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Eco-friendly Chemical-free Dyeing of Polyester/Cotton Blended Fabrics

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Abstract

Dyeing of textile fibres encompasses utilization of various chemicals and auxiliaries for various purposes, such as exhaustion of the dyestuff from the dyeing liquor to the textile substrate, fixation of the dyestuff on the substrate, giving identical and level dyeing results, etc. The utilization of these chemicals in the dyebath adds up to the effluent load after the dyeing is complete, which may cause harm to the environment if they are discharged along with the waste water. Moreover, expensive treatment techniques are utilized for the removal of dyes as well as chemicals from the effluent liquor. The present paper deals with a chemical-free dyeing of polyester/cotton blend; to achieve this, physio-chemical alteration of the blended substrate has been performed with a substantially potential synthetic polymeric compound and a suitable cross-linking agent. The conventional colouration of blends of polyester with cotton and other cellulosic substrates with a dyeing system comprising of disperse and reactive dyestuffs implicate the utilization of acidic and alkaline media respectively for the fixation of these dyestuffs on the respective substrates. The application procedure usually employed is either dyeing in two separate dyeing liquors or in a single dyebath in two different steps. The polyacrylic acid polymer was pretreated onto the blend comprising of polyester and cotton components in presence of a cross-linker and subsequently padded with a liquor containing an admixture of disperse and reactive dyestuffs, followed by drying and curing. The dyeing liquor was maintained at a neutral pH without utilization of any auxiliary or chemical in the padding solution. For evaluation of the dyeing performance, the blend samples, dyed by the modified chemical-free dyeing and the conventional methods, were compared with each other for their colour strength and fastness (wash, light and rub) characteristics. Furthermore, the study of the effluent liquors specifies the permissible limits of various effluent parameters, viz. pH, BOD, COD, etc.; the results obtained emphasizes strongly on no additional effluent treatment for the modified polymer assisted neutral dyeing system, thereby substantially reducing the effluent treatment cost, which is generally must for conventional dyeing of such blended substrates. However, an appropriate dye/colour removal practice may be employed for elimination of residual colour of the dyestuffs left in the effluent liquors. Hence, such chemical-free dyeing of blended textiles may be considered as "Green technological approach" for a textile dyer.

Keywords: Reactive dye, Polyester/cotton blend, Eco-friendly dyeing, Polyacrylic acid, Effluent characteristics.

Introduction

Energy and water are the two main cost factors in the textile industry. Specifically in epochs of high energy price and water inadequacy, improving energy efficiency and developing methods for water conservation should be the primary concerns for textile plants. Moreover, environmental aspects are also gaining importance in the present scenario of preserving the globe from the pollution complications. The chemical wet processing of textiles consumes a large quantity of water and also generate effluent liquor in tremendous proportion. Many issues related to the ecological aspects arise during manufacture and processing, particularly chemical wet processing of textiles, and these complications are further transformed to the final finished product. Hence, it becomes necessary for the textile processor to either curtail the chemical usage during wet processing of textiles or to design eco-friendly processes for performing bleaching, dyeing, printing and finishing of textiles so as to have minimum effluent load. In addition to scarceness, the upsurge in fuel's and other energy resource's value have led the researchers to design processes by reducing time, temperature, etc. without forfeiting the desirable properties or causing any detrimental effect on the textile substrate.

Polyester/cellulosic, particularly polyester/cotton, blends are quite popular worldwide due to specific innovative characteristics of the individual components combined together in the blend substrate during blending. The colouration of polyester/cellulosic blends is a lengthy process and associates enormous usage of auxiliaries and chemicals, thereby leading to consumption of large amount of time and energy as well as generation of massive amount of wastewater. In order to have energy conservation and to meet with various ecological aspects, researchers have implemented various approaches in their research, such as chemical alteration including apparent amendment of cotton surface; utilization of either a resin or a suitable catalyst; usage of various solvents and swelling compounds; etc.[1-7]. During the routine colouration process of blended substrates comprising of polyester and cotton (cellulosic) components, usually dyeing of polyester component is carried out first, followed by the dyeing of cotton component of the blend. Essentially, the application of disperse dyestuffs on polyester may be performed by carrier (exhaust) dyeing, high temperature - high pressure dyeing and thermosol dyeing methods; in each method the dyeing sequence is followed by various after-treatments, such as reduction clearing (to remove the unfix disperse dye from the polyester portion), rinsing, washing, soaping and drying. The disperse-dyed blend sample is subsequently dyed for the cotton component with reactive and various other dyestuffs suitable for the cellulosic substrates; the dyeing process is again followed by rinsing, washing, soaping and drying procedures. The final washing off of the blended material should be performed thoroughly for the removal of any adhered unfixed dyestuff from the surface of the blended fabric; otherwise poor fastness properties of the final product may result. Apart from the two-stage dyeing of the polyester-cotton blended materials, these additional but essential after-treatment procedures substantially reduce the efficiency and enhances the consumption of energy, time and labour. The wastewater generated by such dyeings contains enormous quantity of chemicals and auxiliaries as well as the unfixed dyestuffs, which makes the effluent liquor deeply coloured and polluted.

In order to diminish the contamination burden modelled through the wastewater generated from the above-mentioned colouration processes of the blended substrate and to minimalize the consumption of time and energy, designing of an inexpensive and environmental-friendly route is quite essential during dyeing of polyester/cotton fabric with disperse-reactive dye combination, thereby achieving dyeing of both the components of the blend without varying their individual performance and properties. The present research has been endeavored for the single-stage colouration of a modified blended substrate of polyester/cotton with a dye system comprising of disperse and reactive dyes of similar hue and shade. The modification of the blend was achieved by treatment with a potentially active polymeric compound of acrylic acid (polyacrylic acid, PAA) along with an apposite cross-linker, thereby enabling application of disperse-reactive dye system onto the blended substrate to be conducted in a neutral medium in the absence of any chemicals/auxiliary in the dyebath.

Materials and Methods

Materials:
Substrate: The polyester/cotton blended fabric (comprising of 67% polyester and 33% cotton), selected for the present work, was supplied by Kiran Threads Limited, Vapi. The other specification of the fabrics were: Weight: 123 gm/m^2, Ends/cm: 42, Picks/cm: 35.

The fabric, as obtained from the mill, was in scoured and bleached condition. However, for better performance and to remove the adhered dirt and other stain marks, if any, a mild treatment was given to the fabric in the laboratory with a liquor containing: Sodium carbonate: 2 g/l, Non-ionic detergent (Lissapol N): 2 g/l at boil for 60 minutes. Finally the fabric was neutralized, washed thoroughly and air-dried. The fabric appearance after the above treatment is as shown in the Figure-1.

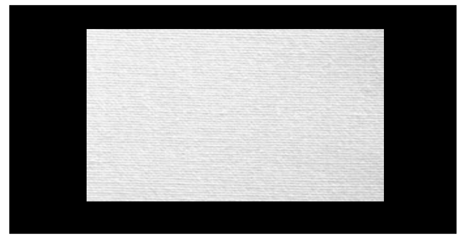


Figure-1
Polyester/cotton blend fabric sample

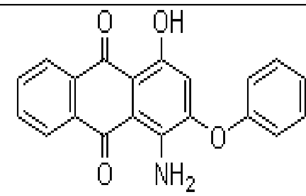
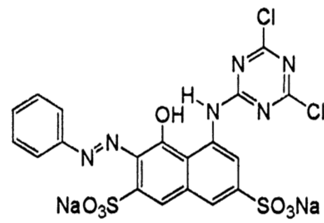
Chemicals: The polymer, polyacrylic acid (PAA; A. R grade) and the cross-linker hydrazine hydrate (HH, nitrogenous type; A. R. grade), used for the exploration, were acquired from Durga Traders, Vadodara. The other supplementary auxiliaries and chemical used during the research were of L. R. grade.

Dyes: A red colour combination, of nearly similar shade, hue and tone, was selected from disperse and reactive classes of dyes. The dyes selected were commercially available dyestuffs and have been utilized directly on the respective substrates without undergoing any supplementary refinement. Some of the specific characteristics (chemical specification, chemical structure, and Colour Index number) of these dyestuffs are stated in Table-1.

Experimental Procedures:
Polymer Pretreatment: The PAA polymer, in presence of HH cross-linker, was padded on the polyester-cotton blended substrate using 2-dip-2-nip technique and 65% padding expression, dried and cured at 150^o C for 5 min, followed by thorough rinsing and drying. Prior to their final application on the substrate, the concentrations of PAA and HH were individually optimized. The assessment of the optimization results was performed on the basis of the dyeing performance of the pretreated sample with 2% depth of shades of disperse-reactive dye system combination (DI + DII; 20 g/l each)) using pad-dry-cure dyeing procedure and evaluated spectrophotometrically for their colour strengths.

Throughout the colouration process, the bath pH has been maintained at 7.0 ± 0.2 without utilizing any additive in the padding liquor. The curing conditions for dyeing were also optimized during the research work and the optimum condition selected for curing were 150^o C for 5 minutes. After completion of the process, the coloured blend fabric was thoroughly rinsed, treated with 2 g/l Lissapol N (non-ionic detergent) and 1 g/l sodium carbonate at 60^o C for half hour using material to liquor ratio of 1:30, washed and dried using ambient conditions.

Table-1
Commercial Disperse and Reactive dyestuffs used

Dyestuff	Chemical specifications	Chemical structure	Colour Index number
DI: Foron Brilliant Red E 2BL	**Chromophoric group:** Anthraquinone		CI Disperse Red 60
DII: Procion Brilliant Red 5B	**Reactive system:** Monochlorotriazine (MCT) **Chromophoric group:** Azo		CI Reactive Red 2

Dyeing Technique: The blend sample, treated with optimum concentrations of PAA and HH was subsequently dyed as follows:

The pretreated polyester/cotton blend was padded on a two-bowl padding mangle by 2-dip-2-nip procedure and 65% padding expression using necessary quantity of disperse and reactive dye solutions (20 g/l each), followed by drying using ambient conditions and curing at 150^o C for 5 minutes. The dyed sample was thoroughly washed, soaped at 60^o C for 5 minutes, washed and dried; the results were then compared with the conventionally dyed blend samples[8].

Testing and Analysis
Mechanical Properties: The blend samples were evaluated on Instron 1121 Tensile Tester for their tensile characteristics, namely tensile strength and extension at break, on the basis of average of 10 readings.

Measurement of Nitrogen Content: Perkin Elmer Model 240 Elemental Analyzer was utilized for the determination of the percentage of nitrogen element present in the modified as well as parent blend samples.

Assessment of Dyeing Performance: All dyed samples were examined for their dyeing behaviour by evaluation of their relative colour strength (*K/S*) values on Data Spectraflash SF 600 Spectrophotometer. The assessment of the colour values utilizes Kubelka-Munk equation[9], by which the measured reflectance values on spectrophotometer are directly converted into the colour strength (*K/S*) values.

Determination of Fastness Properties[10]: Various fastness characteristics (wash, light and rub) were determined using standard procedures. The washing fastness was measured on the Launder-o-meter as per ISO Standard Test No.3; the measurement of light fastness was performed on fade-o-meter using carbon-arc continuous illumination (BS 1006: UK-TN, IS 2454-1985), and the fastness to rubbing (dry & wet) were assessed on Crock meter as per standard procedure (BS 1006: No.X12; 1978).

Measurement of Various Parameters for Wastewater: The wastewater was collected after completion of both modified as well as conventional dyeing processes and were utilized for the studying different characteristics of the wastewater, viz. pH of the liquor, Chemical Oxygen Demand (C.O.D.), Bio-chemical Oxygen Demand (BOD), Total Solids (T.S.), Total Dissolved Solids (T.D.S.) and Total Suspended Solids (T.S.S.). All the parameters were measured using standard procedures[11].

Results and Discussion

In the preliminary trial research work, the pretreatment of the polyester/cotton blend substrate was performed with a substantially active PAA polymer in conjunction with a nitrogenous cross-linker (HH); subsequently the treated fabric was dyed with a carefully selected combination of red disperse and reactive dyestuffs (Foron Brilliant Red E 2BL and Procion Brilliant Red 5B) in a neutral dyebath (pH maintained at 7.0 ± 0.2) without incorporating any additive or chemical in the padding liquor. The successfulness of the treatment was adjudged from the dyeing results, which were reasonably encouraging, consistent and quite comparable with the similar dyeing performed using conventional dyeing procedure.

The research work was further extended for optimization of the concentrations of PA polymer and HH cross-linker as well as the curing conditions for treatment and dyeing. For optimization study of pretreatment, the concentration of PAA polymer was

chosen as 25, 50, 100, 150, 200 and 250 g/l, while that of the HH cross-linker was selected as 10, 25, 50, 75, 100 and 150 g/l. Similarly, for optimization of curing conditions of pretreatment and dyeing, the curing temperature was varied as 120^{o}, 130^{o}, 140^{o}, 150^{o}, 160^{o} and 170^{o} C while the time of curing was kept as 60, 120, 180, 240, 300, 360 and 420 seconds. In all these cases, the individual selection for optimized parameter was done by the assessment of the dyeing results of the dyed fabric from their spectrophotometrically measured *K/S* evaluations. However, the optimization study was a quite long procedure and involved presentation of many results; hence, these results are not mentioned in the paper. However, the final optimized conditions are as mentioned below:
i. Optimum concentration of polyacrylic acid : 200 g/l,
ii. Optimum concentration of hydrazine hydrate: 25 g/l,
iii. Optimized temperature for curing and dyeing: 150^{o}C,
iv. Optimized time for curing and dyeing: 300 seconds (5 minutes).

Morphological and physiochemical changes are found to occur due to the polymeric treatment in the cotton component's cellulosic configuration and also the compacted arrangement in the polyester component; thereby causing some changes in the tensile characteristics of the treated blend sample. Some of the changes are identified as follows:

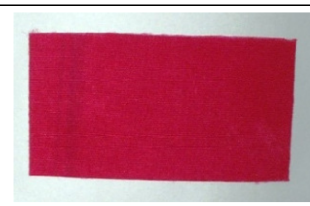
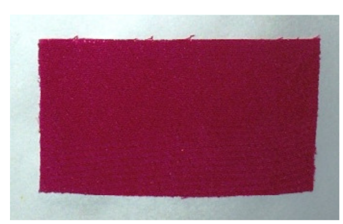
The estimation of nitrogen content on the elemental analyzer revealed the following values for the nitrogen element in the sample: i. Untreated blend sample: 0.008%, ii. PAA treated sample (optimized concentration): 0.012%, iii. PAA + HH treated sample (both optimized concentrations): 0.411%.

From the results, it can be visualized that there has been considerable enhancement in the values of nitrogen content for the treated samples, particularly when the cross-linking agent was utilized along with the PAA polymer; the results support the existence of a cross-linking between the polymer and the blend substrate.

Furthermore, the results of tensile strength analysis also indicate the manifestation of the reaction of cross-linking. The untreated blend sample (control) exhibited 20.2 kg breaking strength and 14.3% elongation-at-break; whereas the blend sample treated with optimized concentrations of PAA polymer and HH cross-linker displayed 17.4 kg breaking strength of 17.4 kg and elongation-at-break of 13.6%.

To examine the feasible mechanism of attachment of disperse and reactive dyestuffs on their respective substrates, namely polyester and cotton, the dyed samples were treated with sodium hydrosulphite (slightly alkaline) and pyridine solution (pure as well as aqueous) separately. It was found that neither disperse dye nor reactive dye stripped out from their respective blend's components when dyed sample was treated with alkaline liquor of sodium hydrosulphite. Moreover, the treatment with pure pyridine and it aqueous solution with water (1:1) also revealed the covalent linkage formation of hydroxyl group of cotton's cellulose with the fibre-reactive dye; thereby confirming reactive dye molecule attachment on to the modified cotton substrate of the blend. From this study, the permanent attachment of disperse and reactive dyestuffs on to their respective blend components may be established.

Table-2
Dyeing performance for conventional and polymer-aided dyeing systems

Dye combination	Colour strength values for	Shades for
Conventional dyeing technique		
DI + D II	11.96	
Polymer-aided dyeing technique		
DI + D II	15.22 (+27.25)	

Note: Data in bracket designates percentage gain over control sample dyed by conventional dyeing method

The commercialization aspects of this new approach of neutral dyeing of an appropriately selected combination of disperse and reactive dyes for the polyester and cotton components of the blend fabric is necessary; to achieve this, the dyestuffs from both the classes of dyes were chosen on the basis of similar depth of shade, hue and tone and were applied on the polymer pretreated substrate for 2% shade by padding technique and the fixation was achieved by curing the samples. The results for the colour strength values and depth of shade for the modified and conventional dyeing samples were compared with each other and are represented in Table-2. From the table, it can be noted that the polymer-aided neutral dyeing technique has achieved excellent performance as compared to the conventional dyeing technique. There has been an enhancement of up to 27 % dye uptake for the red dye combination of disperse and monochlorotriazine type of reactive dyes selected for the present work. The samples dyed by the neutral dyeing method also exhibited adequate washing, light and rubbing (dry-rub as well as wet-rub) fastness characteristics; the results (Table-3) are at par with those of control samples dyed by conventional dyeing method.

Table-4 epitomizes the analysis of effluent parameters for the wastewater generated after dyeing of the blend using traditional two-stage as well as modified polymer-aided dyeing utilizing pad-dry-cure technique in the present study. The standards recommended by the Gujarat Pollution Central Board, GPCB[12] have also been taken into account for the comparison of the results. It must be noted that no specific effluent treatment procedure was adopted for the wastewater generated in either case and the measurement of effluent parameters was done directly for the effluent liquors produced immediately after the dyeing was complete. The results from the study confirms reasonably higher effluent characteristics for the traditional two-step colouration method than those designated in the recommended GPCB norms. However, the respective values for the polymer-aided modified system are relatively in the allowable limits. Furthermore, due to non-incorporation of any additive (acid/alkali, salt, or any other auxiliaries), the effluent produced after the adapted chemical-free dyeing system poses reduced pollution load than that generated by the 2-step conventional dyeing technique. The pH of the effluent after dyeing in the modified approach is nearly neutral (6.8 to 7.2), whereas it is in the range of 4.5 - 5.5 and 9.5 - 10.5 in the disperse colour dyeing and reactive colour dyeing respectively. It is utmost essential to control the BOD and COD parameters in case of conventional effluent liquors, while no such necessity is found for neutral dyeing effluent liquors as the values are reasonably in the acceptable range. Similar interpretation holds true for the TS, TDS and TSS parameters for the modified neutral dyeing approach. From the study of effluent parameters, it can be said that for modified approach, there is no necessity of sending the dyeing effluent for effluent treatment purpose; thereby the requirement for investing on effluent treatment plant is minimized and the overall dyeing cost can be substantially reduced. Thus, polymer-aided, chemical-free neutral dyeing method may be considered as an environmental-responsive scheme for the colouration of disperse/reactive dyestuffs on polyester/cotton blend material.

Table-3
Evaluation of Fastness properties

Dye combination	Fastness grades for							
	Control				Modified			
	Wash fastness	Light fastness	Rub fastness		Wash fastness	Light fastness	Rub fastness	
			Dry	Wet			Dry	Wet
D I + D II	4-5	7	5	4	4	5-6	4	3-4

Table-4
Assessment of Effluent parameters

No.	Dye combination	Effluent parameters					
		pH	B.O.D. (mg/l)	C.O.D. (mg/l)	T.S. (mg/l)	T.D.S. (mg/l)	T.S.S. (mg/l)
		As per GPCB standards					
1	-	6.5 to 8.5	130 to 820	465 to 1400		1200 to 4000	50 to 350
Conventional dyeing							
2	D I + D II	5.6 & 9.7	973	1760	1665	8650	749
Polymer-aided neutral dyeing							
3	D I + D II	7.1	380	462	975	2223	169

Conclusion

Polymeric pretreatment on the polyester/cotton blended substrate, with optimized concentrations of PAA polymer and HH cross-linker, using pad-dry-cure dyeing technique, may be successfully employed for the single-stage application of a disperse-reactive dye combination with improved performance. The treatment substantially enhances the nitrogen content value of the pretreated sample but marginally decreases the tensile strength by 13.86 %; thereby confirming the happening of morphological variations in the blended substrate. Apart from the cross-linking of the polymer with the cotton cellulose, the linkage development through covalent bonding, between the cellulosic fibre-reactive dyestuff and the cellulosic component (cotton) of the blend, is also established by the study. The dyed samples showed improved dye uptake (up to 27 %) and adequate fastness characteristics for the modified chemical-free dyeing in comparison with conventional colouration method. The performance of dyeing with no additive in the padding liquor also substantially reduces the pollution load, thereby minimizing the possibility of effluent treatment. This novel approach of polymer-aided neutral dyeing of polyester/cotton blend substrate may be regarded as "Green processing of polyester/cotton blended textiles" with no harmful effect to the environment.

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