10A05

The effect of anionization of cotton, via photografting or UV/O_3 surface treatment, on its dyeability.

장진호, 고석원

서울대학교 공과대학 섬유고분자공학과

1. INTRODUCTION

While cosiderable interest has been taken in the cationization of cotton both academically and industrially, a few number of work on anionization reported. Most of research was related with improving the dyeability or adsorption of cotton to cationic dyes or metal via introducing carboxylic or sulphonic acid group to cotton.[1-7] Three potential dye resist anionising methods have been evaluated with the aim of reducing the dyeability of cotton to anionic dyes such as direct, reactive, sulfur dyes.[8] This approach may provide a method of introducing pattern images on cotton fabric by differential shading with the same dye. The resolution of the image can be increased by the use of UV light compared to silk printing.

2. EXPERIMENTAL

Materials: Mercerised plain weave cotton fabric(152g/m^2) was used throughout this study. The dyes used are listed in Table 1. The anionic agents used are sodium vinyl sulfate(25% solution, Aldrich) and acrylic acid(99%, Aldrich). As a photoinitiator, Quantacure BTC(4-Benzoyl benzyl trimethyl ammonium chloride, $C_{17}H_{20}NOCl$) was obtained from Octel Chemicals Ltd. Table 1 Dyes used in the present study

Commercial name	Manufacturer	C.I. name
Diazol LT Turquoise JL U	ICI	Direct Blue 86
Procion Red MX-5B	Zeneca	Reactive Red 2
Sulphol Liquid Green QGCF	James Robinson Ltd	Leuco Sulfur Green 2
Sulphol Liquid Brown QNR	James Robinson Ltd	Leuco Sulfur Brown 96
Maxilon Blue BL	Ciba-Geigy	Basic Blue

Photografting and UV/O_3 surface treatment: All fabrics were impregnated by padding through the liquor(wet pick-up: 70-110%) containing anionic monomers and photoinitiator. Photoinitiator concentration was 3% on the weight of monomer. The samples were then dried for 3 minutes at 80°C. Anionic agent padded fabrics were cured using a white light curing mashine(D lamp, 120W/cm)(Jenton Fusion System Ltd). A standard cure time of 2x2 passes(2 passes on each side of the fabric) at the speed of 1.7m/min, namely 730 mJ/cm^2, was used. The uncured agent was washed off with warm water(60°C).

% Grafting = $(w_3-w_1)/(w_1)$, Grafting Efficiency = $(w_3-w_1)/(w_2-w_1)$

where w_1 = initial weight of cotton fabric, w_2 = total weight of cotton fabric after curing, w_3 = final weight of cotton fabric after washing off uncured agent

For UV-ozone treatment, samples were treated in a UVO cleaner model 42-220(Jelight, California) for specified time period. A VG ESCA 3 MKII spectrometer was used to obtain

XP spectra using a non-monochromatic MgKα X-ray source of energy 1253.6 eV under a residual pressure of 4 x 10^{-8} torr. The fabric sample were attached to the probe with double-sided tape. Spectra were charge referenced against the C-C/C-H (1s) peak at 285.0 eV. Quantitative analysis was carried out using the photoelectron peak areas corrected with the appropriate atomic sensitivity factors.

Dyeing of untreated and treated fabric: All direct dyeing was carried out under pH 7 at a liquor ratio of 30:1. Dye bath was kept at 40°C for 10 minutes, then raised to the boil for 30minutes without salt and stayed for 60 minutes. Reactive dyeing condition was described with the results. For sulfur dyeing, dye bath was kept at 40°C for 20 minutes with 10%owf of liquid leuco sulfur dyes(liquor ratio 1:30), 5g/l of sodium hydrosulfide and 5g/l of soda ash without salt, temperature increased until 85°C and stayed for 25 minutes, then the fabric was oxidised with 1% owf of sodium perborate. Basic dyeing was done without salt at 90°C for 1 hr. All dyed fabrics were rinsed thoroughly in water after dyeing and tumble dried.

3. RESULTS AND DISCUSSION

The grafting efficiency of the anionic agent onto cotton and associated colour changes occuring are listed in Table 2 and indicate that vinyl sulfate had higher reactivity than acrylic acid. However acrylic acid cured fabric gave less colour change compared to vinylsulfate treated cotton. X-ray Photoelectron Spectroscopy(XPS) shows that the hydrocarbon surface in cotton partially oxidized by UV/ozone treatment and reduces wetting time, leading to better penetration of the dye. The C(1s) peak for untreated cotton was peak fitted with components at 285.0 eV for aliphatic carbon, at 286.6 eV for carbon singly bound to oxygen and at 289.0 eV for carbonyl carbon. After UV/ozone treatment, both peak areas of C-O and C=O increased, while C-C/C-H dcreased. The dye resist is therefore due to the formation of carboxyl groups, as indicated by the increase in the peak area of 289 eV. The colour yield of modified cotton decreased with increasing anionising agent concentration and the irradiation time because the more anionised surface can enhance the charge repulsion between dye molecules and cotton, helping "exhausted" dyes to be easily washed off, Table 3 and 4. However the decreased colour yield of modified cotton when dyed with 10g/l of salt was not as noticeable as without salt, implying that salt can work as the neutralizer of the more negative charged surface, thus causing the difference in the dyeability of untreated and modified cotton to decrease. In the case of using acrylic acid and vinyl sulfate as anionising agents, colour yield of treated cotton was about half of untreated cotton, although UV ozone treatment gave about 70% of colour yield compared to the untreated cotton. Athough % exhaustion increased in most cases maybe due to increased polarity of modfied cotton, the exhausted dyes were easily rinsed off with cold water owing to the reduced dye/fiber interaction such as stronger repulsion force between cotton and dye unlike cationsed cotton. Reactive dyeing results of anionised cotton with vinyl sulfate shows that the treated cotton had lower dyeability compared to the untreated fabric when dyed with soda ash, Table 5. While dyeing without soda ash the anionised cotton did not show much difference compared to untreated cotton due to the low dyeability of untreated cotton under these dyeing conditions. The addition of salt decreased the reduced dyeability effect by anionisation. Sulfur dyeing results of cotton anionised with vinyl sulfate show that both sulfur dyes showed the decreased dyeability compared to untreated cotton like direct and reactive dyes, Table 6.

As can be seen in Table 7, the anioised cotton with acrylic acid improved the dyeability of untreatd cotton to the basic dye because of increased charge interaction.

4. CONCLUSION

The anionization of the cotton was induced by UV/ozone irradiation treatment as well as the photografting of monomeric acids such as acrylic acid or vinyl sulfate. Anionisation imparted reduced dyeability to cotton with respect to direct, reactive, and sulfur dyes and the enhanced dyeability of the cotton to basic dye.

REFERENCES

1. M.M. Kamel, Amer. Dyestuff Rep., **82(6)**, 36(1993).
2. K. Fukatsu, Text. Res. J., **62**, 135(1992).
3. J.A. Cuculo, Text. Res. J., **41**, 321(1971).
4. T.L. Ward, R.R. Benerito, and R.J. Berni, Text. Res. J., **42**, 119(1972).
5. J.A. Clipson and G.A.F. Roberts, J. Soc. Dye, Col., **105**, 158(1989).
6. K. Cho, M.S. Dissertation, SNU, Seoul, 1997.
7. J. Lee, M.S. Dissertation, SNU, Seoul, 1998.
8. J. Jang, PhD thesis, UMIST, Manchester, 1998.

Table 2. Photografting of two anionic agents to cotton and Yellowness Index(YI) and Whiteness Index(WI) of treated fabric.

Agent	Agent applied(%)	%G (%owf)	GE (%)	YI	WI
Untreated	0	0.00	0.0	3.3	67.1
Acrylic acid	1	0.04	3.7	3.2	67.8
	3	0.25	7.9	3.4	66.3
	5	0.76	14.4	3.4	66.5
	7	1.08	15.5	3.4	66.5
Vinyl sulfate	1	0.10	9.3	3.3	67.0
	3	0.50	14.9	3.7	64.6
	5	1.08	18.5	4.5	64.2
	7	1.37	17.2	4.9	63.0

%G, GE indicate %grafting, grafting efficiency respectively.

Table 3. Dyeing of anionised cotton with Direct Blue 86.

Treatment	Agent Applied(%)	K/S	%E
Untreated	0	2.0(5.8)	13.1(41.9)
Acrylic acid	1	1.2(5.3)	5.2(38.7)
	3	1.0(5.4)	7.9(43.6)
	5	1.0(5.0)	9.3(45.7)
	7	1.1(4.6)	12.2(47.2)
Vinyl sulfate	1	1.5(5.0)	9.8(40.8)
	3	1.3(4.3)	11.3(38.5)
	5	1.1(3.4)	11.3(36.2)
	7	1.1(4.0)	10.9(35.4)

Parenthesis indicate that the sample was dyed with the addition of sodium sulfate(10g/l).

Table 4. The Effect of UV ozone treatment on the dyeing properties of Direct Blue 86, YI and WI.

Radiation Time(mins)	K/S	%E	YI	WI
Untreated	2.0(5.8)	13.1(41.9)	3.3	67.1
1	1.7(8.2)	16.4(39.4)	3.5	66.3
2	1.6(8.1)	16.3(37.5)	3.6	66.1
5	1.4(6.0)	16.5(36.3)	4.5	63.4
10	1.4(4.8)	17.6(36.0)	8.0	53.7
20	1.4(4.0)	24.0(31.1)	12.2	43.4
40	1.4(3.6)	30.0(33.9)	15.7	29.9

For key see Table 3.

Table 5 Dyeing of anionised cotton with C.I. Reactive Red 2.

Vinyl sulfate applied(%)	K/S	%E	K/S[a]	F(%)	T%
0*)	0.3	6.2	0.2	66.7	4.1
1*)	0.4	4.2	0.2	50.0	2.1
3*)	0.3	4.0	0.1	33.3	1.3
5*)	0.4	2.4	0.2	50.0	1.2
7*)	0.4	5.4	0.2	50.0	2.7
0**)	9.1	57.1	7.9	86.8	49.6
1**)	3.9	44.0	3.7	94.9	41.8
3**)	4.0	43.0	3.1	77.5	33.3
5**)	3.6	41.4	2.7	75.0	31.1
7**)	2.5	38.5	2.2	88.0	33.9
0***)	9.0	60.7	7.9	87.8	53.3
1***)	6.8	53.4	6.3	92.6	49.4
3***)	7.0	52.9	5.0	71.4	37.8
5***)	5.4	49.4	4.7	87.0	43.0
7***)	4.6	47.3	3.9	84.8	40.1

dyed with C.I. Reactive Red 2 at 40°C, liqour ratio 1:30 for 1.5 hr.
a), K/S after soaping;
*), **), ***) indicate that this dyeing does not include soda ash, 10 g/l soda ash, 0g/l of soda ash + 10 g/l sodium sulfate respectively.

Table 6. Sulfur dyeing of anionised cotton with C.I. Leuco Sulfur Green 2 and Brown 96.

Dye	Vinyl sulfate applied(%)	K/S	K/S[a]	F(%)
Leuco Sulfur Green 2	0	5.2	3.2	61.5
	1	4.6	2.7	58.7
	3	4.6	2.7	58.7
	5	4.4	2.4	54.5
	7	4.1	2.3	56.1
Leuco Sulfur Brown 96	0	6.3	5.5	87.3
	1	5.9	5.1	86.4
	3	6.0	5.2	86.7
	5	6.2	5.3	85.5
	7	6.2	5.3	85.5

Table 7. Basic dyeing of anionised cotton with acrylic acid.

Acrylic acid applied (%)	K/S	%E
0	1.6	21.3
0[a]	1.1	20.9
1	2.9	49.8
2	3.6	62.1
3	5.3	68.0
5	7.4	76.6

a), the bath contained 10g/l of sodium sulfate.