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Dissolution of Konjac Glucomannan with Room Temperature Ionic Liquids

SHEN Chunhui, LI Denian, ZHANG Ling, WAN Chao, GAO Shanjun*
(School of Materials Sciences & Engineering, Wuhan University of Technology, Wuhan 430070, China)

Abstract: Two kinds of new room temperature ionic liquids (RTILs), 1-allyl-3-methylimidazolium chloride (AMIMCl) and 1-butyl-3-methylimidazolium chloride (BMIMCl), were synthesized and used for the dissolution of konjac glucomannan (KGM). The experimental results showed that the solubility of KGM in AMIMCl was better than that in BMIMCl. Regenerated KGM were obtained by adding anhydrous alcohol to the KGM / ionic liquids solutions. Solubility, molecular weight, structure, and thermal property of the regenerated KGM were investigated by polarized optical microscopy (POM), viscosimetry, infrared spectroscopy (IR), X-ray diffraction technique (XRD), thermogravimetry (TG) and differential scanning calorimetry (DSC). It was demonstrated that the viscosity-averaged molecular weight of the KGM samples decreased after regeneration because of the molecular degradation of KGM. Results from IR and XRD indicated that the chemical structure and the crystalline form of regenerated KGM were not changed. Results from TG and DSC showed that the thermal stability of the regenerated KGM samples only slightly decreased. These results suggest that AMIMCl and BMIMCl are direct and effective solvents for KGM.

Key words: konjac glucomannan; room temperature ionic liquids; dissolution

1 Introduction

Nowadays, exhausting non-renewable resources have posed a great challenge to our environment. Therefore, people are increasingly paying attention to the exploitation of natural polymer. Konjac glucomannan (KGM) has attracted great interest due to its excellent film-forming ability, favorable chemical modification property, good biocompatibility and biodegradability^[1]. KGM, one of the water-soluble and non-ionic natural polysaccharides with high molecular weight, found in tubers of the *Amorphophallus konjac*, is composed of β -(1 \rightarrow 4) linked D-glucose and D-mannose with the molar ratio of 1:1.6^[2]. As to the structure of KGM, there are some branches linked to the backbone, but the exact branched position is still in debate^[3]. There are 5%-10% acetyl-substituted residues in the glucomannan backbone of KGM^[4, 5], and it is widely accepted that the presence of this group confers

water solubility on the glucomannan. KGM has special properties, such as the crystallization behavior^[6, 7], the liquid crystalline, rheological and thermal properties^[8, 9]. It is worth noting that KGM has promising application in edible film and biodegradable film material^[10, 11].

Cellulose, one of the most abundant renewable resources in nature, has the similar structure to konjac glucomannan (KGM)^[12]. Because of their stiff molecules and close chain packing via numerous inter-molecular and intra-molecular hydrogen bonds, it is extremely difficult to be dissolved in water and most common organic solvents. To date, many derivative and non-derivative solvents for cellulose have been found, such as LiCl/N, N-dimethylacetamide (DMAc)^[13], N-methyl-morpholine-N-oxide (NMMO)^[14], and molten salt hydrates. Among the solvents, NMMO/H₂O system has been industrially used to produce regenerated cellulose fibers and films. Homogeneous functionalization of cellulose has been studied for a long time^[15]. Whereas, it has been reported so far that only isoamyl acetate^[16], distilled water^[17], aqueous cadoxen (CdO/ethylenediamine), NaOH/thiourea^[12], NaOH/urea solution^[18] can be used to dissolve and realize the homogeneously chemical modifications for KGM. Heterogeneous functionalization of KGM was realized in N, N-dimethylformamide/pyridine^[19] and water/alcohol^[20]. However, as for the above homogeneous solvents, the prepared KGM solutions

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SHEN Chunhui(沈春晖): Assoc.Prof.; E-mail: shenchunhui@whut.edu.cn

* Corresponding author: GAO Shanjun(高山俊): Prof.; E-mail: sjgao@whut.edu.cn

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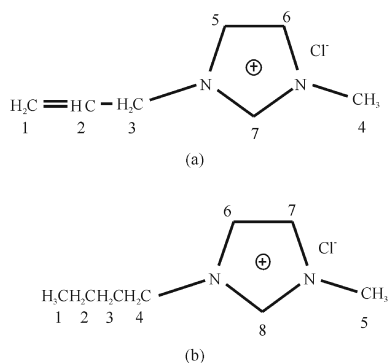


Fig.1 The chemical structures of AMIMCl (a) and BMIMCl (b)

are unstable at ambient temperature, and the synthesis of water-insoluble KGM derivatives cannot be realized in these solvents. Therefore, the study to explore new and direct solvent for KGM is of great significance.

Room temperature ionic liquids (RTILs), being considered as desirable green solvents for great width of liquid range, excellent dissolution ability, low vapor pressure, and easiness to recycling, have been used to replace the organic solvents in many fields^[21]. Furthermore, RTILs may be easily modified through changing the structures of cations or anions, which will broaden their applications. In the present study, two kinds of RTILs (shown in Fig.1), 1-allyl-3-methylimidazolium chloride (AMIMCl) and 1-butyl-3-methylimidazolium chloride (BMIMCl) were synthesized. The dissolution behavior of KGM in these two RTILs was studied. The chemical structure, molecular weight, and thermal stability of KGM regenerated from the RTILs solutions were also investigated.

2 Experimental

2.1 Materials

The raw KGM samples used were purchased from Meili Food Co Ltd. (Wuhan, China) and further purified by mixing with three times weight of 50wt% and 80wt% ethanol for 2 h, respectively, and with waterless ethanol for 4 h, and then vacuum-dried at 60 °C for 4 h. All other reagents were of analytical grade.

2.2 Synthesis of AMIMCl and BMIMCl

The room temperature ionic liquid AMIMCl was synthesized as described in previously reported work^[22]. 1-Methylimidazole (22.1 mL) and allyl chloride (26.9 mL) at a molar ratio 1:1.25 were added to a round-bottomed flask (100 mL) fitted with a reflux condenser for 7 h at 65 °C with stirring. The unreacted chemical reagents and other impurities, such as water, were removed by vacuum distillation, and then vacuum-dried

at 80 °C for 2 days. The obtained product, AMIMCl, was slightly amber. The room temperature ionic liquid BMIMCl was synthesized according to the previous literature^[23].

2.3 Dissolution of KGM in AMIMCl and BMIMCl

Raw KGM is a kind of polysaccharide having relatively low crystallinity, so it presented itself as amorphous^[24]. The dissolution process of raw KGM in the isotropic RTILs can be simply observed by polarized light microscopy. Optical microscopic observation was carried out with a polarized light microscope (CK-005, Shanghai CaiKang Optical Instrument Co., Ltd., Shanghai, China) fitted with a hot stage, a multicolor digital video (TK-C921EC (A), Victor Co., Ltd., Japan) and a computer. The mixtures of KGM powder and AMIMCl solvent were sandwiched between two pieces of glasses and put on the hot stage at 60 °C. The process of dissolution was monitored by a multicolor digital video until the KGM powder in the eyeshot selected completely dissolved.

The raw KGM powder was dispersed into amount of ionic liquids in glass vials, heated with vigorous stirring until KGM samples were completely dissolved and coded as AK0, AK1, AK2, AK3, BK0, BK1, BK2, BK3, respectively, corresponding to the different heating temperature. Finally, transparent KGM solutions were obtained and the dissolution endpoint was judged by polarized optical microscopy (POM). The dissolution processes of KGM in AMIMCl and BMIMCl at different temperature with a concentration of 5 wt% are summarized in Table 1.

2.4 Regeneration of KGM and solvent recovery

Regenerated KGM was precipitated from the KGM solution in RTILs by adding isopropyl alcohol. The KGM precipitate was isolated using a sand filter and washed with isopropyl alcohol and dried at 60 °C in a vacuum oven. A series of regenerated KGM samples were obtained from the solutions and were coded respectively as RAK1, RAK2, RAK3, RBK1, RBK2, RBK3 corresponding to the above solutions. The recovery of RTILs was accomplished by evaporating isopropyl alcohol from the precipitation liquid and dried at 80 °C in a vacuum oven.

2.5 Viscosity measurements

About 29wt% of aqueous solution of ethylenediamine was saturated with cadmium oxide (CdO) in an ice-water bath under vigorous stirring and kept below 5 °C for 2 days, and then the supernatant

was filtered and refrigerated. The cadmium content in cadoxen was about 1.5wt%. The raw and regenerated KGM sample solutions were prepared by mixing KGM powder with required amount of cadoxen and stirred to make it dissolved. The intrinsic viscosity measurements of the solutions were carried out with an Ubbelohde-type viscometer (Ningbo Tianheng Instrument Co. Ltd., China) at 25 ± 0.05 °C. Extrapolation to infinite dilution was made using both Huggins and Kraemer plots. The viscosity-averaged molecular weights (M_v) of the raw and regenerated KGM samples were calculated according to the Mark-Houwink equation $[\eta] = (3.55 \times 10^{-2}) M_v^{0.69}$ [25].

2.6 Characterizations

The structure of AMIMCl and BMIMCl was characterized by ^1H NMR analysis. The RTILs were dissolved in deuterated dimethyl sulfoxide (d_6 -DMSO) and the concentration was adjusted to 5-10 mg/0.5mL for ^1H NMR measurement. ^1H NMR spectra was recorded at ambient temperature at 600 KHz on a Varian INOVA-600 spectrometer.

The raw and regenerated KGM samples were cut into small pieces and vacuum-dried at 80 °C for 24 h before the following measurements. IR spectra of the samples were recorded with a Fourier transform infrared (FTIR) spectrometer (60SXB, NICOLET, USA). The test specimens were prepared by the KBr method.

The X-ray diffraction (XRD) patterns of the samples were recorded with X-ray diffractometer (Rigaku D/Max-III A, Japan). The operation conditions for the data collection were $\text{CuK}\alpha$ radiation, 30 kV, 50 mA. The diffraction angle ranged from 5° to 50° . The crystallinity was calculated by Eq. (1) [26]:

$$X_c = F_c / (F_c + F_a) \times 100\% \quad (1)$$

where, X_c is crystallinity and F_c and F_a are the areas of crystal and no crystalline regions, respectively.

Thermogravimetry (TG) and the differential scanning calorimetry (DSC) analysis of the samples with the weight of around 15mg was performed by a comprehensive thermal analyzer (NETZSCH STA 449C, Germany) under a nitrogen atmosphere with a flow capacity of $25 \text{ mL} \cdot \text{min}^{-1}$ from 40 to 400 °C at a heating rate of $20 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

3 Results and Discussion

3.1 Structure of RTILs and its capability to dissolve KGM

The ^1H -NMR spectra of AMIMCl and BMIMCl were showed in Fig.2. The three signals in the ^1H -NMR spectrum of AMIMCl at $\delta = 5.3 \times 10^{-6}$, 6.0×10^{-6} , 4.8×10^{-6} M correspond to the hydrogen atom located at position 1, 2, 3 in the allyl unit, the single peak appearing at $\delta = 3.8 \times 10^{-6}$ M is corresponding to the hydrogen atom at position 4 in the N- methyl group, the hydrogen atoms at position 5, 6 correspond to the signal at around $\delta = 7.7 \times 10^{-6}$ M. The signal at $\delta = 9.3 \times 10^{-6}$ M is attributed to the hydrogen atom at position 7. As for the ^1H -NMR spectrum of BMIMCl, there are four peaks with different intensities at $\delta = 0.9 \times 10^{-6}$, 1.2×10^{-6} , 1.7×10^{-6} , 4.2×10^{-6} M corresponding to the hydrogen atoms located at position 1, 2, 3, 4 in the butyl unit, respectively. The single peak appearing at $\delta = 3.8 \times 10^{-6}$ M corresponds to the hydrogen atom at position 5 in the N- methyl group and the hydrogen atoms at position 6, 7 correspond to the signals at around $\delta = 7.7 \times 10^{-6}$, 7.8×10^{-6} M. The signal at $\delta = 9.4 \times 10^{-6}$ M is the result of the hydrogen atom at position 8. From above ^1H -NMR, it can be concluded that the obtained products are AMIMCl and BMIMCl, respectively.

The dissolution of KGM in RTILs at different temperatures was investigated and is shown in Table 1. At room temperature, KGM only swelled in AMIMCl

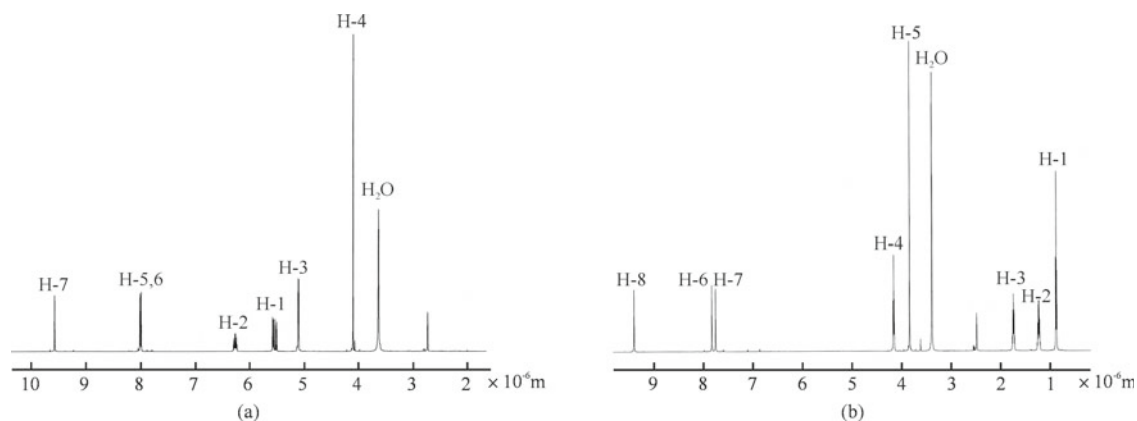


Fig.2 ^1H -NMR spectra of AMIMCl (a) and BMIMCl (b)

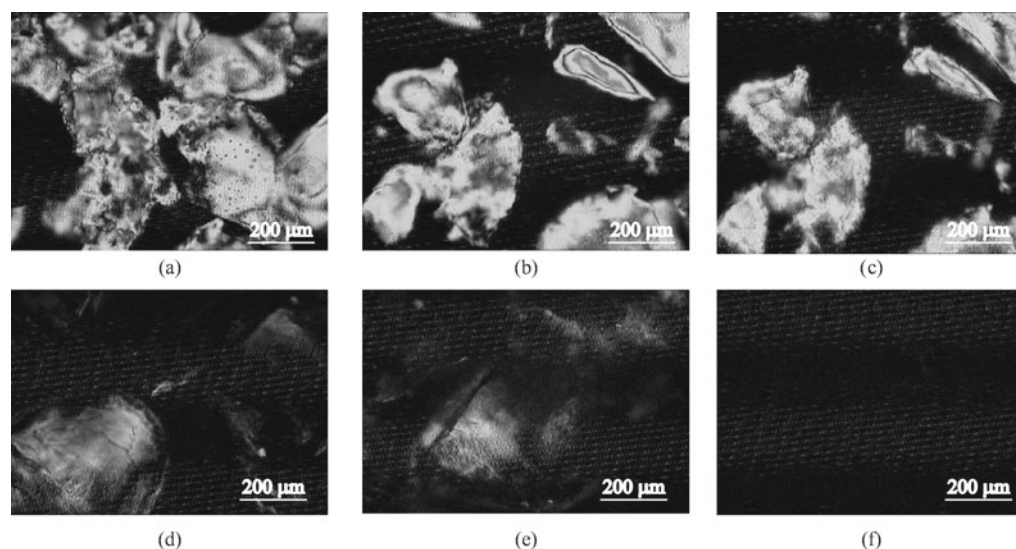


Fig.3 POM images of the raw KGM dissolution in AMIMCl at 60°C at different time: (a)0, (b)8, (c)16, (d)35, (e)52, (f)65min

Table I Solubility of dissolving KGM in ionic liquids with a concentration of 5wt%

Ionic liquids	Code	Dissolution temperature/°C	Dissolution time/min
[AMIM]Cl	AK0	Ambient	Insoluble,swelling
	AK1	60	65
	AK2	70	43
	AK3	80	30
[BMIM]Cl	BK0	Ambient	Insoluble,swelling
	BK1	60	90
	BK2	70	75
	BK3	80	60

and BMIMCl but could not dissolve. However, KGM dissolved readily at 60 °C with stirring. It was observed that KGM with a molecular weight as high as 1.35×10^6 dissolved in AMIMCl with a concentration of 5wt% within 65min, while it dissolved in BMIMCl within 90min at 60 °C. With increasing temperature, KGM dissolved more rapidly in both AMIMCl and BMIMCl and finally formed clear and viscous solutions. Compared with BMIMCl, AMIMCl is more efficient in dissolving KGM under the same condition. Dissolving process of KGM in AMIMCl at 60 °C was monitored by POM and the results are shown in Fig.3. It was in evidence that the diameter of KGM particle was approximately between 100μm and 300 μm. Many KGM particles agglomerated together in the AMIMCl as shown in Fig.3(a). But the agglomerated particles dispersed and became smaller with increasing dissolution time as shown in Fig.3(b, c, d, e). After 65 min, a totally dark field was observed in Fig.3(f) which indicated that homogeneous KGM solution was obtained.

It is widely accepted that the disruption of the great number of inter- and intra-molecular hydrogen bonds existed in KGM solution is favorable for the dissolution of KGM. It is speculated that the high chloride concentration and activity of the cations of the solvents are highly effective in breaking the hydrogen bonding. In comparison with BMIMCl, the cation [AMIM]⁺ has a smaller ion size due to three carbon atoms and a double bond in N-substituted methimidazonium cation of AMIMCl. Furthermore, one substituent on nitrogen is alkenyl in AMIMCl instead of saturated alkyl. It can be reasonably speculated that the small cation [AMIM]⁺ and the unsaturated alkenyl favors the attack on oxygen atom of KGM hydroxyl. Moreover, the less electronic chemical structure caused by alkyl group also enhances the interaction between cations in RTIL and oxygen atoms of hydroxide group in KGM. Therefore, AMIMCl performed more effective capability in dissolving KGM. In order to clearly understand the mechanism of dissolving KGM in RTILs, further investigation is still needed.

Table 2 The viscosity-averaged molecular weight of regenerated KGM samples

Samples	KGM	RAK1	RAK2	RAK3	RBK1	RBK2	RBK3
$[\eta]/\text{cm}^3\text{g}^{-1}$	602.78	374.84	344.52	316.51	387.32	324.40	299.60
$M_v/\times 10^{-4}$	135	68	60	53	71	55	49

3.2 Structure of regenerated KGM

The viscosity-averaged molecular weights (M_v) of the raw and regenerated KGM samples are shown in Table 2.

It is obvious that, with the dissolution temperature increased, the M_v of the regenerated KGM samples decreased to a certain degree. The M_v of the regenerated KGM (RAK1) precipitated from the KGM/AMIMCl solution at 60 °C was slightly lower than the regenerated KGM (RBK1). With the temperature increased, the M_v of the RBK samples decreased more tempestuously than the RAK samples. It is indicated that the high temperature led to the greater degradation of the KGM when dissolving both in AMIMCl and BMIMCl.

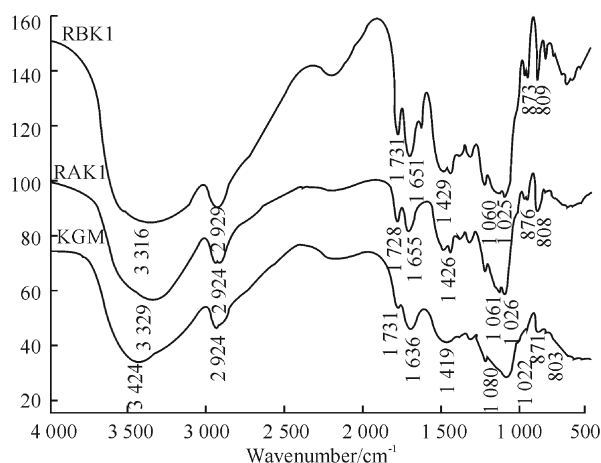


Fig.4 FTIR spectra of original KGM and regenerated KGM from AMIMCl/KGM solution (RAK1) and

FTIR spectras of KGM before and after regeneration are shown in Fig.4. It can be seen that the stretching vibration mode of -OH groups from KGM was a broad band and occurred at 3424 cm^{-1} . The stretching peak at 2924 cm^{-1} was attributed to the stretching of -CH₃ groups and the peak at 1731 cm^{-1} was assigned to the carbonyl of aceto groups^[27]. The absorption band at 1636 cm^{-1} was the intra-molecular hydrogen bonds. The peaks at 1080 and 1022 cm^{-1} were assigned to the stretching of C-O-C. The characteristic absorption peak of the mannose in the KGM appeared at 871 and 803 cm^{-1} . Compared the regenerated KGM spectrum with that of pure KGM, the two spectras of RAK1 and RBK1 are quite

similar to that of the original KGM, and no new peaks appear in the regenerated samples, indicating no chemical reaction occurred during the dissolution and regeneration processes of the KGM sample. That is to say, AMIMCl and BMIMCl are both direct solvents for KGM. The peak at 3424 cm^{-1} , which is broader than that of free hydroxyls, was attributed to the vibration of -OH groups. It is probably caused by the association of the KGM chains due to hydrogen bonds. As for the regenerated KGM, the -OH vibrations of the RAK1 and RBK1 both shifted to a lower frequency (3329 cm^{-1} , 3316 cm^{-1} , respectively). This indicates that the intra-molecular hydrogen bonds have been slightly destroyed. As no new peaks appear in the FTIR spectra, both AMIMCl and BMIMCl can be considered as a true solvent.

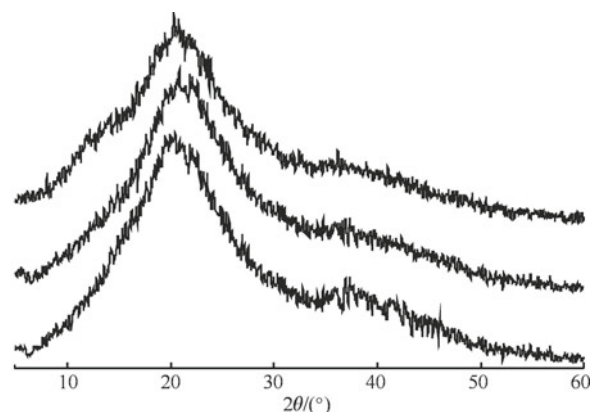


Fig.5 X-ray diffraction patterns of raw KGM sample and regenerated KGM samples prepared from KGM/AMIMCl solution at 60 °C (RAK1) and KGM/BMIMCl solution at 60 °C (RBK1), respectively

The raw KGM samples consist of radial disposed micelles, which have two kinds of crystals: one is α -type (non-crystalline), and the other is β -type (crystalline)^[28]. Fig.5 shows the X-ray diffraction patterns of raw and regenerated KGM sample. The broad diffraction peaks for raw KGM, RAK1, and RBK1 were observed at $2\theta=20.077^\circ$, 21.244° , and 20.279° , respectively. It can be concluded that both the raw and the regenerated KGM show noncrystalline state with amorphous α -type structure. The similarity of the X-ray diffraction patterns of the KGM before and after regeneration indicates that the crystal type has not transformed. It can be seen from Fig.5 that the intensity of diffraction peaks of the regenerated KGM samples decreased

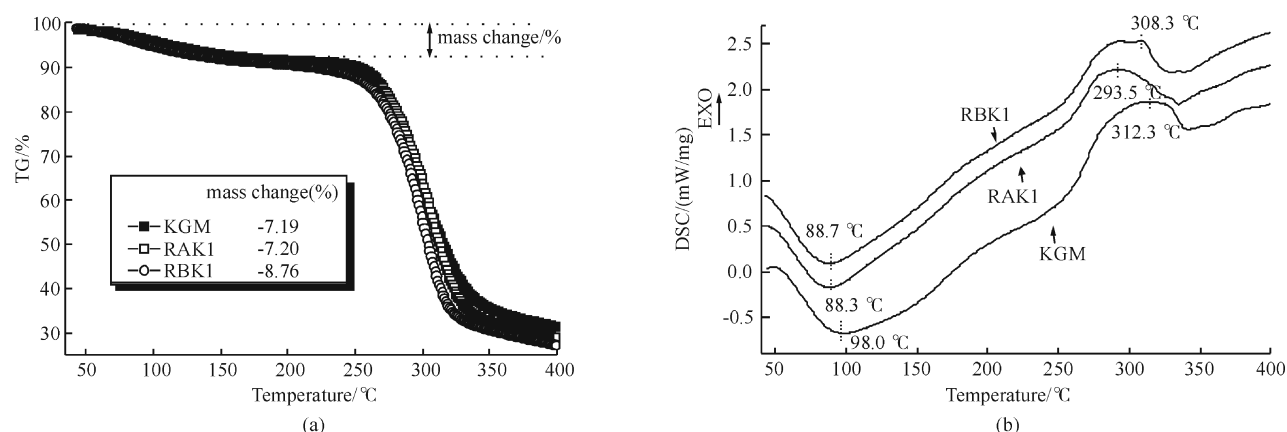


Fig 6 The TG curves (a) and DSC curves (b) of the raw konjac glucomannan (KGM) and regenerated KGM from the KGM/AMIMCl solution (RAK1) and KGM/BMIMCl (RBK1) at 60°C

slightly. The calculated crystallinities of raw KGM, RAK1, and RBK1 were 11.2%, 10.7% and 9.5%, respectively.

3.3 Thermal properties of regenerated KGM

The thermal behavior of the raw and regenerated konjac glucomannan samples were investigated by TG and DSC measurements (Fig.6). It is well known that there are large quantities of hydroxyl groups in KGM which can easily form KGM-water crystalline^[29]. As for the TG curves of the raw KGM and regenerated KGM samples, there are different mass loss before the onset temperature, due to the loss of small amount crystal water. Meanwhile, the thermal decomposition residues at 400 °C of the RAK1 and RBK1 samples are 30.7% and 28.8%, respectively, which are both less than that of the KGM sample (33.25%). From the DSC curves, all the three samples show endothermic peaks at 87-98 °C, corresponding to the loss of crystalline water molecular formed during drying process. This result is in concordance with the mass loss before the maximum decomposition in the TG curves. An exothermic peak of raw KGM, RAK1, and RBK1 respectively appeared at 312.3 °C, 293.5 °C, 308.3 °C, attributed to the greatest thermal degradation due to the disintegration of the molecular chains. Obviously, the thermal decomposition temperature of the regenerated KGM samples slightly shifted to lower temperature. This may be resulted from the degradation of the molecular weight after the regeneration.

3.4 Recycling of the ionic liquid

After the regeneration of KGM, the residual ILs can be easily recovered by simply reducing the pressure and subsequently rotary evaporating to remove water. Because of the salting-out effect, the hydrophilic ionic liquids after adding some inorganic salts can form two-phase aqueous system: an upper ILs-rich phase and a

lower inorganic-rich phase, which can be utilized to concentrate and recycle ILs^[30]. It has been reported^[31] that BMIMCl could be recycled or concentrated from aqueous solution by using aqueous biphasic systems (ABS), in which the BMIMCl solution in water was contacted with concentrated solutions of the water-structuring salts such as K_3PO_4 , and then formed two aqueous phases: an upper ILs-rich phase and a lower K_3PO_4 -rich phase. The same method can also be utilized in the recycling of the AMIMCl and BMIMCl in the present study. Doubtlessly, easiness to recycling of the RTILs will promote their application in dissolution and functionalization of KGM.

4 Conclusion

Room temperature ionic liquids AMIMCl and BMIMCl were found to be effective and direct solvent for KGM. Compared with BMIMCl, AMIMCl is more efficient in dissolving KGM under the same condition. The raw KGM sample can dissolve absolutely in the RTILs and form transparent and viscous solutions. The KGM can be easily regenerated by adding amount of anhydrous alcohol. The analysis by FT-IR, XRD, and DSC/TG for the KGM samples before and after regeneration showed that after the regeneration the structure had not been changed. The viscosity average molecular weights of the regenerated KGM samples decreased with raising the dissolution temperature due to the thermal degradation. Further investigation is still needed in order to understand the mechanism of dissolving KGM in ILs. On the whole, RTILs of AMIMCl and BMIMCl are true solvent for KGM. Regarding the potential of RTILs as promising green solvent, homogeneous functionalization of KGM in RTILs is expected to attract more attention.

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