Evaluation of IR Spectral Analysis and Dyeing Parameters for Plasma and /or Nano-Silver Treatments of Polyester and Nylon Fabrics

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ABSTRACT

In our work of this paper, we study the effect of surface modification of polyester and nylon fabrics induced by DC plasma discharge and/ or nano-siliver treatments .DC plasma discharge was employed at first, as a function of plasma device parameters including different time, different current and different hydrostatic pressure using chemically inert working gas: argon or nitrogen. Optimization of the performance of the applied DC plasma discharge with various applied conditions were performed using Fourier Transform Infra-Red (FTIR) Spectroscopy spectral analysis, by following up the changes in the peak intensity values of the characteristic functional groups that characterize polyester fabric. Then the dyeing properties of different pretreated fabrics with plasma by the best conditions are subjected to nano-silver treatment by concentration 50 ppm under the effect of different dye concentrations, different dyeing temperature and different dyeing time. Finally, the fastness properties to light and washing for the treated samples were studied. The results obtained showed that both of the dyeing parameters and fastness properties were highly improved by the treatment of fabrics by either individual plasma treatment or combined DC cold plasma and nano-silver treatments.

Keywords: Nano-siliver treatments; DC plasma discharge; argon; nitrogen; polyester; nylon; Fourier Transform Infra-Red (FTIR) spectroscopy; dyeing parameters and fastness properties.

INTRODUCTION

The pre-treatment and finishing of textiles by non-thermal plasma technologies becomes more and more popular as a surface modification technique. A non-thermal (or cold or low temperature) plasma is a partially ionized gas with electron temperatures much higher than ion temperatures. The high-energy electrons and low-energy molecular species can initiate reactions in the plasma volume without excessive heat causing substrate degradation. Non-thermal plasmas are particularly suited to apply to textile processing because most textile materials are heat sensitive polymer[1].This treatment does not require the use of water and chemicals, resulting in a more economical and ecological process. Knowledge of plasma characteristics is required to understand fully the effects of the different physical processes taking place in the plasma pretreatment and to deduce from them its properties [2] .The application of plasma treatments for improved wet-ability has been done on all possible fibre types, with varying success. It offers numerous advantages over the conventional chemical processes.

Nano-material is often defined as a material that is less than 100 nano-meters in at least one dimension, as one nanometer is a millionth of a millimeter, or a billionth of a meter. Nano-materials may be either entirely new chemical structures or already known chemical structures at a smaller scale [3]. As a result of their small size, nano-materials may have entirely different properties and functions. Nanotechnology is concerned with forming and using these small structures. Most of the presented methods [4] for stabilizing of inorganic nano-structured materials on the textile surfaces need several steps of preparation, functionalization, final treatment, drying, curing and so on. This is forced high cost and it is very time consuming for high-scale manufacturing production [5].

Many treatments were conducted using "silver", it was then called "high-tech", as well as the high pricing. However, the amount of silver should not exceed a certain level for it may cause harmful effects. Many investigations[6] concerned the treatment of textile surfaces using silver-nano-particles, where they applied new method to stabilize nano-silver on the textile surfaces for gaining permanent antibacterial activity, where, silver is a safer antibacterial agent in comparison with some possible organic antibacterial ones that have been avoided because of the risk of their harmful effects on the human body. When germs of many kinds approached silver-nano-particles, it has the characteristic of easy combining and entering the cell. After the penetration, it will rapidly combine with sulfur and hydrogen based molecule to stop germs from repopulation. In addition, silver-nano-particles kills gems and they are different from traditional antibiotic medical supplies. It will not kill normal molecules, and will left those good cells intact after leaving a human body. Therefore, silver-nano-particles is naturally safe to all living bodies [7].

Polyethylene terephthalate polyester is the leading man-made fiber in production volume and owns its popularity to its versatility alone or as a blended fiber in textile structures. PET is formed through [2] step growth polymerization of terephthalic acid or dimethyl terephthalate with ethylene glycol in the presence of a catalyst at 250°-300°C as in **Figure 1**, The formed degree of polymerization of 80-100.
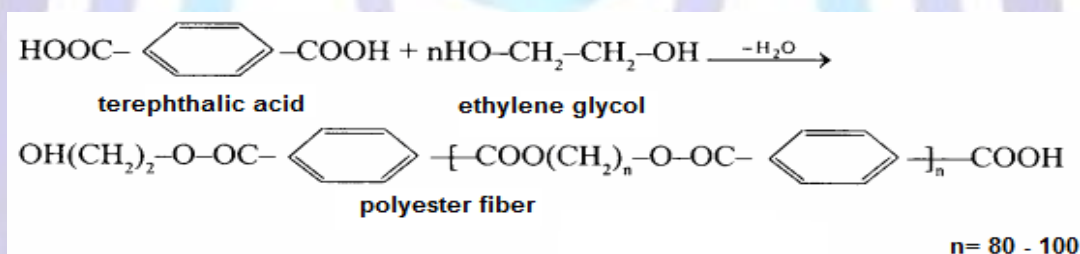

Figure (1): Polyester Formation

Nylon 6,6 is produced by the melt polycondensation of adipic acid and hexamethylene diamine as represented schematically in **Figure (2)**. In melt poly condensation an aqueous salt solution is first prepared from adipic acid and hexamethylene diamine in stoichiometric amounts. The salt solution is heated to remove most of water, further heating under pressure to 275°C gives a pre-polymer of 4000 molecular weight [8] .The pressure is released slowly to eliminate the water from the reaction, while the polymerization is completed at 275°C.
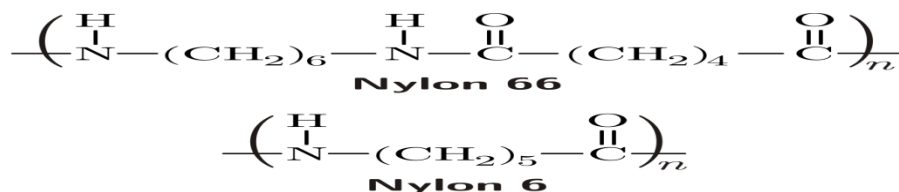

Figure (2): Chemical structure of nylon 6 and nylon 6,6 manufacture

It is well known that the dyeing of synthetic fabrics depends mainly on the nature, chemical and physical properties of substrate and dye applied. Also other factors such as temperature ,time of dyeing and dispersing agents added contribute considerably to the dyeing process [9]. These specific features of the structure and properties of the synthetic fiber render their interaction with dye extremely difficult while allowing their dyeing with disperses dyes [10]. While Nylon 6 possessing

charged amino groups (NH$_2^+$) can be readily dyed with disperse dyes especially those containing sulphonic acid groups[11]. In recent years the process of dyeing with disperse dyes has been extensively studied. Early workers carried out some experiments and showed the mechanism of adsorption of disperse dyes by nylon .It was concluded that adsorption of this substrate is similar to that on cellulose acetate. Disperse dyes provide the simplest and the most direct way of dyeing polyamide and related fibers[12]. They possess the property of covering yarn irregularities better than any other class of dye.

Disperse dyes are traditionally non-ionic chemicals with sparing solubility in water which, consequently, are able to retain comparatively better substantivity for hydrophobic fibres, such as polyester, nylon and acetate. For the sake of efficient diffusion into textiles, the particles of disperse dye should be as fine as possible comprising low molecular weight molecules in the range of 400 – 600. It is essential for disperse dyes to be able to withstand various dyeing conditions, pH and temperature, resulting in negligible changes in shade and fastness. Disperse dyes are often substituted azo, anthraquinone or diphenylamine compounds which are non-ionic and contain no water solubilising groups. The dye particles are thus held in dispersion by the surface-active agent and the dyes themselves are called disperse dyes. They are marketed in the form of either an easily dispersible powder or a concentrated aqueous dispersion and are now the main class of dye for certain synthetic fibres. These dyes are applied from dye-bath containing dispersing agent   and desired dye, in particular, in polyester dyeing the dye –bath must contain acetic acid and a carrier, where this carrier modifies the physical structure of the polyester fiber in such a way that increases dye-uptake and hence accelerates the rate of dyeing [13].

The present work in this paper has focused on evaluating the effect of three different treatments on polyester and nylon fabrics, which are: plasma pretreatments using (Ar or N$_2$) ,silver-nano-particles with different concentrations, and finally ,plasma pretreatments with best conditions combined with silver-nano-particles treatments. The work will be studied in view of fourier transform infrared spectroscopic analysis and dyeing properties of different treated fabrics.

EXPERMENTAL WORK

1) Materials and chemicals

- Woven Polyester fabrics 108 g/m^2 is provided by OUF Son's Company, Cairo. Polyester samples 7.5 cm in diameter were cut from a large piece and fully washed and dried at 80° C .

- Nylon 6 provided by "OUF" son's Company, Cairo. The samples where prepared in the same way like polyester fabric.

- Nano-sized silver powder metal based on size <100mm, 99.5% producing by Aldrich company.

- Disperse dye: disperse red TS-5BL C.I 167 is obtained from Jihua dyes company, China.

2) Instrumentation for plasma production

This instrumentation that used for plasma production to set-up of exposing polyester and nylon textile surface to nitrogen or argon plasma was clearly stated in our previous published work [14]. The pre-washed samples were exposed to DC pseudo plasma discharge treatments employing chemically inert argon or nitrogen as working gases with different electric current, different pressures and different times.

3) Treatment by using nano-sized silver

 Coating the silver nanoparticles on polyester and nylon fabrics surface pretreated with plasma at optimum conditions with solutions of silver nanoparticles of two concentrations (25-50 ppm.) The conditions for the application of silver nanoparticles by an exhaust method were established to be: an acidic pH of 4, a temperature of 40◦C, and a time of 20-30 minutes [14].

4) Dyeing of treated fabrics

Argon plasma treated polyester and nylon samples were separately dyed in a laboratory dyeing apparatus using the conventional exhaustion dyeing method [15], with liquor ratio 1:50. Polyester and nylon samples dyed separately with disperse dye (disperse red TS-5BL C.I. 167) the dyeing -bath contains the following in one litter: 4.0 g/l methylnaphthalene carrier , 1.0 ml dispersing agent, and 1.0 ml acetic acid (pH = 5 ~ 5.5). The dyeing method was carried at three different temperatures of (40 - 80 - 100◦c) for different times of (30 - 60 - 90 - 120 minutes) and different concentrations (0.05 - 0.5 - 1 -1.5 – 2) g of disperse dye. Finally; the samples were removed and washed with tap water and dried at ambient temperature.

5) Characterization of the applied treatments

5.1) Fourier Transform Infrared (FTIR) spectroscopic analysis

The IR spectra of the treated and untreated samples were measured by using Nicolet 380 (FTIR) Spectrometer, USA, in the wavelength range 4000-500 cm^{-1}. The changes in the contents of some chemical groups for each sample were monitored with absorbed IR selected bands [16].

5.2) Dyeing Properties

5.2.a) Color strength (K/S) determination

The Color Strength (K/S) values of the different examined dyed samples are determined from the reflection spectra measurements at the proper wave length of the used disperse dye (C.I. 167) according to kubilka Munk equation [17] using color eye 3100 spectrophotometer SDL, England.

5.2.b) Evaluation of fastness properties

The fastness properties for different examined dyed samples were determined to washing according to AATCC standard method [18]. Also the fastness to light was performed according to standard method of testing [19] using Tera's Light Fastness Tester [20].

RESULTS and DISCUSSION

1. Optimization of plasma treated polyester via fourier transform infra-red (FTIR) spectroscopy

Infrared radiation ranges from about 10.0000 – 100 cm^{-1} is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption vibration spectra appears as bands rather than as lines because a single vibration energy change is accompanied by a number of rotational vibrations particularly those occurring between 4000 and 400 cm^{-1} .There are two types of molecular vibrations [16] involving : stretching and bending, where, stretching vibration is a rhythmical movement along the bond axis resulting in an increase or decrease of the interatomic distance. While, bending vibration resulting from a change in the bond angle between bonds with a common atom. Only, those vibrations that result in a rhythmical change in the dipole moment of the molecule are observed in the IR spectra, thus only asymmetric stretching which result in changing in the dipole moment is IR active and is a point of interest [21]. The frequency or wavelength of absorption depends on the relative mass of the atoms, its geometry and the force constant of the bonds. Fourier transform infrared (FTIR) spectroscopic technique has been employed [22] to study the effect of varying plasma exposure parameters argon or nitrogen plasma treatments for different exposure periods , different exposure pressures and different exposure currents on the behavior of different functional groups that characterize polyester fabric. **Figure (3)** represents the infrared absorption spectra of the blank untreated polyester fabric as a function of wave number in the range from 4000-500 cm^{-1}.
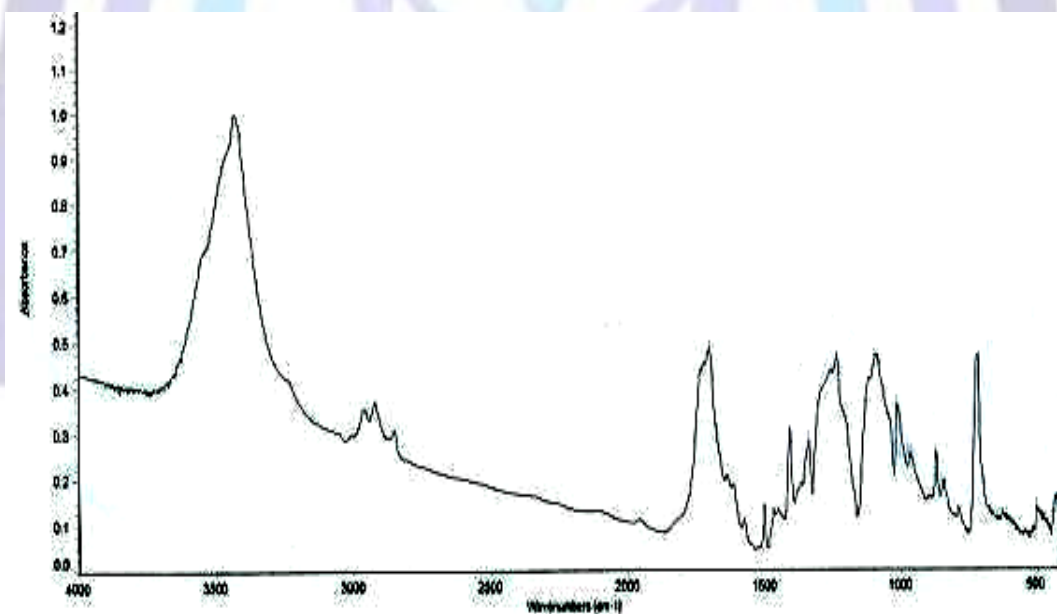

Figure 3: FTIR diagram of blank polyester fabric.

1.1. FTIR-spectroscopy of polyester fabrics exposed to nitrogen plasma

Tables (1-3) and **Figures 4(a-e)** ,**5(a-d) and 6(a-e)**   represent the changes in peak intensity values of the major absorption bands of different functional groups exist in polyester fabrics that exposed to nitrogen plasma for different exposure periods (15 -30 - 45 - 60 and 120 Seconds) , different exposure pressures (0.2 – 0.3 – 0.4 and 0.6 Torr) and different exposure currents (40 – 50 – 60 – 75 and 90 mA.) respectively. These groups are: CH$_2$-anti-symmetric stretching

at v_{CH2} = 2945 cm^{-1}, carbonyl bond stretching at $v_{c=o}$ = 1725 cm^{-1}, standard absorption OH- band stretching at v_{OH}^- = 1410 cm^{-1}, CH-stretching second overtone at v_{CH} = 1143 cm^{-1}, O-CH$_2$ stretching at v_{O-CH2} = 973 cm^{-1}, and benzenoid group at $v_{benzenoid}$ = 868 cm^{-1}.

It is clear that in the case of treatment with nitrogen plasma for different exposure times, there is a gradual increase in peak intensity values of these groups reaching maximum increase at 45 seconds exposure by about: 35%, 99.8 %, 114 %, 79.4% and 148.2% relative to their initial values respectively for the studied groups: CH$_2$-anti- symmetric stretching, carbonyl bond stretching, hydroxyl, CH-stretching second overtone, and benzenoid group respectively. The signal represents O-CH$_2$ stretching, its intensity increases at 120 seconds by a maximum increase of about 61%relative to its initial values.

But, in the case of treatment with nitrogen plasma for different exposure pressures, there is a gradual increase in peak intensity values of these groups reaching maximum increse at 0.4 Torr. exposure by about: 145.7 % , 118 %, 180 %, 110% and 144.5% and 218% relative to their initial values respectively.for; CH$_2$-anti-symmetric stretching, carbonyl bond stretching, hydroxyl, CH-stretching second overtone, O-CH$_2$ stretching and benzenoid group respectively.

Finally , in the case of treatment with nitrogen plasma for different exposure currents, there is a gradual increase in peak intensity values of these groups reaching maximum increse at 75 mA. exposure by about: 145.7 % , 118 %, 180 %, 110% and 144.5% and 218% relative to their initial values respectively.for; CH$_2$-anti-symmetric stretching, carbonyl bond stretching, hydroxyl, CH-stretching second overtone, O-CH$_2$ stretching and benzenoid group respectively.

Table (1): The changes in the peak intensity values with nitrogen plasma exposure times for different functional groups exist in polyester fabrics.

Groups Exposure time (seconds)	CH$_2$-antisymmetric stretching (2945 cm^{-1})	C=O anti-symmetric stretching (1725 cm^{-1})	Standard absorption -OH band (1410cm^{-1})	C-H Stretching second overtone (1143 cm^{-1})	O-CH$_2$ Stretching (973 cm^{-1})	Benzenoid group (868 cm^{-1})
0(blank)	0.368	0.479	0.307	0.470	0.360	0.255
15	0.114	0.606	0.403	0.722	0.457	0.485
30	0.183	0.633	0.416	0.721	0.451	0.501
45	0.496	0.957	0.657	0.843	0.547	0.633
60	0.351	0.833	0.475	0.818	0.433	0.495
120	0.368	0.666	0.503	0.742	0.579	0.502

Figure (4) a :FTIR Diagram of Nitrogen plasma treated polyester fabric at (15) Seconds

Figure (4) b: FTIR Diagram of Nitrogen plasma treated polyester fabric at (30) Seconds
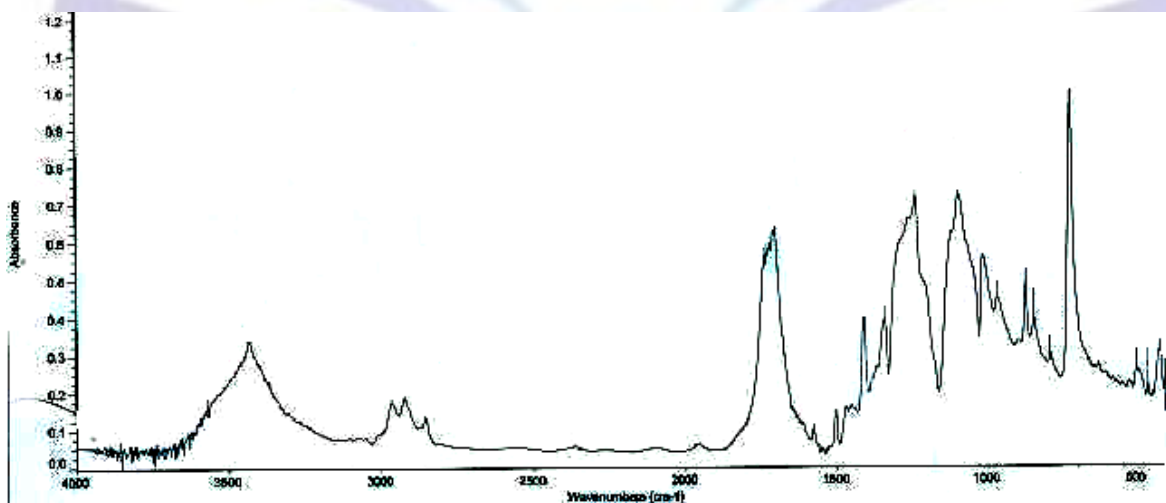

Figure (4) c: FTIR Diagram of Nitrogen plasma treated polyester fabric at (45) Seconds
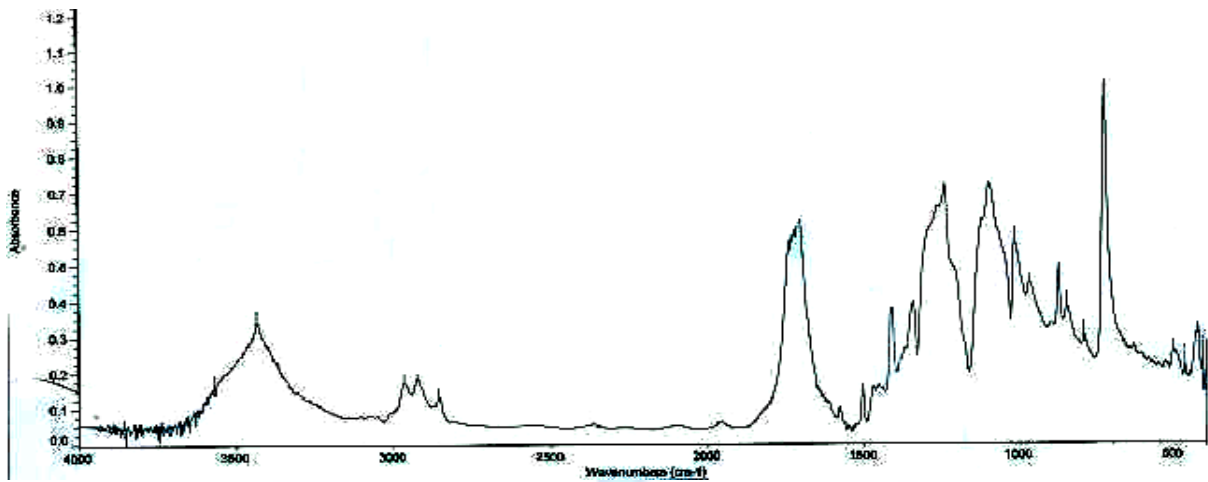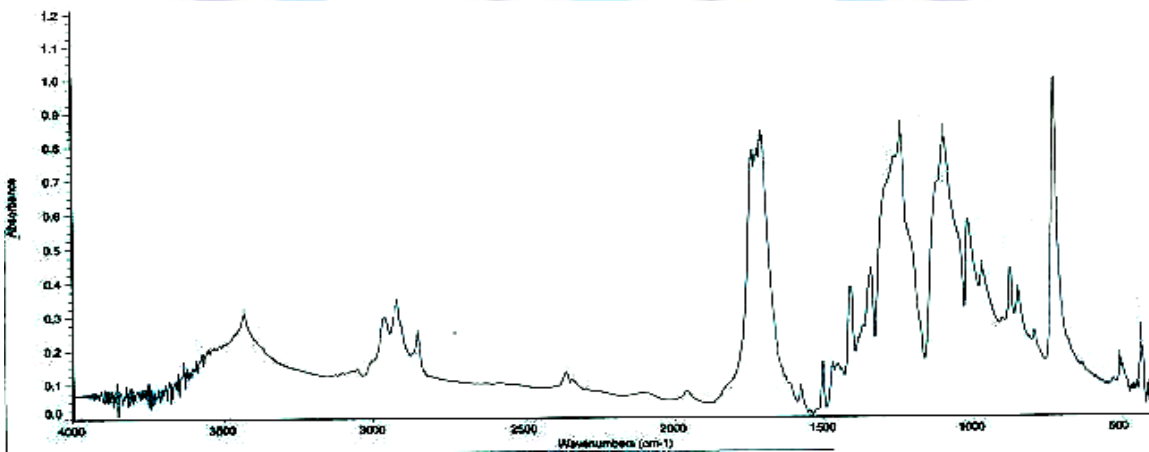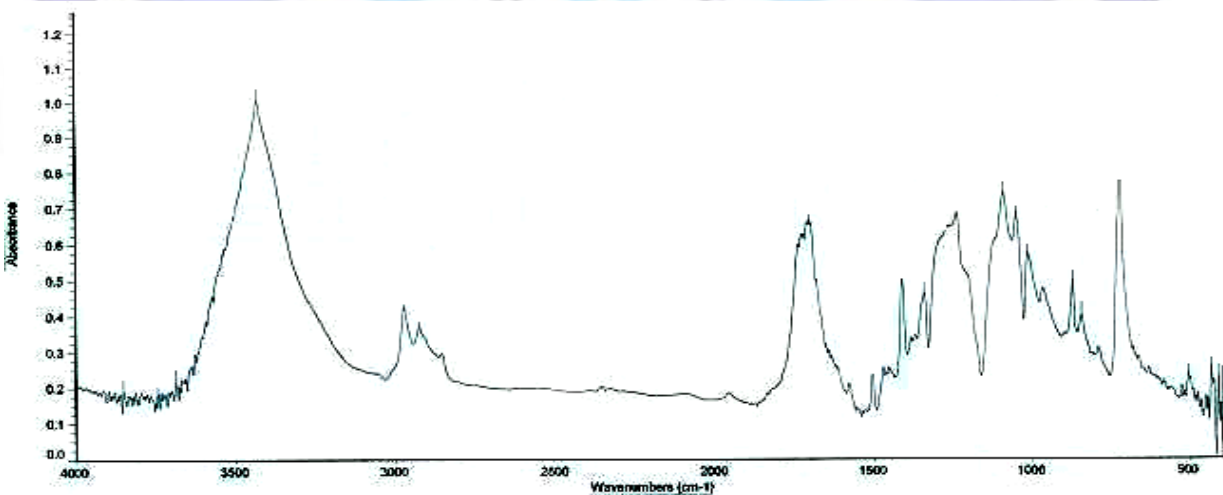

Figure (4) d: FTIR Diagram of Nitrogen plasma treated polyester fabric at (60) Seconds
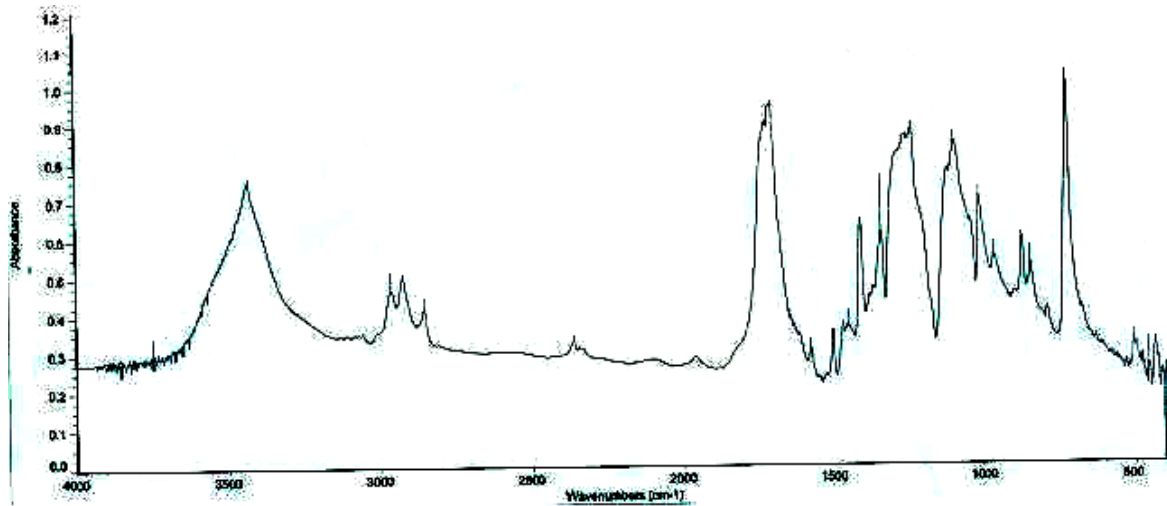
igure (4) e: FTIR Diagram of Nitrogen plasma treated polyester fabric at (120) Seconds

Table (2): The changes in the peak intensity values with nitrogen plasma exposure pressure for different functional groups exist in polyester fabrics.

Groups Pressure (Torr)	CH₂-antisymmetric stretching (2945 cm⁻¹)	C=O anti-symmetric stretching (1725 cm⁻¹)	Standard absorption-OH band (1410cm⁻¹)	C-H Stretching second overtone (1143 cm⁻¹)	O-CH₂ Stretching (973 cm⁻¹)	Benzenoid group (868 cm⁻¹)
0(blank)	0.368	0.479	0.307	0.470	0.360	0.255
0.2	0.442	0.830	0.602	0.845	0.709	0.629
0.3	0.511	0.882	0.651	0.884	0.749	0.660
0.4	0.904	1.044	0.860	0.987	0.880	0.811
0.6	0.499	0.892	0.650	0.843	0.703	0.636

Figure (5) a:FTIR Diagram of Nitrogen plasma treated polyester fabric at (0.2) Torr.

Figure (5) b: FTIR Diagram of Nitrogen plasma treated polyester fabric at (0.3) Torr.

Figure (5) c: FTIR Diagram of Nitrogen plasma treated polyester fabric at 0.4 Torr.
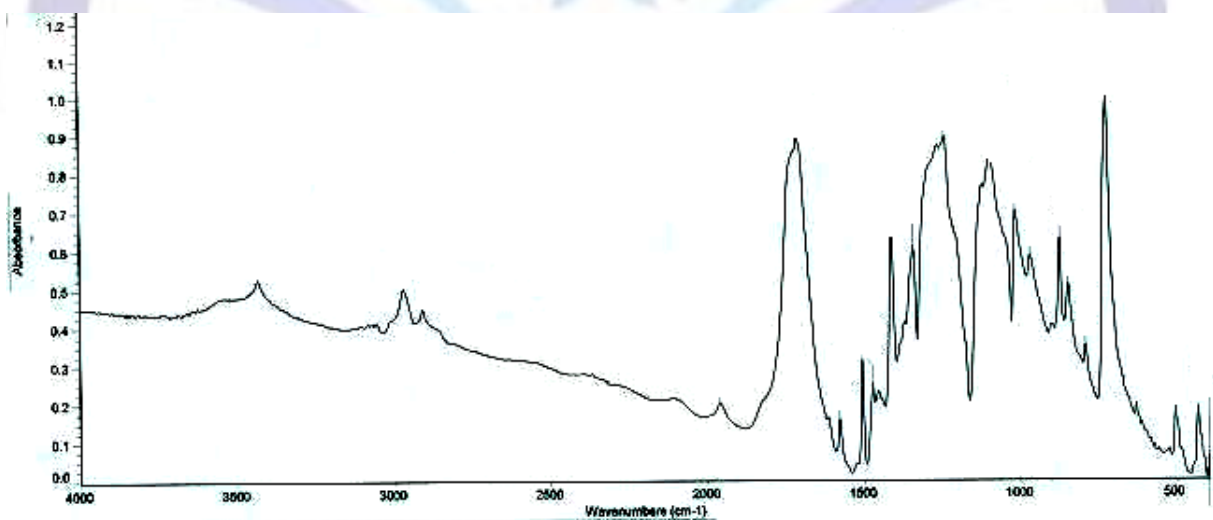
Figure (5) d: FTIR Diagram of Nitrogen plasma treated polyester fabric at 0.6 Torr.

Table (3): The changes in the peak intensity values with nitrogen plasma exposure currents for different functional groups exist in polyester fabrics.

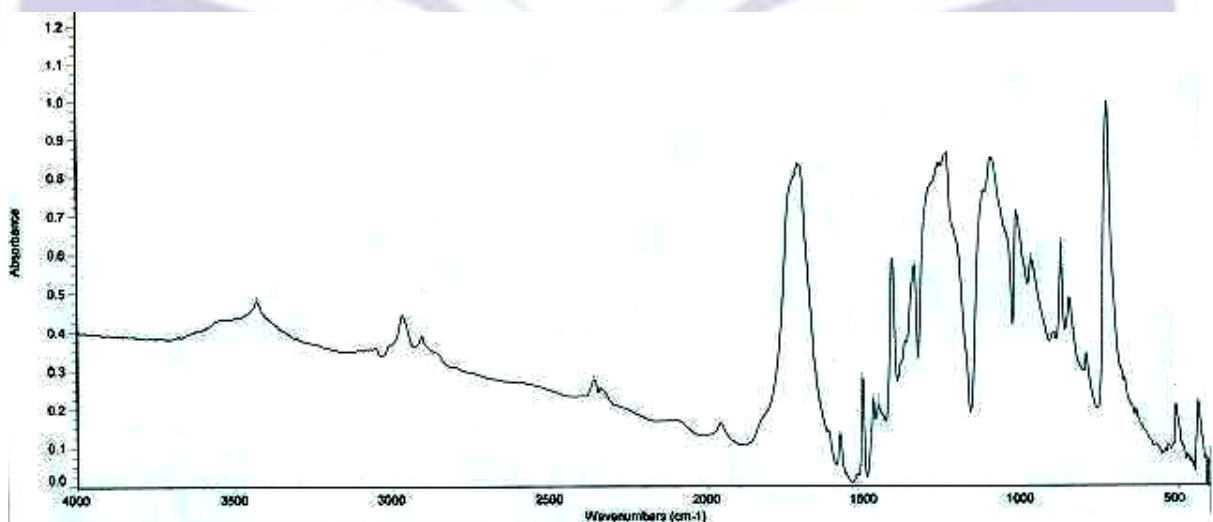| Groups Current (mA)	CH$_2$-antisymmetric stretching (2945 cm^{-1})	C=O anti-symmetric stretching (1725 cm^{-1})	Standard absorption-OH band (1410cm^{-1})	C-H Stretching second overtone (1143 cm^{-1})	O-CH$_2$ Stretching (973 cm^{-1})	Benzenoid group (868 cm^{-1})
0(blank)	0.368	0.479	0.307	0.470	0.360	0.255
40	0.458	0.840	0.601	0.835	0.677	0.603
50	0.527	0.877	0.675	0.857	0.739	0.676
60.	0.484	0.867	0.646	0.867	0.719	0.642
75	0.904	1.044	0.860	0.987	0.880	0.811
90	0.412	0.788	0.559	0.792	0.639	0.575

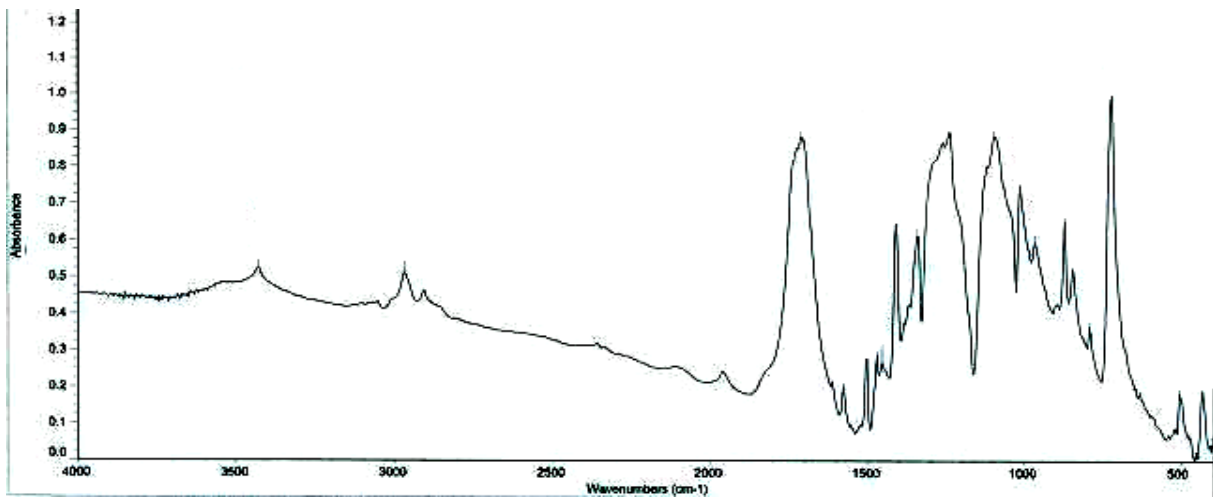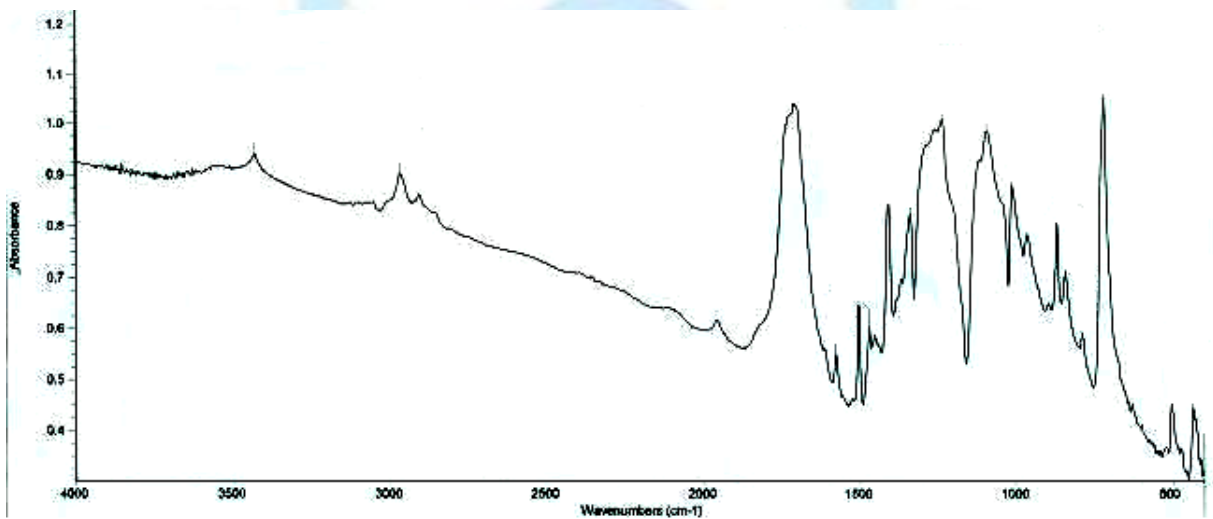**Figure (6) a: FTIR Diagram of nitrogen plasma treated polyester fabric at (40) mA.**

Figure (6) b: FTIR Diagram of nitrogen plasma treated polyester fabric at (50) mA.

Figure (6) c: FTIR Diagram of nitrogen plasma treated polyester fabric at (60) mA.

Figure (6) d :FTIR Diagram of Nitrogen plasma treated polyester fabric at (75) mA.

Figure (6) e :FTIR Diagram of Nitrogen plasma treated polyester fabric at (90) mA.

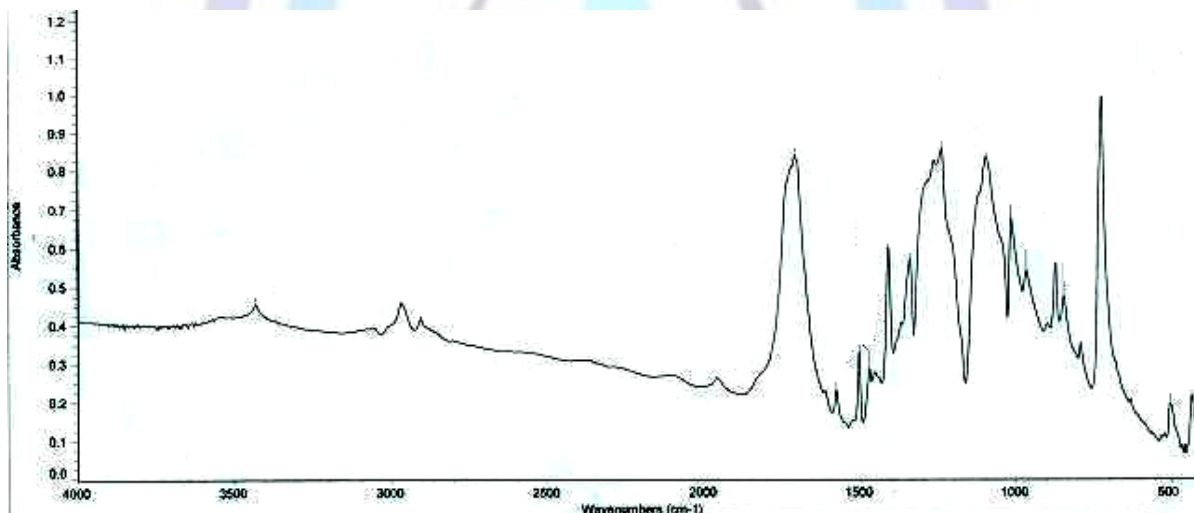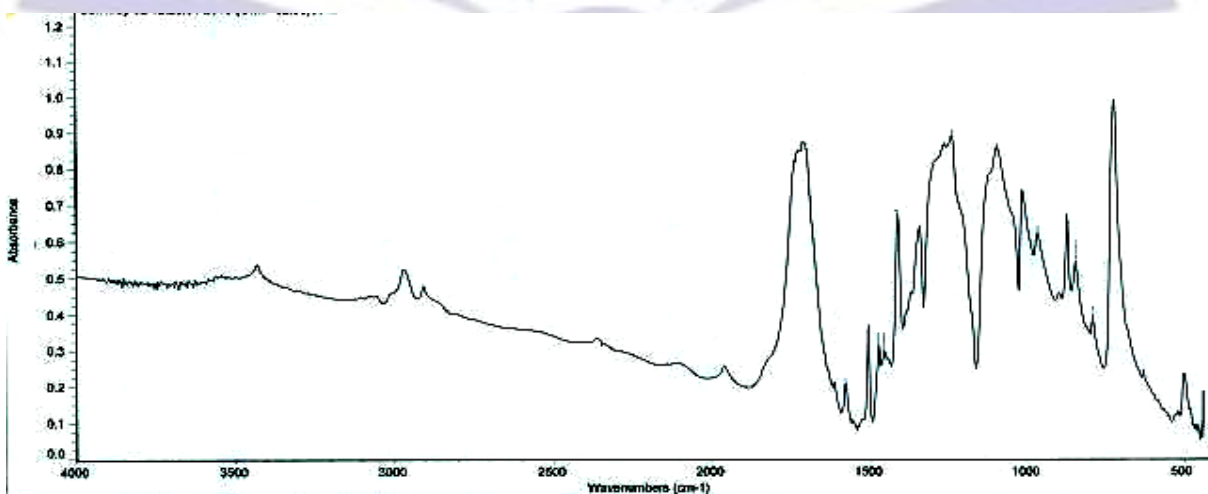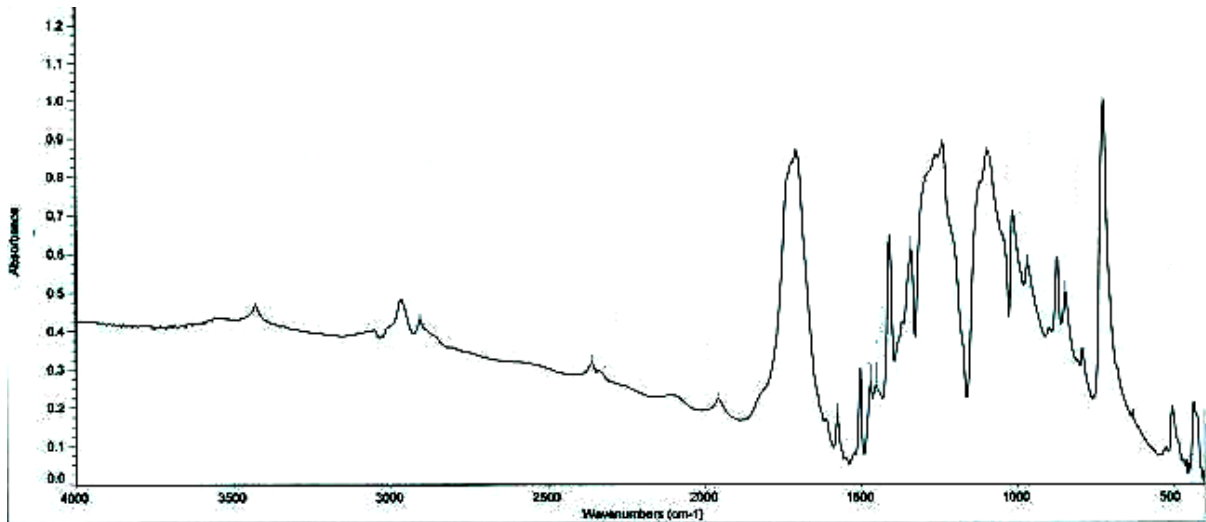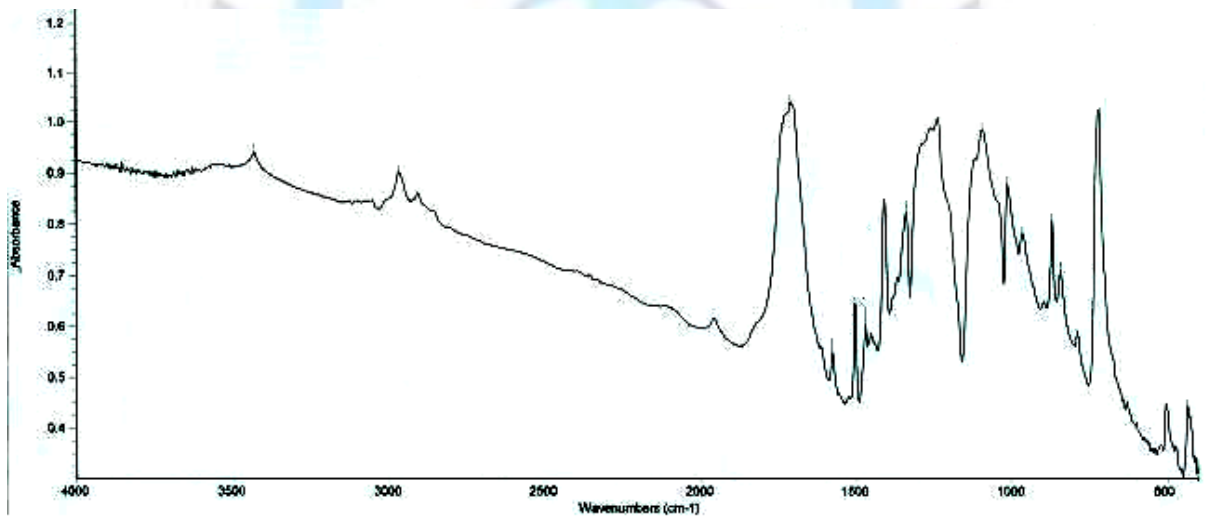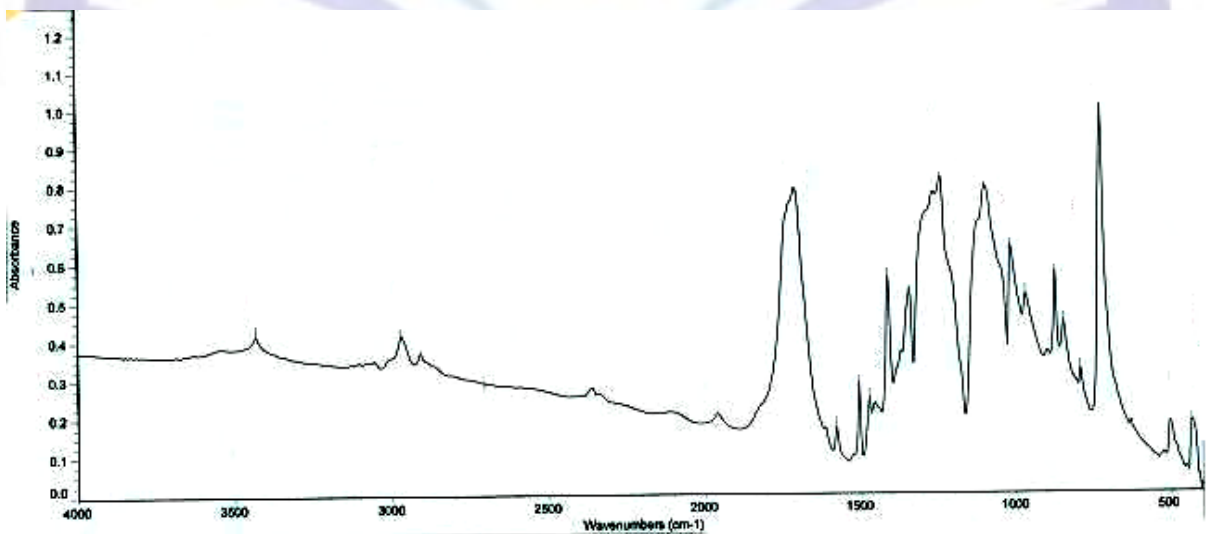## 1.2. FTIR-Spectroscopy of polyester fabrics exposed to argon plasma

Tables (4-6) and **Figures 7(a-e)** ,**8(a-d) and 9 (a-e)** represent the changes in peak intensity values of the major absorption bands of different functional groups exist in polyester fabrics that exposed to argon plasma for different exposure periods (15 -30 - 45 - 60 and 120 Seconds) , different exposure pressures (0.2 – 0.3 – 0.4 and 0.6 Torr) and different exposure currents (40 – 50 – 60 – 75 and 90 mA.).respectively that are: CH$_2$-anti-symmetric stretching at v $_{CH2}$ = 2945 cm^{-1}, carbonyl bond stretching at v$_{c=o}$ = 1725 cm^{-1}, standard absorption OH- band stretching at v $_{OH}^-$ = 1410 cm^{-1}, CH-stretching second overtone at v $_{CH}$ = 1143 cm^{-1}, O-CH$_2$ stretching at v$_{O-CH2}$ = 973 cm^{-1}, and benzenoid group at v $_{benzenoid}$ = 868 cm^{-1} .

Generally it is clear that in the case of treatment with argon plasma for different exposure periods, there is a gradual increase in peak intensity values of these groups reaching maximum increase at 30 seconds exposure by about: 144.02 %, 93.11 %, 135 %, and 93.2% relative to their initial values respectively for; CH$_2$-anti-symmetric stretching, carbonyl bond stretching, hydroxyl, and CH-stretching second overtone respectively. The intensity of the signals for O-CH$_2$ stretching and benzenoid group, increases at 120 seconds by a maximum increases about 120.55% and 184% to its initial values respectively.

In the case of treatment with argon plasma for different exposure pressures, a gradual increase in peak intensity values of these groups reaching maximum increse at 0.4 Torr exposure by about: 101 %, 104.6 %, 163.2 % ,104.5%, 138.7% and 156.1% relative to their initial values respectively for; CH$_2$-anti-symmetric stretching, carbonyl bond stretching, hydroxyl, CH-stretching second overtone, O-CH$_2$ stretching and benzenoid group respectively.

Finally, in the case of treatment with argon plasma for different exposure currents, there is a gradual increase in peak intensity values of these groups reaching maximum increse at 75 mA. exposure by about: 58 % , 87.3 % and 127.4 % relative to their initial values respectively for ; CH$_2$-anti-symmetric stretching, carbonyl bond stretching,hydroxyl respectively. CH-stretching second overtone signal at its intensity increases at 60 mA by a maximum increases about 90%.

The signals v$_{O-CH2}$ = 973 cm^{-1} and v$_{benzenoid}$ = 868 cm^{-1} represents O-CH$_2$ stretching and benzenoid group, intensity increases at 50 mA by a maximum increases about 118.7% and 176.5% to its initial values respectively.

Table (4): The changes in the peak intensity values with argon plasma exposure times for different functional groups exist in polyester fabrics.

Groups Exposure time (seconds)	CH$_2$-antisymmetric stretching (2945 cm^{-1})	C=O anti-symmetric stretching (1725 cm^{-1})	Standard absorption-OH band (1410cm^{-1})	C-H Stretching second overtone (1143 cm^{-1})	O-CH$_2$ Stretching (973 cm^{-1})	Benzenoid group (868 cm^{-1})
0(blank)	0.368	0.479	0.307	0.470	0.360	0.255
15	0.644	0.918	0.704	0.885	0.749	0.682
30	0.651	0.826	0.643	0.696	0.770	0.710
45	0.898	0.925	0.721	0.908	0.604	0.541
60	0.543	0.844	0.635	0.841	0.722	0.663
120	0.626	0.912	0.720	0.899	0.794	0.724

Figure (7) a :FTIR Diagram of argon plasma treated polyester fabric at (15) Seconds.

Figure (7)b: FTIR Diagram of argon plasma treated polyester fabric at (30) seconds.

Figure (7) c: FTIR Diagram of argon plasma treated polyester fabric at (45) Seconds.

Figure (7) d :FTIR Diagram of argon plasma treated polyester fabric at (60) seconds.
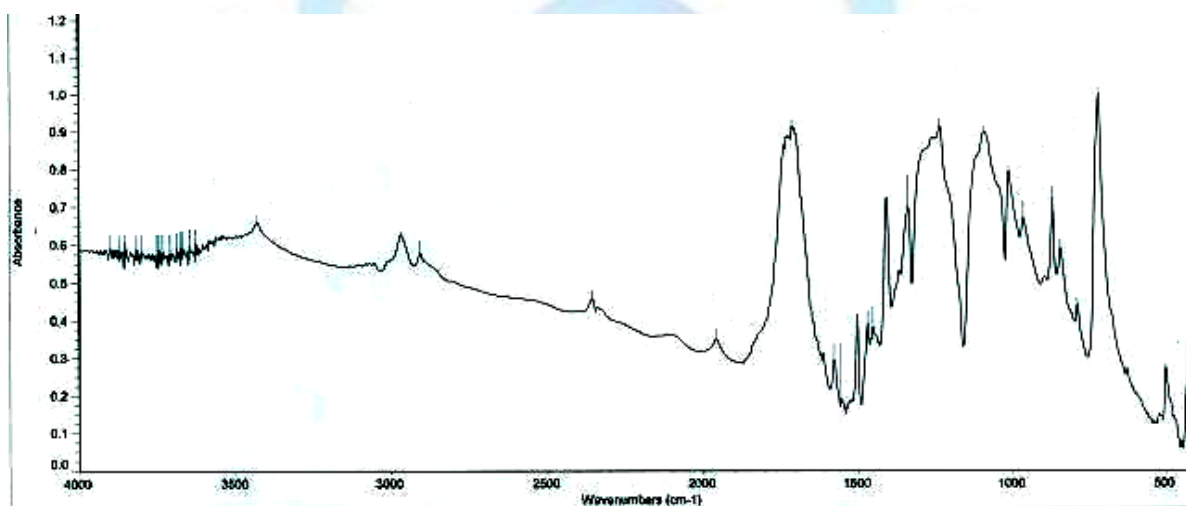
Figure (7) e: FTIR Diagram of argon plasma treated polyester fabric at (120) seconds.

Table (5): The changes in the peak intensity values with argon plasma exposure pressures for different functional groups exist in polyester fabric.

Groups Pressure (Torr)	CH₂-antisymmetric stretching (2945 cm⁻¹)	C=O anti-symmetric stretching (1725 cm⁻¹)	Standard absorption-OH band (1410cm⁻¹)	C-H Stretching second overtone (1143 cm⁻¹)	O-CH₂ Stretching (973 cm⁻¹)	Benzenoid group (868 cm⁻¹)
0(blank)	0.368	0.479	0.307	0.470	0.360	0.255
0.2	0.473	0.859	0.631	0.864	0.728	0.688
0.3	0.483	0.873	0.674	0.893	0.758	0.684
0.4	0.740	0.980	0.808	0.961	0.859	0.816
0.6	0.576	0.891	0.654	0.888	0.749	0.653

Figure (8) a: FTIR Diagram of argon plasma treated polyester fabric at (0.2) Torr.
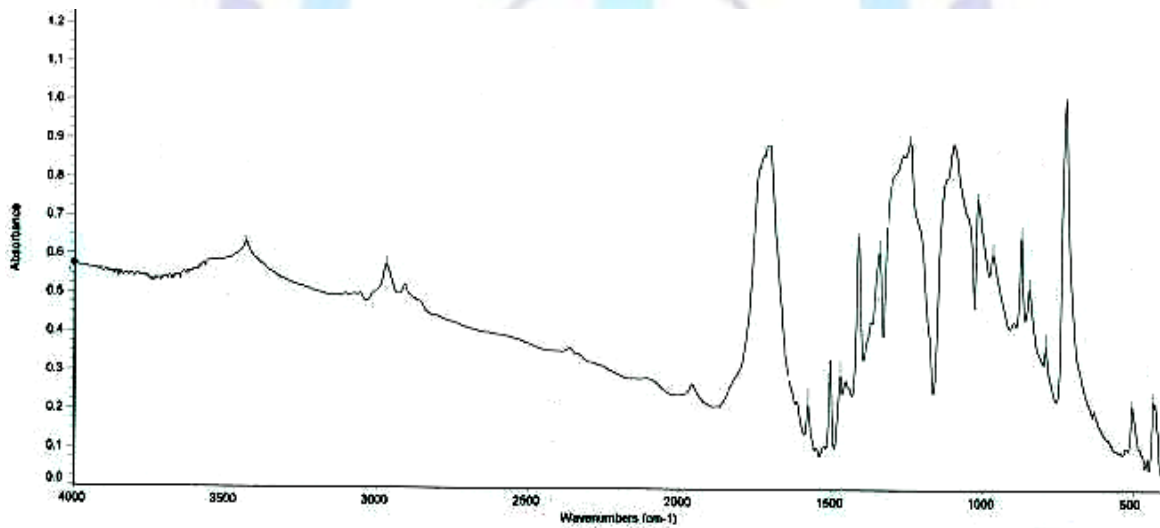
Figure (8) b: FTIR Diagram of argon plasma treated polyester fabric at (0.3) Torr.
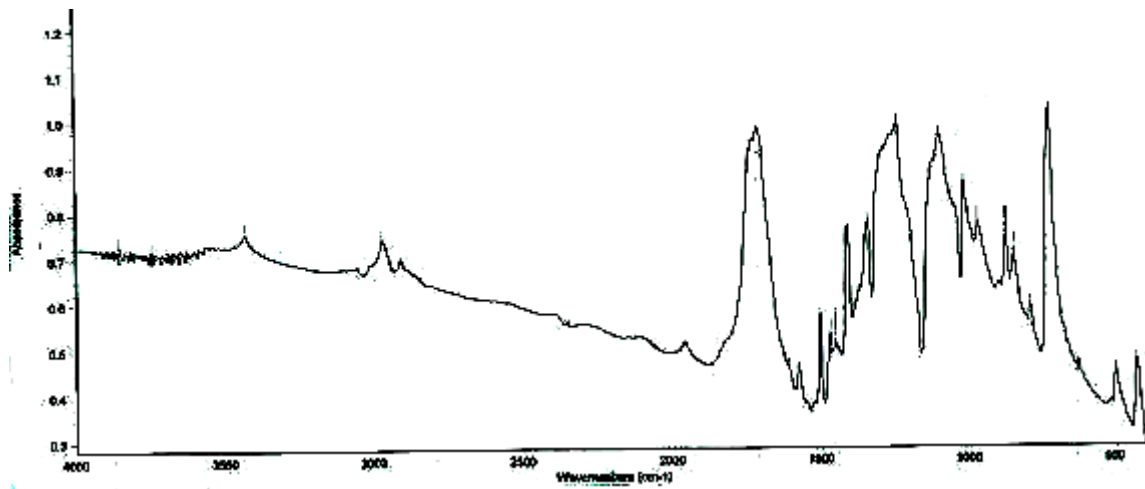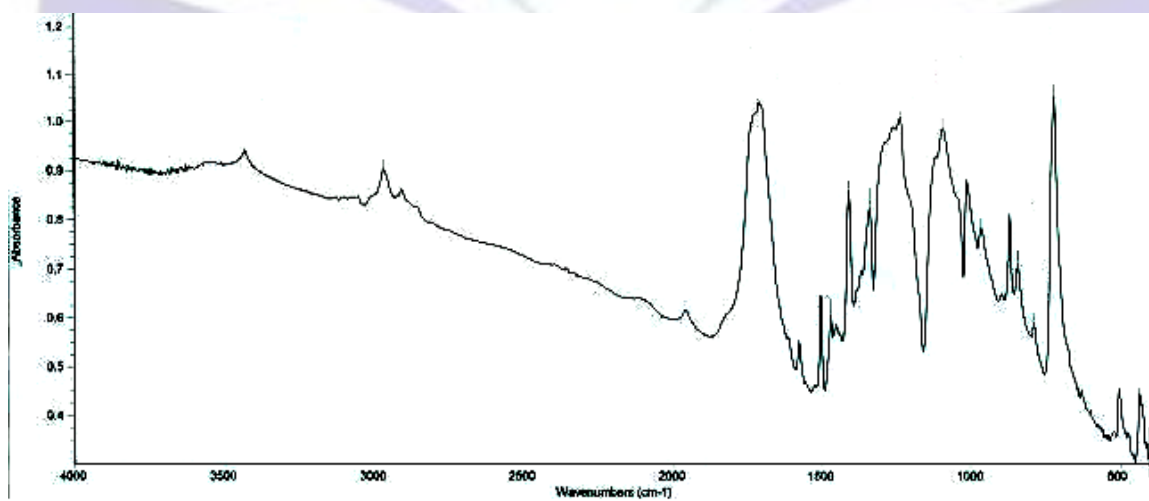
Figure (8) c: FTIR Diagram of argon plasma treated polyester fabric at(0.4)Torr.
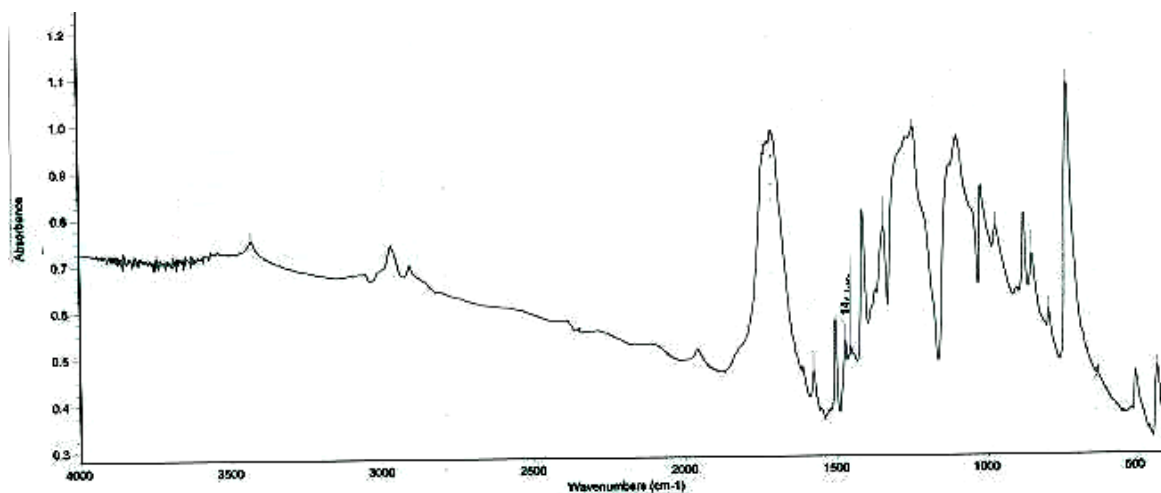
Figure (8) d: FTIR Diagram of argon plasma treated polyester fabric at (0.6) Torr.

Table (6): The changes in the peak intensity values with nitrogen plasma exposure currents for different functional groups exist in polyester fabrics.

Groups Current (mA)	CH$_2$-antisymmetric stretching (2945 cm^{-1})	C=O anti-symmetric stretching (1725 cm^{-1})	Standard absorption-OH band (1410cm^{-1})	C-H Stretching second overtone (1143 cm^{-1})	O-CH$_2$ Stretching (973 cm^{-1})	Benzenoid group (868 cm^{-1})
(blank) 0	0.368	0.479	0.307	0.470	0.360	0.255
40	0.458	0.840	0.601	0.835	0.677	0.603
50	0.527	0.877	0.675	0.857	0.739	0.676
60.	0.484	0.867	0.646	0.867	0.719	0.642
75	0.904	1.044	0.860	0.987	0.880	0.811
90	0.412	0.788	0.559	0.792	0.639	0.575

Figure (9) a :FTIR Diagram of argon plasma treated polyester fabric at (40) mA.
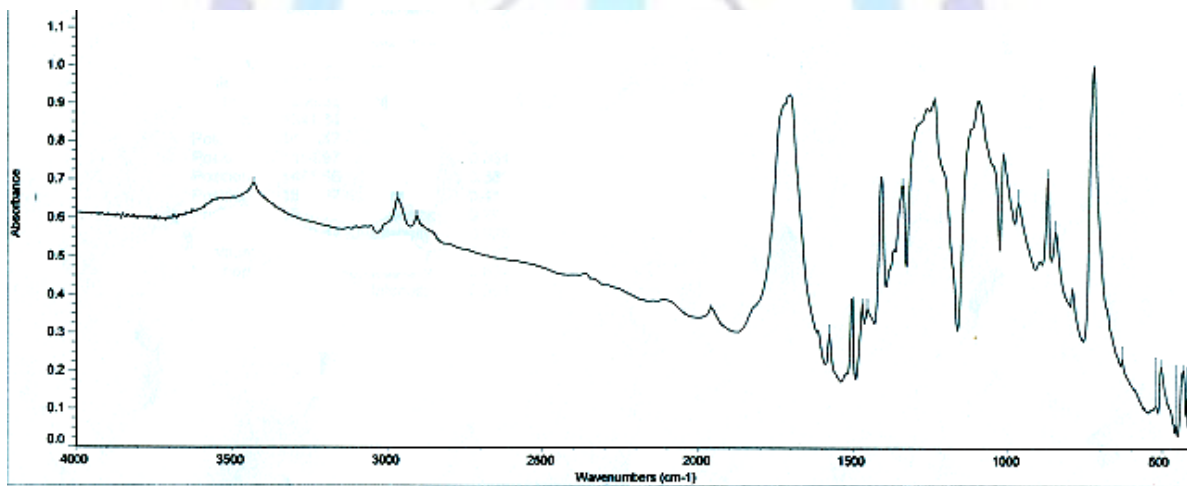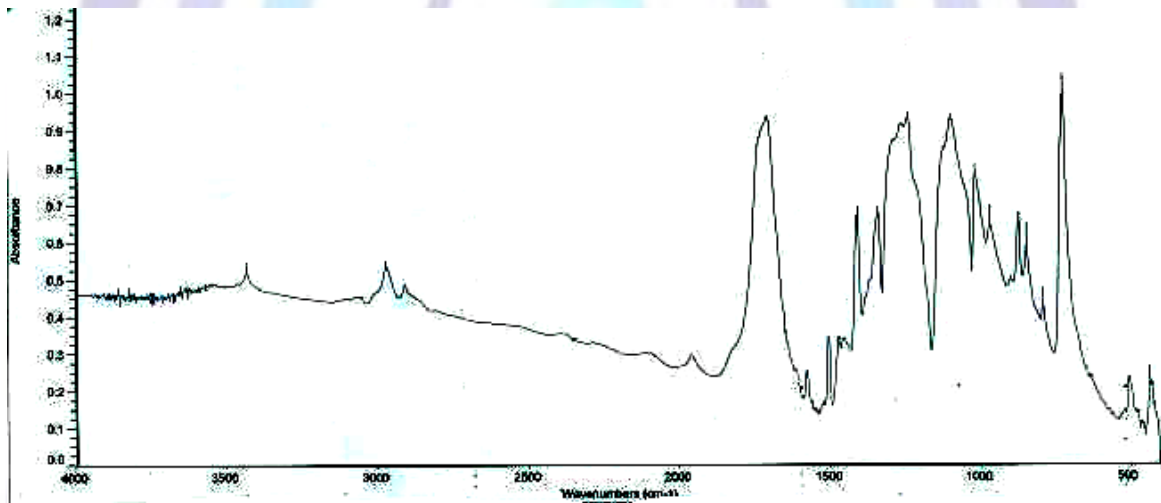

Figure (9) b: FTIR Diagram of argon plasma treated polyester fabric at (50) mA.
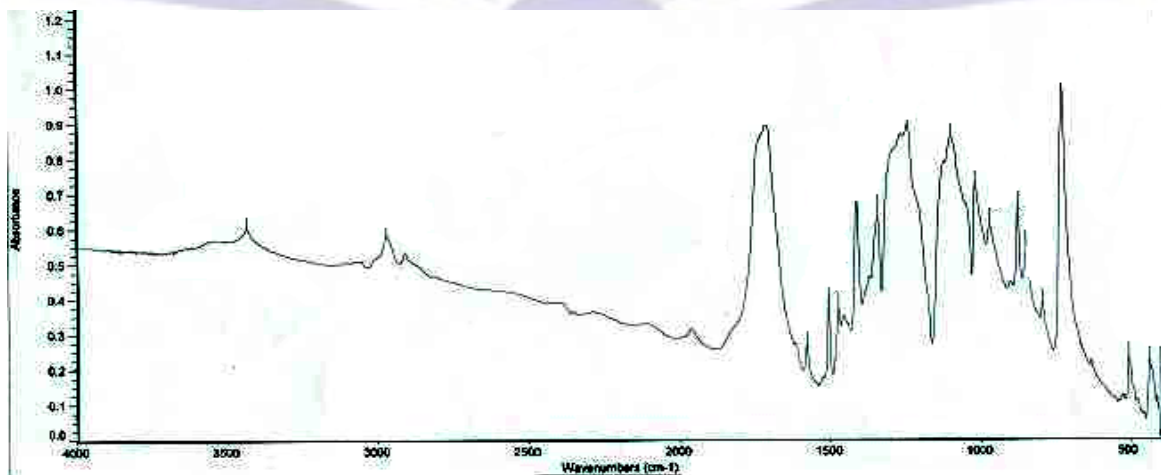
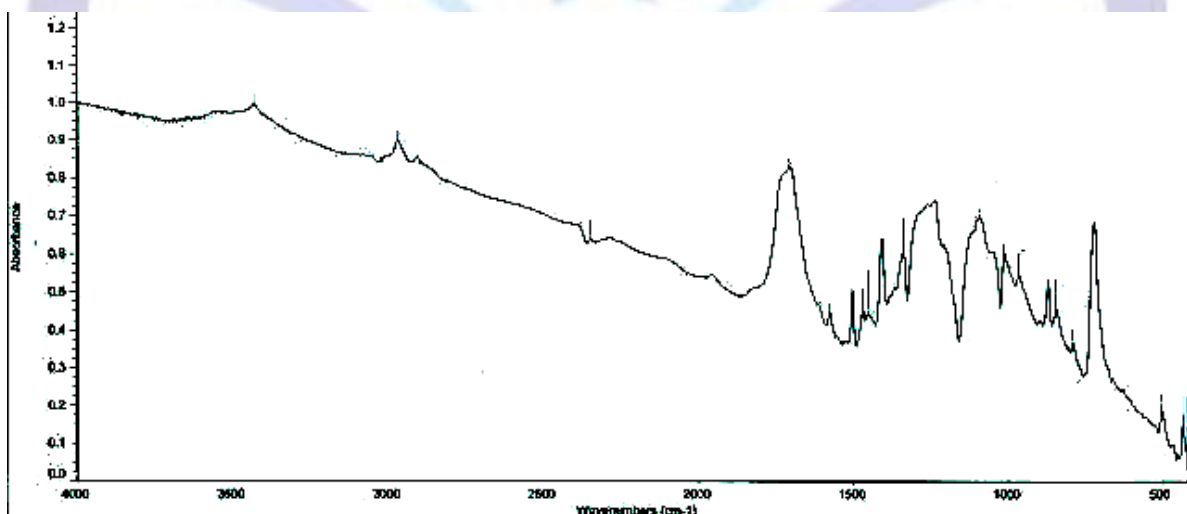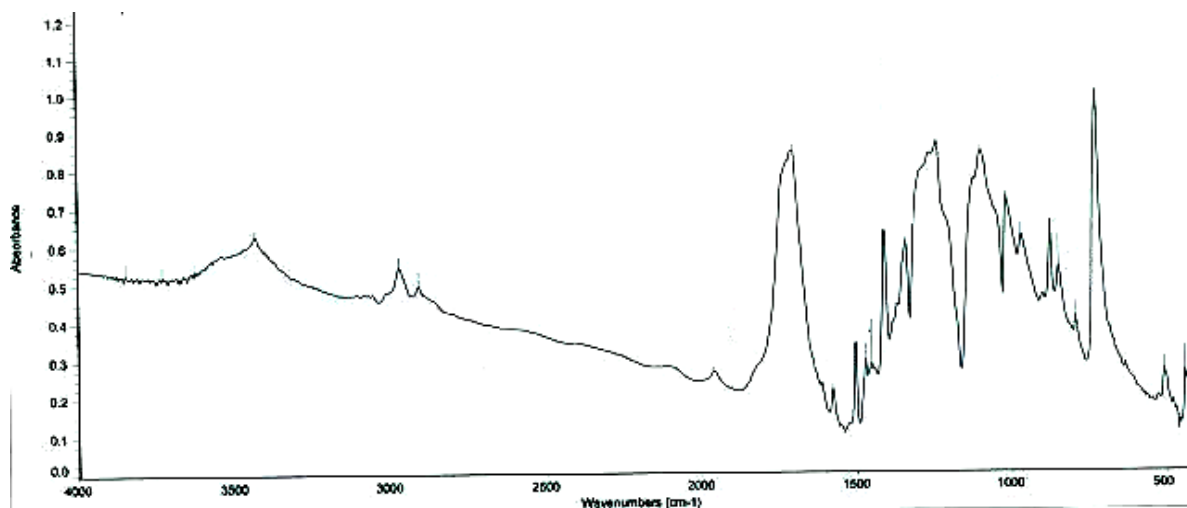**Figure (9) c: FTIR Diagram of argon plasma treated polyester fabric at 60 mA.**
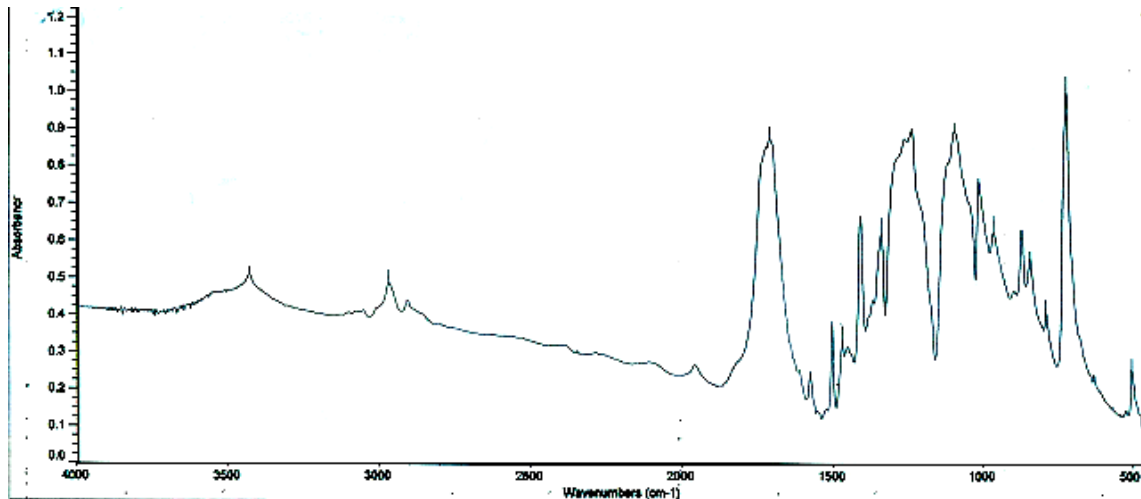
Figure (9) d: FTIR Diagram of argon plasma treated polyester fabric at (75) mA.
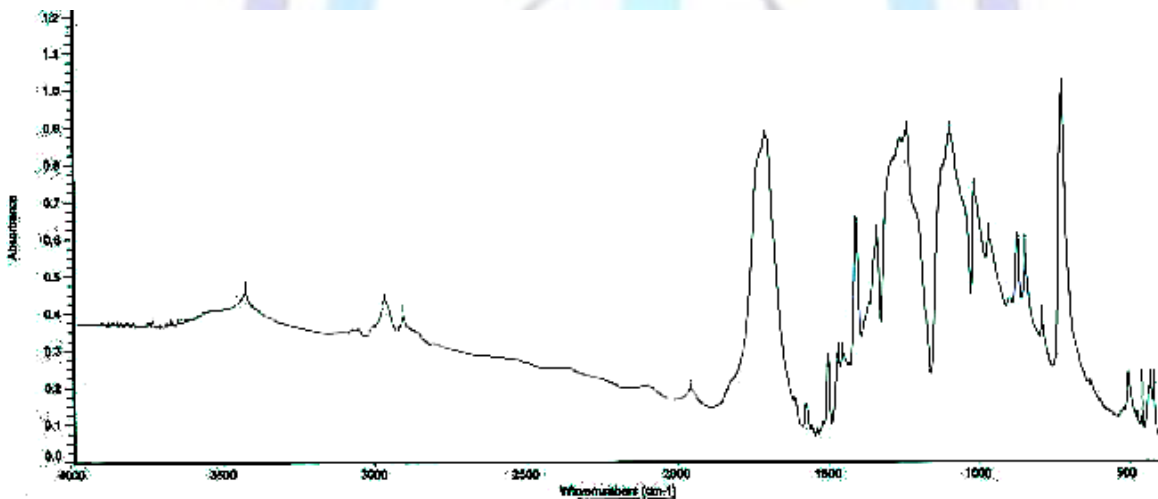
Figure (9) e: FTIR Diagram of argon plasma treated polyester fabric at 90 mA.

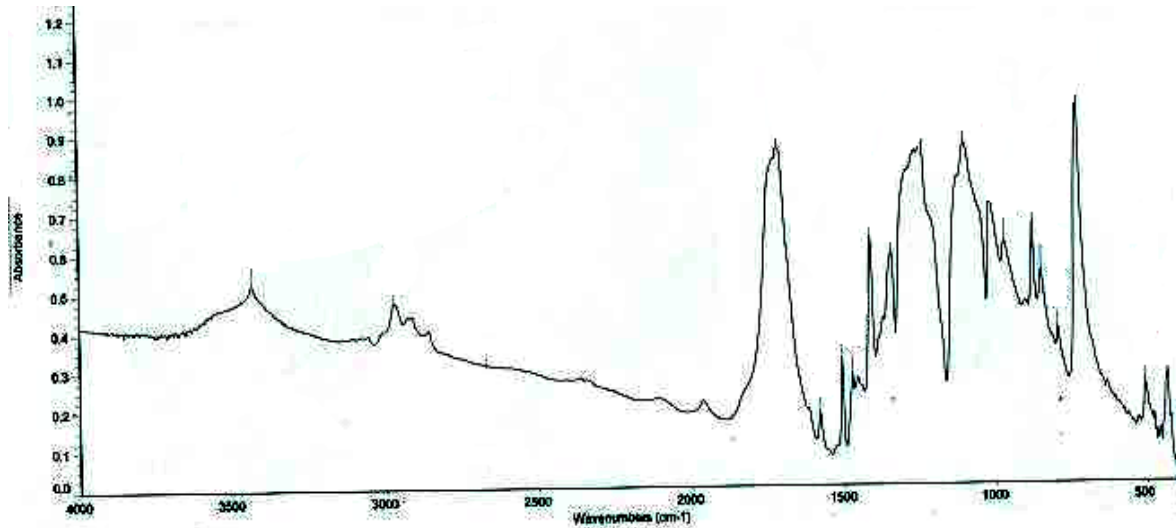## 2. Dyeing properties of the different examined fabric samples

This part was carried out as an applied part to evaluate the effect of the applied plasma and/or nanosilver treatment on the dyeing properties of selected polyester and nylon samples, under the effect of dye concentrations, different dye temperature and different dyeing times plasma. These dyeing conditions are applied on the optimized plasma conditions and /or nanosilver treatment obtained in the last optimization part, where applied gas is argon, exposure time = 30 seconds, pressure = 0.4 Torr , current = 75 mA and nanosilver condition(50 ppm.) the results of this part are summarized in **tables (7-9)** .

2.1. Effect of dye concentration

Tables (7)a-e summarizes the dyeing properties dye-ability (K/S), colour difference (ΔE) and fastness properties of different treated fabrics and disperse dye concentration ranging from (0.05 – 2g/l).

Generally the dyeability (K/S) values increased by increasing dye concentration for all samples continuously, and this increase was enhanced by DC-cold plasma and/or nanosilver treatment of the fabric samples. Where the improvement of dyeability by increasing dye concentration resulting from the greater availability of the dye molecules and/or dye radicals in the vicinity of substrates immobile macro radicals, thus increasing dye diffusion and association. On considering the effect of argon plasma and/or nanosilver treatment on the dyeability (K/S) values, it is clear that maximum dyeability was obtained for plasma and nanosilver treated samples related to their blank dyed mates. This is due to the fact that using argon plasma treatment technique on fibers enhances dyeing properties [23] nanosilver work as mordant in case of argon plasma nanosilver treated samples and also the increased surface area and the modifications of the partition equilibrium of the dye between the dyeing bath and the macromolecular surface in contact with it, can also play a role. Indeed, the

introduction of hydrophilic groups, induced by both reactive and chemically inert plasmas, may increase the water swelling capability and the affinity of the fibers for dyes containing polar groups[24].

Table (7) a: The change of dyeing properties for different examined fabric samples dyed with <u>0.05 g</u>m. disperse dye

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	3	3	4	42.80	0.8779
	Nano.Treated Poly.	3	3	3.5	4.5	44.21	0.9502
	Conventional Dyed Poly.	4	4	4	5	46.15	1.1532
	Plasma Treated Poly.	4	4	4	5	46.41	1.1773
	Plasma Nano.Treated Poly.	5	5	5	7	49.68	1.4663
Nylon	Blank Nylon	3	4	4	4	64.40	5.1287
	Nano Treated Nylon	3.5	4	4	4	65.45	5.6748
	Conventional Dyed Nylon	4	4.5	4	5	67.90	6.5633
	Plasma Treated Nylon	4.5	4.5	4.5	6	71.85	8.4075
	Plasma Nano.Treated Nylon	5	4.5	5	7	74.97	11.5513

* Note: *Dyeing process conditions temp. = 100◦c and Time= 60 min .*

* *The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case*

Table (7) b: The change of dyeing properties for different examined fabric samples dyed with <u>0.5 gm</u> disperse dye

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	3	3	4	46.32	1.2836
	Nano.Treated Poly.	3	3	3.5	4.5	47.32	1.3798
	Conventional Dyed Poly.	4	4	4	5	55.96	2.4794
	Plasma Treated Poly.	5	4	4	6	59.99	3.2554
	Plasma Nano.Treated Poly.	5	5	5	7	63.33	3.9090
Nylon	Blank Nylon	3	4	4	4	78.35	16.2164
	Nano.Treated Nylon	3.5	4	4	4	78.58	16.2559
	Conventional Dyed Nylon	4	4.5	4	5	78.70	16.995
	Plasma Treated Nylon	4.5	4.5	4.5	6	78.72	17.4637
	Plasma Nano.Treated Nylon	5	5	5	7	79.89	18.9329

* Note: Dyeing process conditions temp. = 100◦c and Time= 60 min .

* The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

Table (7)c : The change of dyeing properties for different examined fabric samples dyed with <u>1.00 gm</u> disperse dye

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	3	3	4	46.48	1.4290
	Nano.Treated Poly.	3	3	3.5	4.5	47.61	1.5495
	Conventional Dyed Poly.	4	4	4	5	62.79	3.7423
	Plasma Treated Poly.	5	4	4	5.5	63.01	3.8873
	Plasma Nano.Treated Poly.	5	5	5	7	63.40	4.1084
Nylon	Blank Nylon	3	4	4	4	78.53	17.4637
	Nano.Treated Nylon	3.5	4	4	4	79.36	19.1197
	Conventional Dyed Nylon	4	4.5	4	5	80.07	19.7589
	Plasma Treated Nylon	5	5	5	6	80.17	19.7877
	Plasma Nano.Treated Nylon	5	5	5	7	80.69	20.7192

* Note: Dyeing process conditions temp. = 100∘c and Time= 60 min .

* The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

Table (7) d : The change of dyeing properties for different examined fabric samples dyed with <u>1. 5 gm</u> disperse dye

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	3	3	4	47.92	1.6255
	Nano.Treated Poly.	3	3	3.5	4.5	48.06	1.6292
	Conventional Dyed Poly.	4	4	4	5	62.83	3.8566
	Plasma Treated Poly.	4	4	4	6	63.33	4.0899
	Plasma Nano.Treated Poly.	4	5	5	6	63.41	4.1408
Nylon	Blank Nylon	3	4	4	4	80.08	19.5320
	Nano.Treated Nylon	3.5	4	4	4	80.13	19.6733
	Conventional Dyed Nylon	4	4.5	4	5	80.26	19.7877
	Plasma Treated Nylon	5	5	5	6	80.49	21.0378
	Plasma Nano.Treated Nylon	5	5	5	7	80.71	21.5336

• Note: Dyeing process conditions temp. = 100∘c and Time= 60 min .

* The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

Table (7) e: The change of dyeing properties for different examined fabric samples dyed with <u>2.00 gm</u> disperse dye

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	3	3	4	48.99	1.8648
	Nano.Treated Poly.	3	3	3.5	4.5	49.45	1.7728
	Conventional Dyed Poly.	4	4	4	5	63.31	3.9625
	Plasma Treated Poly.	4	4	4	7	63.65	4.0270
	Plasma Nano.Treated Poly.	4	4	4	7	65.48	5.2361
Nylon	Blank Nylon	3	4	4	4	79.98	19.7017
	Nano.Treated Nylon	4	4	4	4	80.24	20.6254
	Conventional Dyed Nylon	5	5	5	5	80.26	20.7506
	Plasma Treated Nylon	5	5	5	7	80.65	20.9412
	Plasma Nano.Treated Nylon	5	5	5	7	80.79	21.2335

* Note: Dyeing process conditions temp. = 100°c and Time= 60 min .

* The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

2.2. Effect of dyeing temperature

The data presented in **Table (8)a-c** show the effect of dyeing temperatures on the colour strength values of treated and untreated samples. It is clear that the colour strength increased significantly as the dyeing bath temperature were increased within the studied range (40-100) °c. This may be due to the fact that raising the temperature of the dyeing bath had facilitated the transfer of the dye molecules from the dye bath to the fiber surface, adsorption of the dye at the fiber surface and hence diffusion to the inner fiber spaces of the fabrics.

Table (8)a : The change of dyeing properties for different examined fabric samples dyed with disperse dye at <u>40°C</u>

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	4	3	3	4	20.00	0.2261
	Nano.Treated Poly.	4	3	3.5	4.5	21.43	0.1860
	Conventional Dyed Poly.	4	4	4	5	22.50	0.1906
	Plasma Treated Poly.	5	5	5	6	22.67	0.2031
	Plasma Nano.Treated Poly.	5	5	5	7	23.69	0.2338
Nylon	Blank Nylon	3	4	4	4	36.17	0.8429
	Nano.Treated Nylon	3.5	4	4	4	36.24	0.9711
	Conventional Dyed Nylon	4	4.5	4	5	40.57	1.1168
	Plasma Treated Nylon	4	4.5	4.5	6	48.28	1.8185
	Plasma Nano.Treated Nylon	5	4.5	4.5	7	48.63	1.8344

• Note: Dyeing process conditions, dye concentrations= 0.05gm and Time= 60 min.

* The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

Table (8)b : the change of dyeing properties for different examined fabric samples dyed with disperse dye at 80°C

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	3	3	4	31.32	0.3520
	Nano.Treated Poly.	3	3	3.5	4.5	32.59	0.4404
	Conventional Dyed Poly.	4	4	4	5	36.33	0.6657
	Plasma Treated Poly.	5	5	4	7	45.11	1.0586
	Plasma Nano.Treated Poly.	5	5	5	7	45.64	1.3448
Nylon	Blank Nylon	3	4	4	4	50.00	1.9600
	Nano.Treated Nylon	3.5	4	4	4	52.53	2.4435
	Conventional Dyed Nylon	4	4	4	5	54.96	2.7436
	Plasma Treated Nylon	4.5	4	4	6	65.75	5.5998
	Plasma Nano.Treated Nylon	4.5	4	4	7	66.70	5.8028

* Note: Dyeing process conditions, dye concentrations= 0.05gm and Time= 60 min.

* The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

Table (8)c : The change of dyeing properties for different examined fabric samples dyed with disperse dye at 100°C

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	3	3	4	42.80	0.8779
	Nano.Treated Poly.	3	3	3.5	4.5	44.21	0.9502
	Conventional Dyed Poly.	4	4	4	5	46.15	1.1532
	Plasma Treated Poly.	4	4	4	5	46.41	1.1773
	Plasma Nano.Treated Poly.	5	5	5	7	49.68	1.4663
Nylon	Blank Nylon	3	4	4	4	64.40	5.1287
	Nano.Treated Nylon	3.5	4	4	4	65.45	5.6748
	Conventional Dyed Nylon	4	4.5	4	5	67.90	6.5633
	Plasma Treated Nylon	4.5	4.5	4.5	6	71.85	8.4075
	Plasma Nano.Treated Nylon	5	4.5	5	7	74.97	11.5513

- *Note Dyeing process conditions, dye concentrations= 0.05gm and Time= 60 min.*

* The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

2.3. Effect of dyeing time

The colour difference values and (K/S) values of treated and untreated samples as a function of dyeing times are given in **Table (9) a-d**. It is clear that, the colour difference values and (K/S) values increase for both treated and untreated samples by increasing the dyeing time from (30 – 120) minutes. Maximum dye-ability values of these samples are obtained with 120 minutes dyeing time. This my be due to the fact that the increase in dyeing time will give a greater chance to the dye molecule to be absorbed on the fabric surface and also facilitated their transfer to inner fiber spaces of the dyed fabrics thus in creasing the dyeability.

Table (9) a: The change of dyeing properties for different examined fabric samples dyed with disperse dye for <u>30 min</u>.

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	3	3	4	24.85	0.2665
	Nano.Treated Poly.	3	3	3.5	4.5	26.42	0.4032
	Conventional Dyed Poly.	4	4	4	5	28371	0.4825
	Plasma Treated Poly.	5	5	5	6	35.58	0.5612
	Plasma Nano.Treated Poly.	5	5	5	7	36.96	0.6596
Nylon	Blank Nylon	3	4	4	4	59.78	3.9090
	Nano.Treated Nylon	3.5	4	4	4	61.80	4.6375
	Conventional Dyed Nylon	4	4.5	4	5	61.25	4.3143
	Plasma Treated Nylon	4.5	5	5	6	62.31	4.3438
	Plasma Nano.Treated Nylon	5	5	5	7	67.50	6.3124

- Note: *Dyeing process conditions, dye concentrations= 0.05gm and temp. = 100◦c.*

The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

Table (9) b : The change of dyeing properties for different examined fabric samples dyed with disperse dye for <u>60 min</u>.

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	3	3	4	42.80	0.8779
	Nano.Treated Poly.	3	3	3.5	4.5	44.21	0.9502
	Conventional Dyed Poly.	4	4	4	5	46.15	1.1532
	Plasma Treated Poly.	4	4	4	5	46.41	1.1773
	Plasma Nano.Treated Poly.	5	5	5	7	49.68	1.4663
Nylon	Blank Nylon	3	4	4	4	64.40	5.1287
	Nano.Treated Nylon	4	4	4	4	65.45	5.6748
	Conventional Dyed Nylon	4	4.5	4	6	67.90	6.5633
	Plasma Treated Nylon	5	5	5	7	71.85	8.4075
	Plasma Nano.Treated Nylon	5	5	5	7	74.97	11.5513

* Note: *Dyeing process conditions, dye concentrations= 0.05gm and temp. = 100◦c.*

The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

Table (9) c: The change of dyeing properties for different examined fabric samples dyed with disperse dye for <u>90 min</u>.

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	4	4	4	46.30	1.0360
	Nano.Treated Poly.	4	4	4	4	47.82	1.2352
	Conventional Dyed Poly.	4	4.5	4	6	48.67	1.2988
	Plasma Treated Poly.	5	5	5	7	57.43	2.7164
	Plasma Nano.Treated Poly.	5	5	5	7	58.98	3.0552
Nylon	Blank Nylon	3	4	4	4	70.26	8.0692
	Nano.Treated Nylon	3.5	4	4	4	70.82	8.4369
	Conventional Dyed Nylon	4	4.5	4	5	72.07	9.3335
	Plasma Treated Nylon	5	5	5	7	76.30	11.6780
	Plasma Nano.Treated Nylon	5	5	5	7	78.47	15.6817

* Note: Dyeing process conditions, dye concentrations= 0.05gm and temp. = 100◦c.

* The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

Table (9) d : The change of dyeing properties for different examined fabric samples dyed with disperse dye for <u>120 min</u>.

Samples		Washing Fastness			Light Fastness	ΔE	K/S
		Alteration	Staining				
			Wool	S.			
Polyester	Blank Poly.	3	4	4	4	45.22	0.9793
	Nano.Treated Poly.	4	4	4	4	50.81	1.4571
	Conventional Dyed Poly.	4.5	5	5	6	57.72	2.9228
	Plasma Treated Poly.	5	5	5	7	58.97	3.3586
	Plasma Nano.Treated Poly.	5	5	5	7	60.20	3.6018
Nylon	Blank Nylon	3	4	4	4	75.24	9.8223
	Nano.Treated Nylon	3.5	4	4	4	77.10	15.3374
	Conventional Dyed Nylon	4.5	5	5	5	78.70	17.2397
	Plasma Treated Nylon	5	5	5	7	78.74	16.7237
	Plasma Nano.Treated Nylon	5	5	5	7	80.43	18.6206

* Note: Dyeing process conditions, dye concentrations= 0.05gm and temp. = 100◦c.

* The dye-ability is expressed as K/S at the maximum absorption wave length at (λ)max.= 520 nm., and S.: refers to blank untreated sample in each case

2.5. Fastness properties for dyed plasma argon treated samples

2.5.1. Washing fastness

The washing fastness grade was assessed using standard gray scale which ranges from (1- 5), where 5 (excellent), 4 (good), 3 (fair), 2 (poor) and 1 (very poor). While, the staining 5 (no staining), 4 (slightly staining), 3 (noticeable staining), 2 (considerable staining) and 1(heavy staining). Washing fastness values of the examined treated and untreated fabrics

samples dyed with disperse dye produced at different temperature, dyeing time and dye bath concentration are given in **Tables (7-9)**.

The obtained results of fastness to washing revealed that for all examined samples, the alteration ranged from fair- good (3-4) for untreated and nanosilver treated samples and excellent (5) for both argon plasma treated and argon plasma nanosilver treated samples. Staining in general, was small and ranged from slight- no staining (4-5) for untreated and conventional samples and was no staining (5) for argon plasma treated samples and argon plasma nanosilver treated samples.

2.5.2. Light fastness and colour difference evaluation

Visual light fastness rating based on the standard blue scale were assessed and the obtained results are given in **Tables (7-9)** were showed that the dyed argon plasma and argon plasma nanosilver treated samples were the highest value (7) with highest colour difference (ΔE) values, dyed samples obtained from untreated and nanosilver treated their values were of the order (4-5) and conventional dyed samples were of the order (5-6). It is clear that the light fastness values were improved on the argon plasma and argon plasma nanosilver treated samples as a result of increasing the colour strength. The other fastness values were not affected.

CONCLUSION

1-The results obtained from Fourier Transform Infra-Red (FTIR) spectral analysis, a) with nitrogen plasma: i)in the case of treatment with nitrogen plasma for different exposure times, there is a gradual increase in peak intensity values of these groups reaching maximum increase at 45 seconds exposure for the studied groups: CH_2-anti- symmetric stretching, carbonyl bond stretching, hydroxyl, CH-stretching second overtone, and benzenoid group, but $O-CH_2$ stretching, group increases at 120 seconds. ii) Taking into consideration exposure pressures, there is a gradual increase in peak intensity values of these groups reaching maximum increase at 0.4 Torr exposure. iii) Finally, using different exposure currents, there is a gradual increase in peak intensity values reaching maximum increase at 75 mA exposure for the above mentioned groups.

b) with argon plasma:i) at different exposure times, there is a gradual increase in peak intensity values of these groups reaching maximum increase at 30 seconds for; CH_2-anti-symmetric stretching, carbonyl bond stretching, hydroxyl, and CH-stretching second overtone respectively. But for the ,$O-CH_2$ stretching and benzenoid group, their intensity increases at 120 seconds ii)For different exposure pressures, a gradual increase in peak intensity values of these groups reaching maximum increase at 0.4 Torr exposure .iii)Finally, by using different exposure currents, there is a gradual increase in peak intensity values of these groups reaching maximum increse at 75 mA. exposure , while for CH-stretching second overtone its intensity increases at 60 mA.

2-The results of dyeing properties, generally the dyeability (K/S) values increased by increasing dye concentration, dyeing time and dyeing temperature for all samples continuously, and this increase was enhanced by DC-cold plasma and/or nanosilver treatment of the fabric samples.

3- The great effect of DC-cold plasma and/or nanosilver treatment on improving the fastness properties of all examined samples for both washing and light.

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