D M El-Zeer et al Int. Journal of Engineering Research and Applications www.ijera.com
ISSN : 2248-9622, Vol. 4, Issue 3(Version 1), March 2014, pp.756-769

RESEARCH ARTICLE OPEN ACCESS

Effect of Atmospheric Pressure Glow Discharge Treatment on Polymerization of Acrylic Fabric and Its Printing Behavior

D M El-Zeer[1,2], A.A. EL-Halwagy[3], M.A. EL-Kashouty[3], H.M. Ahmed[3], F. F.Elakshar[2] and A A Garamoon[2]

[1]Taif University , Al-khurma branch (for girls) , Applied Phys. Dep, Faculty of Science and Education, KSA.
[2]Center of plasma technology, Al-Azhar University, Nasr City, Cairo, Egypt .
[3] Dyening, Printing and Auxiliaries Department, Textile Division, National Research Center, Cair, Egypt.

ABSTRACT

Acrylic fibers have been treated by atmospheric pressure glow discharge (APGD) plasma in open air to enhance surface antistatic properties. The treated surfaces are investigated by scanning electron microscopy (SEM), Fourier-Transition Infrared Spectroscopy (FTIR) and Atomic Force Microscope (AFM). Plasma treatment of acrylic fabric has been found to increase the surface roughness, modify the nature and density of surface functionalities, and drastically improve the wettability and antistatic ability of acrylic fibers.

Keywords: Atmospheric pressure glow discharge, acrylic treatment, printing properties, polymerization.

I. INTRODUCTION

Polyacrylonitrile which are known as acrylic fibers, have important interest in the textile industry and is considered as one of leading synthetic fibers. They are widely used due to a combination of desirable properties, such as high strength, good elasticity, mechanical properties as well as excellent dyeability. Extensive studies have been carried out in the cationic dyeing of acrylic fabrics (1, 2).

Basic dye is by far the most important class of dye used on acrylic fibers. These dyes dissociate in water to yield colored cations and are characterized by their brilliance and its very high tinctorial strength (3). Basic dyes, which include some of the earliest synthetic dyes, were originally used for dyeing wool, silk and mordant cotton, but poor light fastness of dyeing was obtained until the introduction of acrylic fibers on which the dyes exhibited higher light fastness and very good fastness to wet treatments(4).

Anionic dyes namely reactive acid and direct dyes are not usually used for acrylic coloration and it suffers from being not substantive for the fibers as a result of the repulsive effect that occur between the anionic groups present in the fibers and those present in the dye molecules(5). It has been considered that widening the scope of acrylic coloration using different classes of dyes which facilitate the technical production of different colors of the fiber. According to our knowledge, there is no report as yet appeared in printing acrylic fibers with conventional anionic dyes.

These shortcomings might be overcome by chemical and physical modification of the fiber (6-9). Although chemical modification of the fibers has been somewhat successful in improving hydrophilic and antistatic properties, there are environmental regulations relating to the disposal of chemicals after treatment (10). Plasma treatment, as a clean and environmental friendly physical technique, opens up a new possibility in this field. Plasma treatment can usually induce the processes of generation of polar groups through post-plasma reaction and also generation of increased surface roughness via preferential amorphous structure ablation (11).

Different studies on the surface modification of textile materials by plasma action (11-17) have been carried out. On the other hand very little work has been dealt with the modification of acrylic fibers by plasma treatment(18-21) .

In the present paper a comprehensive study has been carried out on using the APGD plasma in open air. This study includes employing two types of techniques:

(I) Acrylic Fabric Treatment with Plasma only

This technique includes two methods;

a) Treating the acrylic fabric by plasma . printing and then followed by the fixation by steaming.
b) The untreated acrylic fabric has been printed then it followed by the fixation with plasma.

(II) Acrylic Fabric Treatment with Plasma followed by hydroxylamine

II. EXPERIMENTAL DETAILS

2.1. Plasma Set up

The experimental setup (Figure 1) is the same as that in [22] , which consists of two copper plane-parallel electrodes of 2.5 cm diameter. The two electrodes were covered with two porous alumina Al_2O_3 sheets of 3.5 mm thickness and 4 cm diameter. The distance between the two dielectric plates was 1.1 mm. A high voltage transformer (1–10 kV), which generates sinusoidal voltage at a frequency of 50 Hz, was used as an electric power supply to derive the discharge system. The discharge was operated in open air under atmospheric pressure. The applied potential difference (V_a) across the electrodes and the current (I) passing through the system were recorded using a digital oscilloscope (HAMEG HM407—40 MHz). The current was measured by the voltage drop across the resistance R_1 (=100 Ω) connected in series with the discharge system to the ground as shown in figure 1. The voltage across the two electrodes was measured using the potential divider of the resistance system R_2, R_3, where$R_2/R_3 = 500$.

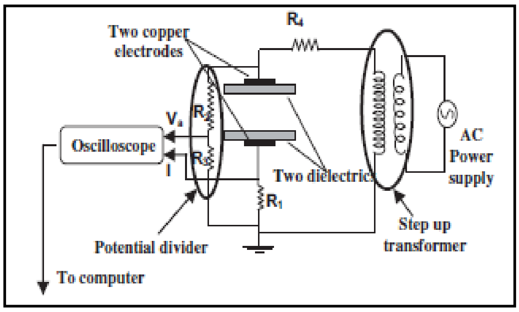


Figure 1: Schematic diagram of the discharge cell used for the treatment of the textile

2.2. Materials

Acrylic fabrics of 172 g / m2 were supplied from Misr for spinning and weaving Co., El-Mahalla El-Kobra, Egypt. The fabric was treated with a solution containing 2 g / L nonionic detergent and 1g / L sodium carbonate at a temperature of 45-50 ^{0}C for 30 minutes, then thoroughly washed and air dried at room temperature. Acetic acid, hydroxylamine hydrochloride, ammonium acetate, urea, ammonium sulphate and formic acid were laboratory grade chemicals. Basic dye Red 46 (Ginacryl Red GRL200%), Reactive dye Bifunction Red 94 were kindly supplied by Misr Color Co. and Acid dye Supralan Blue 2R and blue 225 were kindly supplied by Dystar Co. Commercial sodium alginate of higher viscosity as nature thickener type was supplied by Fluka Chemie GmbH CH-9471 Buchs, Myprogum modified thickener 5% was supplied by ROM STARoim Co. SETA Print and British gum modified thickener 4% was used and supplied by Mahalla El-Kobra, Egypt.

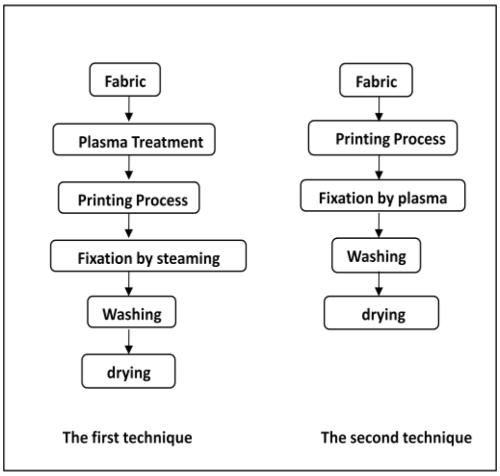
2.3. Experimental procedures

2.3.1. Acrylic Fabric Treatment with Plasma only

Acrylic fabric samples (5x5cm) were placed between the two electrodes and exposed to low temperature plasma of air under atmospheric pressure. This treatment was carried out via two techniques:

I) The first technique, plasma treatment was used to activate the acrylic fabric surface before printing process at discharge power ranges between 0.3 and 2 watts/cm^3 and exposure time ranges from 10 to 60 seconds. Then , the plasma treated acrylic fabrics were printed and followed by the fixation step using the steamer at a temperature of 105 ^{0}C and a fixing time 15 minutes, then it was washed and air dried.

II) The second technique, plasma was used not only for activating the fabric surface but also as a fixation tool-after printing- instead of using the steamer. This, two processes were carried out in one step where, both time and energy could be saved. In this case, the discharge power and exposure time of plasma were changed to compensate for the role of the steamer, where the applied discharge power ranged from 0.3 to 2.0 watts/cm^3 and the exposure time ranged between 0.5 to 5 minutes. The fabric was then washed and air dried. Schematic diagram represents the two techniques is shown as follow;



2.3.2. Treatment with Plasma followed by hydroxylamine

Acrylic fabric samples (5x5cm) were placed between two electrodes and exposed to low temperature air plasma under atmospheric pressure. Then, the plasma treated samples were put into a solution of 10 g/l hydroxylamine hydrochloride and 20 g/l ammonium acetate with a liquor ratio 50:1. This reaction is carried at a temperature of 30 ^{o}C for 30 minutes. Then the samples were thoroughly washed with water and air dried (23).

2.4. Printing methods

a)Printing of plasma treated acrylic fabric

The untreated and plasma treated acrylic fabrics were printed using the conventional silk screen printing technique. The printing paste that is used in the two techniques was the same and was prepared according to the following recipe:

Dye*	0.7	g
Thickener**	89.2	g
Acetic acid	0.1	g
Boiling water	X	g
	100	g

*The dye used was basic Red 46 (Ginacryl Red GRL200%).

** Stock thickener was prepared from 40% British gum which was soaked in boiling water (100 g) and stirred well to prepare the stock paste. After that, the basic dye was added and stirring was carried out for few minutes. Then fixed and washed according to the following steps:-

- Rinsing with cold water
- Soaping with 1g/l nonionic detergent at 40 ^{0}C
- Reduction clear in a solution containing 1-2g/ l sodium hydrosulfate,1-2g/l caustic soda and 1-2g /l nonionic detergent at a temperature 50 ^{0}C.
- Rinsing with water at 50 ^{0}C.
- Rinsing with cold water and air dried

Finally the samples were air dried and assessed for different measurements.

b) Printing of acrylic fabrics treated with plasma and hydroxylamine

The untreated and polymerized plasma LTP treated samples were printed with reactive and acid dye, using silk screen printing technique.
These printed samples were thermo-fixed at 190 ° C for 2 minutes.
The printing paste used was prepared according to the following recipe:

Dye*	20	G
Urea	50	g
Thickener**	50	g
Ammonium sulphate solution (50%)	60	g
Formic acid (85%)	10	g
Water	X	g
	1000	g

*The reactive dye used was Bifunction Red 94 with concentration 4% and the acid dye used is Supralan Blue 2R with concentration 4%.

**Thickener used was either sodium alginate 3% for reactive dye printing or myprogum 5% for acid dye printing.

The stock thickener was prepared by soaking in hot water or cold water for both myprogum and sodium alginate respectively, and well stirred, then the dyestuff was added and complete stirring for few minutes. The samples after printing and fixing were washed as mentioned before and air dried and assessed for color strength and fastness properties.

2.5. Measurements and Material Characterization

The treated and the untreated acrylic fabric samples have been exposed to the following measurements:

2.5.1. Bulk Properties

The percentage weight loss of the acrylic samples before and after plasma treatment was measured according to the weight difference relation (24) . The percentage of the moisture regain of acrylic fabric was determined according to ASTM D2654-89a, where the moisture regains of the fibers treated by oven drying method was calculated using the following formula: Moisture regain %= $[(W_m – W_d) / W_d] \times 100$ where W_d is the dry weight of fibers and W_m is the wet weight wet of fibers under 60% relative humidity for 48 h. The X- Ray crystallinity was measured with a PW 3710 diffractometer (Phillips) (XRD) using $Cu_{k\alpha}$ radiation at an operating voltage of 40 Kv and a current of 35 mA from 5 to 60 angles. Pellets were prepared from 0.25gm fiber and crystalline size was calculated from the equation: $t = k\lambda / \beta \cos \theta$ Where t = the size of crystal (Å), k = shape factor (0.94), λ=wave length of x-ray (1.542Å), β=half-width (radian), θ =Bragg angle.

2.5.2. Surface Morphology and Properties

Changes in fabric whiteness after plasma exposure were measured with an Elrepho 2000 Reflectance Spectrophotometer (Data Color International) according to AATCC test method 153-1985. The wettability was evaluated by measuring the wetting time according to the AATCC method (25). A drop of water is allowed to fall from a fixed hight onto the surface of the acrylic fabric under examination. The time that has been taken for the drop of water to disappear has been measured and taken as wetting time, and the results were the average value of four readings. The antistatic properties of acrylic fabrics were measured using the system FMX-003 SIMCO electrostatic (SiN: R001740 Type, made in Japan). Where the FMX-003 is a compact electrostatic field meter used for location and measuring static charges voltages within +/− 22 KV. The untreated and plasma treated fabrics were investigated by a Scanning Electron Microscope (SEM) JSMT-20, JEOL-Japan, magnification range 1500-2000x, resolution 200A°, and accelerating voltage 19 kV. Before examinations, the fabric surface was prepared on an appropriate disk and coated randomly by a spray of gold. These investigations were carried out at the department of physical chemistry ,NRC Egypt. Fourier- transition infrared spectroscopy (FTIR) was performed using a Pye-Unicam spectra-1000 machine to determine the functional groups on the surface of the acrylic samples. Potassium bromide (KBr) disc was used. Surface morphology of the treated and untreated samples was studied by using a wet- SPM9600 Scanning Probe Microscope (Shimadzu Made in Japan). It uses a probe that has a nanosize tip mounted on a flexible cantilever. The tip was scanned slowly across the surface of a specimen. The force between the atoms on the surface of scanned material and those on the scan causes the tip to deflect. This deflection can be recorded by using a laser focused on the top of the cantilever and reflected onto photo detectors down to the nanoscales. Atomic force microscopy provides high resolution images of surface even if they were nonconducting. In this study, scanning was carried out in contact mode. Scanning range was set at a size of 5.0μm x 5.0μm and scanning frequency is 1.5 Hz. All images were obtained at ambient conditions immediately after plasma treatment.

2.5.3. Printing Properties

The color yield (K/S) of each printed sample was measured using a Data Color SF 600plus Colorimeter using a measured area with diameter of 9mm. All the (K/S) values were calculated by subtracting the (K/S) value of the printed untreated sample from the (K/S) values of the printed treated samples. (i.e values obtained are relative color strength). The dye fixation on acrylic was estimated by extracting equal size (2x2 cm) samples immediately after printing and drying, and after fixation and final soaping, in 85% o-phosphoric acid. The fixation was calculated as follows: Fixation (%) =[$O.D_p$/ $O.D_w$] X 100 Where $O.D_w$ is the optical density of the just printed and dried sample and $O.D_p$ is the optical density of the printed and dried sample subjected to fixation followed by thoroughly rinsing in cold water and soaping at the boil for 5 minutes. The dye-fiber reaction indicated by fixation ratio was estimated by subjecting the printed samples, after soaping at boil, to extraction with 50% urea solution and 1 % nonionic wetting agent for 3 minutes at boil (26). The extent of reaction was calculated by determining the k/S of the printed samples before and after extraction using the reflectance values and Kubelka-Monk function (27). The fixation ratio was calculated by the following formula: Fixation ratio (%) = [$(K/S)_E$ /$(K/S)_W$]X 100 Where $(K/S)_W$ is the Color strength of the printed and dried sample subjected to fixation followed by thorough rinsing cold water and soaping at boil for 5 minutes and $(K/S)_E$ is the Above mentioned soaped samples subjected to extraction with urea solution. Changes in roughness values were measured for the printed untreated and treated acrylic samples using a surface roughness measuring instrument SEM1700α .The results obtained were the average values of three readings. The color fastness of the printed fabrics was assessed by the AATCC Test Method 16-2001(color fastness to light), AATCC Test Method 61-2001(color fastness to laundering) and AATCC Test Method 8-2001(color fastness to rubbing).

III. RESULTS AND DISCUSSION

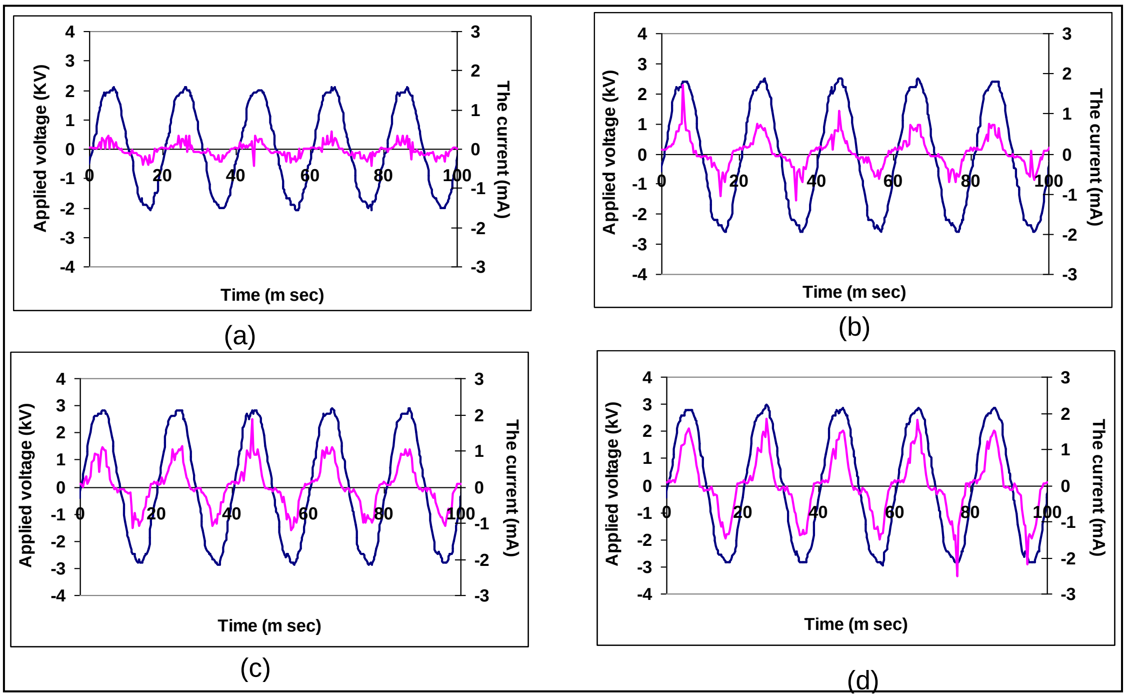
APGD plasma is considered to be an ideal technique to enhance the modification of both physical and chemical properties of acrylic fabric. Hence the surface is exposed to low temperature APGD plasma in atmospheric air. In general, plasma treatment is controlled by several factors such as discharge power, exposure time, gas type and pressure ...etc. In our studies, both power and time are taken in consideration.

3.1. Electrical Characteristics and Power Measurements

3.1.1. Voltage and current wave forms.

Figures 2(*a*)–(*d*) represent the voltage and current oscillograms of the APGD plasma in air and different applied voltages where the currents are a) 0.2 mA, b) 0.6mA, c) 1mA, and d) 1.5 mA respectively.

The APGD plasma is a special type of the dielectric barrier discharge (DBD) plasma. This discharge is characterized by the absence of the micro discharge that are present in the general form of the DBD and causes the formation of short-lived microfilaments (28). If the glow discharge contains some microfilaments then it is called a quasiglow discharge(29). The APGD is considered to be a very important technique in textile treatment because of its homogeneity effect on the textile surface that cause a uniform treatment without burning it.



(a) (b) (c) (d)

Figure 2: Current- voltage waveforms, at the currents are a) 0.2 mA, b) 0.6 mA, c) 1mA, and d) 1.5mA respectively.

Obtaining the APGD by using porous alumina sheets has been found due to the special configuration of the alumina sheets, which are characterized by the existence of micro holes. An internal discharge takes place inside the micro holes and on the surface of the porous alumina. This internal discharge provides seed electrons sufficient for the initiation and growth of the discharge in the APGD form inside gas between the two alumina sheets as it was stated in (30). From figure (1a-d) it can be noticed that the discharge is uniform with a small component of microfilaments that are superimposed on the glow component of the APGD .

3.1.2. The consumed power in the APGD

The mean power consumed in the APGD can be estimated by taking the integration over one cycle of the product of the I(t) and V(t) waveforms (31).

$$p = 1/dST\int_{0}^{T} I_{disch}(t).V_a(t)dt \qquad (1)$$

Where, P : is the power per unit of the discharge volume, V_a : is the applied voltage, I_{disch} : is the discharge current, S : is the electrode surface, d : is the gas gap, and T: is period.

The mean power per cm^3 consumed in the APGD have been calculated at different currents and have been plotted against these currents as shown in Fig. (3). Then, it can be easily calculated the mean power density that consumed in the APGD at different currents from the same Fig (3).

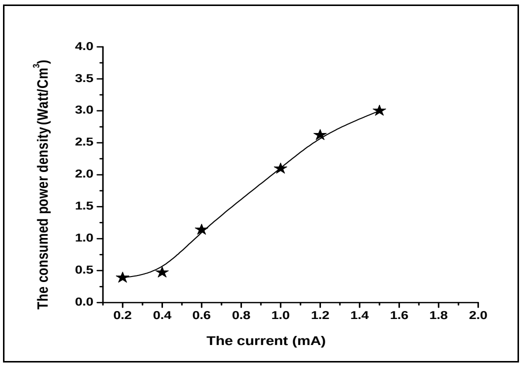


Figure 3: The consumed power density in the APGD at different currents.

3.2. Bulk properties

3.2.1. The percentage of Fabric weight loss

Figure (4) shows the % weight loss behavior of both untreated and treated acrylic fabric with plasma exposure time ranges from 10 to 60 seconds at discharge power varies between 0.3 and 2 watts/cm3. It is clear that, as the plasma exposure time increases, the % weight loss of acrylic fabric increases till it reaches 35 seconds then it starts to decrease. It is also noticed that, this phenomenon holds true regardless the value of the discharge power. This behavior can be interpreted in the light of the fact that: as the treatment time increases the etching processes of the textile surface increase as a result of the its bombardment by electrons, ions and other plasma species that are produced in the plasma environment. This bombardment also cause fragment or breaking up of the bonds, and chain scission (32).

Further increase in the treatment time induces the crosslinking in the acrylic fabric surface which in turns increases the crystalline region of the fabric. This crystalline region hinders and avoids the increase in the weight loss. Therefore, no increase in the weight loss is noticed after 35 seconds, but a decrease is carried out (33). It can be noticed that the highest % weight loss is obtained at the highest discharge power. This is due to the fact that increasing the power causes the increase of the discharge current and in turns the density of the electrons and the ions that bombard the fabric surface increases.

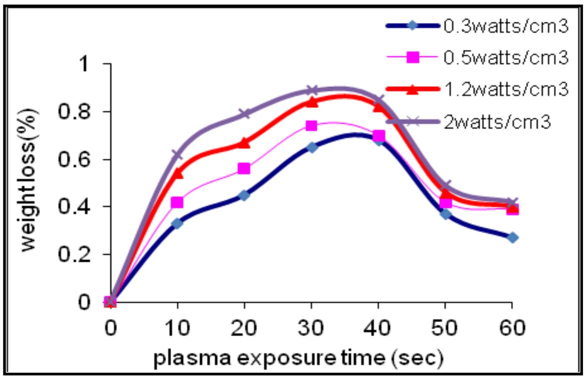


Figure 4: % Weight loss of acrylic fabrics treated with APGD plasma at discharge power (0.3-0.5 1.2- 2 watts/cm^3).

3.2.2 Percentage of Moisture Regain

Figure (5) shows the effect of plasma exposure time on the % moisture content of treated acrylic fabric at different discharge powers. As the treatment time increases, the % of moisture increases until it reaches its maximum value at time 30 second, after that it decreases by further increasing of the treatment time. At treatment times lower than 30 second, the etching process affect the surface of the fabric that forms voids, cracks and fragments on the fabric surface and in turn permits the moisture to migrate and transfer inside the fabric easily. On the other hand further increase in the treatment time causes the formation of the crosslinking beneath the fabric surface that hinders the moisture transport to the interior of the fabric which resulted in a little decrease in the % moisture content (34). Also it can be noticed that increasing the power causes the increase of the % moisture due to the increase of the etching process.

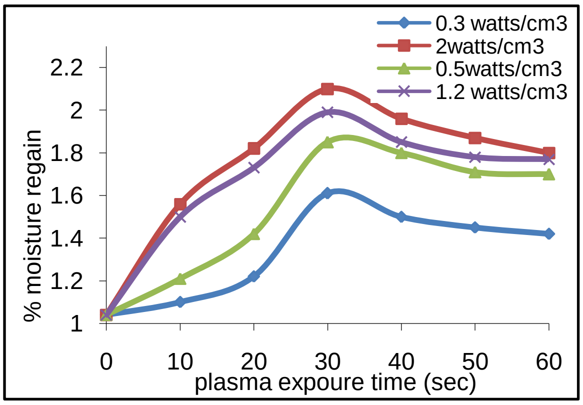


Figure 5: % moisture regain of acrylic fabrics treated with APGD plasma at discharge power (0.3-0.5 1.2- 2 watts/cm^3).

3.2.3. X-Ray Crystallinity

Figure (6) represents a sample of the X-ray diffraction patterns (XRD) of the acrylic fabric treated with APGD plasma in air at different conditions that of the untreated fabric for comparison. It is well known that the sharpness of the XRD peaks reflects the domination of the crystalline phase. On the other hand, decreasing and the broadening of the peaks reflects the tendency of the formation of the amorphous phase in which the atoms are arranged in a short- range order manner.

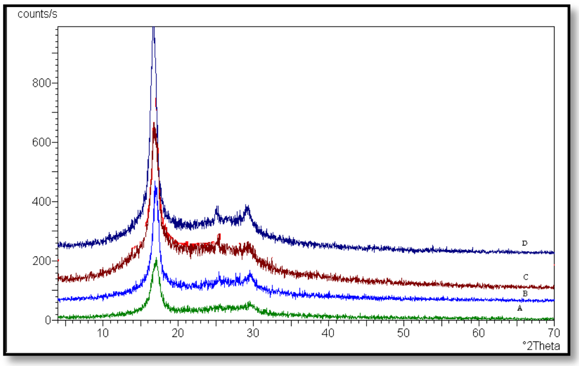


Figure 6: X-ray diffraction patterns of acrylic fabric treated with APGD air plasma at A) 1.2 watt/cm^3 and 30 sec., B) untreated , C) 2 watt/cm^3 and 60 sec. and D) 3 watt/cm^3 and 60 sec.

Table 1 represents the crystalline size that calculated by using the data in the figure (6). It can be noticed that treating the fabric with plasma at low power density such as 1.2 Watts/cm^3 decreases the crystalline size as it compared with that of the untreated one. Whereas, increasing the treatment power causes an increase in the crystalline size rather than that of the untreated one.

Plasma conditions	**Crystallite size (Å) values**
Untreated	18.68
Treated with plasma (1.2 watts/cm^3-30sec.)	12.34
Treated with plasma (2 watts/cm^3-60 sec.)	19.68
Treated with plasma (3watts/cm^3-60sec.)	21.22

Table I: Crystallite size (Å) of acrylic samples treated with APGD air plasma at different conditions of discharge power and exposure time.

This behavior can be interpreted as follows: at low power density the plasma species that bombard with the acrylic surface and cause the formation of cross-linking in the fabric and in turns the atoms of the fabric will be arranged in the short-range order manner and hence the crystalline size decreases. On the other hand, as the plasma power increases, the temperature also increase and hence there will be a chance for the fabric atoms to be rearranged again in a long-range order manner and in turns the crystalline size increase again. The increase in the crystalline phase is simply reflected by a decrease in the amorphous phase (34).

3.3. Surface Morphology and Properties

3.3.1. Whiteness

It is well known that acrylic fabric has no clear white color and also it has a main problem of its yellowness that appears during the dye fixation process. Plasma treatment of the fabric try to overcome this problem. Figure 7 shows the effect of plasma exposure time and the discharge power on the whiteness of acrylic fabric. From the figure it can be noticed that increasing the plasma power and the treatment time, to about 15 sec, causes an increase in the whiteness of the fabric. This may be attributed to cleaning of the fabric surface by plasma species bombardment. Beyond 15 sec, the whiteness can be seen to be saturated.

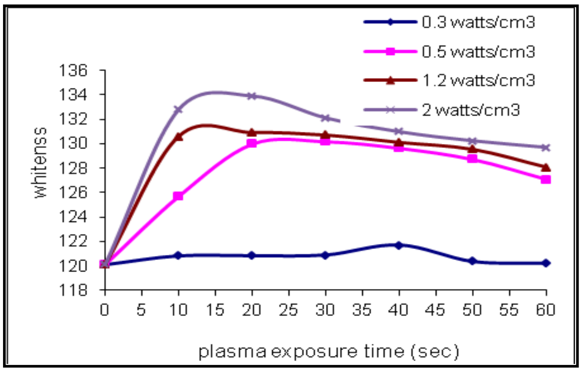


Figure7: Whiteness of acrylic fabrics treated with APGD plasma at discharge powers (0.3-0.5 1.2- 2 watts/cm^3).

3.3.2. Wettability

Figure 8 shows the effect of the treatment time and the power on the fabric wettability. It can be noticed that increasing the treatment time to about 10 sec or increasing the plasma power causes a decrease in the surface wettability. This is due to the plasma treatment that introduces hydrophilic groups onto the fabric surface. These polar groups may be generated either by the nitridation of the fabric surface by plasma nitrogen ions or when the samples are exposed to air after plasma processing(21). Further increase in the treatment time beyond 10 sec causes the saturation in the wettability of the fabric.

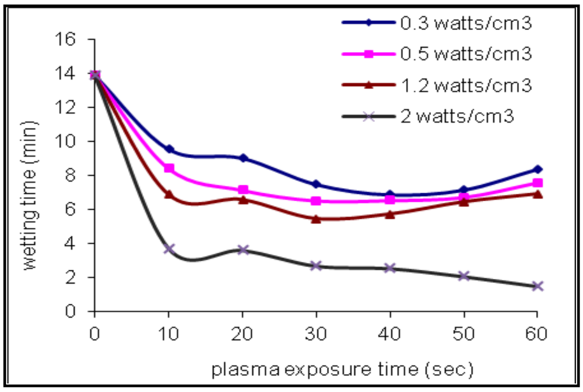


Figure 8: Wettability of acrylic fabrics treated with APGD plasma at discharge power (0.3 -0.5-1.2-2 watt/cm^3).

3.3.3 Antistatic of Acrylic Fabric

The antistatic ability of the untreated and treated samples is shown in table (II).

Sample	Antistatic (Kv)
Untreated	−1.23
Air plasma−treated	
10 sec	−5.5
20 sec	−8.5
30 sec	−12
40 sec	−8.5
50 sec	−8.3
60 sec	−8.0

Table (II) : antistatic ability of the untreated and plasma-treated samples at discharge power 1.2 watts/cm^3.

It can be seen that plasma treatment causes a sharp increase in the negative static voltage of the fibers from –1.23 KV for the untreated samples to about −12 for the treated time of 30 seconds. A slight decrease in the antistatic ability to (-8 KV) has been obtained for all the treatment times above 30 sec. It can be stated that plasma treatment of the acrylic fabric increases the antistatic ability of the fabric and its surface resistivity.

3.3.4. Scanning Electron Microscope (SEM)

It is well known that, plasma etching causes drastic changes on the surface structure of the fabric and gives it other characteristics. Scanning electron microscope measurement is used to investigate surface morphology of the fabric. Figure 9 shows SEM micrographs of the fiber before and after plasma treatment. It is noticed that the untreated acrylic fabric has a smooth surface, while in the treated fabric surface, some voids and cracks are clearly seen. This photo picture agrees with what is mentioned before about etching by plasma species and causes a substantial increase in the surface roughness and may affect the stiffness of the acrylic fabric surface(21).

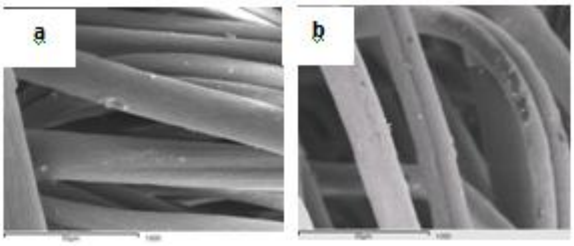


Figure 9: SEM images of the untreated and plasma treated at 1000x(a) untreated acrylic fabric, (b) plasma treated acrylic fabric under atmospheric pressure at discharge power 1.2 watts/cm^3 for exposure time 30 seconds.

3.3.5. Atomic Force Microscope (AFM)

The AFM is used to quantify the change in surface roughness of the treated surface as well as provide high resolution images showing the topography. Therefore, it has been used to assess the topographical and physical changes in structure as a result of plasma treatment, where, it is by far the most commonly used for analysis of plasma-treated textiles. This is due to one of its major benefits of its ability to image surfaces without the need for any complicated surface treatment process. Also it is a technique that can be used in air and imaging can be also done in water(35). Based on a relatively simple concept, the AFM has been partly responsible for the advancing in nano-revolution in material science (36). The surface morphology of the acrylic fabrics in the melt-blown is represented in figure 10. The AFM image in figure 10 (a) shows the relatively smooth surface of original fabric, where the microfiber in the melt blown substrate does not show any fibril structures on its surface. Plasma activation significantly changes the surface characteristic of the fiber as mentioned before. AFM examination, clearly, reveals the effect of the plasma treatment on the surface morphology of the fiber and this can be seen from figure 10 (b). It is clear that, the fabric surface is obviously roughened after plasma treatment due to its activation that forms aggregate structures on the acrylic fabric surface. These aggregates are created by etching effect of plasma species bombardment (37).

Figure 10 (c) shows the surface of plasma treated acrylic fabric followed by hydroxylamine hydrochloride treatment- in the presence of ammonium acetate which causes polymerization for the plasma treated surface of acrylic fabric. The admixtures of reactive ammonia with hydroxylamine into the plasma treated fabric caused strong structure disorder for the fabric surface.

Thus both etching and deposition take place and as a result a nano-porous and crosslinked network with accessible functional groups was obtained. Besides, the surface roughness has been increased remarkably compared to plasma treatment alone, figure 10 (b). Figure 10 (d) shows the surface of printed acrylic fabric after plasma polymerization. It is very clear that; the surface roughness is improved, which may be due to the printing pastes which filled some of the groves formed due to etching process. Thus a smooth surface image-nearly the same as image (a) has been obtained. Thus a great difference between image in (d) and those in images (b) and (c) can be noticed.

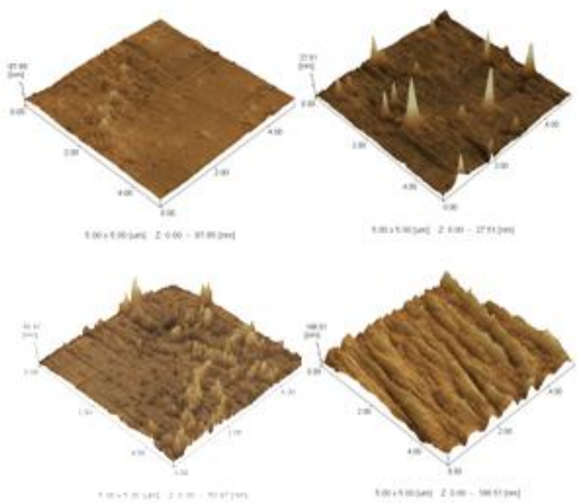


Figure 10: evolution of surface morphology observed by AFM: (a) original acrylic fabric, (b) plasma treated acrylic fabric*, (c) plasma treated acrylic fabric followed by hydroxylamine hydrochloride treatment**, (d) printed acrylic fabric after plasma polymerization.

*Conditions of plasma treatment: 1.2watts/cm^{3}and 30 seconds.
**conditions of polymerization treatment: 10 g/l using aqueous solutions of ammonium acetate 20 g/l at a liquor ratio 50:1 at 30 ^{0}C for 30 minutes

3.3.6. Fourier-Transition Infrared Spectroscopy (FTIR)

FT-IR is often used (alongside XPS) to provide a comprehensive analysis of how the surface of polymer is changed as a result of plasma treatment. Figure 11 shows a typical example of FT-IR spectra in the range of 1000-4000 cm^{-1}. The figure represents the spectra of the untreated (a) and plasma- treated sample (b) as well as the plasma polymerized sample (c). The original sample surface, spectrum (a) shows five distinct components with relative intensities shown in table I are 93, 49, 76.10, 87.37, 77.67 and 70.10ύ, corresponding, respectively to (O – C), (C= O acid), (C≡N), (:CH$_2$) and (O:H) groups. Upon plasma treatment, spectrum (b), the numbers of all these groups are increased while their relative intensities are decreased as shown in table III, in addition to the absence of (O:H) and (C= O acid) groups in spectrum (c), the (C=O amide) and (NH$_2$) groups have been additionally appeared on the sample surface. In the spectrum of untreated acrylic (spectrum a), a strong adsorption band centered at 1651 cm^{-1} can be observed, which attributes to the carbonyl groups of the polyacrylonitrile which lies between peaks 1651 – 1737 cm^{-1}. The weak peak at (1630) cm^{-1} is most likely caused by the impurities of the fibers (38). The increase in the number of polar groups hydroxyl O:H, cyanogens C≡N and carbonyl C=O acid as a result of plasma treatment, is the main reason for increasing wettability of the plasma treated acrylic fabric surface. Spectrum c and table I show introduction of two new species, i.e. carbonyl amide (C=O) at peak 1630 cm^{-1} and amine (NH$_2$) at peak 3628 cm^{-1}. These changes reflect the presence of the oxidation reaction on the surface of plasma-treated samples under open laboratory conditions as well as immersion in the solution of hydroxylamine hydrochloride and ammonium acetate. This oxidation reaction permitted to use different categories of dyes for printing acrylic fabric and this will be discussed later.

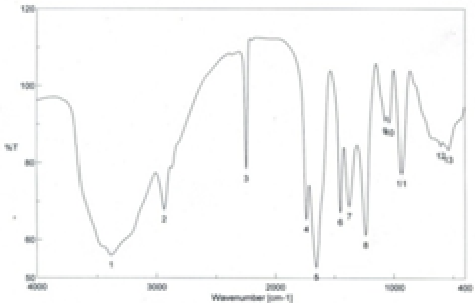


Figure 11a: FTIR of untreated acrylic fabrics

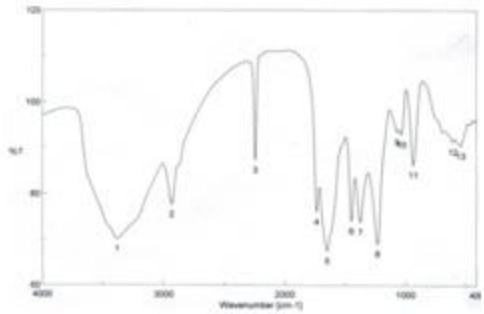


Figure 11 b: FTIR of treated acrylic fabric with plasma at discharge power 1.2 watts/cm^3 for exposure time 30 sec.

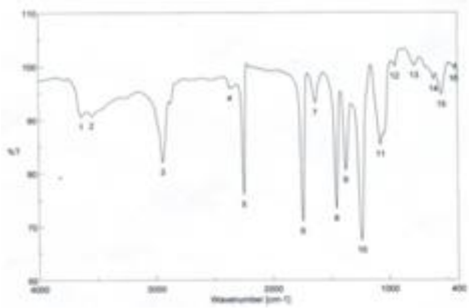


Figure 11c: FTIR of plasma treated acrylic fabric 1.2 watts/cm^3 followed by hydroxylamine hydrochloride treatment 10 g/l using aqueous solutions of ammonium acetate 20 g/l at a liquor ratio 50:1 at 30 ^{0}C for 30 minutes.

It can be also noticed from table III that, in the case of plasma polymerization, while a substantial loss in the relative intensities of cyanogens C≡N and ester groups O:C carried out, a noticeable change is noticed in the methylene groups and which increased to 82.05ύ compared to 67.90 and 77.67ύ for untreated and only plasma treated acrylic fabrics.

Acrylic state	Relative intensities of selected bands in the FTIR spectra of acrylic samples treated with plasma						
	O−H	$-CH_2$	C≡N	C=O (acid)	C=O (amid)	O−C (ester)	$-NH_2$
Untreated	70.1055	77.6776	87.371	76.10515	−	93.4982	−
Treated with plasma	55.9621	67.9084	78.4813	65.3341	−	90.4569	−
Polymerization of treated plasma	−	82.0515	76.0285	−	71.0058	85.3485	90.5519

Table III: FTIR of acrylic samples treated with air plasma under atmospheric pressure and different conditions of exposure time and discharge power

3.4 Printing Properties

3.4.1. Color Assessment

I) Treatment of acrylic fabric by using plasma only

Polyacrylonitrile, or acrylic polymer fiber containing small amount of anionic centers, such as sulphonic acid or carboxylic acid groups, can be dyed or printed with dyes bearing a positive charge, viz, cationic dyes. The cationic dyes are attracted to the fabric and then anchored to the fiber by ionic bonds. Basic dye is -by far- the most important class of dye used on acrylic fabric where it dissociates in water to yield colored cations and are characterized by their brilliance and very high tinctorial strength (4).

Figure 12 represents the effect of the plasma treatment time (in the range of 10 to 60 sec) on the color strength (K/S) at different plasma power densities. It can be noticed that the color strength (K/S) increases with the increase of the treatment time until it reaches its maximum value in the time range (20-40 sec) then it decreases again. This behavior holds true for all power values. It can be stated that as the treatment time increases the etching processes increases by the ion bombardment on the surface and hence it causes the simplicity of the penetration of the printing paste molecules and causes the increase in the (K/S). Also the increase in the (K/S) is attributed to the introduction of polar groups – due to plasma treatment – which incorporate with moisture through hydrogen bonding and help moisture penetration that increases the wettability and also increases the color strength.

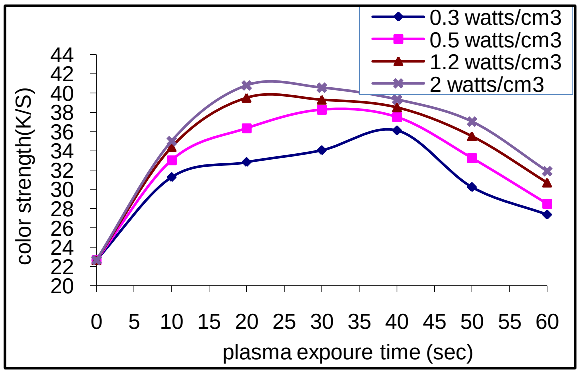


Figure 12: Color strength of acrylic fabrics treated with APGD plasma at discharge power (0.3-0.5 1.2-2 watts/cm^3).

Further increase in the treatment time provides some cross-linking that hinder further penetration of the printing paste into the fabric, therefore the (K/S) decreases. The highest (K/S) is obtained at power 2.0 watts/cm^3 where higher input power causes an increase in the number of high-speed electron in plasma and in turns improve plasma treatment effect,(39) which leds to the increase of (K/S) value of fabric (40).

II) **Treatment of acrylic fabric by using plasma followed by hydroxylamine**

It is well known that anionic dyes namely reactive and acid dyes are not usually used or even suitable for acrylic fabric coloration. These dyes suffer from being not substantive for the fibers as a result of the repulsive effects that occur between the anionic groups present in the fiber and those present in the dye molecules(5). This problem could be overcome by rendering the surface of acrylic fabric with amino groups – via plasma followed by hydroxylamine treatment – to enhance its anionic printability.

Figures 13 and 14 represent the effect of both plasma exposure time and discharge power on the (K/S) of the treated acrylic fabric printed with reactive and acid dyes respectively. It is clear that, the (K/S) values obtained has been improved – to a large extent – by both power and time regardless of the dye type.

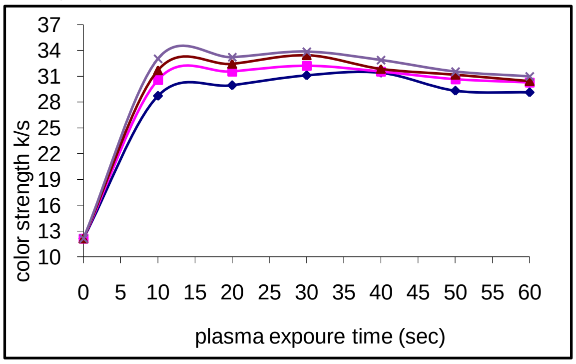


Figure 13: Color strength of acrylic fabrics treated with APGD plasma at discharge power (0.3-0.5 1.2-2 watts/cm^{3}) and polymerization with hydroxylamine hydrochloride (10 g/l) using aqueous solutions of ammonium acetate (20 g/l) at a liquor-to-goods ratio of 50:1 at 30 ^{0}C for 30 minutes and printed with reactive dye.

Figure 13 shows that the (K/S) is increased sharply at the early stages of plasma treatment, where the exposure time of 10 seconds was enough to improve the (K/S) to a higher values regardless the discharge power. After this limit of time, no noticeable increases in the (K/S) but constant values are obtained.

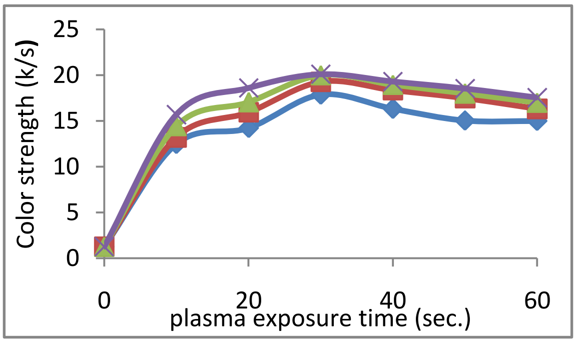


Figure 14: Color strength of acrylic fabrics treated with APGD plasma at discharge power (0.3-0.5 1.2-2 watts/cm^{3}) and polymerization with hydroxylamine hydrochloride (10 g/l) using aqueous solutions of ammonium acetate (20 g/l) at a liquor-to-goods ratio of 50:1 at 30 ^{0}C for 30 minutes and printed with acid dye.

However, figure 14 shows that the ideal exposure time used to get maximum (K/S) values at all discharge power levels is 30 seconds.

III) Effect of fixation temperature on acrylic color strength

The effect of fixation temperature on acrylic color strength (K/S) has been investigated, where after the fabric is treated with plasma followed by the immersion in hydroxylamine hydrochloride in presence of aqueous solutions of ammonium acetate, the resulted fabric is air dried and thermo fixed at 180 ^{0}C for 2 minutes. A yellow colored fabric is obtained with different shades corresponding to the plasma exposure time and the results obtained are represented in figure 15.

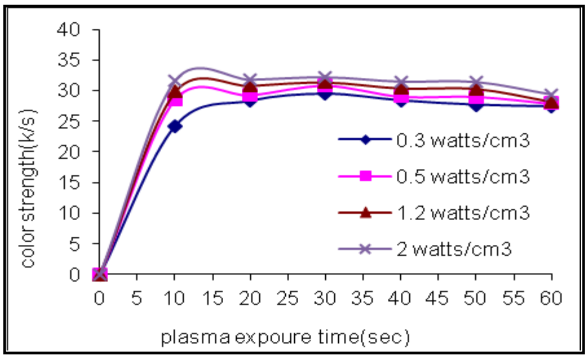


Figure 15: color strength of acrylic fabrics treated with APGD plasma at discharge power (0.3-0.5-1.2- 2 watts/cm^{3}) and polymerization with hydroxylamine hydrochloride (10 g/l) using aqueous solutions of ammonium acetate (20 g/l) at a liquor-to-goods ratio of 50:1 at 30 ^{0}C for 30 minutes then fixed 190 ^{0}Cand give yellow color.

This phenomenon is studied and the FT-IR for this fabric is carried out and its analysis is shown by figure 14. This phenomenon of obtaining yellow colored acrylic fabric – without using any dye – due to its subjection to the fixation temperature at 180 ^{0}C for 2 minutes is explained by the FT-IR spectrum represented in figure 16. It is clear that five important groups has been found at different peaks; the amino NH_2 group at 3628.4 cm^{-1}, the ester O:C group at peak 1035.59 cm^{-1}, the carbonyl C=O amide group at 1630 cm^{-1}, the carbonyl C=O acid group at 1651cm^{-1}, the cyanogens C≡N group at 2243.7 cm^{-1} and the methylene $:CH_2$ group at 2293.2 cm^{-1}. Where their relative intensities, are 86.67, 80.15, 64.34, 70.66 and 77.14 respectively. These values of relative intensities are lower than those obtained in the case of treatment with plasma alone or those with plasma followed by hydroxylamine, which means an increase in all of their groups. This may explain the yellow color obtained that referred to the oxidation of the amino groups created after plasma polymerization and was not present in the untreated fabric. Also, the carbonyl amide group is created due to plasma polymerization and also is oxidized by oxygen in the air plasma giving the yellow color.

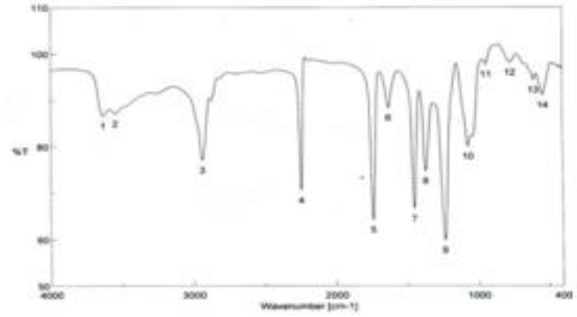
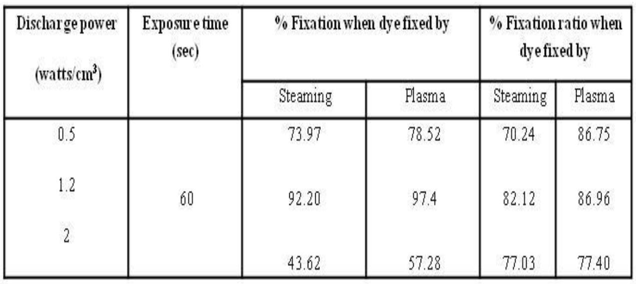


Figure 16: FTIR of acrylic fabrics treated with APGD plasma at discharge power (1.2 watts/cm^3) for exposure time(30 second) and polymerization with hydroxylamine hydrochloride (10 g/l) using aqueous solutions of ammonium acetate (20 g/l) at a liquor-to-goods ratio of 50:1 at 30 ^{0}C for 30 minutes then fixed 190 ^{0}Cand give yellow color.

3.4.2 Percentage of Dye Fixation and Fixation Ratio

Fixation of basic dye on acrylic fabric – as mentioned before – is carried out via two techniques and the results obtained are studied. A comparison between the results of the two techniques are represented in Table IV.

It can be noticed that, the color strength values obtained when using plasma as a fixation step for printed samples are much higher in comparable with that obtained when using steaming method. Higher levels of fixation has been observed in the first case which are in the order of (78.52 - 97.4 %) at 0.5-1.2 Watt/cm^3 discharge power densities compared to the level of (73.97- 92.20 %) obtained in the case of steaming fixation. This phenomenon holds true for discharge powers 0.5 & 1.2 watts/cm^3 while the opposite is obtained at discharge power 2 watts/cm^3. This may be due to the increase in the crystallinity of acrylic fabric at higher power and this agrees with other results of color strength, wettibility and % weight loss. The term 'fixation ratio' expresses the amount of dye bonded to the fabric as a fraction of the dye present in the printed samples after soaping. Table IV, also, shows the results of the fixation ratio (%) for the basic dye fixed by the two methods. The higher values of fixation ratio obtained in plasma fixation method indicates that out of the available dye on the soaped samples maximum amount of dye was bonded with the fiber.



Discharge power (watts/cm^3)	Exposure time (sec)	% Fixation when dye fixed by		% Fixation ratio when dye fixed by	
		Steaming	Plasma	Steaming	Plasma
0.5	60	73.97	78.52	70.24	86.75
1.2		92.20	97.4	82.12	86.96
2		43.62	57.28	77.03	77.40

Table IV: % fixation and % fixation ratio of basic dyes on acrylic fabrics by using steam or plasma in fixation process.

3.4.3. Stiffness

Table V shows the effect of the air plasma exposure time and discharge power on the stiffness of treated printed acrylic fabrics.

Discharge power (watts/cm^3)	Stiffness values of the untreated and plasma treated acrylic fabrics – at different conditions - for various exposure times (sec).																	
	10			20			30			40			50			60		
Different cases	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
untreated	31.47 μm																	
0.3	30.8	30.9	29.7	29.4	30.3	27.7	27.8	27.3	24.9	29.8	28.5	25.7	31	29.2	26.2	31.1	29.8	27.2
0.5	29.6	30.4	28.7	28.6	29	25.2	26.7	24.4	23.7	27.2	26.7	24.6	28.6	27.1	25.5	29.2	27.9	26.3
1.2	28.5	29.8	27.6	27.2	26.3	24.4	22.6	24	22.5	24.4	25.4	23.5	25.6	26.1	24.7	26.7	27.6	26.1
2	25.7	28.2	27	24.9	25.4	23.6	21.5	23.7	21.7	23.5	24.2	22.4	24.9	25.4	23.9	25.6	26.7	25.3

Table V: Stiffness of acrylic fabrics treated with glow discharge plasma under atmospheric pressure.

I-treatment with plasma alone according to the first technique.
II-treatment with plasma alone according to the second technique.
III-treatment with plasma followed by hydroxylamine.

It is clear that, the stiffness values of printed fabric samples that are treated with plasma in all cases gives the highest improvement compared to the untreated fabric. This means that the treated samples become softer regardless plasma exposure times and discharge powers.

3.4.4.Fastness properties

Table VI show the color strength (K/S) and fastness properties of printed acrylic fabric previously treated with air plasma. Samples untreated and treated for different intervals of time at various discharge power levels were investigated. It is observed clearly that, there is a noticeable improvement in the color strength values for the treated samples as compared to the untreated ones, as mentioned before. The overall fastness results – to washing, rubbing, perspiration and light – for the treated acrylic fabric range from very good to excellent.

Discharge power (watts/cm	Time of treatment (sec.)	K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Light fastness
			Alt.	St.	dry	wet	Acid		Alkali		
							Alt.	St.	Alt.	St.	
0.3	–	22.7	4-5	4	4	4	4-5	4-5	4	4	5-6
	10	31.3	5	5	4-5	4-5	5	5	5	5	6
	20	32.8	5	5	4-5	5	5	5	5	5	6-7
	30	34.1	5	5	4-5	5	5	5	5	5	6
	40	36.1	5	5	5	5	4-5	4-5	5	5	6-7
	50	30.3	5	5	4-5	4-5	4-5	4-5	4-5	4-5	6-7
	60	27.4	5	5	4-5	4-5	4-5	4-5	5	5	6
0.5	10	33.0	5	5	4-5	4-5	5	5	5	5	6-7
	20	36.4	5	5	4-5	4-5	5	5	5	5	6-7
	30	38.4	5	5	4-5	4-5	5	5	5	5	6-7
	40	37.6	5	5	4	4-5	5	5	5	5	6
	50	33.3	5	5	4	4-5	5	5	5	5	5-6
	60	28.5	5	5	4-5	4-5	5	5	5	5	5-6
1.2	10	35.9	5	5	4-5	4-5	5	5	5	5	6-7
	20	34.8	5	5	4-5	4-5	5	5	5	5	6-7
	30	34.8	5	5	4-5	4-5	5	5	5	5	6-7
	40	34.2	5	5	4	4	5	5	5	5	5-6
	50	33.7	5	5	4	4-5	5	5	5	5	5-6
	60	30.3	5	5	4-5	4-5	5	5	5	5	5-6
2	10	31.0	5	5	4-5	4-5	5	5	5	5	6-7
	20	30.8	5	5	4-5	4-5	5	5	5	5	6-7
	30	30.8	5	5	4-5	4-5	5	5	5	5	5-6
	40	30.4	5	5	4-5	4-5	5	5	5	5	5-6
	50	30.1	5	5	4-5	4-5	5	5	5	5	5
	60	28.9	5	5	4-5	4-5	5	5	5	5	5-6

Table IV: % fixation and % fixation ratio of basic dyes on acrylic fabrics by using steam or plasma in fixation process.

IV. Conclusion

The APGD plasma treatments of acrylic fabric causes the activation of acrylic surfaces which leads to improve the properties of acrylic fabric. Surface performance of plasma-treated acrylic fabric has been studied morphologically. The investigation shows that treatment of acrylic surface with plasma followed by polymerization with hydroxylamine hydrochloride produced a modified acrylic fabric which could be able to be printed with acid and reactive dye giving higher color strength values and good fastness properties. Characterization of acrylic samples after treatment may help in choosing the optimal conditions of plasma treatment and its relation with the different properties of the fibers.

Reference

[1] **Bird CL& Boston WS (1975).** The theory of Coloration of Textiles. London: Dyers Company Publications Trust.
[2] **Munn DM (1979)**. The dyeing of synthetic-polymer and acetate fibers. England: Dyers Company Publications Trust.
[3] **Kamel M.M, Helmy H.M, Mashly H.M& Kafafy H.H (2010).** Ultrasonics Sonochemistry **17** 92-97.
[4] **David R& Geoffrey H (1990)**. The Chemistry and Application of Dyes, New York and London, 165-166 (Chapter 5).
[5] **Reda M. El-Shishtawy, Nassar S.H.& Nahed S.E.** (2007). Dyes and Pigments **74** 215-222.
[6] **Hsieh Y.L.& Timm D**.(**1987**). Polym. Mater. Sci. Eng. **56** 323.
[7] **Kadash M.M.& Seefried C.G. (1985).** Plast. Eng. **41** 45.
[8] **Keatsu I.& Yoshida M**. **(1979).** J. Appl. Polym. Sci. 24 23.
[9] Munro H.S., Polym. Mater. Sci. Eng. 58 (1988) 344.
[10] Li R., Ye L., Mai Y.W., Composites A 28 (1997) 73.
[11] Sarmadi M., Denes F., Text. Chem. Color. 28 (1996) 17.
[12] Lee S.G., Kang T.J., Yoon T.H., J. Polym. Eng. 18 (1998) 49.
[13] Negulescu I.I., Despa S., Chen J., Collier B.J., Text.Res. J. 70 (2000) 1.
[14] Yamada K., Haraguchi T., Kajiyama T., J. Appl. Polym. Sci. 60 (1996) 1847.
[15] Bhat N.V., Benjamin Y.N., Text. Res. J.69 (1999) 38.
[16] Ryu J., Kawamura H., Wakida T., Lee M., Sen-I Gakkaishi 48 (1992) 213.
[17] Boyd R.D., Kenwright A.M., Badyal J. P., Briggs S.D., Macromolecules 30 (1997) 5429.
[18] Oktem T.N., Seventekin H., Ayhan, Piskin E., Melliand Textil. 82 (2001) 190.
[19] Pane S., Tedesco R., Greger R., J. Ind. Text. 31 (2001) 135.
[20] Tschegolja A.S., Weiman E.J., Beder N.M., Mittschenko J. I., Mellinand Textil. Int. Text. Rep. 9 (1980) 1410.
[21] Yan-Chun Liu, Yan-Xiong, Da-Nian Lu, Appl. Surf. Sci. 252 (2006) 2960-2966.
[22] 22 Garamoon,A.A., and El-zeer,D.M., Plasma Sources Sci. Technol. **18** ,(2009) **3** 194–201.
[23] El-Shishtawy R.M., Ahmed NSE., Color Technol. (2005) ; 121:139 and references cited therein.
[24] Yoon, J., Mc Cord, M.G., Jae, S., & Bok,C.,Text.Res.J., **75**, 11, 771 (2005).
[25] AATCC, Technical Manual, Test Method, 39, (1971).
[26] Dohmyo, M., Shimizu, Y., & Kimura, M., J. Seric. Science, Japan., 54(4), 181-185 (1985).
[27] Garland, C.E., in 'Color Technology in Textile Chemistry; Ed. Gultekin Celikiz and K;ueni G., AATCC, PP 107-112, (1983).
[28] Kogelschatz, U., 2003 Dielectric-barrier discharges: their history, discharge physics, and industrial applications, *Plasma Chem. Plasma Processing* **23** 1–46
[29] Alexandre V., Chirokov, "Stability of Atmospheric Pressure Glow Discharges", A Thesis Submitted to the Faculty of Drexel University, 2005.
[30] Garamoon,A.A., and El-zeer,D.M., Plasma Sources Sci. Technol. **18** ,(2009) **3** 194–201
[31] Gherardi N., Gouda G., Gat E., Ricard A. and Massines F., Plasma Sources Sci. Technol., vol. 9, pp. 340-346, 2000.
[32] Chunying Wang, Chaoxia Wang, Fiber and Polymers (2010), 11, 2, 223-228.
[33] Chen Y.Y., Lin H., Ren Y., J. Zhejiang Uni. Sci., 8, (2004), 918.
[34] Bhat N.V., Benjamin Y.N., Textile Res. J., 69, (1999), 1, 38-42.
[35] Crossley J.A.A., Gibson C.Y., Mapledoram L.D., Huson M.G., Myhra S., Pham D.K., SofieldC.J., Turner P.S., Watson G.S., 31,(2000), 6, 659-667.
[36] Shishoo, R., "Plasma technologies for textiles", Woodhead Publishing Limited, USA, P. 6, 264 (2007).
[37] Qufu W., Yingying W., Xueqian W., Fenglin H., Shengwei Y., J. Appl. Poly. Sci., 106, (2007), 1243-1247.
[38] Sun Y.Y., Shao Z.Z., Ma M.H., Hu P., Liu Y.S., Yu T.Y., J. Appl.Polm. Sci., 65,(1997) 959.
[39] Wang C.X., Qiu Y.P., Surf. Coot. Technol., 201, (2007), 6273.
[40] J. R. Hollahan and A. T. Bell, "Techniques and applications of plasma chemistry", A Wiley Interscience publication, New York, USA, (1947).