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Modification of cellulosic fabric using polyvinyl alcohol, part-II: Colorfastness properties

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ABSTRACT

A series of aqueous solutions of poly(vinyl alcohol) of various commercial products were prepared and applied onto the surfaces of cotton and blends of cotton/polyester fabrics. Fourier transform infrared spectrophotometer was used to confirm the molecular structure of the polyvinyl alcohol used. Performance tests such as colorfastness to rubbing (dry and wet) and colorfastness to washing were determined. The controlling variables affecting the performance properties of the finished substrate such as post-treatment with poly(vinyl alcohol) of various commercial trades, concentration and dilutions were studied. Crocking, washing and hue change of the treated dyed and printed fabrics is accompanied by the formation of semi-inter-penetrated network structure due to the presence of the hydroxyl (–OH) groups which make feasible to a number of grafting and physical cross linking reactions of polymer backbone.

1. Introduction

Polyvinyl alcohol (PVA) is colorless, flammable, odorless and tasteless, translucent, white granular material. It is water soluble, slightly soluble in ethanol, but insoluble in other organic solvents. It has a molecular weight of between 26,300 and 30,000 units and a degree of hydrolysis of 85.5–89% (Sexena, 2004; Ibrahim, Abo-Shosha, Elnagdy, & Gaffar, 2002; Ibrahim, El-Salmawi, & Ibrahim, 2005). The ability of this polymer makes it easily available for numerous applications, such as paper, wood, leather and textile industries, cosmetics, and an important ingredient in agri-products. With respect to biological applications, PVA has been found to be non-immunogenic, i.e. not involving antibody creation, non-mutagenic and non-carcinogenic for human beings. Thus, PVA can be considered as highly efficient polymer in the field of biotechnology (Burkinshaw & Kumar, 2008a, 2008b; Pourciel et al., 2003). Polyvinyl alcohol has been widely used in high tonnage for textile sizing and finishing agent, emulsifier, coating, and adhesive for paper, wood and leather. It has also been used as sizing material for polyester and its blend with cotton and viscose. Due to small, dense and closely packed monoclinic crystallite, PVA films possess tremendous gas barrier properties. Unlike other barrier polymer in the film, PVA exhibits flexibility, transparency, and lower cost (Burkinshaw & Kumar, 2010; Jang & Lee, 2003).

Polyvinyl alcohol is found in several grades, differing in molecular weight and solution viscosity. Polyvinyl alcohol is manufactured by hydrolyzing polyvinyl acetate. The reason is because vinyl alcohol does not exist as a monomer, tautomerization favors the more stable acetaldehyde. Polyvinyl acetate, however, can be hydrolyzed into polyvinyl alcohol under acidic or basic conditions (Zhang, Yang, Wang, & Chen, 2008; Zhang et al., 2011).

Water solubility, solution viscosity and film properties are influenced by the molecular weight and degree of hydrolysis. Fully hydrolyzed (99%) polyvinyl alcohol (PVA) makes strong hydrogen bonding with neighboring chains. Being linear, the chains can align themselves to form a tightly packed array (Zhang et al., 2008; DeMerlis & Schoneker, 2003). Polyvinyl alcohol has been widely used as sizing agents both in warp sizing and adhesive for making nonwoven fabrics. Warp sizing practices demonstrate that while PVA is used as sizing agents, many difficulties in warp sizing operation can be rectified since PVA was introduced as warp sizes in the textile industry. It is worthwhile mentioning that sufficient adhesion to fibers is one of the essential demands for a sizing agent used in warp sizing as well as for an adhesive used in manufacturing of non-woven fabrics (Wang, Yang, Liu, Fu, & Xue, 2009; Zhang et al., 2006). Polyvinyl alcohol (PVA) has multiple applications, such as sizing process of the textile industry and paper coating due to its high tensile strength, better flexibility, high thermal and chemical

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Table 1
Fabrics specification with quality and processed applications.

S. no.	Quality	Construction/count	Blend ratio cotton/polyester	Processed/application
01	Dyed cotton	(100 × 80/40 × 40)	100% cotton	Reactive dyed
02	Printed cotton	(100 × 80/40 × 40)	100% cotton	Pigments printed
03	White bleached cotton	(100 × 80/40 × 40)	100% cotton	O.B. applied[a]
04	White bleached polyester/cotton	(100 × 80/40 × 40)	50/50	O.B. applied
05	White bleached Denier	(76 × 44/30 × 150)	15/85	O.B. applied

[a] Optical brightener.

stability, water soluble and the good film forming ability. Size is normally removed before dyeing and finishing steps in preparation of textile products (Seoudia, Mongyb, & Shabaka, 2008).

It is evident that aftertreatment is normally required to improve the fastness to washing of both acid dyes on nylon and direct dyes on cellulosic fibers if the sample does not come up to the mark. The particular after-treatments employed are similar in that each involves the formation of a large molecular size, low water-solubility complex within the dyed substrate. However, the types of aftertreatment are dye–fiber specific and, therefore, are not interchangeable insofar as an anionic system is used for acid dyes on nylon (Burkinshaw, 1995) while a cationic system (using either a reactive or non-reactive cationic fixing agent) is employed in the case of direct dyes on cellulosic fibers. It was decided to investigate whether an aftertreatment with PVA, which had proven effective in improving the washing fastness of acid dyes on nylon (Burkinshaw & Kumar, 2008a, 2008b), might also enhance the fastness to washing of direct dyes on cotton. In this report the use of PVA in conjunction with an organic titanate, $MgSO_4$ and three protease enzymes, as an aftertreatment of direct dyes on cotton has been well described.

Studies have been made to explore the applications of polyvinyl alcohol as sizing material in textile (Seoudia et al., 2008; Zhang et al., 2006), as coating material for paper, (Pourciel et al., 2003) etc. Very limited literature is available reporting the use of PVA as finishing agents in textile processing. Due to the dearth of report on the application of PVA studying colorfastness properties the present work is planned to study the comparative effect of amount of commercial products of PVA on these properties. In this research solutions of different strength of polyvinyl alcohol were prepared (Zia et al., 2011) by taking three different commercial grades of PVA and applied onto the cellulosic fabrics using pad dry cure method (Zia et al., 2011). The effects of the process parameters were systematically investigated. These parameters include grades and concentration of the polyvinyl alcohol applied onto the fabrics, tone change of the treated dyed and printed fabrics. The treated fabrics were monitored for colorfastness to washing and rubbing, and yellowing on the white fabrics.

2. Experimental

2.1. Materials

2.1.1. Cotton fabric

Mill desized, scoured, bleached, and mercerized (in case of dyed shade) white, dyed and printed, and plain weaved five different fabrics were supplied by Arzoo Textiles Mills Ltd., Khurrianwala, Faisalabad, Pakistan. The characteristics i.e., quality of the fabrics, construction, count, blend ratio, etc., are presented in Table 1. The fabric samples were further decontaminated in the laboratory by washing at 100 °C for 60 min using a solution containing 2 g/L, Na_2CO_3 and 1 g/L, polyoxyethylene glycol octylphenol ethers: $C_8H_{17}–(C_6H_4)–(O–C_2H_4)_{1–25}–OH$: (Triton X-100) a non-ionic surfactant (BASF). The fabric was then washed several times with boiling water then with cold water and finally dried at ambient conditions.

2.1.2. Chemicals

Sodium hydroxide, acetic acid, hydrochloric acid, sodium carbonate, formalin and sodium bicarbonate were of laboratory grade chemicals. Polyvinyl alcohol was procured from Prime Chemicals, Karachi, Pakistan and Sinochem Nanjing Co., Mainland, China. The details regarding sample codes and formulation of the PVA along with suppliers are mentioned in Table 2.

2.2. Preparation of polyvinyl alcohol solution

Six polyvinyl alcohol samples (PVA-1 to PVA-6) were prepared through dilution method following the method reported elsewhere (Zia et al., 2011) with different percentages (e.g., 10%, 13%) using three commercial products of polyvinyl alcohol (Table 2).

2.3. Treatment of cotton and blends of cotton/polyester fabric with PVA

Various dilutions of polyvinyl alcohol, i.e., 25 g/L, 30 g/L and 35 g/L were applied onto the cotton and blends of cotton/polyester fabric. Treatment of cotton and blends of cotton/polyester fabric with polyvinyl alcohol was carried out using pad-dry-cure technique. The fabric samples were treated with various dilutions (i.e., 25 g/L, 30 g/L and 35 g/L each) from stock solutions of polyvinyl alcohol (10% or 13%). After applications, the sample was dried at 100 °C for 4 min. The curing was done at 140 °C (only printed fabrics) and at 180 °C (all other samples) for 5 min.

2.4. Calendaring

Calendaring is a finishing procedure used to generate a shine and better look onto the fabric. In this process the fabric is run through rollers at different applied temperatures and pressure that polish the surface and make the fabric smoother and more lustrous. Fabrics that go through the calendaring process feel thin, glossy and shiny. All the cured fabrics swatches were calendared by this process and then preceded for testing and analysis.

2.5. Analysis and testing

Molecular structure of the used PVA was confirmed using Fourier transform infrared (FT-IR) spectroscopy. Although it is not necessary to confirm the structure of the PVA as nothing has been mixed up with the PVA in the lab. However, FT-IR spectrum of the PVA was taken to confirm that the sample was highly pure. FT-IR spectrum of the PVA samples was obtained in the transmittance mode using a Fourier transform infrared (FT-IR) spectrometer (Model NICOLET 6700; Thermoscientific, USA) at QAU, Islamabad. FT-IR scans were collected on completely dried thin films cast on KBr discs from N,N′-dimethylformamide (DMF) solution. The spectra covered the infrared region 4000–500 cm^{-1}, the number

Table 2
Sample code designation and various formulation of polyvinyl alcohol.

S. No	Sample code	Distilled water (g)	Polyvinyl alcohol (quantity in grams)	Formalin	Polyvinyl alcohol supplier
01	PVA-1	90	PVA 217-PK (10 g)[a]	2–3 drops	Prime Chemicals, Karachi, Pakistan
02	PVA-2	87	PVA 217-PK (13 g)	2–3 drops	Prime Chemicals, Karachi, Pakistan
03	PVA-3	90	PVA BP-26 (10 g)	2–3 drops	Prime Chemicals, Karachi, Pakistan
04	PVA-4	87	PVA BP-26 (13 g)	2–3 drops	Prime Chemicals, Karachi, Pakistan
05	PVA-5	90	PVA 2488 (10 g)	2–3 drops	Sinochem Nanjing Co., Mainland, China
06	PVA-6	87	PVA 2488 (13 g)	2–3 drops	Sinochem Nanjing Co., Mainland, China

[a] Polyvinyl alcohol.

of scans per experiment was 16 and resolution was 4 cm^{-1}. Solid contents of the prepared sample were determined by Refractrometer (Atago). The fabrics after application of PVA were evaluated applying different colorfastness tests, i.e., colorfastness to washing (Society of Dyers and Colorist (SDC), 1990; ISO CO3) and colorfastness to rubbing (SDC, ISO X12). The effect of application of different grades and concentrations of PVA on the shade of different dyed and printed fabrics, and yellowing effect on the white fabrics was evaluated visually by following the standard test methods (AATCC, 1968, 1990, 2000; ASTM, 1995; Cote, 2002).

3. Results and discussion

In this study two stock solutions of each polyvinyl alcohol commercial grades in three dilutions have been applied on different processed fabrics (Table 1). The results of different analytical tests performed on the treated and untreated fabrics are as under:

3.1. FT-IR studies of polyvinyl alcohol

FT-IR spectrum of polyvinyl alcohol (PVA) (Fig. 1) showed very strong and broad peak at 3315.1 cm^{-1} attributed to the hydroxyl (–OH) group (pendant on the alternate carbon atom of the backbone) and at 2906.8 cm^{-1}, which is due to the CH_2 asymmetric stretching. The other sharp peaks appeared at 1732.3 cm^{-1} which is due to ester functional group of unhydrolyzed polyvinyl acetate repeat unit and peak at 1423.4 cm^{-1} due to C–OH stretching. The FT-IR spectrum support that the PVA understudy has been prepared by hydrolyzing the polyvinyl acetate and there is some un-hydrolyzed ester group remained.

3.2. Colorfastness to rubbing and washing

Colorfastness is the resistance of the color to one of the number of parameters, which may effect the certified dry and wet performance tests. The former include wet process such as washing test and later indicate the parched (dry) treatment, i.e., rubbing fastness test. In the presence of soap solutions of various degree of alkalinity there are many factors, which determine the fastness to washing; these include the solubility and the rate of stripping off the dye from the fiber. The results of colorfastness to rubbing (dry and wet) and washing are presented in Tables 3 and 4, respectively.

It is clear from the results (Table 3) that the dyed fabric treated with samples PVA-3 and PVA-4 has shown some better resistance to crocking. However, the samples treated with PVA-1, PVA-2, PVA-5 and PVA-6 has shown some comparable results against crocking fastness. It is obvious from the results that rubbing fastness of all the treated dyed samples improved with the application of the prepared PVA samples. The improvement in the rubbing fastness may come jointly with a remarkable chemical versatility due to the presence of the hydroxyl (–OH) groups. The modification of secondary

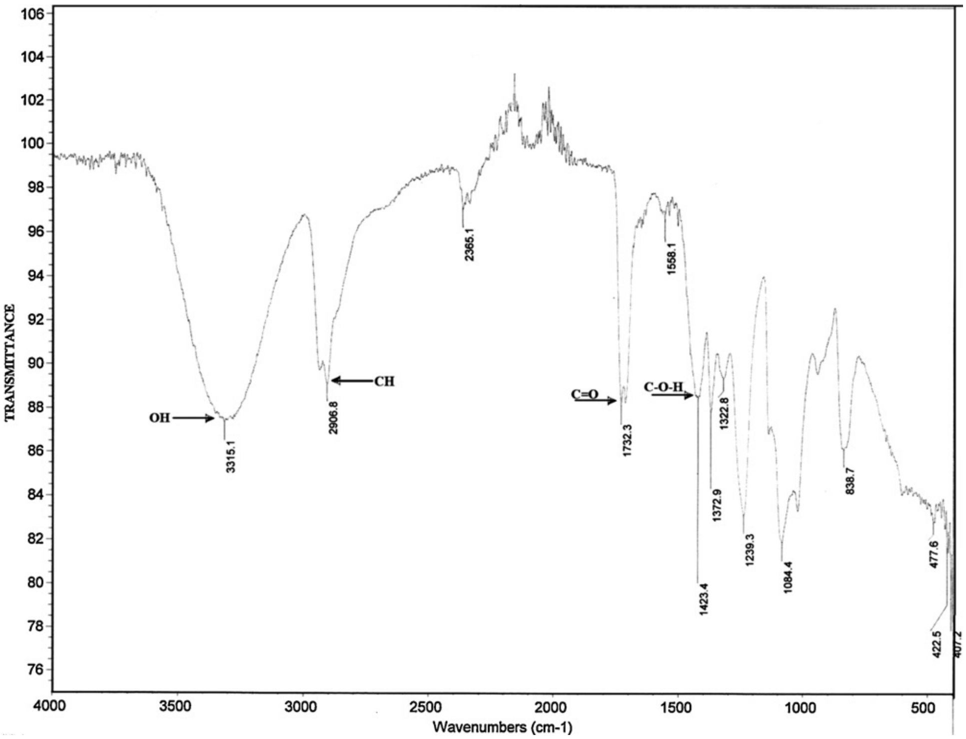

Fig. 1. FT-IR spectrum of poly(vinyl alcohol).

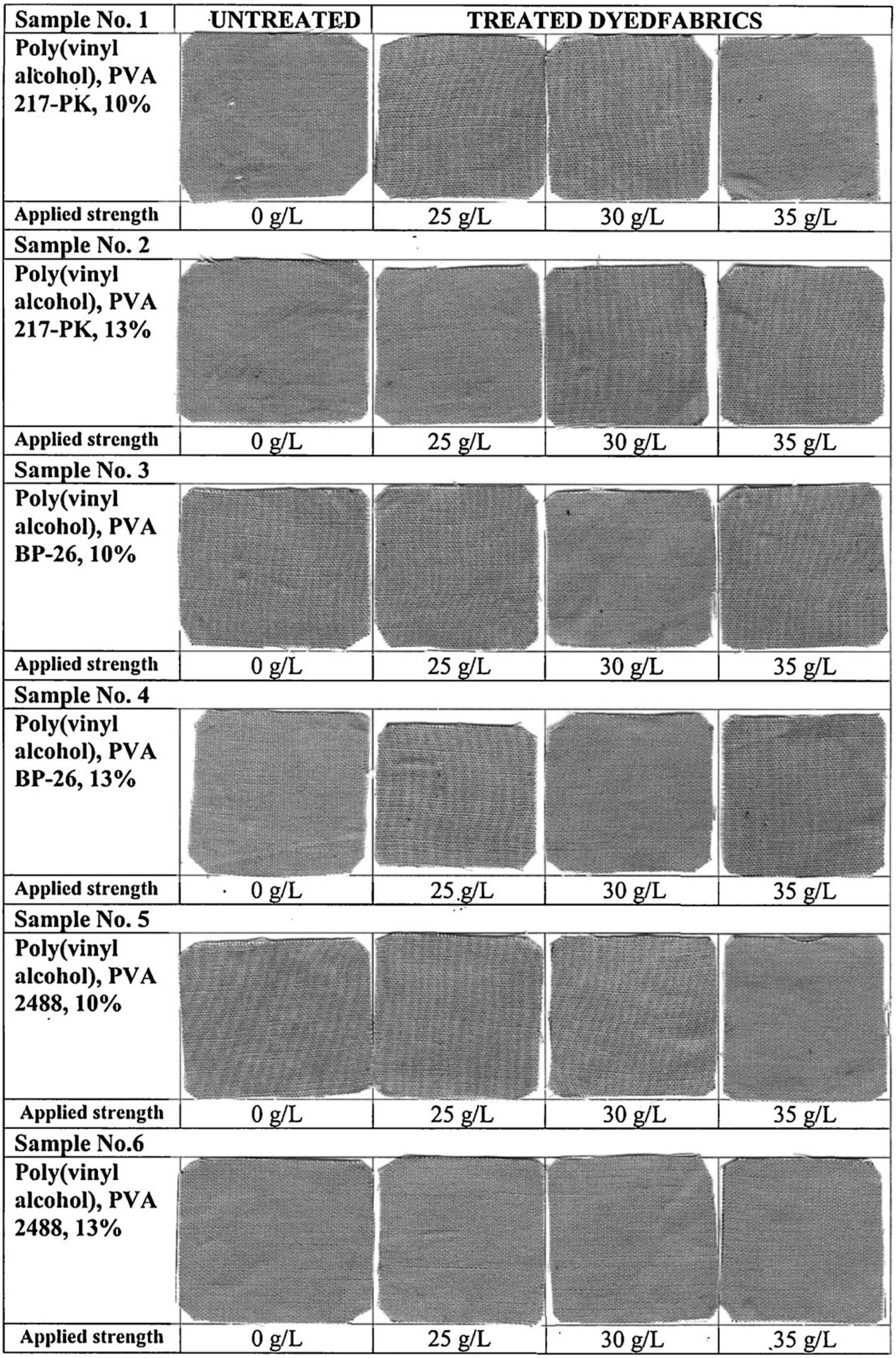

Fig. 2. Variation in the shade change of dyed fabrics after application of different concentration of prepared polyvinyl alcohol.

–OH group of polyvinyl alcohol has been reported in the literature to obtain material with new properties (Burkinshaw & Kumar, 2010; Zhang et al., 2011). However, PVA treated printed fabrics have shown reverse results as compared to the dyed treated fabrics and even untreated printed fabrics. It can be seen that all the treated printed samples have shown poor rubbing fastness as compared to the untreated printed samples (Table 3). This might be because of the presence of the binder layer on the printed surface for the

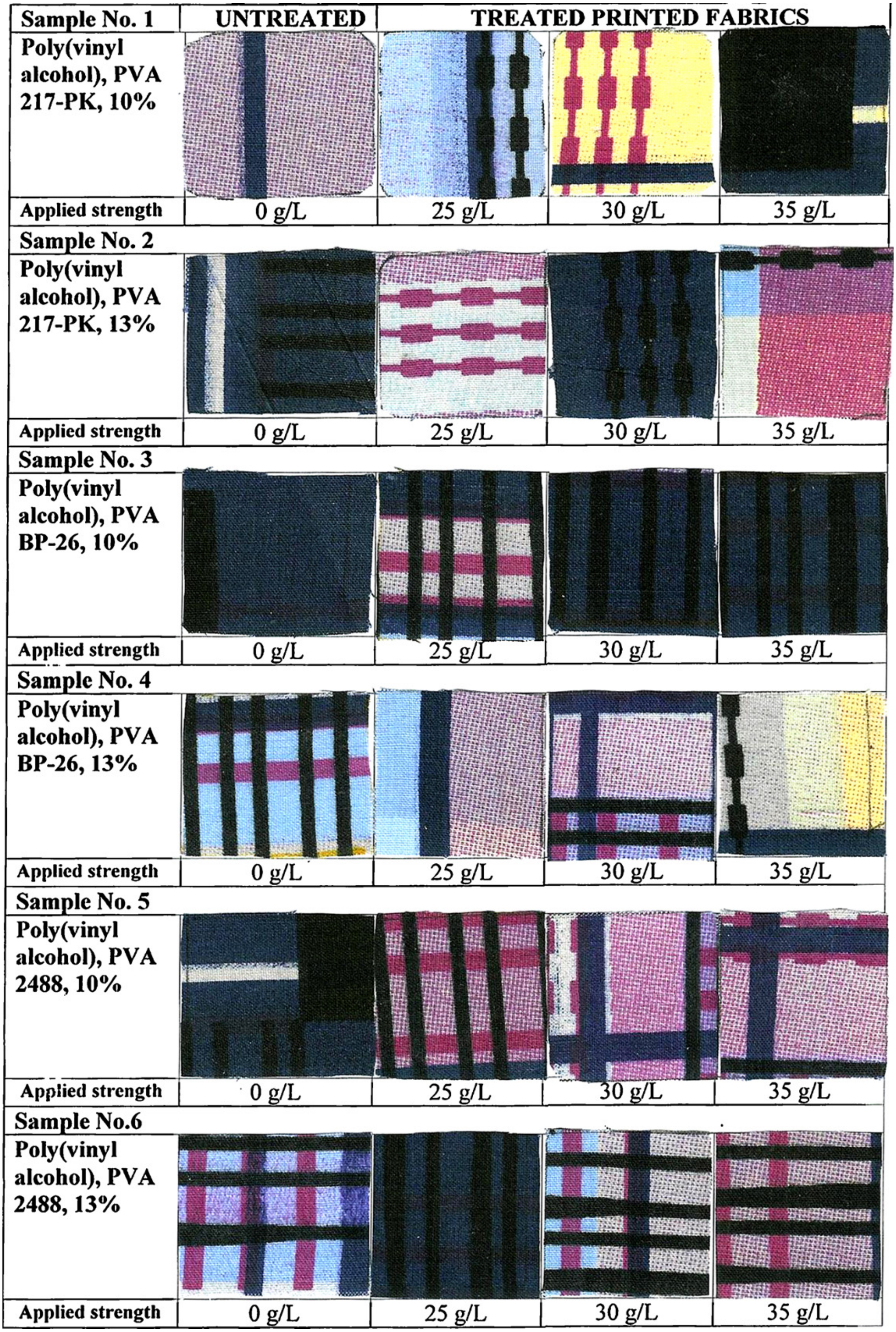

Fig. 3. Variation in the shade change of printed fabrics after application of different concentration of prepared polyvinyl alcohol.

retention of pigment particles. Due to the presence of this film the PVA molecules failed to get polymer interaction with hydroxyl group of the cellulose substrate. Moreover, the bundles of free hydroxyl group of the PVA make it more hydroscopic and keep the surface wet which ultimately may results in poor rubbing fastness. Further more the decrease in rubbing fastness of printed fabrics especially in wet rubbing is attributed to the swelling of acrylic binder in the presence of hydrophilic PVA coating.

Table 3
Colorfastness to rubbing of dyed and printed cotton fabric (ISO X12).

S. no	Strength of the applied PVA[a] sample (g/L)	Type of fabric	PVA-1		PVA-2		PVA-3		PVA-4		PVA-5		PVA-6	
			Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
1	25	Dyed[b]	4/5	3/4	4	3/4	4/5	4	4/5	4	4	4	4	4
2	30	Dyed	4	3/4	4	4	4/5	3/4	4/5	4	4/5	3/4	4	3/4
3	35	Dyed	4	3	4	3/4	4/5	4	4/5	4	4	3/4	4	4
4	25	Printed[c]	4	2	3/4	1/2	3/4	1/2	3/4	2/3	3/4	2	3/4	2
5	30	Printed	4	2	3/4	1/2	3/4	1/2	3/4	2	3/4	1/2	3/4	1/2
6	35	Printed	4	2	3/4	1/2	3/4	1/2	4	2	4	2	3/4	2/3

[a] Polyvinyl alcohol.

[b] Rubbing of untreated dyed fabric (dry, wet) (3/4, 2).

[c] Rubbing of untreated printed fabric (dry, wet) (4, 2/3).

Table 4
Colorfastness to washing on dyed and printed fabric (ISO CO3).

Sr. no.	Strength of solution applied (g/L)	Type of fabric	Polyvinyl acetate 28%		Polyvinyl acetate 30%		Polyvinyl acetate 36%		Polyvinyl acetate 38%		Polyvinyl acetate 48%		Polyvinyl acetate 50%	
			Washing	Staining	Washing	Staining	Washing	Staining	Washing	Staining	Washing	Staining	Washing	Staining
1	25	Dyed[a]	4	2/3	4	3	4	2/3	4	2/3	4	3	4	4
2	30	Dyed	4	2/3	4	2/3	4	4	4	2/3	4	3	4	2/3
3	35	Dyed	4	3	4	3	4	2/3	4	3	4	3	4	2/3
4	25	Printed[b]	4	4	4/5	4/5	4/5	4	4/5	4/5	4/5	4	4	4
5	30	Printed	4/5	4/5	4	4	4/5	4/5	4	4	4	4	4/5	4
6	35	Printed	4	4	4/5	4/5	4	4/5	4/5	4/5	4/5	4/5	4	4/5

[a] Washing of untreated dyed fabric (washing, staining) (4, 1/2).

[b] Washing of untreated printed fabric (washing, staining) (4, 4).

The dyed fabrics have been mercerized during the pre-dyeing operation which improves the cross sectional geometry of the fabrics and increase the surface density of hydroxyl group on the cellulosic fabrics. When the Na-cellulose is neutralized in the final step of neutralization this extend the number of –OH groups present in the amorphous region of the cellulose which show prominent hydrogen bonding with the –OH group of PVA film; so this hydrogen bonding induce the inherent stiffness of PVA film on to the tightly bonded internal cellulose film.

The colorfastness to washing of untreated dyed fabrics has shown; washing 4, staining 1/2 and untreated printed fabric; washing 4, staining 4. The colorfastness to washing of the dyed treated fabric (Table 4) has shown better result regarding staining on the adjacent fabrics, however the shade change rating of the washed fabric swatches remain unchanged. Water soluble dyes usually have lower washing fastness, but the resistance to removal by soap varies greatly with the dye. Since the standard test is carried out for a limited and fixed period, the amount of dye lost, and thus the fastness will depend upon the rate at which it is stripped off from the fiber under mild alkaline conditions. This rate depends on the structure of the dye molecule, especially the number of the anionic group present and to some extent by its molecular weight. It is previously reported in the experimental section that dye containing anionic group (sulphonate group (SO_3^-) in the structure was used during dyeing processing. The larger the number of anionic groups in a given molecular structure, the more stable is the dye under alkaline conditions and the greater is the electrostatic repulsion between the dye anion and the fiber. In alkaline solution the latter carries a charge of the same sign, i.e., negative as that on the sulpho groups. Furthermore it can be believed that sulphonic group of the dye can establish H-bond with the coating of hydroxyl group of PVA and induce ultimate stability of the dye against washing under alkaline conditions.

The results revealed that washing of the printed treated fabric (Table 4) almost unaffected in all the studied samples. It can also be observed that the rating of the untreated printed fabrics is a little better without the application of PVA (Table 4), however, there is slight improvement in the washing and staining of the treated printed fabrics swatches. The self improvement in the washing of the printed fabrics might be due to the involvement of butyl acrylate which has been used in the form of binder during the pigmentation process. It has been reported in the literature (Sultan et al., 2011) that the polyurethane acrylate copolymers are capable of enhancing physicochemical properties of the cellulosic fabrics.

In case of dyed sample the polar interaction of the –OH group with sulphonic acid and amino group of dye help in providing the protective coating of PVA on the dyed surface. However, the improvement in washing fastness is observed, while in case of printed fabrics no significant improvement has been observed. This is might be due to both or any of the reasons. Firstly, the acrylic film that has been bonded does not allow the possibility of the interaction observed in dyed samples. Secondly, most of the pigments lack in such type of polar group.

3.3. Effect of applied polyvinyl alcohol on the tone of the dyed and printed fabrics

The dyed and printed fabric swatches after application of polyvinyl alcohol (PVA) are presented in Figs. 2 and 3, respectively. Each prepared PVA sample was applied after dilution i.e. 25 g/L, 30 g/L and 35 g/L. The results through hand feel revealed that treatment of PVA has imparted stiffness to all the treated (both printed and dyed) fabrics samples. It has been reported in the established literature that different types of water soluble polymers such as modified starch, polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), acrylates are used to protect the yarn. Their protection ability may increases due to the presence of hydroxyl group both in PVA and cellulose. An untreated fabric swatch is also placed at the left of each set of the treated fabrics. It is clear that the tone change is negligible in the comparison of shades of dyed and printed, treated and untreated fabrics. When polyvinyl alcohol is physically cross-linked by the cellulose, though, the physical properties change dramatically, because the strands of PVA are now randomly linked together, with water molecules trapped within the network. The physically cross-linked network structure of the PVA enhances the resistance against any shade change of the treated printed and dyed fabrics.

It can be observed that all the treated dyed and printed fabric swatches (Figs. 2 and 3) have shown an incomparable stiff handle which is attributed to the affinity of hydroxyl groups to fiber and as well as its linkage to the PVA. The improvement in the stiffness of the dyed treated samples was pronounced as compared to the printed treated samples. This is attributed to dyed fabrics swelling as dyed fabrics are more swelled as compared to the printed fabrics due their processing route. All the samples have shown resistance to shade change after the applications of different dilutions of prepared polyvinyl alcohol samples. However, dyed treated fabrics have shown slightly better results as compared to printed treated fabrics. This attributes to the swelling of the fabric, which results in slight increase in weights of the treated fabrics. It is notable that swelling of the fabric enhances the stiffness of the treated fabrics (Zia et al., 2011; Zuber et al., 2011). The swelling of the fabric may result due to the formation of hydrogen bond between the cellulose and poly(vinyl alcohol) using H_2O molecules. During mercerization the number of hydroxyl group on the surface increases which provides better opportunity for hydrogen bonding with applied PVA as finishing agent. The effect of this comes out as stiffness in the fabrics after calendaring.

4. Conclusion

Poly(vinyl alcohol) of various commercial trades were prepared and applied onto the textile cotton and blends of cotton/polyester fabrics. The molecular structure of the diluted poly(vinyl alcohol) was confirmed using Fourier transform infrared spectrophotometer. Colorfastness to rubbing and washing of dyed and printed treated and untreated fabrics were also tested and discussed. The effect of various commercial trades of poly(vinyl alcohol), its concentration and dilutions were studied onto the treated fabrics. It was supposed that fixation of the poly(vinyl alcohol) onto/or within the cellulose structure is accompanied by the formation of semi-inter-penetrated network structure which results in providing good crock and wash fastness with high stiffness.

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