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Pretreatment of Proteinic and Synthetic Fibres Prior to Dyeing

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1. Proteinic fibres

1.1 Wool

1.1.1 Treatment with metal salts

The effect of absorption of some metal ions by wool such as copper, iron, aluminum, cobalt and nickel was thoroughly investigated. The pretreatment of wool with some di- carboxylic acids was studied to present their impact on the amount of metal uptake by wool on its dyeing properties[1-3]. Wool fabric was treated with copper sulphate and ferric chloride solutions (1.5% o.w.f.) at 40° and 60° C for 30 min. The effect of starting pH value of the salt solution on the acquired uptake of copper and iron by wool is illustrated in Fig. 1.1. It can be noticed that the metal uptake increases linearly and strongly for both copper and iron in the range of pH value 3-6 and 1.5-3.5 respectively. Increasing the temperature from 40° to 60°C led to an increase in the amount of metal uptake but the rate was considered to be almost the same or slightly changed. The metal uptake by wool fibres could be enhanced by chemically modifying the fibre with chelating agents able to coordinate the metal ions. It was found that treatment of wool with tannic acid and EDTA has increased the metal uptake by wool and consequently increased the weight gain [4, 5]. Wool was treated with some organic acids such as oxalic, maleic, succinic and adipic acids at 75°C for 90 min. There was a weight gain in wool accompanied to these di-carboxylic acids treatments. The % increase in weights of wool was 3.6, 3.2, 2.6 and 2.5 for wool pretreated with the aforementioned organic acids respectively. These increases in weight were found to correspond to the increase in the carboxyl content of wool from 421.7 meq/100 g fibres for untreated one to 622.1, 530.5, 457.3 and 425 meq/100 g fibres for the treated wool with the aforementioned acids respectively [6]. The metal uptake of treated wool with oxalic acid increases as shown in Table 1.1. Other acids treatment did not enhance the metal uptake property. This may be due to the large molar volume of these acids which might restrict the penetration of metal ions into wool macrostructure [3].

The elongation %, tensile strength at break and alkali solubility of the untreated and treated wool with metal salts solution at 60°C are illustrated in Table 1.2. The results indicated that nearly no changes in the mechanical properties of the treated wool were noticed. It is well known that the tensile properties of wool could be affected negatively during the dyeing process especially at high temperature [7] that might require using of protective agents. This treatment made it possible to dye wool at lower temperature and reflects more protection of wool from damage during the dyeing process (Table 1.2).
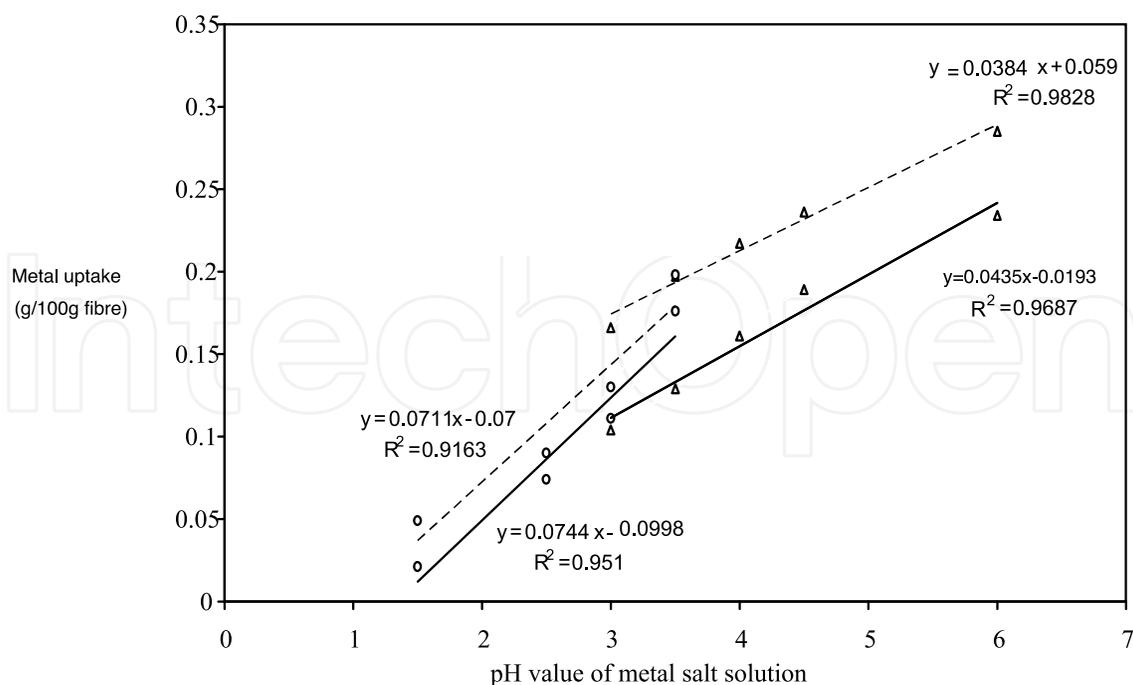
Fig. 1.1. Dependence of metal uptake by wool on the pH value of its solution at different temperatures. Treatment: 1.5 % (o.w.f), Δ-Δ copper sulphate, o-o ferric chloride, ___40º C, _ _60 ºC, 30 min, liq. ratio 1:30.

Wool Samples		Metal uptake (mg/100 g wool)		
		Copper	Cobalt	Nickel
-Treated with metal salts		262.0	154.6	180.5
-Pretreated wool with:	Oxalic acid	366.0	172.1	196.71
	Maleic acid	157.1	21.9	44.3
	Succinic acid	150.4	11.0	19.2
	Adipic acid	129.2	8.2	19.9

Treatment: 0.03 M acid, 75 °C, 90 min., liq. ratio 1:50, 3 % metal salt, 60 °C, 30 min., liq ratio 1:30.

Table 1.1. Effect of pretreatment of wool with some organic acids on its tendency for metal uptake

Type of Sample		Elongation %	Tensile Strength (Kg)	Alkali Solubility
1-Untreated wool		26	41.5	8.82
2-Treated with:	Aluminum sulphate	25	45.5	8.67
	Copper sulphate	20	37.5	8.23
	Ferric chloride	22	43.5	8.42
	Cobalt sulphate	21	41.6	8.81
	Nickel sulphate	21	42.0	8.80

Treatment: 1.5 % (o.w.f.) metal salt solution; 30 min., pH 3.5; liq. ratio 1:30.

Table 1.2. Tensile strength, elongation % at break and alkali solubility of treated wool fibre with metal salts

Dyeability: Four steps could be envisaged in the process of dye uptake: a) diffusion into the fibre surface, b) transfer across the surface, c) diffusion within the fibre to appropriate sites and d) bonding to proper sites. Various algebraic expressions have been derived from Fick's laws of diffusion in an attempt to describe experimental dyeing rates. Near parabolic rates were seen [8]. The equilibrium for the dye- wool interaction could be separated into the following:

$$W - NH_3^+.OOC - W + Dye \rightleftarrows W - NH_3^+.^-Dye + ^-OOC - W$$

$$H^+ + ^-OOC - W \rightleftarrows H.OOC - W$$
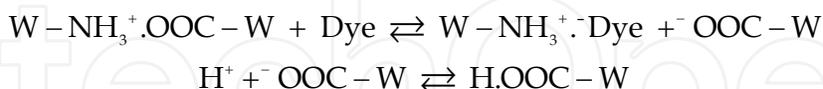
Probably the rate of the second step would be fast and thus the first step would be the rate determining. Combining the metal ions with carboxyl groups led to increasing the reaction in the forward direction and consequently increasing the rate of dyeing.

Pretreatment of wool prior to the metal treatment with some organic acids such as oxalic, maleic, succinic and adipic had enhanced the wool dyeability. Oxalic acid led to nearly complete exhaustion of dye from the dyebath after 30 min at 95°C as compared to 90 % exhaustion for the untreated one dyed for 60 min. at the same temperature (Table 1.3). The dyeing rate constant and the diffusion coefficient increased by the aforementioned treatment while the half dyeing time decreased (Table 1.4). Both alteration (alt.) and staining (st.) washing fastness properties of wool dyed with acid dye at 95°C were found to be good.

Type of Samples		Dye uptake (g dye / 100 g fibre)		
		Cobalt sulphate	Nickel sulphate	*Ferric Chloride
Treated wool		1.89	1.9	1.92
Pretreated wool with:	oxalic acid	2.0	2.0	1.96
	Maleic acid	1.99	2.0	1.96
	Succinic acid	1.94	-	-
	Adipic acid	1.96	-	-

Treatment: 0.03 M acid/100 g fibre, 75 °C, 90 min., liq. ratio 1:50, 3 %metal salt, 60 °C, 30 min., liq ratio 1:30. Dyeing: 2% C.I. Acid Red 41, * C. I. Acid Orange 19, 95°C, 30 min, pH 4.5, liq. ratio 1: 50

Table 1.3. Dyeability of pretreated wool fabric with some organic acids followed by metal treatment

Type of Sample	$t_{1/2}$ min	k^1 x 10^{-4} (cm/sec)$^{1/2}$	D x 10^{-7} cm^2 sec^{-1}
- Untreated wool and dyed at:			
75°C	14.5	4.976	2.7611
85°C	13.3	6.01	2.8151
95°C	9.0	8.12	3.5684
- Treated wool with aluminum sulphate at 40°C, dyed at:			
75°C	12.2	7.417	2.7914
85°C	11.1	8.08	2.9277
95°C	7.8	9.901	4.2467
- Treated wool with aluminum sulphate at 60°C, dyed at:			
75°C	10.0	8.487	3.0113
85°C	8.9	9.343	3.2365
95°C	6.7	10.954	4.5914

Type of Sample	$t_{1/2}$ min	k' x 10^{-4} (cm/sec) $^{1/2}$	D x 10^{-7} cm^2 sec $^{-1}$
- Treated wool with *copper sulphate at 40°C, dyed at:			
75°C	9.3	17.3	3.5014
85°C	8.4	18.762	3.638
95°C	7.4	20.692	4.1716
- Treated wool with *copper sulphate at 60°C, dyed at:			
75°C	8.8	18.1288	3.6961
85°C	8.2	19.6198	3.6427
95°C	6.5	22.3721	4.6041
- Treated wool with **ferric chloride at 40°C, dyed at:			
75°C	12.3	6.668	3.0978
85°C	11.7	7.754	3.2777
95°C	8.6	9.3165	4.3088
- Treated wool with **ferric chloride at 60°C, dyed at:			
75°C	11.7	7.1703	3.1014
85°C	10.5	8.2731	3.3779
95°C	8.0	9.7906	4.5258

Treatment: 1.5 % (o.w.f.) metal salt solutions, 30 min, pH 4.5, **pH 3.5, liq. ratio 1: 30.
Dyeing: 1% (o.w.f.), * 2% (o.w.f) C.I. Acid Blue 221, pH 4.5, liq. ratio 1: 50.

Table 1.4. Half dyeing time ($t_{1/2}$), dyeing rate constant (k') and diffusion coefficient (D) of untreated and treated wool with metal salts.

1.1.2 Treatment with sulphamic acid

Chemical treatments of wool and its blends with synthetic fibres are one of the goals to provide new characteristics and to promote their dyeabilities [10, 11]. The advent of a new practical dye resist treatment, based on sulphamic acid for wool dyeing has brought about renewed interest in its dyeing capabilities especially for its acrylic blend. The application of sulphamic acid onto wool revealed a promoted possibility of cationic dyeing. The dye uptake usually resulted in higher dye exhaustion with level and full penetration of dye molecules into wool fibres. Sulphamic acid treatment offered the possibility of producing deeper shade on wool/acrylic blend without increasing the dye concentration used. Dyeing of the blend could be then achieved with single class of dye and possibly in one bath [12, 13]. Wool fabric was immersed in sulphamic acid solution using concentration of 5-20 % (w/w), padded to pickup 70 %, dried at 80°C for 15 min., and then thermofixed at 160°C for 5 min. The treated wool was subjected to dyeing with cationic dye at 80°C for time intervals of 5–60 min. Wool pretreated with either 15 % (o.w.f) sulphamic acid solution attained nearly the same dye uptake upon dyeing with cationic dye under the same conditions. Alkali solubility of wool before treatment was found to be 15.6 % and that of the sulphamic pretreated wool was found to be 30 %, indicating that there is some damage of wool pretreated under these conditions. Infrared spectroscopy of the untreated and pretreated wool with sulphamic acid shows that no new peak appearance except SO_4^{-2} groups, which appeared at 1150 – 1050 cm^{-1} and also a peak belonging to sulphamic acid groups appeared at 1090 cm^{-1} as compared with the untreated one [14, 15]. SEM of the untreated and the sulphamic acid treated wool shows that most of the scales have disappeared and wool attained a relatively smoother surface than the untreated one (Figs 1.2 and 1.3).

Fig. 1.2. SEM graph of untreated wool.

Fig. 1.3. SEM graph of sulphamic acid-treated wool.

1.1.3 Treatment with chitosan

Chitosan sorption on proteinic fibres is found to be due to ionic interaction between the negative charges of carboxylic groups in the polypeptide macromolecule and the protonated amino groups of chitosan, and possibly due to hydrogen bonding between the hydroxyl or amide groups of polypeptide chains and similar groups in chitosan. The application of chitosan onto wool reveals even dye uptake resulting in higher dye exhaustion with level and full penetration of dye molecules in wool fibres[16]. The treatment of wool with chitosan permits the formation of an approximately uniform sheath on individual fibres. Chitosan treatment does not involve changes in colour fastness of the dyed wool to any extent, but may reveal some problems such as weak binding. Such problems are reported to be overcome upon applying chitosan onto wool with a nonionic surfactant [17, 18]. The possibilities of improving the reactive dye affinity to wool fibres and their protection from damage by conducting chitosan treatments of wool before subjecting it to reactive dyeing were reported [10]. Wool fabric was treated with chitosan and nonionic surfactant using diluted concentrations 0.1- 0.7 % (w/w) and then dyeing the pretreated wool with reactive dye at 80°C for 5-60 minutes. The pretreatment of wool with chitosan enhanced the colour

intensity and the dye uptake as compared with the corresponding untreated one. The rate of dye fixation percentage of the dyed pretreated wool increased as compared with the corresponding untreated one. The rating of crocking and washing fastness was found to be higher than the corresponding untreated ones. Alkali solubility of wool and chitosan treated wool was 18.6 % compared to 15.6 % for untreated one, indicating that there is insignificant damage of treated wool. SEM micrograph of the chitosan treated wool is shown in Fig 1.4. Most of the scales have disappeared and wool attained a relatively smoother surface. Some holes were detected on the surface of treated wool.
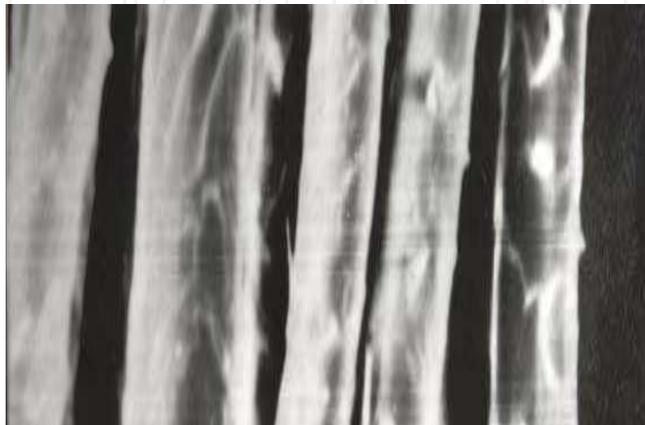

Fig. 1.4. SEM of chitosan treated wool

1.1.4 Treatment with epichlorohydrin and alkoxides

Treatments of wool fabrics were performed using organic acids such as acetic, mono–, di –, trichloroacetic, propionic and butyric acids [19]. Wool fabrics were treated with chitosan at different times and temperatures [17]. The aforementioned treated fabrics were then dyed with reactive dye. The increase in the colour intensity and dye- uptake of the dyed fabrics was found to depend upon the type of the organic acid used in the pretreatment and the pK_a values of the acids used [20, 21]. The acquired colour intensity and dye uptake of the pretreated wool increased compared to those of the untreated one. The dyeability of the treated wool and wool/polyester with some alkoxides using methyl, ethyl, propyl and butyl alcohols is improved towards acid as well as disperse dyes. Treatment of wool with epichlorohydrin [22] was found to improve its dyeability in comparison with the untreated one. Wool fabrics were firstly immersed in sodium thiosulphate or sodium bicarbonate mixture then treated with epichlorohydrin solution (0.25 mol/l) at temperatures 60°C and 80°C for different time intervals 10- 20 min. The treated fabrics were then dyed with a reactive dye for one hour at 80°C and the corresponding dye uptake was determined. Upon increasing the time of wool treatment with epichlorohydrin, an increase in colour intensity and dye uptake were attained. It was reported [23] that serine, tyrosine, aspartic and glutamic acids, arginine, lysine, histidine and the amino end groups in wool macromolecule are possibly the reactive sites for the interactions with epoxides. Water is required to enhance the reaction of epoxide with wool. A wide variety of chemical treatments have been used for wool having the objective of controlling the degradation of the fibre surface, with the least amount of damage. One of the early approaches was the use of alkalies dissolved in aliphatic alcohol to reduce the fibre swelling and to confine the beneficial effects on the fibre surface [24- 27].

1.1.5 Enzyme treatment

The possibility of obtaining various finishing effects on wool by the use of environmentally friendly treatments such as enzymes has been investigated. However the complexity of wool fibre makes it difficult to find the enzymes that are able to modify wool properties without excessive damaging its structure. Application of enzymes, particularly protease, to wool has been studied to achieve a non-felting fibre. The efficiency of shrink-resist protease treatment, the effect of treatment on the absorption of some reactive dyes, and the action of protease enzyme when added to the dyebath was reported to improve the dye absorption by wool fibres. The influence of pretreatment of wool fabrics with a lipase enzyme on its dyeability with reactive dyes was studied [28-30]. The enzymatic treatments by exhaustion technique were performed in a bath of a liquor ratio, 1:40 for different intervals of time (10 min and 24h). The concentration of enzyme ranged between 0.2 - 2.0 % (o.w.f.). The pH of the treatment bath was adjusted to 10.7 using phosphate buffer. The enzyme treated fabric was then squeezed and air dried. Wool fabric was treated by padding technique after immersing in a 3 % enzyme solution buffered to pH 10.7. The fabric was padded and squeezed twice to have a pick up of 70 %. The padded fabric is then stored in an air tight polyethylene bag for 24 h. The treated fabric was then dried at room temperature before dyeing. The pretreatment of wool fabric with lipase enzyme has induced significant improvement on its dyeability with the reactive dyes (C.I. Reactive Blue 203 and C.I. Reactive Red 21). As the amount of the lipase increases, the rate of dye uptake increases. Lipase enzyme has been reported to remove the surface lipids of the fibre and thus enables improved penetration of solutions, including dyes, to the interior of wool fibres [28]. The dye uptake of wool fabric is dependent on time of treatment. A complete exhaustion of C. I. Reactive Red 21 (1% o.w.f.) from the dyebath was achieved after about 10 min of dyeing of the enzyme pretreated wool at 80^0C compared to about 48% exhaustion for untreated one. Complete dye exhaustion has a positive impact on reduction of indoor pollution, cleaner production and energy saving. The half-dyeing time ($t_{1/2}$), specific dyeing rate constant (K') as well as the diffusion coefficients (D) were calculated for untreated and pretreated wool fabric with lipase according to the following equation:

$$K' = 0.5 \cdot C_{\infty} \cdot (d/t_{1/2})^{1/2}$$

$$D = C_t / C_{\infty} \cdot \frac{d^2 \cdot 100}{t}$$

Where C_{∞} is the % dye absorbed on the sample at equilibrium conditions between the sample and the dyebath divided by the weight of the sample, C_t is the dye uptake after 10 min and d is the fibre diameter in cm. Time of half dyeing ($t_{1/2}$) of pretreated wool fabric is less than that of untreated one. This can be contributed to the higher dyeing rate and higher dye diffusion of the treated wool fabric (Table 1.5). Using exhaustion or padding technique in treatment process (for 24 h at room temperature) resulted in the same effect in enhancing the dyeability of wool and reducing the half-dyeing time. The quantity of dye absorbed after short dyeing time (10 min) can substitute the diffusion values, so a modified Arrhenius relationship can be applied as follows :

$$\ln C = \ln C_0 \cdot \frac{-E}{RT}$$

Where C is the dye absorbed after a short dyeing time, C_o is constant, T is the dyeing temperature in ^0K and E is the activation energy of diffusion. Plotting ln C versus $1/T$, two straight lines may be drawn, one at high temperature and the other at lower temperature. The two lines intersect at a point with approximately constant value of 1n C (ln C_i) and $1/T$ is increasing for treated wool fabric. The slope of the straight line is $-E/R$ from which the activation energy of diffusion (E) can be calculated where R is the universal gas constant. For the early stage of dyeing where the outer layers of the fibre are involved, a certain number of dye sites in the outer layer of the fibres saturate slowly; diffusion towards these sites presents high activation energy (E_1) at dye concentration lower than C_i. Evaluation of E_1 for untreated and pretreated wool fabric was 15.4 and 6.6 kJ/kg.mol.^0K respectively. The enzymatic treatments led to first saturation at lower temperature, where it was 102^0C for untreated wool sample and 72^0C for pretreated one. Diffusion towards the other sites follows the first saturation and a decrease in activation energy was observed at a second linear relationship (E_2 at $C>C_i$), it was evaluated by 1.402 kJ/kg.mol.^0K for treated wool fabric. The kinetic investigation of the dyeing process revealed a decrease in half dyeing time, an increase in the dye rate constant and diffusion coefficient and also a decrease in the activation energy of diffusion.

Type of Sample	$t_{1/2}$ min	K' $x10^{-5}$ (cm/sec)$^{1/2}$	Dx10^{-7} cm^2.sec^{-1}
-Untreated	16	1.14	1.980
-Pretreated by:			
exhaustion technique	7.5	2.08	3.803
Padding technique	7.5	2.08	3.803

Treatment: 2% (o.w.f.), 25^0C, 24h, Dyeing: 2% (o.w.f.) C.I. Reactive Red 21, 80^0C, pH 4.5, L.R. 1:50.

Table 1.5. Time of half dyeing ($t_{1/2}$), specific dyeing rate constant (K') and diffusion coefficient (D) of pretreated wool fabric with lipase.

1.2 Silk
1.2.1 Treatment with saccharin
Colouration of wool, silk and polyamide fibres are satisfactorily performed with acid dyestuffs. Energy saving as well as high fastness performance and reduction of costs can be reasonably gained by applying cationic dyes to the fibres used in carpet manufacture. An attempt has been directed to give evidence of the benefits of treatment of silk fibres with saccharin during dyeing [22, 25]. Silk fabrics were treated with saccharin solutions (10 g/l); the treatment was carried out at 90°C for 1h. The effect of this treatment on the dyeing ability of silk fabrics with C. I. Basic Red 18 was studied. The pretreatment with saccharin had enhanced the colour intensity of the dyed fabrics, as compared to the untreated dyed one. The increase in colour intensity was found to be dependent on the temperature and the time of dyeing. The increased affinity of the saccharin treated fabric to the cationic dye can be attributed to the possibility of the breakdown of saccharin molecules liberating carboxylic acid groups. These groups have the ability to trap both cationic moiety as well as the NH_2 group of the fibres.

1.2.2 Treatment with organic solvents
Some studies on the solvent effects on shrink proofing of silk fabrics were reported[31, 32]. The shrink proofing was obtained by treatment with dimethylsulphoxide, dimethylformamide,

dimethylacetamide, sulfolane, and ethylene glycol in a closed curing system. The treatments with hexa-amino-cyclotriphosphazene in dimethyl sulphoxide, ethylene glycol, glycerol and the mixtures of (dimethylsulphoxide, ethylene glycol), and (dimethylsulphoxide, glycerol) were more effective for shrink proofing even with small amounts of resin deposition. These results showed that the molecular orientation and cross linking in medium crystalline regions played the important role for shrink proofing of silk crepe. Dimethylsulphoxide was one of the best solvents for the shrink proofing by phosphoric amides. Some of the fundamentals governing the shrinkage of silk goods were explained based on the release of the strains imposed during manufacturing processes and the swelling produced on wetting. The mechanism of the swelling by organic solvents was explained in terms of the solubility parameter of the solvents and hydrogen bonding and dipolar interactions between silk and the solvents.

1.2.3 Plasma treatment

Chemical modification of textile fabrics was early used as a tool for imparting new fibre properties and increasing its effective applications. However, these chemical methods are not always environmentally friendly and may also produce changes in the mechanical properties of the fabric which makes them less comfortable to wear. Nowadays, physical technologies can advantageously replace some of these chemical modifications as environmental friendly process. Plasma treatment is a rapid, innovative and environmentally amenable method which could replace wet chemical application to modify the surface properties of polymers and textile materials without significant effects in the bulk of fibres. Interest was directed to produce durable silk surface as well as use reactive dye for its printing. Plasma surface treatment of silk was carried out in atmospheric air at different discharge powers for different plasma exposure times. The effect of plasma treatment on the printability of silk fabric with reactive dye using conventional silk screen printing technique is investigated. The printability of silk was found to be markedly improved as well as its fastness properties. The whiteness of plasma treated silk increased by increasing the discharge power. The wettability of treated silk expressed as wetting time was found to depend upon the treatment time and discharge power [33].

2. Man made fibres

2.1 Polyester

Polyester fibers have attained a major position in the textile and non-textile uses, although polyester fibers have several drawbacks vis. low moisture regain (0.4%), a tendency to accumulate static charges, pick up soil dirt during wearing, difficulty of cleaning during washing, pill formation, thus spoiling fabric appearance and flammability. Modifications of polyester fibers can have an effect to overcome these disadvantages and can promote its permeability, hydrophilicity, hand and thermal properties [1, 2]. Modification of polyester fibers is carried out via its treatments with alkalies, combined thermal and alkali, mono or multifunctional amines, organic solvents and acids as well as enzymatic hydrolysis. Thermal treatment of polyester fibers is a well known and important method in modification of the polymeric structure of the fibers. The purposes have increased to concern and cover the specific physico-chemical changes of the fiber structure to induce a certain tendency of crystallinity and orientation.

Unevenness is one of the major drawbacks in their dyeing. Drastic dyeing conditions are usually performed to overcome unevenness, to promote colour homogeneity and depth, which however endanger the properties of the fibres. The lower barré effect appears from the application of dyes having high diffusion efficiency in polyester fibres. It is an oversimplification to deem that polyester is a solid solvent for disperse dyes and other hydrophobic molecules [3]. Some relationships exist between the rate of dye diffusion, temperature, steric structure of the dye, size of voids in the substrate and elasticity of the amorphous regions. Ensuring the benefits of chemical modifications of polyester fibres in order to introduce new possibilities by changing its dyeing characteristics was done [3,4]. It is nearly impossible for a dye molecule to diffuse into the polyester structure at low temperature; adequate rates are only achieved when dyeing temperature exceeds the glass transition temperature of the fibre. Satisfactory dyeing of polyester fibres can be carried out by loosening the fibre structure. This can be achieved by high temperature treatments; or during high temperature –high pressure dyeing or via carrier dyeing. High temperature and carrier dyeing methods succeed in opening the fibre structure. As the fibre is being heated thermal motion of the polymer chains increases, thus allowing dye molecules to diffuse in. Dyeing begins in the least oriented regions of the fibres. The orientation of polymeric, chains directly determines the rate of diffusion and dyeing rate. Treatment with organic solvents increases the dyeability of polyester in spite of a significant increase in crystallinity. Preswelling and plasticization of polyester fibres promote its physico-mechanical properties as well as dyeability characteristics. Plasticizing effects occur due to carrier attack on polyester fibres resulting in larger and more accessible channels and voids giving more porous fibre into which dye and water molecules can diffuse more rapidly and uniformly[5-13].

2.1.1 Treatment with alkali

Alkaline hydrolysis has been used since several years to modify the physical properties of polyester. It is well established that the alkaline hydrolysis of polyester fibers using aqueous sodium hydroxide is confined to the polymer surface [3,4]. When using sodium hydroxide in alcoholic media, the attack is found to be more severe and weight loss occurs more rapidly. Sodium alkoxides form alkyl ester end groups during the ester interchange reaction with polyester, resulting in a more rapid loss in weight than using aqueous sodium hydroxide. Alkali treatment of polyester fibers in glycolic media was also tried. Combined thermal and alkali treatment was carried out [14-21].

Theory of Alkali Hydrolysis: Two separate kinds of chain cleavage may occur. The first may involve the reaction of single hydroxide ion with the chain to produce a carboxylate anion and hydroxyl end groups of the shortened chain. This reaction does not produce a weight loss directly but may increase the weight due to the addition of hydroxide ion. The second reaction involves the attack of two hydroxide ions essentially simultaneously some distance apart along the same polymer chain backbone [22]. In this case, a low molecular weight segment of the chain is removed as a single unit, resulting in a loss in weight from the polymer. Further reaction of these low molecular weight segments occur in liquid phase and do not contribute further to the weight loss of polyester, but it does contribute to depletion of the caustic concentration of the solution. Both of these reactions occur at the interface between the caustic solution (liquid phase), and the fibre surface (solid phase). At the moment of reaction, molecular solvation of the polymer must be minimal. Accordingly, this step of the reaction must be slow. Another kind of reaction is a scission of an already-

cleaved chain at the carbonyl group distal to the free end group of the chain. The free end groups consist of either terephthalate anion or the hydroxyl ethyl group. The reactions leading to elimination of the terephthalate dianion or ethylene glycol by "un- zippering" (i.e., the progressive reaction of the chain with hydroxide ion, beginning at a free end group) occur at locations that may be solvated, and hence can be expected to have rates that are faster than the rates of chain cleavage. Hydrolysis at the end group produces one molecule of either ethylene glycol or the terephthalate dianion for the reaction of each hydroxide ion. Consequently, this sort of reaction is first order in hydroxide concentration, while chain cleavage may be either first order or second order in hydroxide concentration. Neither the density, the intrinsic viscosity, nor the number of carboxyl end groups changes appreciably as compared to the untreated one after treatment with 10% solution of aqueous caustic at 60°C for 2h, as the reaction does not occur in either regions of low order or high order and the attack is at the ends of the polymer [23, 24]. A theoretical model has been developed to describe the kinetics of polyester fiber dissolution in alkaline solutions. The model is based on the surface reaction concept. The rate of dissolution is taken as being proportional to the surface area of fibers and to the concentration of OH⁻ ions raised to a certain power (order of reaction: 0, 1, or 2). Integrated forms of rate laws are derived for all possible orders of dissolution reactions. According to the results, the weight loss is not a simple linear function of time, as usually accepted. The kinetics of the process is characterized by the rate constant, which is, for a given system, independent of the content of OH⁻, fibers, and water in the system [25-28].

Alkali Treatment in Aqueous Medium: Hydrolysis of polyester fabrics with sodium hydroxide was found to improve the hydrophilicity and other comfort-related properties of fabrics. Effect of the reaction parameters such as treatment time, sodium hydroxide concentration, and temperature on the extent of hydrolysis is examined. The modified fabrics are evaluated for their physical, mechanical and physico-mechanical properties [29, 30]. Improved moisture absorbency of polyester fibers can be achieved by introducing hydrophilic block copolymers [31]. In addition, penetration of water into the interior of the fibers has not been clearly shown to improve perceived comfort. Surface modifications can have an effect on hand, permeability, and hydrophilicity. Polyester fibers are susceptible to the action of bases depending on their ionic character. Ionizable bases like caustic soda, caustic potash and lime water only affect the outer surface of polyester fibers. Primary, secondary bases and ammonia can diffuse into polyester fibre and attack in depth resulting in breaking of polyester chain molecules by amide formation [32]. The action of strong base leads to cleavage of ester linkages on the fibre surfaces [33, 34]. The result is the formation of terminal hydroxyl and carboxylate groups on the fibre surface. Hydrolysis is believed to increase the number of polar functional groups at the fibre surface.

Caustic treatment in organic solvent medium

Some methods are involved to overcome the low water absorption of polyester fibers to improve its dyeability. The compactness of the structure of polyester fibers minimizes the rate of the dye diffusion. To overcome this difficulty, swelling agents or high temperature treatments are used. Preswelling and plasticization of polyester fibers promote their physico-mechanical properties, moisture regain, as well as dyeability characteristics. Treatment of polyester fabric with ethanolic sodium hydroxide solution showed a significant improvement in the absorbency behavior of the polyester fabric, such as the decrease in wicking time and relative increase in the moisture regain percentage, as

compared with the untreated mate [35-40]. It can be noticed from the scanning electron micrographs (Figs 2.1 and 2.2) of the untreated and treated polyester fabric with sodium ethoxide that there is a change on the surface of the polyester fabric without whole-fiber damage. This may be due to the use of alkoxide solutions causing a reduction in the whole-fiber swelling and thus imparting beneficial effects on the fiber surface [38].

Fig. 2.1. SEM of untreated polyester fabric [16].

Fig. 2.2. SEM of treated polyester fabric with ethoxide [16].

The dyeability of the pretreated polyester fabric with disperse dye shows some progressive improvements with lowering the dyeing temperature and/or decreasing the time of dyeing. Ethoxide is found to be more effective in enhancing the dyeability of polyester fabric than either methoxide or propoxide. A decrease in the half dyeing time and an increase in the rate of dyeing of the pretreated polyester as compared with the untreated one are noticed [38]. The influence of the variation of dye concentration in the solution on the extent of dyeing is studied by plotting rate of dyeing (tan α) against the dye concentration. This relation is illustrated in Fig. 2.3. The resultant curve is found to rise moderately at low dye concentration up to 0.2 g/L, and then the increase of tan α is slowed down by increasing the dye concentration up to 0.4 g/L for both dyed untreated and pretreated polyester fabric. The assumed equations of the curved line in Fig. 2.3 are:

$$Y = -2.9369x^2 + 2.4799x \quad \text{for untreated polyester fabric;}$$
$$Y = -7.3587x^2 + 5.8675x \quad \text{for pretreated polyester with propoxide;}$$
$$Y = -7.8556x^2 + 6.4022x \quad \text{for pretreated polyester with ethoxide}$$

Differentiating of the previous equations (y`) that represent the tangent of the curve at any point, it is found that $y`_{x=0.1}$ = 1.9 and $y`_{x=0.2}$ = 1.3 for the untreated sample, whereas the corresponding values for the pretreated sample with propoxide are 4.4 and 2.9 and that for the pretreated polyester with ethoxide are 4.8 and 3.2, respectively. These results indicate that the rate of tan α (y`) is found to decrease by increasing the dye concentration. This would enhance the evenness of the dyed pretreated polyester fabric despite increasing the rate of dyeing, as proved by the above-mentioned mathematical analysis [38].
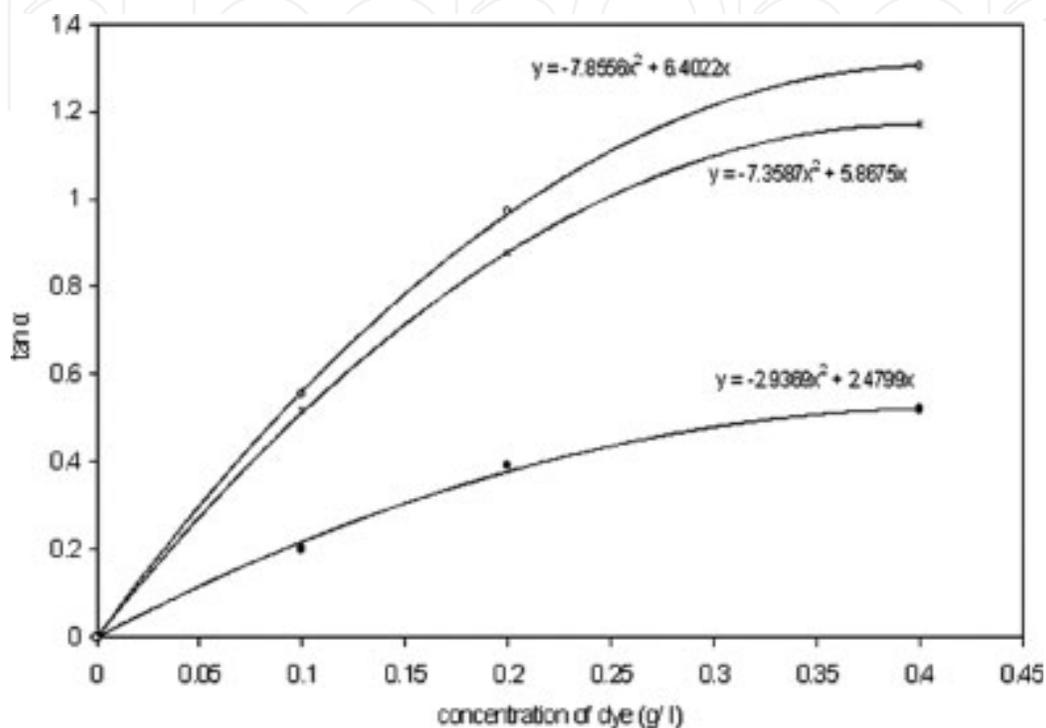
Fig. 2.3. Dependence of tan α value on the concentration of dye used in dyeing of polyester

Ethylene glycol is examined as an accelerating agent, but the improvement is not as good as methanol. Ethylene glycol and glycerin are used to replace the conventional water treatment of the alkaline solution. Both hydrolysis and glycolysis may shorten the treatment time and increase the hydrophilicity and dyeability of polyester [18]. Treatment of polyester fibers with sodium hydroxide using propyl alcohol, propylene glycol and glycerol as a solvent was tried. The degradation rate in both propyl alcohol and propylene glycol is found to increase rapidly. The effect of treatment on some properties of polyester fabric are given through measurements of tensile strength, drapability, permeability, density gradient, crystallinity, moisture regain, and scanning electron microscopy. The use of this treatment can greatly shorten the treatment time to achieve results similar to those with the conventional aqueous system. The effect of concentration of sodium hydroxide in mono-, di- and tri-hydric alcohols on the weight loss of treated polyester fabric is illustrated in Fig. 2.4. The loss in weight resulted from treating of polyester fibres with sodium hydroxide in mono-hydric alcohol (propanol) more than di-hydric alcohol (propylene glycol) more than tri-hydric alcohol (glycerol). The loss in weight is about 10% in case of using propylene glycol corresponds to about 2% in case of glycerol, while using propanol as a medium of alkali hydrolysis leads to complete dissolving of polyester fibres after about 45 min at 65°C with 0.5 M sodium hydroxide [19].
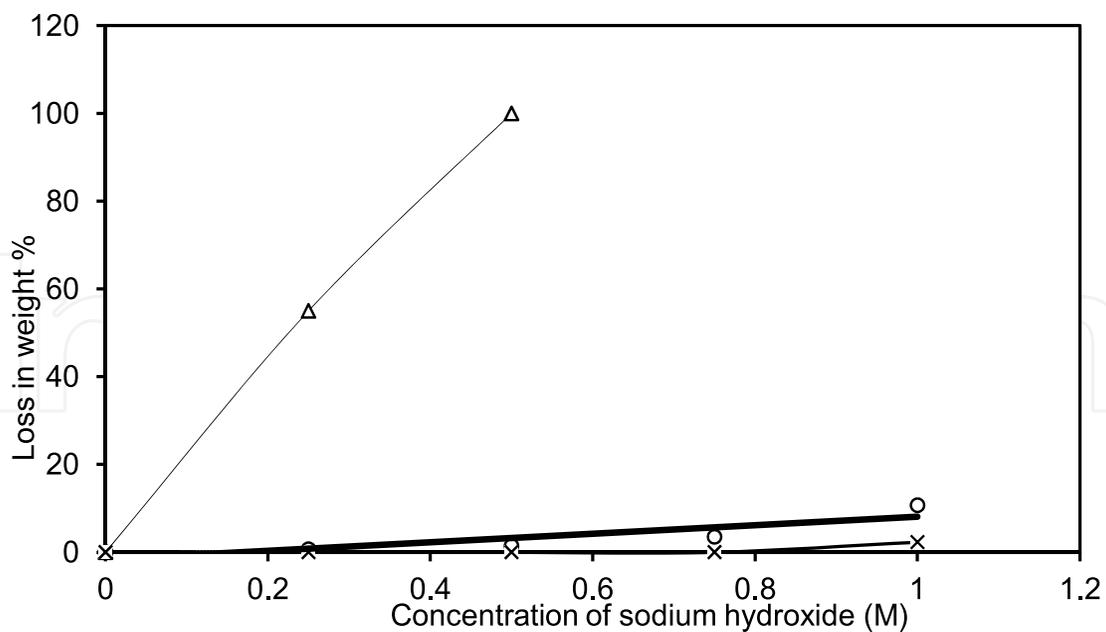
Fig. 2.4. Concentration of sodium hydroxide/ loss in weight of PET fibers, Treatment: 65°C, 45 min, L. R. 1: 25, x-x glycerol, o-o propylene glycol, Δ-Δ propanol

Combined thermal and alkali treatment

In textile processing, polyester fabric is usually heat set to improve dimensional stability and prevent creases during wet processing and handling. Heat setting of polyester fibers is processed to make a change in the fine structure and consequently dyeability and chemical reactivity [39- 49]. The effect of heat setting temperature on the hydrazinolysis of polyester fibers was studied. Polyester partially oriented yarn (POY) is heat set at 100° to 220°C in a fixed state and then treated with hydrazine. Relatively smaller amines, such as hydrazine, swell the less ordered regions of the fibre and attack ester linkages in the molecular chain effectively. The weight loss of thermally treated POY is found to be minimum at 120°C and increased with increasing treatment temperature up to 220°C , while it is recorded to be 160°C for regular polyester because of the difference in the fine structure of the fibers. Hydrazinolysis with 40% aqueous solution of hydrazine monohydrate at 60°C for 120 min incorporates a hydrazide group at the end of the fibre's molecular chain. Hydrazinolysis builds inactive sites for adsorption acid dyes by modified polyester fibers. The crystallinity of the heat-set POY fibers increases with hydrazinolysis as well as the heat setting temperature. Scanning electron microscopy (SEM) photographs of the hydrolyzed POY fibers show appearance of cracks on the fibre surface which differs with variation of heat setting temperature and becomes deeper in the inner regions. Polyester fibre is heat set at 100°-220° C and then hydrolyzed with 10 % aqueous sodium hydroxide solution at 90 °C for 1 and 2h. The disperse dye exhaustion of the heat set/ alkali hydrolyzed polyester is found to decrease with increasing the temperature up to 180 °C. The amorphous/ crystalline ratios are the controlled parameters in dyeing of PET fibre with disperse dye and consequently the applied method in thermal treatment [20]. Other attempts were carried out to improve the dyeability of polyester fabric with disperse dyes at the boil without using carriers or using HT/HP dyeing technique. Some alkyl and/or alkylol amines as well as hydrazine hydrate treatments are carried out by padding technique at room temperature prior subjecting it to the thermal treatment in air and slack conditions. Methylamine, ethylamine, ethanolamine

and hydrazine hydrate (5-20 % v/v) solutions are used in this study as pretreatment reagents by padding technique then squeezed up to 100 % pick up, followed by thermal treatment at 160ºC for 15 min in air under slack conditions. The pretreated fabric is dyed at the boil with disperse dye without using carriers. Treatment of polyester fabric with hydrazine hydrate before thermal treatment led to high enhancement of the fibre dyeability with disperse dyes as well as decreasing the setting temperature of polyester to 160ºC. Applying the padding technique in treatment of PET may decrease the consumption of chemicals in the dyeing process as well as reducing the pollution impacts [40, 48]. The effect of pretreatment of polyester fibers with some amines such as methylamine, ethylamine and ethanolamine followed by thermal treatment is shown in Table 2.1 [40].

PET sample	Color intensity (K/S)					
	0	5%	10%	15%	20%	30%
-untreated	4.9	-	-	-	-	-
-thermally treated	6.1	-	-	-	-	-
-treated with ethanolamine		7.0	9.2	10.0	11.6	-
-treated with methylamine		6.1	6.3	6.5	7.1	8.0
-treated with ethylamine		7.2	7.9	8.3	8.9	9.8

Treatment: 160ºC, 15 min, Dyeing: 1% (owf) C.I. Disperse Red 60, 100 ºC, pH 4.5, L.R. 1:100.

Table 2.1. Dyeability of pretreated polyester fabric with various concentrations of some amines.

The depth of disperse dye inside the interior structure of pretreated PET fabrics increases by the effect of steam and hydrazine hydrate treatments (Table 2.2). Polyester fabrics pretreated with steam have lower Tg values. The chemical/thermal pretreatment of polyester fabrics with hydrazine hydrate causes a decrease in T_g. The glass transition temperatures of pretreated polyester fabric with ethanolamine, ethylene glycol and 2-hydroxy-4-methoxybenzophenone are reported to be 63º, 68 º and 63ºC respectively [40].

Polyester sample	Dye depth in cross section %	T_g °C
-untreated	38.4	72
-hydrate hydrazine treated	46.5	70
-Steam treated	39.5	69.0

Table 2.2. Dye depth and glass transition temperature of polyester fabric.

2.1.2 Enzymatic hydrolysis

Application of biotechnology to textile finishing is an example of more environmentally compatible processes. Enzymes are produced from fermentation of microorganisms (renewable resources) and are biodegradable. Amylases and cellulases hydrolyze starch and cellulose respectively and can be used in desizing of textiles. Hydrolases are capable of hydrolyzing fatty acids or carboxylic esters. Lipases have been reported to biodegrade polyesters. The insoluble nature of polyester fibers in an aqueous medium may limit enzymatic hydrolysis to the surface, thus improving the fibre wettability. The water wetting contact angle of the untreated polyester is evaluated as 75.8º. Polyester fabrics are immersed in the buffer solution (organic and inorganic) at 35ºC for 1h. The organic buffer, tris (hydroxyl methyl)-aminomethane, lowers the wetting contact angle of polyester fabric to

67.5°. The inorganic buffer, sodium phosphate, increases the contact angle to 81.9°. Any improvement in surface wetting can be due to the hydrolyzing action of the lipase. Some types of lipases are found to decrease the water wetting contact angle to 57.4° without significant change in breaking tenacity and strain of pretreated polyester fabric. The lipase hydrolysis resulted in better wetting surfaces than aqueous alkaline hydrolysis. The improved wettability due to enzyme treatment is accompanied by full strength retention compared to the significant reduced strength and mass from alkaline hydrolysis. The water contact angle is found to decrease from 75.8° to about 52°. As the contact angle decreases, the wettability increases and consequently the dyeability is improved [50-56].

2.1.3 Other trends in dyeing

Organic Solvents: The solvent treatment of synthetic fibres influences strongly dye-diffusion characteristics as well as the equilibrium dye-uptake. Interaction of solvents with synthetic fibres can affect fibre swellability, segmental mobility, irreversible structural changes, shrinkage and shifts in glass-transition temperature. Small amounts of organic solvents such as alcohols were added in the aqueous dyeing baths of synthetic and natural fibres to assist the dyeing process [5-13]. The effect of plasticizing of benzyl alcohol /chloroform (6: 4) mixture on polyester is presumed to increase the degree of crystallinity and the perfection of the apparent size of the crystallites. This effect might occur by reducing the forces of entanglement points between the macromolecular chains. Chain segments thereby acquired relatively sufficient free movement into a crystal arrangement. Part of the amorphous region remains intact and tends slowly to crystallize at an extremely slow rate. The solvent molecules were expelled from the crystal, but still persist to influence the amorphous portion, which exhibited some mobility. Change in the tendency of the modified polyester to uptake disperse dyestuff was also noticed. Polyester structure modification due to binary solvent interaction showed some promising improvement in the accessibility of the substrate to dyeing [57, 58]. Treatments of polyester fibres were performed with non-hydrogen bonded solvents vis. 1, 4-dioxan, N, N'-dimethylformamide, cyclohexanone and with hydrogen-bonded reagents such as formic and monochloroacetic acids [59]. The non-hydrogen bonded-type of solvents were found to be more efficient in improving the colour intensity than the pretreatment with some hydrogen-bonded solvents. Adsorption behaviour of these modified polyester fibres is examined via studying the nature of the dye, maximum adsorption temperature, and dipole moment of the dye molecules [60-64].

Acids: Moderate treatment of polyester and Quiana polyamide fibers with sulfuric acid solution is studied [65]. Significant improvements in the dyeabilities of both fibers with cationic dyes below the boiling point, without appreciable reduction of the fabric dimension are attained. Kinetic characterization of the dyeing process reveals that the time of half dyeing decreased pronouncedly in case of the modified substrates and, consequently, the specific dyeing rate constant increases. A rapid decrease in the relative diffusion coefficient of the sulfuric acid pretreated substrates is observed upon increasing the temperature of dyeing. The dye affinities increase and the corresponding heats of dyeing practically decrease for both modified fibers. The kinetic reactions between both polyester and Quiana polyamide fibers and sulfuric acid were studied [66]. The moisture regain and dye uptake of treated polyester increased [67-70].

Super Critical CO$_2$: The dyeing of polyester textile in supercritical carbon dioxide is investigated experimentally. The influence of temperature and density of the SC-CO$_2$ on the

process was studied in the ranges 85−125°C and 400−550 kg/m³. The dye saturation concentration in the polyester increased and the distribution coefficient decreased with temperature, the latter showing a logarithmic dependence on the reciprocal of temperature. Increasing the fluid density led to an increasing saturation concentration and a decreasing distribution coefficient. When the right temperature and solvent density were chosen for the supercritical process, the same dye concentration could be attained as in aqueous dyeing. The experiments showed that the dyeing was exothermic, with a negative change of entropy. The thermodynamic characteristics of supercritical and aqueous dyeing were concluded to be roughly the same, with similar saturation concentrations, thermodynamic affinities and heats and entropies of dyeing [71]. One-bath dyeing of polyester/cotton blends with reactive disperse dyes is investigated using supercritical carbon dioxide (SC-CO₂) as a solvent in the range of 353 to 393° K and 10 to 20 MPa. The dyeing behavior is compared with the thermosol dyeing method using the same dye. Samples are subjected to a color fastness test and colorimetric measurements. Good color intensity and wash fastness are obtained by the SC-CO₂ dyeing method at 393 K and 20 MPa. The color fastness properties of fabrics dyed in SC-CO₂ are superior to those of fabrics dyed by the thermosol dyeing method [72]. Supercritical carbon dioxide is a suitable solvent for dyeing even for the most sensitive textiles up to 140°C. The treatment time at 160°C should not be longer than 1 hour [73]. Supercritical dyeing can be an interesting alternative to traditional dyeing due to the unquestionable advantage of the use of a clean solvent that can be easily recovered and separated from the excess dye at the end of the process. Set up a pilot plant of supercritical dyeing could be performed with yarn bobbins for polyester textiles [74].

Dyeing with Carriers: Carrier dyeing is a method of dyeing polyester materials that is used when necessary. Although usage of carriers in dyeing enables the dyeing of polyester materials at atmospheric pressure, the undesirable properties of the carriers are drawbacks. Disperse dyes are classified under different energy levels and the dyeing methods and color and fastness properties of dyed materials are associated with this classification. Carriers can be used when dyeing at higher temperatures than 100°C to promote the leveling of the more difficult disperse dyes [75, 76].

Dye Absorption after Thermal Treatment: Thermal treatment of polyester fibers can lead to variation in the absorption behavior as appeared in its dyeing properties, iodine sorption as well as swellability. The rate of dyeing of polyester is dependent on temperature, time and thermal history of the polyester fibers. The dye uptake of disperse dyes by thermally- set polyester initially decreases as the temperature of pre-heating is raised. At higher temperatures the dye uptake increases with temperature and can be greater than that of the untreated polyester fibers depending also on the dye molecule [77]. The variations in dyeing properties of polyester fibers in terms of structure is described using two- phase theory of structure involving crystalline and amorphous regions. The competition between crystallization (with reduction of rate of dyeing) and disorientation of the amorphous region (leading to increased dye uptake) explains the variations of dyeing behavior of polyester fibers with heat setting. The effect of heat setting at various temperatures and draw ratios on the diffusion of disperse dyes into polyester fibers is studied in relation to the measurements of the dynamic loss modulus of the fibers. The diffusion is controlled by the chain mobility of polymer as indicated by measuring the glass transition temperature (T_g). The diffusivity and dye saturation values depend on the difference between the dyeing temperatures and glass–transition temperature. The dye molecules penetrate the polymeric fiber structure upon movement of the chain segments producing spaces suitable to the size

of the dye molecules. The larger the dye molecule, the higher might be the dyeing temperature to permit the formation of spaces of sufficient size by the segmental motion of chains [78, 79]. The physical characteristics of polyester fibers such as solubility, dyeability and iodine absorption are related to the orientation and crystallinity of fibers. The absorption of iodine by polyester fibers decreases on increasing the thermosetting temperature from 180° to 220° C. Increasing the applied tension on the fiber during thermal treatment hinders the iodine absorption due to better microstructure orientation [80- 82]. The dyeability of the micro-denier polyester fabric is compared with the normal denier polyester. The rate of dyeing is found to be higher in the case of micro denier polyester. The fastness property has not been influenced by the rate of heating during dyeing with disperse dyes [83, 84].

2.1.4 Plasma treatment

Polyester (PET) swatches are treated with electrical discharge plasma of a reactive atmosphere (tetrachlorosilane) to graft chlorosilane groups, subsequently hydrolyzed to very hydrophilic hydroxysilane groups. The results show that the surface parameters are considerably modified by the treatment [85]. Low-pressure glow discharges are efficient in generating uniform plasmas. They have been applied in the surface modification of a variety of materials. Through the discharge of mixture of argon and oxygen, Ar-O$_2$ (10:1), polyester fabric is continuously modified. The results reveal that the dyeability of the polyester fabric is dramatically improved. The improvement of dyeability is attributed to the introduction of functional groups on the surface during the treatment [86]. Polyester fabrics are treated with radio-frequency plasma (in air) at different power levels and time intervals, and moisture content and surface resistivity behavior. The surface resistivity of polyester is dramatically reduced after plasma treatment. The fabrics are subjected to further plasma initiated grafting of acrylamide and acrylonitrile. Polyester has a moisture content of up to 3% after plasma initiated grafting. The surface resistivity of polyester is drastically lowered after grafting [87]. Polyester fabrics are dyeable and printable with disperse dyes. Since the dyeability of PET fabric has been related to hydrophilicity and/or increase of micro roughness and surface area therefore, plasma treatment can improve the colouration of fibres [88]. The printability of treated fabric with plasma/Al$_2$O$_3$ at 1.3 watt for 2 min was tried. The colour intensity of treated sample increased from 13.4 for untreated sample to 15.2 for treated one. The washing fastness properties of coloured treated samples are almost the same as the untreated one (4-5).

2.1.5 Microwave irradiation

Microwave drying is substantially more effective than convection oven drying. Microwave exposure has no effect on the elongation of polyester [89]. Aliphatic polyesters have been studied mainly for medical applications. High energy radiation induced processing is an established technique that is used in polymer science. Radiation is used to initiate radical polymerizations and for modifications such as degradation, cross-linking, and graft-copolymerization [90].

2.2 Polyamide

Prospects of low waste or clean technology in textile dyeing can be realized by preserving the quality of both fibres and dyeing during processing. To meet new demands for energy conservation, high production rates [1, 2] and strengthening the dye-fibre bond formation,

various redox systems were incorporated in the dyebath vicinity. Redox systems have been utilized to induce covalent fixation of dye moieties on proteinic and polyamide fibres. Radical formation is usually the consequence of a bimolecular reaction between oxidant and reductant. Its rate can be adjusted almost by suitable variation of reactant concentration. The organic substrate may participate in a two-electron transfer process without radical formation [1-5]. Introduction of glyoxal- hydrogen peroxide as a redox system to accelerate the polyamide dyeability with acid dyes is performed. An increase in colour intensity of the substrate dyed in the presence of the redox system as well as rapid exhaustion of the dyebath was observed. Time of half dyeing, specific dyeing rate constant and diffusion coefficient show some advancement as compared with the untreated polyamide. The activation energy of dyeing of the pretreated substrate decreased [1]. Addition of 2 % alcohols to the pretreatment bath reveals nearly complete exhaustion of the dyebath after 30 min. at 70°C. The alcohol effectiveness can be ordered methanol > ethanol > propanol. Complete dye exhaustion at lower dyeing temperature and time can save energy, time as well as minimize pollution effects. Half dyeing time at 60ºC decreased by the applied treatment from 13.5 min for untreated sample to 2.5 min for glyoxal pretreated sample in methanol/water (2:98), as compared with the given t $_{1/2}$ at 80ºC which decreased from 6 min to 1 min. Both dyeing rate constant (k`) and diffusion coefficient (D) at 60ºC and 80ºC have increased by the same pretreatment (Table 2.3).

Type of Sample	t $_{1/2}$ (min)		K'		D (cm ^{2} sec $^{-1}$) x10 $^{-4}$	
	60ºC	80ºC	60ºC	80ºC	60ºC	80ºC
1- Untreated	13.5	6	0.01	0.0245	0.176	0.291
2-Pretreated with glyoxal in:						
-propanol/ water	5.0	1.0	0.0283	0.0632	0.311	0.422
-ethanol/ water	3.5	1.0	0.0338	0.0632	0.328	0.422
-methanol/ water	2.5	1.0	0.04	0.0632	0.345	0.422

Treatment: 0.5 g glyoxal/ 100g fibre , solvent/ water ratio 2:98 , 50ºC, 1h.,Dyeing: 1% (o.w.f.) C. I. Acid Red 41, pH 4.5, liq ratio 1: 100, 0.3 % H$_2$O$_2$

Table 2.3. Half dyeing time (t $_{1/2}$), dyeing rate constant (K'), and diffusion coefficient (D) of polyamide 6 fibres dyed with C. I. Acid Red 41.

The activation energy decreased from 41.5 kJ/g mol for untreated one to 24.9 kJ/g mol for pretreated polyamide 6 fabric with glyoxal/H$_2$O$_2$ in methanol/water (Table 2.4). The decrease in the half dyeing time and the activation energy and the increase in dyeing rate constant and diffusion coefficient led to saving in time. The colour intensity was improved upon applying continuous dyeing technique.

Samples		E (kJ/ g mol)
1- Untreated		41.5
2- Pretreated with glyoxal in:	methanol / water	24.9
	ethanol / water	26.9
	propanol / water	26.9

Treatment: 0.5 g glyoxal / 100 g fibre, solvent / water ratio 2: 98, 50ºC, 1h, Dyeing: 1 % (o.w. f.) C. I. Acid Red 41, pH 4.5, liq ratio 1: 100, 0.3 % H$_2$O$_2$

Table 2.4. Activation energy (E) of dyeing for pretreated polyamide 6 fibres

Techno-economic estimation of dyeing PA6 fabric

The cost of energy is continuously increasing and is becoming a significant share of total cost of processing textiles. Lowering the dyeing temperature brings down the energy requirements which can be done by employing some dyebath additives or by giving some pretreatment to the material to be dyed, during which improvement of the dyeing behaviour of the fibre can be achieved [6]. Pooling of techno-economic knowledge across research and application would improve the productivity when faced by lower cost competition [7]. The intention is to achieve lower machinery cost, less chemicals and energy consumption, easier wash-off, better reproducibility and rapid as well as easier technical changes for higher value-added products. Attempts are undertaken to perform a comparative techno-economic investigation of two dyeing methods of polyamide fabrics; a conventional dyeing method normally as applied in industry versus a proposed modified one which depends on the usefulness of chemical pretreatment of polyamide fabric with acetaldehyde or a redox system at ambient conditions. The economic aspects of the dyeing processes are pursued, where the variables are brought together, to determine the production costs. The pretreatment of polyamide 6 with either reagent reveals some improvements in dyeing characteristics. This is reflected on the possibility of saving considerable amount of energy, shortening the time of dyeing, increasing the production rate and so lowering the total cost of the dyeing process as well as reducing the environmental impacts [8]. Conventional exhaust dyeing of PA-6 fabric was performed at nearly the boil [9]. Pretreated PA-6 wet fabrics with either acetaldhyde or glyoxal/H_2O_2 were exhaust dyed at different temperatures (60°, 70° and 80°C). The pH value of the dyeing bath was adjusted at 4.5 by adding acetic acid (about 1 ml/ litre) and using a liq. ratio of 1:10 [1, 10]. The process is wet on wet. Pretreated PA-6 fabrics with acetaldehyde had exhausted the same amount attained by conventional dyeing method (0.92g dye/100g fibre) after about 45 min at 80°C [10]. Pretreated PA-6 fabric with the redox system exhausts almost completely the dye from the bath at different temperatures (60°, 70° and 80°C) after about 40, 20 and 10 min respectively [8].

Cost of chemicals and water in conventional and modified dyeing method

Table 2.5 illustrates comparatively the cost of chemicals, dyes and water consumed in the investigated dyeing processes. PA-6 fabric pretreated with glyoxal/H_2O_2 attained the lowest cost and on the other hand acetaldehyde pretreated PA-6 fabric is relatively the highest. Specifically, this held true in the element of water consumption.

Dyeing Process	Dye	Chemicals	Water	Total
Conventional dyeing at the boil.	2.0	0.78	0.025	2.805
Dyeing of pretreated fibre with acetaldehyde.	2.0	1.555	0.039	3.594
Dyeing of pretreated fibre with (glyoxal/ H_2O_2).	1.84	0.837	0.015	2.692

Table 2.5. The costs of chemicals and water consumed (LE/kg fabric)

Steam consumption

The amount of steam required to offer necessary heat to the wet processes can be estimated from the following equation [11]:

$$Q = W.\ Cp.\Delta t$$

Where Q is the heat required, Cp is the specific heat of matter to be warmed up, W is the weight of the material to be warmed up; and Δt is the temperature difference involved, An initial temperature of 20°C is assumed for water. The heat loss by radiation and by other means can be calculated by assuming that the total heat is twice the heat required for heating up [12]. Table 2.6 shows the cost of heat energy per kg of fabric. It is clear that the glyoxal / H_2O_2 pretreated fabric attained the lowest value.

Dyeing process		Energy/cycle Kcal	Cost/cycle	Cost/kg
Conventional dyeing Method		497280	29.8368	0.0995
Pretreated with acetaldehyde.		372960	22.3776	0.0746
Pretreated with glyoxal/H_2O_2 and dyed at:	60°C	154716	9.283	0.031
	70°C	162876	9.772	0.0325
	80°C	171036	10.262	0.034

Assuming that 10^6 Kcal energy = 60 LE

Table 2.6. Cost of energy consumption for the different dyeing process in (LE)

Fixed costs

In addition to the expenditure on dyes, chemicals, water and energy, the layout on the equipment and operating personnel carrying out the dyeing process have to be considered, besides the general costs and overheads. The general costs have to be a common item not to be included in the calculations.

Machinery

The suggested dyeing processes have to be compared with the conventional one. The price of Jet machine is considered as one million Egyptian pounds. For suggestion of dyeing methods, a stainless steel tank of 4m³ is required for preparation and storing the pretreatment solutions of either acetaldehyde or glyoxal. A stainless steel pump (5 Hp) is also required. The total cost of the pump and the storage tank is assumed to be about 10.000 LE, supposing the use of two Jet machines in this study.

Depreciation for 10 years as: $\dfrac{1}{10} \ X \ \dfrac{\text{cost of machine}}{\text{production rate (kg/year)}}$

Interest =10 % of the capital cost.

Repairs = 5 % of the capital cost.

Labour /kg fabric = (Man hour x no. of hours/shift x no. of shifts/day x no. of labours/shift) ÷ (no. of batches/day x Production rate/ batch)

Table 2.7 represents the total fixed operating costs/kg fabric for all dyeing processes in this study. It can be noticed that the investigated pretreatments led to decreasing the operating costs as well as increasing the production rate.

Table 2.8 illustrates the total production cost/kg fabric. Glyoxal/H_2O_2 pretreated fabric attained a lower production cost than both conventional dyeing method and that pretreated fabric with acetaldehyde. It can be noticed that pretreatment of PA-6 fabric with redox system (glyoxal/H_2O_2) led to a decrease in the total production cost/kg fabric in the range of 7-11% as well as increasing the production rate/year and decreasing the pollution impacts without impairing the tensile properties of the fibre.

Dyeing process	Depreciation	Interest	Repairs	Labour	Total
Conventional dyeing Method	0.278	0.278	0.139	0.048	0.743
Pretreated with acetaldehyde	0.255	0.255	0.127	0.044	0.681
Pretreated with glyoxal/H_2O_2 and dyed at 60°C	0.255	0.255	0.127	0.044	0.681
70°C	0.234	0.234	0.117	0.04	0.625
80°C	0.2	0.2	0.1	0.034	0.534

Table 2.7. Fixed operating costs in LE/kg fabric

Dyeing process	Variable cost LE/kg		Fixed cost LE/kg	Total LE/kg
	Chemicals	Energy		
Conventional dyeing Method	2.805	0.0995	0.743	3.65
Pretreated with acetaldhyde	3.594	0.0746	0.681	4.35
Pretreated with glyoxal/ H_2O_2 and dyed at				
60°C	2.692	0.031	0.681	3.4
70°C	2.692	0.0325	0.625	3.35
80°C	2.692	0.034	0.534	3.26

Table 2.8. Production costs in LE/kg fabric

2.3 Cellulose acetate

Dyeing acetate fibers is reviewed thoroughly to show some new possibilities of improving its dyeability with disperse, azoic, acid and cationic dyes. The fastness, techniques and conditions of dyeing, dye-absorption, fixation, leveling and vapor phase dyeing of acetate fibers are also reported [1-3].

Dyeing characteristics

Acetate fiber was the first man-made fiber which could not be dyed with conventional dyes used for cotton, wool and silk [4]. Dyeing of acetate fibers by the method used for cellulosic fiber was found to be difficult because of the saponification possibility of acetate groups in alkalies. When dyeing was carried out at room temperature, no swelling of acetate fibers took place; consequently the diffusion of the dye component into the fiber was hindered. Dyeing behavior of acetate fiber was found to be very similar to that of synthetic fibers, particularly the affinity for water-insoluble dyes. Acetate fiber was dyed with selected types of cationic and acid dyes. The former produced a brilliant shade, while the latter produced a medium shade. Disperse dyes are generally suitable. Developing dyes of deep, wet-fast shades can be applied to acetate fibers. Pigment dyes were used only in exceptional cases and only for only pale shades. The effect of aromatic amines on dyeing intensity of triacetate fibers was related to change in the fibers' structure, determined by the interaction of amines with cellulose triacetate fiber [2, 5].

Disperse dyes: The migration of disperse dyes in the dyeing of triacetate fibers was determined by dissolving the fibers in either chloroform or an acetone-water mixture (4:1) [6, 7]. The influences of temperature, liquor ratio, carrier, and acetyl value were determined.

Increasing the temperature accelerated the migration, giving higher values for the desorption constants than for the absorption constants. Increasing the liquor ratio was more favorable for the dyes having a higher solubility in water. Use of carriers promoted the migration because of the increase in dye solubility. When the acetyl value decreased, the rate of migration was found to increase [2, 8]. Acetate fibers were dyed with disperse dyes in tetrachloroethylene in presence of water at a temperature above that of the tetrachloroethylene-water azeotropic mixture under pressure for 30 min. to give fast deep shade. The presence of tetrachloroethylene as a carrier gave fast shade at higher yields than in the presence of aromatic chlorinated hydrocarbons [9-12]. Cellulose triacetate was exhaust dyed at 50°-75° in an aqueous bath containing disperse dye, 10-50% methylene chloride or methylene bromide, and a dispersing agent. The result was a level dyeing with good penetration and excellent fastness [13-15]. Dyeing acetate yarns with dyeing liquor exposed to ultrasonic waves increased the dye absorption. The dyeing liquor was exposed to ultrasonic waves by passing the liquor through an ultrasonic generator. Acetate yarns were immersed in the resulting liquor for 20 min. at 85 °C to give dyed yarns with the amount of the dye absorbed 50% greater than that obtained without passing the liquor through the ultrasonic generator. In the dyeing of triacetate fibers with disperse dyes in organic solvents; the affinity and the heat of dyeing were much smaller than those in an aqueous system. The diffusion coefficients varied with different fiber solvent combinations [13-17].

Acid dyes: Acid dyes are used for dyeing acetate, nylon, and acrylic fibers. These dyes were originated from basic dye acidification and have a complete color range. The light fastness ratings were generally very good and not affected by gas fading [5]. The impregnation of acetate fabrics with liquors containing an acid dye and storing the fabric in ammonia vapor to give dyed fabrics with improved wash fastness was studied. An acetate taffeta fabric was immersed in a bath containing 20% g/l acid dye and 50 g/l thiourea to 50% pick up, dried, and stored in water vapor containing 28% ammonia for 4 h at room temperature, washed, and dried to give dyed fabric with wash fastness rating [2, 18].

Direct dye: Acetate samples treated with methylamine, dimethylamine and trimethylamine and dyed with direct dye gave satisfactory results. The maximum color intensity was obtained in case of the treatment with diethylamine as compared with the relatively lower color intensities for ethylamine and triethylamine. This can be explained on the basis of higher basicity of diethylamine which led to a higher hydrolyzing effect changing the acetyl groups to hydroxyl groups [1].

In dyeing processes, the use of cyclodextrin (CD) can improve the dye uptake of CA because CD increases the tendency of disperse dye solubilization in aqueous solutions. CD is characterized by a hydrophobic internal cavity and by a hydrophilic exterior. This can give different inclusions of dye molecules depending on the size of the cavity. The formation of complexes between the dye molecules and CD has been thoroughly described and can be used as an alternative to dyebath additives. The structure of CD shows an ability of inclusion of complexes with compounds having a molecular size complementary to the cavity dimensions. No covalent bond is established between the dye molecules as a guest in the CD host molecules. Consequently, the dissociation–association equilibrium in solution becomes one of the characteristic features of the guest/host association. One of the modification possibilities of the fiber surface to alter its properties is attained by a successful binding of CD to the fibers [19]. CA samples of known weight were treated with both CD and MCT-CD by a padding technique. The samples were then subjected to the dyeing process. A systematic study on the influence of CD treatments on the dyeing of CA fabric with disperse

dye was performed to optimize new possibilities to dye CA fabric at a lower temperature than the conventional dyeing one without using additives as well as enhancing the fastness properties and increasing the dye penetration into the interior of the fiber structure to ensure homogeneity and leveling of the dye. Disperse dyes are hydrophobic compounds, it was anticipated that CD could serve as host sites if incorporated into the molecular structure of a warp size. CD treatment offered a significant dyeability effect on CA than MCT-CD. The color intensity of the dyed CA was found to depend on the CD concentration. The differential thermal analysis data of the untreated CA and that one pretreated with CD is given in Table 2.9. A slight decrease in glass transition temperature (Tg), crystallinity temperature (Tc), and melting temperature (Tm) was observed. CD treatment of CA fabric imparts no effect on the thermal properties of CA.

CA Sample	Tg (°C)	Tc (°C)	Tm (°C)
Untreated	64.5	168.8	260
Pretreated with CD	62.1	163.0	259

Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 150°C, 3 min.

Table 2.9. Differential Thermal Analysis of Untreated and Pretreated CA Fabric With CD

Scanning electron micrographs (SEM) of the untreated and pretreated CA fabric with CD are depicted in Figure 2.5(a, b). Some changes on the surface features of the pretreated CA were observed. The mean depth of the disperse dye inside the pretreated CA fiber was found to be twice more than that of the dyed untreated one. The % mean depth of dye into the dyed fiber is ranged from 60 to74% for CD-treated CA compared to 20–21% for untreated one. A mean dye depth <30% inside the fiber is defined as ring dyeing.
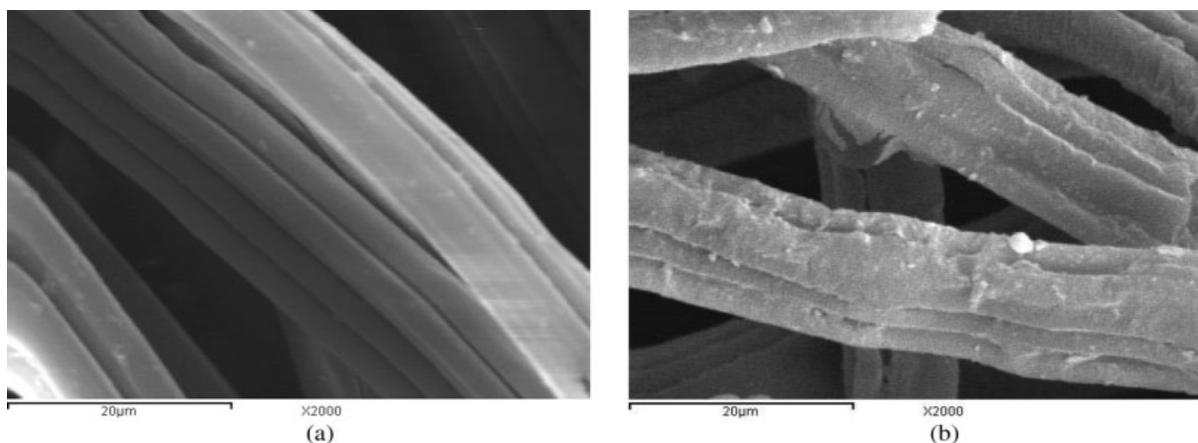

Fig. 2.5. (a) SEM of untreated CA fabric. (b) SEM of treated CA fabric with CD.

Dyeing behaviour of laser treated fabric: The excimer UV-laser treatment can improve the dyeability of polyester fibres. The maximum colour intensity of untreated one could be attained at shorter time. Also, the half dyeing time of laser treated sample decreases from about10min for untreated one to 7 min. The main factor which explains the improvement of the dyeability of the irradiated CA fabric is the increase of the overall surface area as a result of the morphological modification induced by excimer laser. The mean depth % of dye into the dyed treated CA sample is that 43.9 % compared to 20.2% for untreated one [20].

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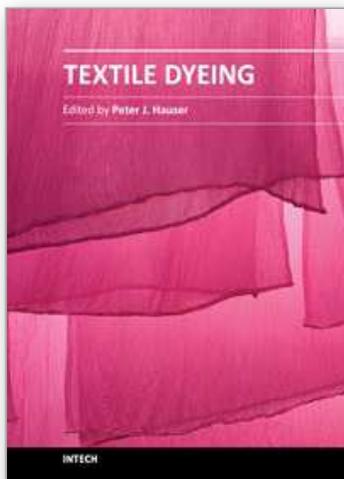
The coloration of fibers and fabrics through dyeing is an integral part of textile manufacturing. This book discusses in detail several emerging topics on textile dyeing. "Textile Dyeing" will serve as an excellent addition to the libraries of both the novice and expert.

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