Single Stage Application of Disperse/Reactive Dye System on Chemically Modified Polyester/Cotton Blend for Improved Performance

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***Abstract*—Wet processing of textiles involves utilization of large amount of chemicals, which ultimately adds to effluent load. The colouration of textiles with various dyes makes the colour of the effluent dark and hence requires expensive treatments for the removal of dyes from the effluent. In the present work, a blend comprising of polyester and cotton components was dyed with disperse and reactive dyes respectively by a neutral dyeing approach. Normally polyester is dyed with disperse dyes in acidic medium, while cotton is dyed with reactive dyes in an alkaline medium for their respective fixation; the application involves either a two bath or one bath/ two-step dyeing procedure to be employed. In this approach, the blend was pretreated with a potential polymer, polyacrylic acid, in the presence of a suitable cross-linking agent and subsequently the pretreated fabric was dyed by pad-dry-cure dyeing technique using both disperse and reactive dyes in the same padding liquor in the absence of any chemical in the bath. Thus, one bath/one-step dyeing method was possible with such neutral dyeing method leading to considerable saving of energy, time, water, labour, etc. These dyeing were compared with the conventionally dyed samples in terms of colour strength (K/S) values, measured on spectrophotometer. The washing, light and rub fastness of the dyed samples were quite good and comparable with the conventionally dyed samples. Effluent characteristics show remarkable results for the new approach and since chemicals were not utilized during dyeing, the pH, BOD, COD, etc. were all in the permissible range, indicating no extra effluent treatment to be used, except removal of dyes/colour from the effluent by a suitable colour removable technique, Thus, the new approach may be considered as "Green processing of cellulosic textiles" without any pollution problem.**

Keywords*— *Reactive dye, polyacrylic acid, cross-linking, effluent characteristics, green processing

I. INTRODUCTION

Ecology and energy conservation are the prime concerns of the textile industry throughout the world. The eco-problems in textile industry occur during some production and wet processing processes and are carried forward right to the finished product. Therefore, it is essential to either develop eco-friendly processes for wet processing of textiles or to minimize the utilization of chemicals. Moreover, with the scarcity as well as increasing prices of fuel, it has become one of the imperative duties of the present day researchers to cut-short the processes, without sacrificing the desirable properties of the product, for economy in general and conservation of energy in particular. To meet the above objectives, in the field of dyeing polyester-cotton blends, various approaches have been adopted, which include chemical modification and/or surface treatment of cotton; treatment with resin and/or cross-linking agent; use of high boiling swelling agents; etc. [1 – 12].

Conventional dyeing of polyester-cotton blend involves various steps, viz. polyester component dyeing – reduction clearing – washing – drying; followed by cotton component dyeing – washing – drying. After the completion of cotton part dyeing, various washing off treatments are necessary to remove the unfixed dye adhered to the fabric surface, which if not done properly will ultimately lead to poor fastness properties of the product [13 – 14]. Thus, severe washing off treatments, reduction clearing and intermediate dyeing steps are involved in two-bath polyester-cotton dyeing, which leads to more consumption of time, man-power, energy and also declination of productivity.

Thus, to conserve time and energy and also to minimize the pollution load posed by the effluent liquors in such dyeings, it is desirable to develop an economical and eco-friendly process, which can dye both components of the blend without altering their respective properties [15 – 16]. Therefore, in the present investigation, an attempt has been made to dye polyester-cotton blend in a single bath with disperse-reactive dye system by suitable modification of the blend with a highly reactive polymer, viz. polyacrylic acid in the presence of a suitable cross-linking agent. This modification makes it possible to perform the dyeing of the blend with disperse-reactive dye system in a neutral medium, without using any chemicals in the dyebath.

II. MATERIALS & EXPERIMENTAL PROCEDURES

A. Materials

1) Substrate: Mill scoured and bleached polyester/cotton blended fabric (composition 67:33; weight 123 gm/m^2; 42 ends/cm and 35 picks/cm) was selected for the present investigation. The fabric was purified in the laboratory by a mild treatment with the liquor containing 2 gpl sodium carbonate and 2 gpl non-ionic detergent (Lissapol N) at boil for 1 hour to remove the impurities, if any; then thoroughly washed till it became neutral and dried.

2) Chemical: Polyacrylic acid and Hydrazine hydrate (nitrogenous type cross-linking agent), used for the

investigation, were procured from Suvidhanath Chemicals and were of Analytical Reagent grade. All other chemical used during the work were of Laboratory Reagent grade.

3) Dyestuffs: Four commercial reactive dyes and two disperse dye were used without any further purification. The dyes were selected in such a way so as to make suitable combination with each other as far as shade, hue and tone are concerned. Thus, two red reactive dyes, containing different reactive groups, were combined individually with a red disperse dye during dyeing. Similarly, two blue reactive dyes, comprising of different reactive groups, were used separately in combination with a blue disperse dye. The specifications of these dyestuffs are mentioned in Table I.

B. *Experimental procedures*

1) Pretreatment: The application of polyacrylic acid and hydrazine hydrate (cross-linking agent) on polyester-cotton blended fabric was done by pad-dry-cure (curing at 150° C for 5 min) technique. The pretreated sample was rinsed with water and dried. The concentrations of polyacrylic acid and hydrazine hydrate were optimized by the assessment of the dyeability (in terms of K/S values) of the pretreated sample dyed with disperse-reactive dyes combination, viz. CI Reactive Red 4 (MCT) + CI Disperse Red 60; and CI Reactive Red 2 (DCT) + CI Disperse Red 60 dyes at 2% depth of shades by pad-dry-cure dyeing technique. During dyeings, no chemical was added to the padding liquor. The pH of the dyebath was maintained at 7.0 ± 0.2. After dyeing, the dyed sample was washed, soaped with a non-ionic detergent, Lissapol N (2 gpl) and soda ash (1 gpl) at 60° C for 30 min using a liquor ratio of 30:1, followed by thorough rinsing and drying.

TABLE I. REACTIVE AND DISPERSE DYES USED

Dye	Reactive system / chromophoric group	Colour Index number
DI: Procion Brilliant Red H7B	**Reactive Group:** Monochlorotriazine (MCT) **Chromophore:** Azo group	CI Reactive Red 4
DII: Procion Brilliant Red M5R	**Reactive Group:** Dichlorotriazine (DCT) **Chromophore:** Azo group	CI Reactive Red 2
DIII: Foron Brilliant Red E 2BL	**Chromophore:** Anthraquinone group	CI Disperse Red 60
DIV: Procion Brilliant Blue H5R	**Reactive Group:** Monochlorotriazine (MCT) **Chromophore:** Azo group	CI Reactive Blue 13
DV: Procion Brilliant Blue MR	**Reactive Group:** Dichlorotriazine (DCT) **Chromophore:** Anthraquinone group	CI Reactive Blue 4
DVI: Foron Brilliant Blue S-R	**Chromophore:** Methine group	CI Disperse Blue 354

2) Dyeing Procedure: The samples treated with optimum concentrations of polyacrylic acid and hydrazine hydrate were then dyed with the following pad-dry-cure (p-d-c) dyeing procedure –

The blended fabric was padded on a two bowl padding mangle with requisite amount of disperse-reactive dye solution (20 g/l each) using 2-dip-2-nip technique (65 % expression), dried at ambient temperature and cured at 150° C for 5 min. After dyeing, the samples were washed and soaped by usual procedure and the dyeings were compared with conventionally dyed samples [17].

C. *Testing and Analysis*

1) Mechanical Properties: Tensile properties, namely breaking strength and elongation at break, of the treated and untreated samples were determined on the Instron 1121 tensile tester. An average of 10 readings was taken.

2) Determination of Nitrogen Content : Nitrogen content of the treated and untreated samples was determined on C, H, N Analyzer (Perkin Elmer Model 240 Elemental Analyzer).

3) Evaluation of Colour Strength: The dyeing performance of various dyed samples was assessed on Data Spectraflash SF 600 Spectrophotometer by measuring the relative colour strength (K/S value) spectrophotometrically. These values are computer calculated from reflectance data according to Kubelka-Munk equation [18].

4) Assessment of Fastness Properties [19]: Wash fastness was evaluated according to ISO Standard Test No.3 on Launder-O-meter; light fastness on fade-O-meter using carbon-arc continuous illumination (BS 1006: 1987) and rub fastness (both dry as well as wet) on Crockmeter (BS 1006: No.X12; 1978).

5) Determination of Effluent characteristics: Various effluent dye liquors, after exhaustion and padding processes, were collected at random after the dyeing process was over. These effluent liquors were used for the studies of various effluent parameters, viz. pH value, chemical oxygen demand (COD), biological oxygen demand (BOD), total solids (TS), total dissolved solids (TDS), etc. The assessment of these parameters was done by standard procedures [20].

III. USING THE TEMPLATE

During trial experimental works, the polyester-cotton blended fabric, treated with polyacrylic acid and cross-linking agent, was dyed with one reactive-disperse dye system (CI Reactive Red 4 and CI Disperse Red 60) without using any chemical in the dyeing liquor and so it was possible to maintain the dyebath at neutral pH (7.0 ± 0.2). The dyeing results obtained were quite encouraging and uniform. Therefore, the concentrations of the polymer and the cross-linking agent were optimized. This was carried out by using various concentrations of polyacrylic acid (25, 50, 100, 150, 200 and 250 gpl) and hydrazine hydrate (10, 25, 50, 75, 100 and 150 gpl) for the pretreatment purpose. The optimized concentrations of these agents were found individually by assessing the dyeing performance in terms of K/S values (not mentioned here) of the respective sample. It was found that optimum concentration of polyacrylic acid was 200 gpl, while that of hydrazine hydrate was 25 gpl.

The treatment undergoes some changes in the morphological characteristics of the cellulose structure of cotton as well as the compact structure of polyester, which

results in variation of tensile properties of the pretreated sample. The nitrogen content value for untreated blend sample was 0.008%; for polyacrylic acid treated (200 gpl/pad-dry-cure process) sample was 0.012% and for the sample treated with polyacrylic acid polymer along with hydrazine hydrate cross-linking agent (25 gpl) sample was 0.411%. The increase in the value of nitrogen content suggests the occurrence of cross-linking reaction with the blend substrate. The sample pretreated with polyacrylic acid and hydrazine hydrate (at optimized concentration) showed 17.4 kg breaking strength and 13.6 % elongation-at-break as compared with 20.2 kg and 14.3% breaking strength and elongation-at-break respectively for untreated sample. The decrease in breaking strength, viz. 13.86 % is also an indicative of cross-linking reaction being taken place.

The attachment of dye molecules onto the partially modified cellulosic substrate is found to be through covalent bonding as no reactive dye strips out from dyed blend sample in pyridine (100%) as well as in its mixture with water (50:50). Moreover, when the blend was treated with slightly alkaline sodium hydrosulphite solution, the disperse dye as well as the reactive dye were not removed from the respective polyester and cotton parts of the blend. These two treatments affirm the permanent attachment of disperse and reactive dyes onto polyester and cotton parts of the blend respectively.

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TABLE II. COLOUR STRENGTH (IN TERMS OF *K/S*) VALUES OF POLYESTER-COTTON BLEND FABRIC DYED WITH DISPERSE-REACTIVE DYE SYSTEM

Disperse + Reactive dye system	***K/S* values for pad-dry-cure dyeing using**
Conventional dyeing methods	
D I + D III	11.96
D II + D III	9.48
D IV + D VI	16.21
D V + D VI	14.53
Polymer-aided dyeing methods	
D I + D III	15.22 (+27.25)
D II + D III	9.23 (- 2.63)
D IV + D VI	19.15 (+18.13)
D V + D VI	14.68 (+1.03)

[a.] Data in parenthesis indicates percentage loss/gain over conventional dyeing

For the commercialization of neutral dyeing of disperse-reactive dye combinations on blended polyester-cotton substrate, four commercial reactive dyes, comprising of MCT and DCT reactive groups were applied in combination with disperse dyes having almost similar hue on blended fabric at 2 % shade by pad-dry-cure dyeing sequence as mentioned earlier. The results are mentioned in Table II. Such dyeings were also compared with conventionally dyed sample. The nature of the dye and the dyeing process utilized is found to have a great influence on the dyeing performances.

It can be observed from the table that the dye combinations, viz. DI + DIII as well as DIV + DVI perform extremely well for the polymer-aided neutral dyeing system. The colour strength (K/S) values for these dye systems are quite high than those of conventionally dyed samples. The values are enhanced up to 27% and 18% for DI + DIII and DIV + DVI combinations respectively. Both these systems contain less reactive monochlorotriazine type of reactive dye along with a disperse dye. These reactive dyes require high temperature for fixation and their fixation might have occurred with ease on the cross-linked polymer-modified substrate.

Further, it can be observed that in case of disperse-reactive dye system containing DCT (cold brand) reactive dyes, the colour strength of treated sample dyed by DII and DIII combination is only slightly lower in comparison with the respective conventionally dyed samples in the pad-dry-cure dyeing sequence used for the study. This may be due to the fact that dichlorotriazine reactive dyes require lower fixation temperature owing to their higher reactivity, and their performance might have been slightly impaired due to high temperatures used for fixation of these dyes during curing. The colour strength value for DV and DVI combination are quite comparable with that of conventionally dyed sample.

The fastness properties of all such dyed sample are quite satisfactory and comparable with conventionally dyed sample (Table III). However, in polymer-aided pad-dry-steam dyeing process (DS II), there is slight impairment in the light fastness for some of the dyes, particularly for DCT dye combinations.

TABLE III. FASTNESS PROPERTIES OF POLYESTER COTTON BLEND FABRIC DYED WITH VARIOUS DISPERSE-REACTIVE DYE COMBINATIONS

Disperse/ Reactive dye system	**Fastness Grades for**							
	Conventional pad-dry-cure dyeing method				**Polymer-aided pad-dry-cure dyeing method**			
	W	L	R		W	L	R	
			Dry	Wet			Dry	Wet
DI+D III	4	6-7	4	3-4	5	6-7	4-5	4-5
DII+D III	4-5	6-7	4	3-4	4-5	6	4-5	4
DIV+DVI	4-5	7	4-5	4	5	7	4-5	4-5
DV +DVI	4-5	6-7	4	4	5	6	4	4

[b.] **W** = Washing fastness, **L** = Light fastness, R = Rub fastness

The effluent parameters of randomly selected polyester-cotton blend samples, dyed by conventional two-step dyeing and single bath one-step polymer-aided neutral pad-dry-cure dyeing method have been mentioned in Table IV. Only a few dyed samples have been selected for characterization and the results are also compared with the norms prescribed by the Gujarat Pollution Central Board, GPCB [21]. It must be noted that all the samples (dyed by conventional as well as neutral dyeing procedures) have been tested without any effluent treatment standardized procedures and hence the values are slightly higher. It can be clearly seen from the table that the effluent parameters for conventional dyeing are comparatively much higher than the prescribed norms of the Pollution Control Board. On the other hand, the comparative effluent parameters for neutral dyeing approach are quite within the permissible range. Hence, the dyeing effluent need not be sent to the effluent treatment plant, which reduces the needs of the plant capacity and investment. It leads to a substantial reduction in the dyeing cost. Thus, the effluent of polymer-aided neutral dyeing method poses lesser loads than that of the conventional dyeing. It is because of no addition of salt and acid/alkali in the dyebath as in the conventional dyeing for such blends. Thus, the pH of the dyebath is near neutral pH, i.e., between 6.8 to 7.2, which minimizes the treatment procedure compared to the conventional dyeing, where the pH is in the range of about 4.5

to 5.5 in disperse colour dyeing and about 9.5 to 10.5 in reactive colour dyeing. The BOD and COD values of conventional effluent liquors are quite high, particularly the COD values and so an extra effluent treatment procedure is a must. The respective BOD and COD values for neutral dyeing effluent liquors are quite less and within the required permissible range. Further, in the padding processes, actually, the liquors are to be completely utilized and so the effluent procedure is negligible. The TS, TDS and TSS values for neutral dyeing liquors are also quite low compared to the conventional effluent liquors and possibly no extra effluent treatment is required as in the conventional dyeing procedures. Thus, polymer-aided neutral dyeing approach, with no utilization of chemical or auxiliary in the dyebath, can be regarded as an environmentally-friendly approach for the application of disperse-reactive dyes on polyester-cotton blend substrate.

TABLE IV. EFFLUENT PROPERTIES FOR CONVENTIONAL AND POLYMER-AIDED NEUTRAL DYEING METHODS

No.	Disperse/Reactive dye system	Effluent characteristics					
		pH	BOD mg/l	COD mg/l	TS mg/l	TDS mg/l	TSS mg/l
1	--	6.5 to 8.5	130 to 820	465 to 1400		1200 to 4000	50 to 350
	CONVENTIONAL PAD-DRY-CURE DYEING METHOD (2 STEP)						
2	DI + DIII	5.4 & 9.8	998	1820	1612	9700	826
3	DV + DVI	5.2 & 9.4	837	1520	1388	8240	684
	POLYMER-AIDED NEUTRAL PAD-DRY-CURE DYEING METHOD						
4	DII + DIII	7.0	380	462	975	2223	169
5	DI + DIII	7.2	420	510	827	2616	193
6	DV + DVI	6.9	365	495	958	2185	145
7	DIV +DVI	6.9	442	516	889	2086	129

CONCLUSION

Polyester-cotton blended fabric was pretreated with polyacrylic acid and cross-linked with hydrazine hydrate cross-linking agent by pad-dry-cure (at 150° C for 5 min) technique. The concentrations for polyacrylic acid and hydrazine hydrate were optimized. There is a drastic increase in the nitrogen content value for the sample treated with polyacrylic acid in the presence of hydrazine hydrate cross-linking agent. There is also a decrease in the tensile strength by 13.86 % for treated sample. These results provide a tool for the occurrence of cross-linking reactions and also manifest the morphological changes incurred in the blend substrate. Such pretreated and partially cross-linked blended fabric can successfully be dyed with various types of disperse-reactive dye system by pad-dry-cure dyeing sequence. The colour strength of all the dyed samples was adequate and quite comparable with conventionally dyed samples. In case of DI + DIII and DIV + DVI disperse-reactive dyeing systems, the dye-uptake was enhanced up to 27 % and 18% with respect to their conventionally dyed samples. The study also revealed formation of covalent bond of the reactive dye with the cotton component of the substrate. The fastness properties of such dyeings were very good. The fabric so dyed did not utilize any salt or acid/alkali during dyeing and after dyeing the effluent treatment is not essential. So, the new approach may be considered as "Green processing of polyester/cotton blended" textiles without any pollution problem. Commercialization of this new approach may be useful for the textile industries from ecological and energy conservation aspects.

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