Surface Modification of Polestar Fabrics by Non-thermal Plasma for Improving Hydrophilic Properties

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Abstract: Polyester fabrics are exposed to glow discharge plasma and the physical and chemical properties of the fabrics were studied. From the vertical dragging analysis, hydrophilic properties of fabrics are improved after the plasma treatment. Group concentration and atomic concentration of the fabric was studied from an X-ray photoelectron spectroscopy and it is seen that the polar groups are increased after plasma treatment. These increasing polar groups are used for improvement of hydrophilic properties of fabrics. Surface analysis was studied using scanning electron microscope.

Keywords: Plasma, Polyester, Polar groups, Hydrophilic, X-ray photoelectron spectroscopy

1 INTRODUCTION

Polymers are applied widely in modern industry and have many obvious advantages. However, bonding and finishing of many polymers present a problem due to the low hydrophilicity of their surfaces because it affects the wettability, printability, colorability, biocompatibility, adhesion, antifogging, anti-electrostatic properties etc., A number of methods have been devised and are commercially used to modify the polymer surface.

The improvement on the wettability of polymeric materials can be obtained by an increase in the surface energy through a chemical or physical activation, which can be done, for instance, by inserting polymeric samples in plasma of gases such as oxygen, hydrogen and nitrogen. Plasma is produced when a gas at low pressure at room temperature is subjected to an electric field. The result is an atmosphere full of ions, atoms, molecules and free radicals. One of the main effects of the interaction between active chemical species due to the plasma colliding with a polymeric surface is the breaking of molecular chain, the formation of new functional groups and morphological alteration, like the formation of micro porosity [2]

Hydrophilic and hydrophobic are clearly related to physico-chemical properties of a fiber surface layer. Textile produced by poly (ethylene terephthalate) fibers cannot usually absorb moisture and be dyed at one atmosphere owing to the high degree of crystalline density and lack of functional polar groups on the fibers surface such as (-COOH) and (-OH). This causes the fiber to have low surface free energy and poor wettability. Surface modification is usually used to roughen fiber surface to enhance mechanical interlocking and form chemical groups on the surface that improve wetting and/ or chemical bonding.

Low temperature plasma has already been used by industry for the treatment of metal and polymer materials. Plasma processes alter the physico-chemical properties of the polymer surface. They improve polymer hydrophilicity, conductivity, adhesion or biocompatibility. Many researchers explained that the improvement of hydrophilicity was induced by formation of new oxygen- containing groups on the surface, such as (–OH), (-OOH), etc. because these groups are hydrophilic [3-5].

The capillary rise method was applied to evaluate the improvement in water uptake of polyester and acrylic fabrics obtained by plasma treatment. Discharge power, exposure time and gas type (nitrogen, air and oxygen) were considered as plasma variable [12]. In this paper, the relations between polar groups and hydrophilic properties by XPS analysis have been investigated.

2 MATERIALS AND METHODOLOGY

The raw material was 100% polyester. Initially the samples were prepared by cutting the fabric into strips measuring 5x5 cm, after that each one was fixed in the sample holder in the interior of the chamber by using an adjustable rod, so that the fabric could be with in a distance of 1cm from the cathode. This distance was proved to be adequate to avoid some thermal alteration in the fabric during the plasma processing.

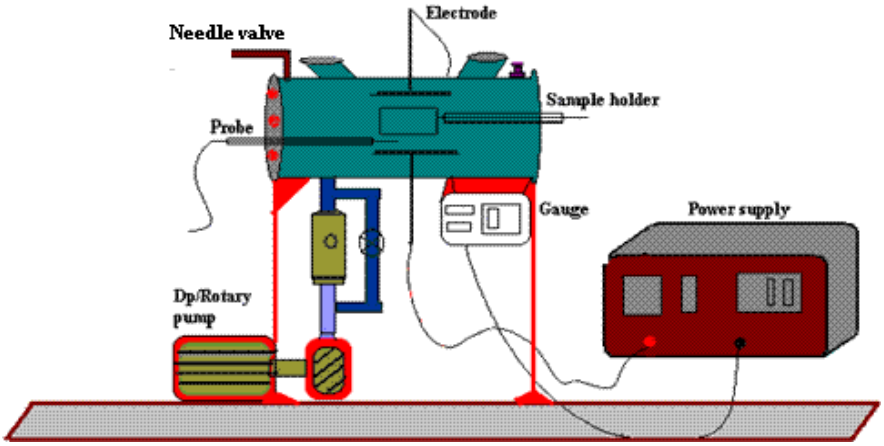

Fig. 1 Schematic for Plasma chamber

The plasma system (Fig. 1) consists mainly of a plasma chamber, a vacuum system, a power supply, one electrode is permanently fixed and another one is movable to maintain a particular distance between the electrodes. A pressure of 0.2 mb is maintained inside the chamber using Wilson joints. A D.C voltage of about 300V is applied between the electrodes. Pressure is measured using a pirani gauge. The fabric is exposed to plasma for a particular time. The experiment is repeated for 325V, 350V, 375V and 400V respectively. Before putting the fabric sample into the plasma, the chamber was cleaned by first distilled water and acetone. Any oxide formation on the electrode was cleaned using an alkali. The electrodes and substrate holder were cleaned by a discharge current of about 1 μA for about 15 minutes.

2.1 Wettability Measurements (Vertical Drag Method)

Low temperature plasma treatment is known as one of the well-recognized and effective means of improving the surface wettabilities of many polymeric surfaces. The improved wettability has been attributed to increasing surface roughness. After plasma treatment, the polyester samples were submitted to wettability test. A simple wettability test can be performed on a fabric strip kept vertically with the lower end immersed in dye solution in a small beaker. The time required for the vertical advancement of each centimeter of the solution was measured, and the results were expressed in the graphical form.

2.2 XPS Measurements

XPS analysis is used to determine the chemical changes on the PET surfaces introduced by plasma treatment. XPS measurements are carried out on a VG Escalab 220 XL system (Thermo Fisher Scientific – USA), using non-monochromatic Mg K□-radiation ($h\nu$ = 1253.6 eV) operated at 15 kV and 20 mA. The angle between the photoelectron emission direction and the plane of the sample is kept constant at 90°. The pressure in the analysing chamber is maintained at 10-7 Pa or lower during analysis and the size of the analysed area is 8 mm x 8 mm . The high-resolution spectra are taken in the constant analyser energy mode with a 40 eV pass energy and the value of 285.0 eV of the C1s core level is used for calibration of the energy scale. Curve fitting of the C1s peak is done using XPS peak 4.1software.

2.3 Surface Morphology Analysis

The morphology of modified and unmodified PET fiber was observed by (model JEOLJSM-J330A) scanning electron microscope. The samples were mounted and gold sputtered to give the samples electronic conductivity under vacuum (prior to bservation).

3 RESULTS AND DISCUSSION

3.1 Probe Measurements

The electron density and electron temperature of plasma plays an important role in surface modification of textile fabrics. A potential of 350 V is applied to the electrodes and the pressure inside the chamber is maintained at 0.3 mb. The electron temperature is measured from I -V characteristics (Fig. 2(a)), the slop of the curve (Fig2. (b)) 0.7854. The electron temperature is calculated from the equation T_e = (e/K)/ slope. From the equation the electron temperature is 1.345 eV and the electron density calculated is 12.9×10^{9} cm^{-3}.

3.2 Hydrophilic Behavior

By wettability test, the vertical dragging method, it was possible to quantify the wettability behavior of the treated fabric by measuring the time required for the solution to advance vertically each centimeter of the sample (Fig. 2). It can be observed from the graph that all samples treated with plasma had a substantial improvement in their wettability when compared with the non- treated one. The wettability

increased due to the upper surface of the polymers being etched by plasma process and due to radicals of the air plasma contents.

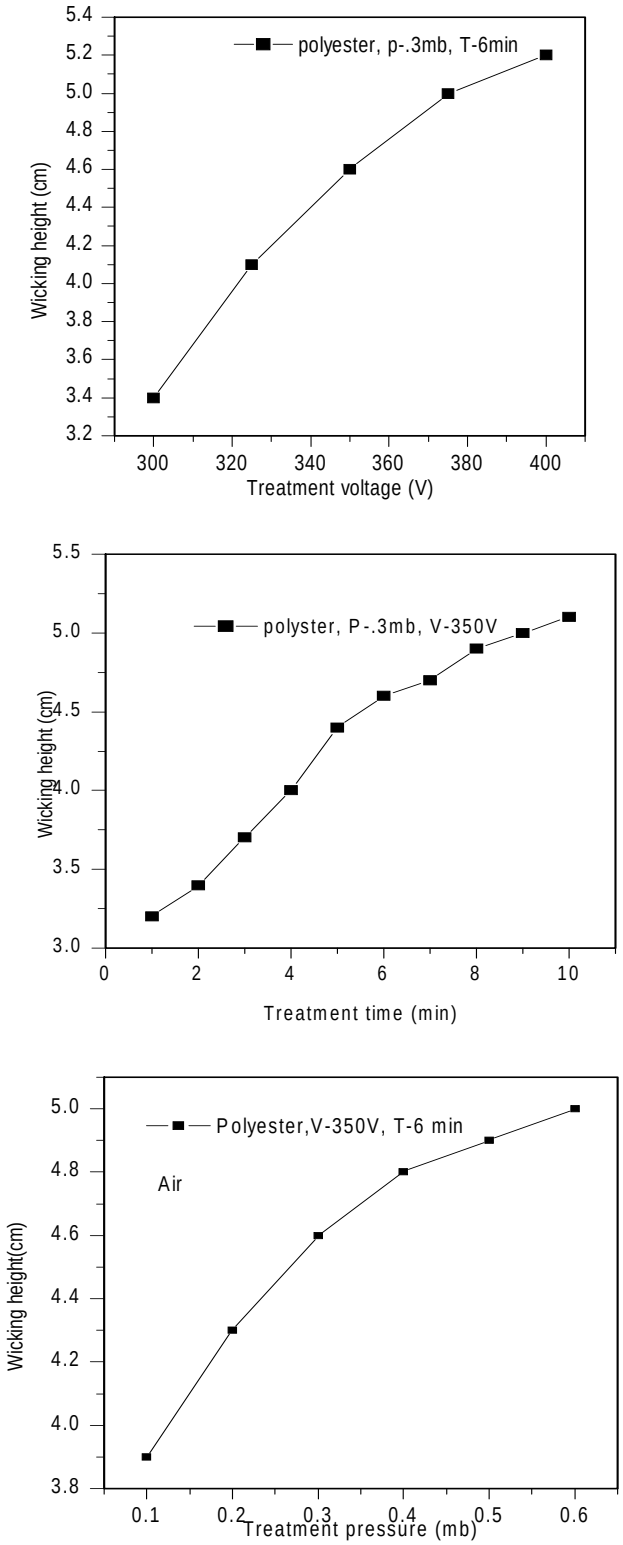

Fig. 2 Wettability analysis of polyester fabric

When the gas pressure was increased, the number of collisions between the charged particles and the neutral atoms increases inside the discharge tube, leading to an increase of electron density. These electrons loose more of their energy in the collisions, so, the electron temperature decreases, i.e, increasing the gas pressure increases the electron density and decreases the electron temperature at the same time. The best surface treatment of polymers is obtained with high plasma density and low energy of electrons or ions, so, that the wettability of the polyester samples increases by increasing the gas pressure [13].

The increase in surface wettability noticed, may be because of the formation of several hydrophilic polar groups such as C-O and O-C=O. The fictionalization in the form of these groups has also been confirmed by XPS analysis. The effect of plasma treatment conditions on the absorbency of the fabric tested by wicking height is shown in Table 1. From the table it is understood that increasing the time and pressure of plasma treatment reduces the wetting time significantly, i.e. improves absorbency.

The improved wettability due to plasma treatment is attributed to increase in amount of polar groups, surface oxidation. The plasma exposure time and pressure are very critical factor, which determines the wettability

The improvement in wettability was also confirmed by Wickability test in terms of wicking height. While untreated polyester fabric showed a wicking height of 1.2 cm (which is depends upon the fabrics warf and weft). The plasma treated (0.5 mbar, 5 mins) showed a wicking height of 4.9 cm.

3.3 XPS analysis - Atomic Concentration

3.3.1 Untreated Polyester

The untreated polyester consisted of oxygen, calcium, carbon, chlorine and silican. The carbon concentration is high that is 81.975% of the sample. Atom 9c concentration of the oxygen is 15.033. Oxygen is second highest concentration of the polyester fabric. The calcium is 1.741 and chlorine, silicon are 0.318 and .933 respectively.

3.3.2 Plasma treated Polyester

Plasma treated (4 min) polyester fabric's carbon atomic concentration is 69.841 it is highest percentage of the fabric but ratio of the percentage is decreased after the plasma treatment from 81.975 to 69.841. And calcium is not presented. The oxygen atomic concentration is increased from15.033 to 21.298 due to plasma treatment. Silicon and chlorine atomic concentration are slightly increased after the plasma treatment. Also copper elements are presented its concentration is 3.188 which is highest concentration of the silicon, chlorine and fluorine. This is due to used copper electrode for plasma treatment. The copper particles are etched from the electrode and deposited on the surface of the

fabric. Copper atomic concentration is increasing with increasing plasma treatment time, which is verified by plasma treatment for cotton fabric using copper electrode.

3.4 Quantitative Data of the XPS Curve: Atomic Concentration (shown in Table 1, Fig. 3))

Table 1 Atomic concentration of treated and untreated polyester fabric

Peak	Untreated polyester		Treated polyester	
	Binding energy Centre (eV)	AT%	Binding energy Centre (eV)	AT%
O1s	532	15.033	531.8	21.298
Ca 2p	347.6	1.741	-----	----
C 1s	285	81.975	285	69.841
Cl 2p	198.2	0.318	198.9	2.89
Si 2p	102	0.933	103.1	1.298
Cu 2p3	------	------	933.4	3.188
F 1s	------	------	685	1.485

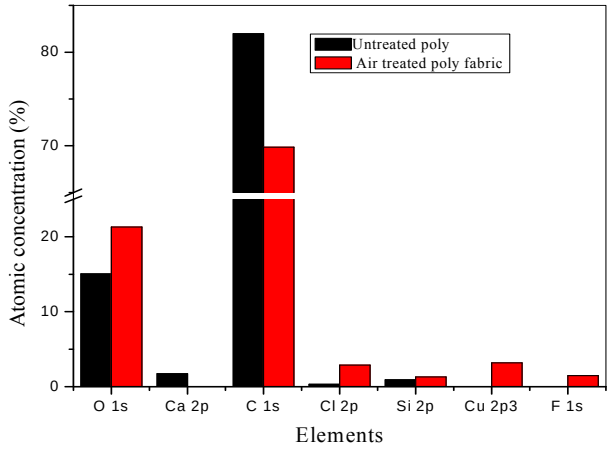

Fig. 3 Atomic concentration of polyester (PET)

3.5 Group Concentration (shown in Table 2)

The group concentration of C-C/C-H is 87.91 in untreated polyester fabric. The C-O and O-C=O concentrations are 6.05. After plasma treatment group concentration of C-C/C-H is decreased from 87.91 to 80.19 but C-O, O-C=O group's concentrations are increased. These increasing polar groups are used for increasing fabrics hydrophilic properties. From capillary rise methods, we are found that increasing wettability of plasma treated fabric so we are ironically said that this wettability property increases by increasing polar groups which is proved by XPS analysis (see Figs. 4-6).

Table 2 Group concentration of polyester (PET) from XPS curve

Group	Binding energy (eV)	Concentration (%)	
		Untreated polyester	Treated polyester
C-C/C-H	285	87.91	80.19
C-O	286.5	6.05	9.02
O-C=O	288.9	6.05	10.79

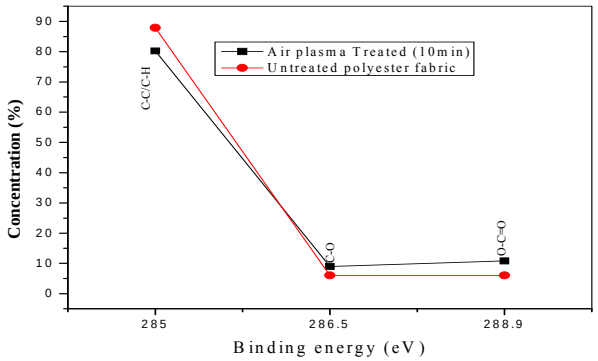

Fig. 4 Graph for group concentration of polyester (PET) from XPS curve

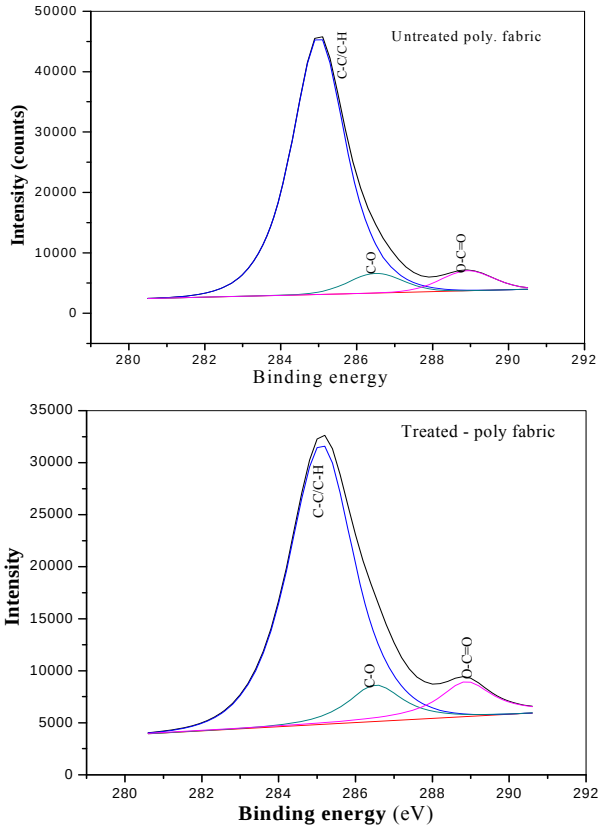

Fig. 5 XPS curve of polyester (PET)

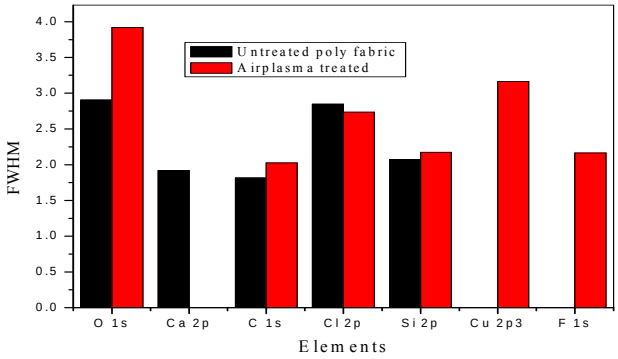

Fig. 6 FWHM diagram of the polyester from XPS data

3.6 Morphology Studies

One of the plasma-acting mechanisms is based on etching as a consequence of the impact of the gas plasma species on the polymer surface. This mechanism increases surface roughness and contributes to better surface wettability. It is possible to quantify the extent of etching caused by plasma treatment by simple weight loss analysis. Weight loss highly depends on the polymer structure and the reactivity of the gas used for the plasma treatment [10]. Degradation of the Polymeric surface leads to a small modification of the surface morphology by increasing the surface roughness [11].

Fig. 7 shows photographs obtained through electron scanning electron microscope of treated samples fibers, as well as the non – treated one. It is clear that the treated samples suffered morphological alteration on their surface, with the formation of fissures and pores, due to plasma etching and plasma particle attack on the sample surface by plasma treatment.

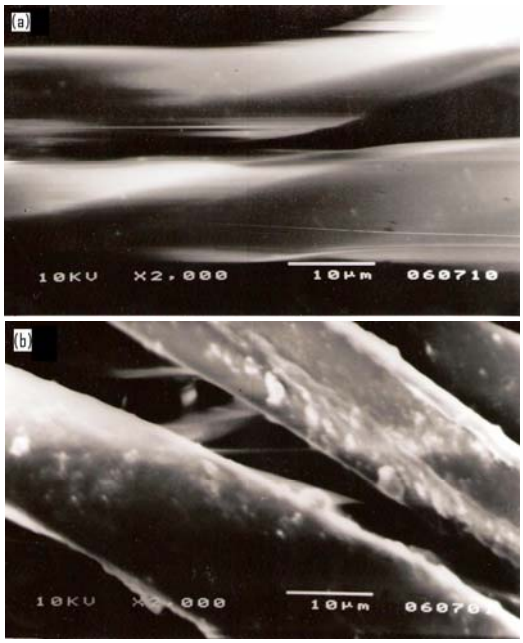

Fig. 7 SEM photograph of a) un treated b) treated polyester

4 CONCLUSIONS

Plasma treatment greatly enhances polar contributions to solid surface energy values and it is indicated that one of the most important plasma mechanism is surface activation due to the formation of polar groups as it can be seen from XPS observations.

Surface performance of plasma treated polyester fabrics have been studied morphologically, chemically and physically. Exposing polyester fabrics to low temperature plasma caused changes in surface geometrical roughness. Rougher fabric surface is important in the conventional aqueous textile finishing and dyeing processing because of higher rate of liquid uptake. It is expected that this technology is being used different branches of the industries.

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