

Dissolving cellulose with twin-screw extruder in a NaOH complex aqueous solution

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Abstract. Novel cellulose dissolution method with twin-screw extruder was developed in order to improve the dissolution property, to simplify production procedure and to produce cellulose spinning dope which is stable and which has a higher concentration of cellulose. Therefore, the extrusion conditions on the cellulose dissolution in NaOH/thiourea/urea were extensively studied in this work. The resulted extrudates of twin-screw extruder dissolution method were characterized by polarized optical microscope image, the solubility experiment and the apparent viscosity. The results revealed that the screw revolution speed of such process could improve the solubility value (S_a) of cellulose, and the solubility of cellulose reached a maximum value of 7.5 wt% at higher revolutions 450 rpm. On the other hand, the cellulose solutions were more transparent and balanced with its apparent viscosity values lower and more stable compare to stirring method, which indicated dissolving cellulose with twin-screw extruder was reliable. Moreover, the whole dissolving time is quite short, and the process is simple. The soluble effect of twin screw extrusion was far superior to traditional stirring, and the most suitable temperature was -2°C.

1. Introduction

Cellulose is one of the plentiful natural and linear macromolecule polymers. The chemical structure of cellulose consists of β -glucopyranose units with 1-4-glycosidic bond linked. It has been classified as environmentally friendly, inexpensive, biodegradable, may and biocompatible be chemically modified to produce functionally products [1-3]. Cellulose, however, cannot melt, dissolution is a key issue. There are a limited number of solvent systems to directly dissolve cellulose, such as inorganic metal complexes (cuam, cadoxen, cuen etc.) [4], lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) [3], N-methylmorpholine-N-oxide (NMMO) [5], dimethylsulfoxide/tetrabutylammonium fluoride (DMSO/TBAF) [6], ionic liquids [7, 8] and aqueous NaOH systems [9-11]. Thus it is a growing urgency to build a new, green, inexpensive solvent for cellulose. Recently, Zhang and co-workers had developed some "green" solvent systems like NaOH/urea [12], LiOH/urea [13], and NaOH /thiourea aqueous solutions [14]. The three solvent systems can dissolve cellulose quickly. Furthermore, Lixia Gu and Jianyong Yu [15, 16] developed a NaOH/urea/thiourea solvent system that is more effective in dissolving cellulose. Moreover, higher concentration cellulose spinning solution is more stable than NaOH /thiourea or NaOH/urea aqueous solution systems. However, cellulose dissolve in the above solvents should be precooled to -12 °C or -10 °C with vigorously stirring, which is not favored for scale up of the cellulose dissolution technology, and is not yet applied for industrial use. Herein, there



is a large space to improve the dissolution property, decrease dissolution time, simplify production procedure, and produce cellulose spinning dope-which is stable and has a higher concentration of cellulose.

Twin screw extrusion is a short-time, high-shear process with the benefit of high can and versatility overcome the problems of dissolving cellulose by conventional stirring method [17].

In this work, we present a new method to dissolve cellulose with twin-screw extruder in an optimal NaOH (9 wt%)/urea (3 wt%)/thiourea (5 wt%) aqueous solution at -2 °C. The extrudates' quality obtained was stable and more productive. Nevertheless, extrusion conditions' effects on cellulose dissolve in NaOH complex aqueous solution have not been discussed before. Moreover, dissolution reliability and dissolving capacity of co-rotating twin-screw extruder are discussed here in detail.

2. Materials and methods

2.1. Materials

Cellulose pulp [α -cellulose > 95%, DP=550] was provided by Longma Corporation (Jiangsu Province, China). As received, all chemicals were of analytic grade and were used.

2.2. Cellulose solution preparation

Dried cellulose pulps were dispersed into NaOH (9 wt%)/urea (3 wt%)/thiourea (5 wt%) aqueous solution at room temperature to prepare cellulose suspension. Then the cellulose suspension was extruded by a twin-screw extruder (D = 16 mm & L/D = 40) precooled to -2 °C to obtain transparent cellulose extrudate very quickly.

2.3. Solubility test

The transparent cellulose solution was obtained through centrifuging the prepared extrudate at 1100 rpm for 10 min at 5 °C. Undissolved fractions were divided and then washed using acetone and water, respectively. Finally, undissolved fractions were dried for 24 h at 60 °C in a vacuum oven. Therefore, the solubility (S_a) value of cellulose in NaOH complex aqueous solution was expressed as

$$S_a = [(W_1 - W_2) / (W_1 - W_2 + W_0)] * 100 \quad (1)$$

Where W_1 was the original cellulose pulp's weight, W_2 was the undissolved fraction's weight and W_0 was the NaOH complex aqueous solvent's weight.

2.4. Characterization

Polarized optical microscope (DM2500P, Leica, Germany) was utilized to observe cellulose's morphological change in NaOH/thiourea/urea aqueous solution at ambient temperature. The cellulose solutions were observed and photographed by pressed between two superimpose glasses.

The apparent viscosity of each prepared solution was carried out on a rotational viscometer (SNB-1, Shanghai Jingtian Electronic Instrument Co., Ltd, China) at 20 °C. The cellulose solution was degassed before testing.

3. Results and discussion

3.1. Effect of screw revolution speed on solubility

Figure 1 showed the dependence of cellulose's S_a values and the cellulose extrudates' polarized optical microscopic pictures on the revolutions of the extruder. Cellulose pulp dissolved in aqueous NaOH/thiourea/urea solution by using a twin screw extruder at -2 °C. The S_a curves sharply increased and reached a maximum value of 7.5 wt% at more than 450 rpm. This stated that the rise in the rates and the shearing force of extruder could reinforce the solubility and dispersion [18]. Also it could be seen from the polarized optical images that cellulose's solubility in NaOH complex aqueous solution could be enhanced considerably by increasing the extruder revolutions.

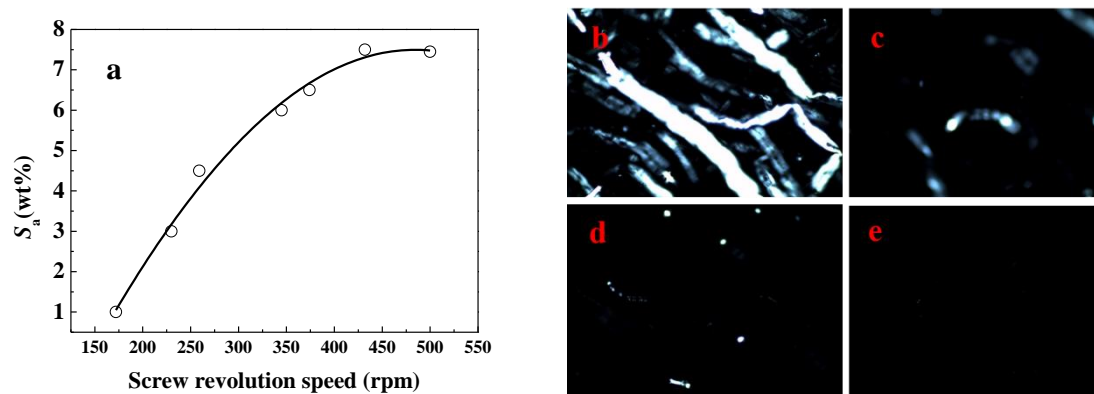


Figure 1. The dependence of cellulose's S_a values and the cellulose extrudates' polarized optical microscopic pictures at 0 rpm (b), 200 rpm (c), 350 rpm (d) and 450 rpm (e) with twin screw extruder at -2°C .

3.2. The dissolution reliability of twin-screw extruder

Twin screw extrusion was a high efficiency and high-shear process, while the related research of the resulted extrudate's uniformity was relatively less. According to this consideration, the polarized optical microscopic image and the apparent viscosity of each prepared cellulose solution were studied to prove the dissolution reliability of twin-screw extruder, which can be seen in figure 2 and 3.

In NaOH/thiourea/urea solvent system, two 7.0 wt% cellulose solutions were prepared. Solution 1 was dissolved by twin screw extruder as mentioned previously and solution 2 was dissolved through stirring method [16]. Figure 2 showed that solution 1 was entirely dissolved, however, solution 2 was not completely dissolved remaining some undissolved cellulose pulp. It is obvious that twin-screw extruder dissolution method is more efficient than the stirring method. Moreover, twin-screw extruder dissolution method can overcome the problems of dissolving cellulose by stirring method and solution 1 was more transparent than solution 2. The undissolved cellulose pulp in solution 2 appeared to be surrounded by the viscous solution, so it was difficult for solvent to enter into the pulp [16]. The solvent seemed to lose its dissolution ability even with prolonged stirring. Therefore, twin-screw extruder dissolution method is conducive to scaling up of the cellulose dissolution technology.

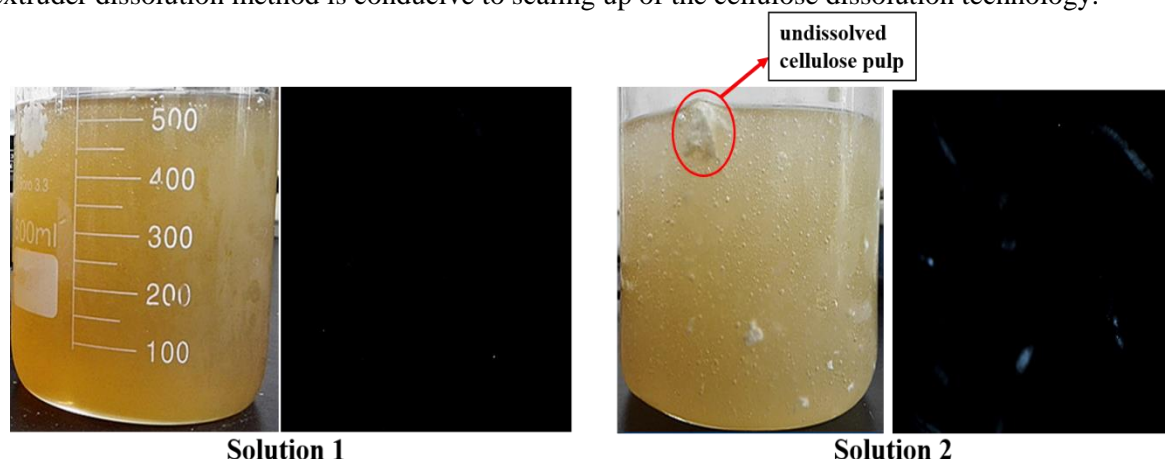


Figure 2. Digital and polarized optical microscopic images of two cellulose solutions.

In figure 3, curve *a* and *b* indicated that the viscosity results of cellulose extrudate were lower than the solution dissolved by conventional stirring. It is necessary for wet-spun process and industrial applications. Curve *c* and *d* represented the random S_a values of the cellulose solution dissolved by

twin screw extruder and conventional stirring, respectively. It could be observed that the S_a values of the cellulose extrudates were relatively more stable than the solution dissolved by conventional stirring. The twin screw extruder has more powerful shearing force, and makes the macromolecular chain less of mutual entanglement and then makes the chain easy to stretch. Meanwhile, the reverse thread element of twin screw extruder can provide enormous pressure to make the small solvent molecules easy to penetrate into the cellulose pulp and promote the solvation effects. However, the mixing dissolution is limited by motor power and the blade structure, lead to the cellulose pulp local diffusion uneven. In order to improve the dissolve ability, conventional stirring need to increase motor power, design the blade structure and avoid the phenomenon of climbing pole. Obviously, twin screw extruder takes more advantages in the preparation of high concentration and high quality spinning cellulose solution.

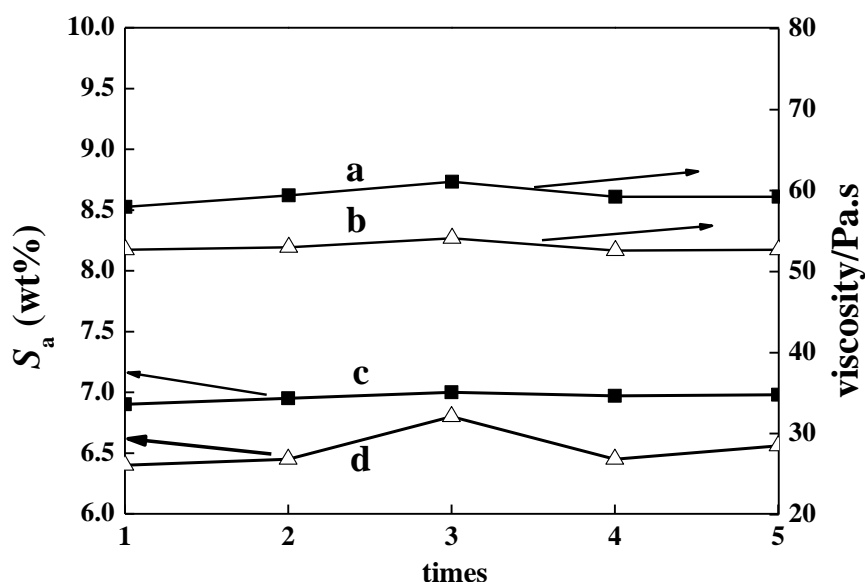


Figure 3. Differences of random S_a values and the apparent viscosity of two cellulose solutions (the results were from 5 times random sampling among cellulose dissolution process).

a, d – stir dissolution method; b, c – twin-screw extruder dissolution method

4. Conclusion

Cellulose pulp (nonactivated or untreated) is able to dissolve in NaOH complex solution directly. The low toxicity's solvent system has more excellent solubility ability for cellulose in comparison with NaOH/urea and NaOH/thiourea. The novel dissolution approach with twin-screw extruder has higher efficiency, and it can obtain an excellent cellulose extrudate, further to obtain a high quality cellulose spinning dope. Furthermore, the whole dissolving time is very short, and the process is simple. The soluble effect of twin-screw extrusion was far superior to traditional stirring, and the most suitable temperature was from -12°C to -2°C . Regenerated cellulose fibers and films with better mechanical properties, which is prepared by this simple, environmentally friendly and inexpensive technology, will be discussed in the further research. Therefore, it is hopeful to replace the viscose production technology that involves serious pollution problems.

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