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Nano Polypeptide Particles Reinforced Polymer Composite Fibers

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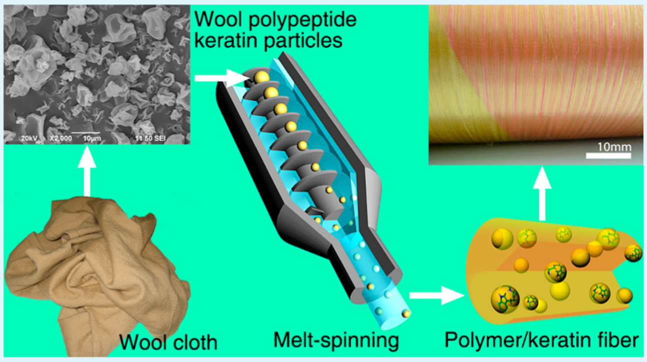
Supporting Information

ABSTRACT: Because of the intensified competition of land resources for growing food and natural textile fibers, there is an urgent need to reuse and recycle the consumed/wasted natural fibers as regenerated green materials. Although polypeptide was extracted from wool by alkaline hydrolysis, the size of the polypeptide fragments could be reduced to nanoscale. The wool polypeptide particles were fragile and could be crushed down to nano size again and dispersed evenly among polymer matrix under melt extrusion condition. The nano polypeptide particles could reinforce antiultraviolet capability, moisture regain, and mechanical properties of the polymer−polypeptide composite fibers.



KEYWORDS: *nitrogen cycling, nano polypeptide particles, melt blending, melt spinning, polymer composite fiber*

Increasing consumption of animal proteins and followed biomass burning and burying play a big part of the emission and deposition of nitrogen (N) in terrestrial and aquatic ecosystems.[1−3] The extra N has aroused concerns about its negative impacts on ecosystem health and services such as air pollution, global acidification, loss of biodiversity, and eutrophication of terrestrial and aquatic systems.[4,5] Improving use efficiency of nitrogenous materials (including wool, silk, hair, feather, etc.) is crucial to slowing down N cycling and its negative impact locally and globally.[6,7] Here we show a strategy to regenerate polypeptides from wool and then to melt-blend them with general engineering plastics. After wool was dissolved by alkali liquor, the hydrolysate was dialyzed and dried to obtain polypeptide powders. Using a two-step melt process method, polypeptide particles were crushed to nano size and homogeneously dispersed into polymer composite fibers without any extra additives. More important, even after two rounds of heat-treatments at high temperatures (up to 260 °C), the remaining nano polypeptide particles still reinforced the antiultraviolet capability, moisture regain, and mechanical properties of these polypeptide−polymer fibers.

In recent years, there has been a great interest in using regenerated natural proteins to develop polymer composite fibers. Natural proteins from agricultural sources or from the agricultural waste stream are sustainable and environmental friendly. Generally, most of the spinning methods with recycled proteins involve extensive usage of solvents, such as wet-spinning, dry-spinning, and electrospinning,[8−10] which are tedious and cause concerns on environmental pollution and sustainability. Alternatively, thermal processing involves little solvents and is widely used to produce polymer composites and fibers in industry. If we develop a technical strategy to thermally process proteins with general polymer materials, it can extend the applications of protein-contained composites/yarns/fibers to a much broader area.

Several research groups reported successful progresses to melt-blend feather keratin into thermoplastics, composites, and fibers.[11−13] Wool, down, and silk were also ground into powders and melt-blended or melt-spun with synthetic polymers to produce protein−polymer composites and fibers.[14−17] Because the average particle size of these protein powders was larger than one micrometer, some plasticizers had to be used to improve the thermoplasticity of the whole blending system. Even so, addition of big protein powders in polymers still destructed the integrity of the fiber and declined the thermal stability and the mechanical properties of the blended materials significantly. Moreover, the low extrusion temperature (≤180 °C) in these explorations limited the compositing of protein with most of engineering plastics.[11−17]

Although mechanical grounding and milling techniques have been developed to recycle the consumed fibers as small

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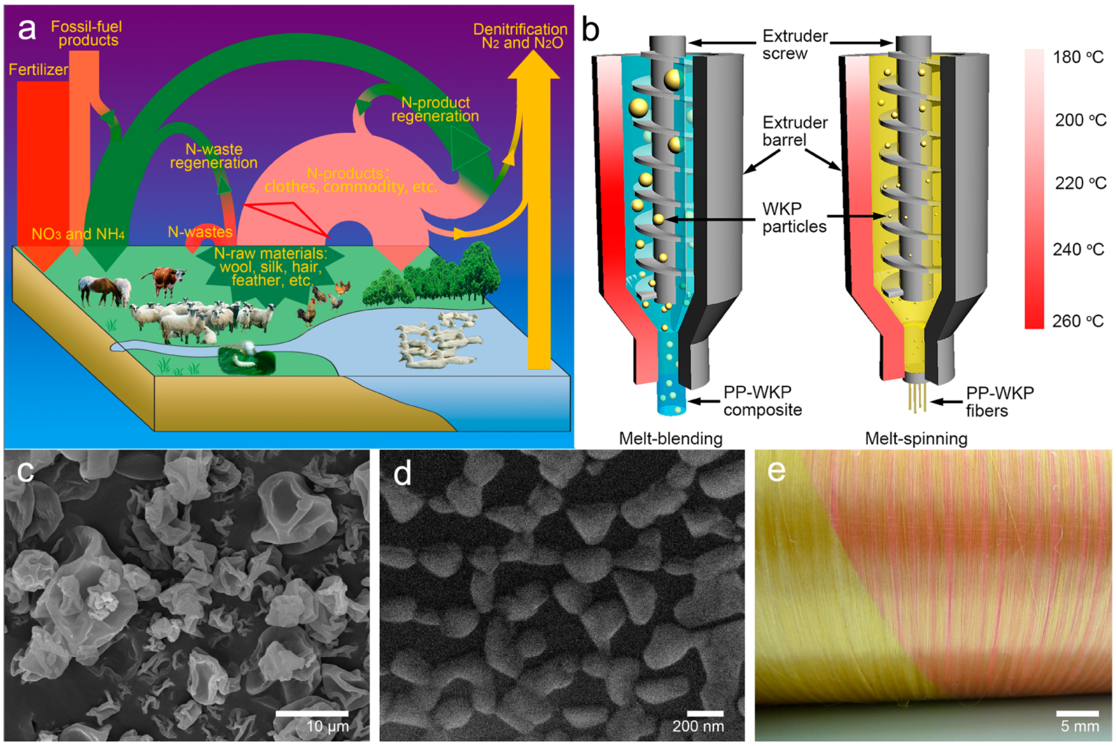

Figure 1. Two-step strategy to melt-spin polypropylene (PP) and wool keratin polypeptide (WKP) composite fibers. (a) Depiction of the nitrogen cycle of nitrogenous materials. (b) Schematic diagram of melt blending and melt-spinning of PP and WKP particles by a single-screw extruder. (c) SEM of spray-dried WKP particles from wool hydrolyzate. (d) SEM of nanosized WKP particles extracted from PP/WKP fibers. (e) Optical image of PP/WKP (5% WKP in weight) fibers.

particles for further applications,[16,17] these techniques can be used only for textiles made from pure protein fibers. However, for most of the organic wastes such as wool textiles and clothes, these materials normally cannot be directly reprocessed because they have been damaged, polluted and entangled, particularly very often dyed and/or blended with synthetic fibers. So it needs to develop novel scientific ideas and technologies to reuse and recycle the consumed/wasted natural fibers and textiles as regenerated green materials with desirable functional properties. To solve this issue technically, we hydrolyzed wool fibers to extract and obtain the wool keratin polypeptide (WKP) solution and powders.[18−21] Briefly, 100 g of waste wool was immersed into 1.0 l of sodium hydroxide solution (0.5 N), and then incubated in 95 °C water bath for 2 h to hydrolyze the wool completely. Afterward, the pH value of hydrolysate of WKP was adjusted to 7.0 by adding 0.1 N hydrochloric acid. After WKP solution was dialyzed against DI water for 3 days, it was air-dried or spray-dried to obtain WKP powder. Under alkaline conditions, the disulfate linkages of cystine could be conversed to cystyl residues (Cy-S$^-$) or dehydroalanine residue (Cy).[22,23] Subsequently, cystyl residues can also react to produce lanthionyl residues (Cy-S-Cy).

$$\begin{aligned}&\mathrm{Cy-S-S-Cy+OH^-}\\&\quad\rightarrow\mathrm{(Cy-S^-+Cy-S-OH)}\\&\qquad\text{or }\mathrm{(Cy+Cy-S-S^-)}\end{aligned}$$

$$\mathrm{Cy+Cy-S^-\rightarrow Cy-S-Cy}$$

Moreover, not only were the disulfate bonds between protein chains broken but also some of the peptide bonds were nonspecifically cut off to form nanosize polypeptide fragments of about a few kilodaltons. Furthermore, we extended the extraction technology of WKP to wool blended fabrics which greatly broadened the sources of raw materials. With excellent biocompatibility, WKP was also used as biomaterials and scaffolds for biomedical applications.[19−21]

For the final powder product of WKP, the nano polypeptide fragments in wool hydrolysate were dried and collected as particles of several micrometers in size. In our preliminary experiments, we found that these WKP particles could be crushed down to nano size again and dispersed evenly among polymer matrix under melt extrusion condition. These exciting research findings initialized the original motivation to extract nano polypeptides from consumed natural protein materials and waste and then to introduce them into engineering polymer fibers using melting process. We believe that it will be an effective way to slow down the nitrogen cycle (see Figure 1a). After N-raw materials (including wool, silk, hair, feather, etc.) were produced, most of them were proceeded to be N-products for human consumption, while some of them went to next cycle as N-wastes. As we proposed, after protein polypeptides were regenerated from N-wastes and consumed N-products, they were melt-processed with general plastics to be engineering materials. By this strategy, the utilization levels for N-raw materials will be improved. Meanwhile, the N cycle will be prolonged accordingly. Moreover, the demand and use of fertilizers and fossil-fuel products will be decreased which are the major contributions of reactive nitrogen to natural system through anthropogenic perturbation.

To compete with petroleum-based materials, protein composites from different biodegradable and renewable sources must have comparable performance levels in terms of thermal and mechanical properties, moisture sensitivity, and cost of production. Therefore, it is essential to develop novel technical

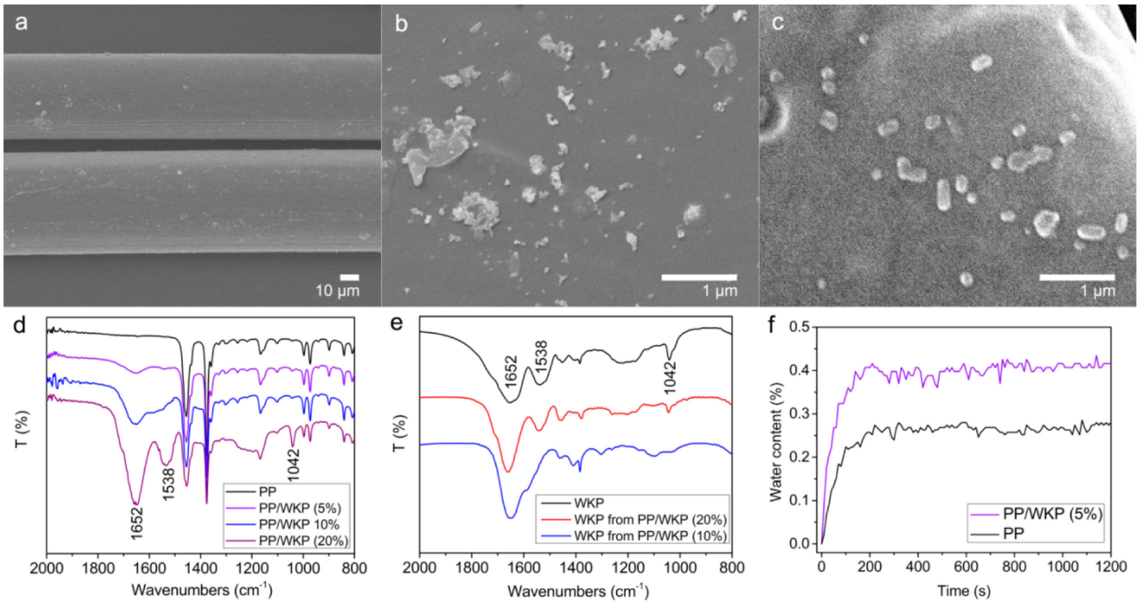

Figure 2. Morphologies and chemical structure of WKP particles in PP/WKP. (a) SEM of PP/WKP (5%) fiber. (b) SEM of WKP particles on the surface of PP/WKP (5%) fiber. (c) SEM of WKP particles on the cross section of PP/WKP (5%) fiber. (d) FTIR of PP and PP/WKP with different ratios of WKP. (e) FTIR of WKP extracted from PP/WKP masterbatch and fibers. (f) Water content of PP and PP/WKP (5%) fiber.

strategies for melt-spinning protein−polymer composite fibers to achieve desirable functional properties. With success in obtaining WKP particles from wool hydrolysate,[21] we explored the possibility of melt-blending and melt-spinning WKP with synthetic polymers under their normal processing temperature by a single screw extruder system. For example, we designed a feasible method to fabricate polypropylene (PP) and WKP composite fibers in two steps (see Figure 1b): (1) melt-blending PP with WKP to get masterbatch (20% WKP in weight) at a higher temperature (260 °C); (2) melt-spinning PP/WKP composite fibers with different ratios of WKP (0.1−10%) at a lower temperature (220 °C).

In the first step, WKP agglomerates (see Figure 1c) were blended with PP and crushed to small particles inside the extruder barrel. Meanwhile, some smoke was released when PP/WKP composite was extruded from the extruder die. In this case, it was hard to draw continuous fibers from the composite melt. After most of smoke was released from composite melt in the first round thermal process, less smoke in the following melt-spinning step had no much effect on the wire-drawing process. Moreover, we set a higher temperature in the first step than that in the second step to remove smokes as much as possible. Furthermore, the size of WKP particles was decreased to nanoscale (see Figure 1d) in the second step and the spinnability of WKP-polymer composite was improved greatly to get fine PP/WKP fibers (see Figure 1e).

During the melt-blending process, high temperatures can induce degradation and rearrangement of protein materials.[23] However, the pyrolysis mechanisms are complex, as protein materials have large variations in structural units, which can contain up to 20 different amino acids. Moreover, temperature, heating rate and isothermal heat treatment below melting point all play key roles to affect the bond cleavage, cross-linking reactions, and solubilization of protein molecules. Although the physical and chemical changes of natural protein materials have been studied under a static heat treatment situation in vacuum or with N_2 atmosphere,[23,24] the pyrolysis mechanisms of protein materials, especially nanosized protein polypeptide fragments, have not yet been investigated in a polymer melt under dynamic thermal process with high shearing force and pressure, such as melt-blending and melt-spinning.

After two melt-blending processes, nano WKP particles were dispersed homogeneously on the surface and the cross section of PP/WKP fibers (see Figure 2a−c). Although it is still unclear which part of WKP is degraded or destroyed during melt process, its amide structures can be detected in PP/WKP masterbatch (20%) (see Figure 2d). The absorption bands of WKP at 1652 and 1538 cm^{-1} are the characteristic peaks of amide I and II, respectively. The amide I absorption band is mainly the C═O stretching of amide groups. Peak at 1538 cm^{-1} is the N−H bending coupled with C−N stretching vibration of amide II.[25,26] For PP/WKP fibers (5% and 10%), amide I is still reserved, whereas the peak of amide II becomes broader and overlaps with amide I. Moreover, the peak of symmetric S−O stretching at 1042 cm^{-1} disappears in the PP/WKP fibers.[26] These results are further confirmed by the FTIR results of WKPs, which are separated from PP/WKP masterbatch and fibers (see Figure 2e). It is expected that the remaining WKP nanoparticles can impart some special functions to the composite fibers. For example, the moisture absorption of PP/WKP (5%) was about 0.4%, which is similar as polyester fibers (see Figure 2f).

With the advances of nanoscience and nanotechnology, some inorganic nanoparticles have been introduced into nanocomposite fibers to modify their mechanical properties. Because of their larger total surface area and surface energy, nanoparticles presented better affinity for fibers and fabrics and increased the durability of their functions. Furthermore, nanostructured nanoparticles could increase the crystallization of PP which had a significant contribution to its mechanical properties. PP has three different morphological forms, α, β, and γ. Theβ-crystalline or pseudohexagonal form generally occurs much more rarely than the α-form unless certain heterogeneous nuclei are present.[27] More importantly, the β-crystalline form contributes unique mechanical properties to PP, such as high tensile elongation and good impact

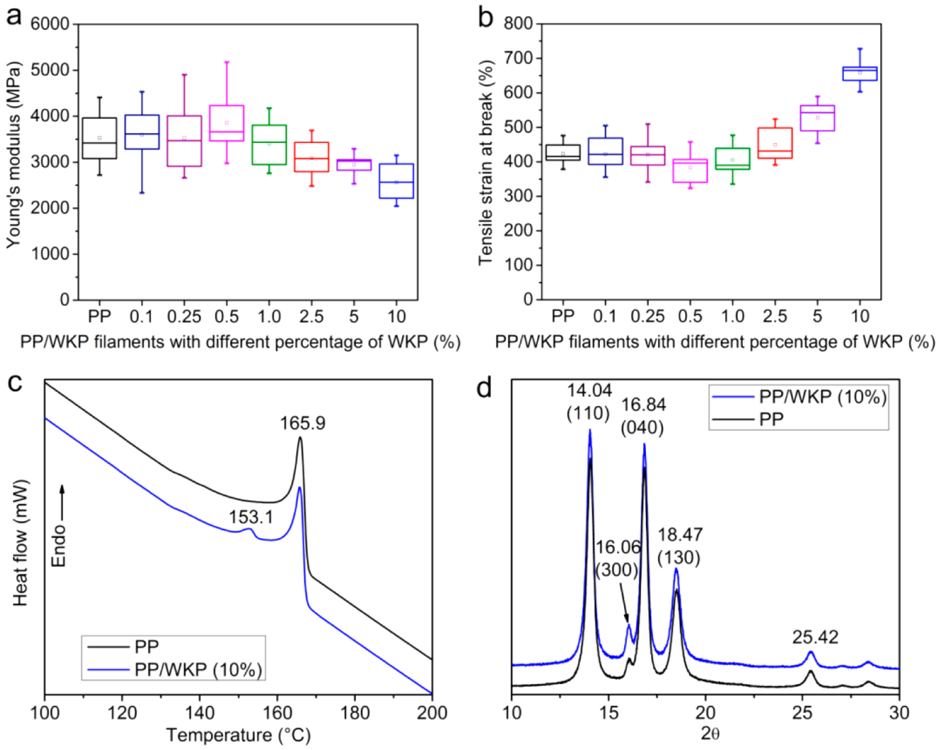

Figure 3. Mechanical properties of PP/WKP fibers with different rations. (a) Young's modulus of PP and PP/WKP fibers with different ratios of WKP. (b) Tensile strain at maximum load of PP and PP/WKP fibers with different ratios of WKP. (c) DSC thermograms of pure PP fiber and PP/WKP (10%) fiber. (d) XRD of pure PP fiber and PP/WKP (10%) fiber.

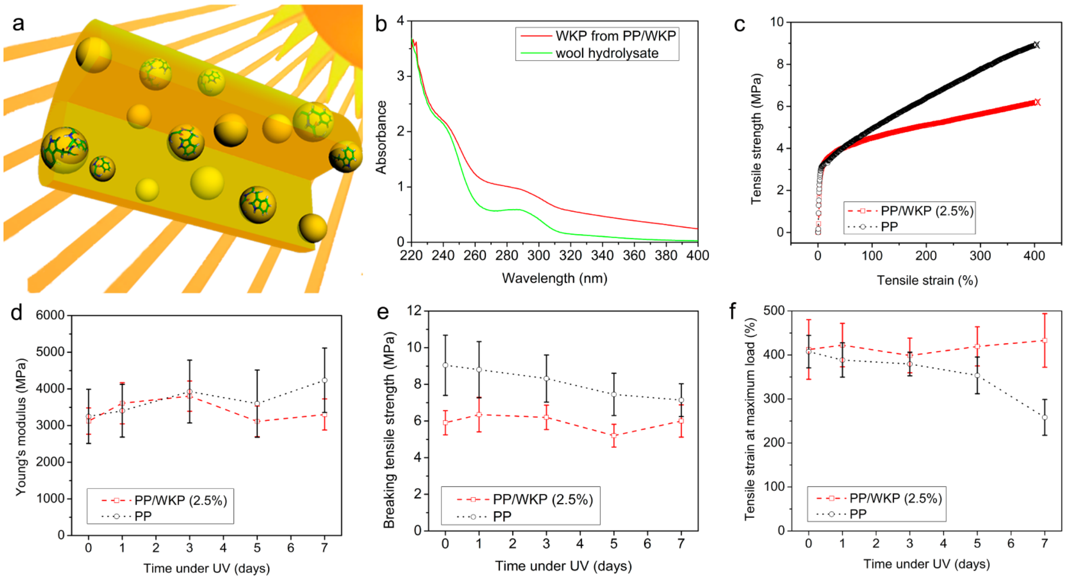

Figure 4. Anti-UV properties of PP/WKP fiber. (a) Schematic diagram of keratin particles with the phenyl structure in PP/WKP fibers. (b) UV absorbance of WKP solution extracted from PP/WKP fibers and wool hydrolysate. (c) Typical strain−load curve of PP and PP/WKP (2.5%) fibers. (d−f) Young's modulus, maximum load, and tensile strain at maximum load of PP and PP/WKP (2.5%) under UV after a certain amount of time.

resistance.[28] For PP/WKP composite fibers, although WKP can increase PP crystallizations, it decreases the density and orientation of PP molecules. Crystallization can improve the Young's modulus, whereas lower density and orientation decrease the modulus. Under these opposed factors, their Young's modulus are not markedly changed (see Figure 3a); the tensile strain at maximum load increased (see Figure 3b). There was only one melting peak of α-crystalline form at 165.9 °C for pure PP fiber. An extra melting peak of β-crystalline form at 153.1 °C appeared in differential scanning calorimetry (DSC) curves for PP/keratin fibers, showing WKP could induce and increase percentage of β-crystalline form in PP/WKP fibers (see Figure 3c).[29] For X-ray diffraction (XRD) results of PP and PP/WKP fibers, peaks at 14.04, 16.84, and 18.47° were all for α-crystalline form.[30] More β-crystalline form (16.06°) was observed on PP/keratin fibers which could increase the toughness of PP (see Figure 3d). According to Turner−Jones formula, the percentage of β-crystalline form

(k_x) of PP/WKP (10%) was 7.49%, whereas the k_x of pure PP fiber was 5.44%.[29] Although the nucleation mechanism of PP has been widely studied, the induction of β-crystalline form by organic particles needs further research.

Because of the ultraviolet absorption of aromatic amino acids (Phe, Trp, and Tyr), wool has good antiultraviolet property (see Figure 4a). The bond energy of benzene ring is higher than C−C (84−85 kcal/mol) and lower than C═C (147 kcal/mol) which survived after alkaline hydrolysis and melt-extrusion under 260 °C.[24] The ultraviolet-absorption curve of WKP after melt-blending and melt-spinning was identical with that of wool hydrolysate (see Figure 4b). So WKP who had benzene rings could absorb ultraviolet radiation and imparted anti-UV function to PP/WKP composite fibers. Although PP/WKP (2.5%) fiber had lower maximum load than pure PP fiber, they had similar Young's modulus and tensile strain (see Figure 4c). Along with ultraviolet irradiation time's extension, the Young's modulus of pure PP fibers increased slightly (see Figure 4d), but the maximum tensile strength and tensile strain at maximum tensile strength decreased gradually (see Figure 4e, f). Meanwhile, all mechanical properties of PP/WKP (2.5%) remained stable. The existence of WKP could decrease the degradation and aging of PP plastics which will extend their longevity and expand their applications.

After polypeptides were extracted from wool hydrolysate, they were melt-blended and spun as composite fibers with engineering plastics by a two-step strategy. Nanosized polypeptide particles were dispersed homogeneously into polymer matrix without any extra additives. With good spinnability, polypeptide−polymer composite fibers could be melt-spun under normal thermal processing conditions. Although the pyrolysis mechanisms of polypeptide during melt-processing are unknown, amide structures did survive in PP/WKP composites and fibers which imparted some special functions to polymer composites and fibers. Meanwhile, nanosized polypeptide particles induced and increased β-crystalline form of PP, which improved the roughness of the final products. With good ultraviolet absorption property, polypeptides provided UV resistance to PP composite materials.

Besides wool polypeptides, we also melt-spun PP and sericin successfully. And we believe that it is feasible to apply this processing strategy to other protein materials, such as hair, fibrin and feathers, and so on. The regeneration and reuse of nitrogenous materials should produce positive effects on slowing down N cycling and its negative impact locally and globally.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Author Contributions

Y. Li and J. Li designed and leaded the project. J. Li wrote the manuscript and prepared the images. J. Li, J. Zhang, G. Li, and Y. Han melt-blended and melt-spun materials. X. Liu, Z. Li, X. Liu, and Z. Zhao provided observations, mechanical tests. All authors discussed the results and provided input on the manuscript. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

WKP, wool keratin polypeptide
PP, polypropylene

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