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Preparation of Regenerated Wool Keratin Films from Wool Keratin-Ionic Liquid Solutions

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ABSTRACT: The regenerated wool keratin films were prepared from the wool keratin/ionic liquid solutions through water, methanol and ethanol as coagulation solvents in this article. It could be suggested from the results that $[AMIM]^+ \cdot Cl^-$ ionic liquid has higher solubility for wool keratin fibers than $[BMIM]^+ \cdot Cl^-$ ionic liquid. IR data showed the part of the disulfide bonds was broken during the dissolution. It could be seen from XRD data that the regenerated films exhibited a β-sheet structure and the disappearance of the α-helix structure. TGA curves indicated that the thermal stability of regenerated wool keratin films decreased slightly compared to nature wool fibers. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: ionic liquid; wool keratin fiber; regenerated wool keratin films

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INTRODUCTION

Wool has immense importance as a renewable raw material in textile industry. A great quantity of short fibers and crude fibers are discarded during wool weaving every year and a mass of waste wool keratin textile fibers are abandoned in our daily life, which does not only cause the waste of keratin resources, but also pollute the environment.[1] Obviously, it has great significance to study the recycling of waste wool fibers for effective utilization. Wool keratin fibers generally include four parts: the epidermis, cortex, medulla, and cell membrane complex of which the main component is the α-keratin. Keratin molecules, not dissolved under normal conditions, are highly crosslinked formed three-dimensional stability structure through disulfide bonds, hydrogen bonds, salt bonds, and other bonds.[2] Therefore, it needs to develop an appropriate process for treating wasted keratin from short wool fibers into the available renewable resources.

Ionic liquids have received much attention as green and designable solvents with the development of green chemistry and the requirement for environment protection. Many applications of ionic liquids in organic synthesis, electrochemistry, chemical separation, material preparation, and catalysis have already been reported.[3] Owing to their special structures compared to the traditional molecular solvents, ionic liquids as solvents for the dissolution and regeneration of cellulose, silk protein, and other natural polymer material have become the new fiber material-processing technologies. Forsyth et al.[4] used dicyanamide anion-based ionic liquids as solvents for the dissolution of carbohydrates. Swatloski et al.[5] reported that $[BMIM]^+ \cdot Cl^-$ was an excellent solvent for the dissolution of cellulose. It is simple to prepare up to 10 wt % solutions by heating in an oil bath at 100°C and 25 wt % using a microwave apparatus. Xie et al.[6] studied the solubility and dissolution mechanism of three types of ionic liquids on wool keratin, and indicated that the process have no chemical changes but dissolved.

In this article, the dissolution of wool keratin fibers in ionic liquids was studied. To regenerate film, different solvents including water, methanol, and ethanol were used and the structures and properties of the regenerated films were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), SEM, and thermogravimetry analysis (TGA).

EXPERIMENTAL

Materials and Chemicals

The wool keratin fibers samples were provided by Ningbo Reward Wool Industry (Zhe Jiang Province, P. R. China) and the acetone, ethanol, and methanol were analytical grade chemicals obtained from Sinopharm Chemical Reagent (Beijing, P. R. China). Detergent 209(*N,N*-sodium oleoyl methyl taurinate) was obtained from Shanghai Jing Wei Chemical (Shanghai, P. R. China). Ionic liquids (1-allyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium chloride) were provided from

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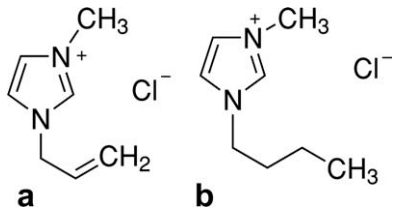

Figure 1. The structure of ionic liquid (a) $[AMIM]^{+}\cdot Cl^{-}$; (b) $[BMIM]^{+}\cdot Cl^{-}$.

Shanghai Cheng Jie Chemical. The structures are shown in Figure 1.

Pretreatment of Wool Keratin Fibers

The wool keratin fibers used in these experiments were first washed by detergent 209 and cleaned by an acetone/ethanol mixture solvent system in a Soxhlet extraction set for 48 h, then rinsed with distilled water, and dried at 100°C for 12 h in an oven prior to solubility experiments.

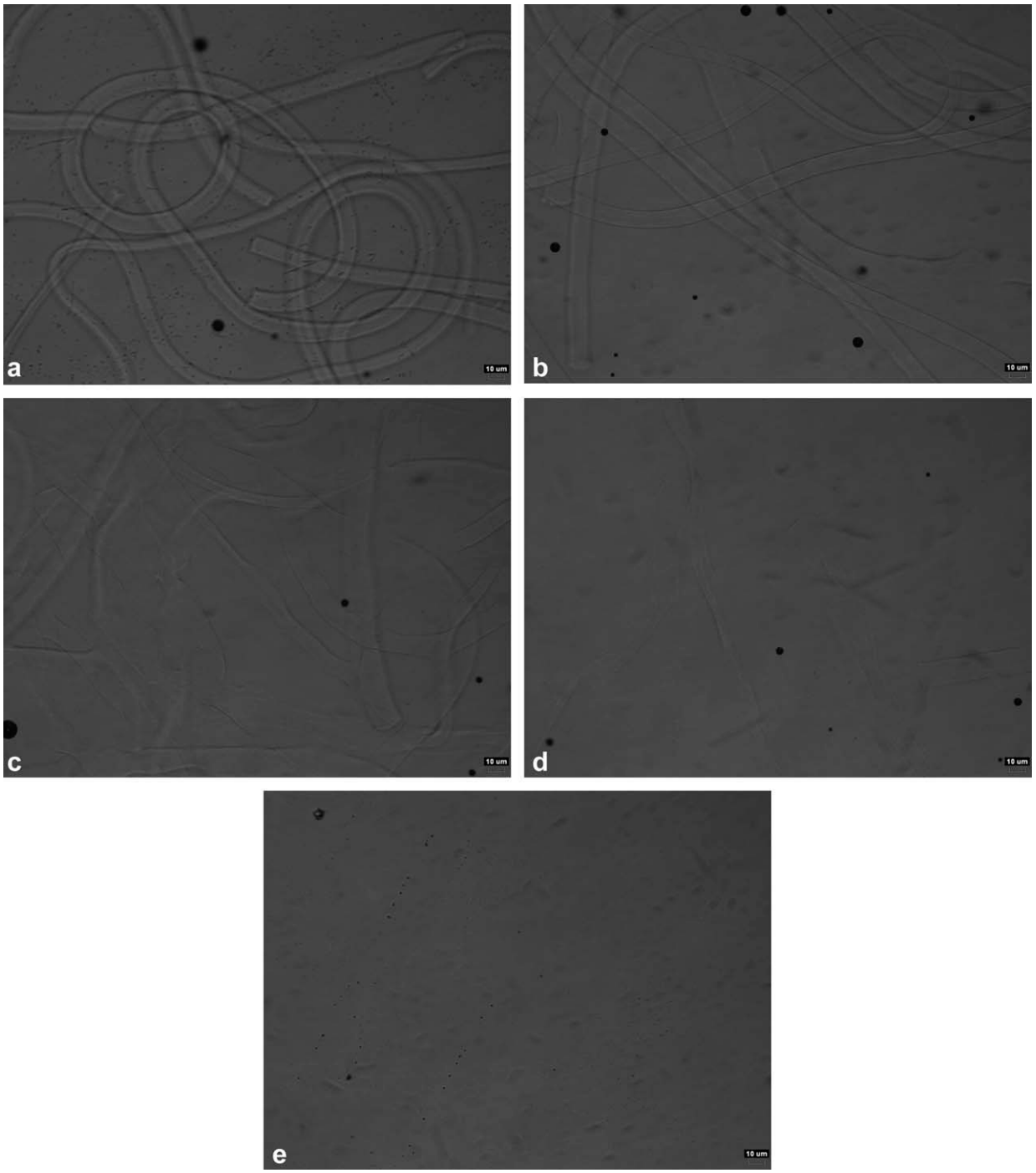

Figure 2. The process of 1 wt % wool keratin dissolved in $[BMIM]^{+}\cdot Cl^{-}$ at 130°C. (a) 1 min, (b) 3 min, (c) 5 min, (d) 10 min, and (e) 15 min.

Table I. The Relationship Between the Concentration of Wool Keratin/Ionic Liquid Solution and Dissolving Time

Concentration wt %	Dissolving time in $[AMIM]^+ \cdot Cl^-$/min	Dissolving time in $[BMIM]^+ \cdot Cl^-$/min
1	3	5
2	15	35
4	55	90
6	105	170
10	180	285
12	275	370
15	390	535
18	515	-
21	640	-
22	-	-

Dissolution of Wool Keratin Fibers

A certain amount of ionic liquid was added in a 50-mL three-necked flask with MR Hei-standard magnetic stirring apparatus produced by Heidolph Instruments (Germany). The temperature of the dissolving process was controlled by an oil bath at 130°C. The wool keratin fibers were added in portions of only 1 wt % of ionic liquid every time until the wool keratin fibers disappeared.

Preparation of Regenerated Films

The wool keratin/ionic liquid solution was spread evenly on the glass, and immersed in water, methanol, and ethanol as coagulation solvents, respectively, for 12 h at room temperature. Then, the regenerated films were cleaned with deionized water and dried at room temperature.

Recycling of Ionic Liquid

Ionic liquid was recycled by removing the solvent from the solution of ionic liquid mixed with water, methanol, or ethanol using an Eyela N-1000 rotary evaporator with a circulation water vacuum pump.

Measurements

FTIR Spectroscopy. Samples for infrared (IR) spectra were measured on a Nicolet Nexus-670 FTIR spectrometer equipped with SMART iTR diamond accessory in Spectral scanning frequency range of 650—4000 cm^{-1} at the spectral resolution of 4 cm^{-1}.

XRD Measurements. The film samples were cut into strips of 10 mm in length and 10 mm in width for the measurements. XRD was performed on a Rigaku-D/Max-2550 PC diffractometer with Cu KR radiation ($k = 1.54056$ Å) at 40 kV, 200 mA in the range of 5–60° at the rate of 0.02°/min.

Scanning Electron Microscope (SEM). The morphology of surfaces of the films was examined with a Hitachi TM-1000 scanning electron microscope (SEM) at an accelerating voltage of 15 kV. The surfaces were coated with thin layers of gold before the observation.

Thermogravimetry Analysis. Thermogravimetry analysis (TGA) measurement was performed on a NETZSCH-TG 209 F1 thermogravimetric analyzer. The measurement was performed using 1–5 mg of the sample under an atmosphere of nitrogen gas. The samples were heated from 30 to 600°C at a rate of 10°C/min.

3 RESULTS AND DISCUSSION

The Solubility of Wool Protein Fiber in Ionic Liquids

The dissolution of wool protein fiber in $[AMIM]^+ \cdot Cl^-$ and $[BMIM]^+ \cdot Cl^-$ was observed by optical microscope. First wool protein fiber was swelled in ionic liquids. With the fibers continue dissolving, the fibers gradually became thin and finally disappeared as shown in Figure 2.

The dissolving time that prepared different concentrations of wool keratin/ionic liquid solutions was measured. According to the method described in Dissolution of Wool Keratin Fibers section, the required amount of wool keratin fibers was added in portions of only 1 wt % of ionic liquid every time until the wool keratin fibers were completely dissolved.

The relationship between the concentration of wool keratin/ionic liquid solution and the dissolving time was researched, as

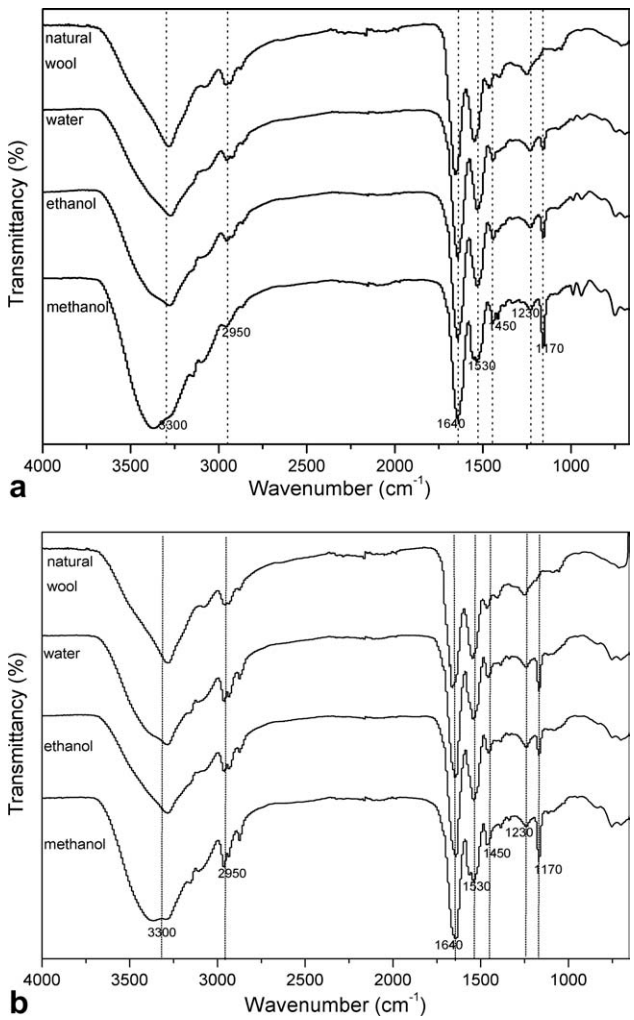

Figure 3. IR comparison of natural wool keratin fibers and regenerated wool keratin coagulated by different solvents from (a) wool keratin/$[AMIM]^+ \cdot Cl^-$ solution; (b) wool keratin/$[BMIM]^+ \cdot Cl^-$ solution.

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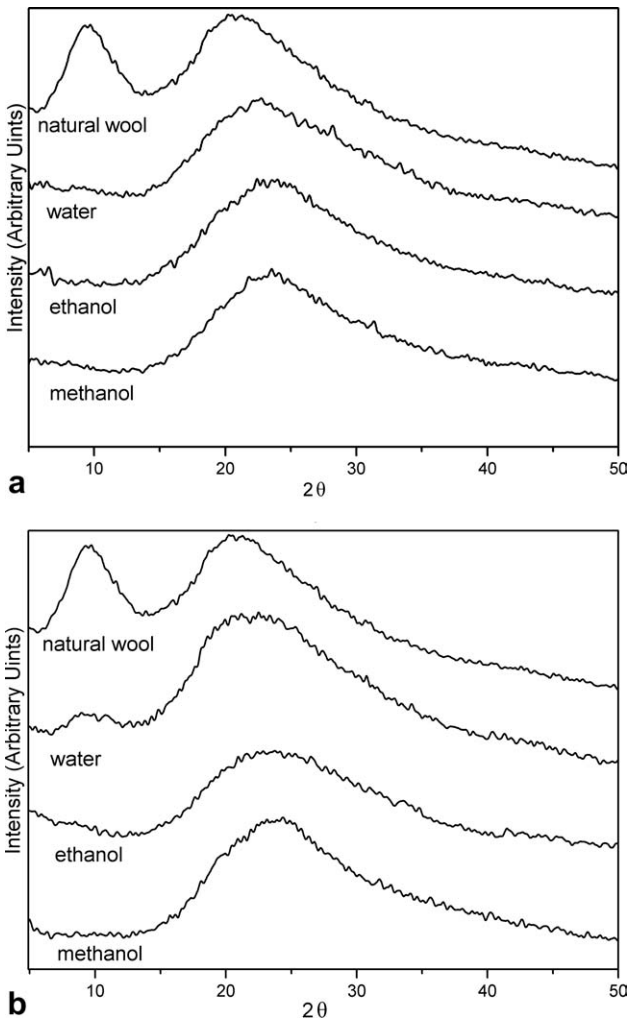

Figure 4. XRD comparison of wool keratin fibers and regenerated wool keratin coagulated by different solvents from (a) wool keratin/$[AMIM]^+\cdot Cl^-$ solution; (b) wool keratin/$[BMIM]^+\cdot Cl^-$ solution.

summarized in Table I. From the solubility results summarized in Table I, it could be concluded that wool protein fibers had high solubility in both $[AMIM]^+\cdot Cl^-$ and $[BMIM]^+\cdot Cl^-$, but $[AMIM]^+\cdot Cl^-$ ionic liquids had higher solubility for wool keratin fibers than $[BMIM]^+\cdot Cl^-$ ionic liquids. It could be concluded the cationic structure of ionic liquid had an important influence on the dissolution of wool protein fibers in ionic liquids.[7]

The Structure Changes of Wool Protein

To further prove the dissolution of wool keratin fibers in ionic liquids, the 10 wt % wool keratin/ionic liquid solutions was taken to prepare the regenerated wool keratin films by addition of methanol, ethanol, or water, respectively.

Molecular structure of wool keratin films could be revealed by FTIR spectroscopy. The IR results of natural wool keratin fibers and regenerated wool keratin coagulated by different solvents from wool keratin/ionic liquid solutions are shown in Figure 3.

Figure 3 shows the IR data comparison of wool keratin fibers and regenerated wool keratin. There were two peaks about 2930 and 3300 cm^{-1} that can be indexed correlated to the C—H and O—H stretching vibration. The peaks at 1450–1500cm^{-1} were related methyl C—H deformation vibration that connected to nitrogen atoms of the protein amide. The protein amide I at approximately 1600–1700 cm^{-1} was connected mainly with the C=O stretching vibration. The protein amide II which absorbed at approximately 1550 cm^{-1} was related to N—H bending and C—N stretching vibrations.[8,9] The amide I band vibrational frequency could be used to determine the secondary structure of proteins because it was particularly sensitive to protein secondary structure.[9–12] For the protein α-helix structure, the amide I, amide II, and amide III typically were in the range of approximately 1648–1660, 1540–1550, and 1235–1250 cm^{-1}, respectively. For β-sheet, the peaks were in the range of approximately

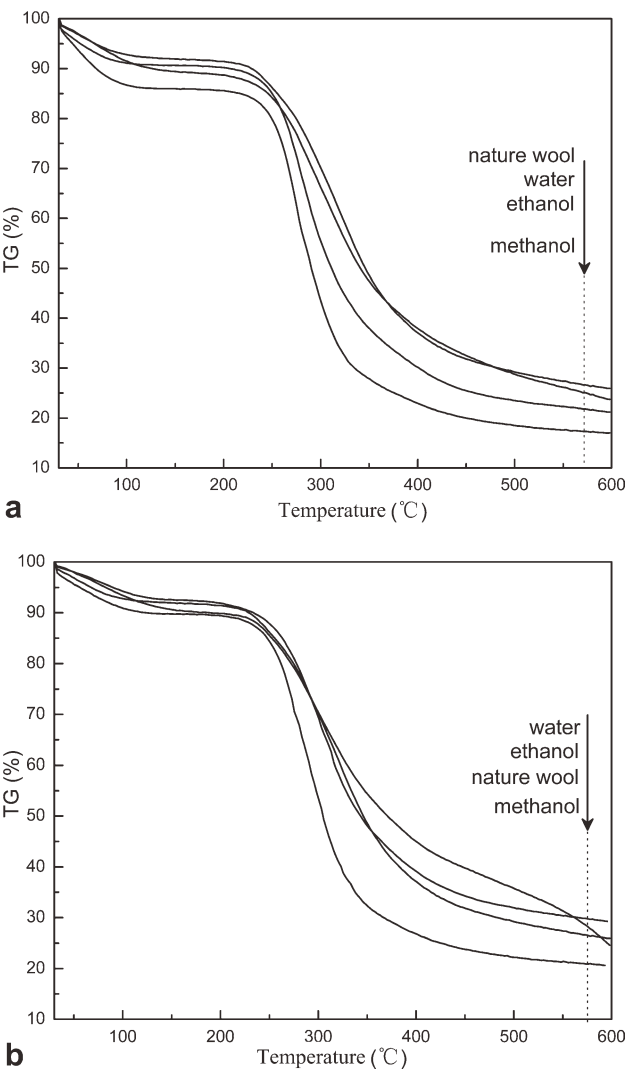

Figure 5. TGA comparison of wool keratin fibers (a) and regenerated wool keratin: (b, c, and d coagulated by water, ethanol, and methanol, respectively, from wool keratin/$[AMIM]^+\cdot Cl^-$ solution; e, f, and g coagulated by water, ethanol, and methanol, respectively, from wool keratin/$[BMIM]^+\cdot Cl^-$ solution).

1620–1640, 1530–1540, and 1220–1235 cm^{-1}, respectively.[11,13] As shown in Figure 3, 1656, 1540, and 1244 cm^{-1} peaks existed in natural wool and 1639, 1530, and 1230 cm^{-1} peaks existed in regenerated wool keratin, which could be suggested that the α-helix structure of keratin changed into β-sheet structure during regeneration of wool keratin films. Figure 3 also shows that regeneration wool keratin films had an absorption peak about 1170 cm^{-1} which could be assigned as the asymmetric S—O stretching vibration of the Bunte salts residues. The S—O band was a product of oxidation reaction of S—H or —S— group in natural wool keratin because there is no S—O group in natural wool keratin.[14,15] It indicated that the part of the disulfide bonds was broken by oxidation reaction during the dissolution of wool keratin fiber in the ionic liquid.

The crystallite alignment of the films was further examined by XRD. These film samples were cut into strips of 10 mm × 10 mm for the measurements.

Figure 4 shows the XRD data comparison of wool keratin fibers and regenerated wool keratin. There was a prominent 2θ peak about 20.78° and several minor peaks that can be indexed correlated to the antiparallel β-sheet structure compared with the natural wool keratin fibers.[16,17] But the disappearance of the peak about 9.31° was consistent with the conclusions of the infrared spectra that the α-helix structure was destroyed by the ionic liquid during the dissolving process. The regenerated wool keratin film precipitated from methanol exhibited a high degree of crystalline compared to other solvents. That was in agreement with the previous literatures which had reported that methanol treatment induced the regeneration of the β-sheet structure of protein polypeptide chains.[18–22]

The thermodynamic stabilities of the natural wool fiber and the regenerated films were measured using thermogravimetric analyzer. The samples were heated from 30 to 600°C at a rate of

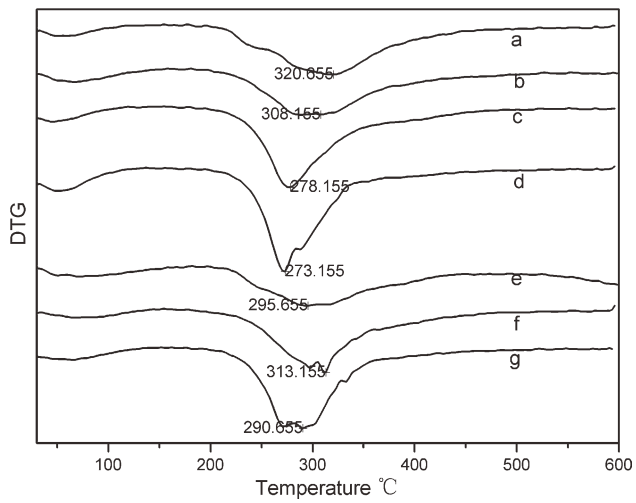

Figure 6. DTG comparison of wool keratin fibers (a) and regenerated wool keratin: (b, c, and d coagulated by water, ethanol, and methanol, respectively, from wool keratin/$[AMIM]^+ \cdot Cl^-$ solution; e, f, and g coagulated by water, ethanol, and methanol, respectively, from wool keratin/$[BMIM]^+ \cdot Cl^-$ solution).

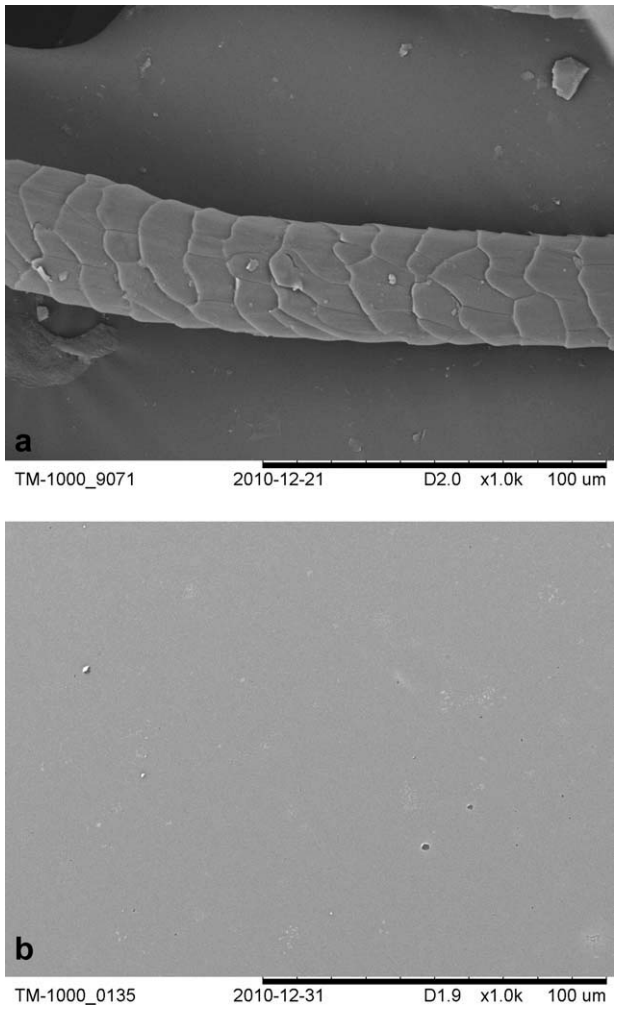

Figure 7. SEM micrograph of (a) nature wool keratin fiber, (b) regenerated wool keratin films (ionic liquid: $[BMIM]^+ \cdot Cl^-$ coagulant solvent: methanol).

10°C/min under an atmosphere of nitrogen gas. TGA curves of wool keratin fibers (a) and regenerated wool keratin are shown in Figure 5 and derivative thermogravimetric (DTG) curves obtained from the derivative of TGA curves are shown in Figure 6.

The comparison of TGA (Figure 5) and DTG (Figure 6) of natural wool keratin fibers and regenerated wool keratin films indicated that it had a significant thermal transition region about 300°C. The weight loss of natural wool keratin fibers and regenerated wool keratin films were about 8% when temperature was heated to 100°C that could be attributed to the loss of water. About 60% of the weight loss from 150 to 500°C might be caused by the destruction of lateral chain of wool protein molecules. Figure 6 shows that the maximum temperature of thermal decomposition of regenerated wool keratin films was slightly lower compared with the natural wool keratin fibers, reflecting that the thermal stability of regenerated wool keratin films decreased slightly. The reason might be that natural wool keratin fibers had high molecular weight and crystalline, but part of the molecular chain of regenerated wool keratin films from

ionic liquids was broken at the role of solvents that made the molecular weight decreased.[23]

The morphology of surfaces of the films was examined with scanning electron microscope (SEM).

Figure 7 shows the SEM micrograph of the surface of regenerated wool keratin films. The films with a homogeneous surface did not show residual wool fiber structure, further supporting the fact that the wool keratin fibers had been dissolved in the ionic liquid.

CONCLUSIONS

The regenerated wool keratin films were prepared from the wool keratin/ionic liquid solutions through water, methanol, and ethanol as coagulation solvents. It could be suggested from the results that $[AMIM]^+ \cdot Cl^-$ ionic liquid has higher solubility for wool keratin fibers than $[BMIM]^+ \cdot Cl^-$ ionic liquid. Compared with the natural wool keratin fibers' structure, the regenerated wool keratin from ionic liquids exhibited a β-sheet structure and the disappearance of the α-helix structure owing to coagulation solvents. The thermal stability of regenerated wool keratin films decreased slightly to some extent because of the part of the molecular chain breakage. But the mechanism of dissolution needed to be further researched.

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