

## Research Article

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# Effect of storage time and temperature on dissolved state of cellulose in TBAH-based solvents and mechanical property of regenerated films

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**Abstract:** Storage of cellulose solution can be practically ineluctable before it is manufactured into various regenerated products (e.g., fibers, films), especially in the case of industrial production. Therefore, it is necessary to evaluate the effect of storage time and temperature on the dissolved state of cellulose in the interested TBAH-based solvents (including TBAH/H<sub>2</sub>O, TBAH/H<sub>2</sub>O/DMSO, TBAH/H<sub>2</sub>O/Urea), as well as on the mechanical property of the relevant regenerated products (films were prepared in this work for the evaluation). The dissolved state of cellulose in these solvents along with storage has been analyzed with the polarized light microscope photographs and Stormer viscosity. Focus on the interested TBAH/H<sub>2</sub>O/DMSO solvent, the effect of storage time and temperature on the solution viscosity, and degree of polymerization of cellulose have been discussed. Critical storage time for different storing temperature has been determined, after where significant cellulose degradation happens. A series of regenerated cellulose films with storage time ranging from 0 to 200 h have been prepared. The optimal storage time and strengthening mechanism for cellulose films regenerated from the solution of cellulose/TBAH/H<sub>2</sub>O/DMSO have been discussed. This work can provide reference about storage time and temperature of cellulose/TBAH/H<sub>2</sub>O/DMSO, especially for the production of pilot-scale, etc.

**Keywords:** storage time and temperature, dissolved state, regenerated cellulose films, mechanical property

## 1 Introduction

Cellulose is one of the most abundant and widely distributed biomass materials in the world [1–5]. Its characteristics of biocompatibility [6,7], renewability [8], biodegradability [9,10], and abundant hydroxyl groups [11] urge scientific researchers to continue its development and utilization [12,13]. At present, the technical route of dissolution and regeneration can be the primary way of utilizing cellulose [14]. Regenerated cellulose materials are usually porous rather than compact [15,16]. On the one hand, some nanoscale pores are ascribed to the solvent exchange during the regeneration process than occupied part of space in the material [11,17–19]. On the other hand, some micron-sized pores are derived from the leaving bubbles in the cellulose solution [20]. These micron-scale voids can serve as defects of the material [21], affecting the mechanical property of regenerated cellulose materials (especially fibers). Therefore, to remove the numerous bubbles in the viscous cellulose solution, a very time-consuming defoaming process is usually necessary. And evaluating the effect of storage time and temperature on the dissolved state of cellulose in the solvent and mechanical property of relevant regenerated films can be an important issue.

About the dissolved state of cellulose, it can be regarded as an aggregate concept of cellulose solubility, rheological behavior of cellulose solution, and degradation of cellulose in this work. There are various methods applied for testing the solubility of cellulose. For example, the solubility of cellulose in NaOH/urea/thiourea solvent can be simply measured by weighting the centrifugal precipitate of cellulose solution [22]. UV-vis spectroscopy [23] or turbidimeter [24] can be used for identifying the

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turbidity of cellulose solution and solubility of cellulose. Besides,  $^{13}\text{C}$  NMR can be used for determining the solubility of cellulose [25]. Compared with the means mentioned above, polarized light microscopy (PLM) can be an easy and fast way of identifying the dissolution condition of cellulose without any complicated process of pretreatment or sample preparation [26]. The transformation from bright to dark in a PLM image of cellulose solution can indicate the dissolution of cellulose. Our previous research has proposed a quantitative analysis method of PLM image for evaluating the dissolution of cellulose in a way of easy, fast, and precise [27]. Here, this method will be utilized for characterizing the tiny difference of dissolution during the storage.

The rheological behavior of cellulose solution is important for confirming the related processing parameters. And ionic liquids (ILs) can be the typical solvent system due to their disadvantages of high viscosity. By decreasing the temperature, the viscosity and activation energy of ILs and their cellulose solution increased exponentially [28]. This brings difficulty for the rheological test since the state of dissolution and rheological property is changing along with temperature and time. Therefore, special precautions, such as nitrogen atmosphere, preheating, and silicone oil protection, are necessary for reducing the experimental errors. However, the instability issue of the dissolved cellulose during rheological testing can be solved by the simplified but effective *in situ* viscosity measurement [29]. Our previous work reported that cellulose/TBAH/ $\text{H}_2\text{O}$ /DMSO tetrabutylammonium hydroxide (TBAH) and dimethyl sulfoxide (DMSO) solution exhibits a similar issue of instability in the air [30]. Therefore, a Stormer viscometer was used for *in situ* viscosity measurement of cellulose solution during the storage in this work for monitoring the change in the dissolved state of cellulose.

Degradation of cellulose during the processing is another issue we are concerned about. Typical examples can be the solvents of ILs [31] or NMMO [32] where cellulose faces the risk of degradation at a high-temperature dissolution process. For TBAH/ $\text{H}_2\text{O}$  solvent, it is reported that cellulose does not degrade during the dissolution [33]. However, with the addition of DMSO, the emerged free radicals will attack the reducing AGU terminals and cause the partial degradation of cellulose [34]. Moreover, it is still unclear what will happen to cellulose during prolonged storage.

In this work, the effect of storage time on the dissolved state of cellulose in the TBAH-based solvents (including TBAH/ $\text{H}_2\text{O}$ , TBAH/ $\text{H}_2\text{O}$ /DMSO, TBAH/ $\text{H}_2\text{O}$ /Urea) has been investigated through characterization of polarized light microscope and Stormer viscometer. Then

the influence of storage time and temperature on the mechanical property of relevant regenerated cellulose films has been further studied for the interested TBAH/ $\text{H}_2\text{O}$ /DMSO solvent. It is expected to figure out whether there are the critical storage time and temperature after when significant changes in the structure and performance happen.

## 2 Experimental

### 2.1 Materials

The cotton pulp cellulose was provided by Bailu Chemical Fiber Group Ltd. (Xinxiang, China), with a DP of 479 and 95%  $\alpha$ -cellulose. The pulp has been smashed and dried in a vacuum oven ( $105^\circ\text{C}$ ) for 2 h before dissolution. The aqueous solution of TBAH (40 wt%) was provided by Runjing Chemical Co. Ltd. (Zhenjiang, China). The TBAH solution was concentrated through distillation under reduced pressure ( $-98\text{ kPa}$ ,  $55^\circ\text{C}$ ). The TBAH aqueous solution of desired concentration can be prepared by attenuation of its concentrated liquor with deionized (DI) water after calculating the content of TBAH by acidimetry. DMSO was supplied by Chengdu Kelong Chemical Reagent Co. (Chengdu, China).

### 2.2 Preparation of cellulose solution and films

Cotton pulp cellulose (17.5 g) was dissolved in a solvent of 232.5 g to form a cellulose solution with 7 wt% cellulose concentration; for TBAH/ $\text{H}_2\text{O}$  solvent, the weight ratio of TBAH: $\text{H}_2\text{O}$  = 1:1; for TBAH/ $\text{H}_2\text{O}$ /Urea solvent, the weight ratio of TBAH/ $\text{H}_2\text{O}$ /Urea = 1:1:0.1; for TBAH/ $\text{H}_2\text{O}$ /DMSO solvent, the weight ratio of TBAH: $\text{H}_2\text{O}$ :DMSO = 1:1:8. First, the mixture of cellulose and solvent was violently stirred using a planetary stirring machine (Marath MV300) at 800 rpm for 30 s, followed by the mechanical stirring at 50 rpm for 1 h under a water bath of  $40^\circ\text{C}$  for the dissolution of cellulose. Then the obtained cellulose solution was stored in an oven with a controlled temperature of 30, 35, 40, 45, and  $50^\circ\text{C}$  before observation and characterization. By using blade coating technology, a thin layer of cellulose solution (approx.  $400\ \mu\text{m}$ ) was coated on a glass plate, followed by aging in the air for 3 h and regeneration in DI water for 3 days. The water needs to be exchanged regularly during the regeneration process. The regenerated film was dried in an oven at  $50^\circ\text{C}$  for 12 h.

## 2.3 Characterization and measurements

For the characterization of cellulose solution, the sample in the center of the solution was extracted for eliminating the possible structural change of the surface layer during the storage. Dissolution of cellulose (cellulose solution) has been characterized by PLM (Leica DM 2700P). To keep PLM images of different samples comparable, the conditions for imaging (including the hardware configuration of the microscope and 970 ms exposure time) had been maintained. Up to five parallel images of each sample had been captured for error analysis.

Stormer viscometer (STM-III, Yonglida, Tianjin, China) was used for measuring the viscosity of cellulose solution. The appropriate amount of cellulose solution was placed in a beaker for keeping the distance of liquid level from the top of the beaker to be about 19 mm. Then the rotor was immersed into the solution so that the liquid level is aligned with the mark on the rotor. Proper weights were loaded to make the rotor rotating at 200 rpm. Then the Stormer viscosity (KU value) was read from the display of the equipment according to the total load (including the weight of the support 30 g).

Ubbelohde viscometer was used to measure the characteristic viscosity of cellulose in TBAH/H<sub>2</sub>O/DMSO (1:1:8) solvent according to our previously proposed Mark–Houwink equation (1) for this solvent [35]. Then the degree of polymerization (DP) of cellulose under different temperatures and storage time for this solvent can be calculated.

$$[\eta] = k \times DP^\alpha = 0.24 \times DP^{1.21} \quad (1)$$

In the formula,  $[\eta]$  represents the characteristic viscosity of cellulose in TBAH/H<sub>2</sub>O/DMSO (1:1:8) solvent; DP represents the degree of polymerization of the cellulose;  $k$  and  $\alpha$  are characteristic parameters for this solvent at 25°C.

The mechanical performance (tensile strength, Young's modulus, elongation at break, and rupture work) of the dried regenerated cellulose films was measured on a tensile machine (XS08XT-3, Xusai, Shanghai, China) at room temperature (25°C, 55% RH). Cellulose films were cut into specimens of 6.5 × 0.5 cm for testing. The testing sample was stretched at a speed of 2 mm/min. Five parallel tests had been carried out to receive the average value of mechanical properties.

Scanning electron microscope (SEM, FEI QUANTA 250, USA) was used to observe the morphology of the stretched section of the regenerated cellulose film with an acceleration voltage of 15 kV. The chemical structure of cellulose was characterized by fourier transform infrared spectroscopy (FT-IR, Bruker Tensor II, Germany) with

attenuated total reflectance (ATR) accessory. The spectrum within the range of 4,000–400 cm<sup>-1</sup> was collected with a spectral resolution of 4 cm<sup>-1</sup>. X-ray diffractometer (XRD, Empyrean, PANalytical B.V., Netherlands) was used to characterize the structure of cellulose materials with a copper target, a working voltage of 60.0 kV, a current of 100.0 mA, and a scan range of 5–50°.

## 3 Results and analysis

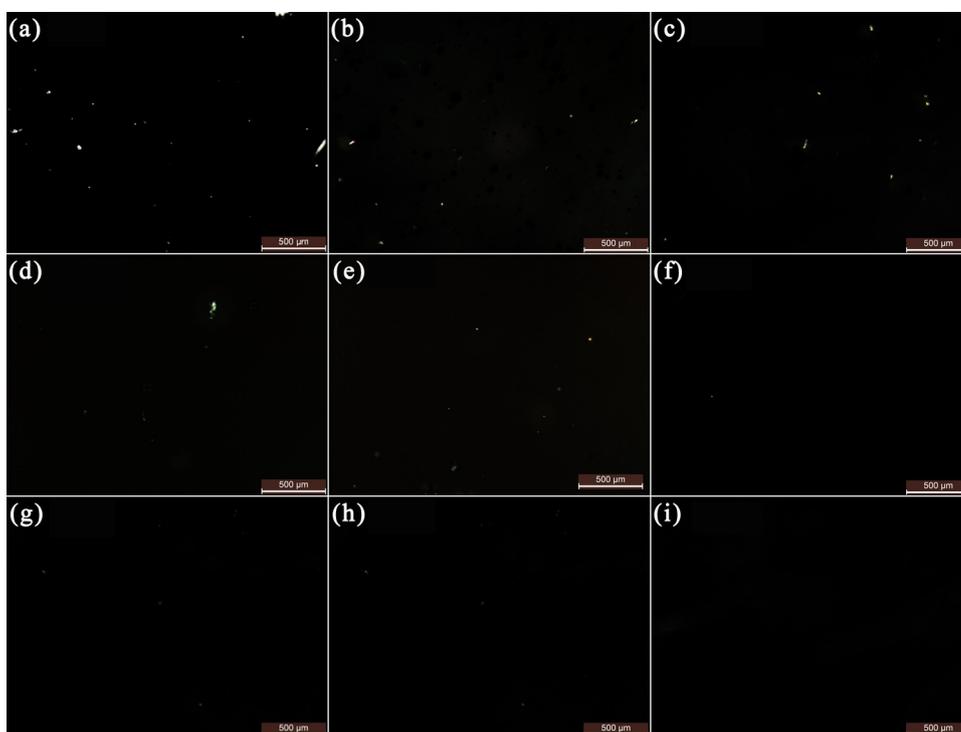
### 3.1 Study on the properties of cellulose solution stored for days

Observation of cellulose solution by polarizing microscope is the very basic and simple method of characterizing the dissolution state of cellulose. The undissolved cellulose retains a crystalline structure, by which the direction of polarized light can be changed by the cellulose crystals, resulting in bright areas in a polarizing microscope. Therefore, people can intuitively judge the dissolution state of cellulose by a polarized light microscope image of cellulose solution. After a dissolution at 50 rpm for 1 h under 40°C water bath, the cellulose solution dissolved in TBAH/H<sub>2</sub>O, TBAH/H<sub>2</sub>O/DMSO, and TBAH/H<sub>2</sub>O/Urea solvents had been stored for different time (0–120 h) and sampled for PLM characterization, as shown in Figures 1–3, respectively. It can be found that there are still a few bright spots in the PLM photos of the cellulose solution stored between 0 and 36 h, indicating that there is still a small amount of cellulose that is not well-dissolved. When the dissolution time is extended to 48–120 h, there is almost no change in the black PLM photos. At this time, the perceptual cognition of the polarized photo of cellulose solution cannot effectively distinguish the tiny difference and describe the trend of dissolution state of cellulose in the solution along with storage time. Therefore, it is necessary to carry out quantitative processing on the polarized photo, which is beneficial to quantitatively analyze and discuss the status and trends of the cellulose dissolved in the solution during the storage progress.

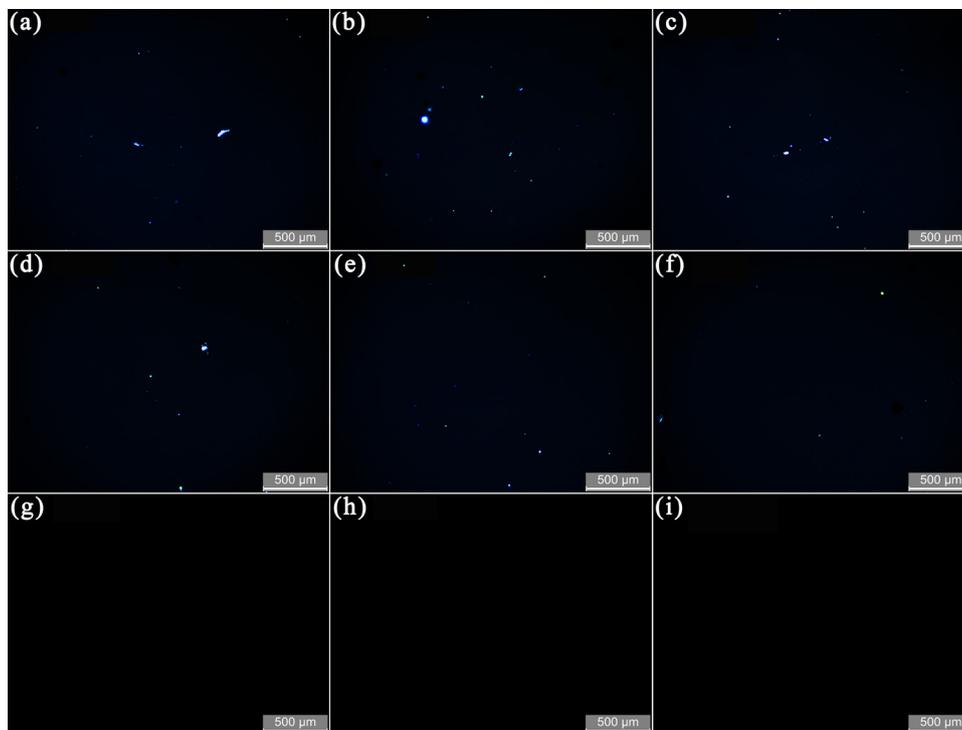
According to the correlation between the bright area and the dissolution state of the cellulose, we previously proposed a method named “Pixel reduced average brightness” (PRAB) for quantitative analysis of PLM images, which helps us better understand the differences in the dissolution of cellulose in the three TBAH-based solvents. Before calculation, the PLM image needs



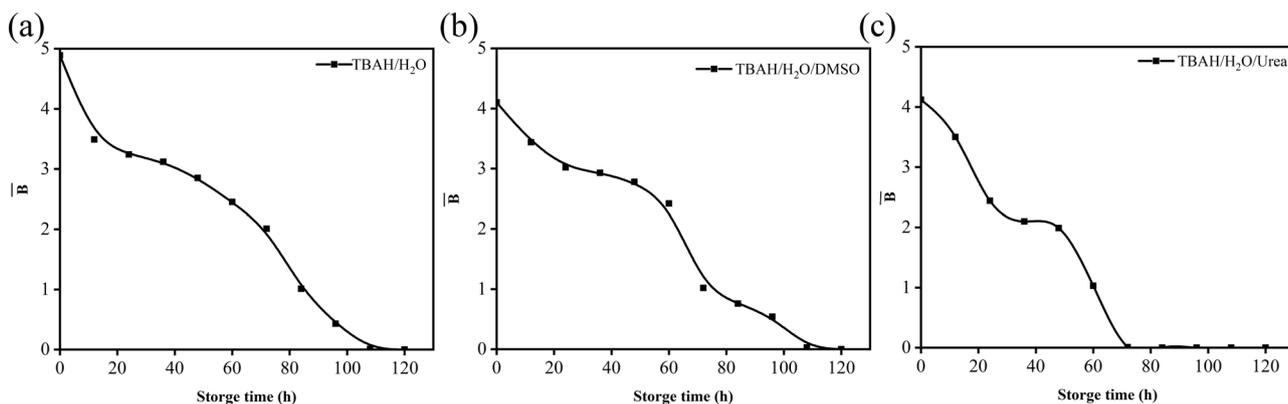
**Figure 1:** PLM photos of cellulose solution dissolved in TBAH/H<sub>2</sub>O solvent at different storage times at 40°C. (a) 0 h; (b) 12 h; (c) 24 h; (d) 36 h; (e) 48 h; (f) 60 h; (g) 72 h; (h) 90 h; (i) 120 h.



**Figure 2:** PLM photos of cellulose solution dissolved in TBAH/H<sub>2</sub>O/DMSO solvent at different storage times at 40°C. (a) 0 h; (b) 12 h; (c) 24 h; (d) 36 h; (e) 48 h; (f) 60 h; (g) 72 h; (h) 90 h; (i) 120 h.



**Figure 3:** PLM images of cellulose solution dissolved in TBAH/H<sub>2</sub>O/Urea solvent at different storage times at 40°C. (a) 0 h; (b) 12 h; (c) 24 h; (d) 36 h; (e) 48 h; (f) 60 h; (g) 72 h; (h) 90 h; (i) 120 h.



**Figure 4:** The trends of the pixel reduced average brightness of cellulose solutions dissolved in the solvents of (a) TBAH/H<sub>2</sub>O, (b) TBAH/H<sub>2</sub>O/DMSO, and (c) TBAH/H<sub>2</sub>O/Urea versus the storage time stored at 40°C.

to be converted into a gray mode to eliminate color influence. The calculation method of PRAB value is shown in equation (2) [27]:

$$\bar{B} = \frac{1}{2^n - 1} \sum_{i=1}^m \frac{g(i)}{m} \quad (2)$$

where  $n$  is the number of bits describing the gray value of the image pixel (assumed to be 8),  $m$  is the number of pixels in the image, and  $g(i)$  is the gray value of pixel  $i$  in the image (ranged from 0 to 255 for an 8-bit grey image).

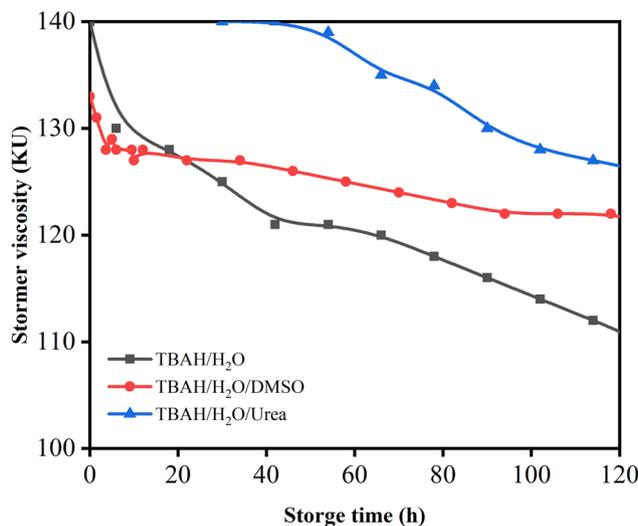
The two extreme situations of the PLM picture need to be discussed in advance to make it easier to understand. If a PLM image with a pure white picture is obtained,  $\bar{B} = 1$  can be obtained through the calculation of the PRAB, which indicates that the PRAB of the PLM image is 100% white. Similarly, for a black PLM image,  $\bar{B} = 0$  can be obtained, which means that the PRAB of the PLM image is 0% white (that is black). For a PLM image of a cellulose solution, its  $\bar{B}$  value should be in the range of 0–1 and is related to the dissolution of cellulose. For each

cellulose solution sample, five parallel PLM images had been collected for error analysis of the dissolution state.

The plots of PRAB values of cellulose solution dissolved in the TBAH/H<sub>2</sub>O, TBAH/H<sub>2</sub>O/DMSO, and TBAH/H<sub>2</sub>O/Urea solvents versus storage time after the dissolution are shown in Figure 4(a)–(c). The PRAB values ( $\bar{B}$ ) of these cellulose solutions all experienced a notable decrease in the initial period of standing (0–24 h), which indicates that 7 wt% cotton pulp cellulose had not been completely dissolved after 60 min of stirring. The undissolved micron-sized cellulose exhibits a slow dissolution in the process of storage for 0–24 h. For the period of 24 to 48 h, the dissolution seems to come to a standstill. The undissolved cellulose began to dissolve at an accelerated rate when the storage time was extended to 48 h. Cellulose is almost fully dissolved from the judgment of PLM characterization (a full black image) when the storage time reaches 120 h.

From the perspective of the dissolving ability (dissolution rate) of the three solvent systems on cellulose during the storing process, the TBAH/H<sub>2</sub>O/Urea system (Figure 4c) completely dissolves cellulose after 72 h of storage, followed by the TBAH/H<sub>2</sub>O/DMSO (Figure 4b) and TBAH/H<sub>2</sub>O (Figure 4a) solvents. Our preliminary research indicates that urea can be served as a hydrophobicity contributor and an amphiphilic modifier of the solvent. When the amphiphilicity property of the solvent matches with that of the cellulose crystal surface, the cellulose can be effectively infiltrated and subsequently dissolved by the solvent.

A Stormer viscometer was used to test the solution viscosity of the cellulose solutions prepared by the three solvent systems at different storage times, as shown in Figure 5. It should be noted that the viscosity of the cellulose solution prepared by TBAH/H<sub>2</sub>O/Urea solvent exceeds the measurement range of the Stormer viscometer used at the initial stage (0–30 h), so the relevant data are missing. The viscosity of the cellulose solutions of the three solvent systems gradually decreases along with increasing the storage time. Kosan et al. studied the cellulose solution viscosity (reflected by the torque of the stirring rod) with the dissolution time during the dissolution of cellulose in NMMO and BmimCl and found that the viscosity of the system will decrease after dissolving [36]. The decrease of the viscosity may be ascribed to the dynamic aggregation of cellulose after the disappearance of the shear field from stirring. There should be a similar situation in the cellulose solutions of the three solvent systems in this study, resulting in a gradual



**Figure 5:** The plot of viscosity of the cellulose solution in the solvents of TBAH/H<sub>2</sub>O, TBAH/H<sub>2</sub>O/DMSO, and TBAH/H<sub>2</sub>O/Urea versus the storage time stored at 40°C.

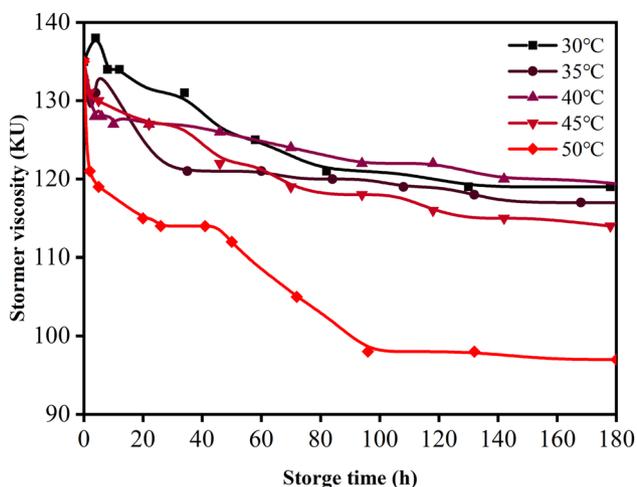
decrease in solution viscosity with the prolonged storage time. However, the analysis of the polarized images of the cellulose solution also shows that the undissolved micron-sized cellulose is gradually dissolving during the storing process, which should lead to an increase in the viscosity of the solution. Therefore, for the cellulose solution prepared with these three solvents, the change of the viscosity may be attributed to the synergistic effect of subsequent dissolution and dynamic aggregation of cellulose during the storing process.

Despite the decreasing trends of viscosity for these solutions, the cellulose solution prepared by TBAH/H<sub>2</sub>O/Urea exhibits the highest viscosity, followed by TBAH/H<sub>2</sub>O/DMSO and TBAH/H<sub>2</sub>O. The viscosity of the cellulose solution can also indicate that cellulose in TBAH/H<sub>2</sub>O/Urea is well-dissolved, followed by TBAH/H<sub>2</sub>O/DMSO and TBAH/H<sub>2</sub>O. This is consistent with the above conclusion based on PLM image analysis that TBAH/H<sub>2</sub>O/Urea exhibits a stronger ability to dissolve cellulose during storage. The stability of the cellulose solution can also be reflected by the evolution of the solution viscosity. The cellulose solution of TBAH/H<sub>2</sub>O/DMSO and TBAH/H<sub>2</sub>O showed a significant decrease in the viscosity within 10 h, which indicates that the cellulose molecules are more unstable in these two solvents and tend to self-assemble into agglomerates after dissolution. We previously reported that the cellulose solution of TBAH/H<sub>2</sub>O/DMSO is easily gelled at room temperature in the air (reach the gel point in about 2,000 s).

### 3.2 Effect of storage temperature on the properties of cellulose solution prepared with TBAH/H<sub>2</sub>O/DMSO solvent

TBAH/H<sub>2</sub>O/DMSO solvent exhibits an outstanding feature of fast dissolution [30]. It is noticed that this feature may be supported by the mechanism that the reducing end of cellulose might be attacked and destroyed by the generated free radicals in this solvent [36]. We wondered if there are side reactions (e.g., degradation of cellulose) in this solvent, especially when the temperature rises. Therefore, cellulose solution of TBAH/H<sub>2</sub>O/DMSO was allowed to be stored at different temperatures, and the viscosity of the cellulose solution was tested using a Stormer viscometer, as shown in Figure 6. There is no big difference in the viscosity of cellulose solution stored at 30–45°C. However, a storage temperature of 50°C seems to be a critical temperature at which the viscosity of the solution decreases significantly (especially when it is left for 0–10 h and 40–100 h intervals). This significant decrease in solution viscosity and the law of nonlinear changes might be derived from the influence of DP of cellulose rather than the temperature-dependent viscosity of the solution.

Usually, DP can be measured through ways of intrinsic viscosity [37] or chromatography (GPC) [38]. The former method is widely used. However, sampling and testing could be kind of tedious with the classical solvent of copper(II) ethylenediamine (CED) [39], since cellulose needs to be regenerated and collected before a test. Our previous work has established the Mark–Houwink equation



**Figure 6:** The plot of viscosity of the cellulose solution in the TBAH/H<sub>2</sub>O/DMSO solvent versus the storage time stored at different temperatures.

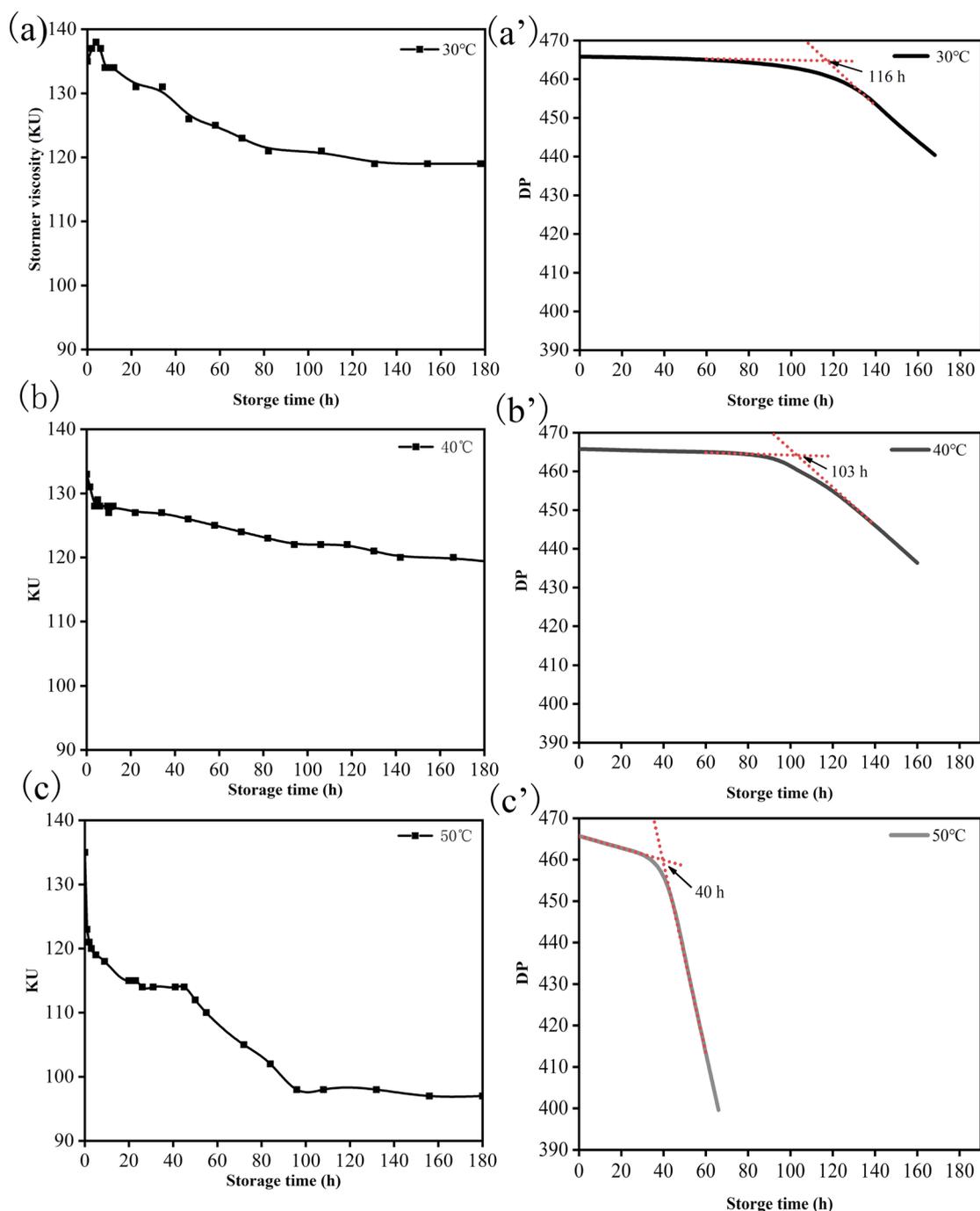
for the dissolution of cellulose in TBAH/H<sub>2</sub>O/DMSO [35]. Therefore, it is easy to measure the intrinsic viscosity and molecular weight of cellulose in cellulose/TBAH/H<sub>2</sub>O/DMSO solution by direct attenuation with this solvent and testing with Ubbelohde viscometer. The DP of cellulose in the solution of storing at 30, 40, and 50°C, as well as the extract plots of viscosity of cellulose solution, versus the storage time, had been plotted, as shown in Figure 7(a')–(c') and (a)–(c).

Judging from the curve of DP, all three conditions exhibit a similar degradation mode. There is a gentle period in the initial stage of storage, during which the DP of cellulose was well-maintained. With the extension of the storage time, the DP of cellulose at different temperatures began to decrease significantly at different times. Tangent lines were drawn at the straight region for identifying the accurate critical time where the degradation of cellulose accelerated. The intersection of two tangent lines was defined as the critical time for accelerated degradation. The results showed that cellulose starts to accelerate the degradation at 116, 103, and 40 h for storing at 30, 40, and 50°C, respectively. Storing at 50°C could significantly accelerate the depolymerization (from more than 100 h to 40 h), causing serious degradation of cellulose (from 5–6% to about 14% loss). Therefore, for the cellulose solution of TBAH/H<sub>2</sub>O/DMSO, the temperature of the solution must be controlled during the process of filtration, vacuum deaeration, transportation, etc., to prevent the degradation of cellulose. A temperature of 40°C can be regarded as a safe temperature.

### 3.3 Effect of storage time on the mechanical properties of regenerated cellulose films prepared with TBAH/H<sub>2</sub>O/DMSO solvent

By the study above, it is concluded that the DP and dissolution state of cellulose, as well as the viscosity of cellulose solution, can be significantly affected by the storage time and temperature. It is wondered whether the storing process may influence the mechanical properties of relevant regenerated cellulose films. Therefore, the effect of the storage time of cellulose solution on the mechanical properties of regenerated cellulose films prepared with TBAH/H<sub>2</sub>O/DMSO solvent had been studied in this section. Cellulose solution was stored at a safe temperature (40°C), as mentioned above.

The plots and table of mechanical property (including strength, elongation at break, Young's modulus, and

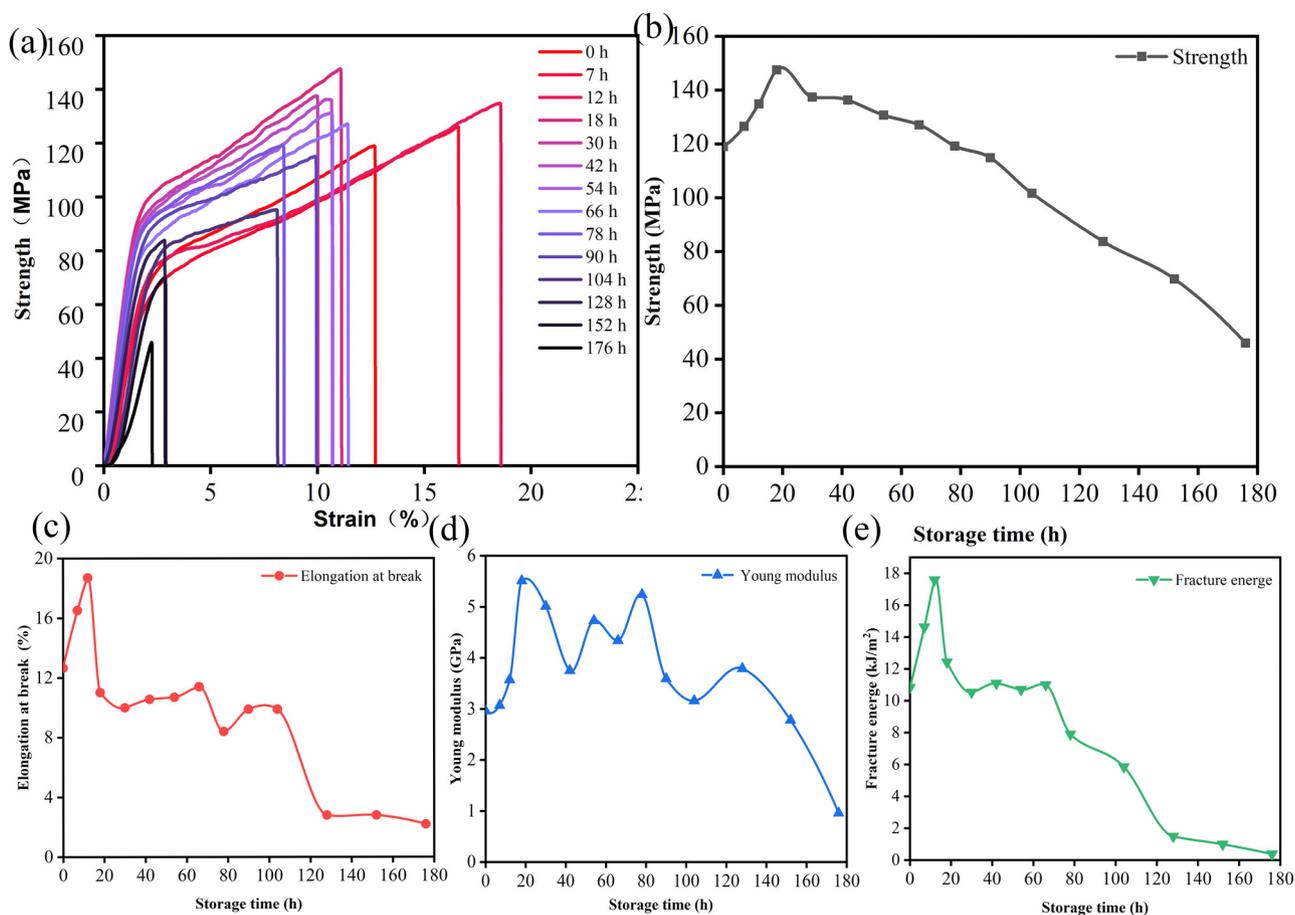


**Figure 7:** Comparisons of the Stormer viscosity of cellulose solution (a–c) and DP of cellulose (a'–c') in the TBAH/H<sub>2</sub>O/DMSO solvent system at different temperatures. (a and a') 30°C; (b and b') 40°C; (c and c') 50°C.

fracture energy) of regenerated cellulose films versus storage time of cellulose solution are shown in Figure 8 and Table 1. Accordingly, these figures can be mainly divided into three stages:

- (1) With storing of 0–18 h, all mechanical properties are generally enhanced. For example, strength can be enhanced from 119.25 to 147.53 MPa (growth of 23.7%)

and elongation at break can be improved from 12.66 to 18.70% (growth of 47.7%). These enhancements can be attributed to the subsequent dissolution of cellulose during the storing process of cellulose solution, as indicated by the PLM characterization of cellulose solution (Figure 2 and Figure 4b). Otherwise, the undissolved cellulose may serve as impurity particles in the



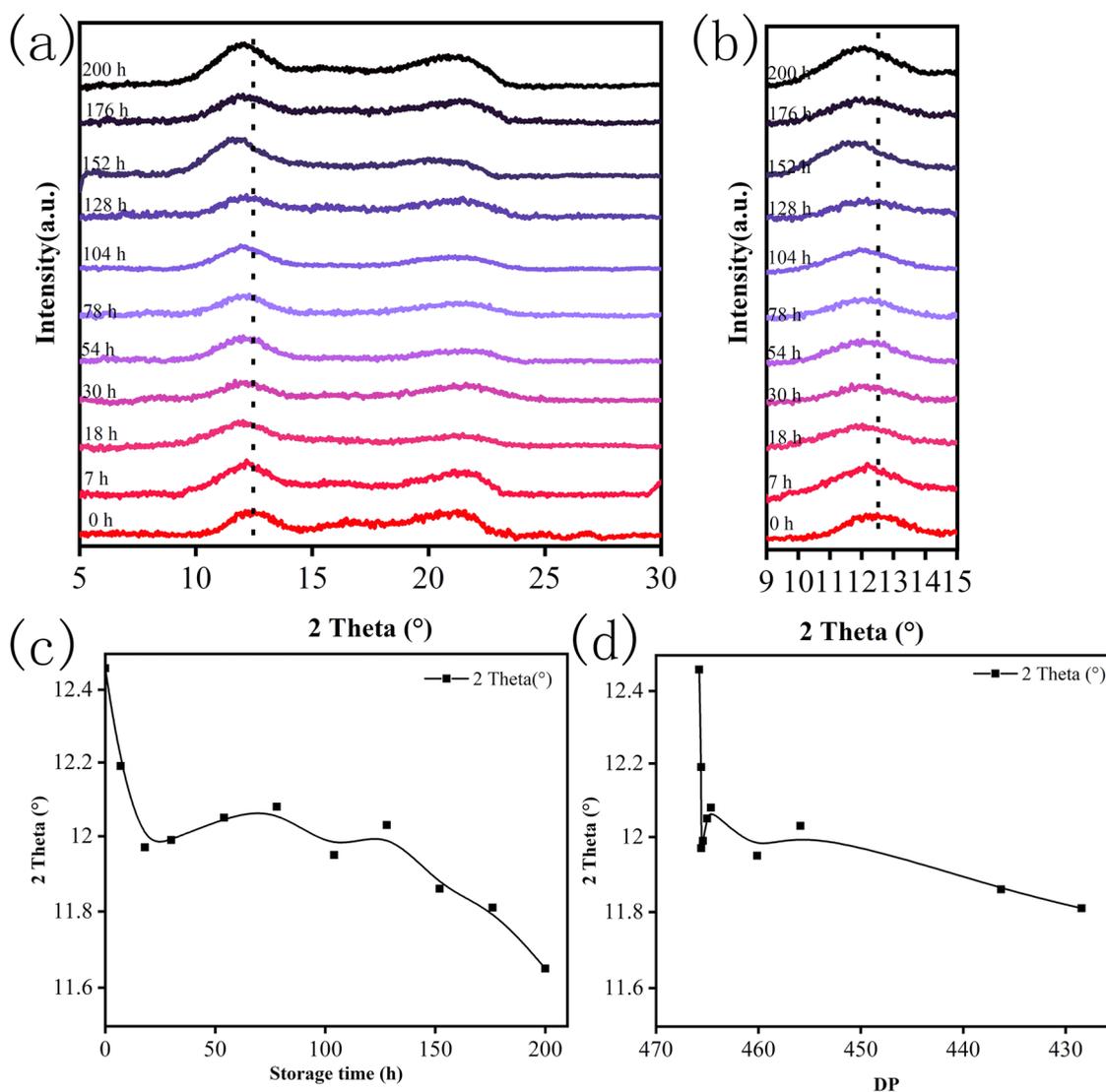
**Figure 8:** Mechanical properties of regenerated cellulose film with different storage times. (a) Stress–strain curve; (b) tensile strength versus storage time; (c) elongation at break versus storage time; (d) Young’s modulus versus storage time; (e) fracture work versus storage time.

**Table 1:** Mechanical properties of regenerated cellulose films with different storage times

Storage times (h)	Strength (MPa)	Elongation at break (%)	Young modulus (GPa)	Fracture energy (kJ/m <sup>2</sup> )
0	119.25 ± 9.25	12.66 ± 0.10	2.96 ± 0.41	10.84 ± 0.01
7	126.50 ± 9.50	16.52 ± 3.09	3.07 ± 0.69	14.63 ± 0.29
12	134.87 ± 8.79	18.70 ± 4.02	3.57 ± 0.71	17.59 ± 0.35
18	147.53 ± 9.50	11.02 ± 2.12	5.01 ± 0.55	12.43 ± 0.20
30	137.41 ± 1.15	10.00 ± 2.44	5.51 ± 0.89	10.53 ± 0.03
42	136.26 ± 7.15	10.56 ± 1.88	3.75 ± 0.19	11.09 ± 0.13
54	130.70 ± 8.51	10.70 ± 2.22	4.73 ± 0.43	10.71 ± 0.19
66	127.10 ± 6.00	11.40 ± 0.56	4.34 ± 0.61	11.00 ± 0.03
78	119.20 ± 7.90	8.40 ± 2.81	5.24 ± 0.32	7.90 ± 0.22
90	114.80 ± 5.30	9.90 ± 0.50	3.59 ± 0.47	13.31 ± 0.03
104	101.60 ± 4.08	9.90 ± 4.77	3.16 ± 0.11	5.86 ± 0.19
128	83.70 ± 2.17	2.80 ± 0.30	3.79 ± 0.75	1.49 ± 0.01
152	69.78 ± 1.19	2.80 ± 0.12	2.78 ± 0.30	1.00 ± 0.00
176	45.90 ± 1.21	2.20 ± 0.16	0.96 ± 0.25	0.38 ± 0.00

regenerated cellulose film, affecting the mechanical properties, and generate big pressure on the filtration system.

(2) With storing for 18–104 h, there is a notably continuous decrease (31% drop) in the strength (from 147.53 to 101.60 MPa). This might be ascribed to the dynamic



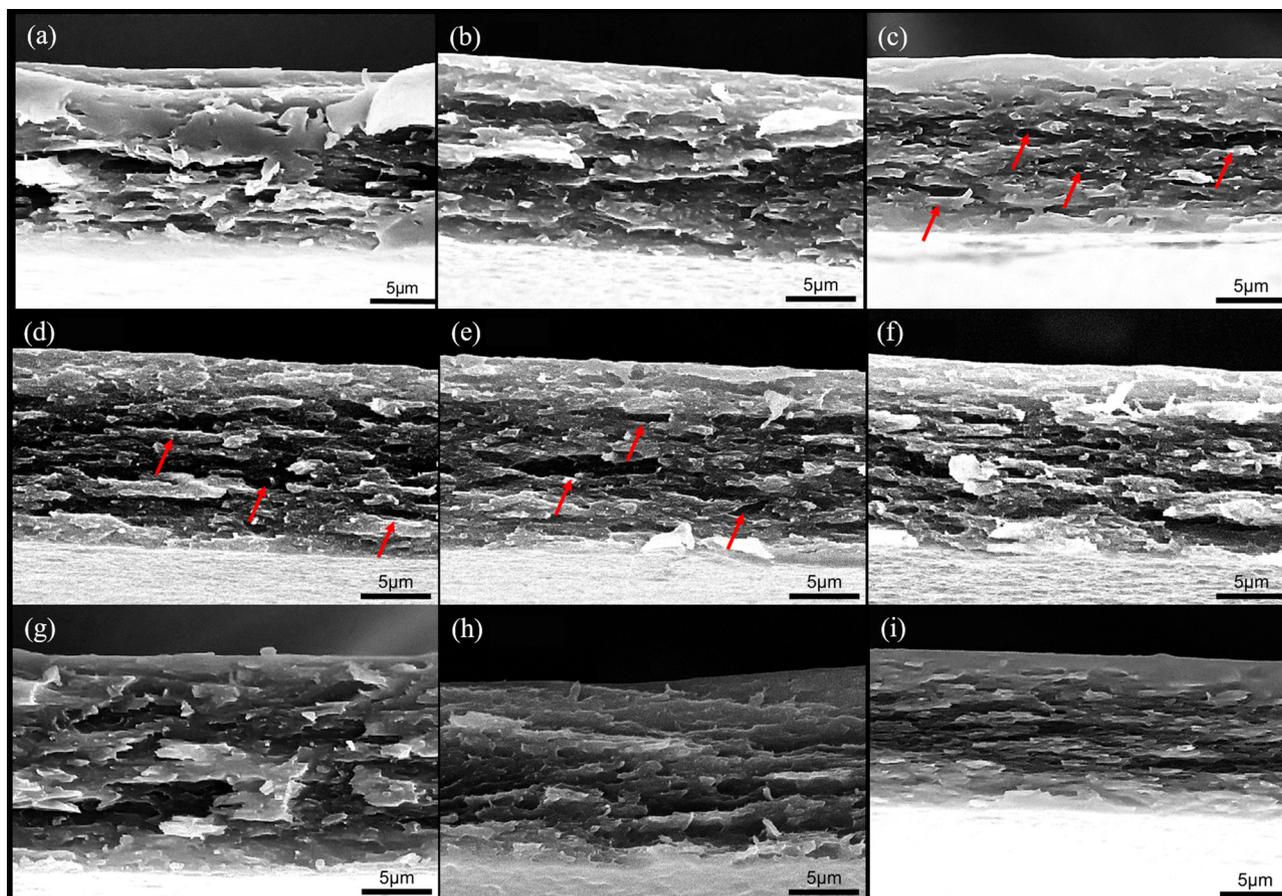
**Figure 9:** Regenerated cellulose films of cellulose solution dissolved in a TBAH/H<sub>2</sub>O/DMSO solvent system at a constant temperature of 40°C for different times; (a) XRD patterns of regenerated cellulose films; (b) zoomed in 9–15°; (c) shift of (110) peak versus storage time; (d) shift of (110) peak versus DP of cellulose.

aggregation of dissolved cellulose, as indicated by the decrease in the viscosity of cellulose solution (Figure 5). Meanwhile, the subsequent dissolution of cellulose comes to a standstill at this time. The aggregation of cellulose exhibits a negative effect on the strength of regenerated cellulose film.

- (3) With storing for 104–176 h, a significant decrease of all mechanical properties can be observed during this stage. It is rational to conclude that these might be primarily ascribed to the degradation of cellulose (as shown in Figure 7).

All regenerated cellulose films with different storage times exhibit similar FT-IR spectra, as shown in Figure S1. This represents that the storage of cellulose solution

within 200 h does not affect the chemical feature of cellulose. The structure of regenerated cellulose films and raw cotton pulp cellulose were characterized by XRD, as shown in Figure 9. Compared to the raw cellulose with cellulose I structure, regenerated cellulose films generally exhibit similar patterns of cellulose II with characteristic peaks of 12° and 20°–22° corresponding to the plane of (110) and (110)/(020), as shown in Figure 9a. However, we noticed that the (110) peak of samples with a long time (e.g., 152–200 h) of storage exhibits a tiny shift toward low 2θ, as shown in Figure 9b. This is consistent with the conclusion that degraded cellulose (low DP) will form less crystalline structure with higher interplanar spacing. According to the relationship between the storage time at 40°C and the DP of cellulose (Figure 7b'),



**Figure 10:** Stretched section of regenerated cellulose film with different storage time in TBAH/H<sub>2</sub>O/DMSO solvent system, the red arrow indicates the pull-out hole. (a) 0 h; (b) 7 h; (c) 18 h; (d) 30 h; (e) 42 h; (f) 66 h; (g) 90 h; (h) 128 h; (i) 176 h.

the plot of (110) peak shift versus DP of cellulose can be drawn, as shown in Figure 9c. One can notice that there is a good linear relationship between the peak shift and DP, except for the initial stage (0–12 h) of storage. This indicates that degradation of cellulose can result in a reduction in structure regularity and the failure of mechanical performance of regenerated cellulose films. The thermogravimetry result of regenerated cellulose films (Figure S2) exhibits a similar trend.

The stretched section morphology of the regenerated cellulose film at different storage times was characterized by SEM, as shown in Figure 10. For samples with a short storage time (0 and 7 h), there is a rough morphology on the stretched section due to the micron-sized cellulose insolubility. By extending the storage time (18, 42, and 66 h), there are pull-out holes in the cross-section, indicating a strong intermolecular interaction among cellulose in the film. For samples with a long storage time (e.g., 176 h), the stretched section is relatively flat. This is consistent with the condition of cellulose with a low DP

and poor mechanical properties (especially lower elongation at break and work of break).

## 4 Conclusion

In this work, the effect of storage time and temperature of cellulose solution prepared with solvents of TBAH/H<sub>2</sub>O, TBAH/H<sub>2</sub>O/DMSO, and TBAH/H<sub>2</sub>O/Urea on the dissolution state and degradation behavior of cellulose, as well as the viscosity changes of cellulose solution and the mechanical properties of relevant regenerated cellulose films, has been studied.

(1) From the characterization of the polarized light microscope, it is proved that the undissolved cellulose still undergoes a slow subsequent dissolution during the storage process for three solvents. The two periods (0–24 h and 38–120 h) of storage are active for the subsequent dissolution. TBAH/H<sub>2</sub>O/

Urea solvent exhibits the most powerful ability of subsequent dissolution, followed by TBAH/H<sub>2</sub>O/DMSO and TBAH/H<sub>2</sub>O.

- (2) A storage temperature of 50°C might be fatal to the cellulose solution prepared with TBAH/H<sub>2</sub>O/DMSO. Compared to the low storing temperature (30–45°C), the solution viscosity and cellulose DP are significantly reduced. The critical time for the degradation of cellulose is advanced from 116 h to 40 h. Therefore, it is necessary to strictly control the temperature of cellulose solution prepared with TBAH/H<sub>2</sub>O/DMSO solvent during the process of filtration, deaeration, storage, and transportation.
- (3) The storage time of cellulose solution prepared with TBAH/H<sub>2</sub>O/DMSO solvent shows a great influence on the mechanical properties of the relevant regenerated cellulose films. The optimal storage time was about 12–18 h, with which the strength and elongation at break of the regenerated cellulose films can be enhanced from 119.25 to 147.53 MPa (growth of 23.7%) and improved from 12.66 to 18.70% (growth of 47.7%).

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