Effect of Plasma Treatment on Surface of Protein Fabrics

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Abstract

Study of the morphology, aggregation structure and properties of Silk and Wool treated by low temperature glow discharge air plasma showed that slight flutes appeared on the surface of silk and wool fibers and that its surface structure changed after plasma treatment. Crystalline structure of the silk fabric also decreased after the plasma treatment. The weight of the fiber decreased after plasma treatment because of etching. The yellowness of the fabrics increased with increasing plasma treatment.

1. Introduction

Plasma surface treatment of fiber or fabrics has been applied in many fields for a long time [1-5] and the main purposes of the treatment is, in analogy with most of the other materials, the improvement of the surface energy by using hydrophilic-natured plasma. Higher surface energy makes adhesion or printability better for plastics or any solid materials. As an application for fabrics (fiber), both organic and inorganic fabrics (fiber) with improved adhesion and compatibility with plastics by plasma treatment is used for fiber-reinforced plastics (FRP), which could raise their performance [6-14]. Another important application of plasma treatment of fabrics utilizing higher surface energy is the improvement of dyeability for clothing use. For the purpose of dyeability or color deepening, plasma treatments for many kinds of fabrics, such as poly (ethylene terephthalate), nylon-6, nylon-66, aramid and wool have been reported [15-17]. In these reports, chemical interaction between fiber and dye seems to be rather important than surface energy.

In addition, as far as color deepening is concerned, surface morphology of fiber caused by plasma etching is also crucial. Until recently, reports on plasma treatment of silk were not too many. With increasing popularity of natural products, demands of silk for not only clothing use but also personal care products and foods have been increasing lately. Nakano et al, measured surface area of O2- plasma-treated silk fabrics with a modified-BET apparatus [18]. It will be very interesting if a relationship between the surface area and color deepness is revealed. As the use of silk fabrics increases, their defects have become clear. In addition to deeper dyeing, improvement of color fastness property is often required. In general, color fastness of silk is not satisfactory. When silk fabrics are rubbed with other clothing, dye on the silk transfers to the other cloths, which is called “color pollution”.

In this study, silk and wool fabrics are treated with air plasma in order to improve color deepness of dyed silk fabrics and improve color fastness to light. The use of plasma technique, in which little waste is produced as a dry process, is also environment-friendly.

2. Materials and Methods

2.1 Materials

Wool and Silk fabric details are given in table-1; they were sourced in their raw/grey form without any previous finishing. They are given soap wash with Sodium carbonate and dried in sunshade before experimenting. The fabrics were prepared in the dimensions of 60 mm x 120 mm for plasma treatments and other subsequent processes. Plasma reactor requires this length and further larger sizes
cannot be treated due to the limitations posed by the machine design. The cut length is used for plasma treatment, yellowness measurement and colour index measurement.

Table 1. Fabric constructional details of wool and silk fabric samples used for plasma treatment and other tests.

| Property      | Wool | Silk |
|---------------|------|------|
| GSM           | 135  | 62.3 |
| Ends/inch     | 50   | 68   |
| Picks/inch    | 32   | 68   |
| Warp Count    | 46 (tex) | 3 (tex) |
| Weft Count    | 42 (tex) | 6 (tex) |
| Weave         | Plain | Plain |

2.2 Weight Loss

The loss in weight of the fabric was calculated using the following expression.

\[
\text{Weight loss (g)} = W_1 (g) - W_2 (g)
\]

\(W_1\) - weight of the sample before plasma treatment

\(W_2\) - weight of the sample after plasma treatment

All the fabric samples were dried at 105 °C for 30 min prior to the measurement for the exclusion of the effect of absorbed water.

2.3 Color index measurement

The Color-i instrument works on the principle of illuminating the sample (fabric to be tested for color) with a monochromatic light source emitted by LED (Light Emitting Diode) and the reflected light is received by a sensor which gives five values \((DL^*, Da^*, Db^*, DC^*, DH^*)\) for the color and the color index is calculated electronically. For the evaluation of color deepness of dyed fabrics, reflectance of visible light from 400 to 700 nm was measured at every 20 nm with a reflectometer (Kurabo, AUCOLOR-10a).

2.4 Colour fastness test (Light fastness)

The AATCC Test Method 16-1978 was used for assessing the colour fastness to light of the dyed wool and silk fabric. Water-cooled Xenon-Arc Lamp was used, while continuous light borosilicate inner filters and soda lime outer filter glasses surrounded the xenon-arc lamp. Blue wool standards were used to control the exposure periods as recommended by AATCC.

2.5 X – ray diffraction

X-ray diffraction spectra were obtained with a model 2027 X-ray detector diffraction system at a voltage of 40kV, current of 30mA and scan rate of 2% per min.

2.6 Scanning electron microscopy

The morphology of modified mulberry silk fiber was observed on model JEOLJSM-J330A scanning electron microscope. The samples were mounted and gold sputtered to give the samples electronic conductivity under vacuum prior to observation.

3. Results and Discussion

3.1 Weight loss

In plasma treatments with non-polymer-forming gases, etching of substrates is not negligible. In general study of plasma treatment of wool and silk fabrics also, etching was observed by weight loss of the fabrics and SEM observation. The degradation rate (weight loss) of the plasma-treated fabric increased with increasing the exposure time due to etching of contaminant layer (Table 2). This contaminant layer is responsible for hydrophobicity of the fabric. This etching process is predominant
on the amorphous region of the surface than the crystalline region [19]. Therefore, it is possible that the initial rate of the etching is more rapid. Once all the amorphous materials on the surface has been removed, the remaining crystalline and tightly bound amorphous regions could not be removed easily, causing decline in the etching rate [20]. After the removal of this waxy layer, the fabric acquires hydrophilicity.

Table 2. Weight loss of wool and silk samples with respect to duration of plasma treatment (p = 0.3 mbar, V = 350 V)

| Treatment time (min) | Weight loss (%) |
|----------------------|-----------------|
|                      | Wool            | Silk            |
| 05                   | 0.005642        | 0.010853        |
| 10                   | 0.004219        | 0.012841        |
| 15                   | 0.007752        | 0.014563        |
| 20                   | 0.009366        | 0.015075        |
| 25                   | 0.00979         | 0.016051        |
| 30                   | 0.012195        | 0.020316        |

Etching may not be limited to just the surface, because the fibers became thinner. Those treated with plasma at 0.3 mbar also showed micro pitting on the surface (Fig.8). Although the surface roughness is not measured quantitatively, the roughness seems to have a correlation with the weight loss.

Figure 1. Variation of weight loss of silk and wool samples with respect to duration of plasma treatment (p = 0.3 mbar, V = 350 V)
As is evident from Figure 1, silk samples show more increase in weight loss when compared to wool samples and it is more gradual. On further treatment after 25 minutes, it drastically increases, which may mean that silk fibers attain a level of saturation and then weight loss increases. It has to be maintained at an optimum treatment time of about 15 – 20 min for plasma without losing much weight. Wool samples show a gradual increase in weight loss when compared to silk and it is more linear, which means that wool fibers never attain a level of saturation and the degradation is proportional to the duration of plasma treatment. It has to be maintained at an optimum treatment time until which the wool does not significantly lose its characteristics like strength, elongation, etc.

3.2 Yellowness Index

Yellowness of the fabric formed after plasma treatment is due to the degradation of fibre surfaces. Plasma treatment vaporizes the fibre surface and results in charring, which appears as yellowness on the fabric surface. The yellowness is removed mostly by washing, some char cannot be removed and this results in poor aesthetic property.

Bleaching completely removes the yellowness with considerable loss in fabric weight, when done after plasma treatment. Table 3 shows the yellowness readings measured with Color I instrument with standard of the untreated fabric. Figure 2 shows the yellowness of fabric samples, silk shows a gradual increase in yellowness with increase in duration of plasma treatment and shows slightly more yellowness at the end. This shows silk fabric surfaces degrade more after 15 minutes of plasma treatment [17,18 &21].

![Figure 2. Variation of Yellowness Index of Silk and Wool samples with respect to duration of plasma treatment (p = 0.3 mbar, V = 350 V)](image-url)
Wool shows a considerable increase in yellowness in the initial stages of plasma treatment and then yellowness increases gradually, showing that the initial degradation and yellowing is due to the charring of the scales present on the surface of wool. Later, the fabric surface starts charring. The ability of plasma treatment in removing scales of the wool fibre surface is proved by this property.

### 3.3 Color Index

Plasma treatment increases the dye affinity of the fibres. The deepening of the shade of the dyed sample fabrics shows increase in dye affinity. The samples are tested for their color value in the Color – I instrument, which gives the values of the colors in three different modules namely, CV-WSUM, CV-SUM and CV-SWL.

**Table 3. Variation of Yellowness Index of Silk and Wool samples**

(p = 0.3 mbar, V = 350 V)

| Sample No | Treatment time (min) | Wool | Silk |
|-----------|----------------------|------|------|
| 1         | 00                   | 15.2 | 1.805|
| 2         | 05                   | 21.98| 2.68 |
| 3         | 10                   | 21.8675| 2.9725|
| 4         | 15                   | 24.515| 3.585|
| 5         | 20                   | 25.915| 5.145|
| 6         | 25                   | 27.0175| 5.785|
| 7         | 30                   | 28.795| 6.14 |
Table 4. Color Index values of silk fabric samples in accordance with duration of plasma treatment and values from different modules of color measurement (CV-WSUM, CV-SUM & CV-SWL). (p = 0.3 mbar, V = 350 V)

| Treatment time (min) | CV-WSUM  | CV-SUM  | CV-SWL  |
|----------------------|----------|---------|---------|
| 00                   | 0.014    | 0.194   | 0.205   |
| 00                   | 0.038    | 0.543   | 0.524   |
| 00                   | 0.042    | 0.594   | 0.572   |
| 05                   | 0.061    | 0.86     | 0.908   |
| 05                   | 0.061    | 0.855   | 0.892   |
| 10                   | 0.053    | 0.743   | 0.735   |
| 10                   | 0.054    | 0.756   | 0.756   |
| 15                   | 0.059    | 0.837   | 0.855   |
| 15                   | 0.053    | 0.745   | 0.765   |
| 20                   | 0.06     | 0.857   | 0.87    |
| 20                   | 0.062    | 0.884   | 0.904   |
| 25                   | 0.063    | 0.898   | 0.922   |
| 25                   | 0.059    | 0.831   | 0.866   |
| 30                   | 0.068    | 0.958   | 0.968   |
| 30                   | 0.06     | 0.841   | 0.863   |

Figure 3. Color Index values of silk fabric samples in accordance with duration of plasma treatment and values from different modules color measurement (CV-WSUM, CV-SUM & CV-SWL). (p = 0.3 mbar, V = 350 V)
The three modules give the total values of a corresponding color of the dyed sample. The tests of the modules and their interpretation of the color value are designed according to AATCC standards. Every color can be expressed with three values of primary colors showing the proportion of each primary color in that particular color. With this above given value (Table 4&5), though the proportion cannot be interpreted but increasing value shows the deepening of all or one of the colors.

As is clear from Fig 3, Silk shows a considerable increase in all the modules with respect to the duration of plasma treatment, later increase in values are low, showing that silk attains a saturation limit after 5 minutes of plasma treatment.

Wool shows a very low increase in color in the initial stages, possibly due to presence of scales. After 10 minutes of plasma treatment, the increase is large; this may be due to the ablation of the outer surface of wool resulting in higher dye absorption (Fig. 4).

Table 5. Color Index values of wool fabric samples in accordance with duration of plasma treatment and values from different modules of color measurement (p = 0.3 mbar, V = 350 V)

| Treatment time (min) | CV-WSUM | CV-SUM | CV-SWL |
|---------------------|---------|--------|--------|
| 00                  | 0.008   | 0.108  | 0.179  |
| 00                  | 0.007   | 0.093  | 0.156  |
| 00                  | 0.009   | 0.12   | 0.203  |
| 00                  | 0.01    | 0.125  | 0.205  |
| 05                  | 0.008   | 0.105  | 0.164  |
| 05                  | 0.008   | 0.11   | 0.173  |
| 10                  | 0.008   | 0.113  | 0.173  |
| 10                  | 0.008   | 0.113  | 0.17   |
| 15                  | 0.019   | 0.259  | 0.324  |
| 15                  | 0.018   | 0.255  | 0.324  |
| 20                  | 0.037   | 0.521  | 0.595  |
| 20                  | 0.037   | 0.519  | 0.584  |
| 25                  | 0.045   | 0.629  | 0.775  |
| 25                  | 0.048   | 0.667  | 0.791  |
| 30                  | 0.04    | 0.566  | 0.606  |
| 30                  | 0.038   | 0.553  | 0.573  |
3.4 Colour Fastness to Light

In the case of wool, color fastness to light is affected by plasma treatment. Color fastness from 4 to 3.4 after 10 min of plasma treatment and then remained constant on further treatment. Silk on the other hand is unaffected and has a good resistance towards plasma treatment. The suspected reason for this reduction of fastness is Physical ablation in which the outer layer is removed or ablated causing the wool fabric to become more vulnerable to UV - Rays and X – Rays. The smooth surface of the silk fabric makes it less vulnerable (Fig.5).

Figure 4. Color Index values of wool fabric samples in accordance with duration of plasma treatment and values from different modules color measurement (p = 0.3 mbar, V = 350 V)

Figure 5. Colour fastness values of wool and silk against light and with respect to duration of plasma treatment (min) (p = 0.3 mbar, V = 350 V)
3.5 Crystalline structure of silk and wool fibers

Crystallinity of silk and wool with air plasma treatment is shown in Table 6. Crystallinity of the silk fibers decreased after plasma treatment. It probably can be explained that the polypeptide chain was broken and macromolecules recombined during plasma treatment. The inner structure of silk fibers became looser. Part of the crystal region was oxidized or decomposed because of etching, so the crystallinity decreased. In accordance with the fact that crystalline region and amorphous region have different contribution to X-ray diffraction, changes of crystallinity of silk, before and after treatment could be observed by X-ray diffraction method (Fig.6a&b). It was seen that the X-ray diffraction patterns of untreated and air plasma treated silk were similar and that there was a broad peak at \(2\theta = 20.58^\circ\) and 20.5\(^\circ\) respectively, which were approximately the same. The diffraction intensity decreased after plasma treatment as compared with control sample. So conclusion could be drawn that crystallinity of plasma treated silk fiber decreased. It confirmed the result obtained by density meter method. Part of the macromolecules on the surface and in the inner part of silk fibers being in the ion field oxidized during air plasma treatment. So the crystalline part became looser and crystallinity slightly decreased [22]. The same results were found in wool fabrics, which are shown in figure 6c &d. The X-ray diffraction patterns of untreated and air plasma treated wool were similar and that there was a broad peak at \(2\theta = 21.43^\circ\) and 21.41 respectively, which were approximately the same.

![Figure 6](image-url)

Figure 6. X-ray diffraction curve of fibres with air plasma: (a) control (silk); (b) 5 min (silk); (c) control (wool); (d) 5 min (wool)
### Table 6. Percentage of Crystallinity of silk and wool fabrics.

| Sample number | Details of samples             | Crystallinity D (Å)\% |
|---------------|-------------------------------|------------------------|
|               |                               | Silk       | Wool     |
| 1             | control                       | 41.37      | 22.13    |
| 2             | 5 min plasma exposed          | 41.039     | 22.07    |

### 3.6 Surface morphology

Changes of the surface morphology of silk and wool fibers after air plasma treatment were investigated using SEM (Fig.7&8). Control sample showed a clean and smooth surface (Fig.7a &8a), while slight longitudinal flutes and small pits were appeared on the surface of treated silk and wool fiber (Fig.7b& 8b respectively). This phenomenon was the result of etching by plasma. Figure 7b &8b, shows surface roughness, which is used to increase wettability, printability, dyeability and adhesion properties of the fabrics. Many researchers have published their work on this aspect [22].

![Figure 7. SEM image of Silk fabrics a) Untreated b) Plasma treated samples](image_url)

![Figure 8. SEM image of Wool fabrics a) Untreated b) Plasma treated samples](image_url)
4. Conclusions

From the above experimental results, we conclude that the Low Temperature Plasma (LTP) treatment appears to be a method for modifying the wool and silk fabrics with quite a significant effect. LTP damages an ultra-thin hydrophobic layer on the protective surface of the fibre. This process occurs only on the surface and does not damage the inner structure. The optimum dose of plasma treatment for silk is 5-10 minutes, whereas for wool, it is 10-15 minutes. The LTP-treated wool and silk fabrics could also meet the performance specification requirements. After the LTP surface modification treatments, significant changes within the surface properties of the fibres were observed.

The substantial shortcoming of plasma treatment of textiles is that it cannot replace all wet processes, but it can be a viable pretreatment, which provides plenty of environmental and economical benefits.

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5. References

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