Cellulose-based Films Prepared Directly from Waste Newspapers via an Ionic Liquid

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Abstract

Waste newspapers, composed of cellulose (>60 wt%), lignin (~15 wt%), hemicellulose (~10 wt%) and other additives, are one kind of low-cost, easily collected and abundant resources. In order to get value-added products from this waste, in this work an attempt was made to directly convert waste newspapers into cellulose-based films by employing an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) as a solvent. Most of the organic substances in this waste were dissolved quickly in AmimCl under mild conditions, and then coagulated and dried. Although containing lignin, hemicellulose and inorganic additives, the regenerated cellulose-based films were smooth, compact and semi-transparent, and exhibited good mechanical properties. If the newspaper/AmimCl solution was filtered to remove undissolved inorganic substances, the regenerated

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films became transparent and had a tensile strength of 80 MPa. Thus, this work provides a new, simple and highly efficient way to achieve a high-valued utilization of waste newspapers for packaging and wrapping.

Key words: Waste newspaper, ionic liquid, cellulose based film, cellulose

Introduction

With the depletion of global petroleum resources and the wide concerns about environmental problems, the utilization of renewable resources has attracted more and more attention in recent years (Cao et al., 2006). As the most abundant renewable natural resource in the world, cellulose has a host of current and potential uses in many fields (Chen et al., 2006; Kadokawa et al., 2009; Klemm et al., 2005), because it can be converted into various regenerated materials (fibers, films, food casings, sponges, etc.) and cellulose derivatives (ethers, esters and grafting copolymers).

However, cellulose is neither meltable nor soluble in common solvents due to its well-developed hydrogen bonding network and partial crystalline structure (Cai & Zhang, 2006; Klemm et al., 2005; Kuang et al., 2008). Currently, most of regenerated cellulose materials are produced by the traditional viscose process, which requires much energy and causes heavy pollution. Therefore, adopting simple, effective and environmentally friendly solvent systems is a hot topic in cellulose chemistry. Many new solvent systems and dissolution methods were

investigated for cellulose dissolution, such as LiCl/N,N-dimethylacetamide system (Roder et al., 2001), NaOH/urea (Cai et al., 2007; Lue et al., 2011), NaOH/thiourea (Cai et al., 2007; Lue et al., 2011), N-methylmorpholine-N-oxide (NMMO) (Fink et al., 2004), ionic liquids (Swatloski et al., 2002; Zhang et al., 2005; Zhu et al., 2006), etc. It is worth mentioning that room temperature ionic liquids (ILs) as a new type of cellulose solvents have advantages of superior dissolving capacity, easy recyclability and good recoverability (Swatloski et al., 2002; Zhang et al., 2005; Zhu et al., 2006; Rahatekar et al., 2009). Moreover, ILs can effectively dissolve cellulose without any activation or pre-treatment steps, thus they are regarded as a class of promising cellulose solvents. Recently, ILs has exhibited great potential applications in cellulose fibers and films industry. (Zhang et al., 2005; Cao et al., 2009; Rahatekar et al., 2009; Zavrel et al., 2009).

So far, the main sources of cellulose in commercial production are high-grade cotton linters and wood pulp, which makes the raw material very expensive. In contrast, the low-cost lignocellulose, which is available in large quantities and widely cultivated in the world, has become attractive. Agricultural wastes, woody biomass, and related resources form promising feedstock for cellulose industry, because they have been underutilized until now. For example, the post-consumer newspapers, containing a large amount of cellulose, lignin and

hemicellulose, contributes close to seven percent of the United States' solid waste (Rawski & Cole, 1996). In China, millions of tons of waste newspapers are generated annually. Currently, most of waste newspapers are simply used as conventional and low-value products, such as recycled newspaper, boxboard, compost, paper insulation, animal bedding and ceiling tile. Therefore, effective utilization of this commonly available biomass resource to prepare high-value cellulose-based materials is an interesting and meaningful task.

Few attempts were made to prepare cellulose materials from waste newspapers during the past several years. After removing the lignin in the newspaper, Rodrigues Filho et al. produced cellulose acetate from a homogeneous reaction, and further prepared membranes of cellulose acetate with a good thermal stability (Rodrigues Filho et al., 2008). Jin et al. prepared cellulose-based aerogels successfully by treating waste newspapers with trimethylchlorosilane (Jin et al., 2015). The resultant aerogels exhibited good absorption performance for oils and organic solvents. Mohamed et al. isolated nanocrystalline cellulose (NCC) through an acid hydrolysis process from recycled newspapers (Mohamed et al., 2015a). The NCC from newspapers was expected to be used as inexpensive bio-based filler in polymer nanocomposites. Furthermore, after completely removing lignin of recycled newspapers, Mohamed et al. also prepared regenerated cellulose membranes via NaOH/urea aqueous

solution system (Mohamed et al., 2015b). Ünlü et al. used the recovered cellulose from newspapers to prepare carboxymethylcellulose successfully in an aqueous alkaline medium without additional organic solvents (Ünlü, 2013).

In this work, we used an ionic liquid, 1-allyl-3-methylimidazolium chloride (AmimCl) as the solvent to dissolve waste newspapers without deliberately removing lignin and hemicellulose. Then, regenerated cellulose-based films with good mechanical properties were obtained after coagulation and drying processes. This study achieves a full use of waste newspapers to prepare high-value cellulose-based films, and thus provides a new choice to replace the traditional high-grade dissolving pulp with the low-value waste newspapers.

Experimental

Materials

Waste newspapers were obtained from the market. Microcrystalline cellulose (MCC, Vivapur 101) with degree of polymerization of 220 was purchased from Beijing Fengli Jingqiu Commerce and Trade Co., Ltd. All the cellulose samples used were dried in vacuum at 100 °C for 12 h before using. The AmimCl was synthesized as described in our previous work (Zhang et al., 2005). All other chemicals were of analytical grade and used as received.

Pretreatment of Waste Newspapers

In order to remove ink and glue, waste newspapers (WNP) were pretreated by a series of chemical extraction (Wang et al., 2013). Initially, WNP were cut into small pieces (1~2 cm) and treated with 2 wt% sodium hydroxide (NaOH) solution at 90 °C for 2 h (Figure S1A). Subsequently, the samples were cyclically treated twice using the acidified sodium chlorite (NaClO₂) solution at 75 °C for 2 h (Figure S1B and S1C). Finally, the samples were treated in 2 wt% potassium hydroxide (KOH) solution at 90 °C for 2 h (Figure S1D). The pretreated waste newspapers (p-WNP) were washed with deionized water until a neutral pH was reached. Finally, p-WNP were dried and kept in vacuum.

Preparation of regenerated cellulose-based films

Scheme 1. The preparation procedure of regenerated cellulose-based films from waste newspapers.

The preparation procedure of regenerated cellulose-based films is shown in Scheme 1. After the pretreatment, 2 g of p-WNP was dispersed into 48 g of AmimCl. Then, the mixture was heated at 80 °C for 3 h under vigorous mechanical stirring, so that a homogeneous 4 wt% p-WNP/AmimCl solution was obtained. The resultant solution was cast onto a glass plate with a spreader to obtain a 0.5 mm thick layer, and immediately immersed into a coagulation bath (deionized water) to form a cellulose-based hydrogel, which was named as Hydrogel. The cellulose-based hydrogel was then washed at least five times with distilled water until the residual AmimCl was removed completely. Finally, after drying at 60 °C, the regenerated cellulose-based film (named as Film) was obtained. The yield of the process was about 80-85 %.

For comparison, in another experiment, the p-WNP/AmimCl solution was filtered with a sintered funnel (G4 porosity frit) to remove the inorganic additives. The filtered solution was regenerated into films in a similar way as above-mentioned. The obtained cellulose materials through filtering were named as f-Hydrogel and f-Film, respectively.

Characterization

The chemical compositions in WNP and p-WNP

Table 1. The mass fraction of cellulose, hemicellulose, lignin and other additives in WNP and p-WNP.

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Other additives (%)
WNP	62.70	9.52	14.05	13.73
p-WNP	74.42	7.79	11.60	6.19

Automatic fiber analyzer (ANKOM 2000i, America) was used to characterize the mass fraction of cellulose, hemicelluloses and lignin in WNP and p-WNP. The results are shown in Table 1.

Physicochemical characterization of waste newspapers cellulose

The degree of polymerization (DP) of cellulose in WNP and regenerated cellulose-based films was determined by Ubbelodhe viscometry using cupriethylenediamine as the solvent at 25 °C (Bianchi et al., 1985; McCormick et al., 1985; Rodrigues Filho et al., 2008; Terbojevich et al., 1985). The DP of cellulose in WNP and Film was 380 and 277, respectively.

Polarized optical microscopy (POM) of p-WNP/AmimCl solution

The solubility of p-WNP in AmimCl was assessed by using a Leica DMLP polarizing microscope (Leica Company, German). A droplet of solution was sandwiched between a clean glass slide and a cover slip, for observing the dissolving situation.

Ultraviolet and Visible (UV-Vis) Spectroscopy of the regenerated cellulose-based films

An Ultraviolet spectrophotometer TU-1901 (Beijing Purkinje General

Instrument Co., Ltd., China) was used to characterize the transparency of films.

Mechanical testing

The tensile strength of the regenerated cellulose-based films was measured on a universal testing machine (Instron 3365, UK) at a crosshead speed of 5 mm·min⁻¹. The specimens with length 50 mm and width 10 mm were used in this test. A gauge length of 25 mm was maintained. For each sample, at least five specimens were tested, and the average value was reported. The mechanical test was done by referring to the standard of ASTM D-882.

Morphology of the regenerated cellulose-based films

Scanning electron microscopy (SEM) was recorded by a Hitachi S-4800 microscope (Japan). The samples were quenched in the liquid nitrogen. Then, the cross-sections were sputter-coated with a thin layer of platinum before observation.

Wide-angle X-ray diffraction (WAXD) of the WNP, p-WNP and regenerated cellulose-based films

The X-ray diffraction patterns with CuK_a Radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 200 mA were recorded at a scan speed of 3 °/min from 5° to 40° (2 θ) with an X-ray diffractometer (D/MAX-2500, Rigaku Denki, Japan).

Fourier transform infrared (FTIR) spectra of the WNP, p-WNP, and regenerated cellulose-based films

A Fourier transform infrared spectrometer (FTIR PE-2000, Perkin-Elmer, the United States) at a resolution of 4 cm^{-1} and 32 scans was used to characterize the chemical structure of samples.

Thermogravimetric analysis (TGA) of the WNP, p-WNP, and regenerated cellulose-based films

The thermal decomposition behavior of the samples was investigated by using a thermogravimetric analyzer (Pyris 1, Perkin-Elmer) under nitrogen atmosphere at a heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$.

Results and Discussions

Pretreatment of Waste Newspapers

In order to remove additives such as ink and glue, WNP were pretreated by necessary chemical processes. After sodium hydroxide (NaOH) solution treatment, WNP suspensions were yellow in color (Figure S1A), then turned white after acidified sodium chlorite (NaClO_2) solution treatment (Figure S1B and S1C). Finally, after potassium hydroxide (KOH) solution treatment, the WNP became fluffy (Figure S1D), which facilitated the dissolution.

Dissolution of Pretreated Wasted Newspapers in AmimCl

Figure 1. POM micrographs of the p-WNP in AmimCl at 80 °C after 0 h (A), 1 h (B), 2 h (C) and 3 h (D).

POM was used to probe the dissolution process of the p-WNP in AmimCl, as shown in Figure 1. It can be seen that p-WNP consisted of many microfibers with diameters of 10-50 μm . As time went on, the number of undissolved fibers decreased. At the end of 3 h duration, a relatively homogeneous clear solution was obtained. These results indicate that most of the organic substance in the p-WNP was dissolved quickly in AmimCl under the mild conditions.

Before and after this dissolution process, the DP of cellulose was measured by the viscosity method with cupriethylenediamine as the solvent. DPs of cellulose in the p-WNP and the regenerated

cellulose-based film (Film) were 380 and 277, respectively. It means that the cellulose only had a light degradation during the dissolution process. Moreover, the DP of cellulose in the regenerated cellulose-based film was higher than that of cellophane (DP~230) produced by the traditional viscose process. Thus, the regenerated cellulose films are expected to possess good mechanical properties.

The p-WNP/AmimCl solution was cast on a glass plate, coagulated, washed and dried to obtain regenerated cellulose-based films (Figure S2). The optical photographs of regenerated cellulose-based gels and films are shown in Figure 2. It can be noted that the regenerated cellulose-based gel (Hydrogel, Figure 2A) and film (Film, Figure 2C) were translucent because of some inorganic additives. When the inorganic additives were filtered from the p-WNP/AmimCl solution, the highly transparent gel (f-Hydrogel, Figure 2B) and film (f-Film, Figure 2D) were obtained. The UV-Vis transmittance of cellulose-based films is increased by filtration from 20-30 % (Film) to 80-90 % (f-Film), as shown in Figure S3. These two kinds of films can meet different demands in industry, and show their potential applications in packaging and wrapping fields where optical transparency requirement is not too high, such as packaging tapes, wrapping papers and so on.

Figure 2. Photographs of regenerated cellulose-based gels and films with and without a filtration of the p-WNP/AmimCl solution. A: Hydrogel, B: f-Hydrogel, C: Film, D: f-Film.

Figure 3. XRD profiles of MCC, WNP, p-WNP, Film and f-Film.

The X-ray diffraction profiles of MCC, WNP, p-WNP, and regenerated films are shown in Figure 3 to display more information about the crystalline phase in these samples. Clearly, the XRD profiles of MCC,

WNP and p-WNP show well-defined peaks at $2\theta = 14.7$, 16.8 and 22.7° , which were assigned to (1-10), (110), and (200) lattice planes of cellulose I (Cao et al., 2010; Mohamed et al., 2015b). After dissolution and regeneration of p-WNP, the XRD profile of the Film gives a broad peak at $2\theta = 20.0^\circ$ and two narrow peaks at $2\theta = 12.5$ and 25.0° , while that of the f-Film exhibits only a main and broad peak at $2\theta = 20.0^\circ$. The broad peak ($2\theta = 20.0^\circ$) is a overlapped peak of two peaks of cellulose II at 20.1° (110) and 21.9° (200) and the peak of amorphous cellulose at 17.3° , indicating there is a crystal form transformation (from cellulose I to cellulose II) during the dissolution and regeneration process (Oh et al., 2005). The narrow peaks at $2\theta = 12.5^\circ$ and 25.0° are attributed to the lattice planes of SiO_2 inorganic additives. Therefore, these two narrow peaks disappear in the XRD profile of the cellulose-based film (f-Film) after the filtration of the p-WNP/AmimCl solution.

Figure 4. FTIR spectra of MCC, WNP, p-WNP, Film and f-Film.

All of the FTIR spectra of WNP, p-WNP, Film and f-Film (Figure 4) are similar with that of MCC, one kind of representative purified cellulose. In addition, compared with the FTIR spectrum of MCC, other four FTIR spectra show an obvious new broad peak at 1510-1720 cm^{-1} , corresponding to an overlapped peak of the characteristic peaks of lignin (1510 cm^{-1} , aromatic ring stretch) and hemicellulose (1740 cm^{-1} , C=O stretch), and a new tiny peak at 1248 cm^{-1} , a characteristic peak of lignin (Himmelsbach et al., 2002; Kaparaju & Felby, 2010; Cao et al., 2010). Therefore, the major component of WNP, p-WNP, Film and f-Film was cellulose. Meanwhile they contained lignin and hemicellulose, which was consistent with the results from the automatic fiber analyzer (Table 1 and Table S1).

It is noteworthy that, in FTIR spectra of WNP, p-WNP and Film, there was a new tiny peak at 798 cm^{-1} , which is attributed to the Si-O symmetrical stretching vibration. After the filtration of p-WNP/AmimCl solution, the tiny peak at 798 cm^{-1} disappeared in the FTIR spectrum of f-Film. Thus, the major component of the inorganic additives was SiO_2 , which was consistent with the XRD results. After the filtration, most of the SiO_2 was removed from the p-WNP/AmimCl solution, so there was few left in the f-Film.

In FTIR spectra of cellulose, the O-H stretching peak ($3000\text{-}3700\text{ cm}^{-1}$) and C-H stretching peak are sensitive to the crystalline state of the samples. In WNP, the maximum absorption of the O-H stretching was located at 3333 cm^{-1} . After the dissolution and subsequent regeneration, the O-H stretching peak shifted to higher wavenumber, 3351 cm^{-1} for Film and 3353 cm^{-1} for f-Film. Accordingly, the C-H stretching peak at 2896 cm^{-1} for WNP shifted to lower wavenumber, 2888 cm^{-1} for Film and 2890 cm^{-1} for f-Film, respectively. Furthermore, the absorption band at 1110 cm^{-1} , which was strong in the spectrum of original WNP, diminished in Film and f-Film. These results indicate that a change of the hydrogen-bonding structure and crystal form occurred during the dissolution and regeneration process (Cao et al., 2010), in conformity with the XRD results.

In addition, compared with the FTIR spectrum of original WNP, no new peaks appeared in the FTIR spectra of the regenerated films (Film and f-Film). Obviously, it was a physical dissolution process of WNP in AmimCl. In other words, AmimCl is a non-derivatizing solvent for WNP. TGA is an important method for characterizing the thermal stability of polymers and polymer composites. Figure S4 demonstrates the thermal stability of waste newspapers and regenerated cellulose-based materials. We can see clearly that the thermogram curves and differential thermogram curves of the raw materials (WNP and p-WNP) and the products (Film and f-Film) are almost entirely the same. The onset decomposition temperature (T_{onset}) and the temperature of maximum weight loss rate (T_{max}) of all samples are about 340 °C and 380 °C, respectively. That means the regenerated cellulose-based films exhibited high thermal stability, which was as good as that of native cellulose materials.

In addition, from Figure S4A, it is clear that the residue weight of WNP, p-WNP and Film was more than that of f-Film at 650 °C. This phenomenon indicates the existence of inorganic substances in WNP, p-WNP and Film. After the filtration of the p-WNP/AmimCl solution, most of the inorganic substance was removed, so the f-Film gave a less residue weight than WNP, p-WNP and Film. This result accords with the XRD and FTIR results in Figure 3 and 4.

Figure 5. Stress-strain curves of regenerated cellulose-based films (Film and f-Film).

The mechanical properties of materials directly correlate with their industrial applications. And hence, the mechanical properties of regenerated cellulose-based films were evaluated. The typical stress-strain curves of these regenerated films are shown in Figure 5. Generally, the tensile strength of polymer materials directly depends on their degree of polymerization (DP). The DP of cellulose, the major component in original WNP, was 380. After the pretreatment, dissolution and regeneration processes, the cellulose in Film only had a light degradation. The DP of its cellulose was still as high as 277, higher than that of cellophane (DP = 230) prepared by a harsh viscose process. Hence, the regenerated cellulose-based films (Film and f-Film) possessed high tensile strengths of 70-80 MPa which are comparable to pure cellulose

films. Moreover, compared f-Film with Film, it can be seen that the inorganic substances decreased the tensile strength from 80 MPa to 70 MPa. It should be noted that the tensile strengths of these regenerated cellulose-based films are much higher than those of conventional commercial polyolefin films, such as polyethylene (PE) and polypropylene (PP), of which the tensile strengths are often in a range of 20-40 MPa) (Cao et al., 2010). The tensile elongation of the obtained cellulose-based films is about 2-4 %, which is similar with cellulose films prepared with ionic liquids (Pang et al., 2013) and other solvent systems (Zhou et al., 2002). Because cellulose has rigid backbone structure, the pure cellulose film is often brittle. However, the toughness of cellulose film can be effectively improved by adding plasticizers, such as glycerol, into washing bath during the preparation process (Zhu et al., 2013). Thus, these regenerated cellulose-based films could replace both PP and PE films for packaging and wrapping purposes in some fields. Compared to non-biodegradable PP and PE, these regenerated cellulose-based materials are fully biodegradable, so that the rest of these packaging materials can be easily deposited on landfill sites.

Figure 6. SEM images of the regenerated cellulose-based films (Film and f-Film). A: the surface of Film, B: the surface of f-Film, C: the cross section of Film, D: the cross section of f-Film.

In order to study the morphology of regenerated cellulose-based materials, SEM micrographs were recorded, as shown in Figure 6. It can be seen that, Film displayed a relatively homogeneous microstructure from the interior to the surface, and was smooth and dense. After the solution filtration, f-Film had more homogeneous microstructure, and displayed a smoother and denser texture, indicating that most of the inorganic particles were removed during the filtration.

Conclusions

By using low-cost waste newspapers (WNP) instead of high-grade pulp as the raw material, regenerated cellulose-based films with good

mechanical property have been successfully prepared. WNP could be directly dissolved in an ionic liquid AmimCl without deliberately removing the lignin, hemicellulose and inorganic substances beforehand. The regenerated cellulose-based films were smooth, compact, and transparent or semi-transparent, depending upon the filtration of the p-WNP/AmimCl solutions or not. They exhibited good mechanical properties, such as high tensile strengths up to 80 MPa.

A deeper analysis has lead to more understanding about this route. FTIR analysis showed that the regenerated cellulose-based films contained cellulose, hemicellulose, lignin, and inorganic SiO₂. Moreover, AmimCl was a non-derivatizing solvent for WNP. The XRD patterns indicated a crystal form transformation (from cellulose I to cellulose II) occurred during the dissolution and regeneration processes. TGA results demonstrated that regenerated cellulose-based materials possessed high thermal stability similar to that of the original WNP. Therefore, the present work provides a simple and effective method to convert low-grade cellulose resource into high value cellulose-based products.

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