(REFEREED RESEARCH)

IMPROVEMENT OF FLAME RETARDANT CHARACTERISTIC OF RAW SILK FABRIC

HAM İPEK KUMAŞIN GÜÇ TUTUŞURLUK ÖZELLİĞİNİN GELİŞTİRİLMESİ

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Received: 22.05.2018 Accepted: 05.09.2018

ABSTRACT

In this study, organophosphorus based flame retardant (FR) agent was used in pad-dry-cure-wash treatment in order to enhance the flame retardant characteristics of raw silk fabrics. Silk material is composed of two cores of fibrion surrounded by a layer of sericin which has to be removed from the whole before any chemical finishing treatment. In order to improve the poor wetting capability arising from hydrophobic character of raw silk fabric, degumming process has been widely used for a long time as a necessary process which consume high amount water, chemicals and energy while causing significant weight-loss after the treatment. In today's conditions, water/chemical-saving methods take important part in textile finishing treatments because of environmental concerns. For this aim; low-temperature plasma treatment with various gases at different exposure times in different exposure power were applied on some of the raw silk fabrics before FR finishing process while some of the raw silk fabrics were undergone through conventional degumming processes. Flame retardancy, hydrophilicty, weight losses of the samples were tested, respectively. Morphological analyses of samples were tested by SEM and chemical structures of the fabrics were analyzed by FTIR-ATR. According to LOI test results, it was determined that especially nitrogen plasma pre-treatment had a significant improvement in flame retardancy of raw silk fabric. It was concluded as an output of this study that plasma treatment as a pre-treatment improved the flame retardancy of raw silk fabrics and had a significant effect on increasing wettability properties of raw silk fabrics without the necessity of conventional degumming process.

Keywords: Silk fabric, flame retardant, plasma treatment, wettability

ÖZET

Bu çalışmada, ham ipek kumaşın güç tutuşurluk özelliğini geliştirebilmek amacıyla, organofosfor esaslı güç tutuşurluk maddesi emdirme-kurutma-kondenzasyon-yıkama işleminde kullanılmıştır. Ipek lifinde, fibroin kısmını çevreleyen serisin yapının herhangi bir kimyasal terbiye işlemi öncesinde uzaklaştırılması gerekmektedir. Ham ipek kumaşın hidrofobik özelliğinden kaynaklanan zayıf ıslanabilirlik özelliğini geliştirmek amacıyla, yüksek miktarda su, kimyasal ve enerji harcayan serisin giderme işlemi uzun yıllardır kullanılan gerekli bir işlemdir. Bugünün koşullarında, çevresel kaygılar nedeniyle su-kimyasal tasarruf eden metotlar tekstil terbiye işlemlerinde büyük önem arz etmektedir. Bu amaçla; güç tutuşurluk bitim işlemi öncesinde, farklı güçlerde farklı sürelerde ve farklı gazlarla düşük sıcaklıkta plazma işlemi bazı ham ipek kumaşlara uygulanırken, diğer ham ipek kumaşlara ise konvansiyonel serisin giderme işlemi uygulanmıştır. Numunelerin sırasıyla güç tutuşurluk, hidrofilite ve ağırlık-kaybı testleri yapılmıştır. Morfolojik analizler SEM ile test edilirken, kumaşların kimyasal yapıları FTIR-ATR ile analiz edilmiştir. LOI sonuçlarına göre, özellikle azot plazma ön işleminin ham ipek kumaşın güç tutuşurluk özelliği üzerinde belirgin bir iyileştirme yaptığı belirlenmiştir. Çalışma çıktısı olarak, ön işlem olarak plazma işleminin yapılmasının hem ham ipek kumaşta güç tutuşurluk özelliğinin geliştirdiği ve hem de ayrıca konvansiyonel serisin giderme işlemine gerek kalmadan ham kumaşta ıslanabilirlik özelliğinin artmasını sağladığı sonucuna varılmıştır.

Anahtar Kelimeler: İpek kumaş, güç tutuşur, plazma işlemi, ıslanabilirlik

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INTRODUCTION

As it is well known, textiles are the materials that could cause serious fire hazards due to their flammability and ignitibility features. Therefore, there has been an increasing consideration to improve the flame retardant property of textiles for the reduction of fire hazard over the past decades. Silk fabric is widely used as pajamas, evening dress, and domestic furnishing materials for its luster, soft handle, wearing comfort, and aesthetic appearance. However, silk fiber continues to burn and cannot self-extinguish once ignited. Its limited oxygen value (LOI) value is about 23% which still needs flame retardancy finish to fulfill the commercial requirements. It is therefore vital to improve the flame retardant property of silk fabrics in which the safety regulations are concerned. Current safety laws and regulations have raised safety and environmental protection standards on flame retardant (FR) agents and support the development of environmentally friendly structures for replacing the halogen based compounds that cause toxic gases during burning process [1-5]. On the other hand, sericin layer of raw silk fabric has poor functional properties, such as dull appearance, stiff handle and hydrophobic characteristics which prevents penetration of finishing or dyeing chemicals into the fiber. Therefore, degumming process is a necessary treatment before any finishing application of silk materials in order to achieve good functional properties [6-11].The surrounding sericin could be removed by enzymes or in hot aqueous solutions containing soap, alkali and synthetic detergents. However, the methods mentioned above, are thermal- and wet-chemical processes increase the cost in effluents treatment which have environmental concern due to waste water discharge. Furthermore, these methods generally consume high amount of water, chemical and energy. They also have the possibility of degradation or fibrillation of fibroin material and uneven chemical absorption in the finishing bath because of using harsh chemicals at high temperatures in degumming process [12-19]. That's why, in today's conditions; it is important to support the improvement of functional properties of silk fabric with an environmental-friendly method which consumes less energy, water and chemical in finishing treatments.

Low temperature plasma treatments are widely used in surface modifications in polymer and textile industries due their remarkable advantages such as being dry and fast process that uses no water, less energy and less chemical that decreases waste water discharge and providing surface modification without affecting bulk properties of the material which could be named as "effective environmental-friendly method". The excited particles, electrons and photons of plasma have high energies that can initiate various chemical reactions which causes obtaining new functional groups on the surface of the treated material [3,6,20].

The aim of this study was improving flame retardant characteristic of raw silk fabric by increasing the penetration of finishing chemicals into the fibers properly with using an environmental-friendly way instead of conventional degumming process which has to be carried out before finishing treatments. Thus, in this study low-temperature plasma treatment was used with various gases as an alternative method which acted as a pre-treatment before FR finishing of silk fabric while taking the advantage of making surface modification on the raw silk fabric without the necessity of using degumming process which uses harsh chemicals at high temperatures. So, by this way, FR property of raw silk fabric was improved and wettability characteristics of raw silk fabrics were enhanced without using conventional degumming processes.

Experimental Details

Material

100 % silk woven plain fabric which is 39.6 g/m^2 (36 warp/cm x 27 weft/cm**)**, supplied by Ödemiş İpek Company (Turkey) was used in this study. Marseilles soap was taken from İpek Sabun, non-ionic surfactant was supplied by Hunstman Textile Effects (Charlotte, USA), polyphosphate and Na_2CO_3 (99.5 %) were purchased from Sigma Aldrich. These chemicals were used for chemically degumming process to remove sericin from raw silk fabrics. Dialkylphosphonocarboxylic acid amide as a flame retardant agent and Invadine PBN as an anionic surfactant were purchased from Huntsman Textile Effects (Charlotte, USA). Phosphoric acid (85%) was used as a catalyzer and an ionic surfactant added into the finishing bath as a wetting agent.

Method

Degumming Process

Silk fibroin fabric was obtained by removing sericin through a degumming process showed in Fig.1, involving boiling the raw silk fabric at a liquor ratio of 1 : 60 with 4-5 g/L Marseilles soap , 1-1,5 g/L non-ionic surfactant, 1-1,5 g/L polyphosphate and 1g/L Na_2CO_3 at 95 ^{0}C for 45 min at pH 9. After thoroughly washing with warm water, the silk fibroin fabric was dried at room temperature (25 ^{0}C).

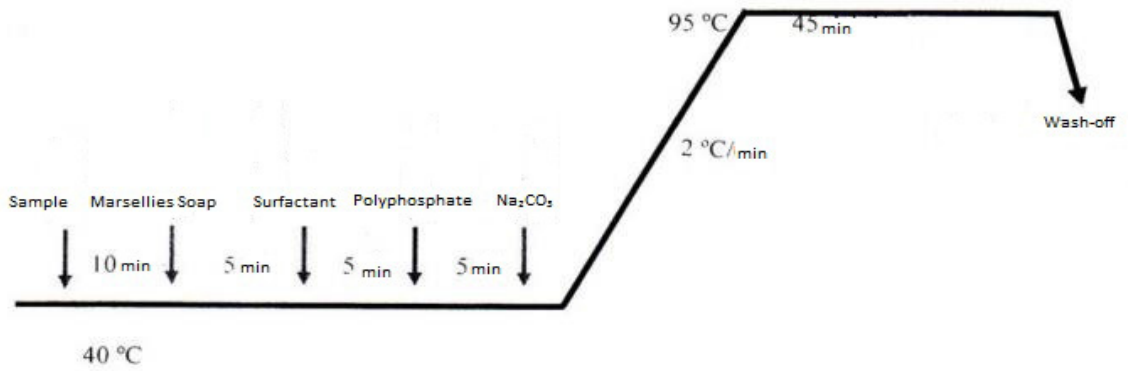

Fig.1. Degumming process of silk fabric

Low Temperature Plasma Treatment

Surface modifications of raw silk fabrics were achieved by low temperature plasma treatment in Diener vacuum plasma (Diener, Germany) in order to investigate the possibility of carrying out plasma treatment for improvement of wetting characteristics of raw silk fabrics instead of degumming silk fabrics with harsh chemicals at hot temperatures before finishing processes. After placing the samples into the plasma device, oxygen, argon and nitrogen gases were discharged into the vacuum chamber, respectively. The process was operated in LF (Low Frequency) generator at a frequency of 40 kHz, at a power of 75 W and 50 W, at a pressure of 0.4 mbar for 1 and 7 min at low temperature (<50^0C). In order to determine the modification effects of plasma treatment and variations in surface characterization of samples, exposure times and power of the treatment were varied in this study. Codes of treated fabrics were showed in Table 1.

Finishing Process

After surface modification and degumming processes, in order to determine the effects of surface modification on the finishing performance of silk fabrics, 250 g/L dialkylphosphonocarboxylic acid amide was used as a flame retardant agent in the recipe of finishing process of treated silk fabrics. 7 g/L phosphoric acid (85%) and 1-1,5 g/L anionic surfactant were used as well in pad-dry-cure system. After applying FR agent in padding bath with a wet-pick-up ratio as 75%, then the fabric was dried at 90^0C for 1-2 min, and then cured at 175^0C for 2 min.In after-wash process, the cured silk fabrics were soaked in water at a liquor ratio of 1:30 containing 2 g/L soap at 60^0C for 20 min, then rinsed with water and then dried at room temperature.

Wicking Hydrophilicty Test

The wicking hydrophilicity test was performed according to DIN 53924. The rising heights of the water of the raw, degummed and plasma-treated raw silk fabric samples with exposure times of 1 and 7 min at a power of 75 W and 50 W, were measured on a scale after 10, 30, 60 and 300 sec.

Weight Loss Test

Weight of treated silk fabrics after treatments were measured on a precision scale and weight losses of the samples calculated as a percentage (%).

Color Spectrum Analysis

Whiteness, yellowness indexes and ΔE values of raw, degummed and plasma-treated raw silk fabrics were calculated by Spectraflash SF 600X Datacolor Reflectance Spectrophotometer in order to determine the changes especially in whiteness and yellowness values of silk fabrics when treated with different gases under specified plasma treatment conditions.

Scanning electron microscope (SEM)analysis

The surface morphology of untreated and treated silk fabrics were scanned by a Hitachi S-3200N electron microscope under a high vacuum at 1500 magnification after being coated with gold-palladium (Au-Pl) at a thickness of 40–50 nm.

Limited Oxygen Index (LOI) Test

The limited oxygen index (LOI) test of samples was performed according to the standard ASTM D 2863-77 after FR finishing process. The numerical index, LOI, is defined as the minimum concentration of oxygen in an oxygen–nitrogen mixture required to just support the downward burning of a vertically mounted test specimen. Thus, a larger LOI value represents a better flame retardancy.

Fourier transform infrared (attenuated total reflectance) spectra FTIR-ATR analysis

FT-IR ATR spectra of the untreated and FR treated silk fabrics were investigated by a Nicolet 510P device in a wave number range of 525–4000 cm^{-1}.

Table1. Codes of treated samples

OP1	Oxygen Plasma 50 W 1 min	**NP1**	Nitrogen Plasma 50 W 1 min	**AP1**	Argon Plasma 50 W 1 min
OP2	Oxygen Plasma 50 W 7 min	**NP2**	Nitrogen Plasma 50 W 7 min	**AP2**	Argon Plasma 50 W 7 min
OP3	Oxygen Plasma 75 W 1 min	**NP3**	Nitrogen Plasma 75 W 1 min	**AP3**	Argon Plasma 75 W 1 min
OP4	Oxygen Plasma 75 W 7 min	**NP4**	Nitrogen Plasma 75 W 7 min	**AP4**	Argon Plasma 75 W7 min
FR-OP1	FR-treated raw silk fabric after oxygen plasma at 50 W for 1 min	**FR-NP1**	FR-treated raw silk fabric after nitrogen plasma at 50 W for 1 min	**FR-AP1**	FR-treated raw silk fabric after argon plasma at 50 W for 1 min
FR-OP2	FR-treated raw silk fabric after oxygen plasma at 50 W for 7 min	**FR-NP2**	FR-treated raw silk fabric after nitrogen plasma at 50 W for 7 min	**FR-AP2**	FR-treated raw silk fabric after argon plasma at 50 W for 7 min
FR-OP3	FR-treated raw silk fabric after oxygen plasma at 75 W for 1 min	**FR-NP3**	FR-treated raw silk fabric after nitrogen plasma at 75 W for 1 min	**FR-AP3**	FR-treated raw silk fabric after argon plasma at 75 W for 1 min
FR-OP4	FR-treated raw silk fabric after oxygen plasma at 75 W for 5 min	**FR-NP4**	FR-treated raw silk fabric after nitrogen plasma at 75 W for 7 min	**FR-AP4**	FR-treated raw silk fabric after argon plasma at 75 W for 7 min

RESULTS AND DISCUSSION

Wicking Hydrophilicity Test Result

Rising height of water after 10,30,60 and 300 seconds of raw and treated silk fabrics were showed in Fig. 2,3,4. As seen below, while raw silk fabric showed a hydrophobic character, plasma-treated raw silk fabrics with different gases enhanced the hydrophilic character of the raw silk fabrics. As seen in Fig. 2, it was determined that, argon-plasma treated silk fabrics showed the minimum increase even at highest exposure time among other plasma treated silk fabrics. In oxygen-plasma treatment showed in Fig.3, increasing both exposure time and power provided more hydrophilic property of raw silk fabrics. When it was analyzed, it could be clearly seen that nitrogen-plasma seen in Fig. 4, had the most significant effect on enhancing wettability properties of raw silk fabrics which the exposure time had more dominant effect compared to effect of plasma power. After 300 sec, the height of water of degummed silk fabric is 10.55 cm that is nearly the same as NP4 (nitrogen-plasma treated raw silk fabric at 75 W for 7 min) which is considered as low temperature plasma treatment could be a better alternative for improving wettability characteristics of raw silk with the advantages of being dry and environmental-friendly process due to consuming less water, chemical and energy, instead of carrying out degumming process with harsh chemicals at high-temperatures. The increases in hydrophilic property of raw silk fabrics attributed to new functional groups such as hydroxyl, carboxyl groups obtained on the surface of silk fabrics via plasma treatment [21-23].

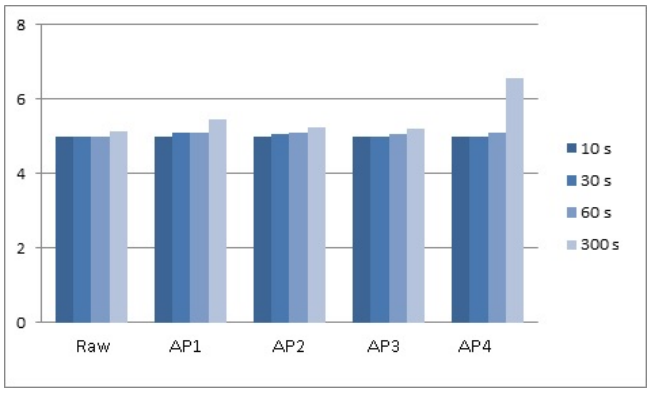

Fig.2. Wicking hydrophilicity results of raw and argon-plasma treated raw fabric

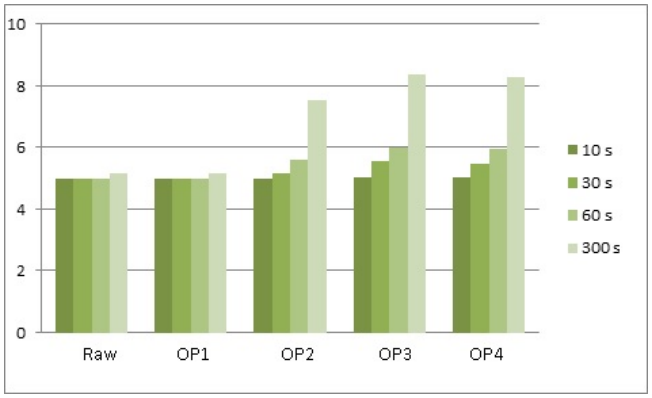

Fig.3. Wicking hydrophilicity results of raw and oxygen-plasma treated raw fabrics

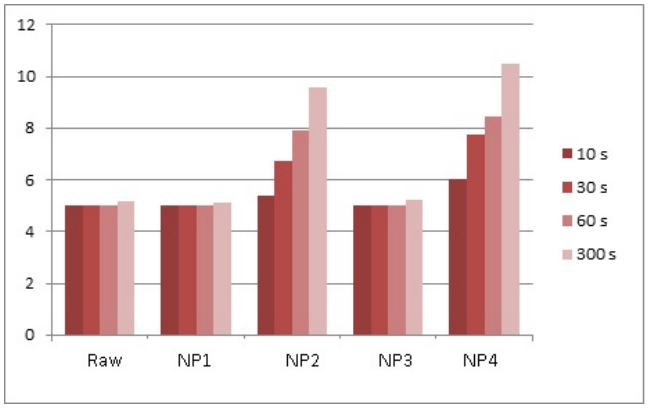

Fig.4. Wicking hydrophilicity results of raw and nitrogen-plasma treated raw fabrics

Color Spectrum Analysis Result

According to the color spectrum analysis; ΔE, yellowness and whiteness indexes of raw, degummed and plasma-treated raw silk fabrics were showed in Table 2. When ΔE of samples were investigated, it was clearly seen that degummed silk fabric had the highest ΔE value among other samples which were treated via plasma process. It was considered that this result was observed because of harsh chemicals usually used in degumming process at high temperatures around 95 ^{0}C, especially for removing sericin layer on it. According to ΔE values, plasma-treated silk high temperature of process around fabrics had less color changes on raw silk fabrics compared to degumming process which was attributed to the mechanism of the plasma process that did not use either chemical or high temperature and had no alterations on bulk properties of treated material but just had a modification effect on surface of raw silk fabrics. However, these ΔE values of plasma-treated fabrics were at certain extent, which was attributed to the effect of enhanced surface roughness by plasma treatment that causes a decrease in amount of reflected fraction of lights from the treated rough surfaces of silk fabrics when compared with untreated smooth surfaces. When whiteness and yellowness indexes were analyzed, it could be indicated that generally plasma-treatment increased the yellowness indexes and decreased the whiteness indexes of silk fabrics which could be considered as it did not have a favorable effect on whitening raw silk fabrics. This increase in yellowness was more obvious when the exposure time and power of nitrogen-plasma were increased. This result was attributed to the formation of chromophoric products containing carbonyl groups on the surface of the material [24].

Weight Loss Test

Weight of raw, degummed and plasma-treated raw silk fabrics and calculated weight losses as percentages (%) were showed In Table 3. As it is seen clearly in the Table 3 that the highest weight loss was belong to degummed silk fabric with the value of 9.30 %. When plasma-treated samples were examined, the highest weight loss (with 6.77 %) of samples among plasma-treated fabrics, was showed in nitrogen-plasma treated raw silk fabrics which were in agreement with Fig. 4 of wettability results of nitrogen plasma-treated raw silk fabrics. It was considered that

plasma etching effect on the surface of the material caused removing sericin from the silk fabric resulting in weight loss of raw silk fabrics. However, it should be emphasized that while both treatment (degumming and nitrogen-plasma treatment) achieved nearly the same level of wettability on raw silk fabrics with the value of 10.55 cm, plasma treatment caused less weight-loss compared to degumming process.

Table 2. ΔE, yellowness and whiteness indexes of raw, degummed and plasma-treated raw silk fabrics

Samples	Yellowness Index (ASTMD1925)	Whiteness Index (Stensby)	ΔE
Raw	18.964	59.606	-
Degummed	12.591	69.284	3.055
OP1	18.328	58.328	1.572
AP1	19.286	58.812	1.714
NP1	19.274	58.664	1.377
OP2	19.047	58.529	1.478
AP2	18.869	58.819	1.317
NP2	23.707	52.957	2.690
OP3	19.742	57.991	1.545
AP3	18.268	58.536	1.100
NP3	20.836	56.418	1.805
OP4	20.378	57.641	1.396
AP4	21.514	55.531	1.908
NP4	23.009	53.524	2.271

LOI Test Results (%)

Limited oxygen index values (%) of raw, degummed and FR treated after plasma treatment of raw silk fabrics were showed in Table 4. As seen in Table 4, raw or degummed silk fabric had no flame retardant effect before finishing process. After padding degummed silk fabric with phosphorus based FR agent, LOI value was increased up to 29.6 %. When FR-treated silk fabrics which were pre-treated with different plasma gases were examined, it could be clearly seen that all plasma applications which were used as pre-treatment before FR finishing, provided enhanced FR characteristics of raw silk fabrics. These results were attributed to the positive effect of plasma treatments on improving wettability properties of silk fabrics due to new functional groups obtained on the surface of the material, so that it increased penetration of FR agent into the silk fabric. It was indicated that highest LOI values were belong to nitrogen-plasma treated raw silk fabric. It was considered that this result could be attributed to the positive synergetic effect between nitrogen-phosphorus compounds on the treated silk fabric.

Results of SEM analysis

SEM micrographs of raw, degummed, plasma-treated and FR-treated after nitrogen plasma treatment at 75 W for 7 min were showed in Fig. 5, respectively. According to the SEM results, it could be clearly seen that untreated raw silk fabric (Fig. 5.a) had a smooth surface whereas fibrillation and degradation was occurred on degummed silk fabric (Fig. 5.b) due to removing sericin layer which keeps the fibroin macromolecules together. During conventional degumming method of raw silk fabric, surrounding sericin is hydrolyzed and the amide bonds of the long protein molecules are broken into smaller fractions, then dissolved in degumming bath containing alkali, soap or synthetic detergents. However, the higher temperature (95 °C) and an alkaline pH (8–9) in the presence of harsh chemicals in the treatment process impose a remarkable unnatural environment on the silk which causes partial degradation of fibroin [8,12,19]. So higher weight losses of silk fabrics after degumming process could be attributed to the harsh parameters taking part in traditional degumming processes. Some chemical residues of FR finishing and also partial roughness of surface modification obtained by plasma treatment could be seen In Fig. 5.d.When nitrogen (Fig.5.c), argon (Fig.5.e) or oxygen plasma treatments (Fig. 5.f) were carried out, roughness could be clearly seen on the surfaces of raw silk fabrics. This result was attributed to the etching effect caused by the physical bombardment of the energetic plasma species on the substrate surface such as fluting and/or grooving observed on materials [3,6].

Table 3. Weight loss (%) of raw, degummed and plasma-treated raw silk fabrics

Samples	Weight Loss (%)	Samples	Weight Loss (%)	Samples	Weight Loss (%)
OP1	5.08	**NP1**	5.93	**AP1**	4.23
OP2	5.08	**NP2**	6.77	**AP2**	4.23
OP3	5.50	**NP3**	5.93	**AP3**	3.38
OP4	5.93	**NP4**	6.77	**AP4**	5.93
Degummed	9.30				

Table 4.LOI results (%) of raw, degummed and FR treated after plasma treatment of raw silk fabrics

Raw	23.8		**Degummed**	23.2	
			Degummed-FR	29.6	
AP1-FR	26.2	**OP1-FR**	26.2	**NP1-FR**	27.6
AP2-FR	26.2	**OP2-FR**	28.5	**NP2-FR**	30.4
AP3-FR	26.4	**OP3-FR**	29.6	**NP3-FR**	32.3
AP4-FR	28.5	**OP4-FR**	31.1	**NP4-FR**	33.1

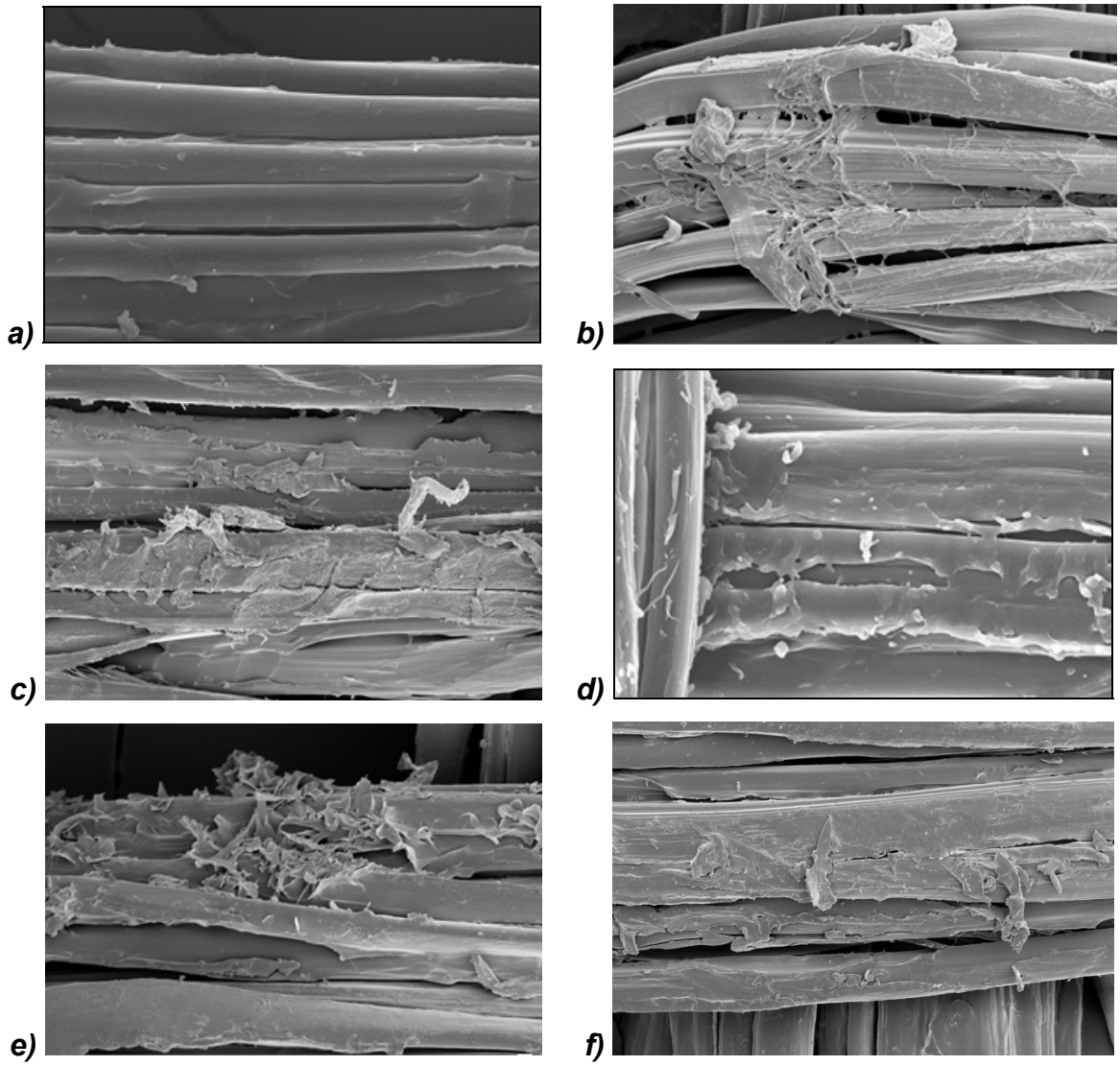

Fig 5. SEM micrographs of raw, degummed and plasma-treated raw silk fabrics a)Raw silk fabric b)Degummed silk fabric c)NP4(Nitrogen-plasma treated raw silk fabric at 75 W for 7 min) d) FR-NP4 (FR-treated after nitrogen-plasma treatment) e) AP4(Argon-plasma treated raw silk fabric at 75 W for 7 min) f)OP4 (Oxygen-plasma treated raw silk fabric at 75 W for 7 min)

Fourier transform infrared (attenuated total reflectance)(FTIR-ATR) analysis results

FTIR-ATR analysis of raw silk fabric, nitrogen-plasma treated raw silk fabric at 75 W for 7 min (NP4) and FR-treated silk fabric after nitrogen plasma application (FR-NP4) were showed in Fig. 6. The FTIR-ATR spectra showed characteristics bands at 1622 cm^{-1} (amide I), which is due to the β confirmation of the crystalline region, while the band appearing at 1515 cm^{-1} (amide II) is due to the random coil conformation of fibroin molecules. The peaks that appeared at 1440 cm^{-1} are attributed to the presence of an amino acid group of CH-stretching of CH_3 deformation of the silk. The appearance of the absorption bands at 3288 cm^{-1} is caused by the free-OH stretching and NH- stretching vibrations [25].

Although for plasma-treated raw silk fabric, maximum effective plasma gas at highest plasma parameters were chosen according to the other performance tests in this study, no significant difference were observed between FTIR-ATR spectra of untreated raw silk fabric and plasma-treated raw silk fabric. This result was attributed to the mechanism of the plasma application which process modification only on the surface of the material without effecting bulk properties. It was also indicated in the literature [26] that infrared equipment by itself may not be the best one to identify chemical changing on the low frequency plasma treated sample's surface unless wet chemical process was carried out after surface modification. However, for the sample of FR-NP4 which had the FR treatment after nitrogen-plasma application, strong band could be seen around 1057 cm^{-1} which indicates P–O–C and C–O–C stretching vibration. Another peak around 1227 cm^{-1} also indicates the absorption overlap of P=O and amide III of silk fibres [4] which caused by phosphorus based FR agent used in finishing treatment.

CONCLUSION

In this study, in order to improve the FR property of silk fabrics; phosphorus based FR agent was used in finishing bath after nitrogen, argon and oxygen-plasma application

which is carried out as pre-treatment. On behalf of making a comparison between conventional method and plasma treatment, some of the samples were undergone through conventional degumming process. After the plasma and degumming treatments, wetting effect of the processes, color spectrums of treated samples and weight losses were investigated. According to the results, it was observed that nitrogen-plasma application was more effective than the other plasma gases on improving the wettability effect of raw silk fabric. When weight losses were examined, it was indicated that degumming processes caused more weight-loss than plasma treatments carried out with various gases. After FR finishing processes, LOI values were examined and it was determined that especially nitrogen-plasma pre-treatment supported the improvement of FR characteristic of raw silk fabrics. In the study, it was considered that plasma treatment could be a better alternative for being used as a pre-treatment of raw silk fabrics when compared to conventional processes.

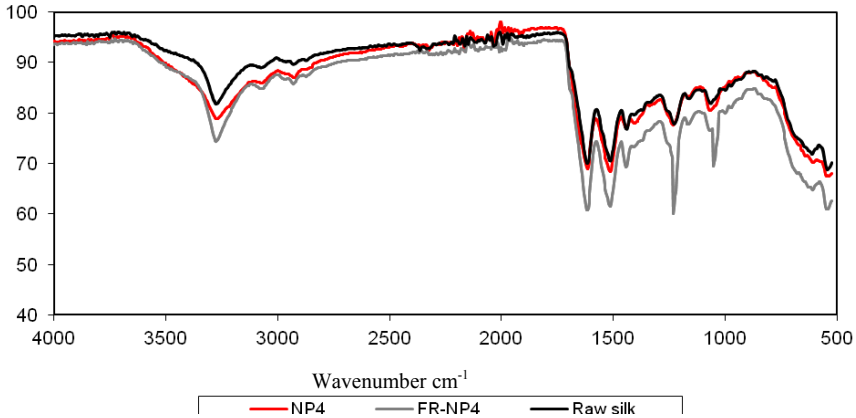

Fig.6.FTIR-ATR analysis of raw silk fabric, nitrogen-plasma treated (NP4), FR-treated silk fabric after nitrogen-plasma application (FR-NP4)

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