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A Bio-antifelting Agent Based on Waterborne Polyurethane and Keratin Polypeptides Extracted by Protease from Waste Wool

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Abstract: A bio-composite made from keratin polypeptides and waterborne polyurethane was firstly employed as a bio-antifelting agent for wool fabric. The keratin polypeptides, extracted from the waste wool fibers with the protease Esperase8.0L, possessed 5271 weight-average molecular weight. The bio-composites containing different contents of keratin polypeptides were applied for wool anti-felting treatment by a pad-dry-cure process. The results indicated that with increasing content of keratin polypeptides from 0 to 6 wt.%, the area-shrinking rate of the treated wool fabrics was decreased from 4.55 % to 0.47 %, respectively. The warp and weft tensile strength at break of the fabric was increased by 8 % and 12 %, respectively and reduced by about 55 % consumption of waterborne polyurethane. The film of bio-composites had more excellent thermal stability, higher mechanical property in elasticity, and better cytocompatibility compared with the pure waterborne polyurethane film.

Keywords: Bio-composite, Polyurethane, Keratin polypeptides, Anti-felting, Elasticity

Introduction

As one of the earliest used natural fiber materials, wool fibers possess many excellent properties that the other fibers are unable to emulate, such as the great resilience, warmth, smoothness, and softness, which make the wool fibers play an important role in the textile materials [1]. However, the cuticle scales on the surface of wool fibers can easily cause the shrinkage of wool fabric subject to the mechanical action. Some processes have been applied to decrease the shrinkage propensity of the wool fabric to meet the machine washable standard. Traditional commercial chemical process to achieve the shrink-resistant performance is the chlorination/ resin method (chlorinate-Hercosett process), which is also adopted in subsequent pilling resistant finishing. However, the harmful absorbable organic halogens (AOX) [2] can be produced into the waste water and released to the environment. In order to solve the AOX release issue, a variety of non-chlorine methods have been tried, for example, enzyme-based anti-felting finishing [3-5] and waterborne polyurethane (WPU) treatment [6] both have better anti-felting performance without chlorine release. Nevertheless, the enzyme-based finishing is always unsatisfactory due to the uncontrollable reactions between the enzymes with the wool fibers. The relative higher concentration of WPU must be applied for coating the fiber surface and the handle of the treated fabric is hard, which limits the application of this technology [7]. Though a thinner film could form on the surface of wool fibers if a small amount of WPU was used, which could endow the wool fabrics a softer handle, the thinner coating should be strong enough to preserve the anti-felting property.

In recent years, some researchers have tried to strengthen WPU by mixing chitosan [8] and cellulose nanocrystals (CNCs) [9], the blended composites acting as a kind of anti-felting agent could achieve great shrink-resistant performance for the wool fabrics, and meanwhile keep the softer handle and reduce the consumption of WPU. However, the chitosan should be dissolved in the acetic acid at first, and the WPU treatment is performed in a weak base condition, which could cause the composite emulsions unstable. The CNCs blended with the WPU can form homogenous composite emulsions, yet the preparation of CNCs is hard to achieve industrialization. Keratin is one of the most abundant proteins widespread in wool, hair, claws, horns, nails, and feathers [10,11]. Million tons of the keratin wastes derive from raw wools not fit spinning, horns, claws, nails, the abandoned feathers [12,13] and byproducts of textile process every year in China. Various attempts have been made to extract the keratin from wool fibers. Besides the conventional reduction method, enzymatic hydrolysis [14] and the ionic liquids [15] have been paid much attention. A large quantity of the chemical additives would be required during the reduction process. Moreover, the ionic liquids always need to be synthesized in the organic solvent before using, along with the high price that limits its application. The enzymatic hydrolysis usually applied in a mild condition without much chemical reagents can be a green method to extract the keratin. Keratin polypeptides (KPs) can be easily extracted from wool fibers in a large scale and have better compatibility with WPU. Recently, modification of polyurethane with

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keratin during the synthesis process has been reported to remove the hexavalent chromium or worked as a biomaterials [16-19]. However, no work focused on the keratin polypeptides blends with WPU for application in the anti-felting process.

In this paper, KPs extracted from the waste wool fibers were blended with WPU, the mixture of WPU and KPs was employed as an anti-felting agent for wool fabrics. The shrinkage rate and the softness of fabrics treated by the composite emulsions with different KPs content were discussed. In addition, the morphology of treated fabric and composite films were investigated by SEM while the mechanical and thermal property of the composite films was investigated by using dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) respectively. The cytocompatibility property of WPU/KPs composite films was also investigated.

Experimental

Materials

Waterborne polyurethane (WPU) applied in the wool finishing was supplied by Shanghai Ruiqi Chemical Co., Ltd. Waste wool fibers used in the extraction process were obtained from Shandong Ruyi Wool Co. (Jining, Shandong Province, China). The enzyme (a serine type protease, Esperase8.0L extracted from *Bacillus subtilis*) and trypsin were both supplied by Novozymes Co., Ltd. (Tianjin, China). Enhanced bicinchoninic acid (BCA) Protein Assay Kit was purchased from Beyotime Biotechnology Co., Ltd. Dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich. Dulbecco's modified eagle medium (DMEM) high glucose, 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2-H-tetrazolium bromide (MTT), and PBS were bought from Sangon Biotech Co., Ltd. (Shanghai, China). Scoured and undyed wool fabric (195 g/m^2, wool 100 %, plain woven) was supplied by Youngor Woolen Textile Co., Ltd. (Ningbo, China).

Preparation of Keratin Polypeptides (KPs)

Waste wool fibers were soaked into a 15 g/*l* Na_2CO_3 solution at 95 °C for 15 min to remove the lipid and damage the layer of the cuticle, and then washed by distilled water to be neutral pH condition. The washed product was placed in an oven for 24 h at 80 °C and subsequently the dried wool fibers were milled into powders, which were collected. Next, the wool powders were placed into a 0.02 M PBS (pH 8.0) containing 5 g/*l* Na_2SO_3 with a liquor to goods ratio of 20:1 and treated at 60 °C for 30 min by using a Roaches Pyrotec 2000 dyeing machine at a 40 rpm shaking rate. The protease was added into the former bath to reach a concentration of 2.0 mg/m*l*, and then the mixed solution was agitated at 40 rpm for 2 h at 65 °C. The enzyme in the mixture was deactivated by raising the temperature to 90 °C for 10 min and maintaining the agitation at 40 rpm. The above prepared suspension was separated by centrifugation at 6000 rpm, 10 °C for 10 min using a Thermofisher Heraeus Multifuge X3 centrifuge. The supernatant liquid was collected and applied in the later wool fabric treatment.

Protein concentration of the supernatant liquid was determined by the BCA assay kit. A gradient concentration (g/*l*) of bovine serum albumin (BSA) standard solution was designed and the absorbance was recorded at 562 nm (A562). A standard curve was automatically generated using the regression equation:

$$y = ax + b \ (R^2 \geq 0.99) \quad (1)$$

where R^2 represented the linear regression coefficient. The absorbance values of the samples were recorded and substituted in the regression equation to calculate the protein concentration of the KPs, and the concentration of the extracted KPs was 62.9 g/*l*. The molecular weight of the wool KPs was determined by gel permeation chromatography (GPC). Samples were carried on a Waters 1525 high performance liquid chromatography (TSKgel 3000 SW_{XL} 300 mm×7.8 mm column) equipped with 2487 ultraviolet detector. The 20 mM PBS (pH 7.0) was used as the eluent and the flow rate was 0.8 m*l*/min. The molecular weight of the extracted KPs was estimated by calibration with the following standards: Bacitracin (molecular weight (M_W), 1422), Carbonic anhydrase (M_W, 29000), bovine serum albumin (M_W, 66000), β-Amylase (M_W, 200000). The results of the GPC measurement was shown in Figure 1, the weight-average molecular weight (Mw) were calculated by the integral of the peak area with the software of Empower3 station, and the Mw was 5271.

Preparation of Bio-composite Films and Anti-felting Treatment of Wool Fabric

Figure 2 demonstrated the processes of the preparation of

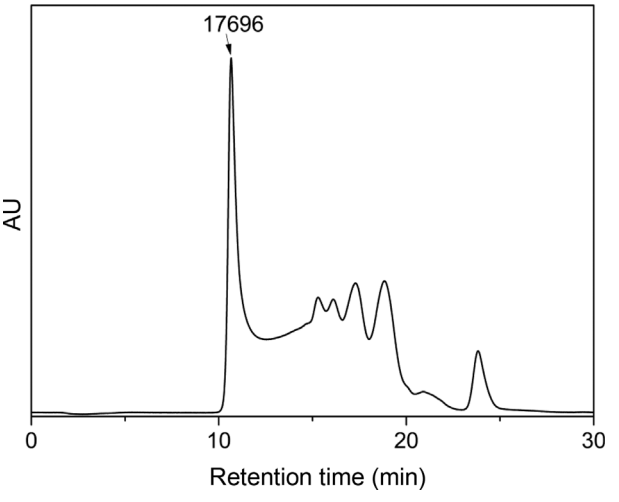

Figure 1. The gel permeation chromatography of the extracted KPs.

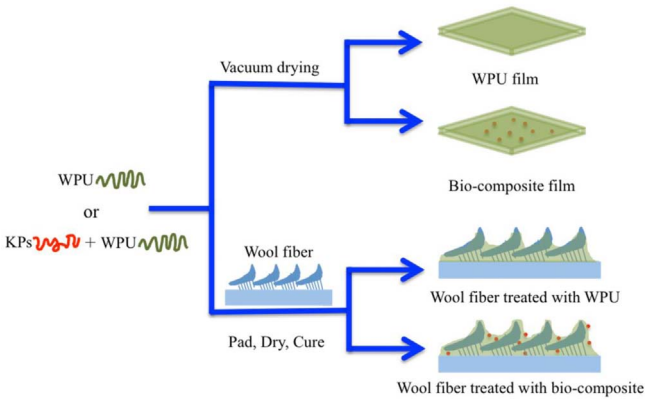

Figure 2. Illustration of preparation of bio-composite film and anti-felting treatment of wool fabric.

bio-composite films and treatment of the wool fabrics. Bio-composite was prepared by a drop-wise process, amount of KPs was added into the weak alkaline WPU emulsion with pH value of 7-8 adjusted by saturated $NaHCO_3$. The concentration of the added KPs was expressed by the mass ratio between protein in the KPs and WPU. The mixture of the bio-composites was ultrasonicated for 1 h at room temperature. Wool fabrics were immersed in these solutions and then padded (pick-up 70-80 %), pre-dried for 3 min at 80 °C and cured at 160 °C for 3 min. The mixture of the WPU/KPs emulsions were heated in a vacuum oven at 60 °C for 24 h. By changing the content of KPs with 1.0, 2.0, 4.0, 6.0, 10.0 % (w/w), respectively, a series of films with a thickness about 0.2 mm were obtained.

Characterization

The measurement of shrinkage due to washing of the treated woven wool fabric was tested according to IWS TM NO.31 using a Washcator FOM71 CLS washing machine for 1×7 A and 3×5 A programs. The area shrinkage was calculated by the following equations:

$$WS\ (\%) = \frac{L_0 - L_1}{L_0} \times 100\% \quad (2)$$

$$LS\ (\%) = \frac{L_0 - L_1}{L_0} \times 100\% \quad (3)$$

$$\text{Area shrinkage}\ (\%)\ \approx \overline{WS} + \overline{LS} \quad (4)$$

where L_0 was the marked length before fabric was washed, and L_1 was the length after standard washing, $\overline{WS}$ was the average value of three *WS* tests of size changing in weft direction (%) and $\overline{LS}$ was the average value of three *LS* tests of size changing in warp direction (%) [9].

Wool fabric samples were conditioned (temperature: 20 °C, relative humidity: 65 %) for 24 h, and then the tensile strength at break was measured in the warp-wise and weft-wise directions using universal testing machine (H5KS) in accordance with the testing standard, ASTM D 5034-95. The fabric samples were cut into rectangular shape (150× 100 mm^2), and every sample took an average value of five replicates.

To determine any changes of the external surface of the fiber and the bio-composite film, micrographs were taken using JSM-5600LV (SEM, JEOL Ltd., Japan). The samples were prepared by attaching a double-sided adhesive carbon tab to an aluminium stub, and then laying the wool fabric and film across the sticky surface of the stub. After that, the samples were sputter coated with gold under vacuum for 50 seconds using an Edwards ES150 sputter coater.

Softness of the fabric was measured according to the AATCC 202-2012 relative hand value of textiles instrument method by the PhabrOmeter 3. The softness value of the untreated wool fabric was set as the control, and the higher the value was, the softer the handle of the fabric would be.

The ATR-FTIR of the films were performed on a Nicolet 670 FTIR spectrometer (Thermal Nicolet Nexus 670, USA) and the spectral scanning frequency range was 600-4000 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans. The storage modulus and the tan δ were determined by a dynamic mechanical analyzer (DMA, Q800, TA instrument) in tensile mode at 1 Hz frequency with a heating rate of 5 °C/min, and the temperature ranged from -80 to 60 °C. Films were cut into rectangular pieces (15×8 mm^2) and were equilibrated at 30 °C for 5 min. The thermal properties of film samples were investigated by using a thermal gravity analyzer (NETZSCH, PHEONIX, TG 209 F1) in a dynamic nitrogen atmosphere, and samples were heated from 25 to 900 °C with a 10 °C/min heating rate. Cell viability of the prepared films was quantitatively assessed using MTT assay. To quantify cell attachment, the fibroblast cells (L929) was cultured in the DMEM, into which we added 10 % fetal bovine serum and 1 % penicillin-streptomycin solution, followed by being incubated at 37 °C with 5 % CO_2 [20]. The next procedures were as followings: make typsin digest L929 and seed them into 24-well plates with a density of 2×10^4 in every well that contains the film, add 0.5 m*l* the medium into per well and incubate for 24 h, and then suck out all of the medium. The films were washed three times with PBS, and 0.4 m*l* of serum-free DMEM medium, as well as 40 μ*l* MTT solution was added into the wells before being continually cultured for 4 h. The solutions in the wells was sucked out, DMSO was added to it, and the plates were shaken for 0.5 h. After that, 0.1 m*l* solution was harvested from each well and the absorbance was determined at 492 nm by using a microplate reader (Multiskan MK3, Thermal Fisher Co., Ltd., USA).

Results and Discussion

Shrinkage and Tensile Strength of Treated Fabric

Shrinkage, tensile strength, and softness of fabrics with

different treatment were shown in Table 1. Untreated wool fabric exhibited an area shrinkage (total shrinkage of warp and weft direction of the fabric) of 13.74 %. When the concentration of WPU was 110 g/*l*, the area shrinkage of the wool fabric was 0.75 %, which met the IWS TM NO.31 technical standard for machine washable wool fabrics with warp and weft direction of the fabric separately ≤3.0 %. However, when the concentration of WPU decreased to 50 g/*l*, the area shrinkage of the treated fabric increased to 4.55 %, failing to meet the IWS technical standard. This result might be explained by the fact that the high concentration of WPU could form more intact film on the wool fabric and should be more advantageous for facilitating the cross-linking between the wool fibers. Nevertheless, the fabric treated with 50 g/*l* WPU and 4 % KPs composites can almost show the same anti-felting property and tensile strength as that treated with pure 110 g/*l* WPU. Besides the higher softness value of bio-composites treated ones indicated that the softer handle had been obtained, and at the same time, WPU consumption was reduced by 55 %. When the KPs content increased to 6 %, the warp tensile strength of the treated fabric reached the maximum value at 528.5 N, about 8 % higher than that of the fabric treated with 50 g/*l* pure WPU, and the weft tensile strength increased by 12 %. This could imply that the mechanical strength of the WPU film was enhanced by blending KPs.

SEM photos in Figure 3 demonstrated the scale morphology of surface of wool. Cuticle edges of untreated wool fiber could be observed clearly from Figure 3(a). Both the treated samples in Figure 3(b) and Figure 3(c) have smoother scale tails than the untreated wool in Figure 3(a). Figure 3(c) image showed that surface effect of bio-composite emulsion was more pronounced and the gaps of the scale layers were more completely sealed than pure WPU (Figure 3(b)) under the same condition. Therefore, excellent anti-felting property could be imparted using bio-composite emulsion.

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR)

ATR-FTIR spectra of KPs, WPU film and WPU/KPs bio-composite film were shown in Figure 4. For the KPs, an absorption peak at 3295 cm^{-1} was assigned to N-H stretching (amide A). Absorption peaks at about 1651, 1519, and 1240 cm^{-1} should be ascribed to amide I, II, III characteristic peaks [21,22]. In the spectra of the polyurethane film, there was a strong peak at about 1716 cm^{-1} for stretching vibration of C=O. At about 1107 cm^{-1}, there was a strong peak for -C-O-C- group. Absorption peaks at 2972 cm^{-1} and 2926 cm^{-1}

Table 1. Shrinkage and tensile strength of the treated wool fabrics

Sample	WPU (g/*l*)	KPs content (%)	Softness	Shrinkage (%)			Tensile strength at break (N)	
				Area	Warp	Weft	Warp	Weft
Untreated[a]	0	0	81.7	13.74	10.28	3.46	427.3	210.3
WPU	110	0	75.2	0.75	0.51	0.24	512.5	258.5
WPU	50	0	78.3	4.55	3.23	1.32	489.9	228.3
KPs-1	50	1	78.0	3.08	2.18	0.90	490.5	245.5
KPs-2	50	2	77.9	1.24	0.84	0.40	507.3	248.3
KPs-4	50	4	77.3	0.58	0.47	0.11	512.0	252.7
KPs-6	50	6	77.1	0.47	0.35	0.12	528.5	255.8
KPs-10	50	10	76.6	0.63	0.41	0.22	525.3	255.0

[a]Raw wool fabric.

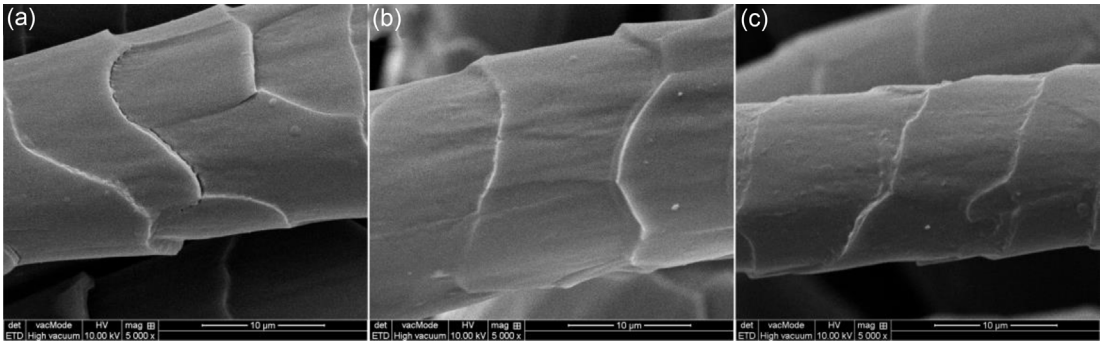

Figure 3. The scanning electron microscopy of (a) the untreated wool, (b) treated with pure 50 g/*l* WPU, and (c) treated with 50 g/*l* WPU/KPs-4 % bio-composite emulsion.

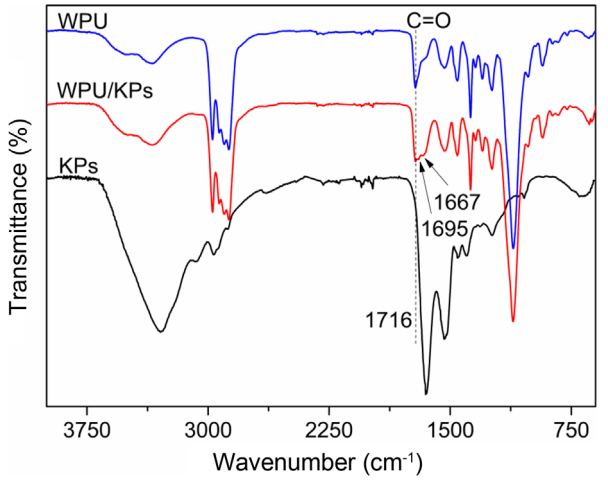

Figure 4. The ATR-FTIR spectra of the KPs, waterborne polyurethane (WPU) film, and the bio-composite film of the WPU/KPs.

were separately the asymmetric stretching vibrations of -CH_3 and -CH_2. After adding KPs into the WPU matrix, WPU and WPU/KPs films represented similar spectra over the whole scanned wavenumbers. However, a new peak appeared at 1667 cm^{-1}, which was related to the urea carbonyl that derived from the reaction between the -NCO of the polyurethane and -NH_2 of the KPs [12], and the 1695 cm^{-1} belonged to the hydrogen-bonded urethane carbonyl absorbance [23]. Therefore, the spectra analysis implied that there were cross-linking and great interaction between the KPs and the polyurethane during curing of the film, which was consistent with the surface morphology of the films (Figure 5).

The Surface Morphology of the Films

Figure 5 showed the effect of the different content of the KPs on the morphology of the WPU films. Compared with the pure WPU film, the bio-composite films showed some creases on the morphology surface. With the concentration of KPs in the bio-composites increasing, the film surface emerged creases and the white dots increased as well. A relative homogeneous distribution of the KPs without large aggregation in the WPU matrix was observed in all bio-composite films, which implied good compatibility between the KPs and the matrix. The phenomenon may be attributed to the interaction between these two materials. Such a uniform distribution of the KPs in the WPU emulsion plays an important role in improving the mechanical performance of the resulting bio-composite films and their anti-felting property.

Dynamic Mechanical Analysis (DMA)

The storage modulus and tan δ of the films were shown as a function of temperature in Figure 6. Storage modulus represents the elastic of the material, and material with higher elastic has greater structure integrity [24]. Therefore, if the elastic character of the WPU/KPs bio-composite films was improved greatly, there would be no need for such high concentration WPU and also achieve a better anti-felting property besides a relative softer handle. The loss modulus (tan δ) versus temperature curve was shown in Figure 6(b), a transition peak can be identified and the temperature at the peak can be assigned to the glass transition temperature (T_g). The storage modulus of the bio-composite films was always higher than the pure WPU film over the whole test process. When the mixed KPs content was 2 % or 4 %, the storage

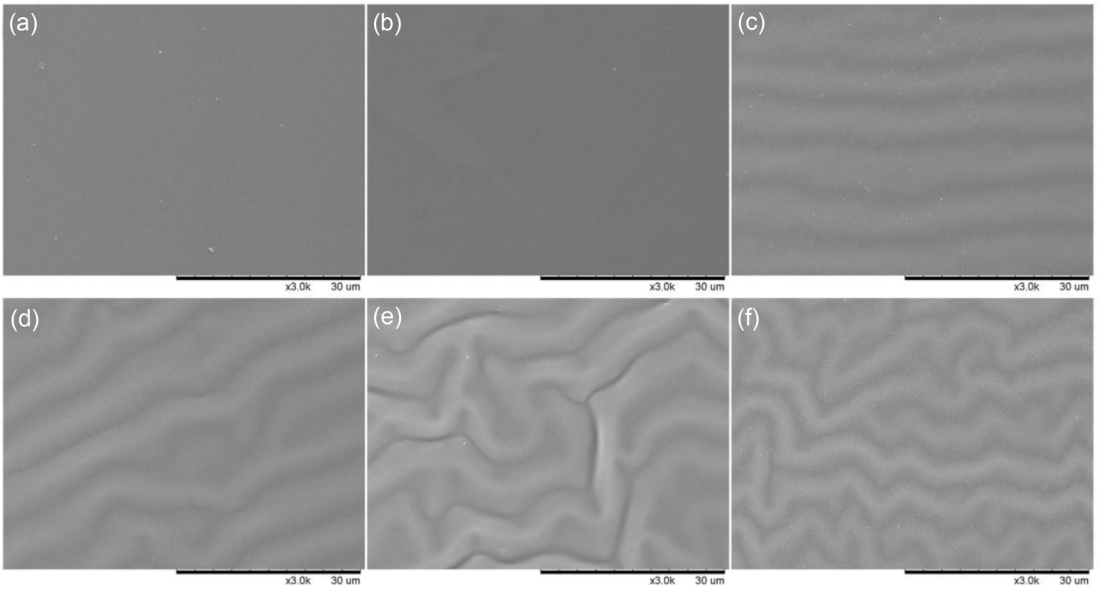

Figure 5. SEM images of the WPU/KPs bio-composite films with different KPs contents; (a) 0 %, (b) 1 %, (c) 2 %, (d) 4 %, (e) 6 %, and (f) 10 % KPs.

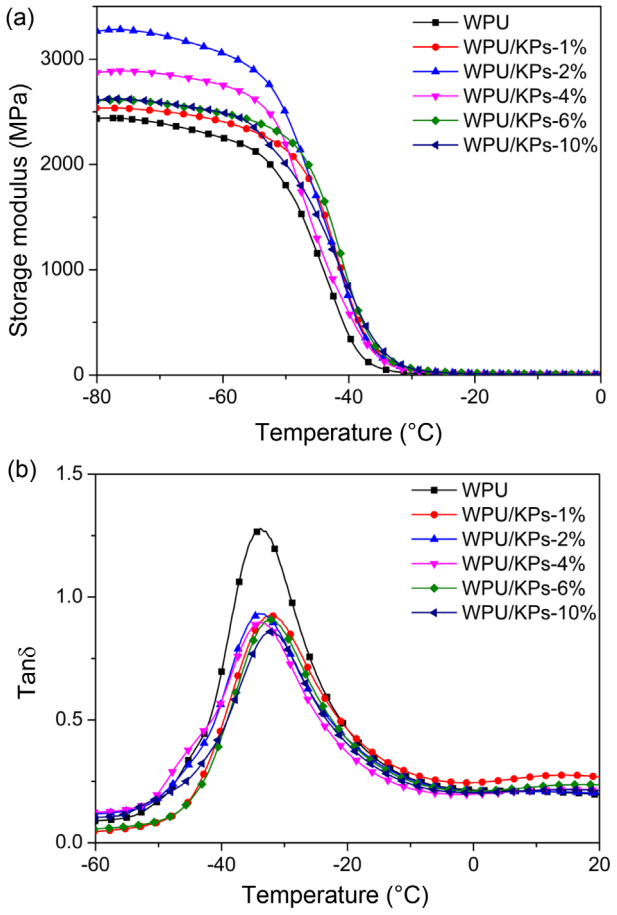

Figure 6. The storage modulus (a) and the tan δ (b) versus temperature for WPU and WPU/KPs bio-composite films varying in KPs content.

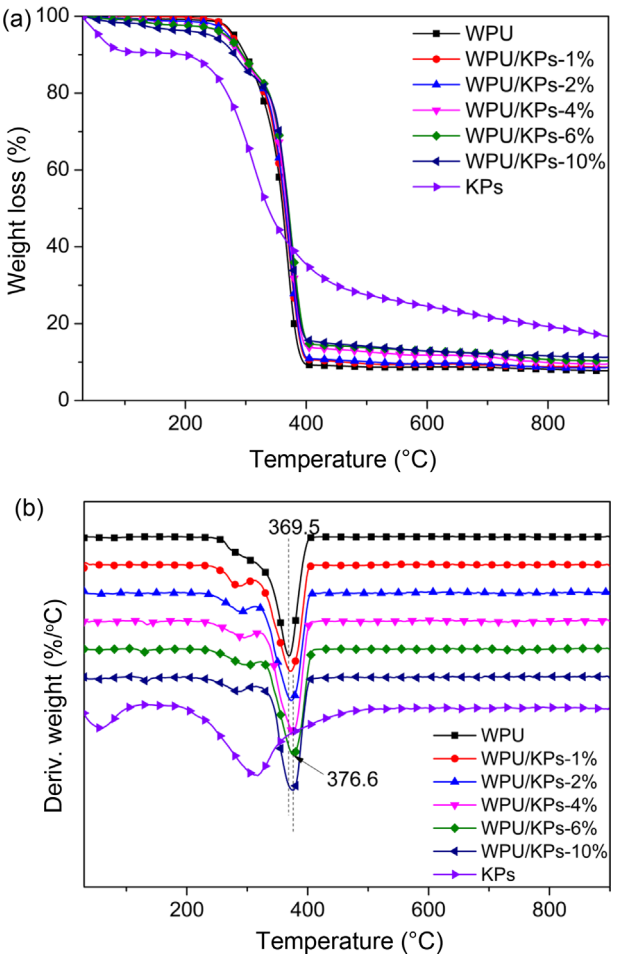

Figure 7. The thermal gravimetric analysis (a) and derivative thermogravity (b) of the WPU and the WPU/KPs bio-composite films.

modulus increased by 2 and 1.5 times respectively, compared with that of pure WPU at T_g. However, when the concentration of KPs increased to 10 %, the storage modulus decreased to 99.9 MPa at T_g, which was consistent with the anti-felting results that the 2 % and 4 % KPs contents could be the better choice to maintain the fabric anti-felting property and softer handle. The growth of the storage modulus could be attributed to the intense interaction between KPs and WPU including the crosslinking between the molecular chains and the hydrogen bonds. However, higher content of KPs above 6 % in the WPU matrix would generate agglomeration and make the material more brittle, which decreased the storage modulus eventually. When 1 % of the KPs was mixed in WPU, the T_g of the WPU/KPs film shifted to a higher temperature from -33.8 to -32.1 °C, which may be ascribed to the crosslinking between the WPU and the KPs [25]. The T_g of the bio-composite films shifted to a slight lower temperature than that of the WPU film when the KPs dosage increased to 2 % and 4 %, (from -33.80 °C to -34.05 °C and -34.12 °C, respectively), and this phenomenon may be explained that 2 % and 4 % KPs mixed in WPU could promote the phase separation of the polyurethane [26]. And the T_g of the bio-composite films increased to -32.43 and -31.67 °C, respectively, when KPs content separately increased to 6 % and 10 % in WPU, which involves the formation of the crosslinking and hydrogen bonds between KPs and WPU.

Thermal Properties of the Films

The thermal degradation behaviors of the KPs and prepared WPU films were investigated by the thermogravimetric analysis (Figure 7(a)) and derivative thermogravity (Figure 7(b)) with a temperature range of 30-900 °C. The KPs possessed relative poor thermal stability at the lower temperature. The first step degradation of the KPs occurred from 30 to 120 °C with a 9 % mass loss, this region was ascribed to the three different types of water loss, which were free water, loosely bonded water and chemical bonded water. The second step degradation temperature of the KPs

occurred from 259 to 356 °C, with a decrease of 60 % in mass, which could be ascribed to the denaturation of the KPs [27,28]. All of the WPU films showed two-step thermal decompositions. With the content of the KPs increasing to above 4 % in the bio-composite films, an obvious weight loss was observed in DTG curves at about 125 °C, which may be ascribed to the improvement of the hydrophilic of the composite films. WPU and bio-composite films were still thermally stable until the temperature increased to 240 °C, and the first-step decomposition temperature range was from 250 to 310 °C, followed by the second-step range from 310 to 410 °C. The bio-composite films presented better thermal stability in the latter step, this could be confirmed by the DTG curves that the temperature at the maximum weight loss rate increased by 1 to 7 °C. Additionally, it has been observed that the temperature at 70 % weight loss increased from 373 °C (pure WPU film) to 382 °C (WPU/KPs-6 % composite film). Such a result implied that the strong interaction occurred between the WPU and the KPs. The lower mass loss rate of bio-composite films compared with that of pure WPU film could be explained by the reaction between KPs and WPU during curing process [29].

Cellular Viability Analysis

In order to study the possible differences of biocompatibility of prepared films, cell viability on the composite films was investigated and results were shown in Figure 8. The optical density (OD) values at 492 nm showed that the cell viability of the films was relative weaker than the control sample (blank glass plate). However, the bio-composite films were more compatible for cell attachment compared with the pure WPU film, and with the content of KPs increasing, the cells toxicity of the bio-composite films was gradually decreased, which could be ascribed to the excellent biocompatibility intrinsic of the KPs and the wrinkle surface morphology of the composite films. Moreover, it was also indicated that the bio-composite films could be potential to present better biodegradability and would reduce the environmental pollution after being abandoned.

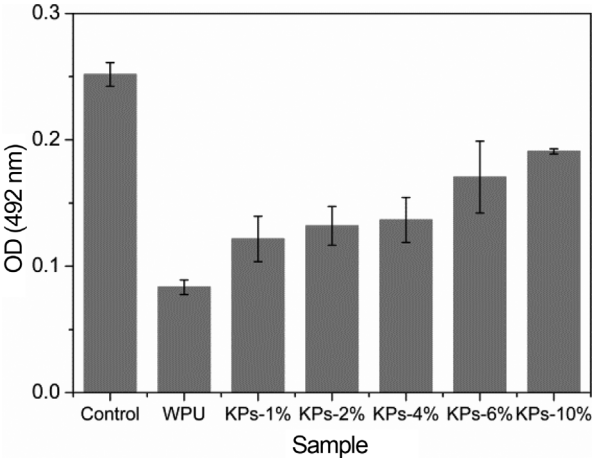

Figure 8. L929 cell viability on the bio-composite films with different KPs ratios.

Conclusion

In this study, a bio-composite prepared from KPs and WPU as a novel anti-felting agent was investigated. The KPs was extracted by 2.0 mg/m*l* protease Esperase8.0L from waste wool in the weak alkaline environment, and possessed a 5271 weight-average molecular weight. The bio-composite emulsions were prepared with different contents of KPs mixed in WPU and the wool fabrics treated with the bio-composite emulsions by a pad-dry-cure process. According to the measurement and analysis of the shrinkage and softness of the treated fabric, a suggested recipe of bio-composite emulsion was 4 % KPs mixed into 50 g/*l* WPU, which could meet the IWS TM NO.31 technical standard for machine washable wool fabrics and reduce the consumption of WPU by 55 %. The SEM photos showed that the gaps of the scale layers were more completely sealed when the wool treated by the suggested recipe, and the KPs can relatively homogeneously disperse in the WPU matrix. ATR-FTIR and dynamic mechanical analysis of the bio-composite films revealed the great interaction between the KPs and WPU, which indicated that the KPs enhanced the tensile strength of wool fabric treated with lower WPU concentration and maintain the good anti-felting property. The thermal gravimetric analysis and the cell viability results demonstrated that the film of bio-composites had more excellent thermal stability, and better biocompatibility. These conclusions could provide a promising strategy to prepare high performance WPU composites by blending renewable waste wool materials with WPU.

Acknowledgements

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