Materials Research Express

**PAPER**

Preparation of cellulose film in ionic liquid by high shearing and application in pineapple preservation

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Keywords: cellulose film, ionic liquid, shearing force, preservation

**Abstract**

In this study, the pineapple leaf cellulose film was prepared in ionic liquid by high shearing force and used for fresh-cut pineapple preservation. First, cellulose was dissolved in ionic liquid (1-butyl-3-methylimidazolium chloride ([Bmim]Cl)) using a high shear mixer. The regenerated cellulose was characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), fourier transformed infrared spectra (FT-IR), and thermo gravimetric analysis (TGA). Results showed that the cellulose was dissolved in liquid at room temperature with a high regeneration rate of more than 95% and for less than 2 min. It was suggested that the network of cellulose was destroyed by high shearing force. Then the cellulose film was obtained by casting on the glass plates. The mechanical properties of the films were evaluated by extension test with the tensile strength of 34 MPa. The proposed film was used for fresh-cut pineapple packaging. Results showed that it could significantly decrease weight loss and maintain the firmness of the pineapple, and thus, improve the quality of the fruit during storage. The findings demonstrate a facile biodegradable packaging route to improve food sustainability and reduce waste.

1. Introduction

Recently, biodegradable food packaging materials using biopolymers have been paid much attention as economic and environmental advantages compared with petroleum based plastic packaging materials [1, 2]. Among them, cellulose is environmental friendly and biodegradable, and it has been successfully used as a packaging material for food preservation [3, 4]. However, due to the strong inter- and intra- molecular hydrogen bonding network, cellulose does not dissolve in common organic and inorganic solvents to further form films. The traditional methods to dissolve celluloses are costly, potentially hazardous and not sustainable [5]. Recently, ionic liquids (ILs) have been successfully employed to process cellulose ascribed to its non-flammability, extremely low vapor pressure and high dissolution ability [6, 7]. However, the dissolution conditions of processing cellulose in IL are little harsh with higher temperature, longer time and less regeneration rate due to its high viscosity and high water absorption [8]. Therefore, several investigations have been carried out in order to increase the solubility of cellulose or to accelerate its dissolution time. Zhang reported that 1-allyl-3-methylimidazolium carboxylates had high cellulose solubility under room temperature. Results showed that solubility of cellulose in [Aminim][CH₃CH₂COO] was as high as 19.0 % at 30 °C [9]. In addition, microwave heating is an efficient heating method for processing wood in ILs [10]. It could cut down four times as the oiled heating. However, no matter heating mode, it is always energy consumption and in the accompany of cellulose degradation.

High-shear mixers are commonly used to disperse ingredients from one phase into another when ingredients are immiscible, and to improve dispersion of ingredients [11]. A common application of high-shear mixing is in the production of foods, such as the emulsification, and encapsulation [12–14]. O’Sullivan’s group
found out that high shear inline mixing provided the most efficient induction of powders. Therefore, it can be used for the dissolution of powders to form homogeneous solutions. As far as to our knowledge, few researches are focused on the dissolution of cellulose in ionic liquid by the high-shear mixers.

In this study, the pineapple leaf cellulose was successfully dissolved in ionic liquid by a high shear mixer with high regeneration rate and less time. Using this dissolution, the self-reinforced regenerated cellulose composite films were prepared. The characterization of film was measured by IR, XRD, SEM and TGA. Moreover, the cellulose film was applied on fresh-cut pineapple and their effects on fruit quality were investigated during storage.

2. Experimental

2.1. Materials
Pineapple leaf fibers were collected from local plantations by agricultural machinery research institute of Chinese tropical agriculture science academy. All chemical reagents were of analytical grade, purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). The ionic liquid of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was synthesized in previous study. Pineapples were bought at a supermarket and selected based on size and color, without signs of damage or decay.

2.2. Dissolution cellulose in ionic liquid
The pulverized pineapple leaf fibers were dried for 12 h at 60 °C. Firstly, 35 g L⁻¹ sodium hydroxyl solution was used to remove the lignin for 6 h at 95 °C, and then 1.5 % sulfuric acid was used to remove the hemicelluloses for 3 h at 100 °C. The solution was washed with distilled water until it was neutral, and then dried. The obtained cellulose was mixed with [Bmim]Cl in a multi-functional emulsifying dispersion machine (magic lab, IKA, German). After shearing rate with 16000 r min⁻¹ for two times, the cellulose was completely dissolved in ILs by rare eyes. The compared sample was cellulose dissolved in ionic liquid by microwave heating (130 °C, 500 W).

2.3. Preparation of cellulose film
Cellulose regenerated films were prepared according to the following procedure. The cellulose/[Bmim]Cl solution was flatted out on a glass plate (15 cm × 25 cm) after ultrasonic treatment for 10 min to get rid of air bubbles. After that, the degassed product was immersed in a certain glycerin solution for a certain time, and then washed with deionized water thoroughly to remove the residual ionic liquid. Finally, the obtained film was dried in a vacuum at 60 °C for 8 h.

2.4. Characterization
2.4.1. Particle size measurements analysis
The regenerated celluloses were diluted in deionized water by ultrasonic dispersion. The particle sizes and distribution of cellulose were surveyed by a photon correlation spectroscopy with a Nano-ZS (Malvern Instruments, UK).

2.4.2. Scanning electron microscopy measurements analysis
The morphology of regenerated cellulose was studied by scanning electron microscopy analysis (SEM). The samples were coated with gold palladium in a sputter coater, and then were observed by field-emission-type high-resolution scanning electron microscope (SEM, S-4800, Hitachi, Japan).

2.4.3. Fourier transform infrared spectrometry measurements analysis
Infrared spectra of cellulose were measured by a Fourier transform IR spectrometer (Spectrum GX-1, PE, USA). The spectra were recorded with the sum of 8 scans at a resolution of 4 cm⁻¹ in the range of 4000–400 cm⁻¹.

2.4.4. X-ray Diffraction (XRD) measurements analysis
Crystallinity of the samples was determined by X-ray diffraction method using a diffract meter (Bruker D8 Advance, Germany). The X-ray diffractor grams were recorded by continuous scanning mode in the angular range of 5°–45° (2θ) with a scanning speed of 4° min⁻¹. The crystallinity index (CI) was measured by Segal’s empirical method.
2.4.5. Thermal stability measurements analysis
The thermal stability of cellulose was carried out with a Synchronous Thermal Analysis (STA449C/4/G, Netzsch, Germany). The analysis was performed at a heating rate of 10 °C min⁻¹ range from 25 to 800 °C under nitrogen atmosphere with a flow rate of 1.0 ml min⁻¹.

2.4.6. Mechanical performance measurements analysis
The tensile strength of the regenerated cellulose films was measured by using a tensile testing machine (UT-2080, U-CAN, Taiwan) fitted with a 200 N load cell with the cross head speed of 0.5 mm min⁻¹. The samples were cut in the rectangular specimens with a width of 20 mm and length of 60 mm, and the initial distance between the grips was 20 mm. Five specimens of each formulation were tested, and the average values were calculated. The measurements were performed under room temperature.

2.5. Pineapple preservation
Fresh pineapples were cut into a certain piece by a shaped knife and then washed. It was coated by the obtained cellulose film and commercial polyethylene film (PE) for the storage at room temperature (25 °C) for several days. The unwrapped fruit was served as controls.

2.5.1. Weight loss
The weight loss of pineapple was determined by drying in an oven at 105 °C until to achieve stable weight. Results were reported as percentage of weight loss, according to following equation:

\[
\text{Weight loss} (\%) = \frac{(\text{initial weight} - \text{final weight})}{\text{initial weight}} \times 100
\]

2.5.2. Firmness
Firmness was measured by a texture tester (CT-3, Brookfield, USA) under TPA test mode. Each sample was taken for determination with a speed of 0.5 mm s⁻¹, a compression rate of 5 mm, and a triggering force of 0.07 N. The parallel determination was carried out for 3 times.

2.5.3. Total soluble solids
A total soluble solid (TSS) was determined using a digital refractor meter (WYT-15, Quangzhou, China). Ten grams of flesh were blended with 40 ml distilled water in a blender.

2.5.4. Vitamin C content
The Vitamin C content was measured by 2, 6-dichloroindophenol method. Extract the sample into juice 2 ml, add 2 ml 2 % oxalic acid solution, and then titrate with the calibrated 2, 6-dichloroindophenol solution to reddish color, and then parallel titrate for 3 times.

3. Results and discussion

3.1. Dissolution cellulose in ionic liquid by high shearing force
It is determinate that cellulose can be dissolved in ionic liquid at high temperature due to the disruption of cellulose hydrogen bond [19]. Literatures reported that the shearing force can also crack the network of the cellulose hydrogen bond [17]. Therefore, a high shear mixer might be worked during the dissolution. In this study, effects of shearing force and cellulose concentration are investigated.

3.1.1. Effects of shearing rate
Figure 1 shows that the regeneration rate and particle size of cellulose under different shearing rates from 10000 r min⁻¹ to 20000 r min⁻¹. From the results we can see that the regeneration rate of cellulose was all above 97 %, which was higher than the one under microwave heating mode [20]. It might be due to the mild shearing pretreatment, avoiding the degradation by the high temperature heating. Besides, when the shearing rate was increased up to 18000 rmin⁻¹, the network of cellulose was broken by the shearing force, and thus, particle size of cellulose gradually decreased. However, the cellulose was observed to be aggregated with increasing shearing rate because of the strong intermolecular interaction between molecular.

3.1.2. Effects of cellulose concentration
The effects of cellulose concentration on the regeneration rate and particle size of cellulose are investigated in figure 2. As can be seen, when the cellulose solution concentration was increased from 1 % to 5 %, the particle size of cellulose showed increased, while, the regeneration rate decreased from 98 % to 90 %. Results showed that
3.1.3. Effects of shearing times

Figure 3 shows the regeneration rate and particle size of cellulose under different shearing times. The particle size of cellulose decreased with the shearing times from one to three. It was indicated that more shearing force could destroy the interaction between the celluloses. However, the particle size of cellulose increased after four shearing times, due to the aggregation of particles. In addition, the regeneration time was less than 2 min, which was much shorter than the one under the microwave heating in our previous work [21].

3.2. Characterization

The regenerated cellulose by high shearing force (SC) was characterized by SEM, XRD, TGA, and FTIR analysis. Also, the original cellulose (OC) and the one by microwave heating dissolution (MC) were the comparison.
3.2.1. SEM analysis
The SEM photographs of three kinds of cellulose are shown in figure 5. The morphology of the material was significantly changed after dissolution, displaying a rough, and conglomerate texture [6]. Compared with MC (figure 4(b)), the SC (figure 4(c)) displayed a much denser texture due to the high shearing force, which would be favored to be modified.

3.2.2. XRD analysis
Figure 6 illustrated that the X-ray diffraction curves of three kinds of samples. The diffraction curve of native cellulose was typical cellulose structure (figure 5(a)). After dissolution, the diffraction curve of regenerated cellulose was the typical diffraction patterns of cellulose II by the presence of the broad crystalline peak at 11.7° and 21.7°. In addition, the crystalline index of shearing dissolution samples by Segal method was 36 %, which was lower than the MC samples (47 %) and the original one (76 %). It indicated that after shearing dissolution, the hydrogen bond interaction was broken more seriously and thus a lower crystalline index.

3.2.3. FTIR analysis
The FTIR spectra of three samples are shown in figure 6. The general similarity of three spectra indicated that there was with no new substance appeared. The characteristic O–H vibration stretching in the range of 3000–3600 cm⁻¹ for cellulose were blue shifted from 3423 cm⁻¹ to 3441 cm⁻¹ after shearing dissolution. It was indicated that the number of hydrogen bond interaction was weakened by high shearing [22]. Therefore, the network of cellulose was cracked, and thus, the crystallization area changed to the amorphous area and the crystallinity decreased. It was in agreement with the XRD results.
3.2.4. TG analysis

The thermal stability of three kinds of cellulose was also studied using TGA (figure 7). Regenerated cellulose after shearing dissolution showed high thermal decomposition temperature at 280.9 °C, lower than the other two celluloses. It suggested that cellulose presented a low thermal stability. This indicated a decrease in the crystallinity of cellulose because of the shearing treatment which in turn was a confirmation of the XRD data.

3.3. Preparation of cellulose film

After shearing dissolution, IL/cellulose solution was casted onto a glass plate and then dipped in glycerin solution. Consequently, the IL was removed and the cellulose film was vacuum dried.

During the shearing dissolution, the shearing force was the main influence factors, and so did the process of the film forming. Figure 8 shows the effects of the shearing rates on the tensile strength of cellulose film. As the
shearing rate increasing, the tensile strength of cellulose film was reduced. This was because that the hydrogen bonds between the cellulose molecules were ruptured and the binding force weakened due to the shearing action. The rigid structure of cellulose film was softened, so the mechanical properties reduced.

Besides, the other conditions, such as the cellulose concentration, glycerin concentration, regeneration time, regeneration temperature were investigated (Data were not shown). Results showed that glycerin could increase the mechanical properties, while more cellulose concentration, the regeneration time and temperature could reduce the tensile strength. Therefore, the optimal condition was 2% cellulose/IL solution after 16000 r min\(^{-1}\) during the shearing dissolution, and then cruded in 2% glycerin for 24 h at 5°C. The tensile strength could be calculated as 34 MPa.

3.4. Effects of film on the storage study of fresh-cut pineapple

Pineapple is a common fruit that is relatively prone to rapid decay compared with most fruits. In this study, the proposed film was used to pack the fresh-cut pineapple. The influences of film on shelf life and quality attributes of pineapple during storage at ambient temperature are investigated in table 1.

Weight loss of pineapple wrapped with cellulose film was slower than that without any wrapping, while a little higher than the commercial PE film. It was due to the more pore structure and high-water vapor
permeabilities of cellulose film. While, as weight loss was increased, firmness was decreased. It indicated that the samples with film presented slightly higher firmness compared to control.

The total soluble solids of pineapple without film increased with time because the fruit lost approximately much more water content. Therefore, it was indicated that the cellulose film as well as the PE film could inhibit fruit soluble solids content rise, making the fruit quality improved.

The Vitamin C content in pineapple in all pretreatment decreased during storage. However, the decline rate was relatively slower in cellulose and PE film. Results showed that the cellulose film can effectively delay the loss of vitamin C in the process of storage, which was conducive to the preservation of vitamin C content in fruit.

4. Conclusion

In this study, the pineapple leaf cellulose film was prepared and used to pack the fresh-cut fruit. The cellulose could be dissolved in ionic liquid by high shearing pretreatment at room temperature. The regeneration rate was almost more than 95 %, and the dissolution time was less than 2 min. The dissolution mechanism was suggested that the number of hydrogen bond interaction was weakened by high shearing force, and the network of cellulose was destroyed, leading to dissolution in ionic liquid. After casting, the cellulose film was obtained and the effects on the storage of pineapple were investigated. The cellulose film could effectively slow down the fruit firmness and vitamin C content, as well as inhibit the weight loss rate and the rise of the soluble solids. Therefore, the proposed film could improve the quality of preservation of fresh-cut fruit.

Acknowledgments

We gratefully acknowledge the financial support from the Central Public-interest Scientific Institution Basal Research Fund for Chinese Academy of Tropical Agricultural Sciences (1630122017018) and the national natural science foundation of China (No. 51805336). The work is also partially supported by Natural Science Foundation of Liaoning Province (No. 2019-ZD-0687) and foundation of Key Laboratory of Tropical Crop Products Processing of Ministry of Agriculture and Rural Affairs, P. R. China (KFKT201902).

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