Surface Modification of Textiles by Glow Discharge Technique: Part II: Low Frequency Plasma Treatment of Wool Fabrics with Acrylic Acid

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ABSTRACT: In this study, wool fibers are modified by low frequency plasma polymerization of acrylic acid regarding to its' hydrophobic character due to cuticular cells at their surfaces. Variables of the plasma glow discharge processes were power (40–100 W) and exposure time (5–45 min). The effect of plasma modification in the performance properties of wool were investigated on the basis of hydrophilicity of wool, average wrinkle recovery angle, and breaking strength. The surface chemical structures of fabrics were examined with x-ray photoelectron spectroscopy. The hydrophobic wool fabric became hydrophilic after all plasma treatments except one (40W–5 min). Average wrinkle recovery angle of the treated fabrics were between 157 and 178°, while that of untreated fabric was 180°. The treated fabrics had a little bit lower angles according to the untreated fabric. However, even the lowest value as 157° means that the fabric has a good crease resistance property. The breaking strengths of fabrics were increased up to 26% after the plasma treatments.
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Key words: textile; wool; plasma polymerization; modification; ESCA/XPS

INTRODUCTION

Chemically reactive plasma discharges are widely used to modify the surface properties of materials. Among numerous traditional and new technologies of surface treatments of textiles and films, the plasma treatment is a powerful tool to fulfill environmental requirements and has very specific functions as it exclusively affects the surface, both chemically and physically. Plasma processing technology is very important to several of the largest manufacturing industries in the world. Plasma-based surface processes are critical for the electronics, aerospace, automotive, steel, biomedical, and toxic waste management industries. Materials and surface structures can be fabricated that are not attainable by any other commercial method, and the surface properties of materials can be modified in unique ways. Surface modification by low pressure plasma treatment illustrates many important advantages over techniques such as environmental safety, uniformity and reproducibility, variety of reagent gases, and selective modification with minimization of bulk property change.[1–4]

The outer layer of the wool fiber is the cuticle. The surface of the cuticle cells (epicuticle) contains a covalently bound fatty acid, the chiral 18-methyl eicosanoic acid (18-MEA). This fatty acid is probably bound via a thioester linkage. This acid accounts for about 70% of the fatty acids covalently bound to the wool fibre.[5] The epicuticle is highly resistant to attack from alkalis, oxidizing agents, and proteoliytic enzymes. It is about 2.5 nm thick and amounts to approximately 0.1% of the weight of the fiber. The wool fiber exhibits hydrophobic properties due to the presence of this fatty layer, which surrounds each cuticle cell.[3,6–8]

Absorption of water to improve the comfort and wear properties of textiles can be enhanced by increasing the hydrophilicity of natural and synthetic fibers. Grafting of hydrophilic monomers is used to give hydrophilic properties to textiles by chemical, radiation, and induced reactions.[9–11] Oxidative plasma (such as oxygen, water vapor) treatments are the other way to give hydrophilicity to textile materials.[12–16] Acrylic acid is well known to give hydrophilicity to materials, which it is applied.[17,18] Although it has been widely used on

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wool and other textile fibers,[19–22] application of plasma polymerization of acrylic acid on wool fabric surfaces has not been encountered in the literature. Leeder et al.,[9] studied the *in-situ* polymerization of acrylamide, acrylic acid, and acrylonitrile within the wool fibers and the water-absorption properties of the resultant wool-polymer systems compared with those of wool and the polymers measured separately. Polyacrylamide and poly(acrylic acid) increased water uptake of wool fibers at both high and low humidity, whereas in the case of polyacrylonitrile, there was a reduction in water content of the wool in the same conditions. Ibrahim et al.[10] modified the surfaces of cotton, cotton/polyester blend, and polyamide 6 fabrics by electron beam radiation induced coating by a solution of polyvinyl alcohol and acrylic acid. Considerable improvement in water uptake as well as crease recovery angle was attained with increasing acrylic acid content in solution in case of polyamide 6, followed by blends and then cotton. El-Gendy and El-Shanshoury[11] grafted acrylic acid (AA), acrylonitrile (AN), and their mixture onto wool fabrics by radiation at a dose rate of 1.38Gy/s. The grafting of AA, AN, and their mixture are confirmed from the dyeing affinity of grafted fabrics toward Sandocryl Blue (SB), a basic dye. They obtained an improvement in the dyeability of the fabrics toward basic dyes. The best result was obtained by grafting of acrylic acid while grafting of acrylonitrile onto wool had no influence on improving dyeability.

Regarding to the extensive potential of textile industry in Turkey, our research group has focused on the technical textiles mainly utilizing plasma processing technology. Due to this fact, in the second part of our study,[23] the effects of plasma polymerization of acrylic acid on the hydrophilicity, wrinkle recovery, breaking strength properties and the surface characteristics of wool fabrics were reported in this article.

EXPERIMENTAL

Materials

Fabrics made of 100% wool were used. The area mass, settings in both warp and weft direction, and linear densities of warp and weft yarns were 274 g/m^2, 37.3 cm^{-1}, 32.0 cm^{-1}, Nm 60/2 and Nm 60/2, respectively. Fabrics were cut into the sizes of 29 $\times$ 14.5 cm^2. They placed on a frame (whose outer sizes were 29 $\times$ 14.5 cm^2 and inner sizes were 27 $\times$ 11.5 cm^2), so that the both sides of the fabrics could be exposed to glow discharge. Acrylic acid (Aldrich Chemical) was used as monomer in low frequency glow-discharge plasma system.

Plasma treatment

Plasma polymerization treatments were carried out in PICO LF (low frequency-40 kHz) Plasma Polymerization System (Diener electronic GmbH + Co. KG, Germany). This system has a horizontally placed cylindrical plasma chamber. The length of its plasma chamber is 32 cm and the diameter is 15 cm.[24] At first, the reactor was evacuated to 15 $\pm$ 5 Pa for 1 h to remove possible physically bound water on wool surface. Then monomer inlet was opened and monomer (acrylic acid) vapor was allowed to flow through the reactor for 10 min to remove impurities and remaining water vapor in the chamber. Monomer flow rate was kept constant at 180 $\pm$ 20 cm^3/min. Then power was adjusted to 40–100 watts and the fabrics were exposed to glow discharge for 5–45 min. At the end of the process, the generator was turned off and argon gas was allowed to flow for 10 min to deactivate free radicals. Wool fabrics were modified in various plasma polymerization conditions (discharge power: 40, 60, 100 W, and exposure time: 5, 20, 45 min). The details of the plasma treatment of the fabrics were given in our previous article.[23] The effects of power and exposure time parameters on the hydrophilicity, wrinkle recovery angle, and breaking strength were evaluated by statistical software, MINITAB® for Windows. The surface chemical composition of the untreated and plasma treated wool fibers were characterized thoroughly by XPS analysis.

Hydrophilicity measurements

Hydrophilicity of fabrics after plasma treatments was measured by means of capillary rise method. For the capillary rise test, fabrics were cut into 20$\times$ 2 cm^2 strips parallel to the warp direction. The strips were mounted in parallel to a millimeter scale and the lower ends of the strips were partly immersed into a diluted (0.01 M) potassium chromate aqueous solution. A light weight, which should not affect the geometrical structure of the sample, was placed at the end of the strip to keep it in a vertical position. Height readings were made at the 10th, 30th, and 60th seconds of the first minute and at time intervals of 30 s in the following 4 min.[25,26]

Wrinkle recovery angle measurements

Wrinkle recovery angle of the samples was performed according to TS 390 EN 22,313. Waiting time under 1 kg weight was 5 min and waiting time after weight removed was 5 min. Wrinkle recovery angle of specimens in warp and weft directions was measured separately then averaged out to obtain the average wrinkle recovery angle.

Breaking strength

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.

XPS analysis

SPECS ESCA (Berlin, GERMANY) system (unmonochromatized Mg Kα radiation source, x-ray gun operated at 10 kV, 20 mA, 200 W) was used to determine the surface compositions of untreated and treated wool fabrics. Pressure of the analyzer chamber was 10^{-8} to 10^{-9} torr. Survey scans of plasma treated and untreated wool fabrics were taken in the range of 0 to 1,050 eV. As wool is an insulator, sample fabrics are significantly charged and their photo peaks are shifted to the higher binding energies. All peaks were charge referenced to the C1s photo-peak of the C-C and C-H species at 285.00eV.[27–31]

RESULT AND DISCUSSION

All form of substrates such as fibers, yarns, and fabrics may be modified by plasma treatments. The surface properties of fabrics are mainly affected by the type of monomer used, flow rate, plasma glow discharge power, generator frequency, and the time of the glow discharge.

In this study, we mainly focused on the effect of a specific monomer, acrylic acid, which is widely used by our group[23] and others[32,33] to increase the hydrophilic character of the surfaces by plasma polymerization technique or by wet chemistry, to enhance the hydrophilicity, total wrinkle recovery angle, and breaking strength of fabrics.

Hydrophilicity of fabrics

The effects of discharge power and exposure time parameters on the hydrophilicity of wool fabrics were evaluated and presented graphically in Figures 1–3. The figures show how exposure time and power affect the capillary rise of fabrics during plasma treatments.

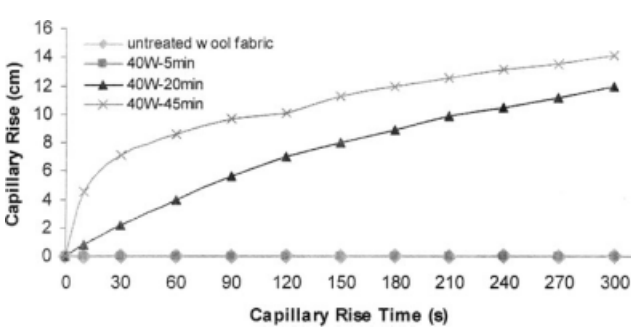

Figure 1 The effect of glow discharge time at 40 W discharge power on capillary rise (cm) of wool fabrics.

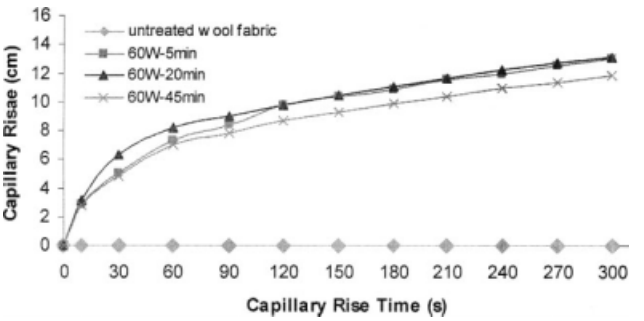

Figure 2 The effect of glow discharge time at 60 W discharge power on capillary rise (cm) of wool fabrics.

As seen in figures, untreated wool fabrics were extremely hydrophobic. Except for 40 W to 5 min, at all plasma conditions, acrylic acid plasma treatments gain hydrophilicity to the wool fabrics. This result is valid for all capillary rise times. The initial wetting property $[\frac{d \text{ capillary rise}}{d\,t}]_{t=0}$ of the treated and untreated wool fabrics were evaluated by the slope of the curve at $t = 0$. It is found that, the fastest transport of water in the modified wool matrix was achieved at 40 W to 45 min plasma conditions. The transport of water in all matrices was followed for 300 s and for none of the matrices a stable rise value was observed. However, it can be said that the gap between all curves getting closed by time and no significant difference was observed. These results are valid for all plasma modifications except 40 W to 5 min. In addition to these, in a very short time of 5 min at 100 W plasma power condition, a good wettability was obtained. The increases in the wettabilities of wool fabrics after acrylic acid plasma treatments can be explained by etching of surface lipid layer and deposition of a few amount of oxygen containing functional groups (increase in the amount of oxygen up to 2.3 times the amount of oxygen on the surface of the untreated fabric) from plasma to the surfaces as can be seen from the results of XPS analysis.

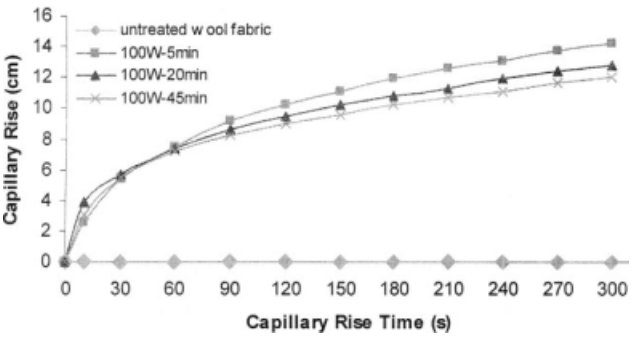

Figure 3 The effect of glow discharge time at 100 W discharge power on capillary rise (cm) of wool fabrics.

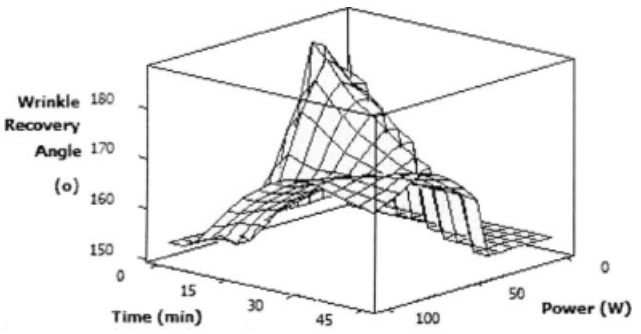

Figure 4 The effect of glow-discharge power and time on average wrinkle recovery angle of wool fabric.

Wrinkle recovery angles of fabrics

The effects of discharge power and exposure time parameters on the wrinkle recovery angle of wool fabrics were evaluated by MINITAB® software and presented in three-dimensional graphics in Figure 4. The figure shows how exposure time and power affect the wrinkle recovery angle of fabrics during plasma.

Figure 4 shows the effects of the discharge power and exposure time on wrinkle recovery angles of wool fabrics. The maximum value was obtained at 40 W to 5 min with the wrinkle recovery angle of 178° where the untreated fabric has 180° wrinkle recovery angle. The high values of wrinkle recovery angles were obtained at the conditions where the wettabilities were low. The wool fibers have the best elastic recovery properties among all natural fibers.[34] Therefore, the crease resistance property of untreated wool fibers is very good. In the energetic medium of plasma, hydrogen bonds of the wool keratin might be damaged and the hydrogen bonds might break due to the deposition of acrylic acid plasma polymer. In addition to this, as seen in Figure 7, the disulphide bonds at the surface of the fibers were somewhat oxidized. Therefore, the wrinkle recovery properties after plasma treatments are worsened, and so the wrinkle recovery angles of wool fibers were decreased approximately 1% to 13% after acrylic acid plasma treatments.

Breaking strengths of fabrics

Figure 5 (a and b) show the effects of discharge power and exposure time on breaking strengths and extension of the fabrics.

The highest breaking strength was obtained at 60 W to 5 min (655.6 N) and lowest breaking strength was obtained at 40 W to 5 min (574.8 N). The extension values for these conditions were 41.88 and 44.04 mm, respectively. The untreated material has a breaking strength of 521.1 N and extension of 49.70 mm. According to results, the breaking strength values of all treated fabrics were higher than the untreated one and the extension values of all treated fabrics were lower than the untreated fabric. The breaking strength values were increased by an average of 20.6% after plasma treatments. However, the extension values were decreased by an average of 10.0% after plasma treatments. The reason of this may be the formation of additional cross-linking due to deposition by plasma polymerization of acrylic acid on the fiber surfaces and between the polypeptide chains. Besides, the disulphide bonds at the fiber surfaces are appeared to be oxidized, however, this effect is superficial and may be insufficient to influence the tensile property of the fabrics.

XPS analysis

As discussed in our previous study[23] and literature, either plasma treated or other chemical methods[10,11] showed that the treatment with acrylic acid enriches hydrophilic properties of materials. This might be regarded as the deposition of hydrophilic groups such as C—O, C=O or due to the nature of the substrate surface and glow discharge conditions on acrylic acid and the etching of the surface.

In our study, XPS spectra of untreated, acrylic acid plasma and oxygen plasma treated wool fabrics are shown in Figure 6. In order to clarify the mechanism of acrylic acid modification on the wool surfaces, the XPS analyses were carried out for the treated fabrics by oxygen plasma at the same plasma parameters (100 W–5 min) with acrylic acid. Due to the

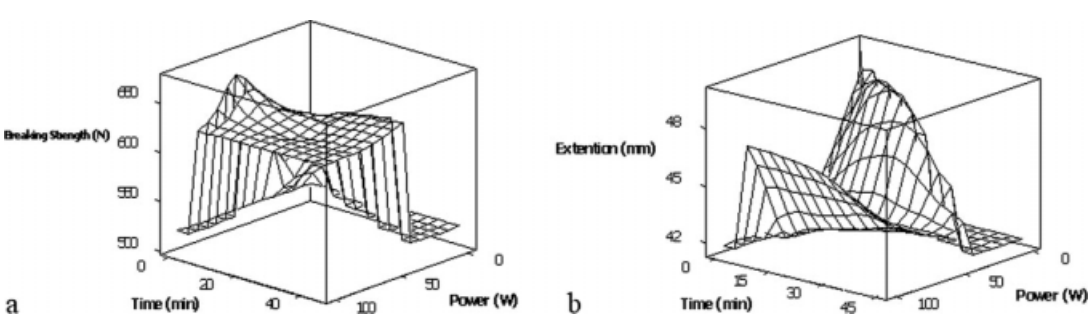

Figure 5 (a) The effect of glow-discharge power and time on breaking strength of wool fabric. (b) The effect of glow-discharge power and time on extension of wool fabric.

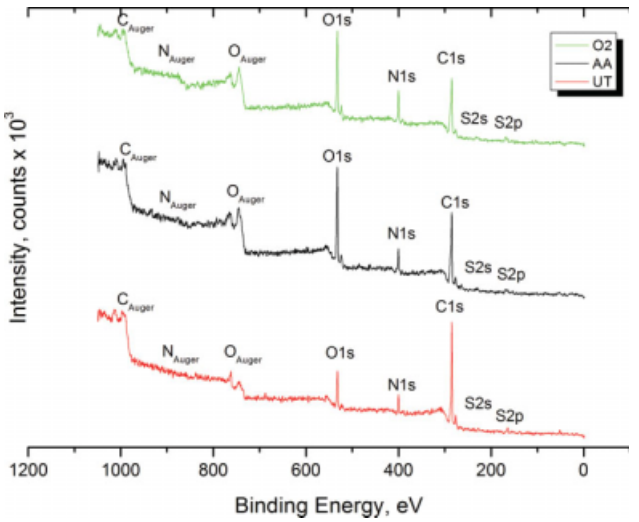

Figure 6 XPS spectra of oxygen (up), acrylic acid (medium) plasma treated and untreated (bottom) wool fabrics. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

very well known fact that the oxygen gas plasma has effective etching influences[35–37]; it can be understood clearly how acrylic acid plasma affects the surface of wool fibers.

Survey spectra show photoelectron peaks at binding energies of ~532 eV, ~400 eV, ~285 eV, ~230 eV, and ~164eV, which can be attributed to the O1s, N1s, C1s, S2s, and S2p respectively. In addition, there are some peaks resulting from Auger electron emission from C, N, and O at higher binding energy part of the spectra. There is no additional peak after acrylic acid plasma because acrylic acid has the same atoms as wool fibers. The compositions of the atoms at the wool surface agreed with previous researches.[38,39] The intensities of C1s, O1s (for both plasmas), and N1s (for only oxygen plasma) peaks are significantly changed after plasma treatments. In Table I, surface elemental compositions (%) and atomic ratios (%) of plasma treated and untreated fabrics can be seen.[29,38,39]

As seen from the Table I and Figure 6, the chemical composition of wool fiber surface changes considerably after only 5 min of oxygen and acrylic acid plasma treatments. Carbon contents of the fiber surface decreased by 24.4% and 29.1% and also oxygen presence increased significantly from 14.1% to 32.4% and to 30.6% after acrylic acid and oxygen plasma treatments, respectively. Additionally, although nitrogen content of surface increased by 67.9% and sulfur content decreased by 10.0% after oxygen plasma treatment, nitrogen and sulfur contents both remained the same after acrylic acid plasma process. The detected sulfur might come from the thioester linkages between fatty acids and protein layer and/or the disulphide bonds present in the protein layer of the epicuticle.[38] The atomic ratio of sulfur was seemed to remain unmodified after acrylic acid plasma treatment; however, changes were found in its chemical form (Fig. 7). The S 2p spectrum of the untreated wool fiber in Figure 7 consists of a single peak centered at 164.0 eV, corresponding to S—S and S—C groups. However, the S 2p spectrum of acrylic acid plasma treated fabric has a shoulder at higher binding energy of 168.0 eV suggesting the presence of the oxidized sulfur species, for instance from cystine to cysteic acid.[31,38,39] Although there was no change in sulfur content of the surface of fibers, there was cleavage of disulphide bonds after acrylic acid plasma process. This might help to explain the decrease in the wrinkle recovery angles of the fabrics, whereas the tensile strength of fibers raised but extension decreased after acrylic acid plasma process. The wrinkle recovery angle decreased because the cystine bridges on the surfaces were broken. The tensile strength increased because the breakage remained only on the uppermost surface and new crosslinkings may arise during the plasma polymerization of acrylic acid on the fibers. The increase in nitrogen content of the surface might be due to the removal of the surface lipid layer (18-MEA) and exposure of the underlying protein in the case of oxygen plasma treatments. There might be also few amount of abrasion of lipid layer in case of acrylic acid as seen in carbon content but it might not

TABLE I
Elemental Compositions Determined by XPS for Untreated and Plasma Treated Wool Surfaces

	Composition (%)				Atomic ratio		
	C	O	N	S	O/C	C/N	S/C
Untreated	75.5	14.1	8.4	2.0	0.187	9.0	0.026
Acrylic acid plasma	57.1	32.4	8.4	2.0	0.567	6.8	0.035
Oxygen plasma	53.5	30.6	14.1	1.8	0.572	3.8	0.034

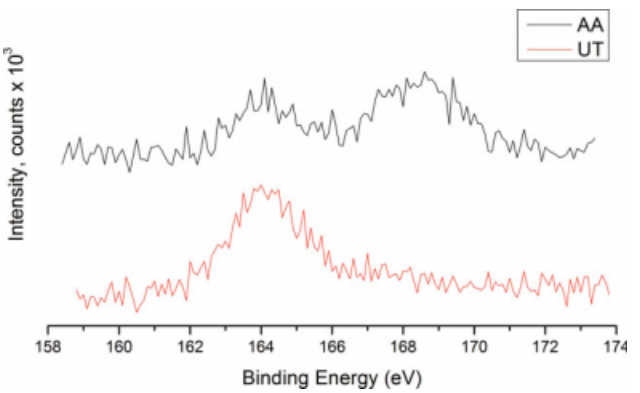

Figure 7 S 2p spectra of untreated (up) and acrylic acid plasma treated (bottom) wool fabric surfaces. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sufficient to remove the entire layer. The C/N ratio is also used to give information about the level of covalently bound surface lipid.[39] The decrease in this ratio might suggest that some fraction of the surface lipid layer was removed. The C/N ratio in our study decreased to 3.7 by oxygen plasma. This value of oxygen plasma treated fabric was almost the same with the value of 3.4 obtained from the amino acid analysis of epicuticle.[31,38,39] This result shows that most of the lipid layer on the surface may be removed by oxygen plasma treatment by the well-known etching effect of the oxygen gas plasma.[35–37] The same nitrogen content as untreated wool surface and the C/N value of 6.8 after acrylic acid plasma treatment indicate that the abrasion of lipid layer of the wool surface may be observed but to a very limited extent. Because of the very little amount of abrasion observed, it can be demonstrated that the increase in hydrophilicitiy of wool fabrics results mostly from deposition of oxygen containing functional groups from acrylic acid plasma and slightly from etching of F-layer of wool fibers. In addition to these, after acrylic acid and oxygen plasma processes, the O/C ratios increased. The increase in the O/C atomic ratio also refers to an increase in the oxygen based functional groups (such as C═O, O─C═O) in the wool surface after both plasmas. Results show that less surface etching and much more oxygen containing group deposition were obtained after acrylic acid plasma polymerization process.

CONCLUSION

The main objective of our research group is to prepare hydrophilic fabrics by a novel technique so called plasma polymerization. In the first part of our study,[23] we have made polyester and polyamide fabrics hydrophilic using acrylic acid as a precursor of plasma polymerization. In this study, as the second step, we attempted to prepare hydrophilic wool fabrics by plasma polymerization of acrylic acid. Besides hydrophilicity, breaking strength, extension and wrinkle recovery angle were measured to investigate the fabric properties. In addition, x-ray photoelectron spectra of untreated and treated fabrics were obtained. Acrylic acid plasma treatments changed the hydrophobic character of wool fibers to completely hydrophilic. The XPS survey scans show that these good hydrophilicity results by acrylic acid plasma were obtained mostly by deposition of hydrophilic groups on the surface and much less by etching of lipid layer of epicuticule of wool fibers, contrary to oxygen plasma treatments. Besides, the tensile strengths of the fabrics were increased by acrylic acid plasma process. Nonetheless, the crease recovery angles were decreased somewhat but still were very good values for wrinkle recovery. It should be noted that, this extreme change in the hydrophobic character into hydrophilic was happened by only "5 minutes" of exposing acrylic acid plasma at low frequency (40 KHz) plasma apparatus. Those promising results have guided us to possible modification of the surface of hydrophobic wool fabrics with low frequency acrylic acid plasma to achieve the highest hydrophilicity on the surfaces in a very short time with an increase in strength.

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