Polymer 49 (2008) 2321–2327

Contents lists available at ScienceDirect

Polymer

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

A novel biomass-ionic liquid platform for the utilization of native chitin

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ARTICLE INFO

Article history:
Received 16 November 2007
Received in revised form 12 February 2008
Accepted 15 March 2008
Available online 19 March 2008

Keywords:
Chitin
Ionic liquid
Solvent

ABSTRACT

A room temperature ionic liquid (RTIL), that is, 1-butyl-3-methylimidazolium acetate (BminAc), is proposed to be a new good solvent for native chitins with different origins and molecular weights. A water and a methanol coagulant were used to regenerate the dissolved chitins and chitin materials with a variety of structures were prepared. Wide-angle X-ray diffraction (WAXD), Fourier transform IR (FTIR), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM) were used to visualize the modifications of the native structures of chitin during the dissolution and the regeneration processes, as well as the morphological features and properties of the reconstituted chitin materials.

1. Introduction

Chitin, structurally similar to cellulose (see Fig. 1), is one of the most abundant polysaccharides with an estimated annual production after cellulose [1]. Chitin forms strong inter- and intramolecular hydrogen bonds, which is difficult to be broken by common molecular solvents. The few true solvents that have been reported to dissolve chitin include a binary solvent system of *N*,*N*-dimethylacetamide(DMAc)/lithium chloride (LiCl) 5% (w/w) [2], an alkaline-ice mixture (2.77 M NaOH) [3], some strong acids such as methanesulfonic acid (MSA) [4], and some fluorinated solvents such as hexafluoro-2-propanol (HFIP) [5]. These solvents are generally volatile and/or corrosive, and the resulting chitin solutions are not stable due to possible hydrolysis in strong acid or basic conditions. The difficulty of dissolving chitin in common organic solvents has limited the utilization of this natural resource to a small area, despite its huge annual production. Up to date, the majority of uses of this natural resource is related to chitosan, a partially or completely deacetylated derivative of chitin.

Recently, ionic liquids (ILs) have been reported to dissolve biopolymers and were regarded as green solvents to replace the volatile organic compounds (VOCs) commonly used in various processing and synthesis industries. In 2002, the first pioneer work on using ILs as solvents for polysaccharides was reported by Swatloski et al. [6] who found that ILs could be used as non-derivatizing solvents for native cellulose and one of the ILs they used, that is, 1-butyl-3-methylimidazolium chloride (BminCl) showed the most excellent solvating ability and up to 25 wt% cellulose could be dissolved under an assistant heating by microwave. The success of dissolving cellulose by ILs has initiated a series of following studies on dissolving other biopolymers and/or developing new ILs. Wu et al. [7] reported that a room temperature ionic liquid (RTIL), that is, 1-allyl-3-methylimidazolium chloride (AminCl), could fast dissolve cellulose without any activation. AminCl, being substituted with an alkenyl in its imidazolium cation instead of a saturated alkyl, has a lower melting point (ca. 17 °C) and lower viscosity in contrast with BminCl which remains as a solid below 65 °C. Fukaya et al. [8] reported that some halogen-free 1,3-dialkylimidazolium formates could dissolve a range of polysaccharides including

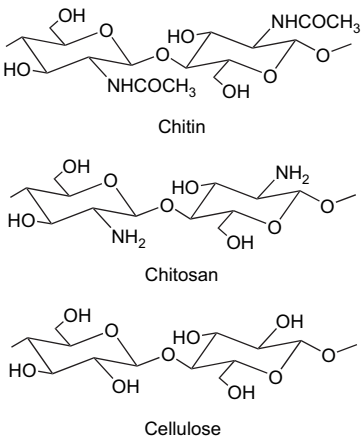

Fig. 1. Chemical structures of chitin, chitosan (fully deacetylated) and cellulose.

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doi:10.1016/j.polymer.2008.03.027

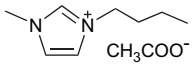

Fig. 2. Structure of 1-butyl-3-methylimidazolium acetate (BminAc) RTIL.

cellulose and amylose. These RTILs, with formate anions, are characterized by very lower viscosity and relatively higher polarity (hydrogen bond basicity), thus, the polymers could be dissolved in high concentration under mild condition.

In contrast to those active studies that have been directed to cellulose, only little information about the dissolution of chitin in ILs can be obtained from literature [9]. Xie et al. used BminCl to dissolve chitin and declared that up to 10 wt% of the polymer could be dissolved within 5 h at 110 °C. However, no detailed information about the molecular structures was given. In fact, we have also attempted to dissolve some native chitin samples with different molecular weights and very high degree of acetylation (DAC) by using BminCl, but no real dissolution could be achieved in any case. We realized that chitins are actually quite diverse considering their different origins, molecular weight and DAC, thus much more work is obviously needed in order to develop a good ionic liquid solvent for various chitins.

The main objective of the present study is to establish a biomass-ionic liquid platform (BILP) based on the dissolution of chitin-based polysaccharides in RTIL. In this paper, we report the dissolution and regeneration of chitin by a new RTIL solvent, 1-butyl-3-methylimidazolium acetate (BminAc, see Fig. 2). Several chitin samples having different origins and molecular weights were used. A series of techniques including polarized optical microscopy (POM), Fourier transform IR (FTIR), wide-angle X-ray diffraction (WAXD), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM) were used to confirm the dissolution of the biopolymers, as well as the changes in structure during the dissolving and the regenerating process.

2. Experimental

2.1. Materials

1-Methylimidazole and *n*-butyl chloride were purchased from Wako Co Ltd., and the former was distilled over KOH and conserved with 4A molecular sieves. The native chitin materials used in this study include an α-chitin (N-α-chitin, Lot. No. 0930-17) from crab ($\eta = 35$ cp and DAC = 99%) and two β-chitins (N-β-chitin-L, Lot. No. 0923-18, and N-β-chitin-H, Lot. No. 060923) from squid-pen with relatively low ($\eta = 15$ cp) and high ($\eta = 278$ cp) molecular weights, respectively. All the three chitin materials were kindly supplied by Koyo Chem. Co Ltd. (Japan). Chitosan (Lot. No. 041116C) with $M_v = 97{,}000$ and DAC = 5% was received from Dainichiseika Chem. Co. Ltd. All the chitin and chitosan materials were used directly after drying without further purification.

2.2. Synthesis of BminAc

The RTIL containing acetate anion was prepared as follows: first, BminCl was prepared by a method described in the literature [10]. An aqueous solution of BminCl salt was allowed to pass through a column filled with anion exchange resin (Amberlite IRA400-OH) to obtain BminOH, as described in the literature [8]. The aqueous BminOH solution was then neutralized with equimolar acetic acid. After removing water by evaporation under reduced pressure, the viscous liquid was thoroughly washed with diethyl ether and finally dried to constant weight to give a pure RTIL BminAc (yield% = 92). The structure and purity of the product were confirmed using ^{1}H NMR, and the characterization results are listed as the following.

BminCl: $\delta_H(CDCl_3) = 10.58$ (s, 1H, N–C*H*═N), 7.82 and 7.64 (s, 2H, N–C*H*═C*H*–N), 4.36 (t, 2H, N–CH_2), 4.14 (s, 3H, N–CH_3), 1.92 (m, 2H, N–CH$_2$CH_2), 1.38 (m, 2H, N–CH$_2$CH$_2$CH_2), 0.96 (t, 3H, N–CH$_2$CH$_2$CH$_2$CH_3).

BminAc: $\delta_H(D_2O) = 8.53$ (s, 1H, N–C*H*═N), 7.28 and 7.23 (s, 2H, N–C*H*═C*H*–N), 3.99 (t, 2H, N–CH_2), 3.69 (s, 3H, N–CH_3), 1.68 (s, 3H, COCH_3), 1.64 (m, 2H, N–CH$_2$CH_2), 1.10 (m, 2H, N–CH$_2$CH$_2$CH_2), 0.71 (t, 3H, N–CH$_2$CH$_2$CH$_2$CH_3).

2.3. Dissolution of chitin in RTILs

Chitin was added in portions of 1.0 wt% of ionic liquid each time and the mixture was then stirred for about 15–20 min at each temperature (controlled by an oil bath) under nitrogen atmosphere. A slight amount of the dispersion mixture was taken out and dissolution was checked using POM. If the polymer was not completely dissolved, the temperature was raised by 5 °C and the mixture was stirred until complete dissolution could be confirmed.

2.4. Regeneration of chitin from ILs

Typically, to prepare the regenerated chitin sample R-CT2 from BminAc, a known weight of chitin was dispersed into 4.0 g of BminAc in a flask, and the mixture was heated at 100 °C and stirred until completely transparent solution was obtained. The solution was cast onto a shaped plastic mold with 1 mm depth and allowed to cool down to room temperature (25 °C). The gel formed in the RTIL was then coagulated in a methanol bath, and rinsed with fresh coagulant to eliminate the RTIL solvent. The obtained semi-transparent regenerated gel was finally oven-dried at 60 °C to obtain a pure chitin film coded as R-CT2. The other three regenerated chitin samples from BminAc (R-CT3, R-CT4, and R-CT6) were prepared in the same way but with different coagulants (water or methanol) and drying methods (oven-drying or freeze-drying). Details of the preparation conditions are shown in Table 1. The RTIL in the coagulants were recycled by evaporating water or methanol and dried in a vacuum oven, and the purity was confirmed by ^{1}H NMR.

Two regenerated chitin samples, i.e., R-CT1 and R-CT5, from BminCl were prepared by the same method as follows: first, the native α-chitin or β-chitin was dispersed in 20.0 g BminCl stirred at 110 °C for 2 h. In both cases, a semi-transparent, viscous slurry was obtained. The slurries were directly added to methanol to precipitate the polymers without filtration. The precipitates were then washed thoroughly with methanol several times and finally dried in vacuo at 60 °C to obtain powdery samples (see Table 1).

2.5. Measurements

An Olympus polarized optical microscopy (POM) was used to confirm the dissolution of the polysaccharides. The IR spectra of the native and regenerated chitin were recorded on a Nicolet Magna

Table 1
Preparation conditions of regenerated chitin samples

Sample	Material	Solvent	Concentration (wt%)	Coagulant	Drying method
R-CT1	N-α-chitin	BminCl	1.0	Methanol	Oven-dried
R-CT2	N-α-chitin	BminAc	4.0	Methanol	Oven-dried
R-CT3	N-α-chitin	BminAc	4.0	Water	Oven-dried
R-CT4	N-α-chitin	BminAc	4.0	Water	Freeze-dried
R-CT5	N-β-chitin-L	BminCl	1.0	Methanol	Oven-dried
R-CT6	N-β-chitin–H	BminAc	1.0	Methanol	Oven-dried

560 FTIR spectrometer by using KBr pellets. The ^{1}H NMR spectra were obtained on a JEOL LA-500 spectrometer operating at a frequency of 500 MHz for ^{1}H. The WAXD experiments were performed on a Rigaku Rint 2100 diffractometer (40 kV, 20 mA), in which Ni-filtered Cu K_α radiation was used. The diffraction intensity profiles were recorded in the region of scattering angle 2°–40°with a scanning speed of 1°/min. Thermal analysis of the chitin samples were carried out on a Shimadzu TA-60WS thermal analyzer under air atmosphere. In each experiment, about 10 mg of the sample was filled into the aluminium pan and the TG and DTA profiles were recorded simultaneously by raising the temperature from 30 °C to 600 °C at a speed of 10 °C/min. Morphological structures of the regenerated chitin materials were observed by a HITACHI S-2600HS scanning electron microscope (SEM) with a 15 kV accelerated voltage. Samples were gold coated by ion sputtering with a JEOL JFC-1100-E and current 10 mA for 90 s before observation.

3. Results and discussion

3.1. Dissolution of chitin in ILs

Natural chitin forms more complex inter- and intra-molecular hydrogen-bond network than cellulose, due to the existence of an additional acetoamide group in its structural repeating unit. In addition, being skeletons of many animals such as crustaceans, chitin is generally found to have larger molecular weights than cellulose which is mainly derived from plants. As a result, it is generally more difficult to dissolve chitin than cellulose materials. Previous studies on dissolving cellulose by ILs have suggested that the solvation mainly involved the interaction of the hydroxyl protons of the carbohydrate with the strong hydrogen bonding and coordinating anions, in particular Cl^- [6]. However, our preliminary experiments showed that those chlorinated ILs reported to be good solvents of cellulose, could not dissolve our chitins with satisfactory results (Table 2). No dissolution could be confirmed when AminCl was used as a solvent, and only limited solvation ability of BminCl to the chitins could be observed at relatively high temperatures. POM observation showed that there existed undissolved crystal domains in the dispersions of 1% N-α-chitin in BminCl. When such a dispersed solution was carefully filtered with a funnel, most of the polymers were obtained from the insoluble solid, and only negligible part (less than 5% of the feed) could be recovered from the filtrate by methanol. Increasing the temperature to 130 °C and stirring time to 5 h did not lead to a complete dissolution of the crystal domains as evidenced by POM, although up to 5% of the polymer could be dispersed to give a more viscous but less transparent dispersion. Therefore, we assume that BminCl can only dissolve the non-crystal domains of a native chitin material but is incapable of dissolving the compact crystal domains.

Thus, we realize that an IL with stronger coordinating anion than chloride is desired in order to disrupt the more complex hydrogen-bond net formed in the chitin chains especially those formed by the *N*-acetyl groups. It has been reported that ILs containing carboxylic acid anions have strong coordinating ability or hydrogen-bond acceptability, and are potential solvents for biopolymer [8,11]. Following this criterion, we have also prepared a 1-butyl-3-methylimidazolium formate RTIL, but found that the formate salt did not dissolve any of our chitins. Therefore, we considered the formate anion, being characterized by stronger hydrogen-bond acceptability than chloride anion [8], may be still too weak to crack the hydrogen bonds formed in native chitin. Therefore, we are particularly interested in the RTILs having acetate anions which are relatively stable and accessible [12]. Acetate anion, being the conjugated base of acetic acid whose acidity is weaker than formic acid, is supposed to be stronger hydrogen bonding acceptor than formate anion. We have thus prepared 1-butyl-3-methylimidazolium acetate (BminAc) and found that it is distinctly better than those chlorinated ILs in dissolving various chitin materials with different origins (see Table 2). In all the cases, the complete dissolutions of the polysaccharides were achieved, and homogeneous solutions were obtained.

The chitin materials, regardless of their origins and molecular weights could be dissolved in BminAc at elevated-temperature (more than 85 °C), and transparent, viscous solutions could be obtained to satisfactory concentrations at 110 °C depending on the origins and molecular weights. The solvability of BminAc shows less important difference between the crystal forms of the chitin samples, that is, α- or β-crystal, but strongly depends on their molecular weights. BminAc could dissolve the chitin with a relatively lower molecular weight (N-β-chitin-L) to more than 6%; while, it could only dissolve 3% of the chitin sample with relatively higher molecular weight (N-β-chitin-H). It is thus suggested from our results that the BminAc RTIL may be used as a potential good solvent for native chitin materials.

Since the two chlorinated ILs dissolve chitosan but not chitin (Table 2), we consider that the dissolution mechanism of chitin by BminAc mainly involves the solvation of the *N*-acetyl group on the repeating unit of chitin. According to the crystal structures of α- and β-chitins proposed by Blackwell et al. [13,14], the amide groups are strongly involved in forming complex inter- and intra-molecular hydrogen-bond (H-bond) networks (–NH···O═C and –OH···O═C) that stabilize their three-dimensional structures in both polymorphs. The dissolution thus is mainly related to the solvation of the polar H-bonds by the polar ionic liquid, especially the anion parts. Acetate anion (Ac^-), being typical ligand, has strong coordinating ability and has been used to stabilize palladium catalysts [15,16]. In addition, as the conjugate bases of weak acids, the RTILs containing Ac^- are characterized by stronger hydrogen bonding acceptability (basicity) compared with those anions derived from strong acids, which have been evidenced by NMR studies [12,17]. Therefore, it is supposed that the acetate anions of the RTIL strongly interact with the H-bond networks in the chitin chains by depriving the proton of the amino (–NH) or hydroxyl (–OH) groups from the carbonyl (C═O) groups and forming more stable associations with the formers. As a result of the cleavage of the H-bond net, the compact crystal structure of chitin was destroyed and thus led to the dissolution of the polysaccharides.

Table 2
Solubilities of native chitins and chitosan in ionic liquids

Polymer	Origin and structural information	Solubility (w/w%) at 110 °C		
		AminCl	BminCl	BminAc (%)
N-α-Chitin	Crab, $\eta = 35$ cp	Insoluble	Partially soluble	6
N-β-Chitin-L	Squid pen, $\eta = 15$ cp	Insoluble	Partially soluble	6–7
N-β-Chitin-H	Squid pen, $\eta = 278$ cp	Insoluble	Insoluble	3
Chitosan	Crab, $M_v = 97{,}000$	8%	10%	12

3.2. Structural characterizations on the regenerated chitin materials

Since BminAc is miscible with water and alcohol which are non-solvents of chitin, the polymers can be directly recovered from water or alcohol coagulants. FTIR and WAXD were then employed to visualize the variation of molecular interactions and the structural modification as a result of the dissolution and the subsequent coagulation.

Fig. 3 shows the FTIR spectra of the native and regenerated chitins. In the spectrum of the native α-chitin (Fig. 3-1), two absorption peaks can be observed at 3263 cm^{-1} (peak **a**) and 3109 cm^{-1} (peak **b**). Peak **a** is generally assigned to the N–H

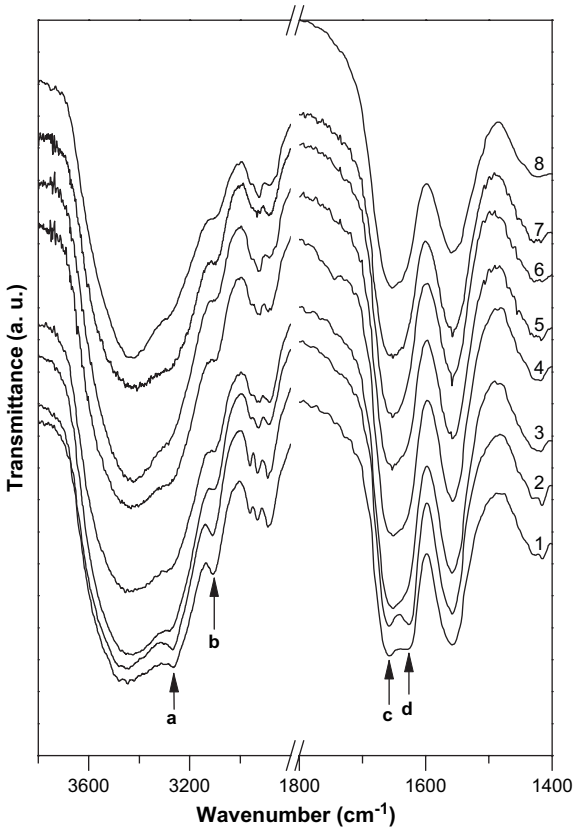

Fig. 3. FTIR spectra of the native and regenerated chitins: 1: N-α-chitin; 2: R-CT1; 3: R-CT2; 4: R-CT3; 5: R-CT6; 6: R-CT5; and 7: N-β-chitin-L; 8: N-β-chitin-H.

stretching restricted by the intermolecular C(2)NH···O═C(7) H-bonds and peak **b** to the O–H stretching restricted by the intermolecular C(6)OH···H–O–C(6′) H-bonds [13,18]. In addition, the spectrum of the native α-chitin is characterized by a splitting of the amide I vibration at 1660 cm^{-1} (peak **c**) and 1629 cm^{-1} (peak **d**) which have been assigned to the stretching of C═O groups hydrogen bonded to N–H groups of the adjacent chain, and the stretching of the C═O groups bifurcated by forming an additional hydrogen bond to the primary OH groups of the same chain, respectively [19,20]. The IR spectrum of the regenerated crab chitin from the BminCl solvent (Fig. 3-2) shows no obvious difference in the above two regions, implying the involved H-bond networks were not distinctly weakened. In contrast, evident differences can be observed when comparing the IR spectra of the regenerated crab chitins from the BminAc solvent (Fig. 3-3 and 3-4) with that of the native one (Fig. 3-1). In the spectra of the two regenerated α-chitins, there can be seen considerable decreases in the peaks **a** and **b**, and thus peak **a** becomes less resolved and peak **b** has a shift around 10 cm^{-1} to a shorter wave number. Besides, the amide I vibration was observed as a single band at 1652 cm^{-1}, instead of a splitting band. These results clearly suggested that the H-bond networks formed in the native crab chitin have been greatly destroyed in the dissolution process by the BminAc solvent, and the H-bond network could not be completely reconstituted during the regeneration process by the coagulants.

The IR spectra of the β-chitin material (Fig. 3-7 and 3-8) show typical absorption bands corresponding to the parallel molecular arrangement with relatively weaker hydrogen bonds than those in α-chitin with anti-parallel arrangement, with peaks **a** and **b** moving to lower wave numbers and single band at 1661 cm^{-1} due to C═O stretching. No obvious differences can be distinguished between the spectra of the regenerated (Fig. 3-5 and 3-6) and the native β-chitin specimens; thus it is very difficult to estimate the changes in the H-bond interactions during the dissolution and the subsequent regeneration processes only from the FTIR results.

The WAXD profiles of the regenerated chitin precipitates from the BminAc and BminCl solutions, as well as the native chitin materials are shown in Fig. 4. The WAXD pattern of the regenerated α-chitins from the BminCl dispersion (Fig. 4b) shows a series of strong diffraction peaks that strongly resemble those observed for the native α-chitin (Fig. 4a). The regenerated β-chitin from BminCl also gave rise to the same WAXD pattern (Fig. 4f) as that of the original one (Fig. 4g). These results indicate that the native crystal structures (both α- and β-chitins) almost remain in the regenerated samples due to incomplete dissolution of both native polymers in BminCl.

In contrast, with BminAc as a solvent, the regenerated chitin samples gave rise to WAXD profiles that are remarkably different from those of the corresponding native ones. It can be seen from Fig. 4c and d (or indices in Table 3) that the two regenerated α-chitin samples (R-CT3 and R-CT2) engender a series of strong diffraction peaks which correspond to the four most intense diffraction peaks appearing in the profile of the native α-chitin, and the intensities are evidently lost compared with those of the native α-chitin. The results indicate that the native crystal structure of α-chitin is barely reconstituted but suffers a remarkable decrease in the crystallinity after being dissolved by the BminAc solvent. It is also interesting to notice that the diffraction peaks revealed in the profile of R-CT3 (regenerated by using water as coagulant) are relatively sharper than those of R-CT2 (reproduced by using a methanol coagulant). In fact, two relatively weak diffraction peaks can be distinguished in the large-angle region (at 29.24° and 35.10°) for the former (Fig. 4c). The results suggest that the chitin

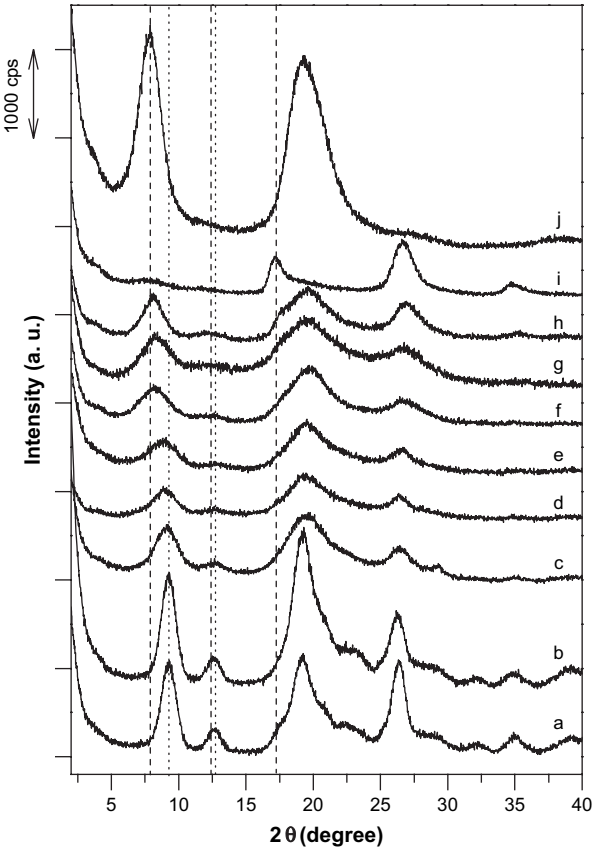

Fig. 4. WAXD profiles of the native and regenerated chitins: a: N-α-chitin; b: R-CT1; c: R-CT3; d: R-CT2; e: R-CT6; f: R-CT5; g: N-β-chitin-L; h: N-β-chitin-H (powder); i: N-β-chitin-H (fibrous, meridional); and j: N-β-chitin-H (fibrous, equatorial).

Table 3
Crystallographic parameters of native and regenerated chitins[a]

Polymer	Miller index	2θ (°) obs.	d-spacing (Å)
N-α-chitin (α-structure)	(020)	9.27	9.53
	(021)	12.66	6.98
	(110)	19.21	4.61
	(130)	22.46	3.95
	(013)	26.36	3.38
	(060)	29.02	3.07
	(142)	32.15	2.78
	(152)	35.02	2.56
	(063)	39.22	2.29
R-CT3 (semi-α-structure)	(020)	9.20	9.60
	(021)	12.70	6.96
	(110)	19.44	4.56
	(013)	26.42	3.37
	(060)	29.24	3.05
	(152)	35.10	2.55
R-CT2 (semi-α-structure)	(020)	8.97	9.85
	(021)	12.76	6.93
	(110)	19.37	4.58
	(013)	26.36	3.38
R-CT6 (semi-α-structure)	(020)	8.93	9.89
	(021)	12.62	7.00
	(110)	19.48	4.55
	(013)	26.60	3.35
N-β-chitin-H (β-structure)	(001)	8.12	10.88
	(011)	12.13	7.29
	(002)	17.20	5.15
	(020)	19.60	4.52
	(121)	26.94	3.30
	(004)	35.24	2.54

[a] Unit cell parameters for α-chitin: $a = 4.74$ Å, $b = 18.86$ Å; $c = 10.32$ Å (fiber axis), $\gamma = 90°$, and β-chitin: $a = 4.85$ Å, $b = 9.26$ Å, $c = 10.38$ Å (fiber axis), and $\gamma = 97.5°$.

coagulated in water has a relatively higher crystallinity than in the alcohol.

As far as the WAXD pattern of the native squid pen chitin (N-β-chitin-H) is concerned, two sharp equatorial diffractions at 7.90° and 19.41° (Fig. 4j), and a series of less strong meridional diffractions at 7.58°, 17.18°, 26.70° and 34.75° could be observed for the fibrous materials (Fig. 4i). A powder x-ray diffraction gives rise to a series of diffraction peaks corresponding to the fibrous diffractions, with the meridional (002) diffraction becoming a shoulder (Fig. 4h or data shown in Table 3), while, the regenerated β-chitin (R-CT6) gives rise to a series of broad and relatively weaker peaks (Fig. 4e), in which the former two diffractions distinctly deviate from those observed in the profile of native samples (Table 3). In addition, the unresolved shoulder peak at 17.20° for the native sample cannot be observed in the profile of the regenerated sample. It is thus suggested that the dissolution and the subsequent coagulation by methanol led to a distinct transition in the crystal structure as well as a decrease in crystallinity in the β-form crystal.

It is interesting to notice that both the WAXD profiles and IR spectra of the regenerated β-chitin and the regenerated α-chitin from the BminAc solvent are hardly distinguishable given the same

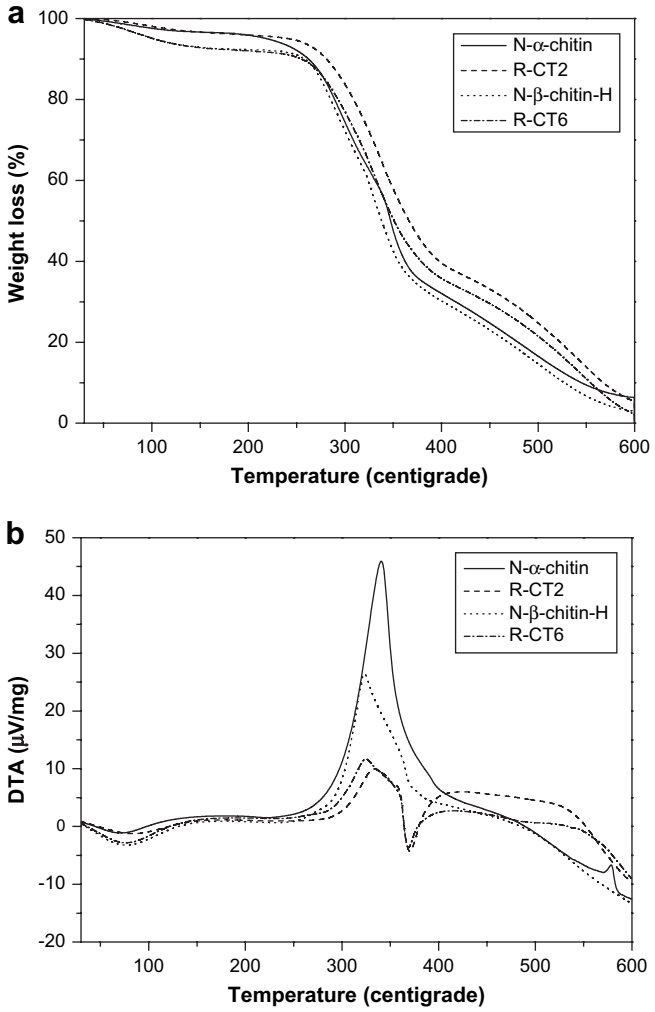

Fig. 6. TG (a) and DTA (b) curves of the native and regenerated chitin samples.

methanol coagulant. Similar phenomenon was also found in a 5% DMAc/LiCl solvent system, which showed that the precipitation treatment of chitins smoothed out the structural differences of the native α- and β-chitins [20]. The WAXD and the FTIR results suggest that the regenerated α- and β-chitins from RTIL have actually similar semi-α-structures which are close to a native anti-parallel arranged α-form crystal (see Fig. 5). In other words, a transition of β-chitin (a metastable chitin polymorphs) to α-chitin (a stable chitin polymorphs) may occur during the dissolving and the recovering processes. In fact, it has been reported that native cellulose I with parallel molecular arrangement (corresponding to β-chitin) transformed to anti-parallel cellulose II structure (corresponding to α-chitin) after being dissolved in another ionic liquid solvent (i.e., AminCl) and regenerated thereof [21].

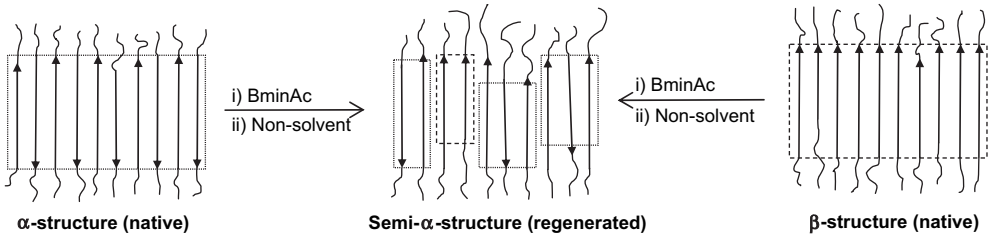

Fig. 5. Schematic illustration of transformations of the native structures of α-chitin (a) and β-chitin (b) during the dissolution in the RTIL and the subsequent regeneration processes. The α-chitin and β-chitin domains are highlighted with dot line and dash line, respectively. The arrows indicate the molecular arrangement direction (polarity) in the crystal domains.

Table 4
Thermal analysis results of the native and regenerated chitins

Polymer	First stage			Second (~third) stage					
	Weight loss (%)	T_1 (°C)	ΔH_{H_2O} (J/mg)	Weight loss at 400 °C (%)	T_{onset}–T_{end}	T_2 (°C)	ΔH_{exo} (J/mg)	T_3 (°C)	ΔH_{endo} (J/mg)
N-α-Chitin	4.3	71.0	0.67	68.0	258.9–367.6	340.6	−14.68	–	–
R-CT2	4.3	83.5	0.90	60.5	271.0–383.6	333.0	−1.57	370.3	0.99
N-β-Chitin-H	7.1	76.8	1.43	69.7	260.6–359.7	323.3	−8.84	–	–
R-CT6	7.2	76.4	1.36	64.2	268.6–372.6	324.6	−2.64	368.7	0.56

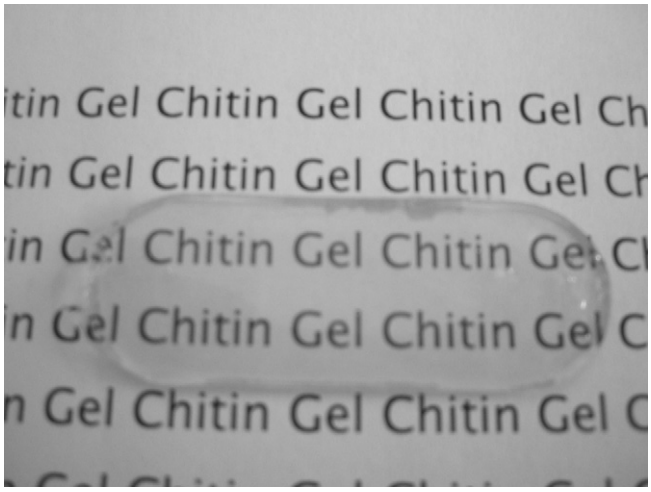

Fig. 7. Digital image of an α-chitin gel prepared by dissolving chitin in the BminAc RTIL.

3.3. Thermal analysis

TG and corresponding DTA curves of the native and the regenerated chitin samples are shown in Fig. 6a and b, respectively. The thermal analysis results are summarized in Table 4. According to the TG results, each chitin sample suffers a small weight loss (4–7%) before 150 °C due to the evaporation of the absorbed water in chitin samples and a sharp weight loss (about 60–70%) at 250–400 °C due to the pyrolysis of polymer chains. In contrast to the two native chitin samples which show double-step decomposition TG curves in the temperature range of 250–400 °C, the two regenerated chitin samples reveal only one-step decomposition TG curves with a little higher onset (T_{onset}) and end (T_{end}) decomposition temperature in the same range. These results indicate that the dissolution and regeneration processes may homogenize the structures of the native chitin samples, and are also responsible for the removal of some relatively unstable impurities and low molecular weight compounds.

On the other hand, the corresponding DTA curves (Fig. 6b) indicate rather different pyrolysis behavior between the native and

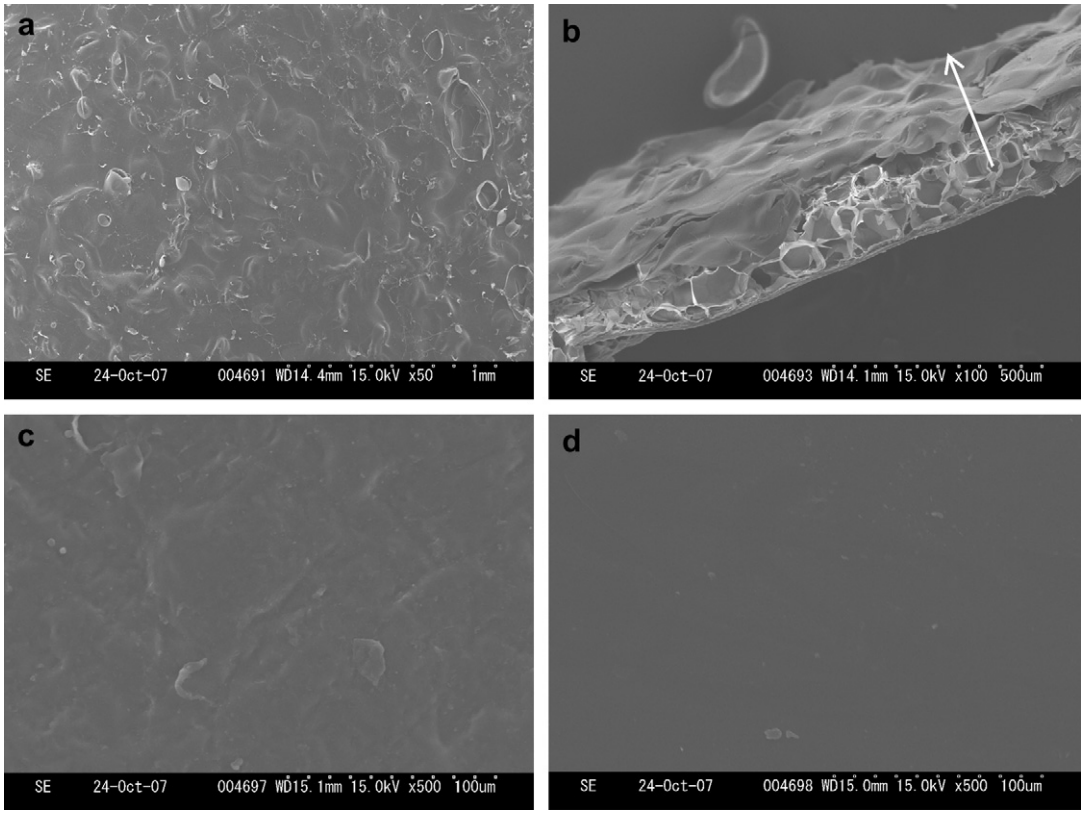

Fig. 8. SEM micrographs of the structures of α-chitin materials: (a) surface and (b) interior structure of freeze-dried chitin sponge (R-CT4); (c) surface structure of oven-dried chitin film (R-CT3); and (d) surface structure of oven-dried chitin film (R-CT2).

regenerated chitin samples, though all of them gave a broad endothermic peak at 70–85 °C (T_1) assigned to evaporation of the absorbed water. For the two native chitins, a sharp exothermic peak due to the main thermal decomposition was observed at 340.6 °C and 323.3 °C for the α- and β-chitin, respectively. While, for the two regenerated chitins, the exothermic peaks were observed at relatively lower temperature or the similar one (T_2) followed by an additional endothermic event which may be ascribed to the dehydrations of the polysaccharide rings at relative higher temperature (T_3). The enthalpy effects (see Table 4) of the exothermic peaks for the regenerated chitins are extraordinarily low compared with those of the native chitins, which may be related to relatively weak inter- and/or intra-molecular hydrogen-bond interactions and poor crystallinity of the regenerated chitins. Again, it is noticed that the two regenerated chitins show similar thermal behavior on the basis of the TG and DTA results, which also gives support to the conclusion that they share similar structures as been indicated by the WAXD and FTIR experiments.

3.4. Morphology observation on the reconstituted chitin materials

The chitin/RTIL solutions were found to form gel after being cooled down to room temperature. Thus, it is quite easy to prepare a transparent soft material (Fig. 7) by casting the as-prepared chitin/RTIL solution to a plastic mold and cooling it to room temperature. In addition, the RTIL in the gels could be extracted out by rinsing the chitin/RTIL gels in water or methanol. The resulting hydrogel and organo-gel were then dried to obtain chitin sponge and films, whose morphologies were investigated by SEM (see Fig. 8). In general, fused and homogenous macrostructures can be observed for the regenerated chitin materials from the SEM results. The regenerated chitin sponge is characterized by a rough surface with bulges, some of which are collapsed (Fig. 8a), and a porous interior structure (Fig. 8b). The two oven-dried chitin films, however, have relatively even and homogenous surface structure (Fig. 8c and d). A water coagulant engendered furrows on the top surface of the regenerated chitin film (Fig. 8c); while, a methanol coagulant resulted in the regenerated chitin film with a plane, featureless surface (Fig. 8d).

4. Conclusion

In this study, we reported a new RTIL solvent, that is, BminAc, for native chitin materials. BminAc could dissolve the chitin materials with different origins (α- and β-chitins) and molecular weights to desirable contents at relatively lower temperature. Cooling the chitin/RTIL solutions to ambient temperature resulted in corresponding chitin/RTIL gels, from which the chitin sponge or film materials were regenerated using water or methanol coagulant. FTIR experiments indicated greatly weakened hydrogen-bond interactions in the regenerated α-chitins from BminAc as compared with that of the native α-chitin. The results from WAXD experiments also suggested that the regenerated α-chitins from the BminAc solvent suffered remarkable decreases in the crystallinity in comparison with the native one, and a methanol coagulant resulted in the regenerated chitin sample with a relatively lower crystallinity than that by using a water coagulant. The regenerated β-chitin sample from BminAc has a crystal structure close to the regenerated α-chitins (semi-α-chitin), implying that a transition of β-chitin (a metastable crystal form of chitin polymorphs) to α-chitin (a stable crystal form of chitin polymorphs) may occur during the dissolving and the recovering processes. The regenerated chitins are thermally more stable than the individual native ones. Morphological studies suggested that the regenerated chitin materials have fused and relatively homogenous macrostructures. On the basis of these results, it is possible to establish a new biomass-ionic liquid platform (BILP) for new processing and homogeneous chemical modifications of native chitin. Such a BILP can be also used as pretreatment technique for many heterogeneous chemical reactions and enzyme degradations in chitin-based polysaccharides.

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