Preparation and Properties of Keratin–Poly(vinyl alcohol) Blend Fiber

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ABSTRACT: Keratin–poly(vinyl alcohol) (PVA) blend fibers containing 13–46 wt % of $-SSO_3^- Na^+$ (S-sulfo) keratin were prepared by the wet-spinning technique. They were formed by dehydration of an aqueous solution of S-sulfo keratin and PVA (spinning dope) in a coagulation bath of sodium sulfate–saturated solution and subsequently drawn. Keratin–PVA fibers showed higher tenacity than that of wool, presumably originating from the high mechanical strength of the PVA component. The heat treatment at about 200°C improved the waterproof characteristics such as shrinkage of keratin–PVA fibers more conspicuously than did PVA fibers. That is, after heat treatment at 195°C for 10 min, keratin–PVA blend fiber shrank 20% in water at 60°C, whereas PVA fiber shrank 56%. Differential thermal analysis suggested the crosslinking of disulfide bonds between keratin molecules during the heat treatment, whereas the additional crystallization of PVA component was not observed. Adsorption of heavy metal and toxic gas to keratin–PVA fibers was also investigated. Keratin–PVA fiber was found to adsorb Ag^+ and formaldehyde gas more efficiently than PVA. Thus, blends of keratin and PVA were advantageous for both polymer fibers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 756–762, 2004

Key words: keratin; poly(vinyl alcohol); fibers; mechanical properties; adsorption

INTRODUCTION

Fibers based on regenerated protein or protein–polyacrylonitrile graft copolymer have been widely investigated to develop new textile fibers and recycle the protein materials. However, proteins investigated so far have been limited to silk, zein, soy been, casein, and collagen.[1–5] Regenerated keratin fibers were never the focus of investigations because of keratin's chemical feature, as described below.

Keratin is the major structural fibrous protein providing outer coverings such as hair, wool, feathers, nail, and horns of mammals, reptiles, and birds.[6] From amino acid analysis, keratin is found to be characteristically abundant in cysteine residues (7–20% of the total amino acid residues).[7] These cysteine residues are oxidized to give both inter- and intramolecular disulfide bonds, which may result in the mechanically strong three-dimensionally linked network of keratin fiber. Therefore, the disulfide bond must be cleaved by reducing or oxidizing reagents for extraction of keratin from wool, hair, and so forth.

Although various attempts have been made to extract keratin from wool or hair, most of them gave keratin carrying chemically modified cysteine.[8–13] Extraction of unmodified reduced keratin solution had never been performed because cysteine residues were unstable. Recently, we reported the preparation of a stable aqueous solution of unmodified reduced keratin.[14] We extracted keratin with not only 2-mercaptoethanol but also sodium dodecyl sulfate (surfactant) to promote extraction and stabilize the keratin solution. Except for reduction with 2-mercaptoethanol, sulfitolysis,[6] which is a kind of reducing reaction, can convert a disulfide bond to –SH and $-SSO_3^- Na^+$ (S-sulfo group) (see Fig. 1). We also extracted S-sulfo keratin by sulfitolysis with sodium disulfite ($Na_2S_2O_5$) and sodium dodecyl sulfate, and subsequently dried the resulting solution with a spray dryer to obtain S-sulfo keratin powder. It readily dissolves in distilled water again and appears to be easy to handle for industrial application.

We attempted to develop regenerated S-sulfo keratin fiber by wet spinning. However, the viscosity of aqueous S-sulfo keratin solution was too low to use in wet spinning. To overcome this problem, a polymer blend is the best choice if both components are compatible.[15] The combination of PVA and S-sulfo keratin is unique in that both polymers are usually dissolved

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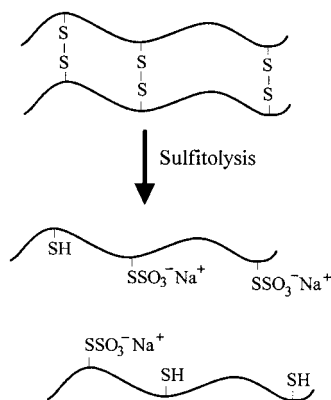
Figure 1 Breakage of disulfide bonds by sulfitolysis.

and coagulated under essentially similar conditions. Furthermore, the obtained keratin–PVA blend fiber is expected to show excellent mechanical properties because of high tensile strength and modulus of poly-(vinyl alcohol) (PVA) fiber.[16] Because wool is known to adsorb toxic substances such as heavy metal ion and formaldehyde gas, the keratin–PVA blend fiber of high S-sulfo keratin content is expected to capture much more toxic substances than PVA fiber.

In the present study, we prepared the keratin–PVA blend fiber of high S-sulfo keratin content, by the wet-spinning technique, to develop a novel fiber and recycle wool. Furthermore, we evaluated water resistance and adsorption behavior of heavy metal ions and toxic gas for the keratin–PVA fibers.

EXPERIMENTAL

Materials

Urea, sodium disulfite ($Na_2S_2O_5$), and sodium dodecyl sulfate (SDS) were purchased from Kanto Chemical Co. (Tokyo, Japan). Poly(vinyl alcohol) powder (OKS-9080N, fully saponified type; average polymerization 4000) was purchased from Nihon Gosei Kagaku Co. (Osaka, Japan). Merino wool was used in this experiment.

Preparation of S-sulfo keratin powder

A 150-g sample of wool was immersed in 1.5 L of aqueous solution containing 8M urea, 75 g of SDS, and 150 g of $Na_2S_2O_5$. The mixture was heated to 100°C, shaken for 30 min, and then cooled in a water bath at 30°C. The resulting mixture was filtered through a stainless-steel mesh. The filtrate was dialyzed against 15 L of water containing 0.1 wt % $Na_2S_2O_5$, with cellulose tubing (molecular weight cutoff of 12,000–14,000 Da) for 6 days, with a change of outer solution twice a day. The protein concentration of the dialyzate was 5 wt % on average, according to the Buiret method.[17] The

dialyzate was condensed by rotary vacuum evaporator (N-11 Tokyo Rikakikai Co., Tokyo, Japan) and dried using a spray dryer (Pulvis Mini-Spray GA32, Yamato Scientific, Tokyo, Japan) to obtain S-sulfo keratin powder.

Gel electrophoresis

SDS–polyacrylamide gel electrophoresis (SDS-PAGE) was performed using a Bio-Rad Mini Protean 3 Cell and 10–20% gradient gel (Bio-Rad Laboratories, Hercules, CA). S-sulfo keratin powder was dissolved in distilled water (0.1 wt %) and boiled with 2-mercaptoethanol for 3 min. Reduced and unreduced S-sulfo keratins were subjected to SDS-PAGE with molecular weight marker (Precision Protein Standards, unstained, Catalog 161-0362; Bio-Rad Laboratories) at 200 V. The proteins in the developed gel were stained by Coomassie brilliant blue G-250 (Bio-Rad Laboratories).

Wet spinning

For preparation of the spinning dope, S-sulfo keratin powder was dissolved in distilled water at room temperature and PVA was then dissolved with stirring at about 90°C. The spinning dopes containing various amounts of S-sulfo keratin and PVA were subjected to the following wet-spinning experiment.

The wet-spinning apparatus used in this work is shown in Figure 2, which consists of a syringe pump, spinneret, coagulation bath, the first drawing roller (DR1), and the second drawing roller (DR2). The syringe pump was filled with 350 mL of spinning dope, which was then extruded at 3.6 g/min through the stainless-steel six-hole spinneret into the coagulation bath containing 400 g/L sodium sulfate aqueous solution. Each hole of the spinneret was 0.5 mm in diameter and its capillary length was 2 mm. Temperature and immersion length of the coagulation bath were 60°C and 1.0 m, respectively. The coagulated fiber was withdrawn by DR1, drawn between DR1 and DR2 at room temperature, and finally collected on
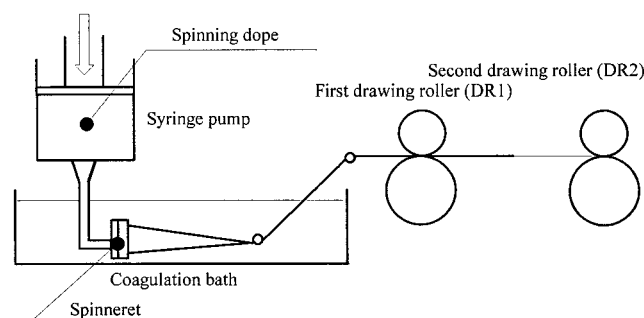
Figure 2 Schematic diagram of wet spinning apparatus.

DR2, where the velocity of DR1 was maintained at 4.2 m/min in all the experiments. The draw ratio was calculated as the velocity ratio of DR2 to DR1. Keratin–PVA fibers of various S-sulfo keratin contents were spun under maximum draw ratio.

Heat treatment

The spun fiber readily shrank or dissolved in water. Thus, heat treatment was conducted under dry hot air (195°C) for 2, 4, 6, 8, 10, and 12 min to evaluate shrinkage or solubility in hot water.

Mechanical properties

Mechanical testing was performed using a Shimadzu Autograph AG-500A (Shimadzu Corp., Kyoto, Japan). Gauge length and crosshead speed were 100 mm and 100 mm/min, respectively. The fiber was preconditioned for 24 h at 20°C and 65% relative humidity before the mechanical testing. Tenacity and elongation at break were determined as the average of 10 tests for each fiber sample, where the dimension of tenacity was centinewton/decitex (cN/dtex). Tex has been defined as a gram per 1000 m of fiber and corresponds to fiber diameter.

Scanning electron microscopy (SEM)

The fiber sample was washed in ethanol and dried under vacuum, then cross-sectionally cut and coated with gold under vacuum before imaging with SEM (JSM-T330 scanning microscope; JEOL Co., Tokyo, Japan). The SEM micrograph provided information concerning surface and cross section morphology.

Shrinkage in hot water

The fiber sample was cut to 100 cm in length and immersed in distilled water at 60°C for 30 min. Subsequently the length of wet sample was measured without tension. The shrinking ratio was calculated according to the following equation: $[(L_{int} - L_{wet})/L_{int}] \times 100$, where L_{int} and L_{wet} are the length of the initial and wet fiber, respectively.

Thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a DTG-60 (Shimadzu). The fiber sample was cut into pieces and weighed in a platinum cell. The weight loss and DTA curve were obtained by heating at 10°C/min, to 600°C under nitrogen.

Heavy metal ion and toxic gas adsorption

A 1-g sample of a fiber was placed in a 100-mL beaker, to which 50 mL of 100 ppm metal solution was added. After shaking for 1 h at 40°C, the residual metal content in the media was assayed by an atomic absorption flame-emission spectrometer AA-640-13 (Shimadzu). The applied heavy metal ions were Ag^+ and Pb^{2+}. To prepare 100 ppm metal solution media, each metal standard solution for atomic absorption spectrometry (1000 ppm; Kanto Chemical Co.) was diluted by distilled water.

A 1-g sample of a fiber was placed in a 5-L gas sampling bag, to which 3 L of 25 ppm formaldehyde gas was injected. After exposure at 20°C for 2 h, the residual gas content was measured by gas detector (Kitagawa Precision Gas Detector, Komyo Co., Tokyo, Japan).

The adsorption of heavy metal ions and formaldehyde gas to keratin–PVA fiber was evaluated from $[(C_{int} - C_{res})/C_{int}] \times 100$, where C_{int} and C_{res} are the initial and the residual contents, respectively.

RESULTS AND DISCUSSION

Characterization of S-sulfo keratin powder

Extraction of keratin from wool was carried out under mild conditions (at 40–50°C for about 5–10 h) to avoid hydrolysis of the keratin in the solution.[8–13] We performed extraction at 100°C for 30 min to enhance the efficiency of extraction. Then, the obtained solution was exposed to hot air (80–90°C) to prepare the powder using a spray dryer. The obtained S-sulfo keratin was subjected to SDS-PAGE analysis under both re-
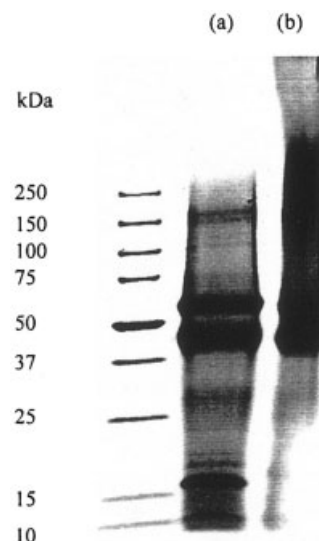
Figure 3 SDS-PAGE of S-sulfo keratins (a) reduced by 2-mercaptoethanol at 100°C for 3 min and (b) unreduced. The molecular weight marker is shown in the right column.
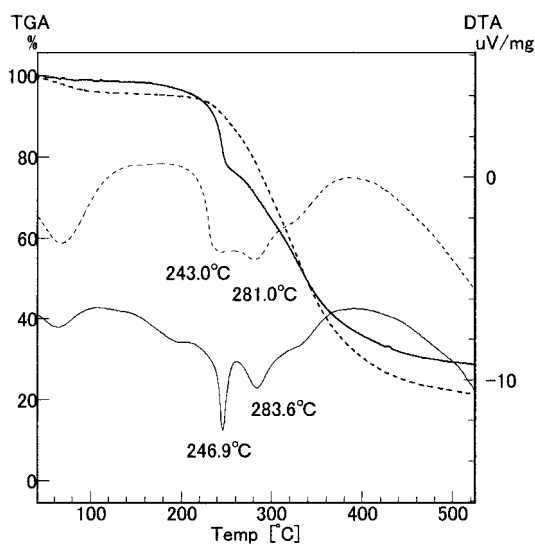
Figure 4 DTA and TGA curves of S-sulfo keratin (solid line) and wool (dotted line).

duced and unreduced conditions (see Fig. 3). Under the reduced condition, S-sulfo keratin gave two major weight fractions (60,000 and 45,000 Da) and a minor fraction (16,000 Da). It was assumed that the two high-weight fractions originated from an α-helical low-sulfur component in a microfibril and the latter from a nonhelical high-sulfur component in a matrix.[18] Thus, S-sulfo keratin was found not to hydrolyze during extraction and spray drying.

SDS-PAGE of the unreduced S-sulfo keratin showed the higher molecular weight fraction over 250 kDa, in addition to those given under reduced conditions [see Fig. 3(b)]. It was revealed that S-sulfo keratin still had the configuration crosslinked by disulfide bonds.

DTA and TGA curves of S-sulfo keratin and wool are shown in Figure 4. Three major endothermic peaks were observed for wool within the temperature range of 200–350°C, from which it has been interpreted that the lowest temperature peak originates from melting or denaturation of the helical component in the microfibril. The DTA curve of S-sulfo keratin was similar to that of wool. It was surprising that the helical conformation was preserved in spite of the extraction under harsh conditions such as the use of a denaturing reagent and high temperature. The weight losses of both S-sulfo keratin and wool started at about 200°C and continued to about 400°C. Spei et al.[19] reported that the endothermic peak of wool and hair around 230–245°C was attributed to helical denaturation superimposed by various decomposition reactions.

Production of keratin–PVA blend fiber

The viscosity of S-sulfo keratin aqueous solutions (5–10 wt %) was so low that they readily dispersed in the coagulation bath after extrusion from the spinneret. To increase the viscosity of S-sulfo keratin solution, PVA was added to the solution. The viscous spinning dope (10–20 poise) could be prepared by dissolving 6–7 wt % of PVA. The combination of PVA and S-sulfo keratin is unique in that both polymers are usually dissolved and coagulated under essentially similar conditions. As a result, keratin–PVA fiber with 13–46 wt % of keratin content could be spun. Table I summarizes the mechanical properties of keratin–PVA and PVA fibers spun under the maximum draw ratio. Keratin–PVA fibers showed higher tenacity than that of wool, which was presumably attributed to high mechanical strength of the PVA component. When the S-sulfo keratin content increased to 45.5 wt %, keratin–PVA fiber became more fragile than wool. From these results, maximum S-sulfo keratin content was determined to be 30 wt %.

Figure 5 shows an SEM micrograph of keratin–PVA fiber with 30 wt % of S-sulfo keratin, which reveals a rough cross section and surface morphology of the fiber. In particular, a "skin–core" structure was observed at cross section. It has been believed that the surface skin layer is formed by rapid coagulation,

TABLE I
Mechanical Properties of Keratin–PVA Fibers Containing Various Amounts of S-Sulfo Keratin

| Fiber[a]	Content of S-sulfo keratin[b] (%)	Tenacity[c] (cN/dtex)	Elongation at break[c] (%)
Keratin–PVA (1 : 7)[d]	12.5	1.57 ± 0.09	41.1 ± 6.4
Keratin–PVA (3 : 7)[d]	30.0	1.49 ± 0.16	22.1 ± 4.4
Keratin–PVA (5 : 6)[d]	45.5	0.77 ± 0.06	12.6 ± 3.2
PVA (0 : 10)[d]	0.0	1.45 ± 0.16	44.5 ± 3.5
Wool	—	1.06[e]	38[e]

[a] Spun under 60°C of coagulation temperature and maximum draw ratio: 3.40 for keratin–PVA fiber and 2.73 for PVA fiber.
[b] Calculated from the concentration of S-sulfo keratin and PVA in the spinning dope.
[c] The data represent means ± SD of 10 measurements.
[d] Each concentration of S-sulfo keratin and PVA in the spinning dope is shown in parentheses. For example, Keratin–PVA (1 : 7) was spun from the aqueous dope of S-sulfo keratin (1 wt %) and PVA (7 wt %).
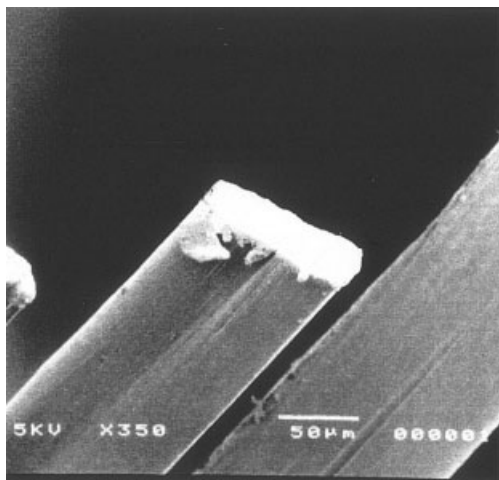[e] From Gillespie.[26]
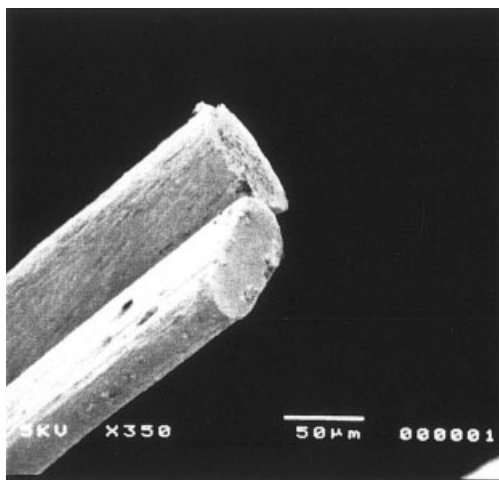
Figure 5 SEM micrograph of keratin–PVA fiber spun at a coagulation temperature of 60°C and draw ratio of 3.40.

TABLE II
Waterproof Characteristics of Keratin–PVA and PVA Fibers Heat-Treated at 195°C for Various Times

Time of heat treatment (min)	Shrinkage in hot water at 60°C[a] (%)	
	Keratin–PVA fiber[b]	PVA fiber[b]
0	ND[c]	ND[c]
2	ND[c]	ND[c]
4	60	ND[c]
6	44	ND[c]
8	40	60
10	20	56
12	8	52

[a] Defined as $(L_{int} - L_{wet})/L_{int} \times 100$, where L_{int} and L_{wet} are the length of the fiber before and after immersion in water (60°C).
[b] Spun under 60°C of coagulation temperature and maximum draw ratio: 3.40 for keratin–PVA fiber and 2.73 for PVA fiber.
[c] Not determined because fiber dissolved in water.

whereas the inner porous core is formed by delayed coagulation, which proceeds under the disturbance of the surface skin.[16] The rough surface and skin–core cross section may affect the mechanical properties. However, it is known that the uniformity of the fiber morphology is given by the use of the coagulation bath of lower temperature to delay coagulation.[16] Actually, the smooth morphology was observed for the fiber spun at 40°C (see Fig. 6).

Waterproof characteristics

PVA fibers, which are spun by wet spinning, are soluble in water. Keratin–PVA fibers also readily shrank or dissolved in water because S-sulfo keratin as well as PVA was a water-soluble component. The heat treatment is known to improve waterproof properties,

Figure 6 SEM micrograph of keratin–PVA fiber spun at a coagulation temperature of 40°C and draw ratio of 3.40.

such as solubility and shrinkage of PVA fibers.[20] The most important change that occurred during the heat treatment is an increase of the crystallinity of PVA through the removal of residual water and the formation of new hydrogen bonds between the molecules.[21] We also treated keratin–PVA and PVA fibers under dry air of 195°C, changing the treating time to improve their waterproof characteristics after the fibers were spun at 60°C of the coagulation temperature and drawn under maximum draw ratio. Although Sakurada et al.[16] conducted the heat treatment of PVA over 200°C, we adopted a slightly lower temperature because S-sulfo keratin showed a weight loss above 200°C on TGA analysis (see Fig. 4).
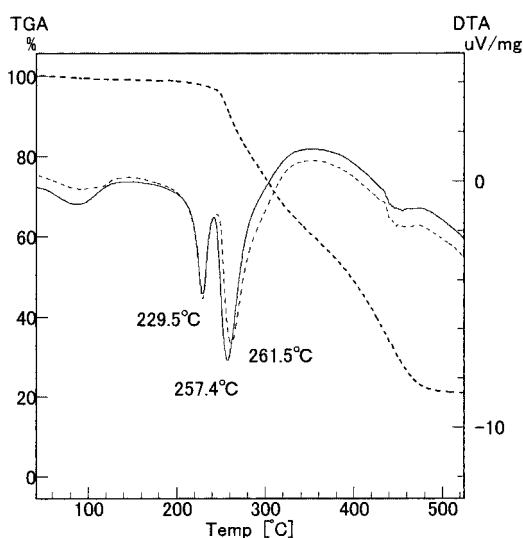
After heat treatment, the shrinkage of the fiber was measured in water at 60°C. The results are shown in Table II. The shrinkage of keratin–PVA fiber significantly decreased as heat treatment time increased, whereas that of PVA fiber was about 50–60% regardless of the length of heat treatment time. These results showed that the heat treatment was obviously effective for keratin–PVA fiber rather than PVA fiber. The heat treatment for more than 10 min turned the color of keratin–PVA fiber from white to yellow probably because of the thermal decomposition of S-sulfo keratin.

Thermal analysis was conducted to evaluate the effect of heat treatment on keratin–PVA fiber. Figure 7 shows DTA and TGA curves of keratin–PVA fiber heat-treated for 8 min and untreated fiber, in which two major endothermic curves were observed. The peak at higher temperature (~ 260°C) was shifted to the lower temperature by 4°C and its area slightly increased after heat treatment. The lower-temperature peak (~ 230°C) was unchanged before and after the heat treatment, although it was attributed to melting of the PVA component.[22] It was assumed that the

additional crystallization of PVA did not occur during the heat treatment. Therefore, PVA fibers were thought to shrink heavily in hot water in spite of the heat treatment as mentioned above. The heat treatment at 195°C was likely insufficient for PVA component. The heat treatment at the same temperature decreased the shrinkage of keratin–PVA fiber in hot water. Reduced keratin carried instable SH and S-sulfo groups that easily formed disulfide bonds and crosslinked intra- and intermolecular bonds. In the thermal analysis of hair, cystine decomposition (i.e., disulfide bond decomposition) was reported to occur in the temperature range of 250–255°C.[19] Therefore, it could be presumed that the change of endothermic peak (∼ 257°C) was attributed to decomposition of disulfide bonds (see Fig. 7), which formed during the heat treatment. Disulfide bond formation might have prevented keratin–PVA fiber from shrinking in hot water.

Heavy metal ion and toxic gas adsorption

Several researchers have reported the interaction of various heavy metal ions with wool. Speakman et al.[23] first reported the binding of mercury compounds to wool. Miyamoto et al.[24] reported that the keratin gel showed very high uptake of heavy metal ions. Toxic gases such as formaldehyde are also known to adsorb onto wool. We evaluated the adsorption of Ag^+, Pb^{2+}, and formaldehyde gas onto the heat-treated keratin–PVA fiber prepared as mentioned above. The results are summarized in Table III. Keratin–PVA fiber adsorbed Ag^+ but PVA fiber did not, indicating that

TABLE III
Adsorption of Heavy Metal Ions and Toxic Gas to Keratin–PVA Fiber[a]

Fiber	Heavy metal ion (%)		Toxic gas (%)
	Ag^+	Pb^{2+}	Formaldehyde
Keratin–PVA fiber[b]	40.5	88.3	48.0
PVA fiber[b]	2.7	86.7	28.0

[a] Adsorption was evaluated by the percentage of adsorbed fraction, which was defined as $(C_{int} - C_{res})/C_{int} \times 100$, where C_{int} and C_{res} are the initial and residual contents, respectively.
[b] Spun under 60°C of coagulation temperature and maximum draw ratio: 3.40 for keratin–PVA fiber and 2.73 for PVA fiber. Fibers were further heat-treated at 195°C for 8 min.

S-sulfo keratin efficiently captured Ag^+. It was suggested that the keratin molecule had the binding site for Ag^+. Pb^{2+} was significantly adsorbed by PVA fiber as well as keratin–PVA fiber; thus it remained unclear whether S-sulfo-keratin adsorbed Pb^{2+}. Shindo and Brown[25] showed that Pb^{2+} would also form a 1 : 1 complex with the cysteine residue (Cys) similarly to Hg^{2+}. Formaldehyde gas was adsorbed by keratin–PVA fiber more efficiently than PVA, similarly to Ag^+.

CONCLUSIONS

S-sulfo keratin was extracted from wool by reducing disulfide bonds with $Na_2S_2O_5$, and its powder was prepared by drying the S-sulfo keratin aqueous solution using a spray dryer. From SDS-PAGE analysis, the S-sulfo keratin seemed not to degrade during extraction and spray drying. Furthermore, DTA showed that helical conformation of keratin molecules was preserved during the extraction under harsh conditions such as chemical and heat treatment.

Keratin–poly(vinyl alcohol) (PVA) blend fibers were prepared by the wet-spinning technique, in the S-sulfo keratin content range of 13–46 wt %. Judging from the mechanical properties of keratin–PVA fibers spun under the maximum draw ratio, maximum S-sulfo keratin content was determined to be 30 wt % and its fiber was stronger than wool. The heat treatment was useful to improve the waterproof characteristics of keratin–PVA blend fiber rather than PVA fiber alone. From DTA and TGA analysis, the additional crystallization of the PVA component did not occur. However, the endothermic peak at 257°C suggested the formation of disulfide bonds of keratin molecules during heat treatment. Adsorption of heavy metal and toxic gas to keratin–PVA fibers was also investigated. Pb^{2+}, Ag^+, and formaldehyde gas were significantly adsorbed by keratin–PVA fiber. In particular, keratin–PVA fiber

Figure 7 DTA and TGA curves of keratin–PVA fibers (solid line) heat-treated at 195°C for 8 min and (dotted line) untreated. Before the heat treatment, keratin–PVA fibers were spun at a coagulation temperature of 60°C and draw ratio of 3.40.

was found to adsorb Ag^+ and formaldehyde more efficiently than PVA did.

Thus, the combination of S-sulfo keratin and PVA was advantageous for both polymer fibers in terms of the mechanical properties, waterproof characteristics, and the adsorption for toxic substances. PVA fiber has been used for various industrial applications such as rope, fish net, hose, fiber-reinforced conveyer belts, and so on because of its high strength.[16] We expect that keratin–PVA fibers will also be widely used for industrial applications, especially as absorbents for the toxic substances such as heavy metal ions and formaldehyde gas.

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