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DYEING PROPERTIES OF POLY GLYCIDYLMETHACRYLATE / NYLON - 6 GRAFT COPOLYMERS WITH ACID AND REACTIVE DYES

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ABSTRACT

Nylon - 6 was copolymerized to different graft levels with poly Glycidylmethacrylate (PGMA)using potassium persulphate and copper sulphate as initiator. The susceptibility of unmodified nylon - 6 as well asthe modified one towards dyeing with acid and reactive dyes was investigated. A kinetic investigation of the dyeing process revealed that the time of half dyeing ($t_{1/2}$ min.) of grafted fibers was hgher than the corresponding values for the ungrafted samples and increased as the graft yield increased. The opposite holds true for the specific dye rate constant (k) and diffusion coefficient (D) . The activation energy of diffusion (E_D) of acid dye was 29.90 and 26.13 K / mole for the grafted and ungrafted nylon - 6 respectively, while it was 82.23 and 76.22 k / Mole in case of reactive dye respectively. Comparison of the values of affinity (U°) and heat of dyeing (H°) for grafted and ungrafted nylon - 6 revealed that, grafting of nylon - 6 with PGMA led to a decrease in its accessibility towards acid and reactive dyes.

The dyeability expressed as the colour strength values (K/ S) of the grafted and ungrafted nylon - 6 dyed, was found to aepend upon the magnitude of grafting level. The grafted and ungrafted nylon - 6 also was found to acquire excellent fastnes properties.

INTRODUCTION

In recent yearsattention has been directed towards improving the properties of polyamide fibers via grafting with vinyl monmers [1-8] . More recently the grafting of nylon - 6 with glycidylmethacrylate without homopolymer formation was developed [9]. Although there is a tremandous volume of work on graft copolymerization of nylon - 6, most of these studies deals with the methods of grafting reactions. Not much work has as yet been publisged on the dyeing properties of nylon graft copolymers. The susceptibility of nylon - 6 copolymerized to different levels with polyacrylamide towards acid and disperse

dye has been investigated early [10]. Recently the susceptibility of nylon - 6 grafted to different levels with acrylonitrile towards dyeing with acid dyestuff and the effect of such modification on the behaviour of nylon - 6 towards printing has been also studied by El-Shahed et al . [11.12].

In the present work, the susceptibility of nylon - 6 copolymerezed to different levels, with GMA towards dyeing with acid and reactive dyes was investigated. Alao the general kinetic chracterization of dyeing the modified and unmodified nylon was illustrated .

EXPERIMENTAL

Materials : Nylon - 6 fabrics (210 dinier / 35 filament yarn), density 1.14 g / cm^3 was soaped at 70°C for 1 hour, thoroughly washed and air dried at room temperature.

- Glycidylmethacrylate monomer (GMA) of pure grade, was freshly distilled at 75° C and 10 mmHg before using .
- Potassium persulphate ($K_2S_2O_8$) and copper suphate (Cu So_4. $5H_2o$) used were analytical grade chemicals.

Dyestuff : Commercial acid dye, Cibalan Greay Blue ($_{max}$. 580 nm) and reactive dye cibacron F. ($_{max}$ 422 nm) and wetting agent, univadine PA, were kindly supplied from CIBA - GEIGY.

- Graft polymerization : Nylon - 6 fabrics were grafted to different graft levels with GMA, using potassium persulphate and copper sulphate as initiator according to the method described inour previous paper [9].

- Dyeing method : Grafted and ungrafted nylon - 6 fabrics (known weight) were dyed inseparate dyeing bathes (1 : 100), containing 3 % acid dye or 2 % reactive dye, and 3 % or 2 % univadine PA (calculated on the weight of the fabric). The PH of the dye bath was adjusted to 4 - 4.5 in case of acid dye and 5 - 5.5 in case

of reactive dye, using glacial axetic acid and sodium acetate, the dyeing was carried out at 80 ° C for different lengths of time. The concentration of the dye exhausted with the fabric was measured spectrophotometrically.

Determination of half - dyeing time ($t_{1/2}$ min) and the specific dye rate constant (K')

Unmodified and modified nylon - 6 fabrics containing differeent amounts of grafted PGMA 5 %, 15 %, and 25 % were dyed at 80° C using 3 % acid dye and 2 % reactove dye (on weight of fabric) for various time intervals to establish equilibrium. Samples were removed from the dye bath immediately after each interval and washed thoroughly 2 times with 25 ml distilled water which was added to the remaining dyeing liquor. The dye concentration inthe dye uptake (g dye / 100 g fabric) versus dyeing time was plotted (Fig. 1-2). The half - dyeing time ($t_{1/2}$ min .) was measured from the corresponding curves. The specific dye rate constant (K') was calculated as follows[13].

$$K = 0.5\ C$$

where: C is the precentqge dye absorbed on the samale at equisibrium conditions beteewn the sample and the dye bath divided by the weight of the sample, and d is the fiber diameter in cm (0.00371).

Determination of the apparent diffusion coefficient (D) (14)

Known weights of modified and unmodified nylon-6 faricl were dyed for a arolonged time (2 hours). Another dyeing was performed formshort time (t = 2 min.) and C & C_t were determined. The values of (C_t / C) werethen calculated, from which the apparent diffusion coefficient (D) could be calculated based on Hill's [14] equation:

Determination of affinity (U°)and heat of dyeing (H°) [15]

A 3% dyeing (acid dye) and 2% dyeing (reactive dye) (dased on weight of fabric) were performed on two samples of polyamide (known weight) at 80°C

for 2 hours, using a liquou ratio (1:100). At the end of the dyeing time, the samples were immediately removed, rinsed several times with cold distilled water. One of the dyed samples was treated with 80 mL of distilled water in a stoppered flask for 2 hours at 80°C. The other one was similarly treated for 4 hours at 60°C. At the end of the presceibed time, the samples were removed, rinsed for 2 times with distilled water (25 mL in each time) and air dried. The amount of the dye in the desorption solution as well as the rmaining part on the treated samples aere determined spectrophotometrically.

Calcuation of the partition coefficient (K), (U°) and (H°) was carriedout according to the following equations:

Determination of Colour Strength (K/S)

The colour strength was determined for both grafted and ungrafted dyed samples, after measurements of the reflection spectra using the UV-300 Double beain recording (Shimadzu Ltd. Kyoto-Japan). The relative colour stuength expressed as K/S values were determined by applying Kubelka Munk equation[16].

Fastness Properties

Exposure to light : Irradiation of the dyed fabrics was done alongside with a blue scale, using the Terra light fastness tester[17]. The exposure was performed for 200 hours continuously at a relativehumidity of 60-65%.

The light fastness properties

The light fastness of the grafted and ungrafted dyed samples were assessed according to the visual assessment inspection against the blue patterns[18]. In this method the visual light fastness rating based on the blue scale ranging from 1 (considerable change) to 8 (unchanged).

RESULTS AND DISCUSSION

Grafting of nylon-6 fabrics with GMA was performed to different add-on. Ungrafted as well as grafted asmples were subjected to dyeing with acid and reactive dyes separately at 80°C for various lengths of time under the same conditions.

Effect of graft levels on the rate of dye uptake

Figures (1,2) show the dyeing fates of acid dyestuff namely Cibalan Greay Blue and reactive dyestuff namely Cibacron F, on nylon-6 containing 5, 15, and 25% of grafted PGMA. The rate of dyeing of unmodified nylon-6 was also included in the figures. It was observed that, the dyeing of the grafted and ungrfted nylon-6 proceeds fast in the eatly stage of the dyeing process, then slows down, and finally levels off. This is observed regardless of the grafting percentage. The rate of dyeing of the grafted samples are lower than that of the ungrafted nylon-6 fabric, furthermore, increasing the magnitude of grafting from 5 to 25% is accompanied by a substantial loss in the rate of dyeing. This indicates that, the presence of PGMA graft on the nylon backbone reduces the susceptibility of the latter towards dyeing with the used acid and reactive dyes. It seems rather likely that, the grafting process on nylon-6 substrate leads to PGMA deposition on the surface of the nylon fabric, which may (a) reduce the noncrystalline portion; (b) block some of the adsorption sites on the backbone; (c) enhance hydrogen bond formation between the epoxy and the hydrogen of the amide groups. The latter interaction may create some negative charges on the surface of grafted nylon-6 which lowers the attraction of the negatively charged acid dye ions leading to a decrease in the dyeing rate. These previously mentioned considerations may inhibit the diffusion of the dyes from the aqueous phase to the fiber phase.

The kinetic characterization of the dyeing process were also investigated to confirm the above suggestions. Tables (1) and (2) illustrate the values of half-dyeing time ($t_{1/2}$),specific dyeing rate constant (K') as well as the diffusion coefficient (D) calculated and grafted nylon-6 samples. Dgiven in tables (1) and (2) indicate

that, dyeing of ungrafted nylon-6 samples proceeds faster than the modified one. Time of half-dyeing was longer in case of grafted nylon-6 fabrics and increases by increasing the percentage of grafted add-on in both acid and reactive dyes. This would contribute to lower dye diffusion of the dye through the substrate and for lower dyeing rates of grafted nylon-6 compared to ungrafted one. Also it is apparint from tables (1) and (2) that, grafting of nylon-6 with PGMA lowers the dye rate constant (K') and the diffusion coefficient (D). The higher the graft level, the lower dyeing rate constant and the lower diffusion coefficient. This again confirms the above finding decreases the dyeing rate of nylon-6. Also it can be seen from tables (1) and (2) that the dyeing rate constant and the difusion coefficient of the reactive dye is much lower than that of acid dye.

Effect of temperature on the dyeing rate of acid and reactive dyes on grafted nylon-6:

Figures (3-6) shows the dyeing rates of the acid and reactive dye on nylon-6 and grafted to the level 15% PGMA at differenrt temperatures (60,70 and 80°C). It can be seen that, increasing the temperature of the dyeing bath is accompanied by enhancement in the dye uptake of the grafted and ungrafted fabrics. However, within the temperature range used, the dye uptake of ungrafted sample is still higher than that of grafted one. Raising the temperature of the dyeing bath from 60 to 80°C may facilitate the transfer of the dye molecules from the dye liquor to the fiber surface, adsorption of the dye at the fiber surface from the surface into the modified and unmodified nylon itself. This would lead to higher dye uptake with increasing dyeing temperature. Tables (3-4) represent data of half-dyeing time, dyeing rate constant and diffusion coefficient at different temperatures for grafted and ungrafted nylon-6 fabrics. It can be observed that raising the dyeing bath temperature from 60 to 80°C is accompanied by a decrease in the half-dyeing time ($t_{1/2}$) for grafted and ungrafted nylon. However the ($t_{1/2}$) for grafted sample was higher than that for the ungrafted one at the same level of temperature, moreover the half-dyeing time ($t_{1/2}$) forgrafted and ungrafted sample in case of reactive dye is still higher than that for the acid dye.

Alos it was found that a significant enhancement was obtained for K' and D at

higher temperature (80°C). The values of K' and D were lower for grafted samples compared to the ungrafted one at the same temperature. The data obtained would confirm the above findings that, at higher temperature, a high dye uptake was observed. Also copolymerized PGMA in the structure of nylon-6 hinders the dye diffusion which leads to lower dye uptake.

The effect of temperature on the process of dye diffusion can also be investigated numerically by calculating the apparent activation energy of diffusion (E_D) from the Arrhenius law:

$$2.303 \log E_D = -E / RT + \text{constant}$$

E_D reflects the changes in diffusion coefficient due to change in dyeing temperature. It may be also regarded as the energy which the dye molecule might acquire in order to be able to move within the fiber matrix. The E_D valuescalcuated from a plot of In D versus figure (7) are 29.90 and 26.13 KJ / mol for grafted (15% PGMA) and ungrafted nylon-6 for the cibalan Greay Blue (acid dye), and 82.23 & 76.22 KJ / mol for the same grafted and ungrafted nylon-6 of cibacron F (reactive dye) respectively.

Affinity and heat of dyeing

Table (5) shows the effect of graft-yield on the partition coefficient of the dye (K) as well as the affinity (- U°) at different temperatures. Also it can be observed that U° has a negative value which indicates that the dyeing process is an exothermic proces. Increasing the magnitude of grafting is accompanied by a decrease in partition coefficient as well as in the affinity of the acid and reactive dyesfor the modified fabric. This is rather expected, since the presence of grafted PGMA in nylon-6 structure seems to cause blcking of the adsorption sites of the nylon-6 backbone which lowers the dye affinity. The heat of dyeing for grafted nylon-6 is represented also in table (5). This again indicated that the susceptibility of ungrafted nylon-6 for fueing with acid and reactive dye is faster than that of the grafted one.

Fastness Properties:

It is clear from tables (6) that the dyeability decreases with the increament of the grafting % and was emphasized by K / S values which was found to acquire higher values at the higher grafting %. Also from the light fastness results, it was concluded that, the light fastness of the acid dye when it was applied on the grafted and ungrafted nylon-6 fabrics was considerably high and ranging over 6, while the reactive dye showed good oight fastness and was in the order 4.5-5.5.

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Table (1): Time of half-dyeing ($t_{1/2}$), specific dye rate constant (K') and diffusion coefficient (D) of modified nylon-6 substrate containing different amounts of grafted PGMA

Amount of grafted PGMA %	$t_{1/2}$ min	k'	D (cm^2. Sec^{-1})x 10^{-7}
0	3	0.05345	1.167
5	4	0.03772	1.140
15	4.5	0.02812	1.06
25	5	0.01471	0.7647

Temperature 80°C, 3% shade, 3% wetting agent, 1:100 liquor fatio; Dye: acid dye, Cibalan Greay Blue.

Table (2): Time of half-dyeing ($t_{1/2}$), specific dye rate constant (K'), anddifusion coefficient (D) of modified nylon-6 substrate containing different amounts of grafted PGMA

Amount of grafted PGMA %	$t_{1/2}$ min.	K'	D(cm^2. Sec^{-1})x 10^{-8}
0	3	0.02145	4.98
5	4	0.01331	4.50
15	4.5	0.006517	4.21
25	5	0.00357	3.64

Temperature 80°C, 2% shade, 2% wetting agent, 1:100 liquor ratio, Dye; Reactive dye, Cibacron F.

Table 3: Time of half-dyeing ($t_{1/2}$), specific rate constant (K'), and diffusion coefficient (D) of ungrafted and grafted nylon-6 fabrics at different temperatures with acid dye : Cibalan Greay Blue.

Dyeing temperature °C	$t_{1/2}$ min		K'		D (cm^2. Sec^{-1})	
	nylon-6	grafted nylon-6	nylon-6	grafted nylon-6 (15%)	nylon-6	grafted nylon-6 (15%)
60	5	5.5	0.01211	0.010258	0.687×10^{-7}	0.557×10^{-7}
70	4	5.0	0.02375	0.01430	0.980×10^{-7}	0.786×10^{-7}
80	3	4.5	0.05345	0.02812	1.167×10^{-7}	1.06×10^{-7}

Dyeing conditions : 3% shade, 3% wetting agent, 1 ; 100 liqour ratio, graft level, 15% PGMA.

Table 4: Time of half-dyeing ($t_{1/2}$), specific rate constant (K'), and diffusion coefficient (D) of ungrafted and grafted nylon-6 fabrics at different temperatures with Reactive dye; Cibacron F.

Dyeing temperature °C	$t_{1/2}$ min		K'		D (cm^2. Sec^{-1})	
	nylon-6	grafted nylon-6 (15%)	nylon-6	grafted nylon-6 (15%)	nylon-6	grafted nylon-6 (15%)
60	7	8.5	0.00967	0.0027	0.910×10^{-8}	0.735×10^{-8}
70	5	5.0	0.0153	0.0044	2.0482×10^{-8}	1.888×10^{-8}
80	3	4.5	0.0214	0.0065	4.98×10^{-8}	4.21×10^{-8}

Dyeing conditions : 2% shade, 2% wetting agent, 1 : 100 liqour ratio, graft level, 15% PGMA.

Table 5: Effect of graft yield on the partition coefficient of the dyes (K), the affinity (-ΔU°) and heat of dyeing (ΔH°).

Amount of grafted PGMA %	Cibalan Greay Blue					Cibacorn F				
	Partition confficient (K)		Affinity (-ΔU°) KJ. mol^{-1}		Heat of dyeing (-ΔU°)	Partition confficient (K)		Affinity (-ΔU°) KJ. mol^{-1}		Heat of dyeing (-ΔU°)
	80°C	60°C	80°C	60°C		80°C	60°C	80°C	60°C	
0	275.36	185.5	16.45	14.43	19.41	529.43	434.7	18.37	16.78	10.00
5	166.6	124.9	14.98	13.34	14.12	335.54	300.7	17.03	15.76	5.29
15	119.2	96.5	14.00	12.62	10.55	140.88	136.57	14.49	13.48	1.76
25	63.3	52.2	12.15	10,93	9.41	71.7	69.81	12.51	11.73	1.17

Figure Captions

Figure (1): Rate of dyein of Cibalan Greay Boue, on polyglycidylmithacrylate -nylon-6 fraft copolymers.
(Dyeing: 3 % shade, 3% wetting agent, pH 4 - 4.5, 80 °C, liquor ratio 1 : 100).

Figure (2): Rate of dyeing of Cibacron F. on polyglycidylmethacrylate-nylon- 6 gragt copolymeres.
(Dyeing: 2; shade, 2% wetting agent, pH 5 - 5.5, 80 °C, liquor ratio 1:100).

Figure (3): Effect of dye bath temperatrure on the dyeability of ungrafted nylon- 6 with Cibalan Greay Blue
(Dyeing: 3 % shade, 3 % wetting agent, pH 4 - 4.5, liquor ratio 1 : 100).

Figure (4): Effect of dye bath temperature on the deability of grafted nylon-6 fabrics with Cibalan Greay Blue
(Graft uield 15 %, dyeing: 3% shade, 3 % wetting agent, pH 4-4.5, liquor ratio 1:100).

Figure (5): Effect of dye bath temperature on the dyeability of ungrafted nylon-6 fabrics with Cibacron F.
(Dyeing: 2% shade, 2 % wetting agent, pH 5 - 5.5, liquor ratio, 1:100).

Figure (6): Effect of dye bath temperature on the dyeability of grafted nylon- 6 fbrics with Cibacron F.
(Draft yield 15 %, dyeing: 2 % wetting agent, pH 5 - 5.5, liquor ratio 1:100).

Figure (7): Effect of temperature on diffusion coefficient of Cibalan Greay Blue and Cibacron F in grafted and ungrafted nylon-6 fabrics.

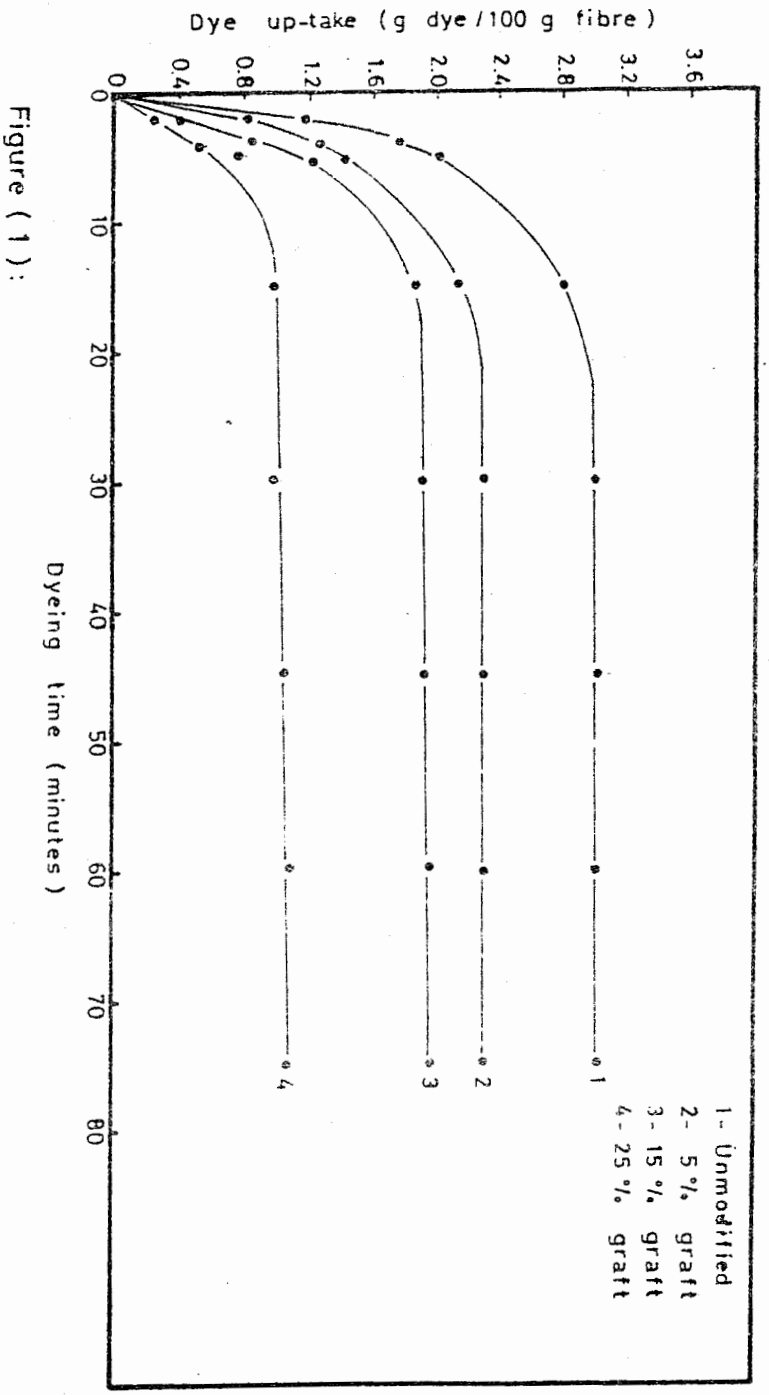
Dye up-take (g dye / 100 g fibre)
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
0
10
20
30
40
50
60
70
80
Dyeing time (minutes)
1
2
3
4
1- Unmodified
2- 5 % graft
3- 15 % graft
4- 25 % graft

Figure (1):

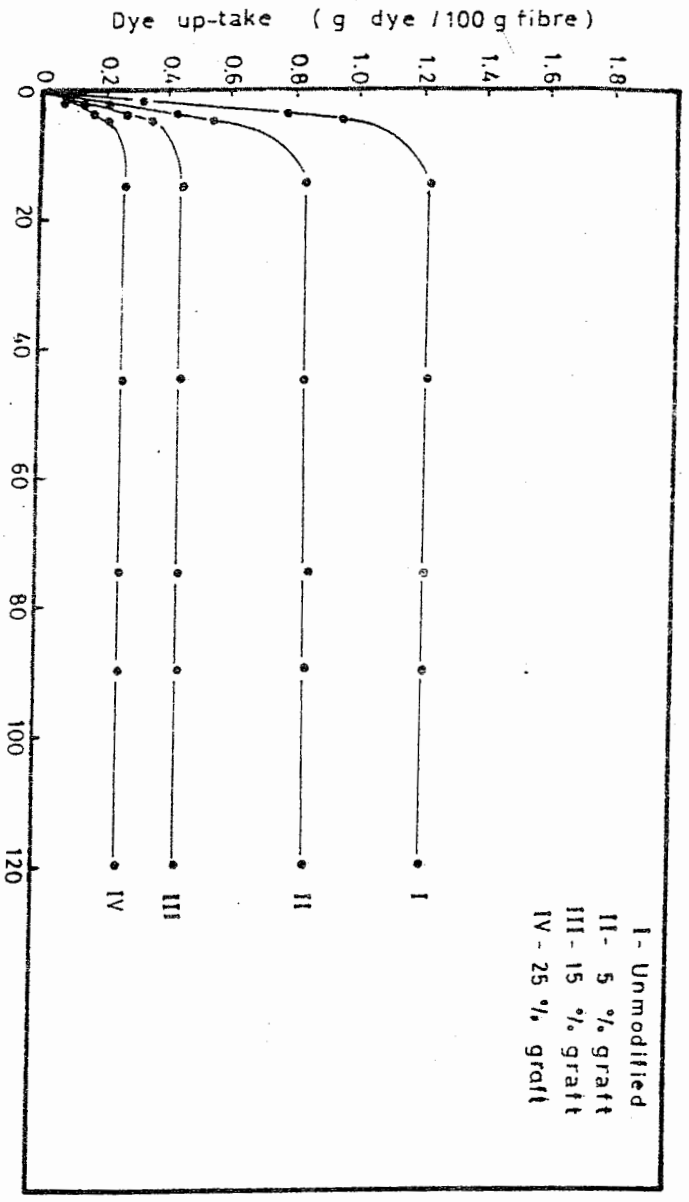
Dye up-take (g dye / 100 g fibre)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
0
20
40
60
80
100
120
Dyeing time (minutes)
I
II
III
IV
I- Unmodified
II- 5 % graft
III- 15 % graft
IV- 25 % graft

Figure (2):

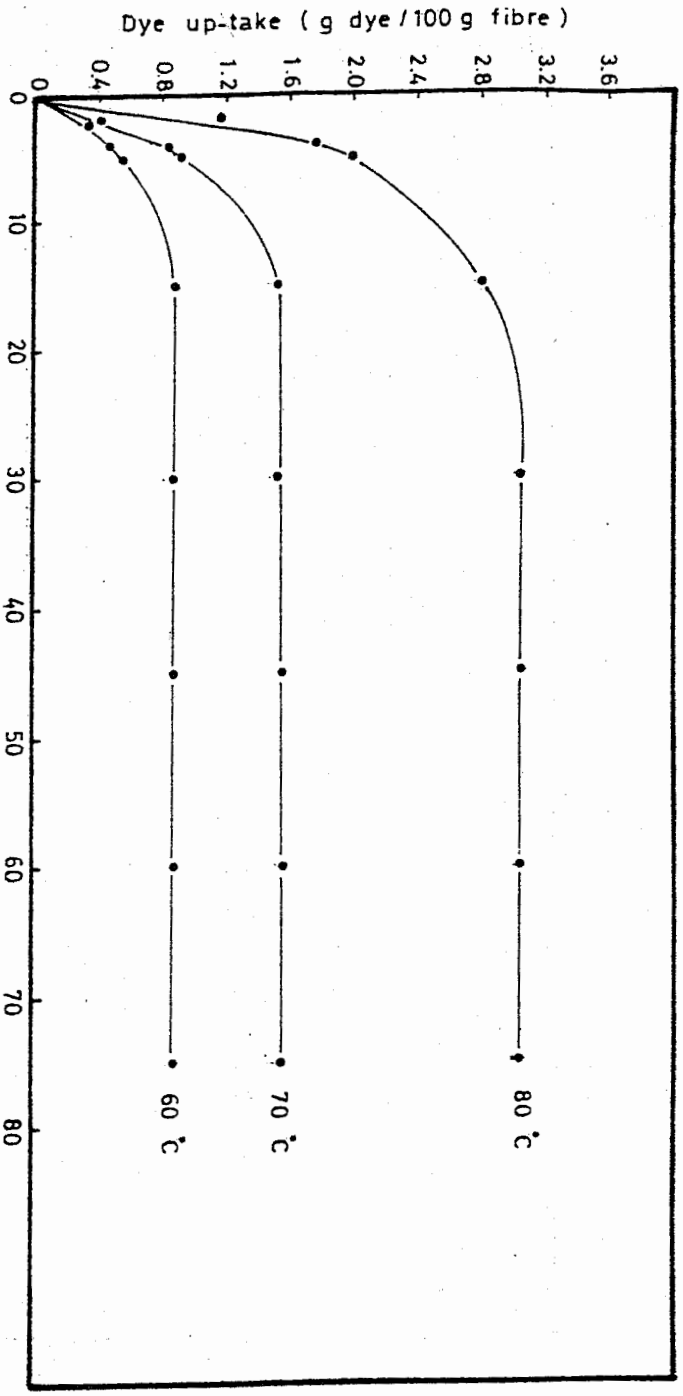
Dye up-take (g dye / 100 g fibre)
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
0
10
20
30
40
50
60
70
80
Dyeing time (minutes)
60 °C
70 °C
80 °C

Figure (3):

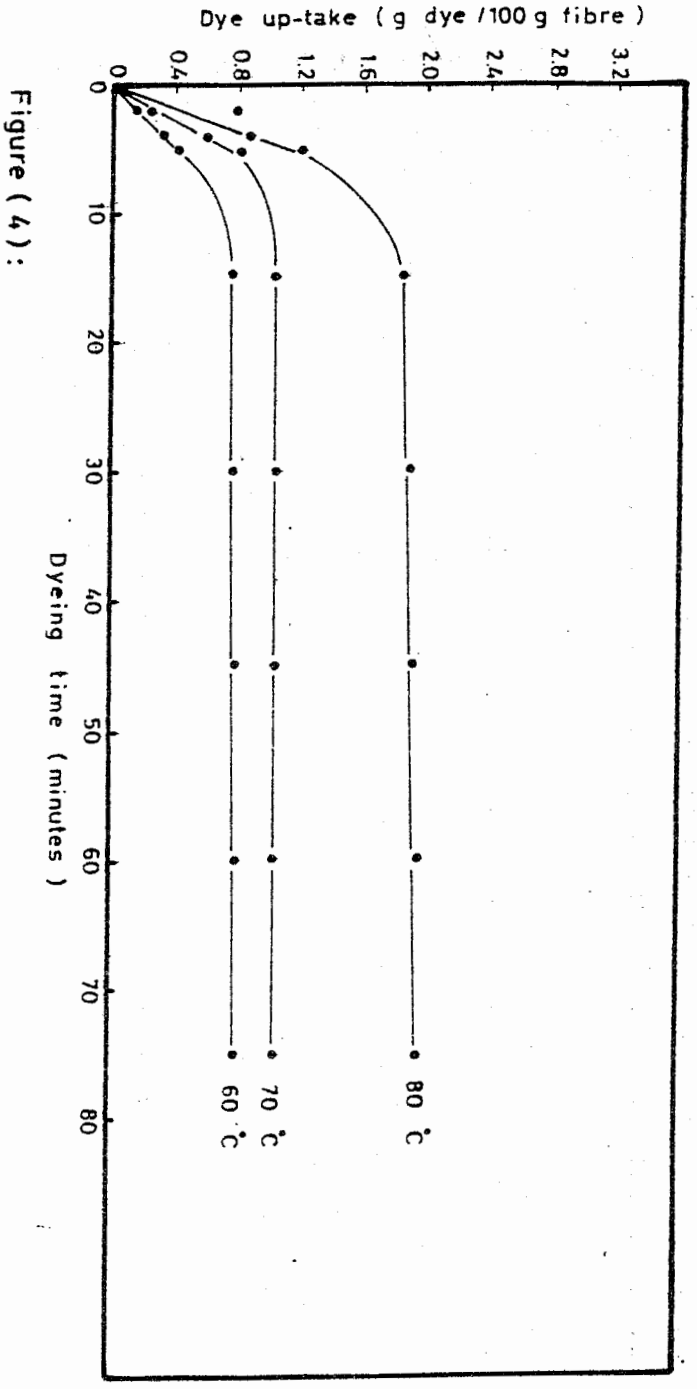
Dye up-take (g dye /100 g fibre)
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
0
10
20
30
40
50
60
70
80
Dyeing time (minutes)
80 °C
70 °C
60 °C

Figure (4) :

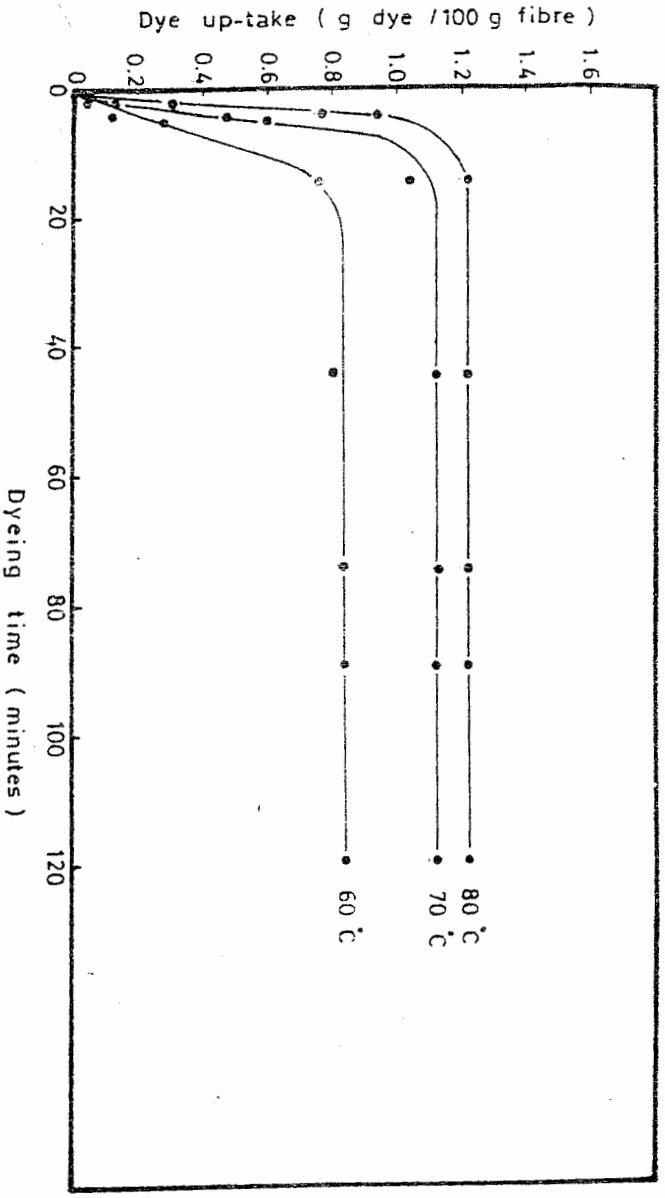
Dye up-take (g dye /100 g fibre)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0
20
40
60
80
100
120
Dyeing time (minutes)
80 °C
70 °C
60 °C

Figure (5):

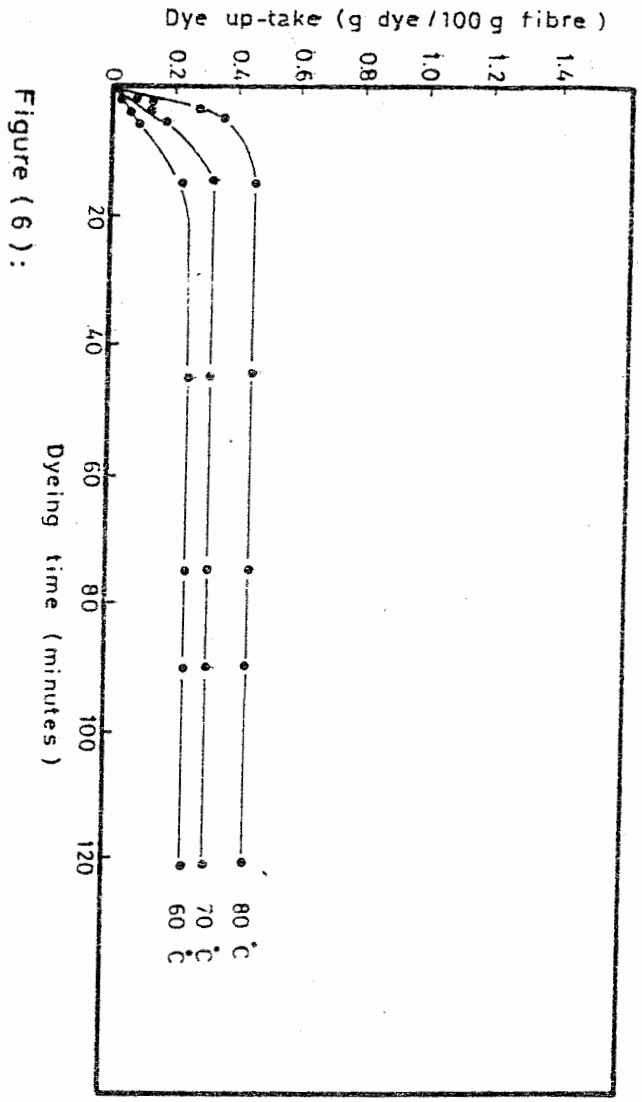
Dye up-take (g dye / 100 g fibre)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
20
40
60
80
100
120
Dyeing time (minutes)
80 °C
70 °C
60 °C

Figure (6) :

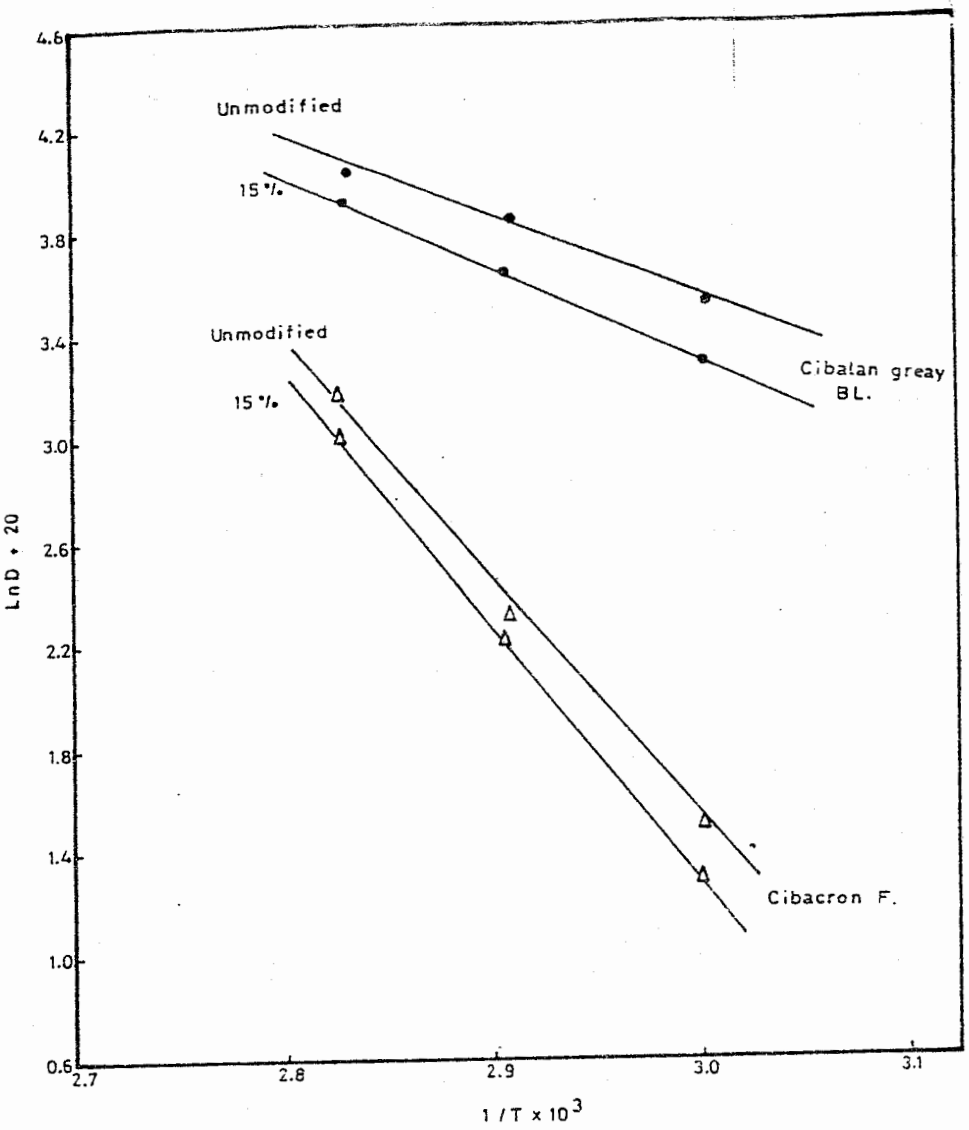
Unmodified
15 %
Unmodified
15 %
Cibalan greay BL.
Cibacron F.
LnD • 20
1 / T x 10^3
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
2.7
2.8
2.9
3.0
3.1

Figure (7):