

# Preparation of Corn Cellulose Films with Controllable Mechanical Property by Using Switchable CO<sub>2</sub>/DBU/DMSO System

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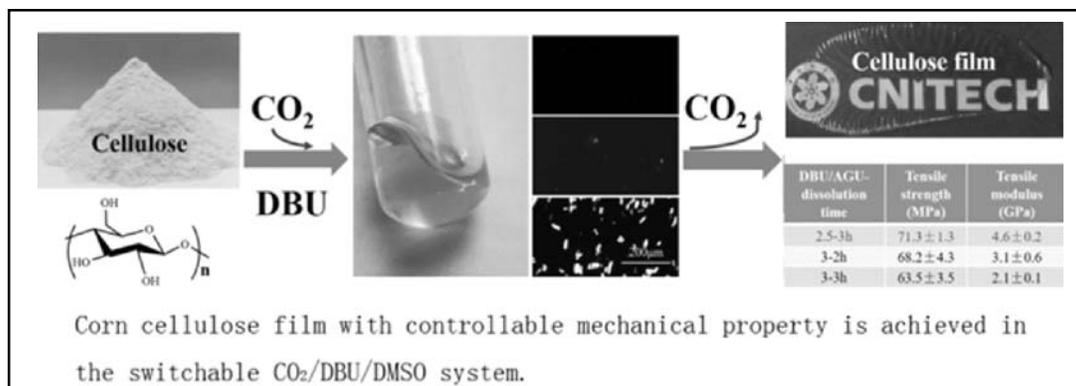
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## ABSTRACT

A switchable CO<sub>2</sub>/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)/dimethyl sulfoxide (DMSO) solvent system is applied to prepare corn cellulose film with controllable mechanical property. By use of the switchable CO<sub>2</sub>/DBU/DMSO system, a rather simple process concerning reacted dissolution and heated precipitation controlled by addition and releasing of CO<sub>2</sub> respectively, to prepare corn cellulose film, is formed. Results exhibit the degree of dissolution of corn cellulose is easily controlled just by adjusting the feeding amount of DBU in the switchable solvent system. Accordingly, some undissolved part of corn cellulose with relative high crystallinity can be appropriately retained to contribute to the improvement of mechanical properties. When DBU/anhydroglucose unit ratio is equal to 2.5:1, corn cellulose film shows the optimal mechanical properties. The tensile strength and tensile modulus respectively reach 71.3MPa and 4.6±0.2GPa. This research provides a feasible technical methodology to prepare corn cellulose film for potential application as a sustainable material in the future.

KEYWORDS: Corn cellulose, Film, Mechanical property.



## INTRODUCTION

Owing to the depletion of fossil resource, exploitation of renewable biomass as substitution or supplement for the sustainable development of energy and material begins to attract great interesting of researchers in recent years<sup>[1]</sup>. Among all the biomass, cellulose is recognized as the most potential one<sup>[2,3]</sup>. It widely exists in various plants with an annual production of over  $1.5 \times 10^{11}$  tons<sup>[4,5]</sup>.

The principal issue for the processing and application of cellulose is to find a suitable solvent. Because cellulose is a hydroxyl-rich polysaccharide formed by the polymerization of glucose with a beta-1,4-glycoside bond, it induces majority intra- and inter-molecular hydrogen bonds among molecular chains and rather strong crystallinity<sup>[6]</sup>. This phenomenon leads to insolubility of cellulose in common organic solvent and water, which makes its processing full of challenge<sup>[7]</sup>. During past decades, some solvents such as *N*-methylmorpholine-*N*-oxide<sup>[8]</sup>, *N,N*-dimethylacetamide/lithium chloride<sup>[9]</sup>, dimethyl sulfoxide/tetrabutyl ammonium fluoride<sup>[10,11]</sup>, and NaOH/urea aqueous solution<sup>[12]</sup> were respectively tried to dissolve cellulose.

With the idea to introduce ion into solvents, the dissolution and processing of cellulose is gradually achieved. In 2002, Swatoski and coworkers<sup>[13]</sup> began to use ionic liquid in cellulose dissolution. This new solvent with strong ion interaction exhibits very good capability to dissolve and process cellulose<sup>[14-17]</sup>.

In 2005, with the thought to less even no use of metal ion and thus to more easily recover solvent, Jessop and coworkers<sup>[18]</sup> noticed a switchable CO<sub>2</sub>/DBU/DMSO solvent system. The particular system can be easily converted from a non-ionic state to an ionic state under mild conditions in 0.1 MPa CO<sub>2</sub> atmosphere at room temperature, and it can be simply recovered to the initial non-ionic state just by removing CO<sub>2</sub> with heating. This solvent system, with gigantic convenience, was immediately used for the dissolution, modification, and processing of cellulose from 2013<sup>[19]</sup>. Accordingly, the investigation of dissolving principle and solution behavior of cellulose in this switchable solvent has been carried out to deeply understanding the physicochemical properties, in the past five years<sup>[20-24]</sup>.

By noticing the great potential of cellulose for the applications in food packaging, the biomedical field, and conductive materials, utilization of the switchable CO<sub>2</sub>/DBU/DMSO system for the modification and processing of cellulose is attached wide attention by researchers. Some literatures focused on the modification of cellulose to make new materials for the potential use in processing by using this solvent system<sup>[24,25]</sup>. Other research is directly committed to prepare cellulose films with superior properties by using this solvent system. From the research work of Xie and coworkers<sup>[26]</sup>, it can be seen microcrystalline cellulose, cotton cellulose, and wood pulp cellulose are emphasized to prepare cellulose films and thus obtained high performances. Accordingly, the use of the switchable CO<sub>2</sub>/DBU/DMSO system suggests a very important thought for the dissolution and processing of cellulose.

In this paper, we will extend the use of the switchable CO<sub>2</sub>/DBU/DMSO system to prepare cellulose film by use of corn cellulose, which is with larger molecular weight (DP ~1440) than the other celluloses. During the research, micro-structure and property of corn cellulose film is researched in detail. After that the advancement to use the switchable CO<sub>2</sub>/DBU/DMSO system in the processing of corn cellulose will be elucidated.

## EXPERIMENTAL

### Materials

Corn cellulose (DP~1440) was obtained from Shengquan Co., Ltd. and dried at 80°C for 12h under vacuum before further use. Dimethyl sulfoxide (DMSO, >99.8%) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, >99%) was purchased from Aladdin Reagent Co., Ltd. and used without further purification. CO<sub>2</sub> (>99.99%) is from Ningbo Wanli Co. Ltd.

### Preparation of corn cellulose film

The process of a typical experiment with DBU/ anhydroglucose units (AGU) ratio of 3:1 is described as following: 1.5mL DMSO, 70mg corn cellulose (4wt%) and 199mg DBU was added in sequence to a 10mL closed high pressure glass vessel with a magnetic stir bar. CO<sub>2</sub> was continuously filled at 50°C. The pressure of CO<sub>2</sub> was maintained at 0.5MPa for some time. After that, a yellow "solution" was obtained and then casted onto a glass plate with a thickness of 0.50mm. A transparent film was formed after dried at 50°C for 48h under vacuum to remove CO<sub>2</sub>. The obtained film was washed in deionized water to remove residual DMSO and DBU. After drying at 80°C for 12h under vacuum, corn cellulose film was finally obtained.

### Characterizations

Scanning electron microscopy (SEM) images were recorded by a Hitachi S4800 scanning electron microscopy using an accelerating voltage of 4kV, platinum was used to sputter the corn cellulose film samples to ensure good electric conductivity. Polarizing microscope (POM) images were performed by an Olympus BX51 Polarizing Microscope after released CO<sub>2</sub> and transferred samples. Crystal structure and crystallinity of the corn cellulose film was tested by X-ray diffraction (XRD, Bruker D8 Advance X-ray Diffractometer). Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/DSC Thermogravimetric Analysis with nitrogen at a heat rate of 20°C/min from 50 to 800°C. Tensile testing was performed by an Instron 5567 universal material testing machine with a 500N load cell at a speed of 5mm/min. The average values and standard deviations were calculated based on more than five samples.

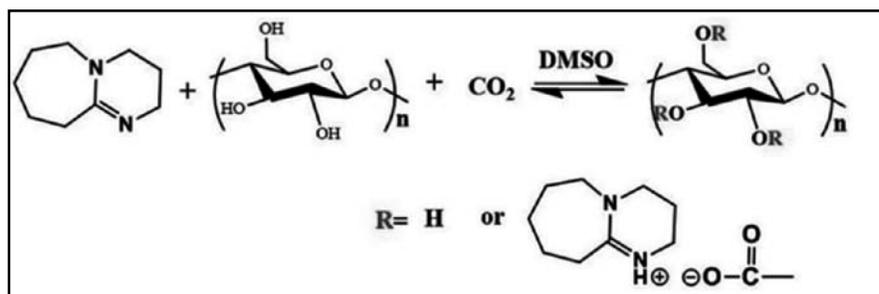
## RESULTS AND DISCUSSION

### Dissolving corn cellulose in switchable solvent

Dissolution of corn cellulose is carried out in the switchable CO<sub>2</sub>/DBU/DMSO system. As elucidated by Zhang, Xie, Meier and coworkers<sup>[20-21,24]</sup>, with the assistance of DBU, CO<sub>2</sub> reacts with the hydroxyl group of cellulose

to form a carbonate (see Scheme 1). The effect of the switchable  $\text{CO}_2$ /DBU/DMSO system is temporarily emerged to change the intrinsic insolubility of cellulose in DMSO. Accordingly, in the experiment, corn cellulose was mixed with DBU at the different ratio (DBU/AGU equals to 2-4) in DMSO. Then,  $\text{CO}_2$  was continuously

injected in the mixture with the pressure of 0.5MPa at 50°C. Under vigorously stirring, the dissolving time was controlled at 0.5-3h. After that, a light yellow transparent DBU/cellulose/DMSO “solution” was obtained. POM was utilized to observe the dissolution of cellulose. As shown in Figure 1(a-d), with the increase of



Scheme 1. Dissolution mechanism of cellulose in switchable  $\text{CO}_2$ /DBU/DMSO system.

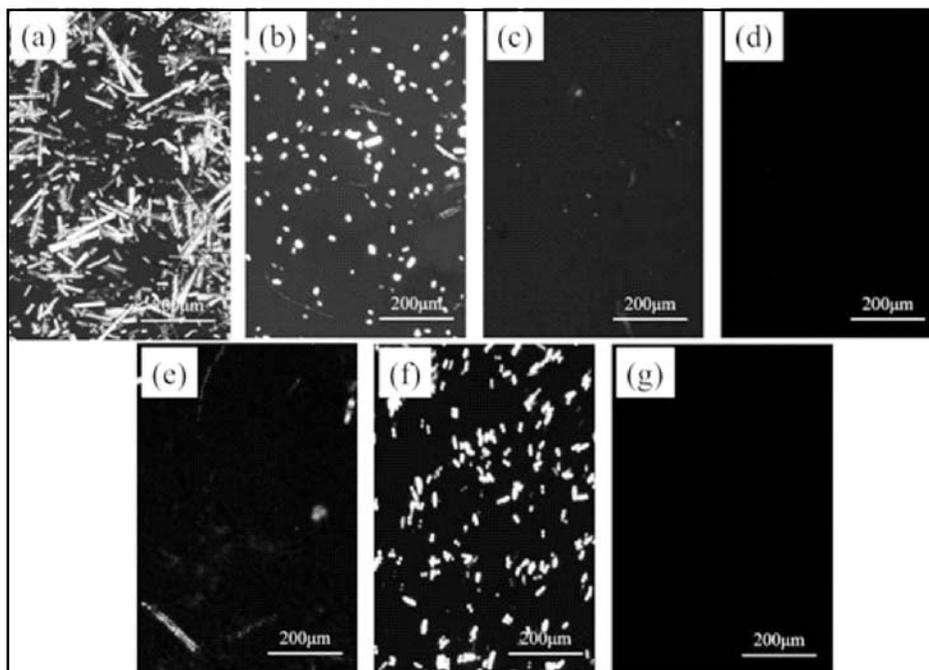


Fig. 1. POM images of corn cellulose after dissolving in DBU- $\text{CO}_2$  switchable solvents with DBU/AGU- dissolution time of (a) 3-0.5h, (b) 3-1h, (c) 3-2h, (d) 3-3h, (e) 2-3h, (f) 2.5-3h, and (g) 4-3h.

dissolving time from 0.5h to 3h, corn cellulose in the solvent with DBU/AGU (3:1) gradually dissolves to completely form a uniform solution.

However, in the system with DBU/AGU (2:1 and 2.5:1), corn cellulose could not achieve complete dissolution (see Figure 1(e, f)). In fact, under these conditions, further extension of dissolving time could still not achieve the complete dissolution of corn cellulose. This is because the dissolving capability of cellulose is decided by the ratio of hydroxyl groups to DBU in order to form carbonate. According to the dissolution mechanism of cellulose in the switchable CO<sub>2</sub>/DBU/DMSO system<sup>[20-21,24]</sup>, one hydroxyl group can only react with one DBU. That is to say, one AGU needs three equivalents of DBU to react. Increasing the ratio of DBU/AGU to higher than 3:1, it will initiate complete dissolution of corn cellulose. In the solvent with DBU/AGU (4:1), corn cellulose is easy to dissolve and then to form a uniform solution (Fig 1(g)).

#### **Formation of corn cellulose film and its microstructure**

All the corn cellulose "solutions" obtained by different solvents and dissolving times were simply casted onto a glass plate and then directly vacuum dried at 80°C to form transparent films. Because of the instability of the formed carbonate, CO<sub>2</sub> can be easily released by heating. This phenomenon reflects the particular advancement of the switchable CO<sub>2</sub>/DBU/DMSO system. Consequently, corn cellulose easily precipitates from the solution to form a film just by simply heating. As to corn cellulose, this particular process is interesting and important. For one thing, the

process to prepare corn cellulose film by using the switchable CO<sub>2</sub>/DBU/DMSO system is very easy to operate. For the other, the extent of dissolution can be easily controlled merely by adjusting the ratio of DBU/AGU. As narrated in previous research<sup>[27]</sup>, partial but appropriate dissolution of cellulose in ionic liquid controlled by dissolving time retain some undissolved part of cellulose, which has rather high crystallinity and probably known as a kind of particular nanocrystals. This partial dissolved cellulose "solution" could be used to prepare a composite film. Within the composite film, the existence of the particular nanocrystals induces the cellulose to produce rather high mechanical property. Noticing the ability to control the degree of dissolution by the switchable CO<sub>2</sub>/DBU/DMSO system, it shows an advancement to contribute an important methodology for the preparation of cellulose film with high properties just by simply adjusting the composition of the system.

SEM was utilized to observe the surface morphology of corn cellulose films. As shown in Figure 2(a), there shows a rather rough surface of corn cellulose film 3-0.5h (DBU/AGU-dissolution time). After increasing the dissolving time to 1h, though the dissolution of corn cellulose is still not complete, the surface of corn cellulose film becomes smoother (see Figure 2(b)). Further increasing the dissolving time to 2 or 3h, the obtained corn cellulose films show more smooth surfaces (Figure 2(c,d)). This result exhibits that the complete dissolution is helpful to the formation of corn cellulose film with high quality. Similar results can be found just by

changing the ratio of DBU/AGU in “solution”. The film obtained from the solvent with DBU/AGU (2:1) only shows a relative rough surface (see Figure 2(e)). However, except for some unsolved corn cellulose, the surface of corn cellulose film 2.5-3h becomes smoother

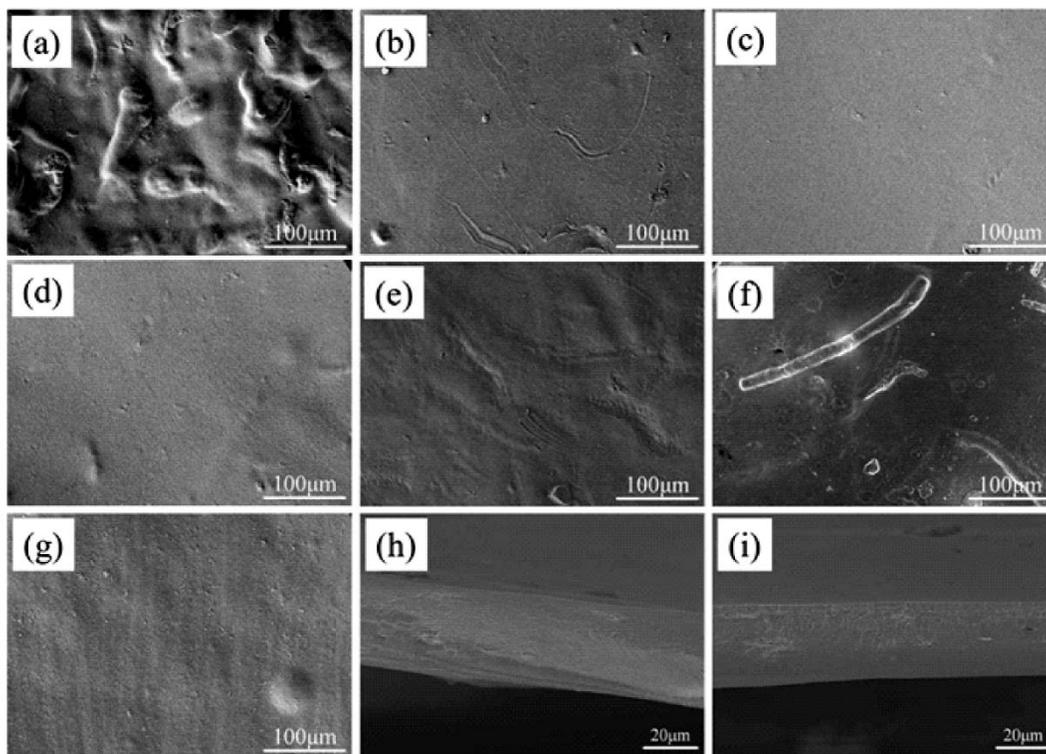


Fig. 2. SEM images of the surface of corn cellulose films of (a) 3-0.5h, (b) 3-1h, (c) 3-2h, (d) 3-3h, (e) 2-3h, (f) 2.5-3h, (g) 4-3h, and the cross section of cellulose films of (h) 2.5-3h, (i) 3-3h.

(Figure 2(f)). After increasing the ratio of DBU/AGU to 4:1, it finally prepares a very smooth corn cellulose film (Figure 2(g)).

From the FTIR spectra of corn cellulose films (Figure 3), all the curves clearly exhibit the -OH stretching vibrations at  $3665\text{--}3000\text{ cm}^{-1}$  and -CH stretching vibrations at  $2903\text{ cm}^{-1}$  respectively. It reflects that the molecular structure of corn cellulose is not destroyed. Figure 4 gives the XRD patterns of raw cellulose

and corn cellulose films. Generally, the raw cellulose shows a strong crystalline peak at  $22.5^\circ$  of cellulose II, together with a broad peak at  $15.8^\circ$  and a weak peak at  $34.6^\circ$  of cellulose I (see Figure 4(b)). By using the solvent with DBU/AGU (3:1), with the increase of dissolving time, the strength of crystalline peaks of corn cellulose film gradually decrease (Figure 4(a)). The results related to the ratio of DBU/AGU are shown in Figure 4(b). Corn cellulose films of 2-3h and 2.5-3h are respectively prepared

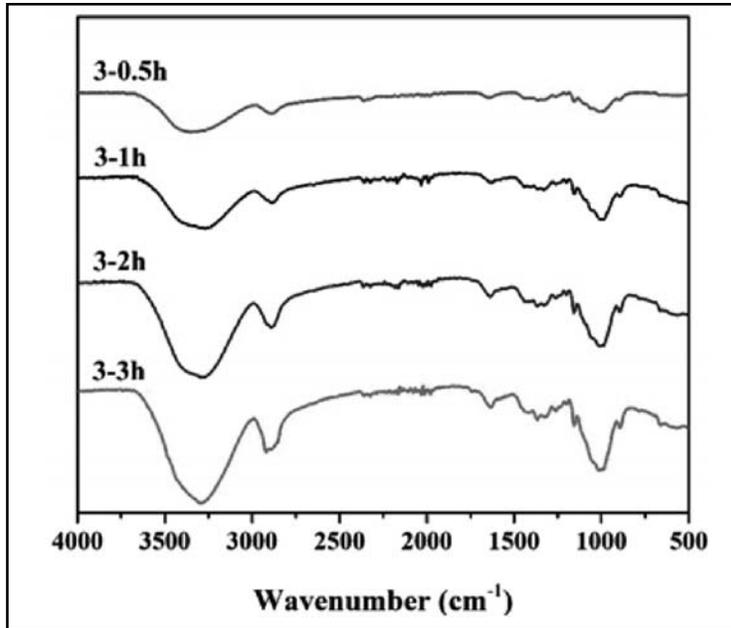


Fig. 3. FTIR spectra of corn cellulose films obtained by means of the switchable CO<sub>2</sub>/DBU/DMSO system.

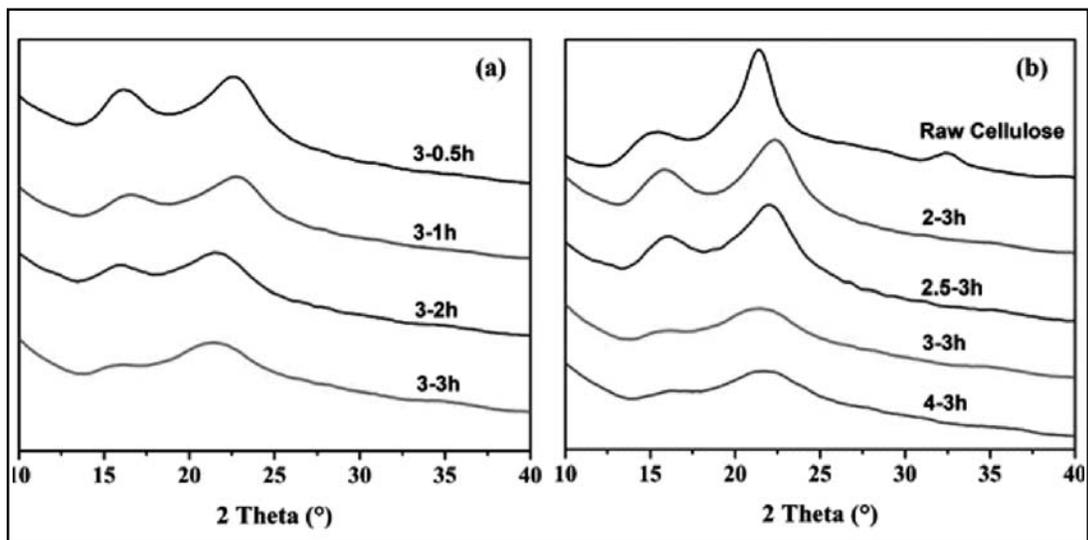


Fig. 4. XRD patterns of raw cellulose and corn cellulose films prepared by means of the switchable CO<sub>2</sub>/DBU/DMSO system of (a) DBU/AGU equals to 3:1 for different dissolving times and (b) 3h dissolving with different ratio of DBU/AGU.

by the “solution” with partial dissolution of corn cellulose in the switchable  $\text{CO}_2$ /DBU/DMSO system. There exist relative weak diffraction peaks of both cellulose I and cellulose II. But corn cellulose film 3-3h and 4-3h are different. Because of they are obtained from the complete dissolved solution, only the diffraction peaks of cellulose II can be observed (see Figure 4).

This phenomenon is similar as the experimental result of Ouajaj<sup>[28]</sup>, that is, cellulose obtained from a process of dissolution and regeneration can only show type-II crystals.

#### Properties of corn cellulose film

The obtained corn cellulose films are all transparent regardless of their different

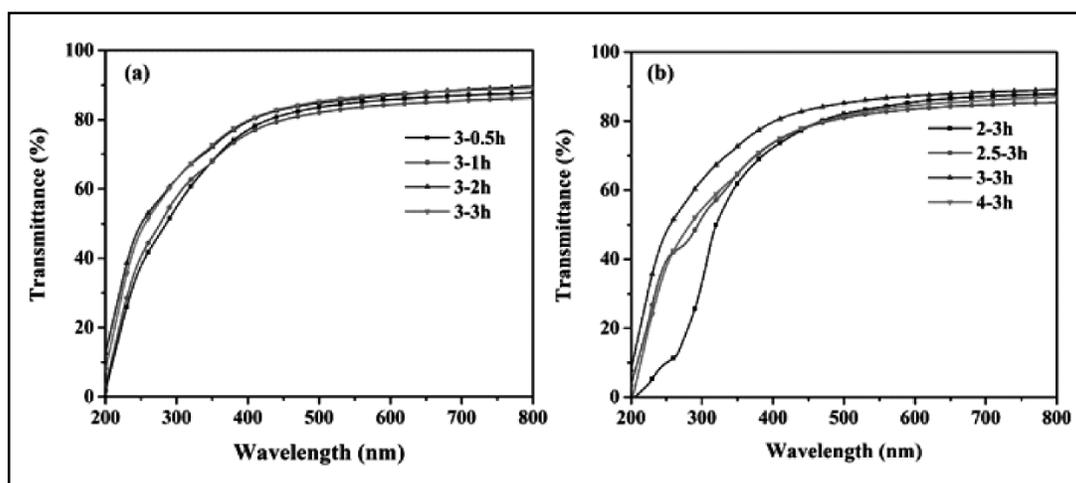


Fig. 5. Light transmittance of corn cellulose films prepared by means of DBU- $\text{CO}_2$  switchable solvents of (a) DBU/AGU equals to 3:1 for different dissolving times and (b) 3h dissolving with different ratio of DBU/AGU.

uniformity, crystallinity, and thickness. The light transmittance in visible light region (400-760nm) of all the corn cellulose films don't exist large difference, which is around 70-80% (See Figure 5).

Mechanical properties of corn cellulose films are also detected and listed in Table 1. By using the solvent with DBU/AGU (3:1), the tensile strength and elongation of the corn cellulose films firstly increase and then decrease with the extension of dissolving time. The tensile strength and elongation of corn cellulose film 3-0.5h is only  $31.5 \pm 3.2$ MPa and  $1.2 \pm 0.2$ %,

respectively. After increasing the dissolving time to 2h, both the tensile strength and elongation increase to  $68.2 \pm 4.3$ MPa and  $13.9 \pm 3.2$ %, respectively. But continuous increase of the dissolving time to 3h, the tensile strength and elongation of corn cellulose film 3-3h reduce to  $63.5 \pm 3.5$ MPa and  $11.0 \pm 2.0$ %, respectively. These results indicate that partial dissolution of cellulose produces defect in corn cellulose film and leads to relative low mechanical properties. Until complete dissolution is basically achieved, the high mechanical properties begin to produce. But the optimal tensile properties appear at the condition of

close to but not complete dissolution. Under this condition, the undissolved corn cellulose doesn't cause the decrease in tensile strength of the film. On the contrary, it forms the enhancement in tensile strength of corn cellulose film as similar as the use of nanocrystals. This phenomenon was similar with the results reported by Zhang and coworkers<sup>[26]</sup>.

With the change of the ratio of DBU/AGU in the switchable CO<sub>2</sub>/DBU/DMSO system, the impact on the mechanical properties of corn cellulose films is also detected. By using the solvent DBU/AGU (2:1), the tensile strength of the corn cellulose film is 44.2±2.4MPa and the elongation is 1.2±0.4%. After increasing the ratio of DBU/AGU to 2.5:1, with the increase of the degree of dissolution, the tensile strength is improved to the maximum of 71.3MPa. With

the continuous increase of the ratio of DBU/AGU to 3:1 and 4:1, the tensile strength of the corn cellulose films decreases to 61-63MPa. In fact, not only the tensile strength, the tensile modulus of cellulose film prepared by the solvent with DBU/AGU (2.5:1) also reaches the highest value at 4.6±0.2GPa. The change in mechanical properties of the corn cellulose film can be equally attributed to the formation of composite film of cellulose, which is narrated above. Understanding from all the experimental results, the corn cellulose film with optimal mechanical properties is obtained by using the switchable solvent with DBU/AGU (2.5:1). These results further reflect the particular advancement of the switchable solvent to accurately control the extent of dissolution of corn cellulose and microstructure of corn

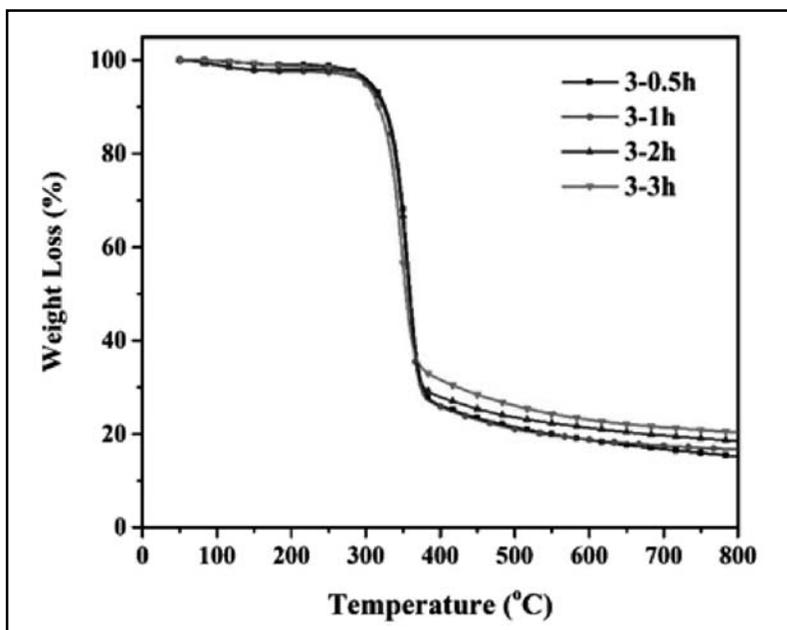


Fig. 6. Weight retention profiles of corn cellulose films prepared by means of the switchable CO<sub>2</sub>/DBU/DMSO system.

cellulose film just by adjusting the composition of DBU/AGU. Simultaneously, the whole process contributes a simple process to prepare corn cellulose film with controllable properties just by design of the composition of the switchable solvent.

The weight loss of corn cellulose film in N<sub>2</sub> atmosphere is also detected in the experiment. As shown in Figure 6, all the corn cellulose films showed almost same weight loss profiles at temperature lower than 300°C. The thermal stability of corn cellulose films is in good consistent with their unchanged molecular structure.

### CONCLUSIONS

The switchable CO<sub>2</sub>/DBU/DMSO system is utilized to prepare corn cellulose film. Due to its particular effect of ionic liquid controlled by injecting or releasing CO<sub>2</sub>, corn cellulose film is easily obtained. The whole process to prepare corn cellulose film is very simple and easy to operate. During the dissolution of corn cellulose, just by adjusting the ratio of DBU/AGU, some undissolved part of corn cellulose with relative high crystallinity can be appropriately retained and accordingly contributes to produce controllable mechanical properties. With the use of the switchable solvent DBU/AGU (2.5:1), corn cellulose film shows the optimal mechanical properties. The tensile strength and tensile modulus respectively reach 71.3MPa and 4.6±0.2 GPa.

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