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Research Article

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Effect of the Dissolving Method on the Dissolution of Dissolving Pulp Cellulose Fibers with Different Dried-States in Different NaOH/additives Aqueous Solutions

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Abstract A NaOH/urea (or thiourea) solvent system capable of dissolving cellulose at lower temperatures is a breakthrough in cellulose chemistry, and it was reported that cellulose rapidly dissolved when it was added to a precooled aqueous solution of sodium hydroxide (NaOH) and additives. Therefore, this work compared the effectiveness of the direct dissolution method and freezing-thaw method in dissolving pulp fiber and pure cellulose. Three aqueous solutions were examined: 7% NaOH/12% urea, 9.5% NaOH/4.5% thiourea, and 8% NaOH/8% urea/6.5% thiourea. The dissolving capacity of three NaOH/additives aqueous solutions was analyzed by polarized optical microscopy and the dissolved cellulose proportion was determined. The results showed that the never-dried softwood dissolving pulp and bamboo dissolving pulp achieved better dissolution using freezing-thaw method than using direct dissolution method in the three aqueous solutions. The dissolving method had a negligible effect on the dissolution of each dissolving pulp in the 8% NaOH/8% urea/6.5% thiourea solution. It seems that the direct dissolution method was more suitable for oven-dried microcrystalline cellulose with a low degree of polymerization (DP) and the freezing-thaw method was more suitable for never-dried pulp cellulose fibers with a higher DP.

Keywords NaOH/additives aqueous solution • Direct dissolution • Freezing-thaw • Dissolving pulp • Microcrystalline cellulose

Introduction

Aqueous NaOH/additives solutions for the dissolution of pulp cellulose have attracted wide attention from researchers because they are inexpensive, eco-friendly, and dissolve rapidly. Many researchers have reported beneficial effects from precooled NaOH-based aqueous solutions [1-4]. The direct dissolution of cotton linter pulp cellulose in any precooled aqueous solution of LiOH/urea, NaOH/urea, or NaOH/thiourea has been found to produce a stable cellulose solution [1, 5-7]. In a study regarding the direct dissolution of cotton linter pulp cellulose in an 8% NaOH/8% urea/6.5% thiourea aqueous solution precooled to -12 °C, it was found that untreated(never dried) or inactivated cellulose was able to dissolve directly and quickly [8,9]. A stable inclusion complex formed by cotton linter pulp cellulose in a NaOH/urea aqueous solution precooled to -12 °C was studied by Qin et al [10]. The dissolving behavior of cotton linter pulp cellulose in a 7%

NaOH/12% urea/0.5% ZnO aqueous solution precooled to -13 °C has also been examined [11]. In these experiments, they investigated the dissolution of cellulose in the precooled NaOH-based aqueous solutions using direct dissolution method, moreover, weight average molecular weight(M_w) and the degree of polymerization (DP) of cellulose used are less than 1.2×10^5 g/mol and 740, respectively. There are also some researchers who have reported the possibility for dissolving more cellulose (DP＞1200) by adding additives to a precooled NaOH systems by direct dissolution [12] and have investigated the influence of additives on cellulose dissolution in an alkali-based solvent[13]. In addition, researchers carried out experiments about the dissolution of cellulose in NaOH/additives aqueous solutions using the freezing-thaw method. The solubility of cellulose from cotton linter, bagasse, alkali-soluble cellulose, and Bemcot non-woven cloth made from cotton linters in NaOH/urea aqueous solution using freezing-thaw method was analyzed by Zhou and Zhang [14]. The dissolution of cellulose powder (M_w = 1.32×10^5 g/mol) in a 9% NaOH/1% PEG aqueous solution using the freezing-thaw method has also been investigated. Namely a room temperature cellulose aqueous solution was frozen at -15 °C for 12 h and then thawed at room temperature under strong stirring, which formed a pure solution of cellulose [15]. And the solubility of wood pulp cellulose in a 10% NaOH/8% urea/4% hexanolactam aqueous solution with the freezing-thaw method was found to be optimal when the mixture was frozen at -10 °C [16].

As we know, the dissolution of cellulose fibers and synthesis of cellulose derivatives on an industrial scale usually use oven-dried (OD) fibers as the starting material. Although the dissolution of OD cellulose in NaOH/additives using direct dissolution method is well studied, recently in our many experiments, never-dried(ND) dissolving pulp(DP＞740) showed better dissolution in NaOH/additives aqueous solution using freezing-thaw method than using direct dissolution method [17-19]. This interesting result led us to plan further experiments shown in this paper. The general thought is that fibers from the ND state will decrease the dissolving strength of the solvent because of the presence of water inside and around the fibers that dilute the aqueous solution. On the contrary, ND fibers in a swollen and more accessible state can absorb more chemicals than OD fibers. Thus, the local decrease in the solvent strength is counteracted by the opening of the structure in the ND state [20-22]. Considering that the influence of the never-dried (ND) state on the swelling and dissolution of cellulose fibers in an aqueous solution was also discussed in some detail [23]. Therefore, to understand how the ND state of a fiber affects its solubility in an aqueous solution, this work examined the dissolution of both ND and OD dissolving pulp fibers in different NaOH/additives aqueous solutions.

Materials and Methods

Materials

Bleached softwood sulfite dissolving pulp (SDP) was provided by Okito Kogyo Co. (Okinawa, Japan). Bleached pre-hydrolysis sulfate hardwood dissolving pulp (HDP) was provided by Hunan Juntai Pulp & Paper Co. (Huaihua, China) and bleached pre-hydrolysis sulfate bamboo dissolving pulp (BDP) was provided by Lee & Man Paper (Dongguan, China). The characteristics of the pulp samples are given in Table 1. The DP of the HDP and BDP was provided by the manufacturer,

while the other parameters were measured in the laboratory. Microcrystalline cellulose (MCC) was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). The MCC was isolated using column chromatography (SN5318X, Sinopharm Chemical Reagent Co., Shanghai, China) and had a particle size of 20 μm to 100 μm (DP＜350). The properties of the cellulose are listed in Table 2.

Table 1 Characteristics of the three commercial dissolving pulps

Parameters		Pulp type		
		SDP	HDP	BDP
	Average degree of polymerization (DP)	1520[a]	800	1228
	α-cellulose content[b] (%)	93.74	98.77	95.45
	Crystallinity[c] (%)	85.0	86.4	77.2
Solubility in 100g/L NaOH aqueous solution S_{10} (%)		6.07	5.03	3.68
Solubility in 180g/L NaOH aqueous solution S_{18} (%)		2.98	2.55	2.50
Fiber quality	0.2-7.5mm L_w (mm)	1.496	0.587	1.490
	Fiber width W_w (μm)	37.2	18.2	21.3
	Content of arithmetic fine fiber(%)	23.2	39.9	61.6
	Kinks index (mm^{-1})	0.937	0.713	0.588
	Coarseness (μg/m)	206.1	53.6	106.7
Neutral sugar	Glucose content (%)	93.03	97.01	94.62
	Xylose content (%)	1.46	2.04	1.91
	Mannose content (%)	5.51	0.23	2.40
	Arabinose content (%)	/	0.72	0.75
	Galactose content (%)	/	/	0.32

Table 2 Properties and dissolving methods of the cellulose fiber samples

Sample	Dissolving Method	State	Moisture (%)	Intrinsic Viscosity (mL/g)
SDP	Direct Dissolution	Oven-dried	0	1010
SDP	Direct Dissolution	Never-dried	5.46	1010
SDP	Freezing-thaw	Never-dried	5.46	1010
HDP	Direct Dissolution	Oven dried	0	565
HDP	Direct Dissolution	Never-dried	6.14	565
HDP	Freezing-thaw	Never-dried	6.14	565
BDP	Direct Dissolution	Oven-dried	0	833
BDP	Direct Dissolution	Never-dried	6.11	833
BDP	Freezing-thaw	Never-dried	6.11	833
MCC	Direct Dissolution	Oven-dried	0	-
MCC	Freezing-thaw	Oven-dried	0	-
MCC	Direct Dissolution	Never-dried	1.48	-
MCC	Freezing-thaw	Never-dried	1.48	-

*Intrinsic viscosity of each cellulose was measured based on the copper ethylenediamine method

The average DP of the SDP was measured using the copper ethylenediamine method. The α-cellulose content was measured using TAPPI T203 cm-99. The crystallinity of the dissolving pulp was calculated using wide-angle X-ray diffraction ((D/MAX-2500, Rigaku Denki Co. Ltd., Tokyo, Japan). The solubility in 100 g/L (S_{10}) and 180 g/L NaOH aqueous solutions (S_{18}) was determined by the titrimetric method (ISO 692:1982). The S_{10} value estimates the hemicellulose fraction, while the S_{18} value estimates the combined hemicellulose and low-M_w cellulose fraction. The fiber parameters of the three pulps were measured with a Lorentzen & Wettre Fiber Tester 912 (Kista, Sweden). The contents of the neutral sugars were measured with ion chromatography (Dionex ICS-5000$^+$, Thermo Fisher Scientific, Massachusetts, USA).

Methods

Observation of the Dissolving Behavior of the Cellulose

A sample from the final pulp fibers-cellulose-solvent mixture or MCC-cellulose-solvent mixture were taken using a toothpick, placed on a microscope slide, and covered with an 18-mm × 18-mm glass plate. The sample was analyzed *via* polarized optical microscopy in the transmission mode (BM-57XCC, Shanghai Biem, Shanghai, China). The magnification of the eyepiece was adjusted to 4 (4×).

Separation of the Cellulose Solution and Insoluble Fractions

The pulp fibers-cellulose-solvent mixture or MCC-cellulose-solvent mixture was centrifuged at 5000 rpm for 10 min at 5 °C (L535-1 low-speed, Changsha Xiangyi Centrifuge Instrument Co., Changsha, China). Part of the supernatant liquid was moved to a transparent plastic sample bottle with a Pasteur pipette for the viscosity measurement. The remaining insoluble fractions in the centrifuge tube were filtrated by a glass sand core funnel and SHZ-D (III) vacuum pump (Lanphan, Henan, China). The filtered material was then washed with the corresponding NaOH/additives aqueous solution three times and further washed with distilled water until it was neutral.

Viscosity Measurement of the Cellulose Solution

The viscosity of cellulose solution produced by dissolution of three dissolving pulps in the different NaOH/additives aqueous solutions was measured by a 0.9-mm to 1-mm Ubbelohde viscometer (Taizhou Jiaojiang District Glass Instrument Factory, Zhejiang, China). Two measurement times were recorded with a timer. One measurement was the time (t) passing through two calibrated lines in the measuring bulb for the cellulose solution. The other measurement was the time (t_o) passing through two calibrated lines in the measuring bulb for the pure NaOH/additives aqueous solvent at the same temperature. The ratio of t to t_o was defined as η_r. The viscosity of each cellulose solution was measured at least three times and the average was calculated. The intrinsic viscosity ($[\eta]$) of the three commercial dissolving pulp samples was measured using the one-point method [5]. The kinetic energy correction was always negligible, so the $[\eta]$ value was calculated with Eq. 1,

$$[\eta]=[2(\eta_r\text{-}1\text{-}ln\eta_r)]1/2\ /c \quad (1)$$

Where η_r is the relative viscosity, and c is the concentration of polymer, g/ml.

Measurement of the Dissolved Proportion of the Three Dissolving Pulps

The insoluble fractions were collected in a plastic culture dish and dried in a vacuum oven (Shanghai Senxin Experimental Instruments Co., Ltd., Shanghai, China) with anhydrous calcium chloride at 50 °C for 6 h. The samples were then weighed and named, depending on the weight of the insoluble fractions and original pulp. The dissolved proportions of the dissolving pulp were calculated with Eq. 2,

$$\text{Dissolved proportion} = (1- W_i/W_o) \times 100\% \quad (2)$$

Where W_o is the dry mass of original dissolving pulps and W_i is the dry mass of the insoluble

fractions of dissolving pulps. The dissolved proportion measurements were repeated three times and the average value was calculated.

Results and Discussion

Dissolution of the Three Dissolving Pulps in the NaOH/additives Aqueous Solutions

The swelling and dissolution of the three dissolving pulp samples in different aqueous solutions were observed by polarized optical microscopy to compare their dissolving behavior. The images clearly showed that the 8% NaOH/8% urea/6.5% thiourea solution had a better dissolving capacity than the 7% NaOH/12% urea and 9.5% NaOH/4.5% thiourea solutions for each dissolving pulp with a DP higher than 740, regardless of which dissolving method was used.

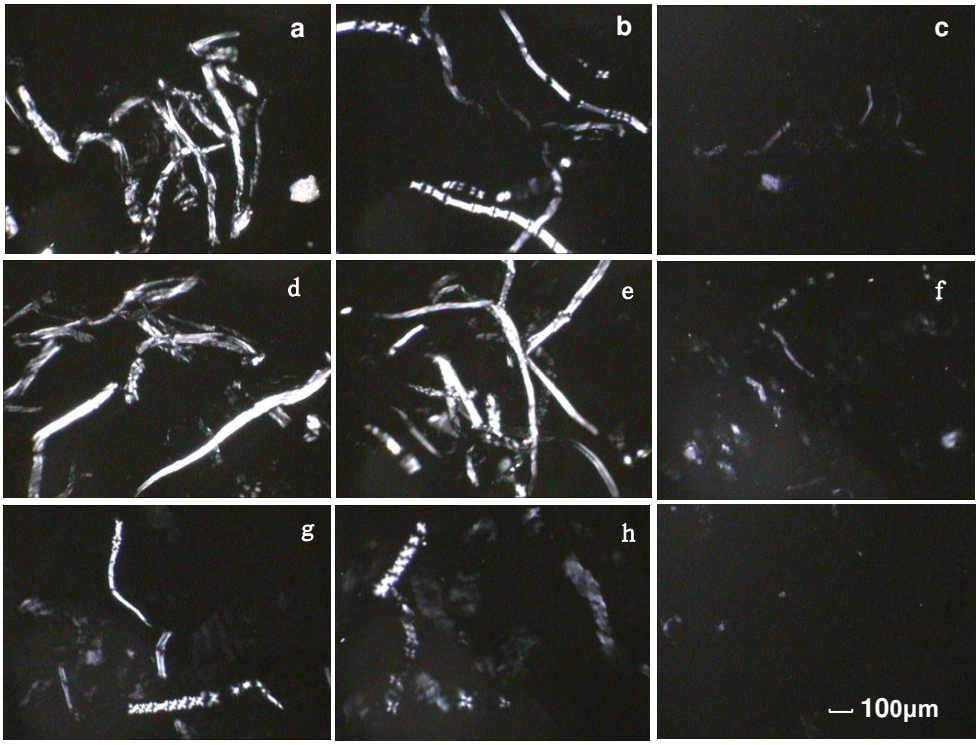

Fig.1 Polarized optical microscopy images of the SDP dissolved in the different NaOH/additives aqueous solutions using direct dissolution method,OD: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; using direct dissolution method,ND: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea and using freezing-thaw method,ND: (g) 7% NaOH/12% urea, (h) 9.5% NaOH/4.5% thiourea, and (i) 8% NaOH/8% urea/6.5% thiourea

The SDP (Fig.1) exhibited good swelling of the fibers. Using freezing-thaw method performed better than using direct dissolution method for the dissolution of SDP in each solvent. The fibers of the HDP (Fig.2) remained thin and short after treatment. There was little difference in the dissolution of the HDP between the freezing-thaw and direct dissolution methods for each solvent. The BDP fibers appeared to be long and stiff (Fig.3). The freezing-thaw method was more effective than the direct dissolution method for the dissolution of the BDP in each solvent. The dissolution of small BDP fibers left many micro-sized fibers in the solvent, which indicated that it was the most difficult to dissolve the BDP cellulose in the NaOH/additives aqueous solutions. These findings were consistent with the results reported by Spinu et al [23]. Namely, the ND state was more reactive for the dissolution of SDP or BDP in NaOH/additives aqueous solutions. The

ND state had no remarkable effect on the HDP, which illustrated that the dissolving capacity of a NaOH/additives aqueous solution depends on the origin of the cellulose fibers, composition of the aqueous solution, and dissolving method. As mentioned in previous studies, ND cellulose fibers are in a swollen and more accessible state, which means that they can absorb more chemicals than OD fibers. The local decrease in the solvent strength is counteracted by the opening of the structure in the ND state at different degrees, which was also affected by different NaOH/additives aqueous solutions.

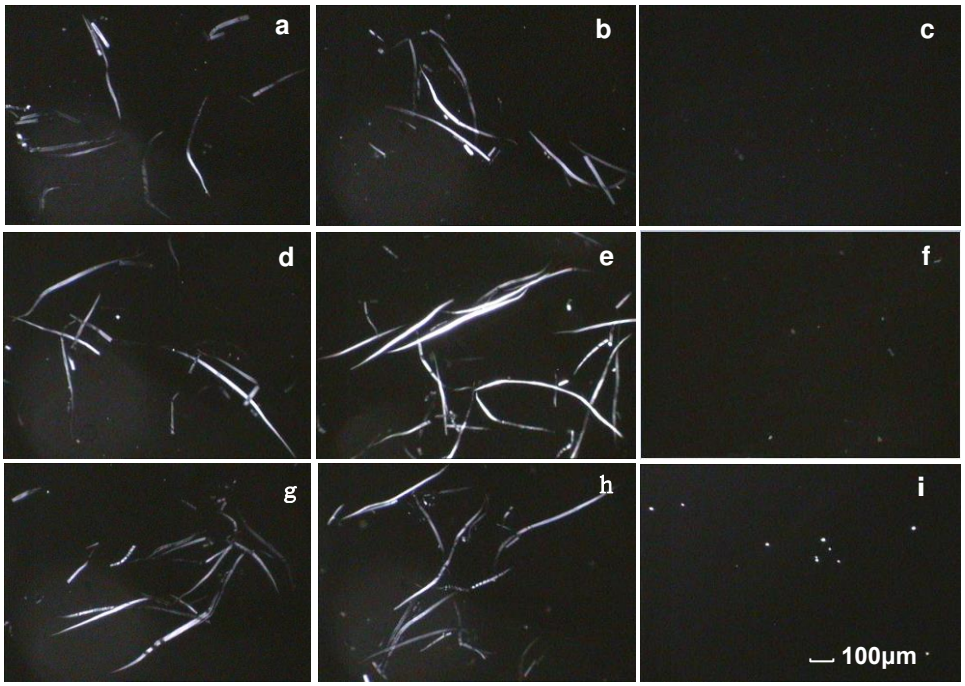

Fig.2 Polarized optical microscopy images of the HDP dissolved in the different NaOH/additives aqueous solutions using direct dissolution method,OD: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; using direct dissolution method,ND: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea and using freezing-thaw method,ND: (g) 7% NaOH/12% urea, (h) 9.5% NaOH/4.5% thiourea, and (i) 8% NaOH/8% urea/6.5% thiourea

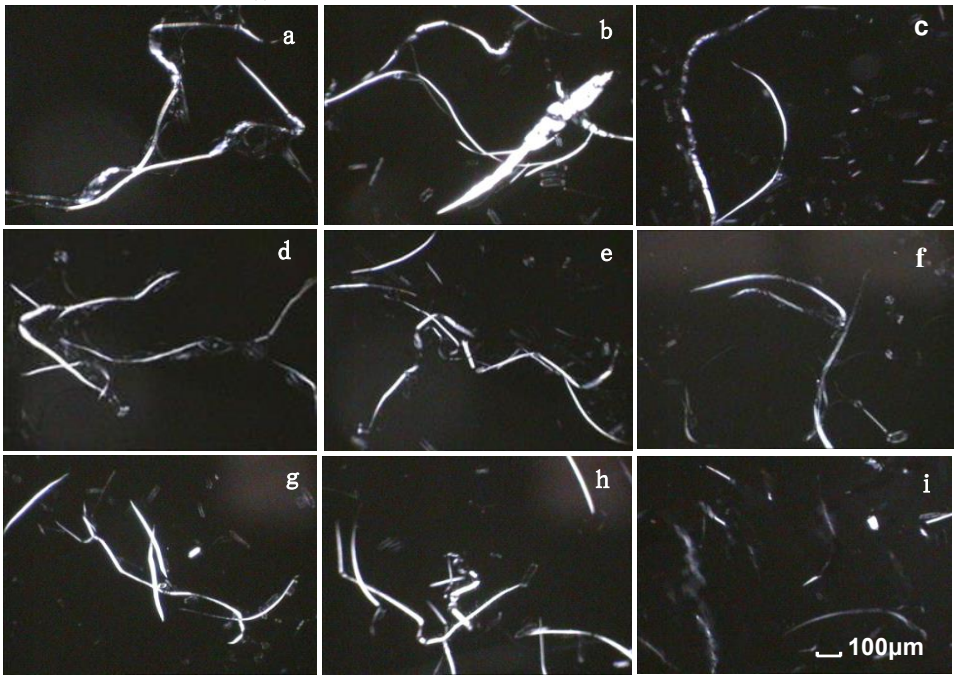

Fig.3 Polarized optical microscopy images of the BDP dissolved in the different NaOH/additives aqueous solutions using direct dissolution method,OD: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; using direct dissolution method,ND: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea and using freezing-thaw method,ND: (g) 7% NaOH/12% urea, (h) 9.5% NaOH/4.5% thiourea, and (i) 8% NaOH/8% urea/6.5% thiourea

Dissolving Capacity of the NaOH/additives Aqueous Solutions

As we know, using polarized optical microscopy to follow the dissolution might be inaccurate because not only crystalline cellulose but a lot of non-dissolved anisotropic cellulose parts can be seen in polarized light. Thus the dissolution degree of the three dissolving pulps was evaluated by recovering the insoluble fiber fractions. The dissolved proportions of all of the samples are shown in Table 3. The dissolved proportions of the samples in the 8% NaOH/8% urea/6.5% thiourea solution were all similar, regardless of which dissolving method was used. However, the dissolved proportions of the samples in the 7% NaOH/12% urea and 9.5% NaOH/4.5% thiourea solutions were higher when the freezing-thaw method was used, rather than the direct dissolution method. While there was a large difference in the solubility for these two systems, there was little difference in the solubility for the 8% NaOH/8% urea/6.5% thiourea solution between the two dissolving methods.

Table 3 Dissolved proportion of each dissolving pulp in the NaOH/additives aqueous solutions

Dissolved Proportion (%)		NaOH/additives Aqueous Solution		
		7%NaOH/12% urea	9.5%NaOH/4.5% thiourea	8%NaOH/8% urea/6.5% thiourea
SDP	Direct Dissolution,OD	47.3±0.4	44.4±0.5	79.8±0.4
	Direct Dissolution,ND	46.2±0.5	42.1±0.3	78.4±0.3
	Freezing-thaw,ND	52.1±0.5	50.5±0.4	80.0±0.3
HDP	Direct Dissolution,OD	44.2±0.4	41.7±0.4	73.2±0.3
	Direct Dissolution,ND	43.0±0.4	39.7±0.5	72.0±0.4
	Freezing-thaw,ND	43.8±0.3	40.1±0.3	72.2±0.4
BDP	Direct Dissolution,OD	43.4±0.2	40.2±0.3	59.4±0.2
	Direct Dissolution,ND	41.5±0.5	38.1±0.5	59.0±0.3
	Freezing-thaw,ND	45.9±0.2	44.2±0.3	61.4±0.4

Table 4 Viscosity of the cellulose solution from the dissolving pulp samples

[η] (ml/g, 25 °C)		NaOH/additives Aqueous Solution		
		7%NaOH/12% urea	9.5%NaOH/4.5% thiourea	8%NaOH/8% urea/6.5% thiourea
SDP	Direct Dissolution,OD	330.2±1.6	343.3±2.3	470.6±1.7
	Direct Dissolution,ND	310.0±2.2	319.1±2.8	440.5±2.7
	Freezing-thaw,ND	340.8±2.3	350.7±2.7	472.2±2.5
HDP	Direct Dissolution,OD	310.3±2.3	257.0±1.9	315.1±2.2
	Direct Dissolution,ND	300.2±0.5	230.8±2.7	299.7±2.0
	Freezing-thaw,ND	304.3±2.1	246.0±2.4	310.4±2.7
BDP	Direct Dissolution,OD	120.5±0.6	130.1±1.1	206.1±1.4
	Direct Dissolution,ND	120.0±1.6	126.9±2.0	180.2±2.2
	Freezing-thaw,ND	149.2±2.1	143.7±2.4	210.0±1.8

Table 4 shows that the 8% NaOH/8% urea/6.5% thiourea solution had a stronger dissolving capacity than the other two solvents for each dissolving pulp sample. The intrinsic viscosity of the cellulose solution from the 8% NaOH/8% urea/6.5% thiourea solution was not too high, which indicated that the cellulose fibers in that solution partially degraded. Measurements from the dissolved proportions and the cellulose viscosity supported the polarized optical microscopy

observations.

Dissolution of MCC in the NaOH/additives Aqueous Solutions

As a candidate of pure cellulose, the dissolution of MCC(DP＜350) in the above mentioned NaOH/additives aqueous solutions was also investigated. Doing this helped to further check the effect of cellulose DP on the dissolving method in the NaOH/additives aqueous solutions. The MCC was dried in an oven at 60 °C before being used to remove the remaining water. The cellulose sample used had a low DP to ensure a good solubility and avoid complications with non-cellulose components, such as hemicellulose and lignin [24].

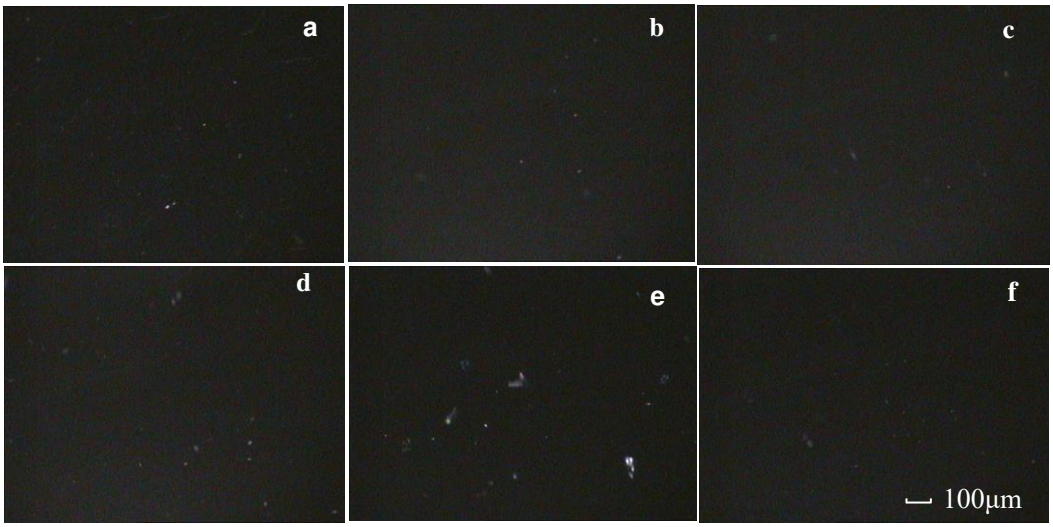

Fig.4 Polarized optical microscopy images of the OD MCC dissolved in the different NaOH/additives aqueous solutions with the direct dissolution method: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; and with the freezing-thaw method: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea

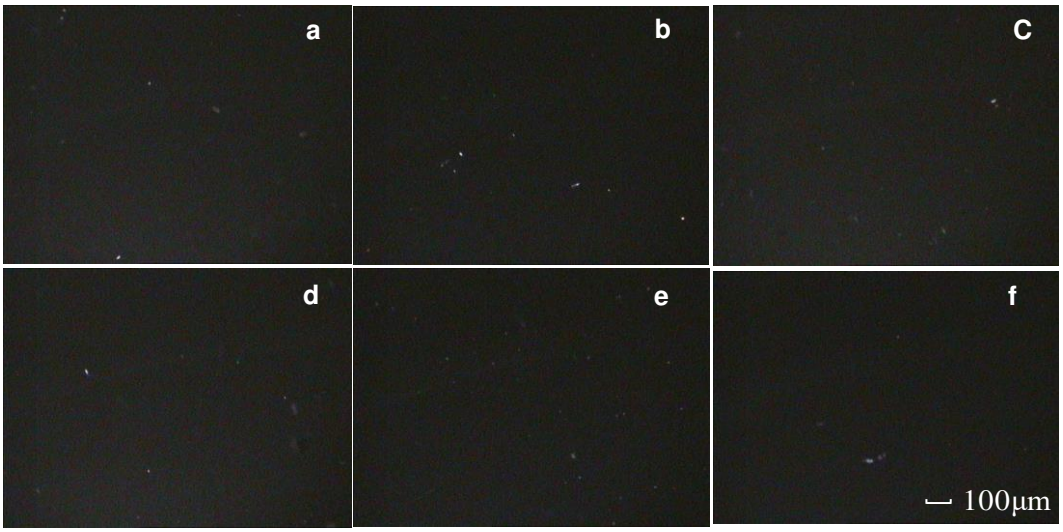

Fig.5 Polarized optical microscopy images of the ND MCC dissolved in the different NaOH/additives aqueous solutions with the direct dissolution method: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; and with the freezing-thaw method: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea

Fig.4 and Fig.5 illustrates the dissolving behavior of the MCC samples in different NaOH/additives aqueous solutions using the direct dissolution and freezing-thaw methods. OD

MCC yielded better dissolution using the direct dissolution method than using the freezing-thaw method. It seems that ND MCC yielded similar dissolution using two dissolution methods, which indicated that the direct dissolution method was best suited for cellulose with a lower DP. And there was no discernible difference in the effects of the two dissolution methods on the dissolution of MCC in the 8% NaOH/8% urea/6.5% thiourea solution.

Conclusions

The dissolving capacity of the NaOH/additives aqueous solutions was dependent on the origin of the pulp fibers, composition of the aqueous solution, and dissolving method. The softwood pulp had a better dissolution when it was prepared in the ND state rather than the OD state. Dryness had no remarkable effect on the hardwood pulp. The direct dissolution method was best suited for OD cellulose fibers with a low DP and the freezing-thaw method was best suited for ND cellulose fibers with a high DP. The dissolving method used had a big difference in the solubility for the 7% NaOH/12% urea and 9.5% NaOH/4.5% thiourea solutions. However, the dissolving method used had little difference in the solubility for the 8% NaOH/8% urea/6.5% thiourea solution. The 8% NaOH/8% urea/6.5% thiourea solution had the best dissolution capabilities for all of the pulp samples and both dissolving methods. The SDP was able to achieve an 80% dissolved proportion in the 8% NaOH/8% urea/6.5% thiourea solution.

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Author Contributions WK: Dissolution experiment, Investigation of polarized optical microscopy, Writing—Original Draft, Plotting. GY: testing of S_{10} value, S_{18} value, and intrinsic viscosity, Investigation. JX: fiber parameters of the three pulps. ML: Conceptualization, Resources, Writing—Review and Editing. YS: Conceptualization, Resources, Review and Editing, Project administration, Funding acquisition, Supervision.

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Data Availability Not applicable. Code Availability Not applicable.

Consent for Publication All authors consent for publication in Journal of Polymers and the Environment.

Compliance with Ethical Standards

Conflict of interest The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Ethical approval Not applicable.

Informed Consent Not applicable.

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Figures

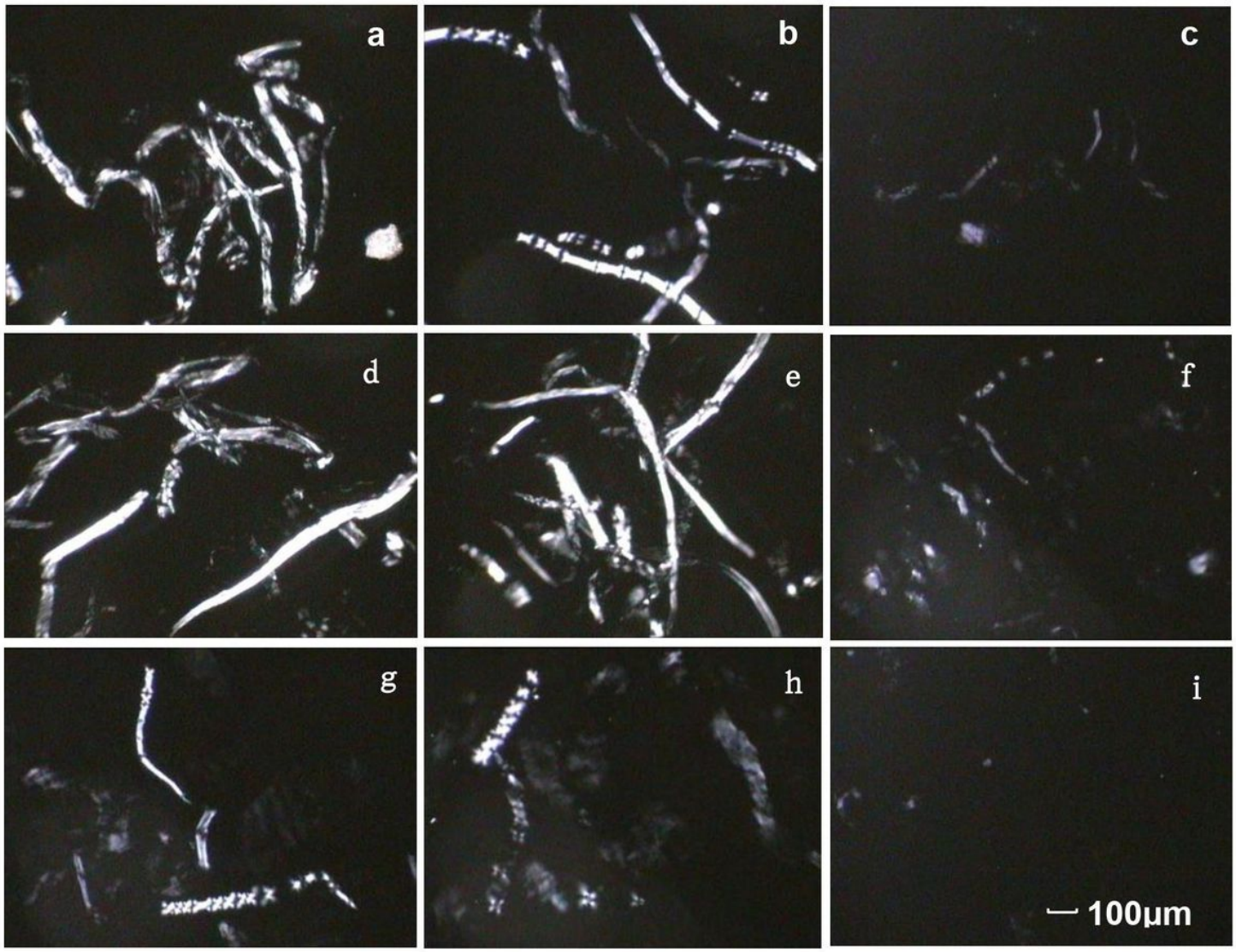

Figure 1

Polarized optical microscopy images of the SDP dissolved in the different NaOH/additives aqueous solutions using direct dissolution method,OD: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; using direct dissolution method,ND: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea and using freezing-thaw method,ND: (g) 7% NaOH/12% urea, (h) 9.5% NaOH/4.5% thiourea, and (i) 8% NaOH/8% urea/6.5% thiourea

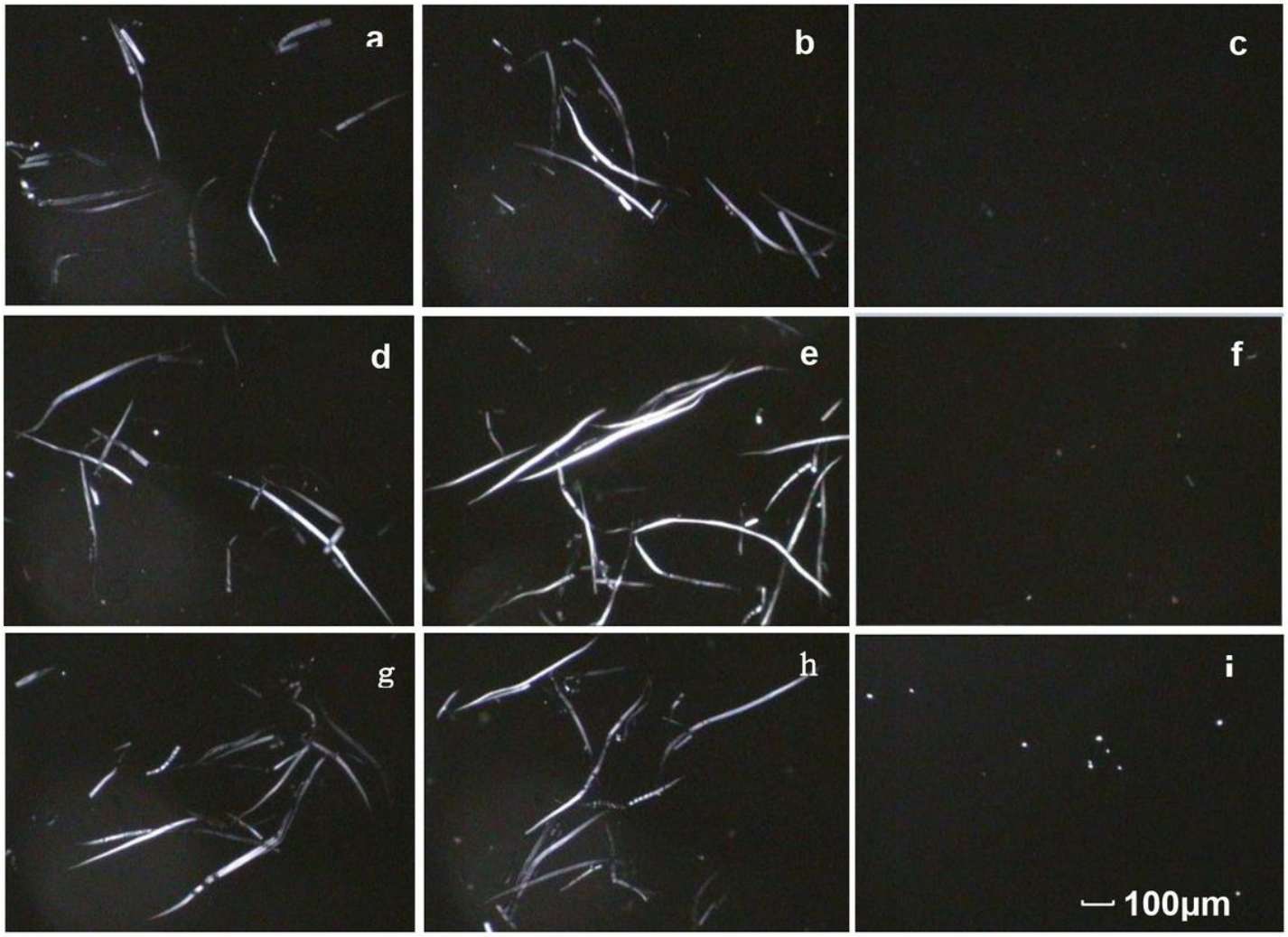

Figure 2

Polarized optical microscopy images of the HDP dissolved in the different NaOH/additives aqueous solutions using direct dissolution method,OD: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; using direct dissolution method,ND: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea and using freezing-thaw method,ND: (g) 7% NaOH/12% urea, (h) 9.5% NaOH/4.5% thiourea, and (i) 8% NaOH/8% urea/6.5% thiourea

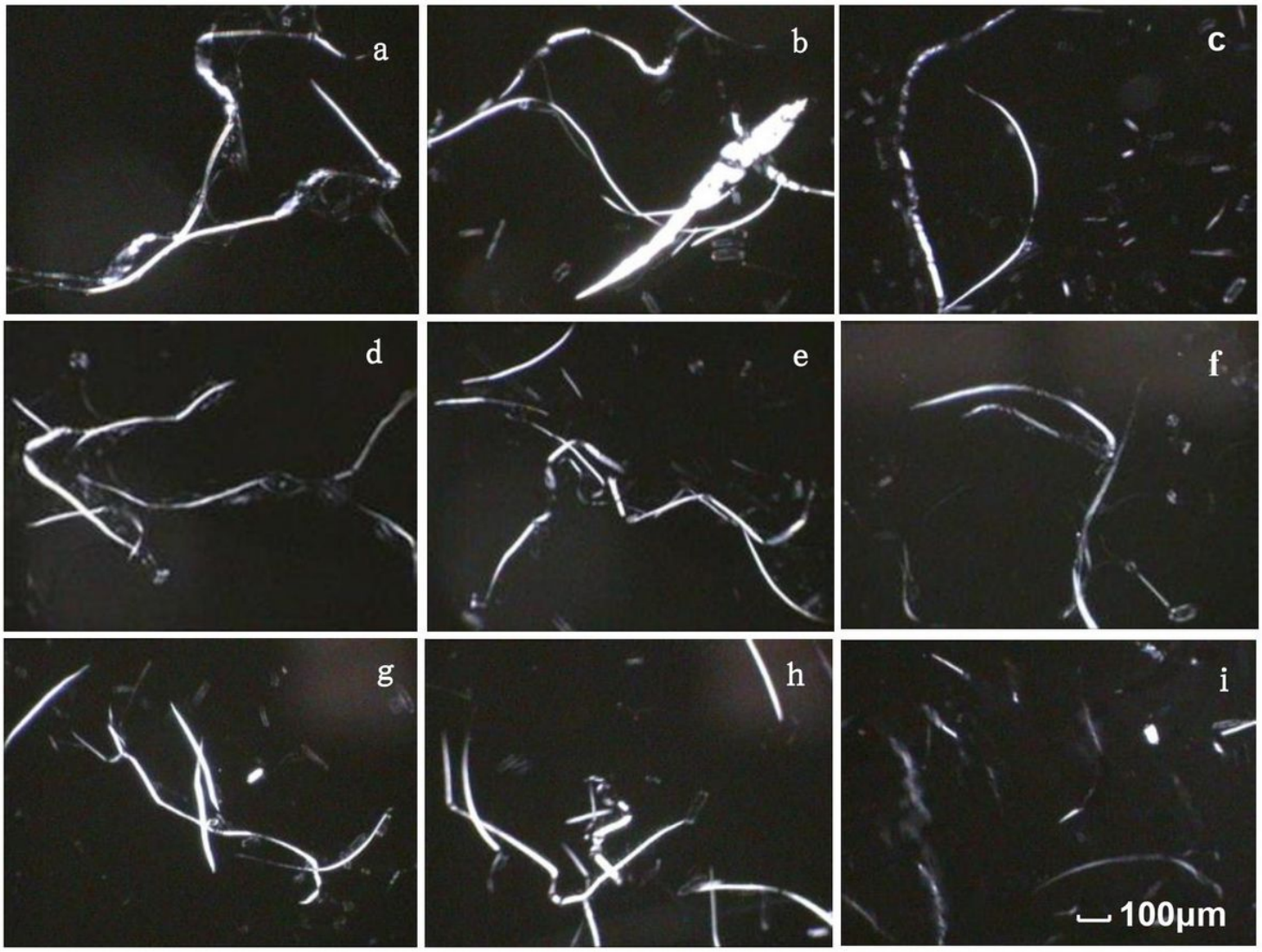

Figure 3

Polarized optical microscopy images of the BDP dissolved in the different NaOH/additives aqueous solutions using direct dissolution method,OD: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; using direct dissolution method,ND: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea and using freezing-thaw method,ND: (g) 7% NaOH/12% urea, (h) 9.5% NaOH/4.5% thiourea, and (i) 8% NaOH/8% urea/6.5% thiourea

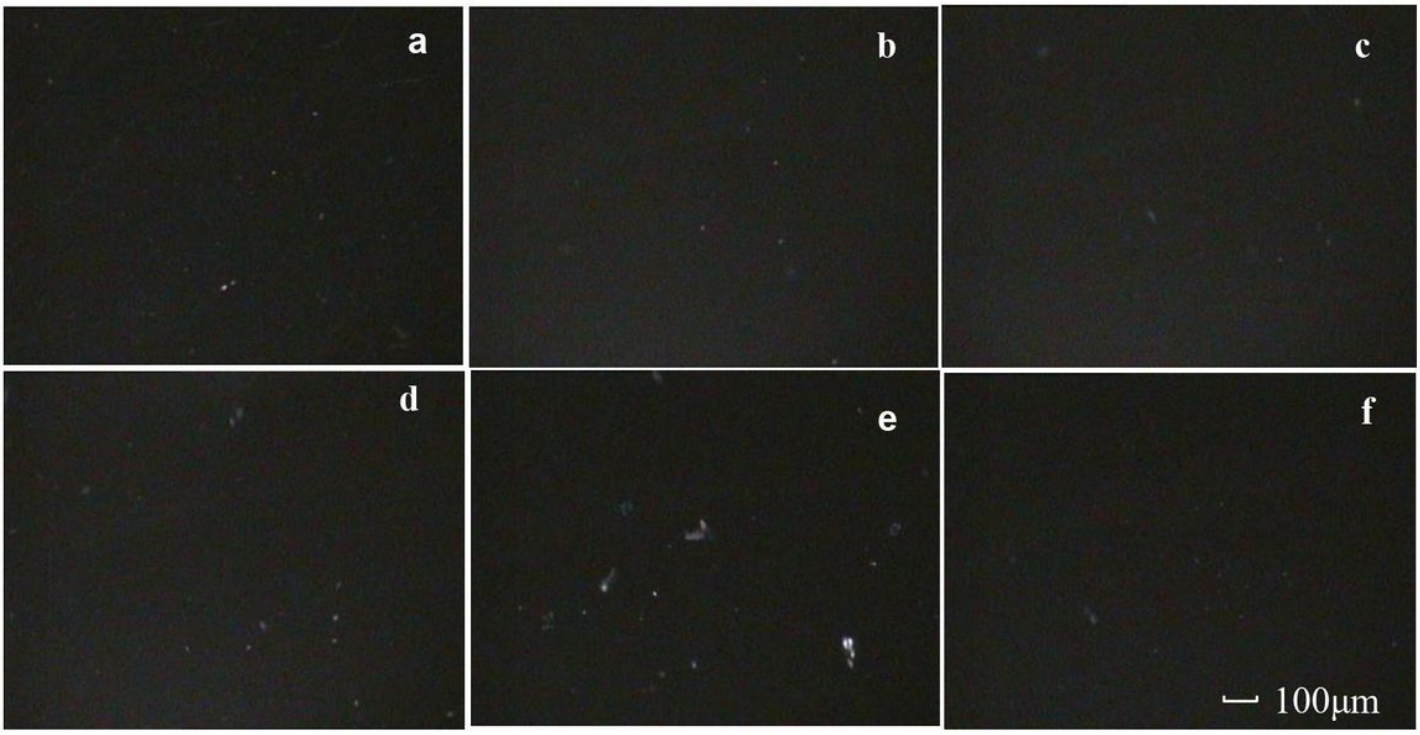

Figure 4

Polarized optical microscopy images of the OD MCC dissolved in the different NaOH/additives aqueous solutions with the direct dissolution method: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; and with the freezing-thaw method: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea

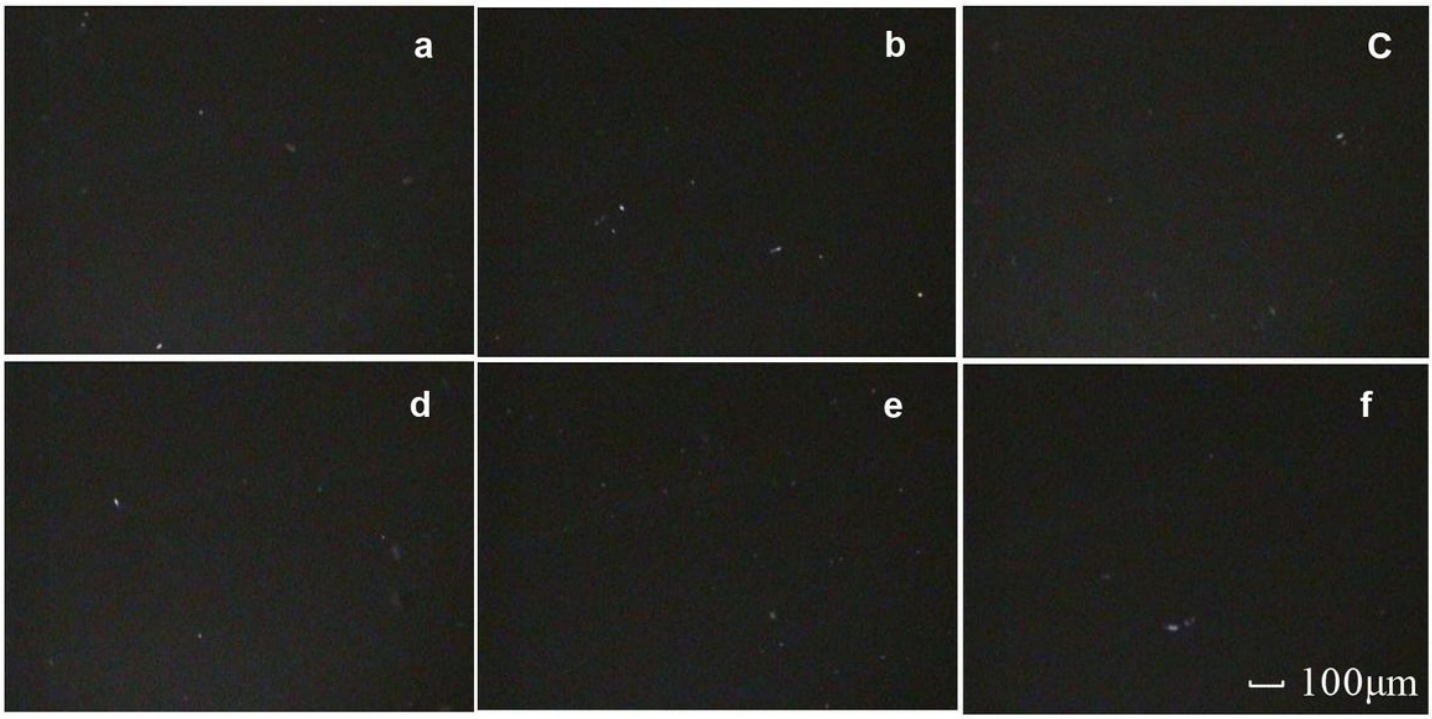

Figure 5

Polarized optical microscopy images of the ND MCC dissolved in the different NaOH/additives aqueous solutions with the direct dissolution method: (a) 7% NaOH/12% urea, (b) 9.5% NaOH/4.5% thiourea, and (c) 8% NaOH/8% urea/6.5% thiourea; and with the freezing-thaw method: (d) 7% NaOH/12% urea, (e) 9.5% NaOH/4.5% thiourea, and (f) 8% NaOH/8% urea/6.5% thiourea