

# Effect of Coagulation Bath Conditions on the Properties of Cellulose Packaging Films From Ionic Liquid [BMIM]Cl

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**Abstract:** By using natural softwood pulp with higher degree of polymerization (DP=1460) as cellulose source and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid as solvent, a novel cellulose packaging film was prepared. The effects of coagulation types, concentration of coagulation and temperature on the structure, mechanical property, permeability for oxygen and water vapor were measured. The investigations suggest that the coagulation bath has great effect on the morphologies of the films, and the films prepared in [BMIM]Cl/water coagulation media show denser structure than those prepared in water, C<sub>2</sub>H<sub>5</sub>OH and DMSO media. When the [BMIM]Cl concentration in the coagulation bath increases, the tensile strength increases at first and then decreases. With increasing temperature of the coagulation bath, the tensile strength decreases slowly while the elongation at break of the films increases at first and then decreases. It was also found that both the oxygen permeability and the water vapor permeability of the films increase with the temperature of coagulation bath and the concentration of [BMIM]Cl in the coagulation bath. The films prepared by using ionic liquid technology would be used in food packaging or other fields as a kind of green packaging material.

**Keywords:** cellulose film; ionic liquid; coagulation bath; packaging material

## 1. Introduction

Cellulose, which is the most abundant natural polymer and contains both amorphous and crystalline structures, has limited applications in preparing packaging films because of chain stiffness and close chain packing via the strong inter- and intra-molecular hydrogen bonding between the hydroxyl groups of the glucose residues [1-2]. Due to the above reasons, cellulose is hard to dissolve in water and most common organic solvents. In the last century, a number of solvent systems, such as DMAc/LiCl, DMF/N<sub>2</sub>O<sub>4</sub>, NMMO, and some molten salt hydrates like LiClO<sub>4</sub>·3H<sub>2</sub>O, have been found to be efficient for cellulose dissolution [3-4]. However, these solvents have some limitations such as volatility, toxicity, cost, difficulty in solvent recovery, and instability in applications.

Within the past several years, ionic liquids (ILs) having the imidazolium structure, such as 1-butyl-3-methylimidazolium chloride [BMIM][Cl] and 1-allyl-3-methylimidazolium chloride [AMIM][Cl], have been reported being used to dissolve cellulose at room temperature. It has also been realized that the integrity of the cellulose chain during dissolution and derivatization in ILs is largely dependent on the purity of these solvents and of the absence of IL-derived byproducts [5-6]. The ILs technology opens up new perspectives also for cellulose film manufacture. In this study, a novel cellulose packaging

film was prepared through the dissolution of cellulose in [BMIM][Cl] by adjusting the coagulation types, concentration of coagulation and temperature. The structures, mechanical property, permeability of regenerated cellulose films were also assessed.

## 2. Materials and Methods

### 2.1. Materials

[BMIM][Cl] (grade of purity >97 %) used as solvent was purchased from was purchased from Shenzhen Tianxudong Keji Co., Ltd, and used as received. Softwood pulp (DP=1460) were provided by Tianjin Zhongchao Paper Industry Co., Ltd. Glycerin, dimethyl sulfoxide (DMSO), absolute alcohol and sulfuric acid (analytical reagent) were analytical reagent grade and were obtained from Jiangtian Chemical Company Co., Ltd.

### 2.2. Preparation of cellulose films

The cellulose films were prepared as follows: The calculated amount of the hard wood pulps and [BMIM][Cl] were added into beaker at 80 °C for 8 h with statistic, in which the concentration of the dried hard wood pulps was 6.0 wt. %. After that, the dissolved cellulose was stirred at 95 °C for 3 h to form a homogeneous and transparent cellulose/ [BMIM][Cl] solution. Then the above mixture was poured and casted with a copper string onto the glass to obtain the films. Subsequently, the obtained

film was soaked quickly into the various coagulation types at 10 - 40°C. Finally, the film was immersed into glycerin solution prior to air-drying.

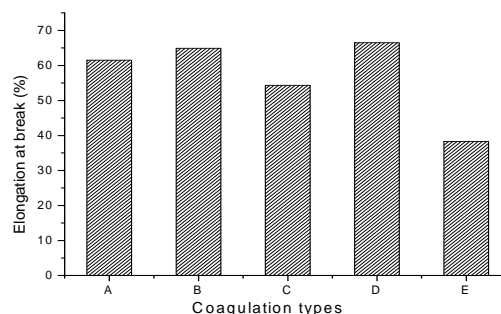
### 2.3. Measurements

The fracture surface of the samples was observed under a JSM-6380LV scanning electron microscopy (SEM). The tensile properties were determined with an RG T-3 universal testing instrument according to a Chinese national standard of GB/T13022-1991. Small dumb-bell specimens with waist dimensions of 80×15 mm were used for tensile mechanical tests, and five measurements were carried out for each data point. The oxygen permeability was performed with differential-pressure method at a Bruger GDP-C instrument according to Chinese national standard of GB/T1038-2000. The water vapor permeability was determined according to a Chinese national standard of GB1037-1988.

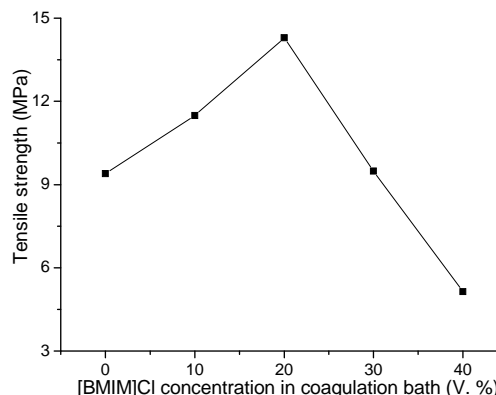
### 3. Results and Discussion

It is known that the exchange rate between the solvent of the cellulose and solvent of the coagulation can impact on the final morphologies of the films during phase inversion technology [7-10]. **Fig. 1** shows the elongation at break of the cellulose films being treated by various coagulation types. It is noted that the cellulose films treated by [BMIM]Cl solution ( $V_{[BMIM]Cl}: V_{H_2O}=1:9$ ) and  $H_2SO_4$  solution ( $V_{[BMIM]Cl}: V_{H_2O}=1:9$ ) have the best elongation (65.0 %) and lowest elongation (38.0 %), respectively. The above phenomenon may be owing to faster rates of phase separation and solidification in the mixture of cellulose and [BMIM]Cl coagulation solution, decreasing the ability to dissolve cellulose caused by stronger complexation between  $Cl^-$  and  $-OH$ , which can prepare the cellulose films with more compact structure and better mechanical properties. However, when the  $H_2SO_4$  or

$C_2H_5OH$  solution are used as coagulations, the slower rates of phase separation accompanying faster rates of solidification in the mixture cause the prepared films with porous structure and worse mechanical properties.



**Figure 1. Elongation at break of the cellulose films as a function of coagulation types: A- $H_2O$ , B- $V_{[BMIM]Cl}: V_{H_2O}=1:9$ , C-  $V_{C_2H_5OH}: V_{H_2O}=2:8$ , D- $V_{DMSO}: V_{H_2O}=2:8$ , E-  $V_{H_2SO_4}: V_{H_2O}=1:9$**



**Figure 2. Tensile strength of the cellulose films as a function of the content of [BMIM]Cl in coagulation bath.**

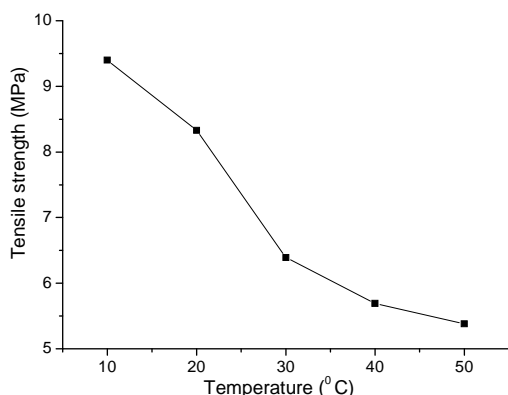
**Table 1. Oxygen permeability (OP) and water vapor permeability (WVP) of the cellulose films prepared under various conditions**

	[BMIM]Cl concentration in coagulation bath (V. %)					Coagulation temperature (°C)				
	0	10	20	30	40	10	20	30	40	50
OP $\times 10^{-13}$ g·cm/cm <sup>2</sup> ·s·Pa	5.81	4.74	9.89	17.2	28.12	3.78	4.95	6.63	10.31	15.20
WVP $\times 10^{-15}$ cm <sup>3</sup> ·cm/cm <sup>2</sup> ·s·Pa	6.78	4.62	9.35	13.89	17.51	4.67	5.28	7.08	9.02	10.94

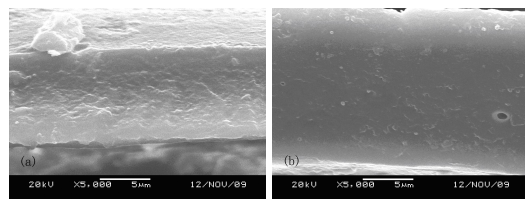
**Fig. 2** and **Table 1** indicate the content of the [BMIM]Cl in the coagulation bath has significant effects on the mechanical and permeability properties of the cellulose films. It can be seen the tensile strength increase from 9.40 MPa to 14.29 MPa with increasing of [BMIM]Cl from 0 wt % to 20.0 wt % in the coagulation, and the tensile strength gradually decreases from 14.29

MPa to 5.14 MPa with increasing the amount of the [BMIM]Cl in the coagulation continuously. When the rates of phase separation match that of solidification, the films prepared with compaction structure and less defects. The lower concentration of [BMIM]Cl in the coagulation bath induces larger exchange rates between solution and non-solution and solidification rates. The above factors

contribute to the films prepared with addition of 10 wt. % [BMIM]Cl in the coagulation bath having both better mechanical properties and permeability for oxygen or water vapor.



**Figure 3. The tensile strength of the cellulose films as a function of the coagulation temperature**



**Figure 4. SEM images of the cellulose films prepared in [BMIM]Cl coagulation at different temperature: (a) 10 °C and (b) 20 °C**

The tensile strength of the cellulose film decreases with increasing of the temperature (**Fig. 3**). One can observe that both the water vapor permeation and oxygen permeability increases with the increase of coagulation temperature (**Table 1**). At lower coagulation temperature, the mass transfer speed decreases with larger resistance, allowing more time at interface to integrate and form a more compact film structure, which can be seen from the SEM images of the cellulose films prepared in [BMIM]Cl coagulation at different temperature (**Fig. 4**).

#### 4. Conclusions

The novel cellulose packaging films were successfully prepared through the phase inversion in [BMIM]Cl ionic liquid solvent. The investigations for the films prepared in water, [BMIM]Cl/water, C<sub>2</sub>H<sub>5</sub>OH and DMSO coagulation media indicate the cellulose films treated by [BMIM]Cl solution and H<sub>2</sub>SO<sub>4</sub> solution have the best elongation (65.0 %) and lowest elongation (38.0 %), respectively. Mechanical and permeability properties of

the cellulose films as a function of the content of [BMIM]Cl in the coagulation bath show the films prepared in [BMIM]Cl 10.0 wt % coagulation bath have better permeability and mechanical properties. The tensile strength of the cellulose film decreases with increasing of the temperature, while both the water vapor permeation and oxygen permeability increases with the increase of coagulation temperature. The films prepared by using ionic liquid technology would be used in food packaging or other fields as a kind of green packaging material.

#### 5. Acknowledgment

The authors greatly appreciate financial support from Key Projects in the National Science & Technology Pillar Program during the Eleventh Five-Year Plan Period (Grant No.: 2006BAD30B02) and China Postdoctoral Science Foundation funded project.

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