

Effects of Plasticization Conditions on the Structures and 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, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid as solvent and glycerol as plasticizer, a novel cellulose packaging film was prepared. The effects of plasticization conditions on the structures, mechanical properties, permeability for oxygen and water vapor were measured by Wide-angle X-ray scattering, thermogravimetric analysis, scanning electron microscopy (SEM), and other techniques. The investigations suggested that the glycerol concentration and plasticizing time had great effect on the properties of the regenerated cellulose films. The crystal transformation of cellulose I to cellulose II occurred during the dissolution and regeneration process, combining with the decrease of thermal stability. The tensile strength decreased rapidly with the addition of glycerol and prolongation of plasticizing time. However, elongation at break of the regenerated

cellulose films increased at first and then decreased with increasing of glycerol concentration and plasticizing time. The morphologies for the fracture surface obtained from SEM images showed transformation of typical brittle fracture to plastic deformation with increasing of glycerol concentrations. It was also found that both water vapor permeability and oxygen permeability of the regenerated cellulose films decreased slowly with increasing of glycerol concentrations and plasticizing time, but water vapor permeability and oxygen permeability presented an almost opposite trend. The films prepared by using ionic liquid technology would be used in food packaging or other fields as a kind of green packaging material. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 704–709, 2012

Key words: cellulose; packaging films; ionic liquid; plasticization conditions

INTRODUCTION

As an important polysaccharide, cellulose is a promising substitute for the petroleum materials in the fields of packaging and textile, because of its renewability, biodegradability, and abundance in nature.^{1,2} However, due to the chain stiffness and close chain packing via the strong inter- and intra-molecular hydrogen bonding between the hydroxyl groups of the glucose residues, cellulose is neither dissolved in common solvents nor thermally processed through the extrusion or the compressed molding, which restricted its wider applications. To date, only a limited number of solvent systems for cellulose has been found, such as DMAc/LiCl, DMF/N₂O₄,

NMMO, and some molten salt hydrates like LiClO₄·3H₂O.^{3–7} In general, the traditional cellulose dissolution processes require relatively harsh conditions and the use of expensive and uncommon solvents, which usually cannot be recovered after the process.^{8,9} With increasing governmental regulations in industries, the need to implement “green” processes for preventing the pollution is becoming increasingly important and acting as a strong driving force to discover effective solvents for cellulose. Recently, ionic liquids have emerged as a new class of solvents for practical applications due to their unique combination of low volatility, chemical stability, high conductivity, wide electrochemical window, ability to dissolve organic and inorganic solutes and gases, and tunable solvent properties. Owing to their specific physical and chemical properties, ionic liquids have been found specific applications in polymer chemistry.^{10–13}

In 2002, Swatloski et al.¹⁴ reported the use of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and other hydrophilic ionic liquids as solvent for cellulose both for the regeneration of cellulose and for the chemical modification of the polysaccharide.

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In 2005, by using 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) as the dissolution and regeneration of cellulose, the regenerated cellulose materials with a good mechanical property was prepared by Zhang et al.¹² 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac), 3-methyl-*N*-butyl-pyridinium chloride and benzyldimethyl(tetradecyl)ammonium chloride were investigated as solvents reaction medium in cellulose functionalization by Heinze et al.¹⁵ In 2010, the regenerated cellulose films were successfully prepared from cornhusks cellulose in room temperature in two ionic liquids [AMIM]Cl and [EMIM]Ac by Cao et al.,¹⁶ and the structure and properties of novel regenerated cellulose films were also studied. Graft copolymers were also prepared by ring-opening polymerization of cyclic esters initiated by HO-groups of cellulose in ionic liquid solution.¹⁷ The use of ionic liquids in the field of cellulose chemistry opens up a broad variety of new opportunities and significantly broadens the modified and tailored of cellulose derivatives, and a number of cellulose-based materials, e.g., gel material, fibrous material, and composites materials have been prepared from ionic liquid.^{18–23}

With the growing global environmental awareness and societal concern, high rate of depletion of petroleum resources and concepts of sustainability, there has been an increasing interest in the development of degradable green packaging materials using cellulose as resource, which offer alternative packaging options, advantageous to the synthetic 'recalcitrant' packaging polymers because they do not contribute to the environmental pollution.^{24–27} Nowadays, considerable efforts are now being made in the research and development of cellulose as the basic material in industrial applications. However, with the molecules structure described above, how to prepare the cellulose packaging films with proper mechanical property and permeability by facile pathway have received considerable attention.

In this study, a novel cellulose packaging film was prepared through the dissolution of cellulose in [BMIM]Cl by using natural softwood pulp with higher degree of polymerization (DP = 1460) as cellulose source, and the effects of plasticization conditions on the structures, mechanical properties, water vapor permeability, and oxygen permeability of the regenerated cellulose films were also assessed.

EXPERIMENTAL

Materials

[BMIM]Cl (grade of purity > 97%) used as solvent was purchased from was purchased from Shenzhen Tianxudong Keji Co. (ShengZhen), and was used as received. Glycerol was analytical reagent grade and

was obtained from Jiangtian Chemical Company Co. (Tianjin). Softwood pulp (DP = 1460) were provided by Tianjin Zhongchao Paper Industry Co. (Tianjin). The content of α -cellulose in cornhusk cellulose was determined according to Chinese national standard of GB/T744-1989, and the content of α -cellulose is 97.3 wt %. The DP of the softwood pulp was determined by Ubbelodhe viscometer using Cuam as solvent at 25°C to be 1460.¹⁶

Preparation of cellulose films

The cellulose films were prepared as follows: The calculated amount of the softwood 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 [BMIM]Cl/H₂O solution (10 vol %) at 20°C. Finally, the above film was immersed into glycerol/H₂O plasticizer solutions (0–45 vol %) for 0–60 min before air-drying.

Characterizations

Wide-angle X-ray scattering (WAXS) was performed with a Rigaku D/max-r C diffractometer (40 kV, 50 mA) with Cu-K α radiation ($\lambda = 0.154$ nm), the diffraction patterns being collected in the 2θ range of 3–90° at a scanning rate of 1°/min. Thermogravimetric analysis (TGA) was performed on a TA instruments Q500 thermogravimetric analyzer from 35°C to 860°C in a nitrogen gas atmosphere with heating rates of 10°C/min. Morphologies of the samples were observed under a JSM-6380LV scanning electron microscopy (SEM). The tensile properties were determined with an RG T-5 universal testing instrument according to a Chinese national standard of GB/T13022-1991. Small dumb-bell specimens with waist dimensions of 80 × 15 mm² were used for tensile mechanical tests, and five measurements were performed for each data point. Oxygen permeability was measured by using a Brruger GDP-C instrument according to Chinese national standard of GB/T1038-2000. Water vapor permeability was determined according to a Chinese national standard of GB1037-1988.

RESULTS AND DISCUSSION

The natural cellulose is a linear but semicrystalline polymer, consisting of highly structured crystalline regions (microfibrils) and amorphous parts. To dissolve cellulose, to disrupt its great number of inter-

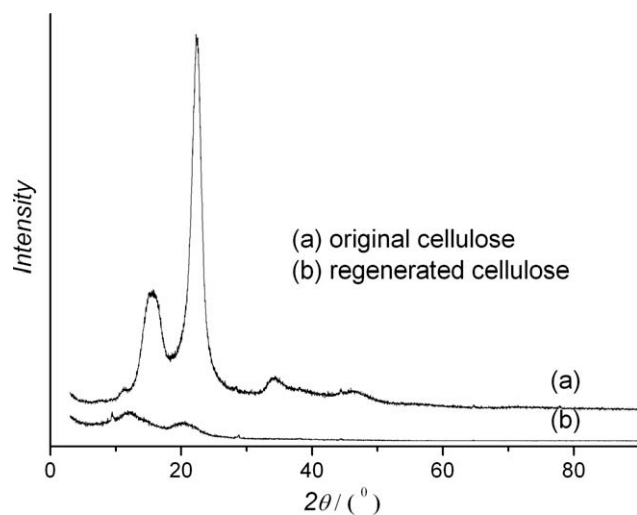


Figure 1 WAXS patterns of the original cellulose (a) and the regenerated cellulose (b).

and intra-molecular hydrogen bonds is required. The mechanism of cellulose in ionic liquids was described as follows: the oxygen and hydrogen atoms of the cellulose form electron donor-electron acceptor complexes with the charged species of the ionic liquid. This interaction results in the separation of the hydroxyl groups of the different cellulose chains leading to dissolution of the cellulose in the ionic liquid.²⁸ When [AMIM]Cl was used as solution to dissolve cellulose, the ion pairs in [AMIM]Cl dissociated to individual Cl⁻ and [AMIM]⁺ ions in solution. Then free Cl⁻ ions associated with the cellulose hydroxyl proton, and the free cations complex with the cellulose hydroxyl oxygen, which disrupted hydrogen bonding in cellulose and led to the dissolution of cellulose.¹² To investigate the effects of ionic liquid [BMIM]Cl on the inner structure of cellulose during the process, the crystalline structures of the

regenerated cellulose and original cellulose were investigated by WAXS measurements (shown in Fig. 1). The original cellulose (spectrum a) showed two well-defined diffraction peaks at $2\theta = 15.7^\circ$ and 22.5° , as the typical diffraction patterns of cellulose type I.^{16,19,29} However, two conspicuous broad peaks at $2\theta = 12.2^\circ$ and 20.2° were observed in the WAXS patterns of regenerated cellulose (spectrum b), which were in accordance with the typical diffraction patterns of cellulose II, accompanying with lower crystallinity. The above phenomena indicates that, during the dissolution process, the original crystalline form and most of the inter- and intra-molecular hydrogen bonding between the hydroxyl groups of the glucose residues were destroyed, and regeneration of cellulose from the [BMIM]Cl solutions might lead to the difficulty in recrystallization of cellulose chains. The crystallinity of the original and regenerated cellulose was 77.3% and 32.9%, respectively. The phenomena obtained were in accordance with the results reported in literatures.^{30,31}

Further evidence for the structure inversion was provided by the TGA measurements in a nitrogen gas atmosphere displayed in Figure 2, which showed the thermal degradation behaviors of the original cellulose and regenerated cellulose samples. The original cellulose showed two steps of weight loss. The first step occurred around 80°C with about 4.7 wt % of weight loss corresponding to the moisture decomposition in cellulose. While the second step exhibited thermal decomposition temperature at 368°C was resulted from the cellulose degradation. However, for the regenerated cellulose, the thermogram showed single step of weight loss. The onset of degradation temperature of the modified cellulose occurred around 230°C . Obviously, the regenerated cellulose started to decompose at a temperature substantially lower than the original one. This behavior

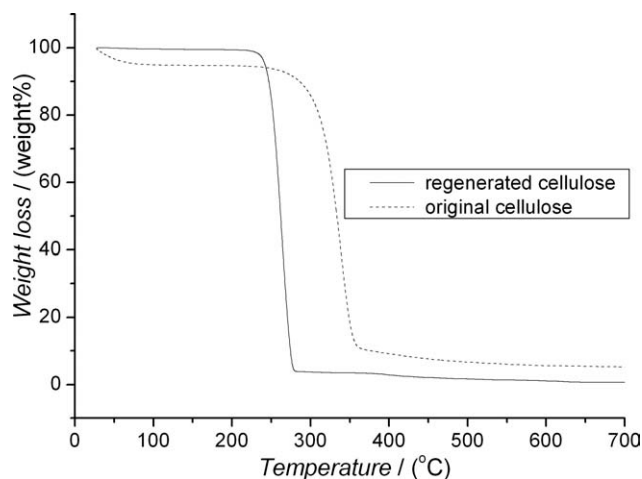


Figure 2 Thermogravimetric analysis (TGA) thermograms of the original cellulose and regenerated cellulose samples in a nitrogen gas.

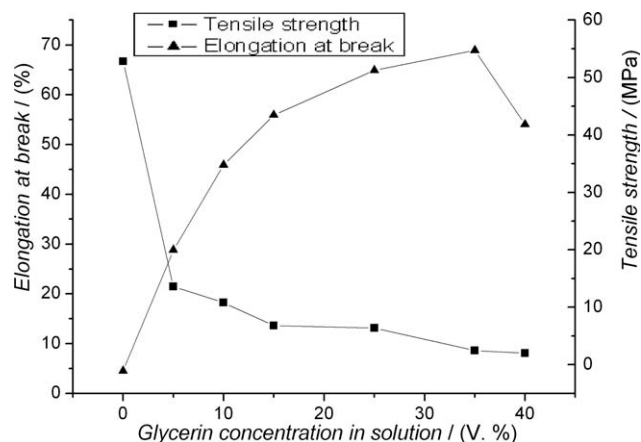


Figure 3 Mechanical properties of the regenerated cellulose films as a function of the glycerol concentration.

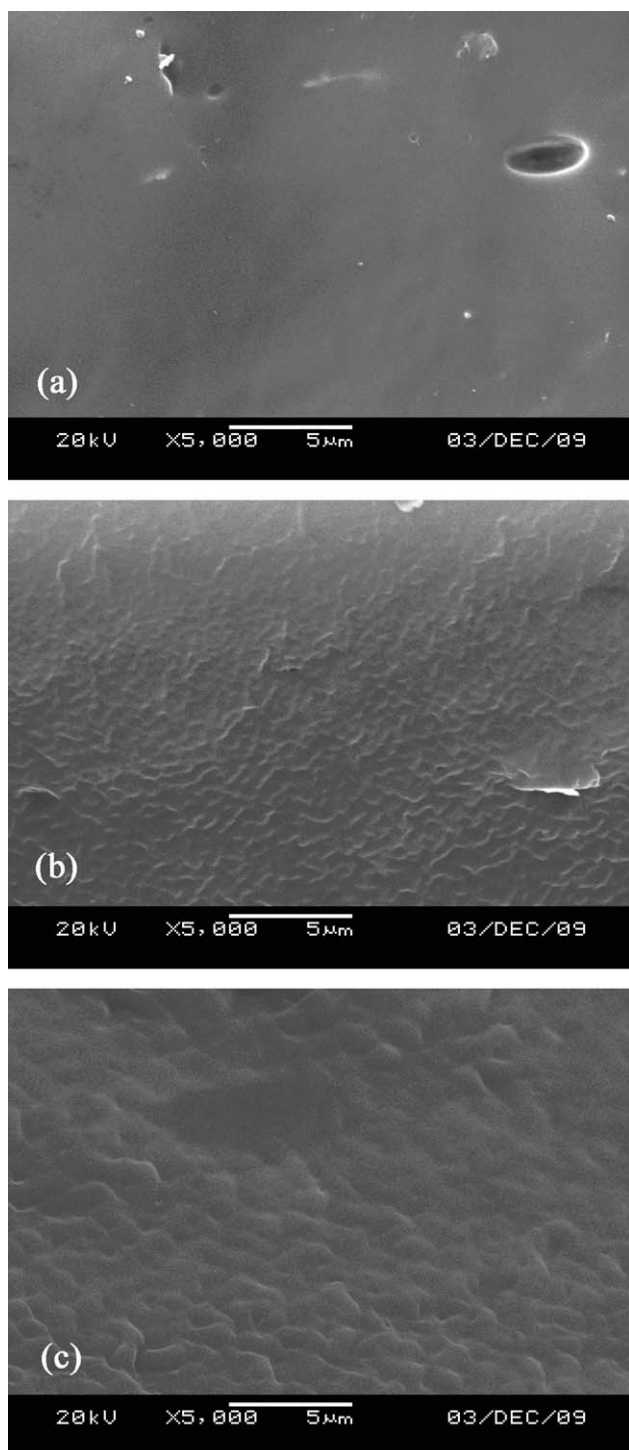


Figure 4 SEM images of the fracture surface of regenerated cellulose films prepared under various glycerol solution: (a) 5.0 vol %, (b) 10.0 vol %, and (c) 35.0 vol %.

was attributed to the disruption of the crystalline regions of cellulose in the samples.

It has been reported by many literatures that cellulose films can be prepared through the phase inversion technology. However, due to the numerous inter- and intra-molecular hydrogen bonds in the cellulose molecular, the films prepared without plasticiz-

ing processing had characters of frangibility and poor toughness and thus could not be used in packaging fields. To get the cellulose films with proper properties, the glycerol was used as plasticizer to treat the regenerated cellulose films in our study. The tensile strength and elongation at break of the regenerated cellulose films as a function of glycerol concentration were displayed in Figure 3, indicating that the glycerol concentration had significant effects on the mechanical properties. For all plasticization systems, the expected effect on mechanical properties (increase in elongation and decrease in tensile with increasing plasticizer amount) was observed except plasticization over 35.0 vol %. With being treated in 5.0 vol % glycerol solution, the tensile strength decreased from 52.8 MPa to 13.6 MPa, but the elongation at break of the regenerated cellulose films increased from 4.5 % to 68.9 %. It is known that plasticizer is a polymer additive that serves to increase the polymer's flexibility, elongation or ease of processing (workability). According to the "gel theory," the plasticizer molecules break up the polymer-polymer interaction by getting in between the chains and "obscuring" these interaction sites from the polymer molecules. In more technical terms, the addition of a plasticizer generally causes a reduction in the cohesive intermolecular forces along the polymer chains. The chains can then move more freely relative to one another, and the stiffness of the polymer is reduced.

Figure 4 showed the SEM images of the fracture surface of regenerated plasticized films in various glycerol concentrations solution. It should be noted that the film prepared with glycerol concentration 5.0 vol % had a glazed fracture surface, indicating a typical brittle fracture behavior [Fig. 4(a)]. One could also see the variation of the fracture surface with plastic deformation as shown in Figure 4(b,c) with the increase of glycerol concentration. In addition, for the films prepared with glycerol concentration

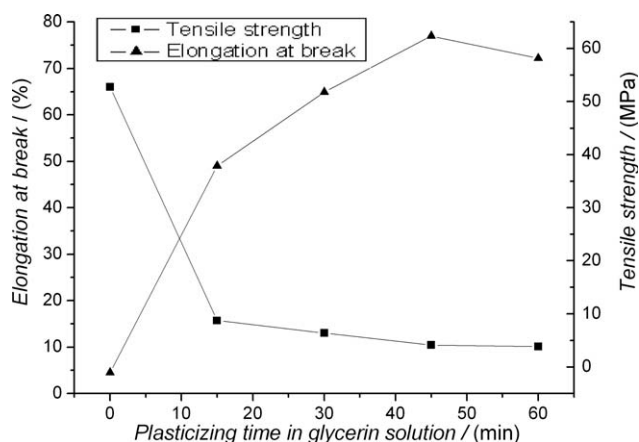


Figure 5 Mechanical properties of the regenerated cellulose films as a function of plasticizing time in glycerol solution.

TABLE I
Oxygen Permeability (OP) and Water Vapor Permeability (WVP) of the Cellulose Films Prepared Under Various Conditions

	Glycerol concentration in solution/(vol %) ^a						Plasticizing time/(min) ^b				
	5	10	15	25	35	45	0	15	30	45	60
OP × 10 ⁻¹⁵ / (cm ³ mm m ⁻² d ⁻¹ kPa ⁻¹)	0.121	0.107	0.102	0.062	0.026	0.017	0.133	0.094	0.062	0.037	0.032
WVP × 10 ⁻¹¹ / (g mm m ⁻² h ⁻¹ Pa ⁻¹)	0.022	0.023	0.024	0.025	0.030	0.038	0.021	0.023	0.025	0.028	0.033

^a The plasticizing time was 30 min.

^b The glycerol concentration in solution was 25 vol %.

35.0 vol %, the SEM image [as shown in Fig. 4(c)] showed clearly its coarse surface, indicating better toughness. These SEM images confirmed the results of mechanical properties obtained from Figure 3.

Plasticizing time is another key parameter during the diffusion process, and the longer plasticizing time means more plasticizer would diffuse and permeate into the composites system of cellulose/glycerol/H₂O. Figure 5 showed the mechanical properties of the regenerated cellulose films as a function of plasticizing time in glycerol solution. One could find that the tensile strength and elongation at break of the regenerated cellulose films showed the similar trends as those in Fig. 1, which could also be explained by the "plasticizer effect on the polymer theory."

Oxygen permeability (OP) and water vapor permeability (WVP) of the cellulose films are important for the films in food packaging fields. Table I showed the permeabilities of the cellulose films prepared under various conditions. It was observed that the cellulose films prepared without being treated by glycerol had the highest oxygen permeability (0.133 cm³ mm m⁻² d⁻¹ kPa⁻¹), and that oxygen permeability decreased slowly with increasing of glycerol concentration and plasticizing time. It was evident that such films with excellent oxygen barriers would be advantageous in food packaging or other fields as a kind of green packaging material. It should also be noticed from Table I that oxygen permeability and water vapor permeability presented an almost opposite trend, which was due to the difference of the molecules polarity in the system, according to the rule "similar-dissolve-mutually." When glycerol, hydrophilic molecular, was used as plasticizer, the permeability for polar molecule H₂O would increase with the concentration of glycerol. However, for nonpolar O₂ molecular, the addition of glycerol might fill in the gap between the macromolecule, hindering the permeation of oxygen molecular.

CONCLUSIONS

The novel regenerated cellulose packaging films were successfully prepared through the phase inversion in

[BMIM]Cl ionic liquid solvent. The results indicated the plasticization conditions had great effect on the structures and properties of cellulose packaging films. The tensile strength decreased rapidly with the addition of glycerol and prolongation of plasticizing time. While elongation at break of the regenerated cellulose films increased at first and then decreased with increasing of glycerol concentration and plasticizing time. Oxygen permeability of the regenerated cellulose films decreases slowly with increasing of glycerol concentration and plasticizing time, but water vapor permeability presented an almost opposite trend. The films prepared by using ionic liquid technology would be used in food packaging or other fields as a kind of green packaging material.

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