

ESTABLISHMENT OF ORDERED KERATIN STRUCTURES AND
CROSSLINKAGES FOR PRODUCTION OF HIGH-PERFORMANCE TEXTILE
FIBERS, ADSORBENTS, AND COMPOSITES FROM CHICKEN FEATHERS

by

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This project focuses on the substantial recovery of ordered keratin structures as well as crosslinkages to produce various high-quality products. For a long time, industrial-scale applications with high-value additions of feathers are limited due to challenges of keratin regeneration including poor recovery of order structures and crosslinkages.

We applied the stepwise oxidation and drawing to pilot-scale spinning for continuous production of regenerated keratin fibers from feathers. Such a technology resulted in the controlled assembly of disulfide crosslinkages, optimum recovery of the secondary structures, satisfactory mechanical properties, and scalable production of keratin fibers. Ordered keratin structures were further crosslinked on a continuous spinning line at low temperatures using saccharide derivatives. Resultant keratin fibers were comparable to wool in toughness. The retention of fiber tenacity was as high as 92% after immersed in water for 1 week.

To achieve high performance of dye sorption, freeze-extrusion was developed to produce 3-dimensional ultra-fine and amorphous keratin-based fibrous matrices. Fibers in matrices were continuous, branched and alignment controlled with high amorphousness, giving fibrous matrices excellent durability and sorption performance. Sorption capacities

of these matrices for textile dyes were as high as 1200 mg g⁻¹. Dye removal efficiency remained high using freeze-extruded matrices after multiple cycles of reuses.

Chitin nanoparticles with engineered deacetylation were used to substantially induce the formation of ordered keratin structures in bio-composites. Via controlled deacetylation, the degree of crystallinity of keratin-based composites increased from 22% to 37%. As a result, the ductility of keratin-based composites increased by 540% compared to keratin films. The weight retention of composites could be up to 94%.

This research shows that stepwise oxidation and drawing, addition of deacetylated chitin nanoparticles induced substantial formation of ordered keratin structures. Sugar-aldehyde crosslinking and deacetylated chitin nanoparticles further reinforced the wet performance of keratin products. Freeze-extrusion helps form fibers with controlled alignments and high amorphousness. Via combination of above techniques, various keratin products with good retention of feather properties have been developed.

DEDICATION

I dedicate this dissertation to my family. My hearty gratitude goes to my loving wife, Qianmei Wu, whose complete trust and unconditional love accompanied me with this long and tough journey. My parents, Mingheng Mu and Jianli Zhang, always show me love and care since I was born and have been very supportive since I made my decision to pursue academic goals.

PREVIEW

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Table of Contents

LIST OF FIGURES	i
LIST OF TABLES	vii
LIST OF EQUATIONS	viii
CHAPTER 1: INTRODUCTION	1
1.1 Restoration of secondary structures in continuously spun keratin fibers from chicken feathers	1
1.2 Improvement of wet performance of keratin fibers via crosslinking using saccharide derivatives	4
1.3 Development of fibrous matrices via freeze-extrusion	7
1.4 Development of keratin-based composites	11
1.5 Objectives of this project	13
CHAPTER 2: EXPERIMENTAL	12
2.1 Materials	12
2.2 Procedures	13
2.2.1 Keratin extraction from chicken feathers	13
2.2.2 Preparation of keratin spinning dope	13
2.2.3 Continuous wet spinning of keratin fibers using stepwise oxidation and drawing	14
2.2.4 Preparation of crosslinkers	16
2.2.5 Continuous spinning with aldehyde crosslinking	16
2.2.6 Formation of fibrous matrices	18
2.2.7 Preparation of chitin nanoparticles with different degrees of deacetylation as composite reinforcements	19
2.2.8 Preparation of keratin/nanoparticle composites	19
2.3 Characterizations	20
2.3.1 Rheological properties of the spinning dope	20
2.3.2 The molecular weight of backbones of keratin from chicken feathers	21
2.3.3 Morphologies of fibers	21
2.3.4 Mechanical properties of keratin fibers from stepwise oxidation and drawing	21
2.3.5 Qualitative measurement of disulfide bonds in keratin using Raman Spectroscopy	21
2.3.6 Quantification of cystine in fibers	22
2.3.7 Determination of sulfur content	22
2.3.8 Analysis of secondary structures	23
2.3.9 Determination of structures of saccharide derivatives	23
2.3.10 Determination of length distribution between aldehydes on saccharide derivatives	24
2.3.11 The molecular weight of crosslinked keratin by saccharide aldehydes	24
2.3.12 Mechanical properties of fibers from aldehyde crosslinking	24
2.3.13 Fibrous matrices morphology	25
2.3.14 Wide-angle X-ray diffraction measurement for matrices	25

2.3.15	Compression test for matrices	25
2.3.16	Pore size and porosity measurement for matrices	26
2.3.17	Determination of specific surface area for matrices	26
2.3.18	Determination of dye removal from water using matrices	26
2.3.19	Analysis of particle sizes of nanoparticles	28
2.3.20	Analysis of degrees of deacetylation of chitin nanoparticles	29
2.3.21	Rheological properties of keratin solutions with chitin nanoparticles	29
2.3.22	Mechanical properties of keratin-based composites.....	29
2.3.23	Wet properties of keratin-based composites.....	30
2.3.24	Statistical analysis	30

CHAPTER 3: CONTROLLED ASSEMBLY OF SECONDARY KERATIN

STRUCTURES FOR CONTINUOUS AND SCALABLE PRODUCTION OF TOUGH

FIBERS FROM CHICKEN FEATHERS..... 31

3.1	Controlled cleavage of disulfide bonds in keratin	31
3.2	Controlled assembly of disulfide bonds during the keratin fiber spinning	34
3.3	Recovered secondary structure in keratin fibers	38
3.4	Continuous spinnability from controlled disulfide cleavages and assembly	40
3.5	Quality of keratin fibers from chicken feathers	41
3.6	Conclusions	45

CHAPTER 4: CROSSLINKING USING STRUCTURE-CONTROLLED

SACCHARIDE DERIVATIVES FOR PRODUCTION OF TOUGH KERATIN FIBERS

FROM FEATHERS WITH HIGH WATER-STABILITY 46

4.1	Structures of engineered saccharides derivatives	46
4.2	Change in molecular weight of keratin after engineered crosslinking.....	48
4.3	Substantial improvement in dry & wet mechanical properties	50
4.4	Improvement in wet stability	53
4.5	Comparison in wet properties with known common fibers	54
4.6	Environmental and economic benefits	56
4.7	Conclusions	60

CHAPTER 5: FREEZE-EXTRUSION FOR CONTROLLABLE ASSEMBLY OF 3-

DIMENSIONAL ULTRA-FINE AND AMORPHOUS FIBROUS MATRICES FROM

CHICKEN FEATHERS: POTENTIAL APPLICATIONS IN SORPTION 62

5.1	Formation of fibrous matrices between ices	62
------------	---	-----------

5.2	Scheme of mechanism	65
5.3	Unique properties of fibrous matrices made by freeze-extrusion	67
5.3.1	Controlled alignment of fibers in matrices	67
5.3.2	Controlled diameters of fibers in matrices.....	68
5.3.3	Limited degrees of crystallinity and drawing of formed fibers by freeze-extrusion	70
5.3.4	Tunable densities of fibrous matrices	71
5.3.5	Durable compressibility of fibrous matrices.....	71
5.4	Performance of dye sorption	72
5.5	Conclusions	77
CHAPTER 6: NANOPARTICLE-INDUCED FORMATION OF ORDERED PROTEIN		
STRUCTURES VIA ENGINEERED CHITIN DEACETYLATION FOR		
PRODUCTION OF TOUGH AND WET-STABLE KERATIN-BASED COMPOSITES		
.....		79
6.1	Properties of chitin nanoparticles with engineered deacetylation.....	79
6.2	Improvement of the toughness of keratin films.....	81
6.3	Improvement of wet properties of keratin-based composites	90
6.4	Comparison of mechanical properties of keratin films with different treatments	92
6.5	Conclusion.....	94
CHAPTER 7: SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH		
.....		96
7.1	Summary	96
7.2	Future research	98
REFERENCES		101

LIST OF FIGURES

Figure 2-1 Diagram of wet spinning sequence on a pilot-scale employed with stepwise oxidation and drawing.....	14
Figure 2-2 Continuous wet spinning for the production of keratin fibers from feathers..	16
Figure 2-3 Continuously spun keratin fibers from chicken feathers.....	17
Figure 2-4 Diagram of continuous and clean keratin fibers spinning with crosslinking using saccharide derivatives.	17
Figure 2-5 Typical images of a) solution of chitin nanoparticles and b) keratin/chitin composite	20
Figure 3-1 Reducing SDS-PAGE. Lane 1: standard protein markers; Lane 2: regenerated keratin; Lane 3: Chicken feathers	32
Figure 3-2 a) Comparison of disulfide bonds in keratin between chicken feathers and spun keratin fibers using Raman spectra. b) Recovery of disulfide bonds in keratin fibers measure by HPLC at different oxidation stages via controlled disulfide bond assembly. 36	
Figure 3-3 a) Relationship between recovery ratio of disulfide bonds in fibers and highest drawing ratio. b) Morphologies in SEM of spun keratin fiber from the highest drawing ratio.	37
Figure 3-4 Morphological change in keratin fibers on a continuous spinning line with controlled disulfide bonds assembly	38
Figure 3-5 XRD spectra and deconvolutions of the ^{13}C NMR spectra (around 170 ppm) of chicken feathers and keratin fibers.	40
Figure 3-6 Unmodified solid ^{13}C NMR spectra of a) chicken feathers and b) spun fibers.	40

Figure 3-7 Continuous spinnings of keratin fibers with stepwise oxidation and drawing	41
Figure 3-8 Keratin filament endured a high degree of twisting.....	43
Figure 4-1 Mass spectra of major oxidized saccharides (ESI mode with positive polarity at a probe temperature of 350 °C and a cone voltage of 60 V using MSQ Plus MS). The first row shows major structures from SU1 and SU3 and the second row shows major structures from RA4. The aldehyde groups on saccharides were derivatized with 2,4-dinitrophenylhydrazine. The mass value was the saccharides derivatized with 2,4-dinitrophenylhydrazine.	47
Figure 4-2 Length distributions between aldehydes from different oxidation conditions	48
Figure 4-3 Reducing SDS-PAGE of fibers with and without aldehyde crosslinking. Lanes 1~4: keratin crosslinked by SU1, SU3 and RA4, and regenerated keratin without external crosslinking. The aldehyde concentrations for each crosslinking condition were 0.52 mol/L. The crosslinking conducted at 50 °C for 1h.....	49
Figure 4-4 a) Effect of temperatures and b) concentrations of saccharide derivatives (aldehyde concentration in solution) on mechanical properties of keratin fibers. The saccharide derivative was SU3, obtained by oxidizing sucrose by a 3-fold molar amount of sodium periodate. For a), a crosslinking bath contained 0.52 M aldehyde.	51
Figure 4-5 a) Typical stress-strain curves for keratin fibers with and without crosslinking using saccharide aldehydes from the continuous spinning line. SU3 was used as the crosslinker. b) Dry and wet mechanical properties of keratin fibers before and after saccharide aldehydes crosslinking (The crosslinking was conducted under 50 °C for 1 h with aldehyde concentration of 0.52 M)	53

Figure 4-6 Effect of crosslinking using saccharide aldehydes on wet stability of keratin fibers immersed in water for 1 week. (The crosslinking was conducted under 50 °C for 1 h with aldehyde concentration of 0.52 M)	54
Figure 4-7 Comparison of annual worldwide production volume of fibers and keratinous wastes. The data from followings work (Shahbandeh, 2018; Statista, 2018).....	57
Figure 5-1 a) Ice formation on the wall of a container (Magnified view on the wall is shown at the right corner). b) PVA precipitated between ices (Magnified view at the rim of solution is shown at the right corner). c) 3-D PVA matrix formation when all liquid water turned into ice. The container of RB 19 dyed PVA solution (1 g/L) was dipped into cooling fluid immediately at -80 °C.	63
Figure 5-2 Observation of 3-D fibrous (a) and non-fibrous (b) PVA matrices via SEM (scale bar = 50 μ m). Solutions contained 0.1 wt.% of PVA in water (a) and DMSO (b) were frozen at -80 °C. Large solubility of PVA in water ensured late precipitation of PVA after the gaps between ices reduced to fibrous level, therefore, fibrous PVA matrix was formed in Figure 5-2(a). Small solubility of PVA in DMSO led to the early precipitation of polymer when the gaps between ices were still large, therefore, ribbon-like matrix was formed in Figure 5-2(b).	65
Figure 5-3 Formation mechanism of fibrous matrices by freeze-extrusion (yellow for polymer, light blue for solvent, dark blue for polymer solution, white for ice). Upper part: Procedures to prepare a 3-D fibrous matrix (in yellow) via freeze-extrusion. Lower part: I, during freezing, ice (in white) forms and grows in polymer solution (in dark blue). II, Polymer precipitates when the concentration exceeds the solubility. When a gap between ices (d) decreases to fibrous level, precipitated polymers within the gap have fibrous	

structure. III, As the growth of ices from rim to center of the container, precipitated polymer accumulates in gaps between ices. IV When all water turns into ice, fibrous polymer matrices form. Due to the random formation of ice at isotherm regions, fibers in matrices have branches..... 66

Figure 5-4 Controlled alignments of fibers in matrices by changing temperature gradients (Scale bar = 2 cm). Fibers are aligned from the bottom up (a), towards the center of the circular plate (b) and center of the sphere (c). polymer with a concentration of 0.1% in water. The freezing temperature was -80°C . Blue arrows indicate directions of fiber orientations in matrices. For a) and b), containers of polymer solution were inserted into coolant at a controlled rate of 2 mm/min and dipped into the coolant immediately, respectively. For c), a spherical vessel holding polymer solution was dipped into coolant immediately to ensure the whole polymer solution to be covered by coolant..... 68

Figure 5-5. a) A high concentration of polymers leads to a large diameter of formed fibers via freeze-extrusion. The freezing temperature was -80°C b) High freezing rate leads to a small radius of formed fibers. Concentration of polymers was 0.025% (w/w). 69

Figure 5-6. 100-cycle compressive fatigue tests with the strain (ξ) of 40% on fibrous matrices with a density of 7.1 mg/cm^3 71

Figure 5-7. a) Dye sorption capacities of RB5 (having negative charges) at equilibrium using freeze-extruded keratin fibrous matrices and keratin feathers, b) Recycle study of Reactive Black 5 removal using freeze-extruded keratin fibrous matrices. The density of fibrous matrices was 7.2 mg/cm^3 ($V_{\text{sorption}}/V_{\text{desorption}} = 4$). 73

Figure 5-8 Sorption isotherm of RB5 and DR80 at room temperatures. Lines are the Langmuir regression fit..... 74

Figure 5-9 Effect of the variation of $V_{\text{sorption}}/V_{\text{desorption}}$ on concentration factor and desorption efficiency. – Optimization of desorption step (sorption step: dye solution pH = 2, dye concentration 200 mg/L, 0.5 g/L keratin fibrous matrices; contact time: 600 min, desorption step: 0.1 g L ⁻¹ NaOH solution, contact time: 600 min).	76
Figure 5-10 Effect of salt concentration on the removal efficiency of RB5 and DR80 by keratin fibrous matrices. (dye solution pH = 2, dye concentration 200 mg/L, 0.5 g/L keratin fibrous matrices; contact time: 600 min)	77
Figure 6-1 Reducing-SDS-PAGE of keratin-based composites. Lanes 1-5: keratin films, keratin films with chitin-0, 1, 2, and 5 nanoparticles. Films were treated at 50 °C for 2.5 h for potential crosslinking between keratin and nanoparticles. 3 wt% of nanoparticles based on the weight of keratin were added.	83
Figure 6-2 Secondary structures of keratin-based composites with deacetylated chitin nanoparticles. 3 wt% of nanoparticles based on the weight of keratin were added.....	85
Figure 6-3 Relationship between degree of crystallinity of composites and degree of deacetylation of chitin nanoparticles. 3 wt% of nanoparticles based on the weight of keratin were added.	86
Figure 6-4 Stress-strain curves of keratin film with and without incorporation of chitin nanoparticles. 3 wt% of nanoparticles based on the weight of keratin were added.....	88
Figure 6-5 Flexibility of keratin/chitin composites (with chitin-10 nanoparticles).....	88
Figure 6-6 Schematics of forces exerted on keratin-based composites a) without the reinforcement of chitin nanoparticles, with b) reinforcement of chitin nanoparticles with controlled deacetylation.	90

Figure 6-7 Changes of swelling ratios and moisture content of keratin film with chitin nanoparticles. 3 wt% of nanoparticles based on the weight of keratin were added.....	91
Figure 6-8 Weight retention of keratin film with and without chitin nanoparticles. Films were immersed in water with a pH of 5 for one week.	92

PREVIEW

LIST OF TABLES

Table 3.1 Rheological properties of 18% keratin solution at 25 °C	33
Table 3.2 Comparison of secondary structures between chicken feather and keratin fibers	38
Table 3.3 Mechanical properties of keratin fibers compared to other common fibers.	42
Table 3.4 Comparison of properties of regenerated keratin fibers developed from various approaches.....	44
Table 4.1 Comparison of mechanical properties of crosslinked keratin fibers to wool fibers	54
Table 4.2 Material cost to produce 1kg of keratin fibers crosslinked by saccharide aldehydes.....	58
Table 4.3 Potential value additions to the poultry industry from various end keratinous products.....	60
Table 5.1 Comparison of the degree of crystallinity for polymer fibers between different preparation methods.....	70
Table 5.2 Relationship among fiber diameter, surface area, and dye sorption capacity...	75
Table 6.1 Particle sizes and polydispersity index of nanoparticles	80
Table 6.2 Degrees of deacetylation of chitin nanoparticles treated with alkali for different times.....	81
Table 6.3 Rheological properties of keratin solution with and without chitin nanoparticles	82
Table 6.4 Different treatments for reinforcement of keratin-based composites and films	93

LIST OF EQUATIONS

Equation 2.1	21
Equation 2.2	26
Equation 2.3	26
Equation 2.4	27
Equation 2.5	27
Equation 2.6	27
Equation 2.7	28
Equation 2.8	28
Equation 2.9	28
Equation 2.10	30
Equation 2.11	30
Equation 2.12	30

CHAPTER 1: INTRODUCTION

1.1 Restoration of secondary structures in continuously spun keratin fibers from chicken feathers

Research on the preparation of high-performance materials through green synthesis technology has received much attention in recent years (Yan Li, Liu, Song, Rojas, & Hinestroza, 2011; Nandgaonkar et al., 2014; Y. Zhang et al., 2018). Meanwhile, there is a trend for utilizations of natural polymers and fibers for green processing (Bingnan Mu, Helan Xu, Wei Li, & Yiqi Yang, 2019) because such utilizations not only reduce environmental pollution but also introduce some unique properties to final products such as low density, moisturizing and biocompatibility (Mu, Xu, & Yang, 2015; Pandey, Ahn, Lee, Mohanty, & Misra, 2010). The implementation of natural fibers in various areas of materials science and technology are becoming even broader. Recent examples include the production of nonwoven membranes from bamboo fibers (Le Phuong, Izzati Ayob, Blanford, Mohammad Rawi, & Szekely, 2019), regenerated fibers produced from whole biomass (Nguyen et al., 2019), and fully recycling and utilization of waste cotton (Y. Ma, Zeng, Wang, & Byrne, 2019). Utilizations of wastes to decrease pollution and increase sustainability are also crucial (Mu et al., 2015; Yang, Kumar, Apblett, & Moneeb, 2017). In terms of textile fibers, more than 80 million tons of synthetic fibers are produced every year globally (Industrievereinigung-Chemiefaser, 2016). Almost all synthetic fibers are petroleum-based and highly stable in the environment (Reddy & Yang, 2005). Therefore, it is important to find sustainable, environmentally responsible, and affordable alternatives to replace petroleum-based fibers (G. Gao, Karaaslan, Kadla, & Ko, 2014; Mu, Xu, Li, Xu, & Yang, 2019).

Keratinous wastes, especially poultry feathers, are abundant, non-toxic, cost-effective, and readily available materials for fiber production (Mu, Li, Xu, Xu, & Yang, 2018). Among all poultries, chicken consumption is the largest worldwide (Allievi, Vinnari, & Luukkanen, 2015). With an annual chicken consumption of about 65 million tons and a subsequent generation of 5 million tons waste chicken feathers worldwide annually (L. Gao, Hu, Sui, Chen, & Chen, 2014), the potential production of protein fibers from chicken feathers is already 2.5 times higher than the current output of both wool and silk. Chicken feathers contain keratin content as high as 90-92% (Reddy, Chen, Zhang, & Yang, 2014). Having linear polymeric backbones and an average molecular weight higher than 10 kDa (Poole, Church, & Huson, 2008), feather keratin meets requirements of molecular structures for fiber spinning. With ~7% cysteine crosslinking sites, feather keratin is expected to possess desirable tensile properties and aqueous stabilities (ARAI, TAKAHASHI, YOKOTE, & AKAHANE, 1983). Regenerated fibers from feather keratin are likely to have smooth touch, moisture transmission, and thermal insulation because of similar chemical structures to those of wool and silk (Bingnan Mu, Helan Xu, Wei Li, Lan Xu, et al., 2019).

Unsuccessful continuous fiber production results from the difficulty in keratin extraction from feathers, incomplete re-dissolution of keratin, limited alignment of molecular chains of protein, and inefficient recovery of disulfide crosslinkages. For a long period, strong alkali solutions were used to dissolve and extract keratin (Tonin et al., 2007). However, high pH not only hydrolyzed protein backbones but also reduced amounts of sulfhydryl groups of keratin (Crewther, Dowling, Inglis, & Maclaren, 1967; Ziegler, 1964). As a result, it was impossible to produce high-quality fibers by those methods. Since ionic

liquids have been used to extract keratin from wastes (Singh & Prasad, 2019; Zheng, Nie, Zhang, Zhang, & Wang, 2015), such liquids have been used to dissolve keratin for spinning. However, the properties of obtained fibers were not satisfactory (Kammiovirta et al., 2016) because keratin cannot fully dissolve in ionic liquids. While ionic liquids could break ionic interactions and hydrogen bonds, they are not able to interrupt disulfide bonds and hydrophobic interactions among keratin molecules.

Our research group developed a non-destructive extraction system and the first regenerated keratin fibers from chicken feathers on a lab-scale (Xu & Yang, 2014). However, such fiber spinning lacked essential techniques to efficiently recover the disulfide bonds and secondary structures. As a result, the spinnability of keratin fibers was inefficient. As a result, the linearity of the regenerated fiber was limited, the distance between keratin chains was long, and the probability for formation of intermolecular disulfide crosslinkages was low. Resultant fibers had a large diameter, low strength, and inflexibility. The tenacity of the regenerated fiber was only 50% of the original chicken feathers and the breaking strain was only 4%. Also, the regenerated keratin fiber did not inherit suitable wet properties from chicken feathers. Although the research regarding fiber production from keratinous waste began in the 1940s (Wormell & Happey, 1949), there were limited efficacious methods developed to continuously produce regenerated pure keratin fibers with high quality. The minimal requirement for fibers is to have stress and strain higher than 100 MPa and 5%, respectively. To achieve above the requirements, most research focused on either post crosslinking or addition of tough polymers such as PVA and cellulose into keratin fibers (Kammiovirta et al., 2016; J. Li et al., 2009;

Yanmei Li, Zhi, Lin, You, & Yuan, 2017; Patil & Netravali, 2019; Rouse & Van Dyke, 2010)

1.2 Improvement of wet performance of keratin fibers via crosslinking using saccharide derivatives

Shortage of natural fibers and sustainable development have become huge concerns today (Jha, 2019; Venkatesan & Periyasamy, 2019). Therefore, it is necessary to initiate the utilization of eco-materials to produce eco-textile fibers. The annual production of fibers only for textile use globally has exceeded 100 million tons while natural fibers such as protein fibers do not show any significant increase in their production volume for nearly a decade (International-Sericultural-Commission, 2017; Q. Jiang et al., 2019; Lenzing, 2017). Though natural fibers are gaining appeal because of their comfortability and sustainability, availability of natural fibers is largely restricted by land, water, and other natural resources required for cultivation and farming (C. Li et al., 2018; Xie, Li, & Zhang, 2005). In terms of synthetic fibers, long-term accumulation of undegradable materials inevitably affects the environment and human health (H. Wang, Wang, & Shahbazi, 2015). It is reported that synthetic polymers are circulating in the atmosphere and ocean after turning into nano- or microparticles (Christensen, 2019; Mu, Xu, & Yang, 2017). Due to the severe environmental impact, many countries including China have issued a ban on post-consumer plastics import. However, some studies show that such bans cannot reverse the damaged ecosystem (Yanan Ren, Shi, Bardow, Geyer, & Suh, 2020; L. Zhang, Xue, & Zhou, 2019). Therefore, the utilization of biobased wastes to develop quality products with desirable degradability should also receive equal attention in the future (Bingnan Mu, Helan Xu, Wei Li, Lan Xu, et al., 2019; Bingnan

Mu, Helan Xu, Wei Li, & Yiqi Yang, 2019; Mu et al., 2015; Yang et al., 2017).

Regenerate protein fibers from poultry wastes are very promising candidates because of their sustainability, biodegradability, biocompatibility, and high-value addition (Mu et al., 2018; Yanfei Ren et al., 2018; N. Zhang et al., 2018). Taking poultry feathers for example, up to 10 million tons of feathers generated annually, far beyond current production volumes of protein fibers. The utilization of such wastes has the potential for significant value-additions.

Due to the uncontrollable morphologies of raw keratinous materials, such materials must be processed through regeneration for different applications. However, there are some key limitations to the industrial-scale application of regenerated keratin fibers (Bingnan Mu, Helan Xu, Wei Li, Lan Xu, et al., 2019). For a long time, keratin fibers after regeneration have had poor properties because of insufficient recovery of secondary structures and crosslinkages, and damages to protein backbones (Mi, Mu, Li, Xu, & Yang, 2020; Singh & Prasad, 2019; Xu & Yang, 2014). As a result, key properties such as toughness cannot meet the actual needs at all.

We achieved a successful production of tough keratin fibers from chicken feathers via a controlled assembly of secondary structures and crosslinkages on a continuous spinning line (Mu, Hassan, & Yang, 2020); the results are shown in Chapter 3. The fibers meet the specifications for basic practical use. However, due to the failure of full recovery of disulfide bonds in keratin fibers, wet strength and wet stability of keratin fibers were low. Additional research and studies were necessary for further improvement of wet properties of fibers so that regenerated keratin fibers can go to the industrial production and application phase.

Physical and chemical methods have been often used to improve the properties of biomass products. The addition of reinforcing nano- or micro- particles was common for physical methods (Mi, Xu, & Yang, 2019). However, for fibers, adding particles would change the spinnability of keratin spinning solutions, which had a side effect on continuous production. Besides, nano- or micro- particles can also substantially affect the properties of micron-sized fibers (Mu et al., 2020). Chemical crosslinking is another commonly used method. However, many crosslinkages required high temperatures, which ultimately deteriorate the properties of final products (Gui-Jie, Peng, Xiang-Sheng, Xing, & Tong, 2006; W. Wang et al., 2016; Woo & Seib, 1997). There is a need to find a new and efficient crosslinking method for production at low temperatures and low toxicity for proteins. Considering that the proportion of amino acids containing amines as the side group in the keratin is as high as 8% (Gregg & Rogers, 1986), it is feasible to crosslink keratin fibers with crosslinkages containing aldehyde groups. However, general aldehyde-based crosslinking agents are generally highly toxic, and the reaction is too fast, making most aldehyde-containing crosslinking chemicals not suitable for sustainable and clean production of desirable keratin fibers (P. Liu, Xu, Mi, Xu, & Yang, 2015).

Saccharide aldehydes were proven to be a safe crosslinker with moderate reactivity (P. Liu et al., 2015). However, challenges exist when applying such crosslinkers for fibers on a pilot and continuous spinning line. Due to the unique molecular arrangement, crosslinking fibers is different from crosslinking other products. There is a discrepancy in properties between crosslinked fibers and other products with the same kind of crosslinkages. General products, such as membranes, have relatively random molecular arrangements and intermolecular lengths. As a result, the relationship between structures