Preparation of Silk Film and Its Plasma Treatment for Better Dyeability

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Silk films were treated with O_2 and NH_3 plasmas for the improvement of dyeability. After O_2 and NH_3 plasma treatment of silk films, chemical composition of O and N on the surface increased, respectively. Also the concentration of acid and base functional groups increased. The silk films were insolubilized so that they could be dyed in an aqueous dye solution. The insolubilization affected the plasma-treatment effect in many surface properties. However, the color deepness of dyed silk film insolubilized after plasma treatment was greater than that of dyed film that plasma treated after insolubilization.

Keywords: plasma treatment, silk film, dyeing, insolubilization

1. Introduction

Silk is one of natural fibers, which has been utilized for more than 3000 years. The price of silk is higher than any other natural and synthetic fibers for ordinary clothing. Especially in Japan, since the produced amount of silk is very small, it is expensive and thought to be a high-grade fiber. However, the price of silk in Japan has been at the lowest level for the last twenty years and is still gradually decreasing. Recent years, in addition to the price down, increasing popularity of natural products has pushed up the consumption of silk. When the consumption of silk increases and is used casually, some new defects of silk emerge. Color fastness of dyed silk fabrics is one of them, which is required immediate improvement. We have achieved better dyeability of silk fabrics by plasma treatment, but the color fastness has not been improved so far [1].

In this paper, in order to dye silk fabrics effectively through chemical interaction, we prepared silk films and plasma treated them for better dyeability. The reason for the use of silk films is that the surface analysis can be proceeded easily.

2. Experimental

2.1. Materials

Silk fabrics used in this study were provided by Chuo Sen-i Co., of which specification is described in our previous paper [1].

O_2 and NH_3 , obtained from Iwatani Sangyo, were used as plasma gases. NaOH and HCl (both special grades) were purchased from Wako Pure Chemical Industries.

C.I. (Color Index) Reactive Black 5 (DyStar Inc., Remazol Black B) was used as a dye, of which structural formula is shown in Figure 1.

2.2. Preparation of Silk Film and Its Insolubilization

Silk fabrics were dissolved in 9 M LiBr aqueous solution. The solution was dialyzed for 24 h to be pure silk solution. The silk solution was cast on glass or acrylic plate and heated at 60 °C for 90 min.

Thickness of the films, measured with a surface profile measuring system (ULVAC Dektak3 ST), was 2 to 30 μm , depending on the concentration of the silk solution.

The obtained silk film (as-prepared silk film) is water soluble and difficult to be handled. Therefore, the silk film was insolubilized by dipping in 75% ethanol solution at 20 °C for 30 min.

Figure 1. Structural formula of C.I. Reactive Black 5.

2.3. Plasma Treatment

Plasma polymerization was carried out with a plasma polymerization apparatus shown in Figure 2. Plasma was created between a pair of stainless steel electrodes (160-mm d., 60-mm gap). Three pieces of silk fabrics or films (ca. 40 × 70 mm) were placed on the bottom electrode. The reactor was evacuated with both a rotary vacuum pump and a mechanical booster for 1 h for the pressure to be less than 1 Pa, then the mechanical booster was turned off. Plasma gases were introduced into the reactor through a mass flow controller (Tylan FC-770A) and the flow rate was adjusted. The pressure of the system was monitored with an absolute pressure gauge (MKS Baratron 122AA). Capacitively coupled plasma was created with an rf generator of which power was supplied to the upper electrode.

2.4. Surface Analysis

Chemical composition of plasma-treated silk film surfaces was analyzed with X-ray photoelectron spectroscopy (XPS, Shimadzu, ESCA-750). Chemical structures of the film surfaces were investigated with ATR-FTIR (Shimadzu, FTIR-8000). Surfaces of plasma-treated silk films were

observed with scanning electron microscope (SEM, Elionix, EXM-3500). Contact angle of silk films was measured on an enlarged view of water droplet (0.06 mL) on the films captured through a digital microscope (Keyence VH-8000).

2.5. Quantitative Analysis of Acid and Base Functional Groups

Amount of acid functional group on the surface of silk fabrics was measured by a back titration of 0.01 M NaOH solution, which had been previously reacted with silk fabrics, with 0.01 M HCl solution. Amount of base functional group was measured by the same way with the reversed use of NaOH and HCl.

2.6. Dyeing

Plasma-treated silk films were dyed in a 10% dye solution at 20 °C for 60 min. Following the dyeing the silk film was rinsed with water at 20 °C for 60 min and dried at room temperature.

2.7. Color Measurement

As an index of color deepness of dyed silk films, absorbance at 600 nm was measured with UV-vis spectrometer (Shimadzu UV-1200).

3. Results and Discussion

3.1. Insolubilization of Silk Film

Since as-prepared silk film is soluble in water, in order to dye it in an aqueous dye solution, we must insolubilize the silk films. The insolubilization was carried out by dipping of the film in 75% aqueous solution of ethanol. This process was quite simple, but the concentration of ethanol was found to be very important. At 60% or lower concentration, silk films dissolved, while at 80% or higher, insolubilization was not achieved.

Figure 3 shows ATR-FTIR spectra of as-prepared silk film, insolubilized silk film with ethanol, and their difference spectrum. In the treatment with ethanol, fibroin protein molecules form hydrogen bondings to be a cross-linked structure, or the second-order structure. Because of the formation of hydrogen bonds around the peptide carbonyl groups, absorption around 1600-1700 cm⁻¹ shifted clearly after the ethanol treatment.

Because of the formation of the second-order structure, the film seems to shrink: the thickness of

Figure 2. Schematic illustration of apparatus for the plasma treatment of silk films and fabrics.

Figure 3. ATR-FTIR spectra of silk films before and after insolubilization and their difference spectrum.

the film decreased about 10% to 15%. (Thickness of the film is discussed later in this section.) Also, surface property of the film changed by the insolubilization.

Since as-prepared silk film is soluble in water, it is very hydrophilic and contact angle cannot be measured. On the contrary, insolubilized silk film became less hydrophilic, and its contact angle was as high as 80° . This high contact angle is unusual as a silk because ordinary silk fabrics (higher ordered structure) is so hydrophilic that it absorbs water immediately.

Contact angle is also changed by the

Figure 4. Contact angle of O₂ and NH₃ plasma-treated silk films at different discharge power at 30 sccm.

○, Plasma treatment → insolubilization;
●, insolubilization → plasma treatment.

insolubilization even after plasma treatment. Figure 4 shows contact angle of plasma-treated and insolubilized silk films. Plasma-treated insolubilized films are very hydrophilic and the contact angle is very low at most of the conditions for both O₂ and NH₃ plasmas. On the contrary, that of the films insolubilized after plasma treatment remained high. These results imply that the insolubilization ruins or resets the effect of the plasma treatment on the surface.

This significant change of the surface property may be supported by the surface chemical composition measured by XPS. Table 1 shows

Table 1. Atomic ratios of the surface of various silk films.

Treatment	O/C	N/C
As-prepared	0.20	0.19
Insolubilized	0.22	0.20
O ₂ plasma → insolubilized	0.29	0.18
NH ₃ plasma → insolubilized	0.19	0.20
Insolubilized → O ₂ plasma	0.69	0.37
Insolubilized → NH ₃ plasma	0.22	0.44

Plasma condition: 50 W, 30 sccm, 15 min.

Figure 5. Thickness of O₂ plasma-treated silk film at various conditions.

□, Insolubilization → plasma treatment; ■, plasma treatment → insolubilization; ●, before insolubilization.

atomic ratios (O/C and N/C) for silk films treated variously. These atomic ratios for as-prepared and insolubilized silk films were almost identical, because only hydrogen bondings are formed in the ethanol treatment. However, the atomic ratios of plasma-treated films showed different trend by the order of plasma and ethanol treatments. As seen in this table, O/C ratio increased largely after O₂ plasma treatment of insolubilized film, while it did not increase so much after insolubilization of O₂ plasma-treated film. In NH₃ plasma, the same things can be explained for N/C ratio.

Thickness of the film is also different by the order of insolubilization and plasma treatment. Figure 5 shows thickness of O₂ plasma-treated silk films at various conditions. The thickness of the films insolubilized after the plasma treatment changed little, while those plasma treated after insolubilization decreased clearly. In the plasma treatment of insolubilized film, cross-linking or some other reactions took place on the surface, which

Figure 6. Atomic ratios and acid and base functional groups after O₂ and NH₃ plasma treatment of silk fabrics.

Figure 7. SEM photographs of O₂ plasma-treated silk films.

might have protected the ethanol treatment. However, we could not point out the fact that only plasma treatment insolubilizes silk films.

3.2. Plasma Treatment of Silk Film

After O₂ plasma treatment of silk fabrics or films, oxygen content increases significantly in most of the plasma conditions. After NH₃ plasma treatment, on the other hand, nitrogen content also increased but the increment was not so large. Examples of the change of atomic ratios of O/C and N/C on plasma-treated silk fabrics are shown in Figure 6 (solid line).

We also measured the amount of acid and base functional groups of plasma-treated silk fabrics. The results are shown in the same figure (dotted line). There are naturally some acid and base functional groups on untreated silk fabrics: their concentrations are 0.055 and 0.11 mmol/g(fabrics), respectively. After the plasma treatments, the functional groups increased. In the figure, there seems to be a correlation between atomic ratio and amount of functional group.

Although it was clear that the number of the functional groups increased by the plasma treatment, little change of the surface chemical structure in the measurement of ATR-FTIR was observed. If a great number of functional groups are introduced on the surface, they can be detected by ATR-FTIR. However, the implantation of the functional groups by the plasma treatment in this research seems not to be sufficient.

3.3. Surface Morphology of Plasma-Treated Silk Films

Figure 7 shows SEM photographs of O₂ plasma-treated silk films. Photo A is as-prepared silk film, which is very smooth. There was almost no change on the morphology of insolubilized film. Also, photograph of NH₃ plasma-treated film is omitted because it did not show any difference from untreated

Figure 8. Absorbance of dyed O₂ plasma-treated silk film at various conditions.

○, Plasma treatment → insolubilization;
●, insolubilization → plasma treatment.

one (Photo A) in any conditions even after 30-min treatment. Photo B is O₂ plasma treated film after insolubilization. O₂ is well known as a good etching gas in plasma. In the most of the plasma conditions,

rough surface of the silk film is observed. The geometrical pattern is very interesting.

The rough surface obtained by O₂ plasma treatment became smoother after insolubilization (Photo C). As we stated earlier that the plasma-treatment effect was spoiled by the insolubilization, the surface morphology also became moderate. Taking into account the dyeability, surface roughness may be an important factor in addition to surface functional groups. Therefore, less rough surface obtained by the insolubilization is thought not to be favored for better dyeability.

3.4. Color Deepness of Dyed Plasma-Treated Silk Film

As for NH₃ plasma-treated films, we expected good results because the dye used has many acid functional groups. However, since we have not obtained reproducible results so far, we focus in O₂ plasma-treated films. Figure 8 shows color deepness (absorbance) of dyed O₂ plasma-treated silk films. We prepared and examined two kinds of silk films: one is plasma treated and insolubilized film, and the other is insolubilized and plasma-treated film. In all plasma conditions, as we expected, the absorbance increased. In the comparison of the two kinds of films, however, unexpectedly the film insolubilized after O₂ plasma treatment showed greater absorbance in all plasma conditions. As we

stated repeatedly in this paper, the insolubilization diminishes the effect of plasma treatment. As far as the dyeability is concerned, however, the silk film insolubilized after O₂ plasma treatment was the best. The reason of this result is now under consideration.

4. Conclusion

Silk films were prepared from silk fabrics for easier surface analysis, and were insolubilized by dipping in 75% ethanol solution. The silk films were treated by O₂ and NH₃ plasmas for the implantation of functional groups for better dyeability. By the insolubilization, the surface property of silk films was altered. The insolubilization after plasma treatment diminished the effect of plasma treatment. However, insolubilized silk film after plasma treatment showed rather better dyeability.

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Reference

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