

Effect of PVAmHCl Pre-treatment on the Properties of Modal Fabric Dyed with Reactive Dyes: An Approach for Salt Free Dyeing

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Abstract

In this research, polyvinylamine chloride (PVAmHCl) was used as a physical modification agent on regenerated cellulosic fabric such as modal by a pad-batch process. The modified modal samples were dyed with different reactive dyes containing various reactive groups. The dyeability of the modified modal samples with reactive dyes without electrolyte was significantly improved due to an increase in the ionic attraction between the reactive dyes and modified modal fabrics. It has been confirmed through zeta potential analysis, as well as the result of various fastness properties such as light, wash and rubbing fastness of polyvinylamine chloride pre-treated modal with different reactive dyes are similar to those of untreated modal fabric. Also, the tensile strength, flexural rigidity and crease recovery angle of pretreated sample were determined, out of that crease recovery angle and flexural rigidity of pretreated sample showing significant improvement.

Keywords: Dyeing; Modal; Pre-treatment; PVAmHCl; Reactive dyes; Salt free reactive dyeing

Introduction

Modal (CMD) is a regenerated cellulosic fiber from Lenzing and it is extracted from Beechwood trees [1]. Modal has all the benefits of being a regenerated cellulosic fiber, and also it is fully biodegradable, higher soft in nature, excellent moisture absorbent and outstanding in handling properties; and possible to blend with all types of fibers [2]. It has a relatively high strength, which allows for the production of finer yarns and lighter fabrics as compared to another regenerated fiber such as viscose rayon. As a result, fabrics produced from modal are breathable and moisture absorbent and have high dimensional stability [3].

Cotton and regenerated cellulosic fibers can be dyed with various classes of dyes [4]. Most prominently, reactive dyes are widely employed for dyeing cellulose fibers because of their brilliance, wide shade gamut, and excellent fastness properties [5]. However, dyeing of cellulose fibers with reactive dyes still suffers from two major disadvantages; one is poor dye uptake and other one is unsatisfactory dye fixation, both were leads to environmental pollution [6]. Poor dye uptake is related to the existence of the charge barrier effect between the negatively charged fiber surface and anionic reactive dyes. This problem can be solved by adding a large amount of electrolytes, to the dye bath in order to suppress the negative charge on the fiber surface and then allowing reactive dye molecules to diffuse inside the fiber [7]. In the case of poor dye fixation, the contributing factor is the presence of inactive hydrolyzed dye [8]. Since fixation of reactive dyes onto cellulose fibers requires alkaline dyeing conditions in order to activate the hydroxyl group of cellulose to be able to react with the dye, some of the reactive dye can inevitably undergo the competing hydrolysis reaction with hydroxide nucleophiles [9], resulting in a reduction in the efficiency of the reaction with the cellulose substrate [10].

Increasing concern on environmental impacts has prompted regulators to enact rigorous environmental legislation to mandate dye users to minimize color in the dye-house effluent [5,11]. To meet such requirements, the dyeing industry has to adopt a more efficient dyeing process as well as selecting dyes which have a high dye fixation value [12]. Reactive dyes, the newest addition of existing dyes are the center of attraction in dyestuff research. Several new reactive systems have been introduced from time to time, hot brand reactive dyes have been widely considered due to their higher fixation yield on various fibers

[13]. Theoretically, Poly functional reactive dyes contain more than one reactive group in each molecule [5,14]. In practice, these additional reactive groups can have an impact on important physical properties such as solubility, aggregation, substantivity, and migration, which offers a very high level of fixation and it leads to low color usage to achieve a given depth of shade and a lower unfixed color load in effluent [15]. These multifunctional reactive dyes were especially designed for cellulosic fibers, and are claimed to save energy and time and reduce water consumption; a special auxiliary to assist the washing-off of unfixed dyes [16]. PVAmHCl has been used as a physical modifying agent for cellulosic materials [17]. It has been used for modification of cotton as well as other regenerated fibers for salt free dyeing as been previously reported [16,17]. Interest in PVAmHCl arises from the presence of a large number of cationic sites NH_3^+Cl^- which illustrated in Figure 1 [18] conclude in their research, dyeability for the cotton fabric significantly improved after pretreatment with PVAmHCl without addition of electrolyte as exhausting agent.

In this study, various reactive dyes with two different reactive groups which including bi-functional and polyfunctional were applied onto the PVAmHCl pre-treated (modified) modal fabrics. The dyeing was performed with and without electrolyte (Na Cl). To determine the modification of modal fabric samples was done by zeta potential, retained

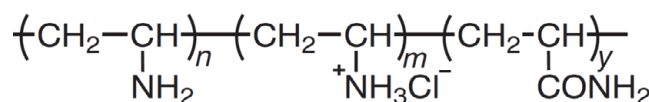


Figure 1: Chemical structures of PVAmHCl (Ma et al. [18]).

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water quantity, TDS, color strength, fastness properties and various physical properties like tensile strength, flexural rigidity, fabric crease recovery angle were also determined to examine the effect of PVAmHCl.

Materials and Methods

Materials

100% Modal (bleached and desized) plain woven fabric was used for this study, which is having Aerial density of 102 g/m² and it has been obtained from Texpert, Mumbai, India and the fabric characteristics are listed in the Table 1. The reactive dyes used with different reactive groups, including bi-functional and polyfunctional which are listed in Table 2, and both were procured from Huntsman, India. PVAmHCl (Laboratory reagent grade) were purchased from Triveni chemicals, Chennai, India and all other chemicals such as Sodium carbonate, Sodium hydroxide, Potassium di hydrogen phosphate, Sodium chloride, acetic acid were supplied from color chemicals, Tirupur, India, and above these reagents were used in laboratory reagent grade.

Pre-treatment and dyeing of modal fabric

Pretreatment: Various concentrations of PVAmHCl (2.5, 5.0, 10, 15 and 20 g/L) solution was applied to the modal fabric by padding technique. The wet pick up was 100% and the room temperature (30-35 °C) was maintained during the padding. The pH of pretreatment liquor was maintained at 7 by using of buffer comprising potassium dihydrogen phosphate (7 g/L) and sodium hydroxide (1.4 g/L). The padded fabric was put in the polyethylene sheet for 6 hours to prevent chemical migration and water evaporation. After 6 hours, the padded fabric was dried at room temperature and baked at 102 °C for 10 min in rapid baker. After baking the pre-treated fabric was washed with dilute acetic acid and followed by water till neutralization, finally the fabric was dried at room temperature. Table 3 shows sample labels and treatment parameters.

Dyeing: Dyeing of both unmodified and modified (pre-treated) modal samples was carried out using an Infrared dyeing machine at the liquor ratio of 20:1. Dyeing with both unmodified and modified modal fabrics with reactive dyes was performed according to the procedure which offered by the dye manufacturer. 1% o.w.f dyes was added for both bi-functional and polyfunctional reactive dyes. The procedure for poly functional reactive groups shown in the Figure 2a and 2b, 30 g/L NaCl, 15 g/L of Na₂CO₃ (Figure 2a) was used for unmodified modal fabrics and for the no salt dyeing procedure, 15 g/L of Na₂CO₃ (Figure 2b) was used for the modified modal samples. Similarly the procedure for bi-functional reactive groups shown in the Figure 2c and 2d (Figure 2c, 40 g/L NaCl, 15 g/L of Na₂CO₃) was used for unmodified modal fabrics and for the no salt dyeing procedure (Figure 2d, 15 g/L of Na₂CO₃) was used for the modified modal samples. After dyeing both unmodified and modified modal fabrics was removed from the bath and rinsed consecutively in cold, hot and cold water. The dyed fabric was boiled in a 2 g/L solution of anionic detergent ladiquest 1097 liq (Pure chem, India.) for 15 min until the complete surface or undiffused was removed, and then rinsed, and then the fabric was allowed to air dry in room temperature.

Testing

Dye Exhaustion, color strength and Fixation: The dye uptake for the modal fabric was determined with the help of UV-Visible light spectrophotometer and the dye-bath absorbance was measured at the wavelength of maximum dye absorption (λ_{max}). The exhaustion of the dyebath can be calculated by the Eq. (1).

Warp density, ends /inch	Weft density, picks/inch	Arial Density (g/m ²)	Warp yarn count (Ne)	Weft yarn count (Ne)
106	96	102	40	40

Table 1: Characteristics of used modal fabrics.

Commercial name	C.I. Number	Reactive groups	Amount (% o.w.f)
Novacron Blue FN-G	C.I Reactive Blue 268	Bi-functional	1
Novacron Red FN-R	C.I Reactive Red 238		1
Novacron Yellow FN-2R	C.I Reactive Yellow 206		1
Avitera Blue SE	C.I Reactive Blue 281	Poly-functional	1
Avitera Red SE	C.I Reactive Red 286		1
Avitera Yellow SE	C.I Reactive Yellow 217		1

Table 2: Characteristics of different reactive dyes used for this research.

Designation	Treatment
CS	Conventional dyeing with salt
CW	Conventional dyeing without salt
P2.5	Pre-treatment of fabric with 2.5 g/L of (PVAmHCl) and followed by dyed.
P5.0	Pre-treatment of fabric with 5 g/L of (PVAmHCl) and followed by dyed.
P10.0	Pre-treatment of fabric with 10 g/L of (PVAmHCl) and followed by dyed.
P15.0	Pre-treatment of fabric with 15 g/L of (PVAmHCl) and followed by dyed.
P20.0	Pre-treatment of fabric with 20 g/L of (PVAmHCl) and followed by dyed.

Table 3: Sample labels and treatment parameters.

$$E\% = \frac{(1-A)}{A_0} \times 100 \quad (1)$$

Where A_0 and A are the absorption of the dye solution at the maximum wavelength before and after dyeing process [10]. After dyeing, reflectance spectra of each sample were measured with the help of Minolta spectrophotometer CM-3600A. A color depth of the dyed fabrics was analyzed by measuring the (K/S) color strength values of samples. It seems the higher value of color strength is nothing but higher the dye absorption by the fabric. Color strength values of the dyed samples were calculated using the following instrument settings (illuminant D65, 10 supplemental standard observers, specular included, UV included). The effective color, strength value was calculated by summation of the color strength values at 10 NM intervals from the wavelength of 360-750 nm. While testing, the sample was folded two times. Each sample was measured ten times by changing the measuring point randomly to calculate the average value [19]. Color measuring instrument (spectro-photometer) determines the color strength value of a given fabric through Kubelka-Munk Eq. (2).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (2)$$

Where R =reflectance percentage, K =absorption and S =scattering of dyes.

The fixation of adsorbed dye (F) can be calculated by using of the Eq. (3) and the total fixation of the originally applied dye (T) can be calculated by using Eq. (4).

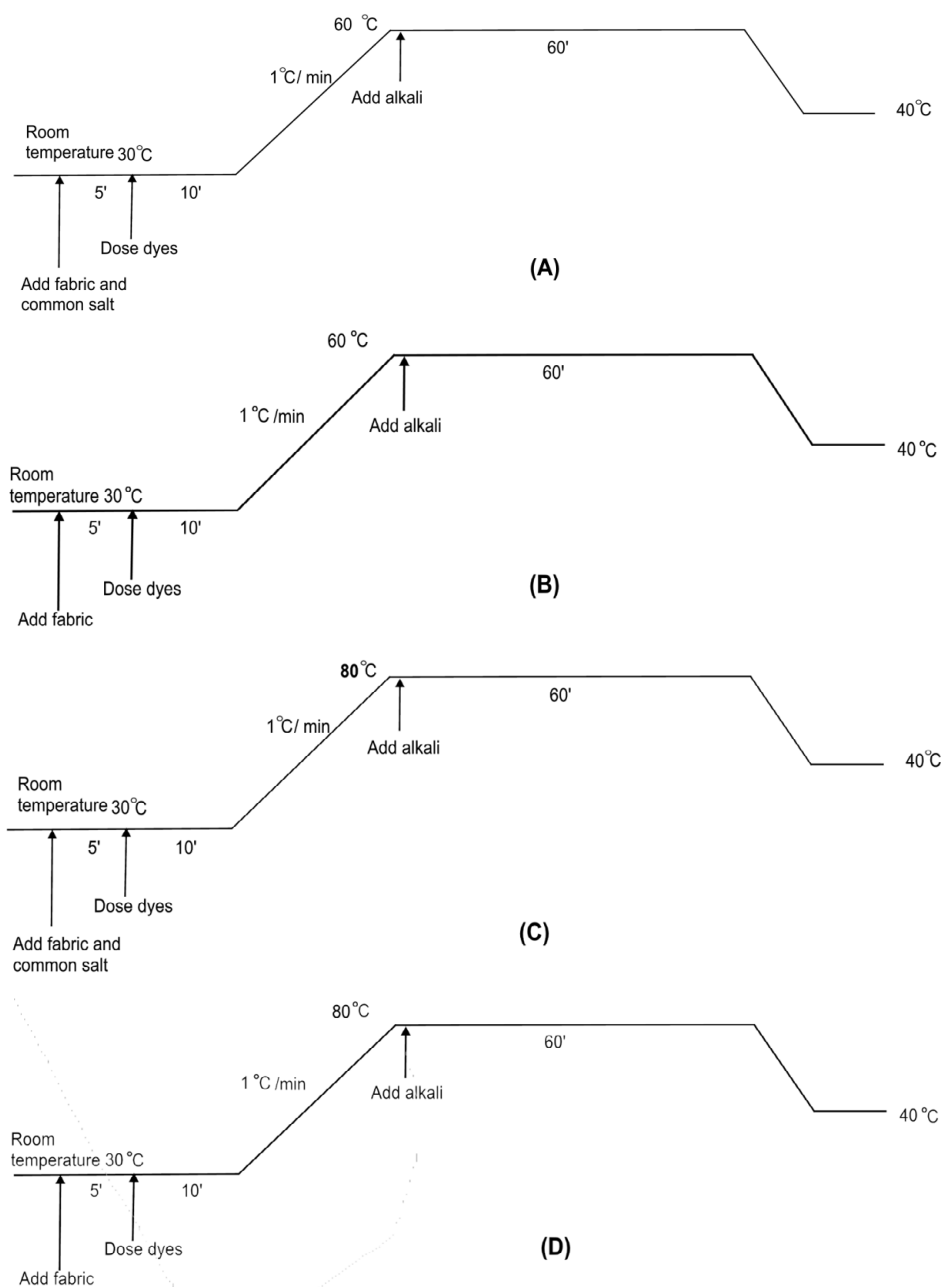


Figure 2: Dyeing procedure for control and treated modal fabrics. (a) Conventional dyeing procedure for unmodified modal fabrics with poly functional reactive dyes. (b) Conventional dyeing procedure for modified modal fabrics with poly functional reactive dyes. (c) Con-ventional dyeing procedure for unmodified modal fabrics with bi-functional reactive dyes. (d) Conventional dyeing procedure for modified modal fabrics with bi-functional reactive dyes.

$$F\% = \frac{(K/S)_1}{(K/S)_2} \times 100 \quad (3)$$

$$T(\%) = E \times \frac{(K/S)_1}{(K/S)_2} \times 100 \quad (4)$$

Where $(K/S)_1$ and $(K/S)_2$ indicates the before and after soaping respectively [10].

The percentage of dye intensity increases (I) on PVAmHCl pre-treated samples compared to untreated sample was obtained from the following Eq. (5).

$$I\% = \frac{(K/S)_a - (K/S)_b}{(K/S)_b} \times 100 \quad (5)$$

Where $(K/S)_a$ refers to modified modal fabric samples and $(K/S)_b$ is to samples without pre-treatment and dyed with salt (CS).

Evaluation of zeta potential: The electrokinetic potential of pre-treated and untreated modal fibers were measured by the streaming potential (U_p) and streaming current (I_p) method using Brookhaven-Paar Electrokinetic Analyzer (EKA). The ζ -potential for the modal fabric was measured by streaming current method depending on

pH values of 0.001 M KCl solution in a pH range of 2 to 10. The zeta potential was calculated according to the Helmholtz-Smoluchowsky Eq. (6).

$$\zeta = \frac{U_p \cdot \eta \cdot L}{\varepsilon \cdot \varepsilon_0 \cdot Q \cdot R \cdot \Delta p}$$

or

$$\zeta = \frac{I_p \cdot \eta \cdot L}{\varepsilon \cdot \varepsilon_0 \cdot Q \cdot R \cdot \Delta p}$$

where ζ : zeta potential (mV), U_p : streaming potential (mV), I_p : streaming current (mA), ε : permittivity electrolyte solution (Fm^{-1}) ($\text{Kgm}^{-3}\text{S}^4\text{A}^2$) η : dynamic viscosity of solution (Pas) ($\text{Kgm}^{-3}\text{S}^4\text{A}^{-1}$), ε_0 : vacuum permittivity (Fm^{-1}) ($\text{Kgm}^{-3}\text{S}^4\text{A}^2$) Δp : pressure difference between capillary ends (Pa) (Nm^{-2}), L : capillary length (m), R : electrical resistance (Ω), Q : capillary cross-section (m^2) [17,20,21].

Evaluation of TDS: Total dissolved solids (TDS) were measured through a process of evaporation. During the first rinse of the dye bath, dye liquor samples were collected for measurement of TDS. The TDS for the dye liquor samples were determined by gravimetric method that involved evaporating the liquid solvent to leave a residue that can subsequently be weighed with a precision analytical balance (normally capable of 0.0001 gram accuracy). The TDS (mg/L) in the effluent was determined with the help of Eq. (7).

$$TDS(\text{mg/L}) = \frac{(A - B) \times 1000 \times 1000}{\text{Sample volume}} \quad (7)$$

Where, the final weight (A) is the weight of the dish plus the dried residue in gram and the initial weight (B) is the weight of the dish in gram.

Note: TDS were tested for the all concentration of PVAmHCl with respect to Reactive Blue 268 only.

Water retention value: To identify the water retention values, pre-treated and untreated modal fabric sample has to be immersed in distilled water for 24 hours and then centrifuged at 7800 min^{-1} for 2 minutes, then it should be dried for 105°C . The water retention values can be calculated by this Eq. (8).

$$WRV(\%) = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{wet}}} \times 100 \quad (8)$$

Where W_{dry} , W_{wet} refers the mass of dried and before dried the samples [2,3,17,20-24].

Evaluation of fastness properties: Washing fastness test for the dyed samples were performed as per the AATCC 61-2003 by using the Texcare Launderometer. A multi-fiber test fabric was attached to each sample to evaluate the staining and the test conditions were set according to the standard. Color fastness to rubbing was measured according to AATCC 08-2003 and both dry and wet crocking test were measured using the AATCC automated crockmeter. The washing and rubbing fastness results can be given grading with the help of appropriate gray scale. Perspiration fastness for the dyed samples was carried out according to the ISO 105-E04 test method. The light fastness was performed as per the ISO 105 B02:1994, standard method and the degree of color fading were assessed by using of SDC blue wool scales.

Evaluation of mechanical properties: The mechanical properties of fabrics, such as tensile strength were measured in Instron tester (3300 series) as per ASTM D5034-95; flexural rigidity was measured in

Taber fabric stiffness tester as per the BIS BS 3356-1991; crease recovery angle was measured in James Heal crease recovery tester as per AATCC 66-2003 standard. Five samples were tested for each test and calculated average values for the results.

Results and Discussion

Zeta potential

Generally, ζ -potential for textile fibers are negative, it is due to negative charge developed on the fiber surface. Modal is a cellulosic fiber and having the $-\text{COO}^-$ groups which arise the ionization or dissociation reaction on the surface. The results of Zeta potential (ζ), Iso electric point (IEP), Point of Zero charge (PZC) and Specific surface charge (q) of modal fabrics were summarized in the Table 4, which specify the dissociation of functional groups such as hydroxyl ($-\text{OH}$), carboxyl acid ($-\text{COOH}$) groups of modal fabric and it introduces the negative charge. The result shows that untreated (CW) modal fabric surface has lowest ζ -potential (negative charge) in whole pH range. The ζ -potential for PVAmHCl pre-treated fabric was increased to positive charge at low pH range. This is probably because of the presence of PVAmHCl and it has a larger number of cationic sites (NH^+) and it gains the H^+ ions in the liquid phase which helps to change the positive charge of the fabric from:

$\zeta = -20.4 \text{ mV}$ for CW to $\zeta = -14.7 \text{ mV}$ for P2.5, $\zeta = -12.8 \text{ mV}$ for P5, $\zeta = -11.7 \text{ mV}$ for P10,

$\zeta = -9.4 \text{ mV}$ for P15 and $\zeta = -7.2 \text{ mV}$ for P20 at pH 10. It clearly shows that how PVAmHCl can enhance the adsorption of reactive dyes on modal fabric. Apart from the ζ -potential at pH 10, it is necessary to know the impact of Iso electric point (IEP) and Point of zero charge (PZC) on dyeing, because both are directly influenced on the dyeing process. The results of Iso electric point (IEP) and Point of zero charge (PZC) are shown in the Table 4 and Figure 3, results indicates that there is no IEP for untreated (CW) sample, because the ζ -potential for untreated sample have only negative values in the whole pH range. An IEP for modified modal samples moved towards the higher pH values when the concentration of PVAmHCl is increased, the range lies between 5.4 to 6.7. The point of zero-charge (PZC) was determined in the pH 10, because the fixation of reactive dyes can occur in this pH and also the ζ -potential can become higher and reaching the constant value. Results shows that PZC values are highest in the case of untreated samples (CW=69.76), and it decreases with increasing the concentration of PVAmHCl, for pre-treated samples having the PZC of 62.54 (P2.5) to 43.41 (P20), it seems that PVAmHCl have significant relationship with point of zero charge. The specific amount of surface charge can be determined with the help of back titration. The values were shown in the table and it concludes, the untreated fabric shows the negative values due to the higher negative surface charge. However, PVAmHCl pretreated samples were showing negative values in $q = -1.0210, -0.8754$ in case of P2.5 and P5 respectively. It seems that ionic modification for these (P2.5 and P5) samples have less as compared to higher concentrations of PVAmHCl. So the modified fabrics have

Sample	ζ at pH 10 (mV)	IEP (at pH)	PZC ($\mu\text{g/mL}$)	q (C/g)
CW	-20.4	-	69.76	-2.3472
P2.5	-14.7	5.4	62.57	-1.0210
P5.0	-12.3	6.1	57.43	-0.8754
P10.0	-11.6	6.3	53.94	0.1220
P15.0	-10.8	6.4	49.77	0.4527
P20.0	-10.2	6.7	43.41	0.9456

Table 4: ζ -potential for the control and treated samples.

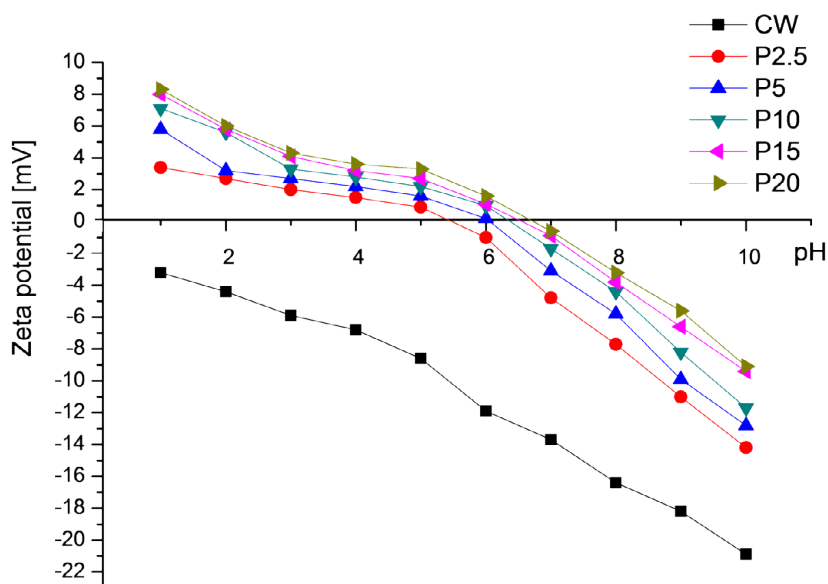


Figure 3: Zeta potential for modified and unmodified modal fabric with different concentration of PVAmHCl with respect to pH of electrolyte 0.001 M KCl.

significantly positive charge and therefore respective samples having good adsorption towards anionic dyestuffs without using of electrolyte (common salt) as well as surfactants.

The effect of PVAmHCl pretreatment on the dyeing performance

To determine whether the PVAmHCl modified modal fabrics would have enhanced dyeability with reactive dyes, the untreated modal fabric and PVAmHCl modified modal fabrics were dyed subsequently with six different reactive dyes for the concentration of 1% (o.w.f), the dyeing carried out with and without electrolyte, but in the presence of alkali, dyeing results are listed in Table 5. The results showed that all six dyes were given color strength (K/S) values for the PVAmHCl pretreated modal fabric was giving much higher value than the untreated samples. For untreated modal fabrics with salt (CS) shows higher K/S values (lowest K/S=2.5 and highest K/S=4.1 values are achieved) than the untreated modal fabric without salt (CW). In the case of untreated modal fabric without salt (CW) shows very low K/S values ((lowest K/S=0.7 and highest K/S=1.4 values are achieved). From the result, the K/S values for the treated modal fabric shows twice than the untreated samples. The K/S values were increased with the increasing concentration of PVAmHCl, but it started to reduce at 15 g/L and above the concentration of PVAmHCl. The decrease in color strength value may be due to, when excess of PVAmHCl was padded on the fabric, the bonding between the fiber and some cationic polymer become weak, and repulsion force also existed within the cationic sites of PVAmHCl. This would lead to presence of unbound polymer in the dye bath, thereby hindering the absorption of dye and possibly causing it to flocculate.

Low color strength values of the both untreated samples (CW and CS) are due to the negative zeta potential for the dyes and fiber and resulting the maximum dyes were never exhausted. However, unexhausted dyes go to pollution treatment plant and it also creates many issues while removing the color. It clearly shows that the importance of electrolyte in dye exhaustion and followed by color strength. Above observations indicate that the pretreatment of modal fabric increases dye uptake. This confirms the effectiveness of

pretreatment in enabling the fabric to be dyed without salt. It is also observed that there is a statistical significant difference in color strength of both dyes of which poly-functional reactive dyes has higher values than bi-functional reactive dyes. As compared to bi-functional reactive dyes, polyfunctional reactive dyes, having many advantages like higher color strength, good exhaustion as well as fixation.

It can be seen from Table 5 that dye reactivity on pretreated fabric was greater, due to presence of primary amino groups provided by the PVAmHCl, this is due to the maximum cationic sites on the surface of modified modal fabrics. However, the exhaustion values (%) may vary from dye to dye and concentration of PVAmHCl (highest exhaustion found 96% for Reactive Blue 281, similarly the lowest exhaustion was found in 88.5% in Reactive Red 238). Exhaustion values of C.I. Reactive blue 268 with respect to CS and CW shows 81%, 1168% less values than treated modal fabric. Generally, the treated fabrics have positive zeta potential at lower pH and it initiates the strong attraction between the anionic dyes on the cationic sites of modified modal fabric and the anionic dyes (reactive dyes) are highly exhausted without the presence of electrolyte in the dyebath. The results for color intensity on modified modal fabric show higher values than the untreated samples. Increased color intensity values are due to the reduction of zeta potential in the dye bath at lower pH.

The effect of PVAmHCl pretreatment on total dissolved solids

The presence of total dissolved solids (TDS) in water makes high hardness which disturbs the osmotic balance of native species. Disposal of the salt laden effluents into ground and surface water bodies cause pollution and render them unfit for any purpose namely agriculture, domestic. The quality of irrigation water mainly depends on its salt content and the proportion of sodium to other ions. Sodium chloride corrodes steel and sodium sulfate corrodes concrete. So it is necessary to determine the TDS values of the polluted water. The TDS was measured from the first rinse of the exhausted dye bath. The TDS (mg/L) values for the dyeing of modified and untreated modal fabrics are presented in Table 6. The results show that the TDS of the effluent obtained from the dyeing of PVAmHCl pretreated samples shows less compared to untreated samples. This is due to a PVAmHCl pre-

Dye (1% o.w.f)	Sample	E (%)	F (%)	T (%)	(K/S)	I (%)
Reactive Blue 268	CS	51.8	82.1	42.5	2.8	-
	CW	7.3	90.9	6.7	0.8	-
	P2.5	88.9	90.6	80.5	3.2	14
	P5.0	92.6	92.1	85.3	3.8	36
	P10.0	92.6	95.1	88.0	4.1	46
	P15.0	90.6	95.0	86.1	4	43
	P20.0	91.6	94.9	86.9	3.9	39
Reactive Red 238	CS	54.1	88.0	47.6	2.5	-
	CW	11.2	87.5	9.8	0.8	-
	P2.5	88.5	96.7	85.5	6	140
	P5.0	89.6	96.8	86.7	6.2	148
	P10.0	92.1	95.5	87.9	6.6	164
	P15.0	93.2	96.2	89.7	6.6	164
	P20.0	90.8	97.3	88.4	6.4	156
Reactive Yellow 206	CS	47.4	83.9	39.8	3.1	-
	CW	11.2	80.0	8.9	1.1	-
	P2.5	89.6	85.1	76.3	4.7	52
	P5.0	94.5	88.0	83.2	5	61
	P10.0	95.9	92.5	88.7	5.3	71
	P15.0	93.2	93.7	87.3	5.2	68
	P20.0	90.8	91.9	83.4	5.4	74
Reactive Blue 281	CS	61.3	87.9	53.9	3.3	-
	CW	19.4	85.7	16.6	1.4	-
	P2.5	88.9	93.2	82.8	5.9	79
	P5.0	92.9	92.2	85.6	6.4	94
	P10.0	96.0	96.2	92.3	7.8	136
	P15.0	93.9	94.9	89.1	7.8	136
	P20.0	93.4	94.7	88.5	7.6	130
Reactive Red 286	CS	62.2	87.8	54.7	4.1	-
	CW	21.0	75.0	15.8	1.2	-
	P2.5	89.8	92.1	82.8	7.6	85
	P5.0	91.6	90.2	82.7	8.2	100
	P10.0	95.1	90.8	86.4	8.7	112
	P15.0	93.3	91.0	84.9	8.9	117
	P20.0	92.9	92.0	85.5	8.8	115
Reactive Yellow 217	CS	63.4	91.3	57.9	2.3	-
	CW	20.5	85.7	17.6	0.7	-
	P2.5	89.6	93.2	83.5	5.9	157
	P5.0	92.4	93.7	86.5	6.3	174
	P10.0	95.4	93.8	89.4	6.4	178
	P15.0	92.2	92.4	85.3	6.6	187
	P20.0	91.3	88.7	81.0	6.2	170

Table 5: Color strength value of control and treated samples.

treated modal fabric does not require any electrolyte for exhaustion of reactive dyes. Utilization of electrolyte in the dyeing may increase the TDS values and it shows (for CS) 18550 mg/L, whereas the PVAmHCl treated sample shows the range of 6400 to 6980 mg/L. It is nothing but, approximately 3 times less TDS value as compared to the untreated and dyed (CS) sample. The fabrics with the lowest percentage of PVAmHCl pre-treatment have slightly lower the TDS values than the fabrics with the highest percentage of pre-treatment. This may be some complex interaction between dyes and the pre-treatment chemicals which, is outside the scope of this study. The higher TDS values (CS=18550 mg/L) are necessary to reduce and it requires many ETP processes which increase the overall process cost (power cost, energy cost, manpower and etc), whereas PVAmHCl pre-treated sample does not requires as much.

The effect of PVAmHCl pretreatment on water retention values

The water retention value (WRV) is an important parameter for the fibers, due to many of the chemical processing such as dyeing and finishing were done by using water or liquids as a medium. Wetting, repulsion and transportation is a complex phenomena which depend on many parameters, namely, fiber surface morphology, functional groups or chemical composition of the fiber and structure of the fiber porous can decide the hydrophilic or hydrophobic characteristics of the fiber. Functional groups or chemical composition is one of the parameters which decide the hydrophilic characteristics of modal fabrics, it is necessary to determine the WRV for PVAmHCl pre-treated fabrics. The WRV results were shown in the Figure 4, which clearly explain the WRV values for treated and untreated samples. The overall WRV has been decreased for the pre-treated samples as compared to untreated samples; this is due to, while treatment with PVAmHCl were blocking the hydroxyl groups of cellulose and probably the pore structure of the fabric was slightly changed which resulting decrease the WRV. But this change is very small (maximum 10%) and it never affects the dyeing or finishing process.

The effect of PVAmHCl pretreatment on colorfastness properties

While usage of dyed or printed fabrics was frequently subjected to various conditions such as washing, rubbing, light radiation and perspiration. It is necessary the respective dyestuff has to withstand with respective conditions, which generally called as good fastness property. Related to this research, it is mandatory to determine the impact of pre-treatment on the dye fastness properties with respect to washing, rubbing and light are summarized in Table 7. In overall, pre-treated fabrics showing excellent results as compared to conventional dyed and without salt (CW), whereas it shows almost the same results to the sample which dyed conventional with salt (CS). Generally, (CW) dyed fabric without salt shows poor to moderate (rating 1-2) in some dyes; it is because of the poor exhaustion and followed by fixation of reactive dyes. In particularly, the washing fastness for pre-treated and dyed with poly-functional reactive dyed modal fabrics against staining of its adjacent fabrics (wool and cotton) was excellent in few cases (5), and the color change was also in the acceptable range which is (2-3). It seems that the results of washing fastness are excellent for the salt free dyeing and it is due to the effectiveness of dye fixing due to the pretreatment with PVAmHCl. Regarding to the rubbing fastness, dry rubbing results for the majority of the cases are showing 4 which namely called as a good fastness property. In case of wet rubbing the results were showing (3-4) which is called average and it is due to the residual unfixed dyes on the surface of the fabric even after soaping process. Owing to the solubility of reactive dyes the unfixed and the surface dyes will dissolve in water during wet rubbing and get transferred to the crocking cloth. As seen in the Table 7, the ratings for color fastness to light in terms of the degree of color change and color staining were good to very good (rating 5). The results for the perspiration fastness under acidic and alkaline conditions were shown in the Table 8. There is no obvious improvement in perspiration fastness properties in most cases with, related to the concentration of pre-treatment. The result of the color change is showing (2-3) under acidic and alkaline conditions, it seems, dyed fabric have sensitive towards pH, and there is no significant difference between pre-treatment and perspiration fastness. However, the staining towards to the acidic conditions is (4-5), whereas in alkali conditions, it shows (3-4) similarly the result for (CW) dyed in conventional method without salt shows moderate to good (rating 3

Dye (1% o.w.f)	Sample	TDS (mg/L)
Reactive Blue 268	CS	18550
	P2.5	6400
	P5.0	6550
	P10.0	6800
	P15.0	6900
	P20.0	6980

Table 6: TDS value of control and treated samples.

Dyes	Sample	Wash fastness			Rubbing fastness		Light fastness
		Evaluation of color change	Evaluation of staining		Evaluation of staining		
			Cotton	Wool	Dry	Wet	
Reactive Blue 268	CS	3	4-5	4-5	4	3-4	3
	CW	2-3	2	2	1-2	1-2	2
	P2.5	2-3	4	4	4	4	5
	P5.0	2-3	4	4	4	4	5
	P10.0	2-3	4-5	4-5	4	4	5
	P15.0	2-3	4-5	4-5	3-4	3-4	5
	P20.0	2-3	4-5	4-5	3-4	3-4	4
Reactive Red 238	CS	2-3	4-5	4-5	4	3-4	3
	CW	2-3	2	2	1-2	1-2	2
	P2.5	2-3	4-5	4-5	3-4	3-4	5
	P5.0	2-3	4-5	4-5	3-4	3-4	4
	P10.0	2-3	4-5	4-5	3-4	3-4	4
	P15.0	2-3	4-5	4-5	3-4	3-4	4
	P20.0	2-3	4-5	4-5	3-4	3-4	4
Reactive Yellow 206	CS	3	4-5	4-5	4	3-4	4
	CW	2-3	2	2	1-2	1-2	3
	P2.5	2-3	4-5	4-5	4	4	5
	P5.0	2-3	4-5	4-5	4	4	5
	P10.0	2-3	4-5	4-5	4	4	5
	P15.0	2-3	4-5	4-5	3-4	3-4	5
	P20.0	2-3	4-5	4-5	3-4	3-4	4
Reactive Blue 281	CS	2-3	4-5	4-5	4	3-4	3
	CW	2-3	2	2	1-2	1-2	2
	P2.5	2-3	4-5	4-5	4	4	5
	P5.0	2-3	5	4-5	4	4	5
	P10.0	2-3	5	4-5	4	4	5
	P15.0	2-3	5	5	4	4	5
	P20.0	2-3	5	5	4	4	4
Reactive Red 286	CS	2-3	4-5	4-5	4	4	3
	CW	1-2	2	2	2	2	2
	P2.5	2-3	4-5	4-5	3-4	4	4
	P5.0	2-3	5	5	4	4	4
	P10.0	2-3	5	5	4	4	4
	P15.0	2-3	5	5	4	4	4
	P20.0	2-3	5	4-5	4	3-4	4
Reactive Yellow 217	CS	3	4-5	4-5	4	3-4	4
	CW	1-2	2	2	1-2	1-2	3
	P2.5	2-3	5	5	4	4	5
	P5.0	2-3	4-5	4-5	4	4	5
	P10.0	2-3	5	5	4	4	5
	P15.0	2-3	5	5	4	4	5
	P20.0	2-3	5	4-5	4	3-4	5

Table 7: Wash, Rubbing and Light fastness for control and treated samples.

Dyes	Sample	Perspiration fastness					
		Evaluation of color change		Evaluation of staining			
		Acidic	Alkaline	Acidic		Alkaline	
wool	cotton			wool	cotton		
Reactive Blue 268	CS	2-3	2-3	4-5	4-5	4-5	2-3
	CW	2-3	2-3	4	4	4	3
	P2.5	2-3	2-3	4-5	4-5	4-5	3-4
	P5.0	2-3	2-3	4-5	4-5	4-5	3-4
	P10.0	2-3	2-3	4-5	4-5	4-5	3
	P20.0	2-3	2-3	4-5	4-5	4-5	3
Reactive Red 238	CS	2-3	2-3	4	4	3-4	3-4
	CW	2-3	2-3	4-5	4	3-4	3
	P2.5	2-3	2-3	4-5	4	4-5	3-4
	P5.0	2-3	2-3	4-5	4	4-5	3-4
	P10.0	2-3	2-3	4-5	4	4-5	3-4
	P20.0	2-3	2-3	4-5	4	4-5	3-4
Reactive Yellow 206	CS	2-3	2-3	4-5	4-5	4-5	3-4
	CW	2-3	2-3	4-5	4-5	4	3
	P2.5	2-3	2-3	4-5	4-5	4-5	3-4
	P5.0	2-3	2-3	4-5	4-5	4-5	3-4
	P10.0	2-3	2-3	4-5	4-5	4-5	3-4
	P20.0	2-3	2-3	4-5	4-5	4-5	3-4
Reactive Blue 281	CS	2-3	2-3	4-5	4-5	4-5	3-4
	CW	2-3	2-3	4-5	4-5	4-5	3-4
	P2.5	2-3	2-3	4-5	4-5	4-5	3-4
	P5.0	2-3	2-3	4-5	4-5	4-5	3-4
	P10.0	2-3	2-3	4-5	4-5	4-5	3-4
	P20.0	2-3	2-3	4-5	4-5	4	3
Reactive Red 286	CS	2-3	2-3	4-5	4-5	4-5	3-4
	CW	2-3	2-3	4-5	4-5	4-5	3-4
	P2.5	2-3	2-3	4-5	4-5	4-5	3-4
	P5.0	2-3	2-3	4-5	4-5	4-5	3-4
	P10.0	2-3	2-3	4-5	4-5	4-5	3-4
	P20.0	2-3	2-3	4-5	4-5	4-5	3
Reactive Yellow 217	CS	2-3	2-3	4-5	4-5	4-5	3-4
	CW	2-3	2-3	4-5	4-5	4-5	3-4
	P2.5	2-3	2-3	4-5	4-5	4-5	3-4
	P5.0	2-3	2-3	4-5	4-5	4-5	3-4
	P10.0	2-3	2-3	4-5	4-5	4-5	3-4
	P20.0	2-3	2-3	4-5	4-5	4-5	3

Table 8: Perspiration fastness for control and treated samples.

and 2-3). It is due to the stability of the bonds leads to alkali hydrolysis. The results for perspiration fastness were observed quite similar for all six kinds of reactive dyed fabric. Hence there is no impact on the pre-treatment.

The effect of PVAmHCl pretreatment on mechanical properties

The results of various physical properties of pre-treated samples were summarized in the Table 9. The crease recovery behavior of

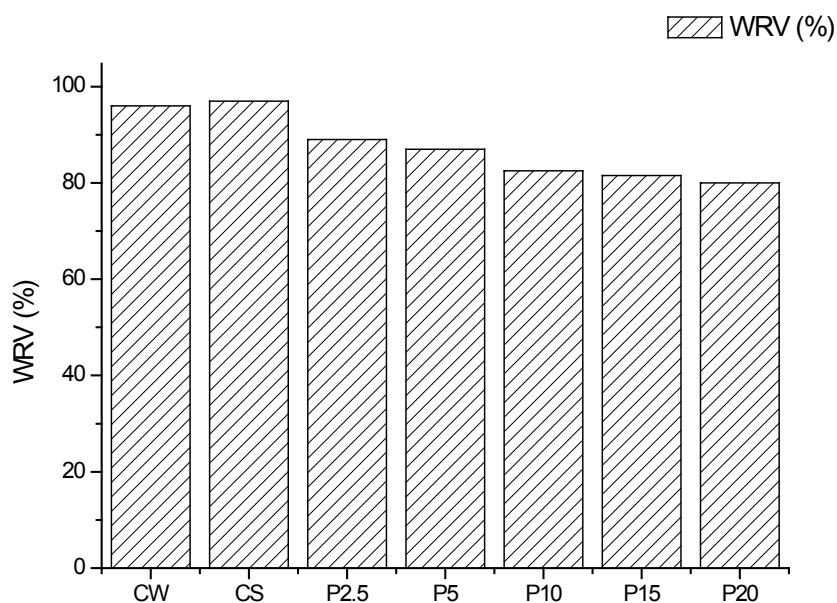


Figure 4: Water retention values (WRV) for control and PVAmHCl treated modal fabrics.

Sample	Tensile Strength				Flexural Rigidity mg.cm		CRA degrees
	Warp way		Weft way		Warp way	Weft way	
	Values, lbs	Loss, %	Values, lbs	Loss, %			
Raw fabric	75	--	60	--	108.5	87.2	132
CS	73	3	59	2	109.2	87.8	135
CW	72.5	3	59	2	109.5	88.1	134
P2.5	70	7	55	8	110	89.8	141
P5.0	69	8	54	10	111.4	91	148
P10.0	68	9	52	13	112.8	91.2	156
P15.0	66	12	51	15	114.3	95	155
P20.0	66	12	50	17	117.5	96.9	156

Table 9: Physical properties of control and treated samples.

all the PVAmHCl pre-treated samples were observed to be good, Crease recovery angle (CRA) has been increased with increasing the concentration of PVAmHCl. Maximum CRA was obtained for (P20) have 156 degrees; whereas raw fabric has 132 degrees only. Increasing the CRA is due to cross-linking of PVAmHCl between the cellulose molecules. These cross-links hinder the molecular and fibrillar slippage and stabilize the structure, thereby increasing the crease recovery angle. The effect of cross linking of PVAmHCl with cellulose generally results in excellent crease recovery behavior, but at the same time the strength loss also associated. The tenacity of pre-treated fabric is decreased with concentration of PVAmHCl is increased; the tenacity decreased 12% and 17% for warp way and weft way respectively at the 20 g/L concentrations of PVAmHCl (P20); it seems that the tenacity is directionally proportional to the PVAmHCl concentrations, it is due to the formation of intermolecular an intermolecular crosslinks reduce the possibilities of equalizing the stress distribution, it ceased to reduce the capacity to withstand towards the load. Generally Flexural rigidity is nothing but resistance to flexibility, flexural rigidity has increased in the range of 8% and 10% in war and weft ways. Increase in flexural rigidity shows that the fabric becomes slightly stiff because of cross linking of cellulose with PVAmHCl; it can be solved by adding a softener during the finishing treatment.

Conclusion

The main purpose of this work is to increase the dyeability of modified modal fabric with reactive dyes were carried out without utilization of electrolyte. Modification of modal fabric with different concentration of PVAmHCl which significantly decrease the negative surface of the pre-treated fabric, it has been confirmed during the zeta potential measurement. Generally the PVAmHCl can adsorb on the modal fiber surface and it increases the positive values of zeta potential. These results can lead good affinity towards to the reactive dyes (anionic) on modified fabric via good ionic interaction. All dyes have good exhaustion towards modifying fabrics, but out of that, polyfunctional reactive dyes have better exhaustion as compared to bi-functional reactive dyes, this is due to the number of reactive groups which help higher exhaustion. The color strength (K/S) values for the modified fabric gave better color strength than the comparable to dyeing without salt by conventional dyeing method (CS), almost the same results as compared to dyeing with salt by conventional dyeing method (CW). The water retention values (WRV) for the modified modal have gradually decreased when the concentration of PVAmHCl has been increased, this is because PVAmHCl can be blocked the hydroxyl groups which available on the surface of fabric, which lead to reduce the water retention capacity. After dyeing, modified modal fabric shows the very less total dissolved solids (TDS) values (approximately 4 times less than conventional dyed fabric with salt (CS), it seems, this method of dyeing can help to save environment from the pollution, as well as the saving the energy which can utilize for the pollution treatment plant. Wash, Rubbing, Light fastness of modified fabrics is showing approximately the same result like conventional dyed fabric with salt (CS). Fabric crease recovery and flexural rigidity increased because of the pretreatment. There is no change in the tensile strength of the fabric because of the pretreatment. Pretreatment with PVAmHCl on modal fabrics having the following advantages are observed.

- Elimination of salt as an electrolyte
- Maximum fixation of dye
- Improve the exhaustion and lead to reduce the hydrolysis of dye

- Significant saving in process cost (for after treatments and pollution treatments)
- Reduction of pollution load up to 80%.

It is considered that PVAmHCl is found to be effective for pretreatment in salt less dyeing of modal fabrics.

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