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Dissolution of wool in the choline chloride/oxalic acid deep eutectic solvent

Dongyue Wang, Ren-Cheng Tang *

National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, 199 Renai Road, Suzhou 215123, China

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ABSTRACT

A great amount of wool wastes are produced every year in the world, leading to the discard of keratin resources and causing environmental pollution. The recycling of wool is of great significance for the application of keratin. In this work, the dissolution of wool in a benign choline chloride/oxalic acid (ChCl-OA) deep eutectic solvent (DES) solvent was presented, and the dissolution conditions were discussed. After dissolution, keratin was separated by dialysis, filtration and freeze-drying. The resulting keratin powder was characterized by X-ray diffraction, thermogravimetry/differential scanning calorimetry, protein electrophoresis, scanning electron microscope, and amino acid analysis. The optimized dissolution conditions were the following: ChCl-OA molar ratio 1:2; wool-DES weight ratio 5%; 110–125 °C; 2 h. In the dissolution process, the disulfide bonds of wool molecules were broken, and the α-helix structure of wool was destroyed. The molecular weight of the as-prepared keratin was between 3.3 kDa and 7.8 kDa, and the freeze-dried keratin displayed flake structures.

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1. Introduction

Keratin universally exists in animal organs such as hairs and feathers. In agricultural and industrial production, a great quantity of wool and feather wastes are produced every year in the world, leading to the abandoning of keratin resources and causing environmental pollution. Because keratin can be applied in multiple fields including fertilizers, biomaterials, composites materials, reinforcements, absorbents, cosmetics, leather and textile processing, and environmental remediation [1,2], the recycling of waste wool is of great significance and has become a research hotspot. In this regard, the dissolution of keratin substrates is the first problem to be solved.

Up to now, the abandoned wool wastes from farms, slaughterhouse and woolen mills have not been efficiently recycled. To extract keratin from these rejectamenta, various approaches for dissolving wool have been attempted, such as reduction, oxidation, sulfitolysis, alkaline hydrolysis, superheated water treatment, and ionic liquid extraction [3–6]. These approaches have different extraction efficiency, potential for upscaling and environmental safety, and produce keratin proteins with different molecular weights [3,4]. Some methods are limited for their long time, high temperature and rigorous reaction conditions, and the others use toxic and harmful reagents. Thus, more dissolution methods deserve to be studied.

Deep eutectic solvent (DES) is the mixture of two or three components acting as either a hydrogen bond receptor or a hydrogen bond donor. The concept of DES was first proposed by Abbott et al. in 2003 [7]. One of the notable features of DES is that the freezing point is significantly lower than its pure material, which allows it to react at a lower temperature [8]. Beyond that, DES has many advantages including good biocompatibility, environmental protection, innocuity, and low-price [9]. A benign choline chloride (ChCl)-urea DES melt was utilized to dissolve wool [10], where the dissolution mechanism of wool is to destroy the macromolecular structures by weakening the intramolecular and intermolecular interactions of wool [10]. Recently, we employed the combination of ChCl with urea, glycerol, ethanol, oxalic acid (OA), citric acid and acetic acid as DES solvent to dissolve wool, and found that the ChCl-OA solvent displayed the best dissolution effect on wool. Additionally, ChCl-OA could effectively extract collagen peptides from cod skins [11]. Therefore, in this work, the mixture of ChCl and OA is used as DES to dissolve wool; the dissolution conditions and mechanism of wool in the ChCl-OA solvent are discussed and the resulting wool keratin is characterized.

2. Materials and methods

ChCl and OA were both chemical pure reagents without further purification. Two compounds were mixed at a 1:2 mol ratio and

* Corresponding author.
E-mail address: tangrencheng@suda.edu.cn (R.-C. Tang).

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stirred at 70 °C for 20 min to give a transparent and homogeneous DES solvent. To dissolve the sheared wool, the following procedure was used: wool was firstly accurately weighed, and then immersed in DES (20 g); the mixture was stirred at the desired temperature for a set period of time; afterwards the cooled solution was dialyzed for 2 days using the dialysis bag with a theoretical molecular weight cut-off of 3000 kDa; after dialysis, samples were frozen using the 25EL freeze-drying machine (Virtis, USA) for 2 days to obtain keratin powder. The detailed dissolution conditions were described in Fig. 1. The keratin obtained under the following conditions was used for instrument characterization: ChCl-OA molar ratio 1:2, wool-solvent weight ratio 5%, 110 °C and 2 h.

The solubility of wool was determined using the following equation:

$$\text{Solubility}\,(\%) = \frac{W_0 - W_1}{W_0} \times 100$$

where W_0 and W_1 represent the weight of wool before and after dissolution, respectively.

The UV–Vis absorption spectrum of wool keratin solution was characterized by the Shimadzu UV-1800 spectrophotometer (Shimadzu Co., Japan). The infrared measurement was conducted on the Nicolet 5700 FTIR spectrometer (Thermo Fisher Scientific Inc., USA). The XRD analysis was performed on the X'Pert-Pro MPD X-ray diffraction (PANalytical B.V., Almelo, Netherlands). The TG analysis was measured on the Diamond 5700 instrument (Perkin-Elmer, USA) at 10 °C/min in nitrogen. The molecular weight distribution of keratin was tested on the PowerPac universal type protein electrophoresis by SDS-PAGE (Bio-Rad Laboratories Inc., USA). The morphology of keratin was observed by the S4800 scanning electron microscope (Hitachi High Technologies America, Inc., USA). The free amino acid residues of wool and keratin were measured on the L-8900 automatic amino acid analyzer (Hitachi, Japan).

3. Results and discussion

Fig. 1 shows the solubility of wool and the absorbance of dissolved products under varying conditions. As shown in Fig. 1a, when the molar ratio of ChCl-OA decreased from 3:1 to 1:3, the wool solubility increased totally, but the absorbance of keratin solution increased at first and then decreased. This might be associated with the increased quantity of free hydrogen protons with increasing OA concentration, leading to stronger binding between hydrogen protons and imino and amino groups in proteins, and more OA to be attracted by proteins, which make the intramolecular and intermolecular hydrogen bonds in proteins damaged [11]. During dialysis, keratin with low molecular weight was removed, resulting in decreased absorbance. Fig. 1b shows that the solubility of wool decreased and the absorbance increased as the wool-to-DES weight ratio increased from 1% to 9%. The decreased solubility is caused by the increased quantity of wool, whereas the increased absorbance is due to an increase in the absolute quantity of dissolved keratin. Fig. 1c and d show that both the solubility and absorbance increased markedly with increasing temperature and time. On the basis of the solubility and absorbance assessments, the optimized dissolution conditions were the following: ChCl-OA molar ratio, 1:2; wool-DES weight ratio, 5%; temperature, 110–125 °C; time, 2 h.

The UV–Vis and FT-IR absorption spectra of keratin are shown in Fig. 2. Fig. 2a clearly shows that the keratin solution had an absorption peak at 275 nm, corresponding to the absorption of aromatic amino acid sequences. The comparison between the FT-IR spectra of wool fiber and keratin in Fig. 2b revealed that keratin did not show great variations in the positions of absorption bands, but the intensity of some bands changed. In particular, Amide II shifted to a lower wavenumber and a novel shoulder peak appeared at 1170 cm^{-1} which is assignable to the asymmetric S–O stretching vibration of water-soluble cysteine. The appearance

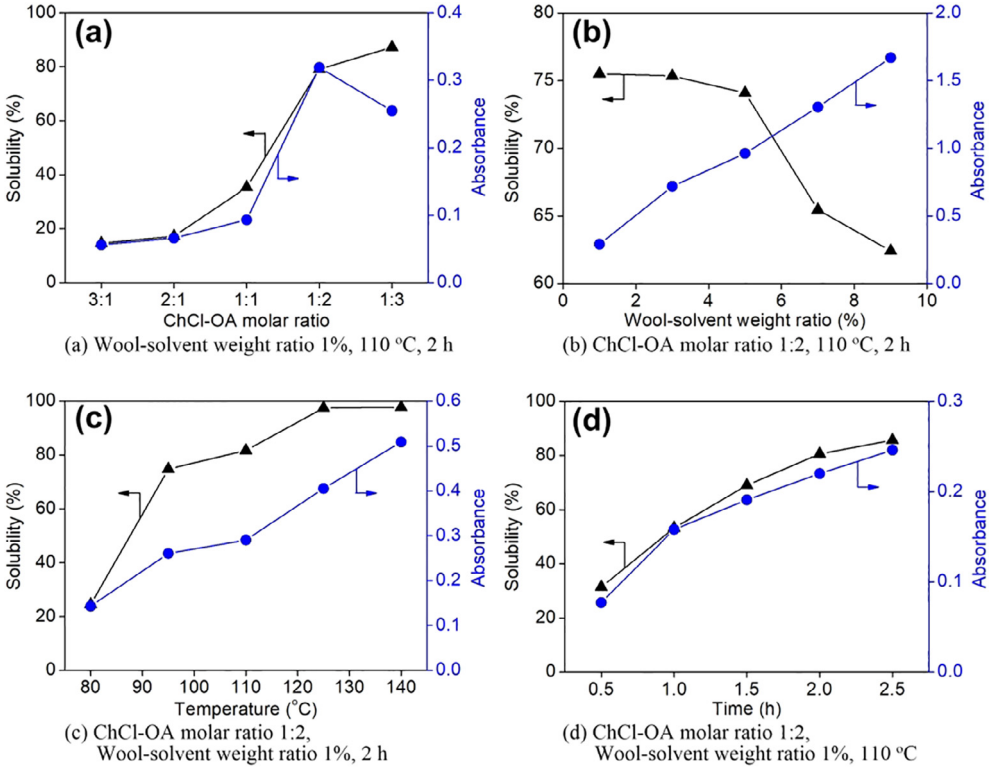

Fig. 1. Solubility of wool in the ChCl-OA DES solvent in various conditions.

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