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Effect of UV Irradiation on Polyester Printing

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Polyester fibers & blends of polyester/cotton fibers are commonly used in the textile industry. Properties of polyester depends on the production method. Beside the advantages of polyester, there are certain disadvantages that affect the dyeability & dyeing process. By the application of chemical process, such as surface hydrolysis, using of solvents, surfactants & enzymes or physical process like using Plasma, Gamma & UV irradiation some improvement can be made. The UV irradiated fabric (Wavenumber of UV Irradiation is 230-280 nm) was dyed with Disperse & Cationic Dyes, which showed high improvement in dyeability of the fabric with cationic dyes, whereas no pronounced effect was noticed with disperse dyes.

Key words: Polyester, Chemical Modification, Dyeing, UV Irradiation.

Polyester fiber refers to polymers which have a large number of ester groups in their main chain. The ester groups, are the result of the reaction between alcohols &divalent carboxylic acids.

Polyesters are usually result ofcondensation polymerization reaction of bicarbonates acid with di-OL (Both of these compounds are bifunctional group) or perform a self-compacting polymerization reaction of carbonate acid or reaction similar compounds are produced corresponding three or more functional groups.

The main raw material to produce PET (one of the most important types of polyester) is, polyethylene terephthalate. The reaction of polyethylene terephthalate polymerization begins in the form of dimethyl terephthalate through an indirect esterification reaction & pure terephthalic acid through a direct esterification reaction.[1, 2, 3]

Microscopic image sections of polyester fibersis smooth as well as other synthetic fibers produced by melt spinning, but the addition of additives such as Titanium dioxide pigment causes very slight roughness on the surface of the fibers. The cross-sectional area of the fibers according to the cross section of producing process can be circular hollow, trefoil, starry[1]

Polyester physical & mechanical properties such as tensile strength, elongation to rupture, modulus of elasticity, etc. depending to the type of application can be changed by changing production conditions. The most important factor that influences the properties of the fibers is tension. The molecular structure of polyester fiber largely depends on spinning speed, as the spinning speed increases causes to the increased orientation of polymer macromolecules in the direction of the fibers& the crystalline regions in the fibers increases[4]

Polyester fibers are flammable, most of the finishing materials (besides the flame finishing) enhance the combustion process of burning fibers

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and the duration of burning. Polyester general resistance against corrosive chemicals is relatively good. Polyester resistance against mineral acids and organic solventsat room temperatureis good and in most cases their resistance to boiling conditions also remain good[5]

Polyester resistance against, concentrated mineral acids, such as phosphoric acid hydrofluoric acid, at room temperature is very good, but concentrated sulfuric acid at room temperature dissolves the fiber. At very low temperatures, the strength& elastic modulus slightly increased and elongation torupture of the fiber greatly decreased[2]

Different methods for surface modification of polyester fiber includes the following:

- Reaction with sodium hydroxide[4, 7]
- Hydrolysis with sodium hydroxide in a non-aqueous solvents[4]
- Reacts with calcium hydroxide[5]
- Surface modification by enzymes[3]
- Surface modification using plasma[5, 7]
- Modification byusing a variety of radiation, such as gamma radiation

Ionizing radiation is consist of high-energy particles or waves that can separate at least one electron from an atom or molecule. The ability of ionization depends on the energy of each particle or radiation and is independent of the number. In general, the particles which have sufficient energy to eject electrons from atoms rays and molecules that collide with them, such as water and protein, this process called ionization[8]

Ionizing radiation are divided into three categories: the first type are ionizing radiation particles, the second type are ionizing radiation and gamma rays, which are electromagnetic waves. The third type of ionizing radiation are radioactive rays[9]

Common synthetic polymers that can be attacked include polyester and LDPE, where tertiary carbon bonds in their chain structures are the centers of attack. Ultraviolet rays interact with these bonds to form free radicals, which then react further with oxygen in the atmosphere, producing carbonyl groups in the main chain. The exposed surfaces of products may then discolor and crack, and in extreme cases, complete product disintegration can occur.

UV rays and gamma rays ionize any molecules or atoms. In the study of effects of radiation in the long chain polymers, it must be considered that the energy absorption of the radical, radical reaction or ion-induced crosslinking systems break the chains of polymers and affectr chemical properties. This chemical changes affect physical properties such as modulus of elasticity, solubility, swelling, and reduction ofviscosity.The main changes in the behavior of polymers are of most recent type[10-13]

Destruction is an important factor that weakens the beneficial properties of the polymeric materials. Physical destruction of the surface indicates that photo-chemical reactions resulting in the formation of smaller molecules increasing the polymer break-chain.These small molecules can be formed together and are improved polymer structure[14-15]

UV light is electromagnetic radiation with a wavelength shorter than visible light and longer than x-ray. UV radiation has very limited ability to penetrate in polymer &influence inside polymer, and reactions are carried out at surface[14] In the chemical degradation, the degree of damage depends on the wavelength of UV light and environmental conditions.Polymer radiation in sunlight and artificial light sources cause some degradation of polymer &reduction in physical properties such as strength and elasticity.The destruction associated with reduction in weight and formation of CO2, CO and changes in the chemical structure of the polymer molecule. Destruction main products involved amounts of hydrogen, methane, water, ethylene, ethane, COOH methanol, butane, acetic acid, formaldehyde, benzene and toluene[15-18]

The overall weight Reduction of the polyester in wider wavelength is more noticable. In general it can be said that no significant difference in the primary photocatalytic processes in the lower wavelength radiation can be seen[19-20]

When the radiation is perform in the absence of oxygen, cause a certain yellowness. However, if radiation performed in an oxygenated environment little yellowness is seen but series of fluorescent compounds (monohydroxy compound) is formed[17]

Radiation reduce the tensile strength and elongation at rupture of irradiated samples. The rate of reduction for both in high doses approximately 10%.Flexural rigidity and bending hysteresis at high doses, respectively, 20% and 50% increases.Increase the bending characteristics may cause difficulties to produce. In particular increase the bending hysteresis, it is extremely evident.In general, less hysteresis bending moment values leads to the ability to return more.Large increase in the flexural properties in irradiated sample lead to decreased flexibility and lower recover bending, will affectthe drape & coverage[21-22]

Titanium dioxide is used as a cheap, non-toxic light catalyst for effective purification purposes. Another application of titanium dioxide is for UV protection. This combination produces hydroxyl radicals and superoxide anions in the presence of O2 or H2O at UV radiation[21]

MATERIALAND METHODS

Fabric samples were prepared in accordance with the table-1, each sample was prepared according to standard conditions illustrated in figure-1. Samples were remain under UV light under condition of different intensity &different times. Then irradiated fabrics dyed with natural dyes at various conditions, and changes in the samples examined.

Samples are with dimensions of 5 x 10 cm, and for consistency and accuracy of test results a stencil was used to form both part (irradiated& non-irradiated) on a single sample. Samples remain for 8, 24 and 48 hours at a distance of 15 cm under the radiation of UV lamps with two power of 20W. & 10W. at wavelength of 230 nm. The fabrics were dyed according to the following processes illustrated at figure-2.

Cases that the samples were analyzed are as follows:

•The presence of titanium dioxide in cationic dyeing: such that the fabric in a solution of 75% titanium dioxide was padded and then irradiated by UV lamp for 24 hours, then dyed with cationic dyes.

•Reflective color coordinates, using a spectrophotometer at a wavelength of 100 to 750 nm and calculate component values for color samples under the standard light source D65, 1964 and measuring the L^*, a^*, b^*

•Sample tensile properties using the Instron at a temperature of 25C and measuring the elongation to rupture, by the specimen elongation rate of 200m / min

•Check samples washing fastness using standard*Wash Test No.2, 500c, ISO/R 105/IV, Part 9*

•Check samples rubbing fastness using standard*Rubbing, ISO/R 105/IV, Part 18, Crockmeter*

•Evaluation of light fastness of samples using standard *Xenon Lamp, ISO /R 105/V, Part 2*

•Check the fiber irradiated surface using a scanning electron microscope SEM

•Check the yellow index of the samples in accordance with ASTM Method 1965 using the following equation:

$$Y.I. = \frac{127.50X - 105.84Z}{Y}$$

•Check of water changes using immersion time of the irradiated and non-irradiated samples

RESULTS DISCUSSION

•The effect of carrier on the dye depth of irradiated and non-irradiated polyester samples dyed with disperse dyes

Color difference equationof the results obtained of a, b &L axes, that shows the difference between the two colors, is as below:

$$\Delta E = \Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}$$

In all samples, irradiated and non-irradiated using carrier increased dyeing depth.

• **Comparison of the effects of UV radiation on polyester dyed with different colors**

In the following charts,figure-3,color depth K/S for samples dyed with different dyes have been shown together

•Trasil Blue 3RL: increasing the dye concentration also increase color depth, as well as with increasing duration of exposure to radiation also increase color depth. But generally increasing dyeability using this method is less compared using carrier.

•Magenta Cationic dye: by increasing the concentration of Magenta cationic dye, color depth in modified and unmodified areas increases but the color depth difference between irradiated and non-irradiated samples in dyeing with cationic dyes, are much more compared to disperse dyes, due to radiation at the product level, hydrophilic and negatively charged groups are created & attract more cationic dye so color depth can be increased. Radiation causes very significant difference in the depth of dyeing with cationic dyes.

•Cationic dye Maxilon Red GRL: for the irradiated samples increasing concentration of cationic dye, cause to significant increase in color depth. For irradiated sample dyed with cationic dyes, color depth are much more thandisperse dyes using the same concentration.

According to all three charts it can be seen that increasing duration of exposure to radiation, increases samples color depth.

•Cibanon Brown 2BR: Samples remain 24 hours under UV radiation with intensity of 20 watts had been used in this dyeing process, and results showed that due to the formation of hydrophilic groups on the surface of polyester,Vat dyes disposed on the surface,so Color depth decreased after exposure. Table-3 shows color difference in sample exposed to UV irradiation and dyed using1%solution of Vat dye.

Overall color difference between the control sample and irradiated sample dyed with cationic dyes is more than others, and dyed with Vat dyes is less than others.

Hydrophilic negatively charged groups that are formed by UV radiation on polyester surface, increaseabsorbance of positively charged cationic dye&absorption of nonionic disperse dye. Vat dye absorption increases slightly because of negative charge of Vat dye itself. It is described as increasing in polyester hydrophilic groups and physical changes to surface.

•**The effect of the UV light intensity on color depth**

According to figure-4increasing used UV light increases the K/S increase in sample B (sample

Table 1. Sample properties

Characteristics	Type of fabric
Woven	100% Polyester
Woven	viscose
Woven	100% cotton
Woven	67% polyster+33% cotton

Table 2. Color differences between irradiated and non-irradiated samples dyed with disperse dyes with the exposure time of 8 hours with the power of 20W

Sample ID	ΔE	ΔL*
1&4	7.189	7.625
2&3	5.925	3.204
1&2	10.829	9.027
3&4	9.294	8.903

Table 3. Compare K/S of samples dyed using Cibanon Brown 2BR

Sample type	Dyed after irradiation	Sample control
K/S	1.2	0.763

Table 4. K/S for viscous samples irradiated for 24 hours, padded with a solution of titanium dioxide and dyed with concentration of 2% Magenta cationic dye

Sample	Control sample	Irradiated & dyed	Padded & dyed	Padded, irradiated & dyed
K/S	4.192	5.955	8.427	3.333

Table 5. Color difference of viscose samples

Sample ID	ΔE	ΔL*
28 & 29	11.300	6.745
29 & 30	13.624	8.711
31 &32	4.471	3.567

Table 6. Other samples color difference

Sample	K/S
Cotton- irradiated & dyed	4.700
Polyester- irradiated & dyed	14.788
Cotton/Polyester- irradiated & dyed	13.181
Cotton-TiO2padded, irradiated & dyed	7.649
Cotton- TiO2 padded, irradiated & dyed	11.742

dyeing with cationic dyes) shows a higher rate.

•The effect of presence of titanium dioxide in irradiation process on dye depth

The effect of titanium dioxide on viscose, polyester and cotton-polyestersamples were studied. The following table (table-4) summarizes the results of the color depth in the viscose sample:

It is clear in table that color depth of viscose irradiated &dyed is more than non-irradiated & dyed sample, & for thesample padded with a solution of titanium dioxide& dyed color depth is greater than the control sample. It seems dye absorption of viscose sample in the presence of titanium dioxide increases. In general, UV radiation increases the color depth of the viscose& table-5 confirms this.

Table-6 illustrates K/S differencebetween

Table 7. Values of K/S of polyester with different exposure times

Radiation duration	K/S
24 hr.	5.523
300 hr.	11.305

Table 8. Polyester tensile properties of control sample and modified samples (24 and 300 hours of irradiated)

Irradiation duration	Rupture force	Elongation at rupture (%)	Rupture time (s)	Strength reduction (%)
-	789.09	42.50	25.50	-
24 hr.	675.30	32.40	16.50	16.701
300 hr.	590.51	20.83	12.50	25.165

Table 9. Yellow index of polyester samples

Radiation duration	Y.I.	Y.I. increase (%)
-	13.128	-
24hr.	22.423	41.452
300 hr.	38.685	66

Table 10. Samples water absorption

Radiation duration	Immersion duration
-	7 min
24hr.	2 min
300 hr.	15 min

Table 11. Effect of radiation on rubbing fastness of samples

Rubbing fastness		Dyeing agent	Radiation intensity	Radiation duration
dry	wet			
4	4	Magenta-Maxilon	-	-
3-4	4	Magenta	10	12
4	4	Maxilon	10	12
4-5	4	Magenta	20	75
4-5	4	Magenta	20	150

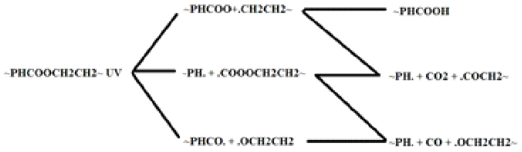
Table 12. Washing fastness of samples

Staining		Washing fastness	Dyeing agent	Radiation intensity	Radiation duration
Polyester	Wool				
4	4	4	Magenta-Maxilon	-	-
4	4	4	Magenta	20	12
4	4	4	Maxilon	20	12
4	4	4-5	Magenta	20	75
4	4	4-5	Magenta	20	150
4	4	4-5	Magenta	20	300

Table 13. Light fastness of polyester fibers

Light fastness*	Dyeing agent	Radiation intensity	Radiation duration
4	Magenta-Maxilon	-	
2	Magenta	20	24
3	Magenta	20	150
4	Magenta	20	300
2	Maxilon	20	24
3	Maxilon	20	150
4	Maxilon	20	300

*all dyeing process was performed with 1:1 standard depth



Scheme 1. The polymer chain cleavage reactions caused by UV radiation

three samples dyed with 2% concentration of Magenta dye after radiation treatment.

Color depth increase in irradiated polyester and polyester/cotton blend is more significant than in cotton sample. Because of negatively charged hydrophilic groups formed in the polyester and polyester/cotton surface cationic dye absorption increase. In each sample, titanium dioxide decrease color depth.

•**Effects of UV radiation duration & penetration on the physical structure of the samples**

In table-7, K/S values for two polyester samples, which have been exposed to radiation one for 24 hours and another 300 hours and then dyedwith cationic dye,Magenta,are shown.

According to the above table for 300 hours irradiated sample color depth is more thanthesample that is irradiated for 24 hours. In fact, by increasing the exposure time of the samples hydrophilic groups formed by radiation so water&color absorption into the structure of the samples become much easier & even back of the samples were affected.

•**The effects of radiation on the strength of polyester**

Elongation at rupture, torn strength and torn time of samples (at 25C) was obtained using the strength tester (Instron). The results are summarized in the table-8 below.

According to the table-8,control sample rupture force is more than polyester with exposure times of 24 and 300 hours. This is due to damaged polyester chain and the formation of new functional groups. The rupture time and elongation at break of non-irradiated sample is greater than the irradiated sample, which indicates that the radiationdecrease strength.

•**Yellow index**

Asa visual effect yellow index is described on the surface which have been burned or destroyed by light and chemical processes.

As is shown in table-9, increase the exposure time of the samples, increases yellow index level. In fact, by increasing the exposure time,chemical& physicaldestruction occur more often.

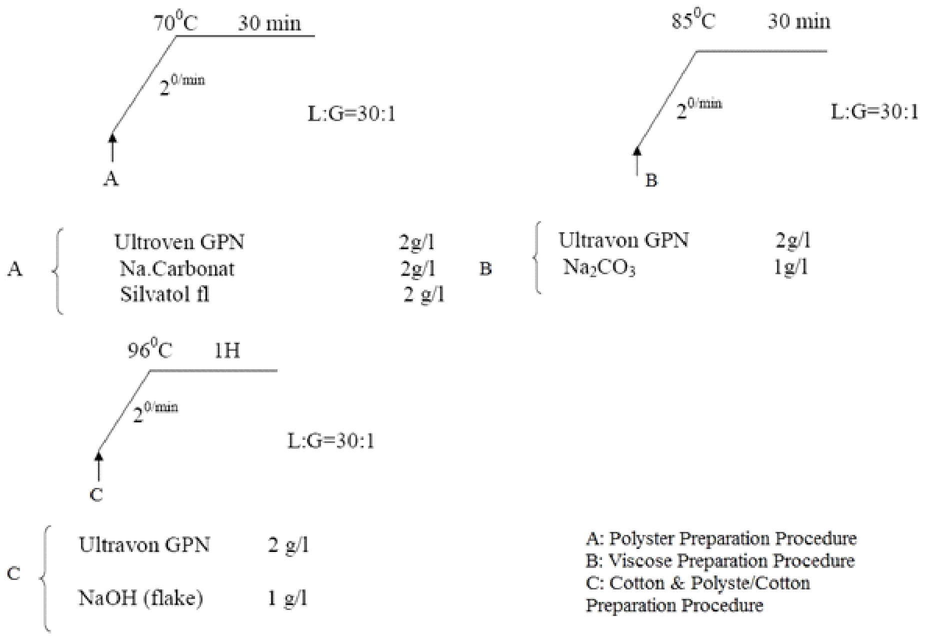
•**The moisture/water absorption of polyester**

The results of test Immersion are summarized in Table-10:

According to the table-10, increasing exposure time, reduce immersiontime and polyester water absorption increase. It is because of increasing the exposure time increase forming of carboxylic acid groups in the sample surface which are so hydrophilic. The water will act polyester variability can be attributed to the increase in the sample hydrophilic groups. Also as a result ofradiation some physical changes in samples surfaceoccur that part of this increase can be attributed to this physical changes.

•**The effects of radiation on the rubbing fastness of sample**

Polyester dyed using Magenta dye shows more rubbing fastness compered to dyed using Maxilon dye. In addition, by increasing the



Fi. 1. Sample preparation graph separated by sample properties

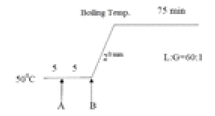
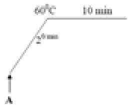
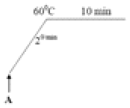
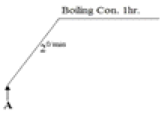
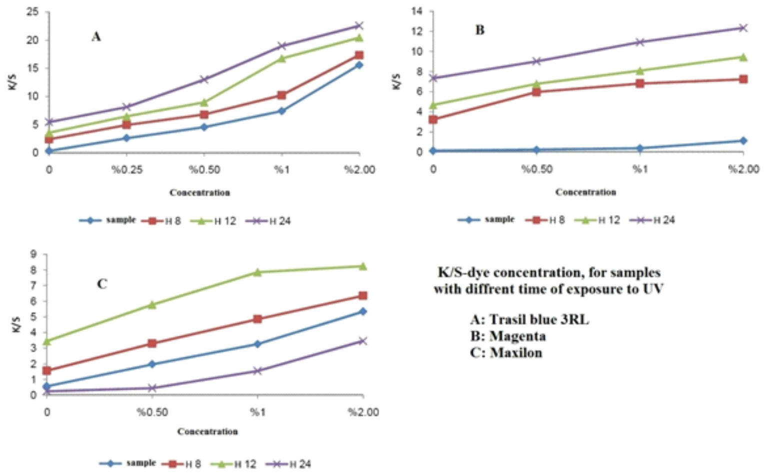
Dying Agent	Concentration	UV Lamp Power	UV Exposed Time	Dying Procedure	Washing Procedure
Disperce Dye (Career)	0.02	10 & 20	24	 A: 0.5g/l Eroipon OL 2 g/l Invalon HTB B: 2% Dye (Terasil Blue 3RL)	Reduction Clearing  A Tinegal W 2g/l Sodium Dithionate 2g/l NaOH (36^0Be) 2cc/l
Disperce Dye (High Temp.)	0.25%-0.5%-1% &2%	10 & 20 W.	8,24 & 48 hr.	Eroipon OL 0.5% HCOOH 1cc/l (pH=4-4.5) Dye(Terasil Blue 3RL) 0.25%, 0.5%, 1%, 2% Temp. 120^0C Time 45min	 A Tinegal W 2g/l Sodium Dithionate 2g/l NaOH (36^0Be) 2cc/l
Cationic Dye	1% & 5%	10 & 20 W.	8,24 & 48 hr.	 A Eroipon OL 0.5% Acetic Acid 3%(pH=4.5) Basic Dye 0.5% , 1%	Washing Using Cold Water
Cibanon Brown 2BR	0.03	10 & 20 W.	8,24,48 hr.	 A 3% Dye 8 cc/L NaOH 32% 3 g/L Na_2SO_4	5cc/l H_2O_2(37%) 1cc/l CH_3COOH Temp. 40^0C Time 10min

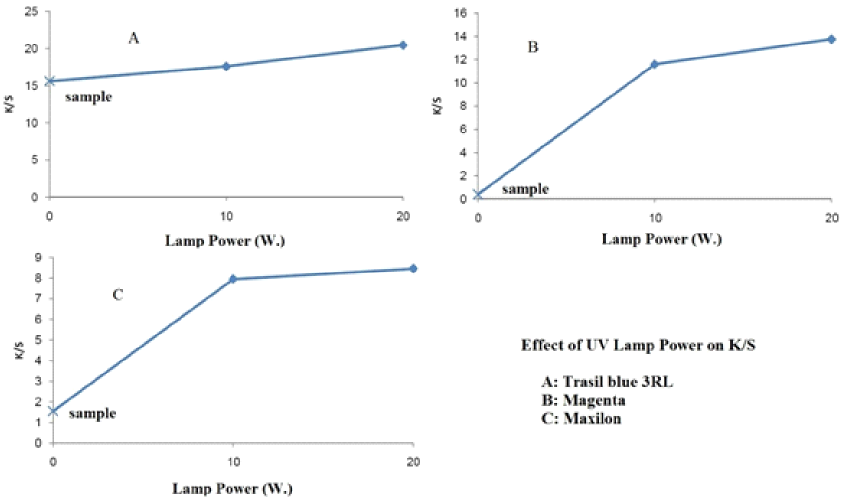
Fig. 2. Dyeing treatment conditions used to separate items



K/S-dye concentration, for samples with diffrent time of exposure to UV

A: Trasil blue 3RL
B: Magenta
C: Maxilon

Fig. 3. Color depth charts K/S for samples dyed with different dyes



Effect of UV Lamp Power on K/S

A: Trasil blue 3RL
B: Magenta
C: Maxilon

Fig. 4. Comparison of K/S for different dyes using different UV radiation intensity

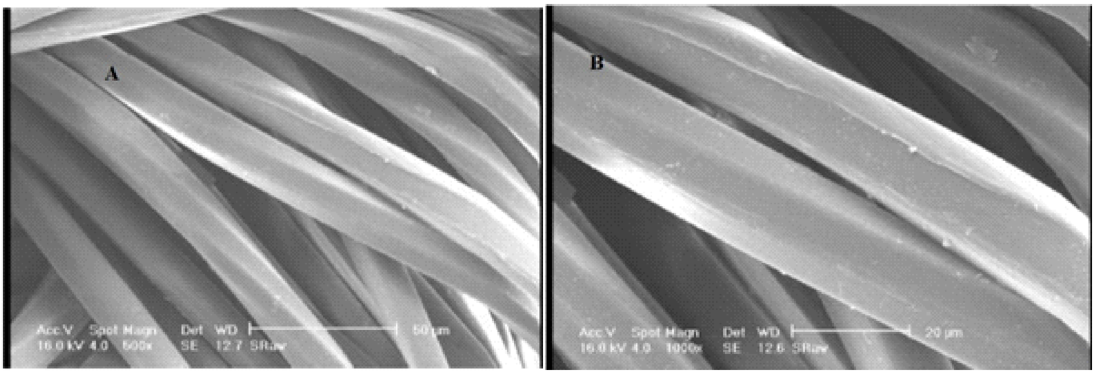


Fig. 5. Control sample; A: scale 1:500, B: scale 1:1000

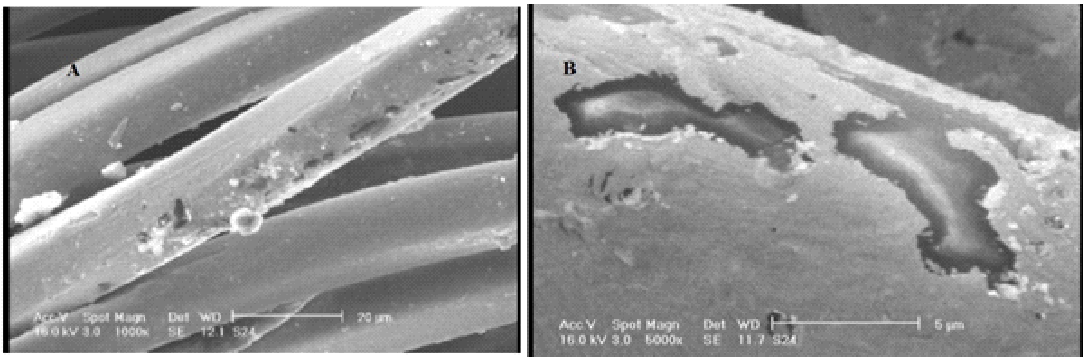


Fig. 6. 24 hour irradiated sample; A: scale 1:500, B: scale 1:1000

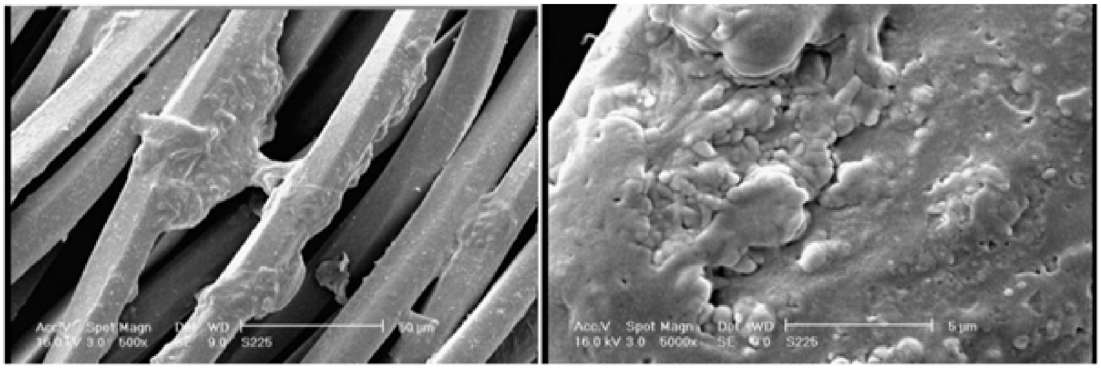


Fig. 7. 225 hour irradiated sample; A: scale 1:500, B: scale 1:1000

exposure time abrasion fastnessincrease, which is due to radiation penetrates deep into the fabric.

•**The effects of radiation on the washing fastness**

Based on the results of standard tests, Table-12, increasing exposure time,increases washing fastness slightly.Also by increasing the exposure time, number of negatively charged groups formed on the surface increase, and connection between dyeing agent and fibers increase.

•**The effects of radiation on light fastness**

The results of both cationic dyes shows increase light fastness increasing exposure time from 24 hours to 300 hours, which could be due to increase inradiation penetration.

The effects of radiation on the surface of polyester fibers using a scanning electron microscope SEM

In Figure-4~9 photographs taken of polyester surfaceirradiated 24 hours and 225 hours compared with the control sample is shown. With increasing exposure time, damage to the surface of the polyester increases.

CONCLUSION

In this study, polyester fabrics modified using UV-radiation. Radiation effect on polyesterdyeability using different dyes were studied. Color depth on polyester samples dyed using disperse dyes increase in the irradiated areas compared tonon-irradiated area.

It should be noted that color depthusingdisperse dyes in presence of career is more than irradiated samples in any case. Dyeing of polyester goods with cationic dye is applicable only in irradiated cases & non-irradiated fiber is not dyeable with cationic dyes. The color depth in polyestersamples irradiated and dyedwith cationic dye is more thancases irradiated & dyed using disperse dyes.Studies show that increasing exposure time and lamp power increases difference color depth.Strength of irradiated and non-irradiated samples, obtained using Instron gauge indicates the fiber strength decrease, increasing exposure time.

To study the moisture/water absorption

of irradiated polyester, immersion test was carried out.By increasing the exposure time, immersion time decreased.Irradiated polyester water absorption can be related to increase in the production of hydrophilic groups on the surface, as well as changes in polyester physical properties.Pictures taken from the irradiated polyester surface using SEM electron microscope, show that by increasing the exposure time, damage on the surface increase, which enhances the dye to the surface of fibers.

Since dyeing irradiated areas, the backward areas cannot be dyed and color is only on the surface of the irradiated areas&creates printing effects on the samples surface, it can be said that changes are in the surface & radiation effects cannot penetrate to the depth of fabrics. By increasing duration of exposure, color depth in affected areas is much increased &radiation penetratesinto the fibers.So it can be concluded that by increasing duration of exposure to radiation it penetrates deep to fibers.The results of rubbing fastness also confirms this conclusion. With increasing exposure time rubbing fastness increases.In this study, titanium dioxide was used as an auxiliary agent in radiation treatment.First, polyester samples was padded with a solution of titanium dioxide and then irradiated with UV radiation and eventually dyed with cationic dye. Color depth in this sample is less than the polyester sample which was not padded with titanium dioxide.So titanium dioxide used as a protective factor against UV effects to reduce its effects and reduces the color depth.While titanium dioxide itself increases the color depth in polyester fibers, which is due to the connection between the dye and titanium dioxide particles.

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