Upcycling of Keratin Wastes in Sustainable Textile Fiber Applications

Wenwen Fang,* Ruxia Fan, A. Sesilja Aranko, Michael Hummel,* and Herbert Sixta

ABSTRACT: The textile industry is facing growing pressure to adopt sustainable practices, including the development of biodegradable and recyclable fibers derived from waste streams. In this study, we explored the use of keratin from waste textiles as a potential raw material for sustainable fiber production. We investigated the dissolution of keratin in 7-methyl-1,5,7-triazeabicyclo[4.4.0]dec-5-ene (mTBD)-based ionic liquids (ILs) and its regeneration in various coagulation solvents. The viscoelastic properties of the keratin solution were characterized using small angle oscillatory shear rheology (SAOS), and the results showed that the keratin solution was not suitable for the dry-jet spinning process and the pure regenerated keratin fiber was too weak to hold the stretching in fiberline. To bypass these issues, we blended high molar mass cellulose with keratin during the dissolution step to adjust the rheological properties and mechanical strength of the extruded fibers. The resulting hybrid fibers exhibited high strength, low fibrillation tendency, and soft texture. We also demonstrated the further processability of these fibers by spinning a yarn and knitting a piece of fabric. Our findings suggest that hybrid fibers derived from keratin waste textiles and cellulose could be promising materials for sustainable fashion applications.

KEYWORDS: fiber spinning, ionic liquid, textile recycling, wool waste, ion-cell technology

INTRODUCTION

The textile industry is confronted with increasing pressure to move away from fast fashion business models toward sustainable and circular clothing production due to the growing awareness of its environmental and social impact. The recent EU strategy for sustainable and circular textiles envisions all textile products placed on the EU market to be repairable and recyclable, to a great extent made of recycled fibers and free of hazardous substances. (The Commission’s 2030 Vision for Textiles) Meanwhile, the fiber market is expected to increase by 34% in 2030 (Textile Exchange); therefore, it is urgent to exploit biodegradable and recyclable textile fibers regenerated from waste streams to satisfy the market needs and reduce the microplastic pollution.

Cellulose has been studied widely as an alternative to high-performance synthetic fibers due to its excellent mechanical properties and abundance.1 In addition to cellulose, keratin wastes generated from the textile industry, butchery, and breeding are estimated to be more than 5 million ton/year worldwide, representing a high potential renewable resource.2 A distinction of keratin from other proteins is the high content of cysteine residues, which contain a thiol group that can give rise to cross-linking disulfide bonds. In wool keratin, there is typically 10–14 wt % cysteine depending on the wool sources.3 In addition, over 30 wt % of amino acids in keratin contain charged side chains, e.g., carboxylic acids and amines.3,4 Derived from its unique chemical composition, it has a natural odor and flame resistance, representing high potential in textile applications.3–5

Dissolution of keratin without excessive hydrolysis is a key step for the recycling of the keratin wastes and conversion into high value-added products. However, due to the high content of disulfide cross-links and hydrogen bonds, keratin is chemically stable and difficult to be dissolved and extracted in regular solvents. Various chemical methods have been investigated to cleave the different linkages present in the structure to facilitate dissolution. The disulfide bonds can be disrupted via oxidation or reduction using peroxides, sulfites, and thiols,5,10 while the hydrogen bonds and ionic bonds are disrupted by urea and SDS, respectively.11 An aqueous solution containing different amounts of urea, SDS, and disulfide bond cleavage agent is commonly used for the extraction of keratin.11,12,13 This method requires an alkaline condition

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In addition to imidazolium-based ILs, super and the zero-shear viscosity, ranging from 20,000 and a strain of 1%. The zero-shear viscosity, 

\[ \eta_0 \] 

and fiber strength.

The dissolution of keratin. In 2005, it was reported for the first time that wool keratin could be dissolved and regenerated using 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]). Since then, various ILs have been employed to process keratin. In addition to imidazolium-based ILs, super base–based ILs, specifically 1,5-diaza-bicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]), have exhibited promising dissolution capacity for both chicken feather and wool keratin. [DBNH][OAc] was initially developed as a novel solvent for cellulose dissolution and fiber spinning, demonstrating excellent spinnability in air-gap spinning. However, due to the hydrothermal instability of DBN, hydrolysis byproducts can form during the thermal removal of water from the IL-water mixtures, reducing the dissolution capacity of the recycled [DBNH][OAc]. In response to this issue, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-enium acetate [mTBDH][OAc] was developed as an alternative cellulose spinning solvent, exhibiting excellent recyclability and high tolerance to impurities in the IL, e.g., water and hydrolysis compounds.

In this study, we investigated the dissolution of wool keratin in mTBD-based ILs and their regeneration in different coagulation solvents. The dissolved keratin was then spun into a fiber via an air-gap spinning process. However, due to the relatively low molecular weight (\( M_w \)) of wool keratin (10–50 kDa), the extruded keratin fibers have poor mechanical strength, making it challenging for the air-gap spinning. One way to overcome these limitations is to blend in high molecular weight biopolymers, e.g., cellulose, which modifies the rheological properties and subsequently improves spinnability and fiber strength. For this purpose, we utilized dissolving pulp with an average \( M_w \) of 200 kDa as the source of cellulose. Various proportions of cellulose and keratin are blended during the dissolution process, and their viscoelastic properties are then analyzed by using oscillatory shear rheology in order to investigate the correlation between rheology and spinnability. To further demonstrate its feasibility in textile recycling, a preconsumer cashmere textile is used as the keratin raw material and blended with cellulose to produce hybrid fibers using multifilament spinning. The regenerated fibers were spun into yarn to produce a knitted fabric piece.

**MATERIALS AND METHODS**

**Materials.** A sulfite pulp made from spruce wood with an intrinsic viscosity of 571 mL/g was used in this work as the cellulose resources. The chemical composition and molar mass distribution of the pulp are presented in Table S1 (Supporting Information). The pulp sheets were ground using a Wiley mill, and the dry matter content was determined before dissolution in an ionic liquid. The wool used in this work was provided by a local farm in Finland. It was cleaned and defatted by a two-step washing procedure. It was first washed by hands in a bucket using detergent to remove the dirt and grease and then dried at ambient conditions. After the first round of washing, the wool still had a greasy hand feel. Therefore, it was washed again by bath sonication using 0.02 M Na_2CO_3 at 80 °C for 30 min with a solid/liquid ratio of 1:10 (w/v), followed by rinsing with water and then acetone to remove the residual Na_2CO_3. The washed wool was dried under ambient conditions for further use. mTBD was neutralized with an equimolar amount of levulinic acid (Lev, natural, 99%, Merck, Germany) at room temperature under stirring. The solution mixture was subsequently stirred for another 30 min to ensure complete conversion to [mTBDH][Lev]. [mTBDH][OAc] was prepared by neutralizing mTBD with an equimolar amount of acetic acid (OAc, 100%, Merk, Germany) at 85 °C under stirring.

**Dissolution of Wool/Cashmere in Ionic Liquid.** The dissolution of wool/cashmere in [mTBDH][Lev] and [mTBDH]-[OAc] was performed in a vertical kneader at 85 °C under stirring (30 rpm) and vacuum (30–40 mbar). To monitor the dissolution of wool/cashmere, a sample was taken from the kneader every hour and assessed via polarized optical microscopy (POM). The microscope (Zeiss Axio, LTS420) was set to a cross-polarized light mode. Wool and cashmere fibers exhibit birefringence when illuminated with cross-polarized light, resulting in a bright coloration. Upon dissolution, the fibers lose their birefringence, indicated by the disappearance of bright coloration.

The cellulose/wool hybrid dopes (10–20 g) with varying mass ratios (87:13, 77:23, 50:50) were prepared by first dissolving wool in the IL at 85 °C for 2 h and then adding cellulose pulp to the solution and continuing the dissolution for another 2 h. The dopes were then filtered using a heated hydraulic press filtration system with a 5–6 μm mesh metal filter. The IL was heated to its spinning temperature, determined by its rheological properties, using temperature superposition principle.

**Rheology Measurement.** The viscoelastic properties of cellulose/keratin dopes under shear stresses were measured using an Anton Paar MCR 302 rheometer equipped with 25 mm diameter parallel plate geometry and 1 mm gap size. The viscoelastic behavior was studied by conducting dynamic frequency sweeps at various temperatures ranging from 25 to 80 °C, within an angular velocity range of 0.01–100 s<sup>−1</sup> and a strain of 1%. The zero-shear viscosity, \( \eta_0 \), was determined by fitting the complex viscosity data to the Cross-viscosity model, assuming that the Cox-Mertz rule is valid. The master curves of spinning dopes at their spinning temperature were generated based on the time–temperature superposition principle.

**Gel Electrophoresis.** The supernatant of wool/cashmere samples was concentrated by Vivaspin centrifugal concentrators (Sartorius) with a cutoff of 3000 MWCO followed by buffer exchange into MQ water using the centrifugal concentrators. The wool/cashmere samples were dissolved in 8 M urea with vigorous stirring. The soluble fractions were collected for analysis by sodium dodecyl-sulfate polyacrylamide gel electrophoresis (SDS-PAGE) by centrifugation (13,333 × g, 10 min). All samples were mixed with the SDS-PAGE loading dye and heated at 95 °C for 5 min prior to gel electrophoresis. All samples were analyzed on precast gradient gels, 4–20% SurePAGE, Bis-Tris (GenScript). After running, the gels were stained by Coomassie blue staining and imaged by Biorad ChemiDoc.

**Rheology Measurement.** The viscoelastic properties of cellulose/keratin dopes under shear stresses were measured using an Anton Paar MCR 302 rheometer equipped with 25 mm diameter parallel plate geometry and 1 mm gap size. The viscoelastic behavior was studied by conducting dynamic frequency sweeps at various temperatures ranging from 25 to 80 °C, within an angular velocity range of 0.01–100 s<sup>−1</sup> and a strain of 1%. The zero-shear viscosity, \( \eta_0 \), was determined by fitting the complex viscosity data to the Cross-viscosity model, assuming that the Cox-Mertz rule is valid. The master curves of spinning dopes at their spinning temperature were generated based on the time–temperature superposition principle.

**Fiber Spinning.** Monofilament Spinning. A small amount of dope (approximately 20 g) was placed into a monofilament dry-jet wet spinning unit (manufactured by Fourne Polymertechnik) and heated to its spinning temperature, determined by its rheological properties. Our previous study revealed that a stable spinning is achieved when the angular frequency of the crossover point (COP) is approximately 1 s<sup>−1</sup> and the zero-shear viscosity, ranging from 20,000...
Therefore, the spinning temperature can be predicted by the rheology data. The capillary had a diameter of 100 μm and a length of 200 μm. The dope was then extruded through an air gap of 1 cm into a coagulation bath containing either water or ethanol, and the cellulose was regenerated.

The extrusion velocity was kept constant at 1.3 m/min, while the take-up velocity (the speed of the godets collecting the fibers) was varied to collect fibers at different draw ratios (DRs). The collected filaments were cut into 8 cm long pieces and washed with 80 °C water for 2 h to remove any residual IL.

**Multifilament Spinning.** The spinning process for multifilament spinning is similar to that of monofilament spinning, but it involves a larger amount of dope, approximately 1 kg. The spinning dopes were preheated in the spinning cylinder for 2 h at around 85 °C to remove any residual IL, which was prepared using a small vertical kneader at 85 °C under 30 rpm stirring.

**RESULTS AND DISCUSSION**

**Dissolution and Regeneration of Wool/Cashmere.** The dissolution of virgin wool and preconsumer cashmere textiles in mTBD-based ILs combined with different anions has been investigated using polarized optical microscopy (POM). A 13 wt % dope was prepared at 85 °C using a vertical kneader, which exerts sufficient shear force to assist with fiber disintegration. Shear force was found to be essential for accelerating the dissolution process.

**Elemental Analysis.** The elemental analysis (EA) was performed on a CHN 2400 Elemental Analyzer (PerkinElmer). Prior to testing, the fiber samples were finely cut into particles and dried in an oven. Each sample was measured in triplicate using approximately 2 mg of sample per measurement. To minimize interference from residual IL, the nitrogen content of pure cellulose fibers was also measured and used as a reference. The nitrogen content in the cellulose/keratin hybrid fibers was then calculated by subtracting the nitrogen content of the pure cellulose fibers from the total nitrogen content of the cellulose/keratin hybrid fibers.

**Fibrillation Test.** The fibrillation test of the hybrid fibers was conducted based on a modified procedure of a previous study. Briefly, 200 mg of air-dried regenerated fiber was cut into approximately 5 mm short fibers and diluted with 200 mL of water. The fiber suspension was then mixed in a house-built blender with a rotational speed of 1500 rpm for 20 or 30 min. The suspension was then filtered subsequently, and the collected fibers were then cut into approximately 2 mm fibers. The shortened fibers were dispersed in 1% gelatin solution (as a fixed medium) and imaged with an optical microscope (Olympus BX53M). The fibrillation index (I) was calculated as follows

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I_f = \frac{\sum l}{L}
\]

The overall length of the fiber (L) and the microfibrils on the fiber surface (l) were measured using ImageJ software.

**Scanning Electron Microscopy.** The surface and cross-section of the fibers were imaged using scanning electron microscopy (SEM, Sigma VP Zeiss) under the acceleration voltages of 2 or 3 keV. All of the samples were sputter coated with gold/palladium (80 Au:20 Pd) for 45 s with Q150R S plus (Quorum) to improve the conductivity.

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**RESULTS AND DISCUSSION**

The dissolution of virgin wool and preconsumer cashmere textiles in mTBD-based ILs combined with different anions has been investigated using polarized optical microscopy (POM). A 13 wt % dope was prepared at 85 °C using a vertical kneader, which exerts sufficient shear force to assist with fiber disintegration. Shear force was found to be essential for accelerating the dissolution process.
POM analysis revealed strong birefringence of both wool and cashmere fibers due to their crystalline structure and showed that the fibers swelled and gradually dissolved as the dissolution process began (Figure 1). We tested the dissolution of cashmere using mTBD-based ILs with two different anions, acetate (OAc) and levulinate (Lev). [mTBDH][Lev] demonstrated faster dissolution rates. Additionally, [mTBDH][OAc] has a relatively high melting temperature of approximately 76 °C, whereas [mTBDH][Lev] remained in a nonsolidified state even at a remarkably low temperature of −60 °C, as evidenced by the DSC measurements (Figure S3 in Supporting Information). This characteristic renders [mTBDH][Lev] significantly more convenient to handle during the processing phase. Therefore, we decided to focus our further investigations on [mTBDH][Lev]. Despite having similar chemical compositions, wool and cashmere fibers have different dimensions, with Finnish wool fibers having a diameter of 15−30 μm and cashmere fibers ranging from 10 to 20 μm. These differences in size contribute to varying dissolution rates. Additionally, the processing of cashmere fibers resulted in partial removal of the cuticle layer (as shown in Figure S1 of the Supporting Information), which enhanced the dissolution efficiency. It was found that the dissolution of the cuticle layer was much more challenging due to the higher content of disulfide bonds compared to the cortex. 28

During the dissolution, we observed that the wool dope got very “dry” as shown in Figure S2 caused by the absorption of IL into the wool fiber. To further investigate the swelling and dissolution of wool fiber, a freshly prepared 13 wt % wool in [mTBDH][Lev] mixture was placed between the plate−plate geometry in a rheometer and the change of G' and G'' over time was monitored at 85 °C (Figure S2, Supporting Information). At the beginning of the experiment, the wool fibers were suspended in the IL without significant interactions, resulting in a low modulus value of less than 100 Pa. However, between 30 and 60 min, a sharp increase in the modulus was observed due to the swelling of wool fibers, resulting in an approximate modulus surge to 10 kPa. This swelling-induced rise was driven by heightened interfiber friction. The dissolution of wool fibers started after the IL was absorbed into the fibers, and this process lasted for approximately 24 h, during which the modulus exhibited a decline to less than 100 Pa. The extended dissolution time is due to the lack of mechanical forces to disintegrate the fibers. At the dissolution stage, the storage modulus was larger than the loss modulus, indicating a dominance of the elastic behavior. After the wool fibers were completely dissolved, the viscous behavior started to dominate. The viscoelastic properties of the wool dope were investigated by oscillation shear rheology measurements at different temperatures ranging from 30 to 70 °C. The 13 wt % wool dope displayed a shear-thinning behavior and the loss modulus is higher than the storage modulus, indicating the dope is more viscous than elastic (Figure S4 in Supporting Information).

Combining rheological measurements with POM allowed us to gain a better understanding of the wool fiber dissolution process. The strong swelling phenomenon of wool fibers in [mTBDH][Lev] is largely attributed to the unique core (cortex)—shell (cuticle) structure. The cuticle layer, with its layered scale structure, allows the IL to penetrate into the cortex while also having a higher chemical resistance due to the high content of disulfide bonds.

The coagulation solvent is critical for determining the precipitation yield of the dissolved polymers and the formation of their secondary structures. In our previous study of cellulose-keratin hybrid fibers, only 50% of the keratin was retained in the fibers, with the rest got lost during the regeneration process in a water bath. 19 This observation led us to hypothesize that water may not be an optimal coagulation solvent for keratin and that the dissolution process may lead to keratin degradation and the formation of short-chain keratin that cannot be regenerated. Therefore, we conducted a comparative study of the regeneration of wool and cashmere using both water and ethanol as coagulation solvents and subsequently analyzed the molar mass of the regenerated keratin using electrophoresis.

As shown in Figure 2, a complete precipitation of keratin can be achieved in an ethanol bath, whereas regeneration of wool keratin in water was limited to 40−50%, and cashmere keratin regeneration reached 60−70%. The electrophoresis result showed that the Mr of the main fragment obtained from the regenerated keratin is approximately 37 kDa, in addition to which smaller fragments of 10 kDa were observed. This result is consistent with previously reported values for keratin extracted from wool using moderate methods, such as enzymatic extraction with keratinase or urea/cysteine extraction. 9,29 The amount of wool keratin regenerated in water is lower than that of cashmere keratin, and SDS-PAGE analysis reveals that the intensity of the 37K band in wool is lower than that of cashmere. This indicates that less high molar mass wool keratin coagulates in the water bath.

Single-Filament Fiber Spinning of Cellulose/Wool Hybrid Fiber. Dry-jet wet spinning involves extruding a polymer solution through a spinneret, stretching the resulting
filaments in an air gap, and then regenerating them in a coagulation bath to obtain the final fibers. To ensure stable spinning, it is essential to assess the viscoelastic behavior of the polymer dope. In a previous study, we performed a systematic rheology-spinnability correlation analysis using blended pulps with different molecular weight distributions (MWD). We found that spinnable dopes should have a zero-shear viscosity ($\eta^0$) between 20,000 and 30,000 Pa s and a crossover point (COP) between 2000 and 4000 Pa at their spinning temperatures.

Zero-shear viscosity refers to the viscosity plateau at an infinite low shear rate, which cannot be measured directly but requires extrapolation. For non-cross-linked linear polymer solutions, the entangled polymer chains will be oriented under shear force, resulting in a shear-thinning behavior. The COP is the intersection of $G'$ and $G''$ as a function of angular frequency, which describes the transition of the polymer dope from viscous-dominated behavior to elastic-dominated behavior. Samples with broader MWD have been shown to have a COP at lower modulus than samples with narrower MWD.\textsuperscript{31,32}

The viscoelastic behavior of polymer solutions is influenced by multiple factors, including the MWD and interactions between blended polymers. In this study, we investigated the effect of varying the keratin/cellulose mass ratio on the viscoelastic properties of the resulting hybrid polymer dope. SDS-PAGE electrophoresis measurements indicated that keratin has a smaller $M_w$ range (10k–50k) compared to cellulose (average $M_w$ of 200 K). The addition of low percentages of keratin increased the viscosity of the cellulose solution, which is typically not the case when low $M_w$ molecules are added. However, the viscosity decreased again when the amount of keratin reached 50 wt %. The positive net charge of wool keratins at neutral conditions (isoelectric point in the range of 4.7–5.4) leads to electrostatic interactions with the slightly negatively charged cellulose.\textsuperscript{15} These interactions are thought to lead to the formation of more entangled polymer networks, which can increase the viscosity of the hybrid polymer dope. The COP modulus decreased with an increasing amount of keratin, indicating the apparent MWD is becoming broader with the addition of keratin.

The rheological behavior of cellulose/keratin hybrid dopes at their spinning temperatures is extrapolated by utilizing time–temperature superposition (TTS) analysis (Figure 3). TTS analysis enables the prediction of the master curves of the dopes at longer time scales than those measured experimentally, thereby providing valuable insight into their processing behaviors. The hybrid dopes are found to exhibit different viscosity and modulus at their spinning temperature depending on the cellulose/keratin ratios. However, the frequency of COP, and thus the characteristic relaxation time associated with it, falls into the same range for all the hybrid dopes.

The moderate high mechanical strength and stretchability of virgin wool fiber are derived from their complex hierarchical structure, where the cortex consists of an assembly of keratin fibrils, protected by a dense shell called the cuticle.\textsuperscript{33} In addition, the secondary structure of keratin is stabilized by a range of noncovalent interactions, including electrostatic forces, hydrogen bonds, and hydrophobic forces and covalent disulfide bonds.\textsuperscript{34,35} However, during the dissolution process, the fiber structure is deconstructed, and the protein constituents undergo denaturation, and it is challenging to rebuild this structure during the regeneration process. As a result, regenerated wool fibers typically exhibit poor mechanical performance with a tensile stress of less than 100 MPa.\textsuperscript{36,37}

A recent investigation introduced an approach for revitalizing
the disulfide linkage through the application of dithiothreitol (DTT) as a chain extension agent. This method yielded keratin fibers exhibiting a remarkable tensile strength of 180 MPa. However, the cost-intensive nature of DTT and its substantial consumption at 13 wt % rendered it impractical for extensive large-scale manufacturing endeavors.

In this work, we did not succeed in spinning a pure regenerated wool fiber. The filaments spun from pure keratin solutions were too weak to withstand the elongational stress in the air gap. Thus, we added pulp cellulose as a rheological modifier. Wool and cellulose were blended during the dissolution process to create a continuous hybrid fiber, taking advantage of the excellent mechanical properties of Lyocell-type cellulose fibers. The cellulose/wool hybrid dope demonstrated good spinnability. The stress−strain curve of the resulting fibers at both conditioned and wet states is presented in Figure 4. At 65% RH, both the maximum elongation and tenacity decreased with increasing amounts of keratin, yet the ultimate strength of fiber with 50% wool could still reach ca. 300 MPa, which is comparable to that of the native wool fiber (Figure S5, Supporting Information). Under wet conditions, the mechanical strength of both pure cellulose fiber and hybrid fibers decreased compared with that measured at 65% RH. Simultaneously, the elongation increased. This trend is typical for manufactured cellulose fibers and hybrid fibers for viscose fiber than for Lyocell-type fibers due to the lower crystallinity of viscose fibers. Also for the hybrid fibers, the elongation at break is clearly increased when the fiber is hydrated in water. Water molecules play an essential role in governing the structure, stability, dynamics, and function of proteins.38

The surface morphology and inner structure of regenerated hybrid fibers were analyzed by SEM (Figure 5). It revealed that as the amount of keratin incorporated into the fibers increased, strips appeared on the fiber surface, and larger pores formed inside the fiber. Additionally, the cross section of the fiber became nonhomogeneous, suggesting a phase separation of cellulose and keratin within the hybrid fiber. There have been few attempts to fabricate cellulose/keratin hybrid fibers, and different extent of phase separation has been observed.19,39,40 Depending on the keratin resources, ILs, and coagulants used, the morphology of the keratin domain in the cellulose matrix also varied, e.g., forming a keratin shell, microspheres or scattering inside of the fiber body.19,39,40 The mechanisms underlying phase separation and structure formation in cellulose/keratin fibers remain unclear. According to the elemental analysis, the retention rate of wool keratin in the regenerated hybrid fiber is in the range of 40−60 wt % using both water and ethanol coagulation baths (Figure S6, Supporting Information). Notably, the loss of keratin during the coagulation process was not solely due to its dissolution into the coagulation solvent, as the precipitation test of pure keratin dope revealed complete keratin precipitation in the ethanol bath (Figure 2). Our hypothesis is that differences in the regeneration kinetics of cellulose and keratin may have contributed to the loss of keratin particles into the ethanol bath. Specifically, the fast rebuilding of cellulose fibrils may have expelled slower regenerating keratin, resulting in its

**Figure 4.** Mechanical properties of the regenerated cellulose/wool keratin hybrid fibers measured at 65% RH (left) and in the wet state (right). The presented curve is the average of 10−15 individual tests. Water is used as the coagulation solvent. The linear density for cellulose/wool (C/W)100:0, C/W 87:13, and C/W 77:23 fiber is approximately 1.2 dtex. In the case of C/W 50:50, the linear density is approximately 1.7 dtex.

**Figure 5.** Surface morphology and cross section of cellulose/wool keratin hybrid fibers imaged with SEM. Water was used as the coagulation solvent. The DR for the cellulose/wool fibers with a ratio of 100:0, 87:13, 77:23, 50:50 is 11, 10, 10, and 6, respectively.
partial loss. Furthermore, due to its smaller molar mass compared to cellulose, keratin may accumulate on the fiber surface without high interfacial adhesion to cellulose, making it prone to detachment.

**Recycling of Cashmere Textiles.** Preconsumer cashmere textiles were dissolved together with cellulose and processed into regenerated hybrid fibers using multifilament spinning. The collected fibers were then used to fabricate a demonstration fabric piece (Figure 6a). Initially, 30 wt % of cashmere was added to the cellulose dope, and the final cashmere content in hybrid fiber was approximately 20 wt % based on elemental analysis. The tenacity of the hybrid fiber was around 38 cN/tex (ca. 600 MPa), which is comparable to that of commercial Lyocell-type cellulose fibers. The excellent mechanical properties of Lyocell-type fibers can contribute to their high crystallinity and molecular orientation. In such fibers with high-crystalline orientation, the lateral cohesion between crystalline sheets is often weak. This eases the delamination of the fibril structure on the axial of the fiber, in particular upon mechanical stress under wet conditions. The incorporation of proteins into the cellulose fiber enhanced the lateral cohesion between the fibrils, thereby reducing the tendency for fibrillation. We conducted a fibrillation test for both pure cellulose fibers and cellulose/cashmere hybrid fibers at different draw ratios (DRs) (Figure 6b). The extent of fibrillation under shearing forces was quantified via the fibrillation index calculated by dividing the total length of the fibrils by the length of the fiber. As shown in Figure 6c, the cellulose/cashmere hybrid fibers at both DR6 and DR8 exhibited less tendency for fibrillation compared to pure cellulose fibers.

**CONCLUSIONS**

In summary, our study has demonstrated the potential for upcycling industrial keratin waste streams, such as cashmere textiles, using ionic liquids as solvent coupled with a dry-jet spinning technology. Our investigation on dissolving keratin in mTBD-based ionic liquids revealed that [mTBDH][Lev] was more efficient for dissolving cashmere compared to [mTBDH][OAc], with a dissolution capacity of 13 wt % at 85 °C in 3 h. However, due to the low molecular weight of keratin, the pure keratin dope had viscoelastic properties that were not suitable for dry-jet spinning. The addition of high molecular weight cellulose allowed adjustment of the rheological properties, enabled spinning, and enhanced the ultimate fiber strength.

It is noteworthy that nearly half of the introduced keratin was lost during the fiber-spinning process. Our hypothesis is that the slower regeneration rate of keratin in contrast to cellulose leads to keratin’s repulsion from the fiber and consequent loss in the coagulation bath. To address this, our forthcoming research will investigate the coagulation kinetics, monitor the interaction between keratin and cellulose, and optimize the coagulation solvent to prevent keratin loss. The heterogeneous nature of keratin’s composition might also play a role, potentially suggesting the utility of keratin fractionation.

Nevertheless, our study demonstrated the successful fabrication of cellulose/keratin hybrid fibers with a 20 wt % keratin content using a multifilament spinning unit. The hybrid fibers have a high tenacity of approximately 38 cN/tex or 600 MPa. Moreover, cellulose/keratin hybrid fibers were less prone to fibrillation compared to pure cellulose fibers. As a proof of concept, we spun the fabricated cellulose/keratin hybrid fibers into yarns and knitted them into a piece of fabric.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c04987.

Yarn spinning and fabric knitting; chemical composition and molar mass distribution of cellulose pulp; SEM images of wool and cashmere fibers; dissolution of wool in [mTBDH][Lev] monitored by rheology; DSC measurements of [mTBDH][OAc] and [mTBDH]-
[Lev]; rheology of 13 wt % wool dope at different temperatures; tensile testing of wool fibers; incorporation rate of wool keratin in cellulose/keratin hybrid fibers after regeneration in water/ethanol coagulation baths (PDF)

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Author Contributions

W.F. contributed to the study conception and design, data collection and analysis, and writing and revising the manuscript. R.F. and A.S.A. contributed to the protein analysis. M.H. and H.S. secured the funding and supervised the work. All authors participated in the revision of the manuscript. All authors read and approved the final manuscript.

Notes

The authors declare no competing financial interest.

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