Carbohydrate Polymers 121 (2015) 71–78

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Comparison of physical properties of regenerated cellulose films fabricated with different cellulose feedstocks in ionic liquid

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ARTICLE INFO

Article history:
Received 29 October 2014
Received in revised form
23 November 2014
Accepted 27 November 2014
Available online 31 December 2014

Keywords:
Cellulose film
Ionic liquid
Mechanical property
Thermal stability

ABSTRACT

With the serious "white pollution" resulted from the non-biodegradable plastic films, considerable attention has been directed toward the development of renewable and biodegradable cellulose-based film materials as substitutes of petroleum-derived materials. In this study, environmentally friendly cellulose films were successfully prepared using different celluloses (pine, cotton, bamboo, MCC) as raw materials and ionic liquid 1-ethyl-3-methylimidazolium acetate as a solvent. The SEM and AFM indicated that all cellulose films displayed a homogeneous and smooth surface. In addition, the FT-IR and XRD analysis showed the transition from cellulose I to II was occurred after the dissolution and regeneration process. Furthermore, the cellulose films prepared by cotton linters and pine possessed the most excellent thermal stability and mechanical properties, which were suggested by the highest onset temperature (285 °C) and tensile stress (120 MPa), respectively. Their excellent properties of regenerated cellulose films are promising for applications in food packaging and medical materials.

1. Introduction

Nowadays, the public have more and more concerns with the environmental problems such as "white pollution" and the decrease in natural resources. However, the demand for petroleum based materials is increasing day by day (Satgé, Granet, Verneuil, Branland, & Krausz, 2004; Mahmoudian, Wahit, Ismail, & Yussuf, 2012). Therefore, more efforts on the exploitation of new materials from biomass resources as alternative for petroleum based materials have been made in recent years (Liu, Pang, Zhang, Wu, & Sun, 2013).

Cellulose is the most abundant natural polymer and renewable resource on the earth (Jia, Li, Ma, & Sun, 2012). As the prime source of biofuels and value-added product, cellulose is considered as a promising alternative to non-renewable natural resources for the sustainable supply of fuel and chemicals in the future due to its significant industrial applications and unique physicochemical properties like biocompatibility and biodegradability (Klemm, Heublein, Fink, & Bohn, 2005; Jia, Li, Ma, Sun, & Zhu, 2011; Wan, Wu, Yu, & Wen, 2006). Recently, extensive research is being carried out worldwide to identify and study chemical or biological transformation pathways to convert cellulose into biofuels, feedstock chemicals and bio-based materials (Turner, Spear, Holbrey, & Rogers, 2004). Until now, several successful studies about cellulose fibers, beads, films, and cellulose derivatives have been reported (Luo & Zhang, 2009; Zhang et al., 2009).

Nevertheless, application of cellulose is limited due to the rather complex fashion of cellulose where an extended intra- and intermolecular network of hydrogen bonds is indicated as the basis of cohesion between cellulose molecules. It is believed that intramolecular hydrogen bonds provide chain stiffness, while, on the other hand, intermolecular hydrogen bonds allow the linear polymer molecules to assemble in sheet-like structures (Medronho & Lindman, 2014). Therefore, such a stable structure of cellulose resulted in the insolubility of the biopolymer in almost all common organic and inorganic liquids. Various more or less exotic solvents were developed to overcome this problem and to make cellulose accessible for tailored modification (Liebert, Heinze, & Edgar, 2010). Over the past decades, several cellulose solvent systems were reported for dissolving cellulose, such as *N*-methylmorpholine-*N*-oxide (NMMO) (Swatloski, Spear, & Holbrey, 2002), ammonium fluorides/dimethylsulfoxide (DMSO) (Köhler & Heinze, 2007), and NaOH/urea aqueous solution (Tang, Chang, & Zhang, 2011). Although several of these as solvents for fabricating of cellulose films, fibers, beads and few as homogeneous reaction media for the preparation of cellulose derivatives had been

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http://dx.doi.org/10.1016/j.carbpol.2014.11.067
0144-8617/

successfully investigated. These solvents possess several undesired properties, like uncontrollable side reactions, limited dissolving capability, high toxicity and thermal instability. Therefore, there is still a strong demand for new "green" cellulose solvents for making cellulose-based materials under homogeneous conditions (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009; Pang, Liu, Zhang, Wu, & Sun, 2013).

Recently, room temperature ionic liquids (ILs) as new "green" solvents has been widespread concerned in the public due to their various advantages such as eco-friendly, good chemical and thermal stability, lower hydrophobicity, low flammability, low melting point and ease of recycling (Peng, Ren, & Sun, 2010). Furthermore, it had also been reported that ionic liquids exhibited outstanding dissolving capability for cellulose (Liu et al., 2013). The application of cellulose was fueled by the discovery of ILs as proper cellulose solvents. It had been proved that the unique properties of ILs can be permitted transform of cellulose into a broad variety of new, eco-friendly materials for numerous commercial purposes such as bio-plastics, and also into high value products (Liebert et al., 2010). The fabrication of chitin/cellulose composite films using ionic liquids of 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-allyl-3-methylimidazolium bromide (AmimBr) as solvents had been investigated by Takegawa, Murakami, Kaneko, and Kadokawa (2010). The results showed that BmimCl was good solvent for the regeneration of microcrystalline cellulose, the obtained cellulose films were transparent and flexible. Moreover, with the increase in the proportion of chitin and cellulose, the mechanical properties of the films were significantly improved. In addition, the microcrystalline cellulose (PMCC)/nanocrystalline cellulose (NCC) composite films with a significant enhancement in thermal stability and mechanical properties was also studied by Ma, Zhou, Li, and Ou (2011). Furthermore, different film materials possessed various properties had been successfully prepared and investigated in previous reports(Peng, Ren, Zhong, & Sun 2011; Zhong, Peng, Yang, Cao, & Sun, 2013; Hameed, Guo, Tay, & Kazarian, 2011).

At present, extensive work has been done to study the commercial potential of celluloses-based materials using different ionic liquids. However, the exploitation of cellulose-based materials using different kinds of biomass as raw materials in ionic liquid has not been reported yet. In this study, in order to compare the structure and properties of cellulose films prepared from different kinds of cellulose, four kinds of cellulose including pine, cotton, bamboo cellulose and microcrystalline cellulose (MCC) were chosen as raw materials to elaborate eco-friendly cellulose films with ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc) as solvent. In order to evaluate the desirability of their applications in the packaging and functional materials fields, the morphology, surface and mechanical properties of different kinds of cellulose regenerated films were comparatively characterized by SEM and AFM, contact angle measurement and tensile stress. This work presents a facile approach to environmentally friendly prepare high-strength cellulose films with different kinds of cellulose as raw materials.

2. Materials and methods

2.1. Materials

In order to compare the film properties obtained from different cellulose raw materials, four kinds of cellulose raw materials including cotton linter, microcrystalline cellulose and raw cellulose materials from pine and bamboo were used in this study. Cotton linters were kindly supplied by Silver Hawk Fiber Corporation (Shandong province, China). Microcrystalline cellulose (MCC) was purchased from Sinopharm Chemical Reagent Corporation Limited. The raw cellulose materials from pine and bamboo were obtained by delignification followed by removal of hemicelluloses, and the procedures were consistent with the literature described by Liu, Sun, Zhang, and Ren (2007). Ionic liquid, 1-ethyl-3-methylimidazolium acetate (EmimAc), with purity ≥95%, was purchased from Lanzhou Institute of Chemical Physics. All chemicals were analytical grade reagents and used as received without further purification.

2.2. Preparation of regenerated cellulose films

Cellulose regenerated films were prepared according to the following procedure. The mixtures (around 5 wt.%) were prepared by dissolving the different kinds of cellulose samples (5 g) in EmimAc (100 g) under magnetic stirring at 80 °C for 0.5 h. The mixtures were then degassed by being kept standing at 80 °C for 1 h. After that, the cellulose films were fabricated by casting the homogeneous mixture on glass plate. The obtained cellulose films were soaked in deionized water and washed thoroughly to remove ionic liquid. Finally, the cellulose films were dried in atmosphere for 48 h and stored in moisture controlled desiccators.

2.3. Characterization

The degrees polymerization (DP) of all the cellulose raw materials and regenerated cellulose films were measured by TAPPI test method using copper ethylenediamine (CED) as a solvent and a capillary viscometer to give an indication of the average degree of polymerization of the cellulose materials. The viscosities determined as centipoises (cP) were converted to degree of polymerization (DP) based on the following formula:

$$DP^{0.905} = 0.75 \times [954 \times \log(X) - 325],$$

where X = TAPPI viscosity in cP.

Film thickness was studied with a micrometer (Lorentzen & Wettre, precision 1 μm). The thickness of six different locations on film was detected, and the average values were used in the calculation of the mechanical test.

The morphology of cellulose films were studied by scanning electron microscopy analysis (SEM). The regenerated cellulose film samples were coated with gold palladium in a sputter coater (E-1010, Hitachi, Japan), and then were observed with a scanning electron microscope (S-3400N, Hitachi, Japan) at acceleration voltages of 10 kV.

Atomic force microscopy (AFM) (SPM-9600, Shimadzu) was used to study the nano-morphology of film surface. Small pieces of films were glued onto metal disks and attached to a magnetic sample holder located on the top of the scanner tube. Phase images were recorded under ambient air conditions. All of the images were recorded in contact mode in air using silicon cantilevers.

Infrared spectra of cellulose film samples were recorded with a Fourier transform IR spectrometer (FT-IR TENSOR27, Germany) in ATR mode. The scan range was 400–4000 cm^{-1}, and the resolution rate was 2 cm^{-1}.

The surface free energies of the cellulose films were measured by the contact angles analysis (Krüss DSA100 Germany). The measurements were performed at room temperature by the sessile drop method using a goniometer equipped with a high-speed camera (OCA 20, Data physics Ltd., Germany).

Crystallinity of the regenerated cellulose film samples was determined by X-ray diffraction method using XRD-6000 instrument (Shimidzu, Japan). The X-ray diffractograms were recorded in reflection mode in the angular range of 5–40° (2θ) with a scanning speed of 5°/min.

Thermal analysis was determined by using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (SDT Q600 TGA/DSC, TA Instrument). The