

IONIC LIQUID BASED ON ALKYL IMIDAZOLIUM CATION: SYNTHESIS AND APPLICATION

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A novel ionic liquid (NIL) was successfully synthesized using N-vinylimidazole and 2-chloroethanol and applied to reed cellulose as a green and recyclable solvent. The structure of the NIL was characterized by Fourier transform infrared (FT-IR) spectroscopy and hydrogen nuclear magnetic resonance (^1H NMR). The chemical structure, crystalline structure, thermostability and surface morphology of the reed treated by NIL (TR) and the untreated reed (NR) were investigated by FT-IR, X-ray diffraction (XRD), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM), respectively. The results showed that reed cellulose was directly dissolved in the NIL very easily without derivatization and degradation, retaining the characteristics of cellulose perfectly. During the process of treatment, the crystalline structure of NR was completely transformed (from cellulose I to cellulose II) along with a decrease in the crystallinity. Compared to the NR, the TR exhibited a lower onset temperature and more residues of the thermal decomposition. At the same time, the thermal stability of TR at high temperature was improved.

Keywords: ionic liquid, reed cellulose, synthesis, application

INTRODUCTION

Cellulose, a natural polymer obtained from abundant renewable resources, is characterized by good biodegradability and biocompatibility.¹⁻⁴ It can be derivatized to yield various useful products.⁵⁻⁷ With the depletion of oil resources, making full use of the rich resources of natural cellulose has far-reaching significance. Reed cellulose is lightweight, easily available, inexpensive and renewable with a short growth cycle. Besides, it is also biodegradable and does not leave toxic by-products. However, there are a lot of intramolecular and intermolecular hydrogen bonds in reed cellulose, which makes it difficult to dissolve in ordinary solvents.⁸⁻¹⁰ This is a significant drawback that limits the application of reed cellulose in reinforcing materials.

Dissolving cellulose in ordinary solvents is a traditional method. Although this method is simple, the use of such solvents leads easily to

environmental pollution. In recent years, ionic liquids have widely attracted the researchers' attention. Their use has been investigated in catalytic reactions,^{11,12} organic syntheses,^{13,14} extraction separations^{15,16} and electrochemistry^{17,18} due to their high thermal stability, non-toxicity, wide liquid temperature, good chemical stability, low vapor pressure, good dissolving ability and devisable structure. Consequently, ionic liquids have many interesting applications in the biopolymer field, including their use for cellulose regeneration,¹⁹ derivatization,²⁰ hydrolysis²¹ etc. Kyllonen *et al.*²² used various ionic liquids to study the solubility of wood cellulose. However, their results showed that intact wood cellulose was not soluble and only its swelling could be achieved in ionic liquids, unless special treatments were applied to modify the cellulose. In order to overcome the above disadvantages, a novel

1-ethenyl-3-hydroxyethyl imidazolium chloride ionic liquid (NIL) was synthesized in our study. As far as we know, there has been no systematic investigation of reed cellulose dissolution in alkyl imidazolium ionic liquids.

On the basis of the above background, the aim of the present work was to synthesise an imidazole ionic liquid (NIL), using N-vinyl imidazole and 2-chloroethanol as a green and recyclable solvent for reed cellulose. The chemical structure, crystallinity, thermal properties and surface morphology of the reed treated by NIL (TR) were analysed by FT-IR, XRD, TGA and SEM, respectively. The dissolution of the treated reed cellulose was compared with that of the untreated one to investigate the dissolution performance and recyclability of the synthetic ionic liquid. This would provide important information for further research and application of ionic liquids for cellulosic materials.

EXPERIMENTAL

Materials

Reed cellulose was supplied by Haining Anjie Composite Materials Co., Ltd., China. N-vinylimidazole was purchased from Henan Boailipu Co., Ltd., China. 2-Chloroethanol was obtained from Chengdu XiYa Chemical Technology Co., Ltd, China.

Synthesis of the ionic liquid

The ionic liquid was synthesized as follows. N-vinylimidazole (54 ml) and 2-chloroethanol (30 ml) at a molar ratio of 1:1.2 were added to a round-bottomed flask fitted with a reflux condenser and a magnetic stirrer. The reactive mixture was stirred at 90 °C for about 10 h. The unreacted chemical reagents and deionized water were removed by filtration. The precipitate was dried in a vacuum oven at 80 °C for 12 h. The product was 1-ethenyl-3-hydroxyethyl imidazolium chloride ionic liquid with light amber colour. This ionic liquid was named NIL. The synthesis route is illustrated in Scheme 1.

Preparation and treatment of reed cellulose

The reed cellulose sample was ground into powder and dried in vacuum at 60 °C for 5 h before dissolution. The reed cellulose was then dispersed in the NIL and the mixture was heated at 100 °C for 4 h under vigorous

mechanical stirring. Deionized water was used as a regeneration agent for the cellulose. The mixture was separated by filtration. The TR was washed three times with distilled water, and dried in vacuum at 80 °C for about 24 h. The synthesized ionic liquid, and the first and second recovered ionic liquids from the reed cellulose solutions were named NIL, NIL-1 and NIL-2, respectively.

Characterization

FT-IR spectroscopy

The untreated reed cellulose NR and the treated reed cellulose TR were respectively ground into powder for FT-IR spectroscopy. FT-IR spectra were recorded on an infrared spectrometric analyser (Spectrum One-B, Perkin Elmer Co., Ltd., USA) using KBr pellets. Meanwhile, the ionic liquid samples (NIL, NIL-1 and NIL-2) were also characterized by this technique.

¹H NMR spectroscopy

The degree of substitution upon the use of the NIL ionic liquid was determined by hydrogen nuclear magnetic resonance (¹H NMR), which was performed on a Bruker AV400 (400-MHz, Bruker Technologies & Services Co., Ltd, China) NMR spectrometer with DMSO-*d*₆ as a solvent.

SEM analysis

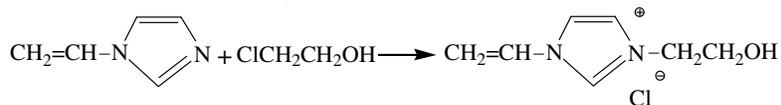
Examination of the microstructure of the reed cellulose before and after treatment by the NIL ionic liquid was conducted using a Hitachi S-3000N microscope (Suzhou Precision Instruments Co., Ltd, Japan) in vacuum. The powder was previously coated with a conductive gold layer.

XRD analysis

XRD was performed at room temperature using a Rigaku D = max-3B, X-ray diffractometer (40 kV, 20 mA) (Japan) with C_{Kα} (λ = 1.540 Å) irradiation at a scan rate of 2° min⁻¹ in the range of 1.5-20°.

Thermal gravimetric analysis

Thermal gravimetric analysis (TG) and derivative thermal gravimetry (DTG) were performed with a Seiko Instruments TG/DTG 6200 thermal analyser (Seiko Instruments, Inc., Japan) at a heating rate of 20 °C/min under nitrogen atmosphere from room temperature to 500 °C. Samples were heated from 30 °C to 500 °C.



Scheme 1: Synthesis route of 1-ethenyl-3-hydroxyethyl imidazolium chloride

RESULTS AND DISCUSSION

Structural characterization of the ionic liquid

FT-IR spectrum analysis of NIL

Figure 1 shows the FT-IR spectrum of the NIL ionic liquid. Two strong characteristic bands at 3369 cm^{-1} and 914 cm^{-1} were attributed to the absorption of the -OH. The adsorption peaks at 3102 cm^{-1} , 1498 cm^{-1} and 964 cm^{-1} were due to the -CH=CH₂ stretch vibration, unsymmetrical bending vibration and rocking vibration, respectively. The absorption at 2880 cm^{-1} was due to the stretching vibration of -CH₂CH₂OH. The

peak at 1650 cm^{-1} was attributed to the absorption of the C=C stretching vibration. The characteristic bands at 1552 cm^{-1} and 754 cm^{-1} were assigned to the stretching vibration and deformation vibration of the imidazole ring, respectively. The symmetry deformation vibration peak of the C-H in the side chains appeared at 1373 cm^{-1} . The absorption at 1079 cm^{-1} was attributed to the C-O stretch. The above results proved that the target product was synthesized.

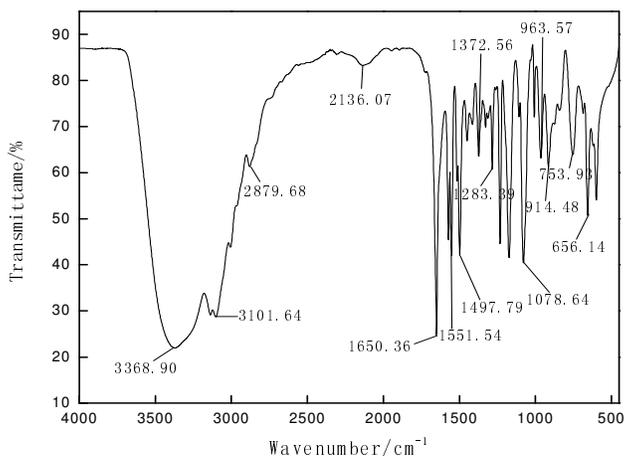


Figure 1: FT-IR spectrum of 1-ethenyl-3-hydroxyethyl imidazolium chloride

¹H NMR spectrum of NIL

The ¹H NMR spectrum of the NIL ionic liquid, shown in Figure 2, further demonstrated its structure. The chemical shift at 9.8 ppm could be assigned to the tertiary hydrogen of the imidazole ring. The chemical shifts at 7.4-7.6 ppm resulted from the vinyl hydrogens of the imidazole ring. The chemical shift at about 7.1 ppm was from the tertiary hydrogen of the side chain vinyl directly linked with the imidazole ring. The chemical shifts at 3.7-5.4 ppm were from the hydrogens of the hydroxy. The chemical shifts at around 3.6 ppm were assigned to the hydrogens of the side chain vinyl groups. These data show that the chemical structure of the synthesized NIL was that of an ionic liquid. The results of ¹H NMR are in good agreement with those of FT-IR spectroscopy.

Effect of NIL on the structure of reed cellulose

The FT-IR spectra of TR and NR are shown in Figure 3. The position of the characteristic peaks

of TR is nearly the same as that for the NR, which indicated that there were no other derivative reactions in the process of dissolving reed cellulose. Thus, the chemical structural of the reed cellulose was preserved. The decrease of the hydrogen bonding interactions of TR was evidenced by weakening of the stretching vibration peaks whose position occurred in the region of 3400 cm^{-1} .

Effect of NIL on the crystallinity of reed cellulose

The X-ray diffraction patterns of TR and NR are shown in Figure 4. In the XRD pattern of NR, the three diffraction peaks at 2θ were 16.22° , 22.76° and 35.14° , respectively. This indicated that NR had a cellulose I crystalline structure. In the XRD pattern of TR, the three weakened diffraction peaks appearing at 2θ were 16.34° , 22.96° and 35.14° , respectively. The crystallinity of reed cellulose thus decreased from 37.7% to 16.3%.

The results revealed that TR had a cellulose II crystalline structure, and the original straight parallel chain structure of cellulose had been reformed perfectly during dissolution and subsequent crystallization from the NIL ionic

liquid. This result was also in conformity with the weakened hydrogen bonds in the FT-IR spectra.

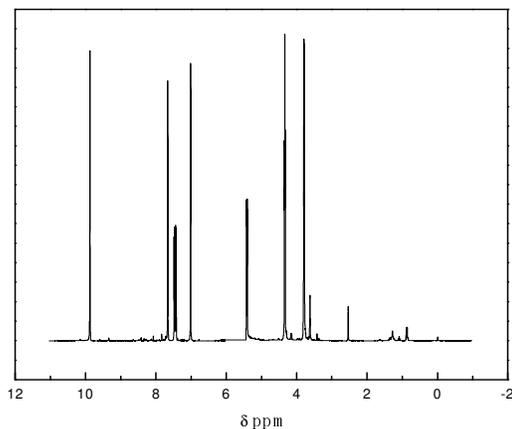


Figure 2: ^1H NMR spectrum of the synthesized ionic liquid

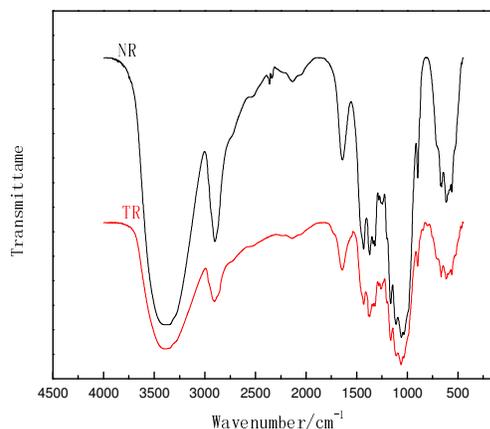


Figure 3: FT-IR spectra of NR and TR

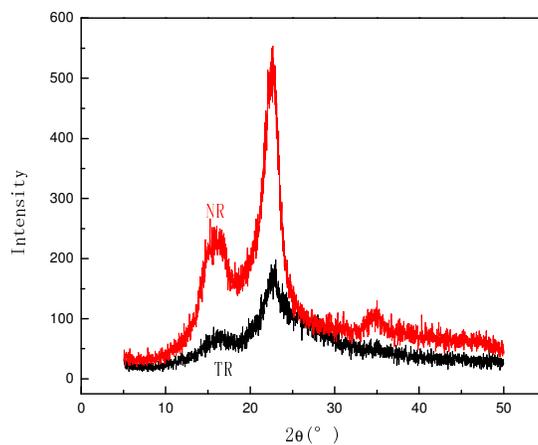


Figure 4: XRD curves of NR and TR

Effect of NIL on the morphology of reed cellulose

Figure 5 shows the SEM images of NR and TR. As may be remarked, the NR had a linear, compact shape before dissolving, and the surfaces of NR were smooth. Unlike it, the structure of TR (after being treated by NIL) was loose, and the surfaces were not clear. In addition, there were a lot of grooves and gullies on the surfaces of TR. Thus, the NIL can improve the compatibility between TR and non-polar materials, which will expand its application range.

Effect of NIL on the thermal properties of reed cellulose

Figure 6 shows the TG and DTG curves of NR and TR. As can be seen, the initial decomposition temperature of TR reduced from 261 °C to 242 °C, which was slightly lower than that of NR. The temperature at which the maximum degradation rate was reached also reduced from 341 °C to 290 °C. This phenomenon could be explained by breaking of a large number of hydrogen bonds in TR molecules. The separation distance among the molecular chains increased, which greatly reduced the degree of crystallization. So, the molecular chain of TR could move more freely, and the initial

decomposition temperature and maximum degradation rate temperature decreased. These results are also in line with those of the XRD analysis, indicating that the degree of crystallinity decreased.

The TR had a higher amount of char residue at

temperatures exceeding 500 °C. As shown in Table 1, the char residue of TR was 15% at 500 °C, compared to only 3% for the NR, which indicated that the thermal stability of the reed cellulose was improved after being treated by the ionic liquid.

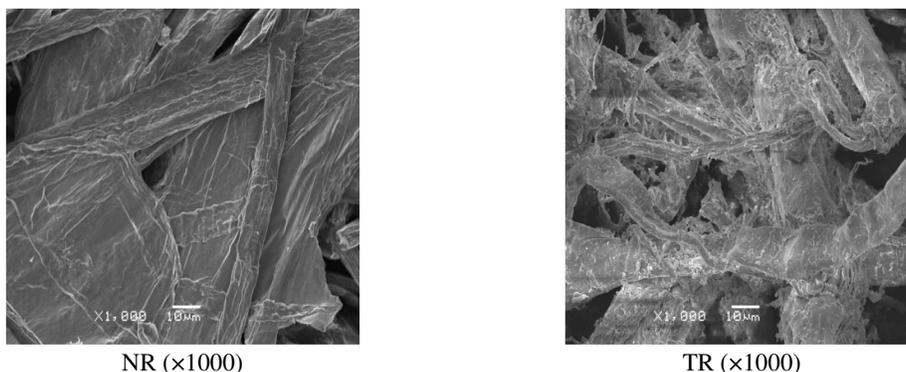


Figure 5: SEM micrographs of NR and TR

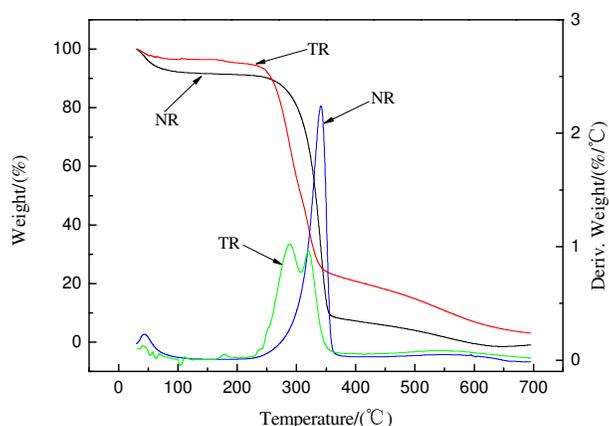


Figure 6: TG and corresponding DTG curves of NR and TR

Table 1
Main data of TGA and DTG

Reed cellulose type	$T_{0.1}$ (°C)	$T_{0.5}$ (°C)	T_{max} (°C)	Char residue at 500 °C (%)
NR	261	332	341	3.25
TR	242	307	290	15.86

$T_{0.1}$ and $T_{0.5}$ – temperature where 10 wt% and 50 wt% weight loss occurred, respectively; T_{max} – peak temperature of DTG

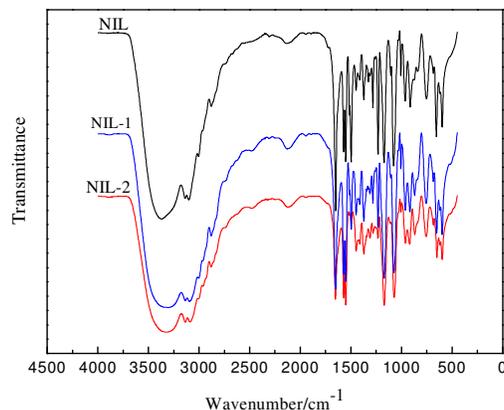


Figure 7: FT-IR spectra of NIL, NIL-1 and NIL-2

Recyclability of the ionic liquid

In order to explore whether the NIL ionic liquid can be recycled, the precipitated cellulose filtrate was evaporated in a rotary evaporator to recover the ionic liquid. The FT-IR spectra of the ionic liquid recovered the first and second time, and that of the initial NIL are shown in Figure 7. It may be observed in all the three spectra that the peak near 3400 cm^{-1} appears widened because of the overlapped hydroxyl peak and water peak, which demonstrated that the NIL, NIL-1 and NIL-2 could absorb water easily. As can be also seen from Figure 7, the position and intensity of the characteristic peaks of the ionic liquid recovered the first and second time were almost the same as those of the initial ionic liquid. In conclusion, these results illustrated that the synthesised ionic liquid could be easily recycled.

CONCLUSION

1. The imidazole ionic liquid, 1-ethenyl-3-hydroxyethyl imidazolium chloride (NIL), was successfully synthesised and used as a green and recyclable solvent for reed cellulose.
2. After the treatment by the ionic liquid, the crystalline structure of the reed cellulose changed from cellulose I to cellulose II, and the degree of crystallinity decreased. This meant that the solubility of the reed cellulose was effectively improved by the NIL ionic liquid.
3. Although the thermal decomposition rate at high temperature of the NIL treated reed cellulose decreased, its char residue increased. Thus, the ionic liquid improved the thermal stability of reed cellulose.
4. Also, it was established that the ionic liquid had good recycling performance. In conclusion, the

present study demonstrated the high potential of 1-ethenyl-3-hydroxyethyl imidazolium chloride as a new environmentally friendly solvent for dissolving cellulose.

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REFERENCES

- ¹ T. Miyamoto, S. Takahashi, H. Ito, H. Inagaki and Y. Noishiki, *J. Biomed. Mater. Res. Part A*, **23**, 125 (1989).
- ² R. L. Anderson, J. W. Owens and C. W. Timms, *Cancer Lett.*, **63**, 83 (1992).
- ³ R. Q. Xie, X. Y. Li and Y. F. Zhang, *Cellulose Chem. Technol.*, **46**, 349 (2012).
- ⁴ E. S. Sashina, D. A. Kashirskii and K. N. Busygin, *Cellulose Chem. Technol.*, **50**, 199 (2016).
- ⁵ H. Awada, D. Montplaisir and C. Daneault, *Bioresources*, **7**, 2090 (2012).
- ⁶ H. Awada, D. Monplaisir and C. Daneault, *Bioresources*, **9**, 3439 (2014).
- ⁷ A. K. Mohanty, M. Misra and L. T. Drzal, *J. Polym. Environ.*, **10**, 19 (2012).
- ⁸ Y. Li and Y. Luo, *Chinese Journal of Solid Mechanics*, **31**, 36 (2010).
- ⁹ H. Saba, Y. Zhang and H. Wang, *Rev. Adv. Mater. Sci.*, **40**, 215 (2015).
- ¹⁰ C. Asasutjarit, S. Charoenvai, J. Hirunlabh and J. Khedari, *Composites Part B Eng.*, **40**, 633 (2009).
- ¹¹ J. Dupont, R. F. Souza and P. A. Z. Suarez, *Chem. Rev.*, **102**, 3667 (2002).
- ¹² H. P. Zhu, F. Yang, J. Tang and M. Y. He, *Green Chem.*, **5**, 38 (2003).
- ¹³ Y. Q. Deng, F. Shi, J. Beng and K. Qiao, *J. Mol. Catal. A: Chem.*, **165**, 33 (2001).
- ¹⁴ W. X. Qian, E. L. Jin, W. L. Bao and Y. M. Zhang, *Angew. Chem. Int. Ed.*, **44**, 952 (2005).

- ¹⁵ Y. C. Pei, J. J. Wang, K. Wu, X. P. Xuan and Q. J. Lu, *Sep. Sci. Technol.*, **64**, 288 (2009).
- ¹⁶ Y. C. Pei, J. J. Wang, X. P. Xuan, J. Fan and M. H. Fan, *Environ. Sci. Technol.*, **41**, 5090 (2007).
- ¹⁷ W. Kubo, T. Kitamura, K. Hanabusa and S. Yanagida, *Chem. Commun.*, **4**, 374 (2002).
- ¹⁸ M. C. Buzzeo, R. G. Rvans and R. G. Compton, *Chem. Phys. Chem.*, **5**, 1106 (2004).
- ¹⁹ Y. Cao, H. Q. Li, Y. Zhang, J. Zhang and J. S. He, *J. Appl. Polym. Sci.*, **116**, 547 (2010).
- ²⁰ C. F. Liu, R. C. Sun, A. P. Zhang, J. L. Ren, X. A. Wang *et al.*, *Carbohydr. Res.*, **342**, 919 (2007).
- ²¹ F. R. Tao, H. L. Song, J. Yang and L. Chou, *Carbohydr. Polym.*, **85**, 363 (2011).
- ²² L. Kyllonen, A. Parviainen, S. Deb, M. Lawoko, M. Gorlov *et al.*, *Green Chem.*, **15**, 2374 (2013).