L H_2SO_4 at various temperatures

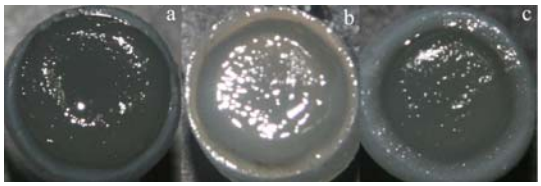

Figure 10: Cross-section of cellulose samples after 400 s of submersion in 1 mol/L H_2SO_4 at (a) 12 °C; (b) 22 °C and (c) 34 °C

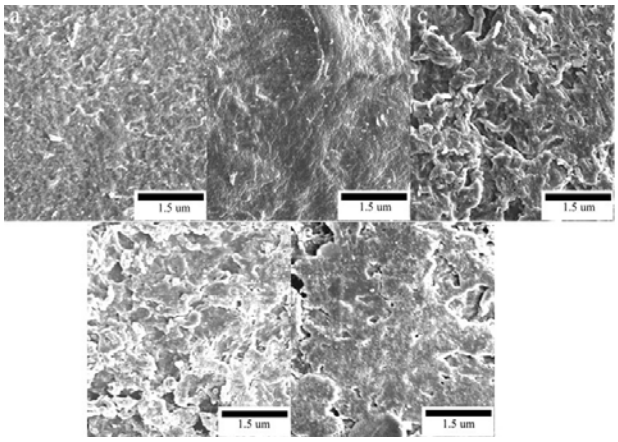

Figure 11: Free surface of cellulose samples after 400 s of submersion in 1 mol/L H_2SO_4 at (a) 12 °C; (b) 22 °C and (c) 34 °C. Images of the sample after coagulation from 1 mol/L H_2SO_4 for 1600 s and 2500 s at 22 °C (d and e)

This interesting phenomenon was believed to be a result of the nucleation and growth mechanism for the slow solidification process, to be possibly explained by the fact that, when the coagulation temperature was low, the exchange rate of solvent and coagulant was also slow.

Thus, nuclei were formed adequately in the polymer solution. These nuclei grew into droplets until they touched each other and coalesced, or until their growth was stopped by solidification of the surrounding polymer solutions. Figure 10 also shows that the increase of coagulation time has a similar effect with the improvement of coagulation temperature, on enhancing sample coagulation, that is, a too long coagulation time would also lead to too much contraction and more macrovoids (Fig. 11 d, e).

The coagulation rates increased with increasing temperature. It is well known that, generally, diffusion behaves as a rate process. A free energy of activation required for the movement of diffusing species (precipitant) from one site to another in a medium must be gained before diffusion takes place.[31] The relationship between the coagulation rate and temperature agrees with the following Arrhenius equation:

$$\ln\frac{\xi}{\sqrt{t}} = \ln \mathrm{A} - \frac{E_a}{\mathrm{R}T} \qquad (4)$$

where $\xi/\sqrt{t}$ represents the coagulation rate, T is the coagulation bath temperature, *E*a is the activation energy of precipitant, and A is the intercept (constant).

To study the effect of coagulation bath temperature on the coagulation rate, a 5.5 wt% cellulose solution in 1 mol/L H_2SO_4 aqueous solution was employed. Figure 12 illustrates the Arrhenius plot of the coagulation rate of different precipitants *versus* the coagulation bath temperature. The activation energy of cellulose-NaOH/thiourea/urea/H_2O coagulation in 1 mol/L H_2SO_4 aqueous solution was calculated (Fig. 12 and Table 5). They are situated within the same order of magnitude as those reported for other coagulation systems, such as cellulose/NH_3/NH_4SCN in methanol, 1-propanol and 2-propanol (5.148-16.024 kJ/mol), and cellulose xanthate/NaOH in an aqueous H_2SO_4 bath (7.866 kJ/mol).[9,12,32]

Effect of cellulose content on coagulation

A cellulose solution ($\bar{M}_\eta$ = 10.2×10^4) with a concentration of up to 6.5 wt% was prepared by using the novel solvent – NaOH/thiourea/urea aqueous solution. Measurements were performed at 3.5-6.5 wt% concentrations of cellulose solutions, in 1 mol/L H_2SO_4 at 22 °C (Table 2). It seems that an increase in the cellulose content leads to a significant increase in the coagulation rate, as well. On the one hand, the increase of cellulose content accompanies the increase in viscosity and the reduced mobility of both solvent and precipitant, a lower coagulation rate thus resulting. On the other hand, a higher polymer content enhances the intermolecular affinity caused by the high density of polymer chains, and further enhances the driving force for

coagulation. In this case, the latter has a dominant effect on the coagulation rate of cellulose in a NaOH/thiourea/urea aqueous solution. It should be noted that the cellulose solution is difficult to filter and degas, if its concentration exceeds 6 wt%, which may be attributed to its high viscosity. On the other hand, a cellulose solution with a too low concentration may lead to poor mechanical properties of the regenerated fibers. A 5.5 wt% cellulose solution is therefore always prepared for spinning or coagulation experiments.

Table 5
Regression equation for the relationship between $\ln \xi/\sqrt{t}$ and $1/T$

Precipitant	$\ln \xi/\sqrt{t} - 1/T$ regression equation	*E*a (kJ/mol)	Regression values	Standard deviations
1 mol/L H_2SO_4	$\ln(\xi/\sqrt{t} \times 10^5) = 6.32 - 1.3 \times (1/T \times 10^3)$	10.808	0.97203	0.05562

Table 6
Experimental value of $\xi/\sqrt{t}$ of 3.5-6.5 wt% cellulose gel samples coagulated from 1 mol/L H_2SO_4 at 22 °C

Contents of cellulose in gel (wt%)	3.5	5.5	6.5
$\xi/\sqrt{t} \times 10^5$ (m/s$^{1/2}$)	6.18	6.55	7.221
Regression values	0.99708	0.99668	0.9946
Standard deviations	0.08085	0.09143	0.12056

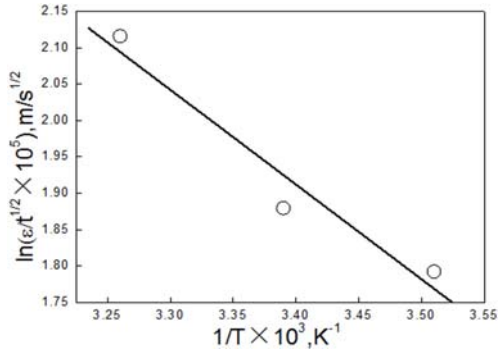

Figure 12: Arrhenius plot of coagulation rate *versus* coagulation bath temperature

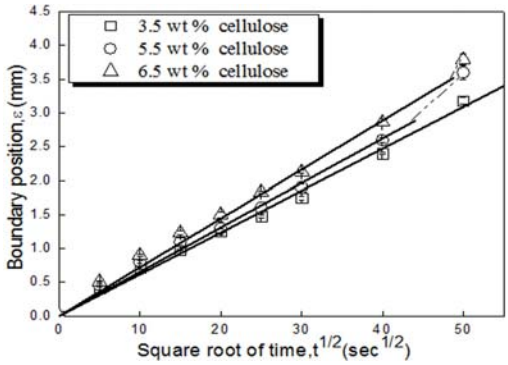

Figure 13: Adherence to Fick's law when the boundary motion is compared with the square root of time for 3.5-6.5 wt% cellulose gel samples coagulated from 1 mol/L H_2SO_4 at 22 °C

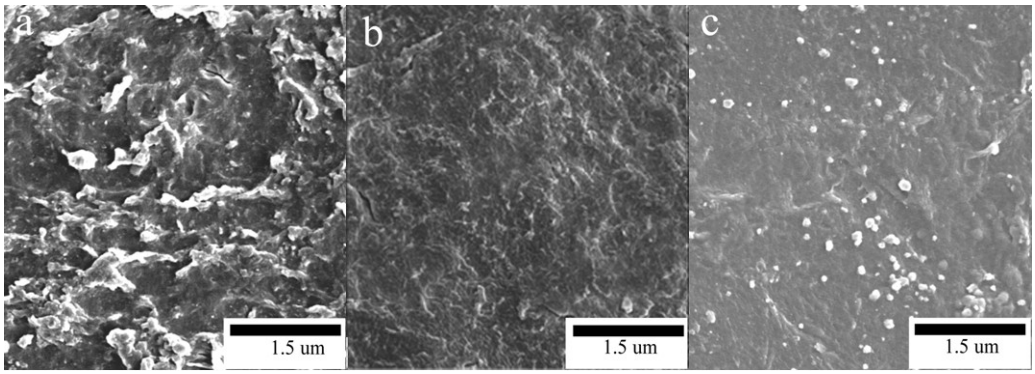

Figure 14: Free surface of: (a) 3.5 wt%; (b) 5.5 wt%; (c) 6.5 wt% cellulose samples after 400 s of submersion in 1 mol/L H_2SO_4 at 22 °C

Effect of cellulose content on the morphology of regenerated cellulose

With increasing the cellulose content in the solution, the surface morphology of the coagulated cellulose became denser, while the pore size decreased. The 3.5 wt% coagulated sample had a distinct asymmetrical structure, including the free surface with many macrovoids (Fig. 14 a). As the cellulose concentration increased to 6.5 wt%, the structure of the coagulated "skin" became even denser (Fig. 14 b, c). With the increase in cellulose concentration, the cellulose poor phase decreased, leading to the formation of a denser structure and to a smaller pore size in the coagulated layer. Therefore, the diffusion and convection processes between the cellulose solution and the coagulation conditions could change the morphology of fibers and films.

The coagulation mechanism

According to the results obtained, the whole coagulation process can be described as follows: when the cellulose solution contacts the preciptant, a counter-diffusion and chemical neutralization process between the solvent in the cellulose solution and the non-solvent from the coagulant occurs. However, the experimental fact that the coagulation rate was greatly affected by changes in the coagulation temperature, coagulation time, and cellulose concentration indicated that it is the counter-diffusion between solution and precipitant which mainly control the coagulation process, and not the neutralization reaction. The coagulation process can be therefore regarded as a diffusion-controlled chemical reaction, or it can be simply considered as a two-phase separation process.

A rapid neutralization reaction occurs on the contact surface between the precipitating bath and the cellulose sample in the initial seconds, meanwhile one or more of the bath components diffuse into the cellulose solution and the solvent in the solution diffuses outside it, the exchange and reaction of the solvent with the precipitant going on simultaneously during the same counter-diffusion process, leading to the regeneration of cellulose molecules and to the reformation of the intra- and intermolecular hydrogen bonds, which results in a loss of cellulose solubility, while the freshly formed fluid gel containing cellulose, water, etc., is gradually converted into a semisolid state to precipitate and regenerate.

CONCLUSIONS

An extensive study on the coagulation of cellulose from cellulose-NaOH/thiourea/urea aqueous solutions is presented. The investigation of the kinetics of diffusion processes during the coagulation of the cellulose solution under the action of various coagulation baths, by observing the optical moving boundary using a microphotography assembly, permitted a quantitative estimation of the process. The depth of the boundary movement $\xi(t)$ was found to be directly proportional to the square root of time, for each precipitant tested. Out of all 4 precipitants, 1 mol/L H_2SO_4 aqueous solution has been proved to have the most effective coagulation ability in the real wet spinning process. In this way, the relationship between coagulation rate ($\xi/\sqrt{t}$) and time, temperature and cellulose concentration has been demonstrated in detail. The coagulation rate was enhanced with the increase in the coagulation temperature, while it decreased with increasing cellulose concentration, which can be possibly attributed to the variable structure and permeability of the solidified layer. The coagulation mechanism can be described as a diffusion-controlled chemical reaction process occurring in two stages: a neutralization reaction in the initial few seconds, and a subsequent counter-diffusion.

REFERENCES

[1] T. Yamashiki, T. Matsui, K. Kowsaka, M. Saitoh, K. Okajima and K. Kamide, *J. Appl. Polym. Sci*., **44**, 691 (1992).

[2] T. Yamashiki, M. Saitoh, K. Yasuda, K. Okajima and K. Kamide, *Cellulose Chem. Technol*., **24**, 237 (1990).

[3] T. Yamashiki, T. Matsui, M. Saitoh, K. Okajima, K. Kamide and T. Sawada, *Brit. Polym. J*., **22**, 73 (1990).

[4] T. Yamashiki, K. Kamide, K. Okajima, K. Kowsaka, T. Matsui and H. Fukase, *Polym. J*., **20**, 447 (1988).

[5] J. P. Zhou, L. N. Zhang and J. Cai. *J. Polym. Sci*., *Pol. Phys*., **42**, 347 (2004).

[6] J. Cai and L. N. Zhang, *Biomacromolecules*, **7**,

183 (2006).
[7] L. N. Zhang, D. Ruan and S. J. Gao, *J. Polym. Sci., Pol. Phys.*, **40**, 1521 (2002).
[8] H. J. Jin, C. X. Zha and L. X. Gu, *Carbohydr. Res.*, **342**, 851 (2007).
[9] C. K. Liu, J. A. Cuculo and B. Smith, *J. Polym. Sci., Polym. Phys.*, **27**, 2493 (1989).
[10] J. J. Hermans, *J. Colloid. Sci.*, **1**, 387 (1947).
[11] D. Vermaas, *Text. Res. J.*, **32**, 353 (1962).
[12] A. Takizawa, *Sen'i Gakkaishi*, **16**, 839 (1960).
[13] A. Takizawa, *Sen'i Gakkaishi*, **16**, 842 (1960).
[14] A. Takizawa, *Sen'i Gakkaishi*, **16**, 850 (1960).
[15] A. Takizawa, *Sen'i Gakkaishi*, **16**, 955 (1960).
[16] A. Takizawa, *Sen'i Gakkaishi*, **17**, 31 (1961).
[17] A. Takizawa, *Sen'i Gakkaishi*, **17**, 36 (1961).
[18] A. Takizawa, *Sen'i Gakkaishi*, **17**, 129 (1961).
[19] M. E. Epstein and A. I. Rosenthal, *Text. Res. J.*, **36**, 813 (1966).
[20] M. Inamoto, I. Miyamoto, T. Hongo, M. Iwata and K. Okajima, *Polym. J.*, **28**, 507 (1996).
[21] R. Gavillon and T. Budtova, *Biomacromolecules*, **8**, 424 (2007).
[22] D. R. Paul, *J. Appl. Polym. Sci.*, **12**, 383 (1968).
[23] A. Ziabicki, in "Fundamentals of Fibre Formation", John Willy & Sons, London 1976, p. 21.
[24] J. Z. Knaul and K. A. M. Creber, *J. Appl. Polym. Sci.*, **66**, 117 (1997).
[25] C. K. Liu, J. A. Cuculo and B. Smith, *J. Polym. Sci., Pol. Phys.*, **28**, 449 (1990).
[26] K. Kamide, H. Iijima and S. Matsuda, *Polym. J.*, **25**, 1113 (1993).
[27] J. R. Booth, *Appl. Polym. Symp.*, **6**, 89 (1967).
[28] D. R. Paul and O. M. Ebra-Lima, *J. Appl. Polym. Sci.*, **15**, 2199 (1971).
[29] G. Pinto and V. Lorenzo, *Polym. Eng. Sci.*, **38**, 461 (1998).
[30] Y. Mao, L. N. Zhang, J. Cai, J. P. Zhou and T. Kondo, *Ind. Eng. Chem. Res.*, **47**, 8676 (2008).
[31] R. J. Borg and G. J. Dienes, in "An Introduction to Solid State Diffusion", Academic Press, San Diego, 1988, pp. 73-76.
[32] C. K. Liu, J. A. Cuculo, T. C. Allen and A. W. Degroot, *J. Polym. Sci., Pol. Phys.*, **29**, 181 (1991).