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Modification of cellulosic fabric using polyvinyl alcohol—Part-I: Physicochemical properties

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ABSTRACT

A series of poly(vinyl alcohol) of different commercial grades were prepared and applied onto the surfaces of cotton and blends of cotton/polyester fibers. The molecular structure was confirmed using Fourier Transform Infrared spectroscopy. Physicochemical properties such as viscosity and solid contents (%) were determined and discussed. Factors affecting the performance properties of the finished substrate such as post-treatment with poly(vinyl alcohol) of different grades, concentration and dilutions were studied. Fixation of the poly(vinyl alcohol) onto/or within the cellulose structure is accompanied by the formation of semi-inter-penetrated network structure thereby enhancing the association as well as providing very high stiffness. The results revealed that applications of poly(vinyl alcohol) on the textile fabrics in the finishing processes enables to enhance the stiffness as well as helps to improve its pilling resistance.

1. Introduction

The hairs of the seeds of the genus gossypuim and/or all vegetable fibers are known as cotton. Cotton is mainly composed of cellulose which consists of two glucose units held together by the glycosidic linkage (Bender, 2004; Patra, Arora, Arora, & Nigam, 2004; Schindler & Hauser, 2004). There are three hydroxyl groups for every glucose unit. The molecular structure of cellulose is presented in Fig. 1(a).

Polyvinyl alcohol (PVA) is colorless, flammable, odorless and tasteless, clear, white granular fine particles. It is water soluble, slightly soluble in ethanol, but insoluble in other organic solvents. Generally, its molecular weight is between 26,300 and 30,000 unit and a degree of hydrolysis of 85.5–89% (Ibrahim, Abo-Shosha, Elnagdy, & Gaffar, 2002; Ibrahim, El-Salmawi, & Ibrahim, 2005; Sexena, 2004). The ability of this polymer makes it easily accessible for numerous applications, such as paper, wood, leather and textile industries, cosmetics and agribusiness. 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 for biotechnology (Burkinshaw & Kumar, 2008a, 2008b; Pourciel et al., 2003). Polyvinyl alcohol has been aggressive in various branches of science and technology, such as textile sizing and finishing agent, emulsifier, photosensitive coating, paper adhesives and finishing chemicals for wood and leather. Due to small, dense and closely packed monoclinic crystallite, PVA possess tremendous gas barrier properties. Unlike other barrier polymers, PVA exhibits flexibility, transparency within economics feasibility. For food packaging application PVA has also been developed as a barrier film (Burkinshaw & Kumar, 2010; Jang & Lee, 2003). The chemical structure of polvinyl alcohol is given in Fig. 1(b).

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. Either method leaves undesirable salts that are difficult to remove. This accounts for both lower molecular weight and linearity of the PVA (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 bond with neighboring chains. Being linear, the chains can align themselves to form a tightly packed array (DeMerlis & Schoneker, 2003; Zhang et al., 2008). Polyvinyl alcohol has been widely used as

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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	Combination of reactive dyes
02	Printed cotton	(100 × 80/40 × 40)	100% cotton	Combination of pigments
03	White bleached cotton	(100 × 80/40 × 40)	100% cotton	Optical brightener
04	White bleached polyester/cotton	(100 × 80/40 × 40)	50/50	Optical brightener
05	White bleached Denier	(76 × 44/30 × 150)	15/85	Optical brightener

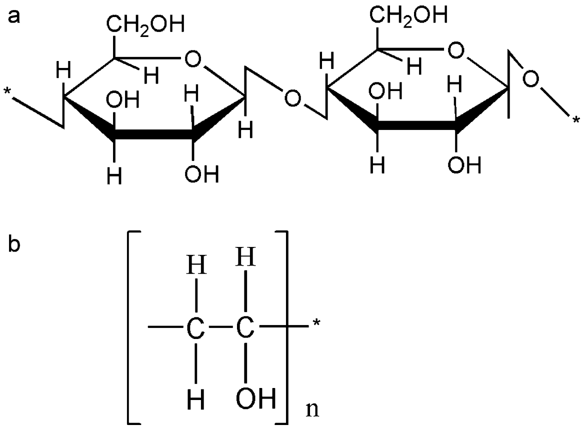

Fig. 1. Molecular structure of (a) cellulose and (b) poly(vinyl alcohol).

adhesives and sizing agents both in warp sizing and making non-woven fabrics. Warp sizing practices demonstrate that, by using PVA as sizing agents, many difficulties in warp sizing operation to synthesize finishes can be overcome. It is important to mention 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 manufactures of non-woven fabrics. The main function of adhesion is to adhere to the fibers in warp yarns and non-woven fabrics in order to increase their strength (Wang, Yang, Liu, Fu, & Xue, 2009; Zhang, Li, Li, Li, & Xiao, 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 stability, water solubility and the good film forming ability. Polyvinyl alcohol (PVA) is broadly used as sizing agents for cotton yarns due to its appropriate mechanical properties and tremendous film-forming characteristics. These sizing agents normally removed before dyeing and finishing steps (Seoudia, Mongyb, & Shabaka, 2008).

It has been reported in the established literature (Sultan et al., 2011) that polyurethane acrylate copolymers are capable of enhancing physicochemical properties of the cellulosic fabrics. In this research work polyvinyl alcohol has been used to modify the properties of the cellulose fabrics. Attempts have been made to apply the polyvinyl alcohol as sizing material (Seoudia et al., 2008; Zhang et al., 2006), paper coating (Pourciel et al., 2003), etc. Very limited literature is available reporting the use of PVA as finishing agents. Due to the dearth of report on the application of PVA studying physicochemical properties and surface morphology with increase in concentration using various trades of PVA, the present work is planned. In this research work different percentage of polyvinyl alcohol were prepared varying trade of the PVA and applied onto the cellulosic fabrics using pad dry cure method. The effects of the process parameters were systematically investigated. These parameters include viscosity and solid contents of prepared samples and, grades and concentration of the polyvinyl alcohol applied onto the fabrics. The treated fabrics were monitored for surface stiffness, smoothness and yellowing.

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, five different fabrics, plain weave (Table 1) 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 was further purified 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)–$(O\text{-}C_2H_4)_{1-25}$–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 detail regarding samples code and formulation of the PVA along with suppliers are mentioned in Table 2.

2.2. Preparation of polyvinyl alcohol solution

First of all, glass wares, reaction kettle were washed with distilled water to remove dirt and all types of other specific matters. The water was taken into the reaction kettle as per different grades and percents of PVA. Six samples (PVA-1–PVA-6) were prepared with different percentage (i.e., 10% and 13%) using three trades of polyvinyl alcohol (Table 2). Continuous heat was supplied to the

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	[a]PVA 217-PK (10 g)	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)	2–3 drops	Sinochem Nanjing Co., Mainland, China

[a] Polyvinyl alcohol.

reaction vessel, when temperature of the reaction vessel containing water was increased to 65 °C; the polyvinyl alcohol (PVA) granules were added slowly with continuous stirring. It is worth mentioning that the solubility of polyvinyl alcohol in water causes to an exothermic process. The addition of PVA granules was stopped when temperature of the reaction vessel approached to 85 °C, simultaneously the supply of heat was stopped, however stirring was continues till the completion of solubilization. The resulting solution formed as a uniform gel. To prevent the attack of any microbes on the prepared polymer solutions, 2–3 drops of formalin as antimicrobial agent was added within 96 h. The other polymer samples varying the trade name and percentage of the understudy PVA samples were prepared following the formulation given in Table 2.

2.3. Measurements

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 transmission 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 of scans per experiment was 16 and resolution was 4 cm^{-1}. Solid contents of the prepared samples were determined by Refractrometer (Atago) and reported. The viscosity of the samples was determined with the help of Brookfield viscometer. For the purpose the spindles Nos. 1–4 was used according to thickness and different rpm speed. However, the values were obtained by using the spindle No. 4 at 12 rpm.

2.4. Treatment of cotton and blends of cotton/polyester fabric with polyvinyl alcohol

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 samples and blends of cotton/polyester fabric with polyvinyl alcohol was carried out using pad-dry-cure technique. The fabric samples were treated with an aqueous solution of polyvinyl alcohol (10% or 13%) with various dilutions (i.e., 25 g/L, 30 g/L and 35 g/L), 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.

2.5. Calendaring

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

2.6. Testing and analysis

The effect of application of different commercial grades and concentrations of PVA onto the shade and visualization of the dyed, printed and white fabrics was evaluated and reported. The stiffness and smoothness were evaluated following standard methods (AATCC Standard test methods; ASTM Standard test methods; Cote, 2002).

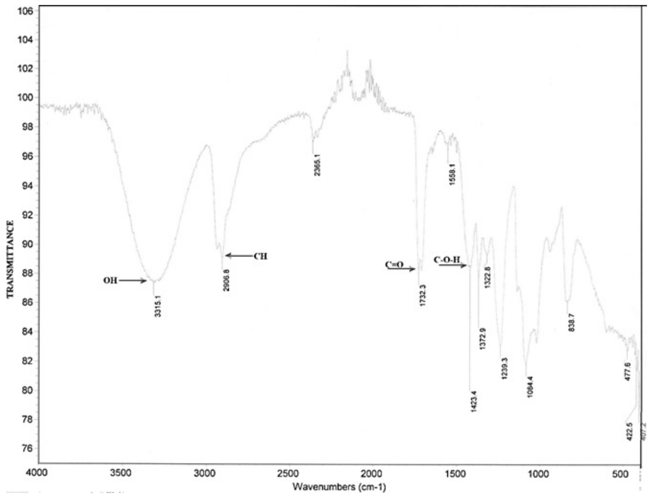

Fig. 2. FT-IR spectrum of poly(vinyl alcohol).

3. Results and discussions

Polyvinyl alcohol is biodegradable, biocompatible and non-toxic polymer with various industrial applications. These properties come jointly with a remarkable chemical versatility due to the presence of the hydroxyl (–OH) groups, which make feasible a number of grafting and crosslinking reactions of polymer backbone. The modification of secondary –OH group of polyvinyl alcohol has been reported in the literature to obtain material with new properties (Burkinshaw & Kumar, 2010; Zhang et al., 2011). In this report solutions of polyvinyl alcohol have been applied on different processed fabrics (Table 1). The results of treated and untreated fabrics have been reported and discussed.

3.1. FT-IR studies of polyvinyl alcohol

FT-IR spectrum of polyvinyl alcohol (PVA) (Fig. 2) showed very strong peak at 3315.1 cm^{-1} attributed to the hydroxyl (–OH) group (a backbone of PVA) 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} is correspond to unhydrolyzed ester functional group of polyvinyl acetate and other peaks at 1423.4 cm^{-1} attributed to C–O–H stretching and C=O of ester group. The FT-IR spectrum support that the PVA under examination has been prepared by hydrolyzing the polyvinyl acetate and there is some unhydrolyzed ester group remained.

3.2. Viscosity and solid contents of the prepared PVA samples

Physical properties such as viscosity (cps) and solid contents (%) are determined in order to know about the active ingredient in the polymer and rheology. The viscosity (cps) and solid contents (%) of the polymer samples are reported in Table 3. It can be seen that the viscosity of the different commercial trade PVA samples having various percentage of PVA ranges from 47,500 (cps) to 78,000 (cps). Among different commercial trades PVA 2488 has shown maximum viscosity and PVA PK-217 has lowest, where as PVA BP-26 remained in between these two samples. The results reported in Table 3 clearly indicates that solid contents of different grades of PVA has no remarkable difference, however there is slight increase in viscosity with increasing the percentage of the ever grade of PVA. Ultimately the viscosity will result to increase

Table 3
Solid contents (%) and viscosity (cps) of the prepared polymer samples.

S. no.	Sample code	Specification	Viscosity (cps)	Solid contents (%)
1	PVA-1	10% PVA[a] 217-PK	47,500	9.80
2	PVA-2	13% PVA 217-PK	55,000	13.0
3	PVA-3	10% PVA BP-26	52,000	11.5
4	PVA-4	13% PVA BP-26	70,000	13.8
5	PVA-5	10% PVA 2488	75,000	10.0
6	PVA-6	13% PVA 2488	78,000	12.20

[a] Polyvinyl alcohol.

with increase in solid contents and vice versa. The above reported results of viscosity and solid content will certainly alter the surface properties of the treated fabric which has being discussed in subsequent reactions.

3.3. *Surface smoothness, pill evaluation and GSM of the treated fabrics*

Quite a large amount of fabric is finished so as to have a firm handle and stiffness, for it may be recalled that various parts of fabrics have to be re-enforced so that they may preserve their shape and size much bitterly. The stiffness so produced is due to swelling of the surface of each cotton fiber so that gelatinous outer layer is formed. Polyvinyl alcohol (PVA) has been used as filling agent for all types of fibers especially, as additives in resin finishing. The PVA provides the full to stiff handle for white good and compatible with resin finishing agents. It has good wetability and imparts to improve the fastness to dry rubbing.

Pilling is the undesirable rolling together of fibers ends released from yarns by bending and abrasion on the surface of fabrics into the clusters of tufts or knots. These clusters are called pills. These contain fibers that are still partially embedded in the yarns and hence secured to the fabric surface. When the fabrics are stressed, the pills appear as "*bur*" like parts. The pilling result of dyed (100% cotton), printed (100% cotton) and white (100% cotton) white PC (polyester/cotton 50:50) blends and denier fabrics of all the studied samples are presented in Table 4. The prepared samples of PVA were applied after dilutions (i.e., 25 g/L, 30 g/L and 35 g/L). It is clear from the results (Table 4) that treatments of fabric with different concentration of the prepared polymer have remarkable anti-pilling property to the dyed and printed fabric. Moreover the fabrics composed of with blends of polyester/cotton have shown higher pilling rating because the pilling is the tendency of the polyester fiber. The results revealed that there is improvement in pilling rating of polyester/cotton (PC) fabric by using the ever prepared sample. Here one thing is noticeable that untreated printed fabrics with almost same blend ratio as that of white PC (i.e., polyester/cotton, 50:50), have good anti-pilling property as compared to white PC (Table 4). It is worth to mention that wet processing (dying or printing) eventually helps to impart the pilling resistance as can be seen from the reported results. In comparison with untreated fabrics, all the prepared PVA samples have shown better results. It is clear from the reported results that the treated samples with dilution of 25 g/L have shown

Table 4
Pilling tests results of, treated, untreated, white, dyed and printed fabrics.

S. no.	Strength of solution applied (g/L)	Type of fabric	PVA-1 pilling rating	PVA-2 pilling rating	PVA-3 pilling rating	PVA-4 pilling rating	PVA-5 pilling rating	PVA-6 pilling rating
1	25	Dyed[a]	4/5	4/5	4/5	4/5	4/5	4/5
2	30	Dyed	4/5	4/5	4/5	4/5	4/5	4/5
3	35	Dyed	4/5	4/5	4/5	4/5	4/5	4/5
4	25	Printed[b]	4/5	4/5	4/5	4/5	4/5	4/5
5	30	Printed	4/5	4/5	4/5	4/5	4/5	4/5
6	35	Printed	4/5	4/5	4/5	4/5	4/5	4/5
7	25	PC[c]	3/4	3/4	4	4/5	4	4/5
8	30	PC	4/5	4	4/5	4	4/5	4/5
9	35	PC	4/5	4/5	4/5	4/5	4	4
10	25	Dinnier[d]	1/2	1/2	2	2	2	2
11	30	Dinnier	1/2	2	1/2	2	2	2
12	35	Dinnier	2	2	2	2	2/3	2/3

[a] Pilling of untreated dyed fabric = 4.
[b] Pilling of untreated printed fabric = 4.
[c] Pilling of untreated white polyester/cotton (PC) fabrics = 3/4.
[d] Pilling of untreated dinnier white fabrics = 1/2.

Table 5
Weights (GSM) of treated, untreated, white, dyed and printed fabrics.

S. no.	Strength of solution applied (g/L)	Type of fabric	PVA-1 GSM (g/m^2)	PVA-2 GSM (g/m^2)	PVA-3 GSM (g/m^2)	PVA-4 GSM (g/m^2)	PVA-5 GSM (g/m^2)	PVA-6 GSM (g/m^2)
1	25	Dyed[a]	124	124	124	125	123	124
2	30	Dyed	126	126	126	123	124	123
3	35	Dyed	127	125	123	124	125	128
4	25	Printed[b]	126	125	124	126	124	124
5	30	Printed	128	125	129	124	124	129
6	35	Printed	128	124	128	124	126	127
7	25	PC[c]	110	111	110	111	111	110
8	30	PC	112	112	111	110	110	110
9	35	PC	111	110	110	112	111	111
10	25	Dinnier[d]	49	49	46	47	47	45
11	30	Dinnier	47	48	45	48	47	47
12	35	Dinnier	46	46	45	46	48	45

[a] Weight of untreated dyed fabric = 123 g/m^2.
[b] Weight of untreated printed fabric = 124 g/m^2.
[c] Weight of untreated white polyester/cotton (PC) fabrics = 110 g/m^2.
[d] Weight of untreated dinnier white fabrics = 45 g/m^2.

better result to improve the pilling of the treated polyester/cotton (50:50) fabric as compared to all the other dilutions. Therefore it is recommended that 25 g/L of the prepared sample must be applied onto the fabrics. It is worth to mention that fewer dilutions of the prepared PVA samples may create some difficulty in their application that results in lesser networking of the PVA with the cellulose or cellulose/polyester fabrics. The comparison of PC (50/50) and the denier fabrics has indicated that PVA-5 and PVA-6 has shown better result as compared to all the other PVA samples. The reason of this contradiction is beyond the scientific approach.

The stiffening and weighing of a textile material can be varied within very wide limits and it is quite possible to increase weight. The results of weight (GSM) of treated; untreated, dyed and printed fabrics are presented in Table 5. It can be seen that there is a remarkable increase in weights of treated fabrics as compared to the untreated fabrics. All the treated samples (dyed, printed, white PC and denier) have shown comparable increase in weights in all the studied samples. This is attributed to the swelling of the fabric which results to slight increase in weights of the treated fabrics. It is notable that swollen of the fabric helps to enhances stiffness of the treated fabrics (Zia et al., 2011; Zuber et al., 2011). The swollen of fabric may result due to the formation of hydrogen bond and or covalent ether bond between the cellulose and poly(vinyl alcohol).

4. Conclusion

Poly(vinyl alcohol) of different grades were prepared and applied onto the textile cotton and blends of cotton/polyester fabrics. Fourier Transform Infrared spectrophotometer was used to confirm the molecular structure of the diluted poly(vinyl alcohol). Viscosity and solid contents (%) of the diluted poly(vinyl alcohol) of different trades were also determined. The effect of different 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 high stiffness and pilling resistance.

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