Preparation and study on the structure of keratin/PVA membrane containing wool fibers

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Abstract. The urea / sodium sulfide / sodium dodecyl sulfate (SDS) method was used to dissolve the wool in this study. Then the Wool fiber/keratin/PVA composites with different proportions were prepared, and the surface morphology, molecular structure, mechanical property of the composite films and the influence of the proportions on their structure and properties were studied. The results showed that, there are $\alpha$-helix structure, $\beta$-sheet and random coil conformations in the pure keratin film, as well as in the wool fiber. Compared with wool fiber, the crystallinity of keratin decreased. PVA can obviously improve the mechanical property of the blended film. When the blended ratio of keratin/PVA is 20/80, the mechanical property of the blended film is greatly improved. The composite films with 8%-16% of wool fibers have better flexibility than those without wool fibers.

1. Introduction

Every year, numerous organic wastes from fiber byproducts of the wool textile industry, poor quality raw wools not fit for spinning, horns, nails and feathers from butchery are disposed. These wastes are abundant in keratin which is a renewable material [1]. Keratin has good biocompatibility, cell affinity, biodegradability and safety with living tissue and also has a certain mechanical properties, processability, sterilizability and other advantages, contributing its application in biomaterials [2]. In this study, urea/sodium sulfide/SDS (sodium dodecyl sulfate) method was used to dissolve the wool to extract the keratin. Then the keratin/PVA (polyvinal) composites containing wool fibers with different proportions were prepared. And the surface morphology, molecular structure and mechanical property of the composite membranes were studied, aiming to understand the potential application of keratin in the field of biomedicine, degradable wrapper, and cosmetics membrane, and provide a new way to reuse keratin wastes.
2. Materials and methods

2.1. Materials
Degreased wool fiber, urea, sodium sulfide, SDS and PVA (with an average polymerization degree of 1700) were all commercially obtained.

2.2. Methods
2.2.1 Extraction of wool keratin. Keratin was extracted from wool fibers according to method introduced in our previous work [3]. In short, 5g degreased wool was stirred in the solution containing 42g urea, 1.9g sodium sulfide and 0.8g sodium dodecyl sulfate dissolved in 100ml distilled water. The blended solution was put into the 35°C thermostatic water bath for 14 hours. After filtration and dialysis, the wool keratin solution was achieved, and it is inspissated to 2% in mass concentration.

2.2.2 Preparation of keratin/PVA membrane. The keratin solution and PVA dissolved in water solution (2%) were blended in different proportions, and the wool fibers cut into a certain length were cast into the blended solution. Thereby, various keratin/PVA composite membranes containing wool fibers with the ratio of keratin/PVA 80/20, 60/40, 40/60, 20/80, 0/100 respectively were formed through pouring the solution into a flat box and drying at room temperature. The ratio of the wool staple to the solution was 0%, 4%, 8%, 12%, 16%, 20%, respectively.

2.2.3 Structure and mechanical property analysis. The morphologies of keratin/PVA composite membranes were observed by using a VHX 1000 hyperfocal digital microscope (KEYENCE, Japan), and the magnification was 500 times. The distribution of fibers in the membranes were observed by using MC2001 image acquisition microscope (LABOMED, America), and the magnification was 40 times.

The Fourier transform infrared (FT-IR) spectrum measurement was performed with Nicolet 5700 infrared spectrometer (Thermo Fisher Scientific Inc., USA), using the KBr pressing plate method and the film was cut into powder before testing.

The X’PERT PRO MPD X-ray instrument (PANalytical Company, Netherlands) was used for wide-angle X-ray diffraction analysis, and the testing condition was set at CuK alpha target, current 35mA, Voltage 40KV and scanning speed 8°/min.

Tensile properties were tested by using Instron 3365 electronic strength tester (Boston, USA), and the test condition was 10mm in specimen width, 90mm in length, 30mm in clamping distance and 10mm/min for stretching speed. Each sample was tested for 10 times, and took the average as result. Before test, the specimen were previously placed in standard condition (20°C and 65% RH) for 24 hours, and measured by digital micrometer on average thickness.

3. Result and discussion

3.1. Morphological structure
The morphological structure of keratin/PVA membrane is shown in Figure 1. By observing, we can see that the pure keratin membrane is fragile and is hard to be a whole. With the increase of PVA content, the surface of the blended membrane gradually turns from coarse to smooth. It is inferred that
keratin and PVA are only physically mixed, resulted in two phases macroscopically and the separation appears to be more obvious with the high ratio of keratin.

![Figure 1](image)

Figure 1. Morphological structure of keratin/PVA composite membrane.
The ratio of keratin/PVA: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, (f) 0/100

The distribution of wool fiber in composite membrane with different ratio of wool fiber is shown in Figure 2. The length of fibers in composite membrane varies approximately from 0.2 mm to 2 mm, and most of them are in length of about 1 mm. As it can be seen, fiber distribution is quite uniform when composite membrane contains not more than 20% wool fibers, resulted from that higher content of wool fiber could lead to fiber aggregation.

![Figure 2](image)

Figure 2. Distribution of wool fiber in composite membrane.
Wool fiber content: (a) 0%, (b) 4%, (c) 8%, (d) 12%, (e) 16%, (f) 20%
(The ratio of keratin/PVA was set at 40/60)

3.2. FT-IR analysis

The Infrared spectrum of pure keratin membrane and wool fiber is shown in Figure 3. It indicates that both keratin membrane and wool fiber have the property of hydrogen bond, amide I band, amide II band and amide III band. Amide I band absorption peak is considered to be related to stretching vibration of C=O bond, which is located in 1644 cm⁻¹ on both the curve of wool fiber and keratin membrane. The absorption peak of the amide II band of wool fiber is at 1518 cm⁻¹ while the that of keratin membrane is at about 1529 cm⁻¹, resulted from the N-H bending vibration shifting to higher wave number. The absorption peak of the amide III band of wool fiber and keratin membrane lies in 1235 cm⁻¹ and 1239 cm⁻¹ respectively, mainly related to the combination effect of N-H Stretching vibration and C=O bending vibration. Since organic solvent was added when dissolving the wool fiber to get keratin film, the macromolecular chemical bonds and hydrogen bond were broken so that small offsets have been showed in characteristic peaks positions.

It is accepted that α-helix structure exists in peak spectroscopy of amide I band in 1651 cm⁻¹ - 1657 cm⁻¹, random coil conformations locates near 1670 cm⁻¹ and β-sheet structure ranges from 1680 cm⁻¹ to 1694 cm⁻¹[5]. In this study, the characteristic peak at 1529 cm⁻¹ states the presence of α-helix
conformation, and the characteristic peak at 1239 cm$^{-1}$ indicates the existence of β-sheet structure, while the strong absorption peak at 1664 cm$^{-1}$ shows that it has a random coiled conformation in keratin. To sum up, compared with wool fiber, α-helix structure, β-sheet and random coil conformations are proved to exist in extracted keratin as well.

![Infrared spectrum of pure keratin membrane and wool fiber.](image)

**Figure 3.** Infrared spectrum of pure keratin membrane and wool fiber.

### 3.3. X-ray diffraction analysis

The X-ray diffraction patterns of pure keratin membrane and wool fiber is shown in Figure 4. It shows that two strong diffraction peaks appear in the 2θ angles of the wool fibers at 9.34° and 20.40°, respectively, and the one at 20.40° performs wider than the other, which might be caused by the overlap of two typical β-sheet structure [1]. The pure keratin membrane has a weak diffraction peak near the 2θ angle at 9.34°, while a strong peak at 19.90°, a little offsetting to a lower diffraction angle in comparison with wool fiber. The diminution in diffraction peak area of keratin indicates that crystallinity decreases after wool dissolved into keratin.

![X-ray diffraction pattern of pure keratin membrane and wool fiber.](image)

**Figure 4.** X-ray diffraction pattern of pure keratin membrane and wool fiber.
3.4. Mechanical property

Figure 5 shows the influence of PVA content on mechanical property of keratin/PVA membrane. It can be seen that, pure keratin membrane is rigid and brittle while pure PVA membrane has a much greater breaking strength and elongation combined with good flexibility. With the increase of PVA content, the breaking tenacity of the blended membrane increased, reaching the maximum value when the proportion of PVA is 80%. Meanwhile, the breaking elongation of the keratin/PVA blended membrane is much lower than that of pure PVA membrane, anyhow, increased with the increasing PVA content. It is inferred that when the ratio of PVA reaches 80%, the mechanical property of keratin/PVA blended membrane is greatly improved, exhibiting more firm and flexible.

**Figure 5.** Influence of PVA content on mechanical property of keratin / PVA membrane.

Figure 6 illustrates the influence of fiber content on mechanical property of keratin/PVA composite membrane. The ratio of keratin/PVA is 20/80. It can be seen that the breaking tenacity of the keratin/PVA membrane containing wool fiber is lower than that of the membrane without wool fibers and slightly decreased with the increasing fiber content, possibly due to the uneven distribution of the fibers in the membrane. Whatever, the composite membranes display higher breaking elongation when containing 8% - 16% wool fibers, and they have better flexibility than those without wool fibers.
Figure 6. Influence of fiber content on mechanical property of keratin/PVA (20/80) composite membrane.

4. Conclusions
Keratin was extracted from wool and wool fiber/keratin/PVA composite membranes were prepared in this study. The results showed that there are $\alpha$-helix structure, $\beta$-sheet and random coil conformations in the pure keratin membrane, as well as in the wool fiber. Compared with wool fiber, the crystallinity of keratin decreased. PVA can obviously improve the mechanical property of the blended membrane. When the blended ratio of keratin/PVA is 20/80, the mechanical property of the blended membrane is greatly improved. The composite membranes with 8%-16% of wool fibers have better flexibility than those without wool fibers.

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