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Comparison of Effects of Several Oxygen Containing Low Frequency Plasmas on the Removal of Silk Sericin Layer of Raw Silk Fabrics

Oksijen İçeren Farklı Düşük Frekans Plazmalarının Ham İpek Liflerinden Serisin Giderilmesine Etkisinin Karşılaştırılması

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Araştırma Makalesi / Research Article

**COMPARISON OF EFFECTS OF SEVERAL OXYGEN
CONTAINING LOW FREQUENCY PLASMAS ON THE
REMOVAL OF SILK SERICIN LAYER OF RAW SILK FABRICS**

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ABSTRACT: This study focuses on changing the surface properties of raw silk fibers to simplify the degumming process. Because the conventional degumming processes may be harmful for fibers, they must be applied moderately. Utilizing the novel techniques and technologies, researchers are trying to find alternative ways in order to achieve effective sericin removal without damaging the fibroin part of the silk. In this study, one of the novel technologies, low-pressure plasma technology was used to remove sericin layer by etching. Air, oxygen and water vapor plasmas were applied to raw silk fabrics under different time and power conditions. Weight loss, breaking strength, scanning electron microscopy and fourier transform infrared spectroscopy-attenuated total reflectance were used to characterize the effects of plasma treatments.

Keywords: Plasma etching, silk, degumming, FTIR-ATR

**OKSİJEN İÇEREN FARKLI DÜŞÜK FREKANS PLAZMALARININ HAM
İPEK LİFLERİNDEN SERİSİN GİDERİLMESİNE ETKİSİNİN KARŞILAŞTIRILMASI**

ÖZET: Bu çalışmada, ipek liflerinden serisin gidermenin kolaylaştırılması üzerine odaklanmıştır. Konvansiyonel serisin giderme işlemleri lifler için zarar vericidir, bu nedenle ılıman bir şekilde uygulanmaları gerekmektedir. Araştırmacılar, yeni teknik ve teknolojiler kullanarak ipek fibroinine zarar vermeden serisin uzaklaştırmak için alternatif yollar aramaktadır. Bu çalışmada düşük basınç plazma teknolojisi, aşındırma ile serisin giderme amacıyla kullanılmıştır. Hava, oksijen ve su buharı plazmaları farklı süre ve güç koşullarında uygulanmıştır. Plazma işlemlerinin etkisi ağırlık kaybı, kopma mukavemeti, SEM ve FTIR-ATR analizleri ile karakterize edilmiştir.

Anahtar Sözcükler: Plazma ile aşındırma, ipek, serisin giderme, FTIR-ATR.

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1. INTRODUCTION

Silk fibers are important for the production of luxury fabrics and medical products with its outstanding properties like handle, luster and comfort for former case and like biocompatibility, mechanical properties and ability to withstand *in vivo* conditions during a suitable time. Raw silk fiber, which is 10-25 μm in diameter, is produced as secretion by silkworms and is composed of two different protein parts: sericin and fibroin. The silkworm cocoon shell consists of 75% fibroin and 25% sericin, approximately [1-5]. Sericin is the glue-like matrix material that protects and holds two triangular fibroin macromolecules together. The 30% of the sericin protein consists of serine aminoacid and the second most common aminoacid in sericin structure is a dicarboxylic acid named aspartic acid and this accounts for 18% of the sericin. Due to these types of aminoacids, 77% of the sericin is polar and its outermost layer (α -sericin) can be soluble in hot water. However, coming close to the fibroin part, inner structure of sericin (β -sericin) becomes insoluble. The α -sericin contains less C and H and, more N and O than the β -sericin. Alanine and glycine aminoacids together, whose side groups are $-\text{CH}_3$ and $-\text{H}$, respectively, account for the 70% of the total composition of the fibroin. One part of fibroin is made up of aminoacids with a low molecular weight (glycine, alanine, serine) and offers crystalline regions which confer a high degree tenacity on the fiber. The other part has amorphous areas composed of aminoacids of a relatively higher molecular weight (i.e. tyrosine). The presence of these two regions makes silk a natural block copolymer and gives fiber the combined properties of strength, flexibility and elasticity. Because the sulphur containing side groups are absent and the ionic side groups are present only in small quantities, the links between the molecule are hydrogen bonds between main and side chains and salt linkages between side chains [1, 3, 6-11].

Production of silk fabric from cocoons is comprised of steps as reeling, weaving, degumming, dyeing/printing, finishing. Degumming is to remove the sericin layer from the fibroin fibers, because it is the cause of poor properties in raw silk form like dull appearance, harsh and stiff handle and has problems with biocompatibility causing host immune response activation [4, 7]. Conventionally, thermochemical methods are used such as soap degumming, alkali degumming. Sericin is hydrolyzed and its amide bonds are broken into small molecules and sericin is dissolved in degumming solutions, while fibroin can be also affected inevitably from the harsh treatment conditions of the process [7, 12]. Degumming of the silk fibers is commonly realized in very hot water containing Marseille soap for a long time. In addition to altered mechanical properties of the fibroin fiber, this industrial processing loads wastewater and causes increased cost of effluent cleaning. Due to these disadvantages, alternative, environmentally friendly and mild degumming methods are investigated by researchers worldwide [3, 4, 11-13].

Cold plasma technologies have been popular and very promising processing methods for polymeric materials like textiles for enhanced hydrophilic/hydrophobic characteristics, biocompatibility, increased dye/chemical uptake, etc. [14-18]. The plasma treated surfaces have some properties that cannot be obtained by

conventional techniques and the method has effects only at the surfaces of the materials. Plasma treatments are realized without water releasing almost no waste; therefore, this technology is a non-polluting method and contributes to conservation of insufficient water on the earth [19]. In the plasma medium several simultaneous reactions occurs. In case of oxygen plasma, etching (due to formation of volatile products) and formation of oxygen containing functional groups are two simultaneous reactions observed [5].

Chen et al. applied oxygen plasma on silk yarns and found weight and crystallinity decreased, β -sheet conformation increased and breaking strength decreased slightly after plasma treatments. Radio frequency (RF) oxygen plasma was applied by Fang et al. to improve inkjet printing performance on silk fabrics and color yields and pattern yields were enhanced by plasma treatment. Riccardi, Barni and Esena, reported RF plasma processing for etching and fluorine grafting (SF_6 gas) and described the use of atmospheric pressure plasma for coating of silk fibers. They concluded that it was possible to obtain partial degumming but for a complete plasma degumming it is required to make fine tuning of operating conditions in order to etching selectivity and to prevent fiber damage. Fluorine grafting for water repellence and atmospheric hexamethyldisiloxane deposition could be efficiently realized. Long et al., suggested a method combining RF argon plasma and a subsequent mild chemical treatment for degumming of silk fibers [3, 20-22]

In this study, raw silk fabrics are treated with various gas plasmas with the aim of understanding whether any of these plasmas can help to moderate the degumming conditions which might be decreased the results as fibrillation and decrease in the mechanical integrity as a result of treatments in hot temperatures for a long time [11]. In order to change the surface properties of the raw silk fibers to remove sericin layer, low frequency (LF) low-pressure plasma was used. The penetration rate of low-pressure plasmas is high into textiles and it effectively influences the surfaces of all single fibers with stronger and more stable effects [3]. In the starting work of this study, raw silk fabrics were exposed to oxygen and air plasmas. Weight differences of treated and untreated fabrics and weight differences after hot rinsing was found [23]. Oxygen containing plasmas, (i.e. water vapor plasma in addition to oxygen and air plasmas) were chosen as low frequency plasma gases for this study, as their etching capabilities are known and in order to obtain degumming as an extraction process [24]. Besides, air and oxygen plasmas were found more effective on removing the sericin layer than nitrogen and helium plasmas in radio frequency [22]. In addition to types of gases, the other plasma parameters in this study were discharge power and plasma treatment time. After plasma treatments, a rinsing process was realized to see whether it was easy to remove the remaining sericin by only water.

2. MATERIALS AND METHOD

2.1 Plasma Treatments

Low frequency (LF-40kHz), cold air, water vapor or oxygen (99.9%) gas plasma was investigated for the surface modification

of plain-woven %100 raw silk fabrics, having area weight of 23.2g/m² and settings of 28ends/cm and 35picks/cm. A continuous mode power was supplied by a low frequency plasma system (Diener, Germany) between 50W and 200W. Discharge time and plasma pressure were changed between 1-20 minutes and 30-60 Pa, respectively. Vacuuming to pressure 20Pa, gases were allowed to flow to remove the impurities; then glow discharge was initiated and continued during predetermined plasma process time. Before taking out the sample, argon gas was flowed through the chamber to terminate free radicals in the medium.

For determination of effects plasma treatment on silk fabrics, weight loss, breaking strength measurements and surface characterization techniques were used and compared with the values of untreated fabric.

2.2 Rinsing

After plasma treatments short hot water rinsing was realized at boiling water for 5 minutes.

2.3 Degumming

Mild conventional degumming was applied as a two-step thermochemical degumming treatment and followed by warm and cold rinsing for comparison with plasma degumming. For this process, silk fabrics were treated by Marseille soap at a concentration of 20 g/l in water at boiling temperature for one hour and second step is the repetition of the first step [25].

2.4 Morphology of Silk Fibers

The samples for SEM imaging were firstly coated with gold. Imaging was realized by Quanta 250 SEM scanning electron microscope at 2kV to characterize their surface morphology. The images were obtained between 500X and 50000X magnifications.

2.5 FTIR-ATR Analysis

The device used to obtain the IR spectras of the fibers was Perkin Elmer FTIR System Spectrum BX. Investigated wavenumber range and the resolution were 650-4000cm⁻¹ and 4cm⁻¹, respectively. 25 scans were applied for a spectrum.

2.6 Weight Loss Determination

Weight losses were measured after all plasma treatments, after rinsing processes and after degumming treatment. Weight loss was calculated as follows:

$$\text{Weight Loss (\%)} = ((W_b - W_a) / W_b) * 100$$

Where W_b refers to weight in grams before treatments (plasma or rinsing) and W_a refers to weight in grams after treatments. The effects of plasma power and exposure time parameters of weight loss measurements after plasma and rinsing processes are evaluated by MINITAB for windows.

2.7 Tensile Strength Measurement

Breaking strength measurements of fabric was realized at Instron 4411 Universal Tensile Tester, according to ISO 13,934-1. Test length was 10 cm and speed was 100 mm/min.

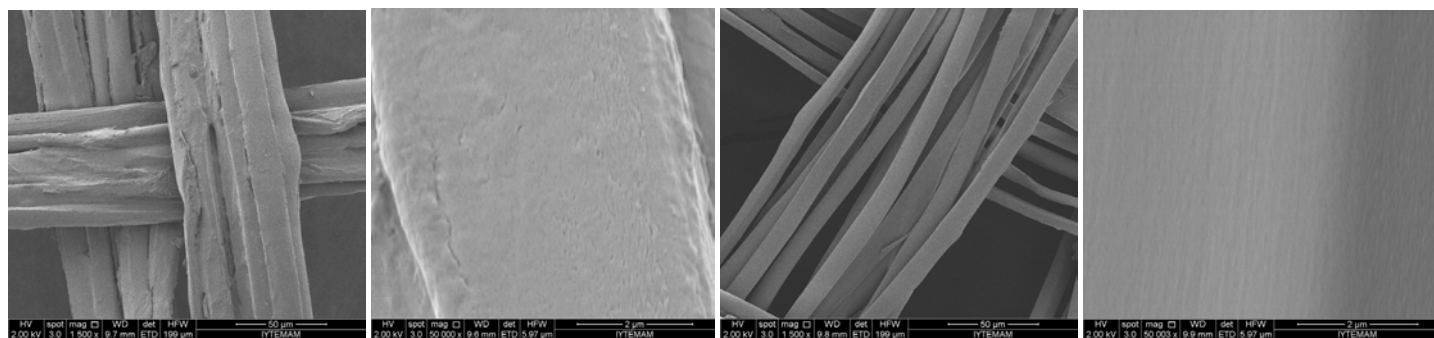
3. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy

To get information about the changes of surface morphologies of raw, degummed and plasma treated silk fibers, scanning electron images were obtained. Air plasma was the most effective plasma treatment after rinsing and oxygen plasma was the most effective after plasma but after rinsing its effectiveness reversed completely. Therefore, the fabrics treated with these two plasmas were chosen to get images. In Figure 1, the SEM images of raw and degummed silk fibers can be seen.

The sericin matrix can be clearly seen from the images of raw silk fibers. In the images of degummed silk fibers that have the smoothest surface, pure fibroin is seen.

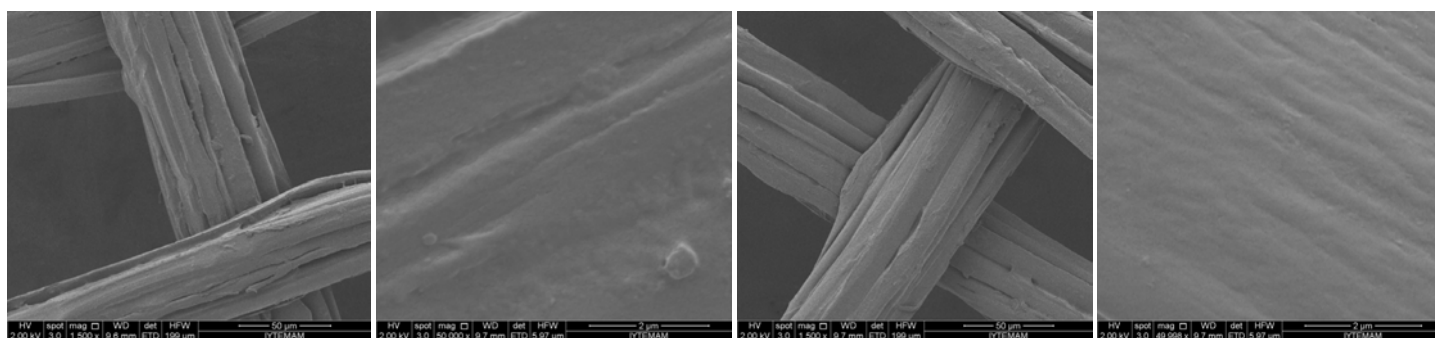
Figure 2 presents the images of plasma treated silk fibers at different magnifications. Figure 2 (a) and (b) show the pictures of treated silk fibers with the conditions of 50W-1min air and oxygen plasma, respectively. These plasma conditions are the mildest conditions. The pictures seem like raw fibers having smooth surfaces. Figure 2 (c) and (d) depict the pictures of 200W-20min conditions of air and oxygen plasma, respectively.



(a) Raw silk fibers at 1500X and 50000X

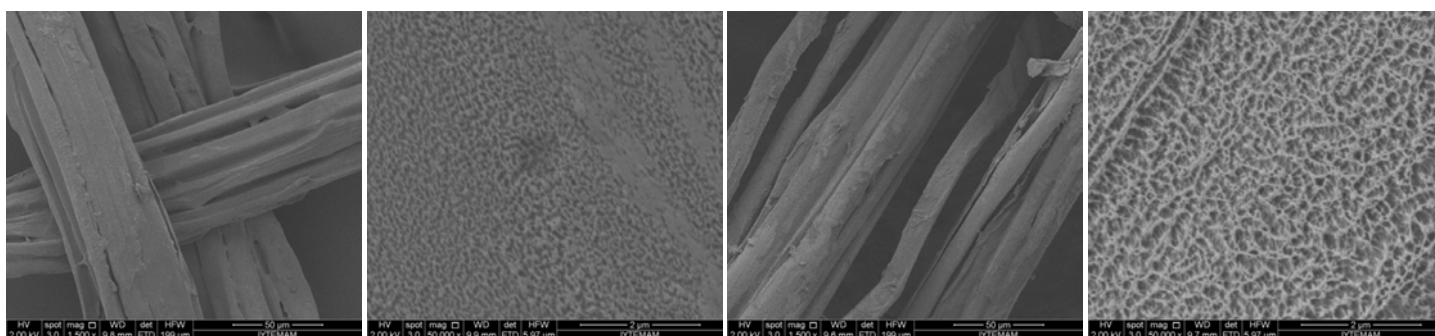
(b) Conventionally degummed silk fibers at 1500X and 50000X

Figure 1. SEM images of raw and conventionally degummed silk fibers at 1500X and 50000X magnification



(a)50W-1min Air plasma-1500X and 50000X

(b)50W-1min Oxygen plasma-1500X and 50000X



(c) 200W-20min Air plasma-1500X and 50000X

(d)200W-20min Oxygen plasma-1500X and 50000X

Figure 2. SEM images of 50W-1min and 200W-20min- air and oxygen plasma treated silk fibers at 1500X and 50000X magnification

Comparing with the untreated raw silk fibers, the surfaces of the fibers for both 200W plasmas are covered with hills and holes, showing a notable plasma etching effect. Deeper pits and grooves were produced on the surface of 200W-20min oxygen plasma treated silk fabrics than air plasma treated ones. Figure 2(d) shows the separation of fibers from each other like the degummed fibers in Figure 1(b). Therefore, 200W air and oxygen plasma, but especially the oxygen plasma, easily broke the outer sericin layers of raw silk fibers.

3.2 FTIR Analysis

FTIR analysis was also conducted to understand the surface structure of untreated and treated fibers. Figure 3 presents the FTIR spectrum of surface of raw silk fibers (i.e. silk sericin).

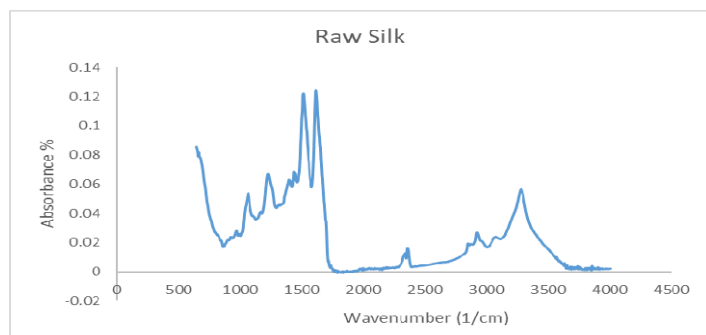


Figure 3. FTIR spectrum of surface of raw silk fibers

In this spectrum, characteristic peaks of silk sericin can be seen. These peaks are N-H hydrogen bond at wavenumber of 3278.12

cm^{-1} , N-H stretching vibrations at 3073.41 cm^{-1} , C=O stretching and N-H deformation peaks from the amide I and II band (due to beta-sheet conformation of protein fibers), and they are at 1620.78 and 1513.08 cm^{-1} respectively. There is also amide III (C-N stretching) band at 1228.09 cm^{-1} . At 2956 cm^{-1} CH_3 stretching vibrations and at 1170.78 cm^{-1} C-C linkage O-H bending peak can be seen. In addition, two bands between $2300\text{-}2400 \text{ cm}^{-1}$ are attributed to asymmetric stretching vibrations of CO_2 results from atmospheric CO_2 in measurement operating conditions. Therefore, these are not considered in interpretation [5, 26-28].

In Figure 4, spectrum of the most effective plasma condition of 200W-20 min oxygen plasma treated silk fiber, together with spectra of raw and degummed silk fiber were plotted.

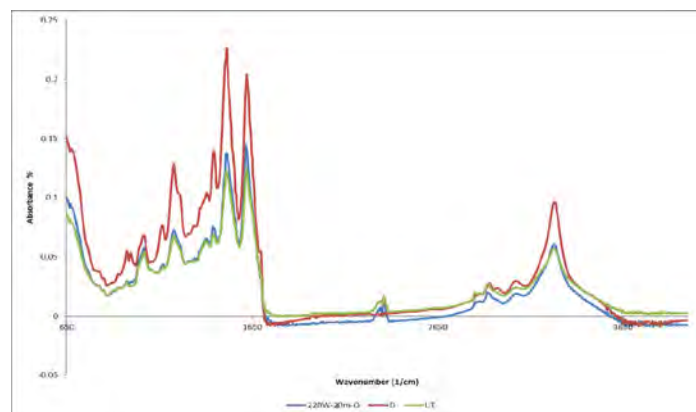


Figure 4. FTIR-ATR spectra of raw (green), degummed (red) and 200W-20min oxygen plasma treated (blue) silk fibers

In raw silk spectrum, the bands attributed to N-H deformation (1513.08 cm^{-1}) and C=O stretching (1620.78 cm^{-1}) have similar intensity. However, for degummed silk fibers, the C=O band at 1650 cm^{-1} became shorter than N-H deformation band. This may indicate the lack of oxygen containing groups at pure fibroin structure. For oxygen plasma treated silk fibers, C=O band is higher than the N-H, due to oxygen based functionalization, C=O carbonyl feature formation of the fiber surfaces after oxygen plasma. The peaks around 995 cm^{-1} and 967 cm^{-1} are the sign of crystalline structure and can be attributed to glycine-alanine-glycine linkage of fibroin [5, 29].

3.3 Weight Loss Measurements

Results of weight loss measurements after air, oxygen water vapor plasma treatments versus plasma parameters were drawn in three-dimensional graphics in following Figures 5a, 5b and 5c.

From the figures, the weight losses can be clearly seen and this shows the etching effect of the plasma treatment. The decreases of the weights of the fabrics were increased by increasing time and LF power conditions of these oxygen containing plasmas. Although the general reduction trends of the graphs are similar, air plasma has less effects than the others for etching of sericin layer. The highest weight loss of air plasma treated silk fibers is almost half of the highest weight loss values of water vapor and oxygen plasma treatments.

Figure 6 shows the weight loss values after plasma and rinsing processes in graphics. The trend of changes of weight loss results with increasing power and time conditions seem to change after rinsing processes.

The changed effects on sericin removal of plasma and rinsing processes can be seen from the Figure 6. In contrast to effects of plasmas, almost all values of oxygen and water vapor plasma with rinsing are lower than the values of air plasma. For air plasma, the weight losses decreased by increasing plasma power, especially at long time conditions. The two highest values are higher than 10% and obtained at 100W-5min and 50W-20min air plasma conditions. For the graphic of oxygen plasma and rinsing (Figure 6.b), near plain surface is obtained meaning almost all weight losses after rinsing were around 6.26%. For water vapor plasma with rinsing, the results show that the total weight losses were a bit lower than oxygen plasma-rinsing treatment as an average of 5.98%. The reason for the lower values of oxygen plasma with rinsing may be the cross-linking of the surface chemical groups under the influence of oxygen plasma. Surface cross-linking may occur when degrading polymeric materials by plasma etching. The specific behavior of each polymer can be the oxidation, crack stability of the backbone, the tendency to branch and crosslink the super-molecular structure including crystallinity, stretching, orientation. The scission of chemical bonds in polymer chain may be resulted in recombining to cross-link neighboring polymer chains. Therefore, in this study, the strong etching effects occurred under pure oxygen plasma treatment and loss values before rinsing were higher than the others. However, plasma has multifunctional effects simultaneously and here more crosslinking occurred in pure oxygen plasma, too. As a result of that, rinsing was not as efficient as the other plasma treatments [29-31].

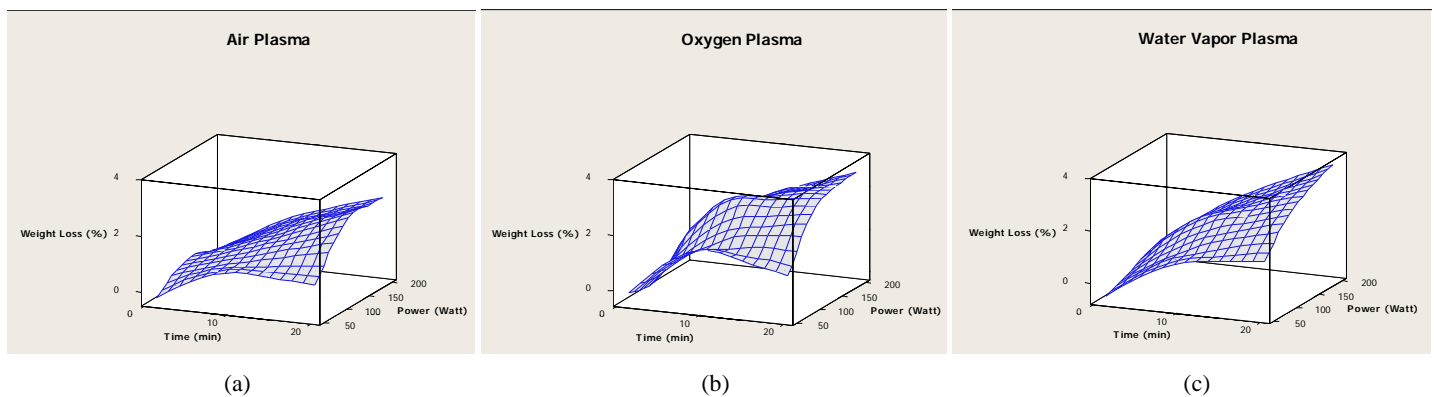


Figure 5. Effect of plasma parameters on weight loss after (a) air plasma, (b) oxygen plasma and (c) water vapor plasma

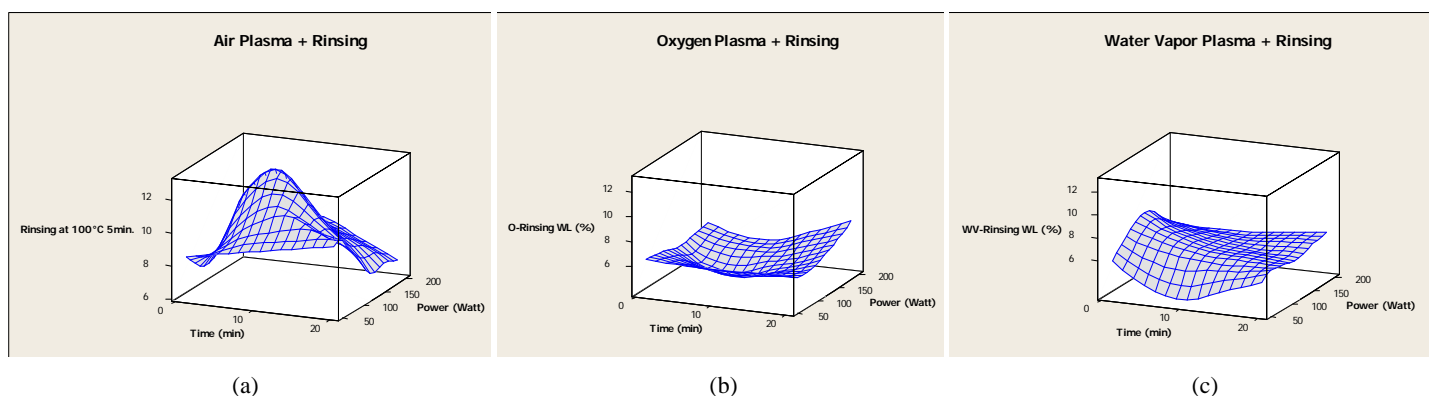


Figure 6. Weight loss values based on plasma conditions after air (a), oxygen (b) and water vapor (c) plasma and rinsing treatments

Sericin is 25-30% of total silk fiber. Therefore, after conventional degumming treatments, this amount is removed from the fiber. In this study, similar amount was obtained after soap degumming as 29.2% weight loss. Besides, after rinsing of raw fibers, the weight loss was 7.62%. Weight loss experiments show higher weight loss for air plasma-rinsing than raw silk rinsing. Thus, this air plasma-rinsing method, with some enhancements, may be a facilitating, ecological, water saving alternative to remove sericin layer of silk fibers.

3.4 Breaking Strength Measurements

Breaking strength and elongation values of raw, degummed and plasma treated silk fibers are seen in Figure 7 (left) and (right).

Tensile strength values seem similar to the raw silk fibers after plasma treatments except for longest time condition of 200 W plasmas. Although there was no remarkable decrease, the most effective plasma was oxygen plasma. In addition, the breaking strength value of degummed silk fibers (108.50 N) was lower than half of the breaking strength value of raw fibers (223.00 N). Similarly, elongation at break values at 200W-20 minutes condition of plasma treated fibers are the lowest values among others. Generally, the shortest time value of 1 minute seems to have no apparent effect on elongation values. Again, elongation value of degummed silk fibers is very low comparing to the others.

According to the results of 200W- 20 min plasmas, the oxygen plasma seems to be the most effective to etch the sericin layer at

the highest rate. Similarly, elongation value after oxygen plasma at this condition is lower than the others. This strengthens the idea of the formation of crosslinking between the macromolecules that limit the mobility of macromolecule chain when tensioning.

4. CONCLUSIONS

Oxygen, air and water vapor plasmas were used to ease the removal of sericin layer from raw silk fibers to establish an environmentally friendly and harmless mild degumming method in combination with a hot water rinsing. An effective etching was obtained after plasma treatments, especially after oxygen plasma at 20min-200W condition and this was observed by SEM and FTIR-ATR analyses. However, oxygen plasma treated sericin is hard to solve in hot water. Air plasma was the most successful among all, especially 100W-5min and 50W-20min conditions. Because after air plasma, remained sericin was easily removed by hot water rinsing without chemicals (up to 11%).

Comparing with the conventional method, this combined method as air plasma with hot water rinsing has comparable weight loss values deserving to be developed. Because, in addition to being an environmentally sustainable choice, air plasma with rinsing method has steps without water using zero chemicals. The difference from the literature were conservation of breaking strength values, i.e. mechanical properties, after plasma treatment (with air plasma it is almost the same as that of raw silk fibers) and application without chemicals using only air and water.

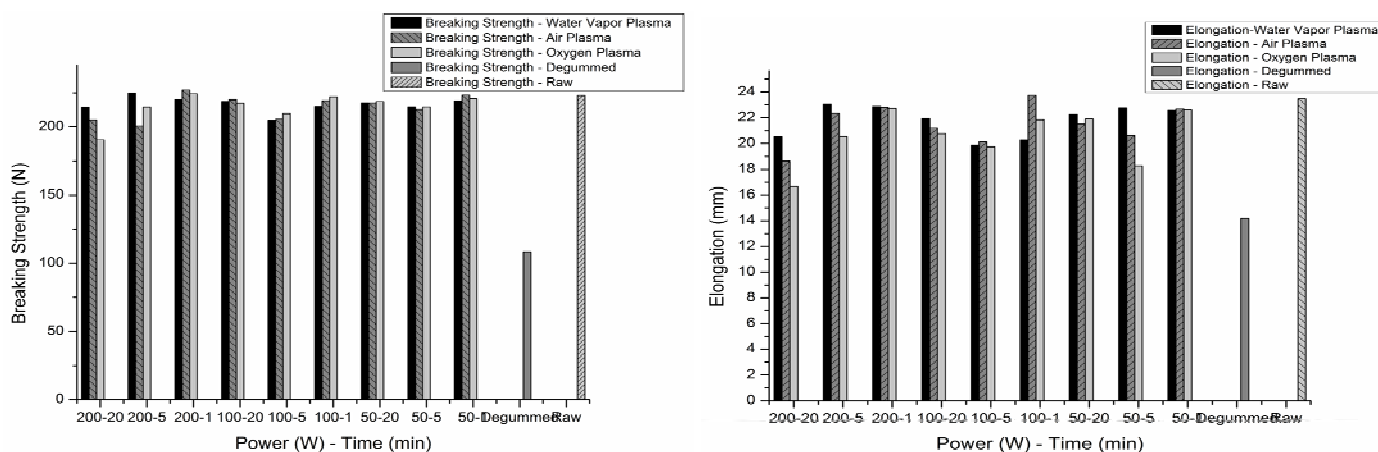


Figure 7. Breaking strength and elongation values of raw, degummed and plasma treated silk fibers

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