Surface modification of polyester fabric using polyvinyl alcohol in alkaline medium

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Chemisorption of polyvinyl alcohol (PVA) onto polyester fabric in alkaline medium has been conducted. The treated fabric is characterized by scanning electron microscope, ATR-FTIR spectroscopy, contact angle, differential scanning calorimetry and dyeability. The PVA treated polyester fabric shows improved hydrophilic character over intact and sodium hydroxide treated PET fabrics.

Keywords: Contact angle, Differential scanning calorimetry, Polyester fabric, Polyvinyl alcohol

1 Introduction
Polyethylene terephthalate (PET), commonly called as polyester, is the widely used polymer for the production of synthetic fibres over the past 50 years. The wide use of PET is the result of its strength combined with its resistance to chemicals, abrasion, stretching, shrinking and wrinkling. However, the disadvantage of PET fibre is its low hydrophilic character and inactive surface. PET is a hydrophobic fibre with a moisture regain of only 0.6 - 0.8% even at 100% relative humidity. The basic requirement of fabric worn next to skin is that it should assist for moisture release to the atmosphere1. The conventional modification of PET fibre properties is through strong alkaline treatment under high processing temperature. Alkaline finishing of polyester fabric with sodium hydroxide changes fabric weight, strength, wettability and aesthetics2,3.

Altering the surface characteristics of polyester is rather difficult due to its inactive chemical structure. However, modifications of PET surface have been reported using various techniques, such as chemical introduction of sugars onto PET fabric using cyanuric chloride4, protein immobilization on PET film5, application of silk sericin to polyester fabric6 and cyclodextrin based finishes for polyester fabric7.

In the present work, adsorption of PVA onto polyester fabric has been carried out to modify the surface properties of base polymer, to make it hydrophilic and to improve its comfort characteristics. Polyvinyl alcohol has been used in textile industries8, as a sizing agent since it is a biodegradable polymer9. In this work, efforts have been made to chemically bind PVA onto PET surface in alkaline medium. Treating polyester structures with polyethylene glycol and metal hydroxide has been reported previously10. Modification of the fabric surface without involving hazardous organic solvents and achieving permanent hydrophilic character is the advantage of the chosen method.

2 Materials and Methods

2.1 Materials
The materials used in this study were (i) 100% polyester fabric (plain weave, 55 gsm; epi 92, ppi 80) and polyvinyl alcohol (C2H4O)n having 1700-1800 degree of polymerization (Loba Chemie Pvt Ltd, Mumbai, India).

The chemicals used in this study, such as hydrochloric acid, sodium hydroxide and sodium sulphate, were of analytical grade. A basic dye (supplied by Burgoyne & Burbridges & Co, Mumbai) para-rosaniline hydrochloride (CI Number 42500) was used for dyeing on polyester fabric.

2.2 Methods
2.2.1 Pretreatment of Polyester Fabric
Polyester fabric was immersed in 10 g/L HCl at 40°C and treated for 1 h at the same temperature with material-to-liquor ratio 1:50 to get rid of the added impurities11.
2.2.2 Application of PVA onto Polyester Fabric
The pretreated PET fabric was immersed in 1N NaOH solution containing 1.5% by weight of PVA. It was kept in the bath at boil for 1 h. Then the fabric was taken out and immersed in water at boiling temperature for 10 min and soaped to remove the physically held PVA, washed and dried at room temperature.

In a separate bath, similar treatment was carried out on polyester fabric without PVA. This sample was considered as control fabric.

2.2.3 Test Methods

Moisture Regain
Moisture regain of the polyester fabrics (intact, control and PVA treated) was determined as per the AATCC test method 20A-1995, RA 24. The moisture regain values were calculated using the following equation:

\[
\text{Moisture regain} = \frac{\text{Weight of conditioned fabric} - \text{Weight of dried fabric}}{\text{Weight of dried fabric}} \times 100
\]

Water Retention
Absorptive capacity of polyester fabrics (intact, control and PVA treated) was measured by standard AATCC 21-1978 test method.

Identification of PVA in Fabric
The polyester fabrics (intact, control and PVA treated) were tested for the presence of PVA. All the samples were spotted with a drop of reagent A (boric acid) and a drop of reagent B (iodine solution). Photographs were taken after 5 min. Polyvinyl alcohol reacts with boric acid and iodine to form a blue colour.

Water Contact Angle
Water contact angle was measured on the polyester fabrics (intact, control and PVA treated) using contact angle measuring system (model Phoenix 300 Plus, M/s Surface Electro Optics Co, Ltd, Korea). Drops of water (volume 8.0 µL) were placed on the fabric samples using a microsyringe. The measurements were taken immediately after placing the water drop and the variations followed for 10 min.

SEM Analysis
The surface morphology of polyester fabrics (intact, control and PVA treated) was observed on SEM (JOEL JSM-6360 model microscope, Japan).

FTIR Study
The ATR-FTIR measurements were carried out on polyester fabrics (intact, control and PVA treated) using an infrared spectrophotometer (Thermoscientific Nicolet iS10). Attenuated total reflectance (ATR) spectra were recorded at a resolution of 4 cm\(^{-1}\) and accumulation of 32 scans.

DSC Study
The differential scanning calorimetry (DSC) for intact, control and PVA treated PET fabrics was carried out using Pyris 6 DSC thermal analyzer. The rate of heating was adjusted at 10\(^\circ\)C/min. DSC traces were recorded from 25\(^\circ\)C to 400\(^\circ\)C under nitrogen atmosphere.

Dyeing of Fabric
The dyeability of polyester fabrics (intact, control and PVA treated) was studied using basic dye (para-rosaniline hydrochloride). Dyeing was carried out at boil for 2 h with a material-to-liquor ratio of 1:100 at pH 9 (using sodium hydroxide). Sodium sulphate was used as an exhausting agent. The dyed samples were washed with hot water, soaped and dried.

Colour Strength
Colour intensities of the dyed PET fabrics were measured using spectrophotometer (model: Premier colour scan ss 5000 A) within the range of 400-700 nm. Reflectance values were measured and the relative colour strength (\(K/S\)) was calculated using Kubelka Monk equation.

3 Results and Discussion
Many trials were carried out on polyester fabric using sodium hydroxide alone (0.25-2.0 N) and with PVA at different concentrations (0.25-2.0% by weight of PVA), time (15 min to 3 h) and temperature (30-120\(^\circ\)C) in different proportions. The weight loss in the polyester fabric and characteristic changes are considered. The effect of the PVA application on polyester fabric in alkaline medium at low concentration, low temperature and short duration is found to be negligible, whereas at higher conditions of concentration, temperature and time, the average weight loss on the PET fabric is more than 25%. Based on these, the optimized conditions for application on the polyester fabric using sodium hydroxide (1 N) and PVA (1.5%) have been fixed as mentioned earlier in section 2.2. The data are presented in Tables 1 and 2 and the effect is shown in Figs 1-4.
3.1 Wetting Behavior of Polyester Fabric

The water retention values of polyester fabric treated with PVA in alkaline medium, sodium hydroxide alone, and intact polyester are 99.115 and 144 % respectively. The PVA treated fabric exhibits about 45% and 29% rise in water retention capacity, compared to the intact and sodium hydroxide treated polyester fabric respectively. This may be due to the effect of PVA which is bound to the polyester fabric and enhances the ability of PET fabric to hold more water molecules. Trials have been carried out for moisture regain of these polyester fabric samples, however only PVA treated fabric shows marginal increase of around 1%.

3.2 Spot Test Effect of Polyester Fabric

The PET fabrics (intact, control and PVA treated) were tested for the presence of PVA after 10 washes. Photographs of fabrics subjected to spot tests are given in Fig 1. When the PET fabrics are spotted with reagents, blue colour is developed in the PVA treated sample, and no colour is obtained on the control and intact PET fabrics. The development of blue colour in the PVA treated PET fabric confirms the permanent nature of attachment of PVA to PET in alkaline medium. Intact and control fabrics do not develop colour confirming the absence of PVA as well as starch which, if present, will develop purple colour with this reagent.

3.3 Water Contact Angle in Polyester Fabric

Water contact angle of intact, control and PVA treated PET fabrics is given in Table 1. When a water droplet is placed on these fabrics, it spreads completely within 5 min in PVA treated PET fabric, whereas on the control and intact PET fabrics even after 10 min the water droplet does not spread fully. PVA treated PET fabric shows a static water contact angle of 67.31° (<90°), indicating that the fabric is wetted by water easily. The control and intact PET fabrics show static water contact values > 90°, which

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Untreated</th>
<th>Control</th>
<th>PVA treated</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>124.24</td>
<td>116.75</td>
<td>67.31</td>
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<tr>
<td>1</td>
<td>119.56</td>
<td>107.52</td>
<td>56.79</td>
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<td>2</td>
<td>113.88</td>
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</tr>
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<td>3</td>
<td>104.24</td>
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<td>6</td>
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<td>8</td>
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<td>10</td>
<td>33.91</td>
<td>59.13</td>
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<table>
<thead>
<tr>
<th>PET fabric</th>
<th>Temperature peak, °C</th>
<th>ΔH, J/g</th>
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<tr>
<td>Untreated</td>
<td>254.04</td>
<td>81.327</td>
</tr>
<tr>
<td>Control</td>
<td>253.69</td>
<td>43.592</td>
</tr>
<tr>
<td>PVA treated</td>
<td>247.07</td>
<td>29.617</td>
</tr>
</tbody>
</table>

Fig. 1—Spot test on (a) untreated PET fabric, (b) control PET fabric, and (c) PVA treated PET fabric

Fig.2—SEM photograph of (a) intact PET fabric, (b) control PET fabric, and (c) PVA treated PET fabric
reveals their hydrophobic character. Thus, this result shows the enhanced hydrophilic character of PVA treated fabric.

3.4 Spectral Investigation of Polyester Fabric

3.4.1 SEM Analysis

The surface morphology of intact, control and PVA treated PET fabrics is shown in Fig. 2. Figure 2c shows the presence of PVA on the surface of PET fabric, it does not fill up the interstices. SEM photograph of sodium hydroxide treated control fabric (Fig. 2b) shows that sodium hydroxide influences the swelling of PET fabric than that of intact fabric (Fig. 2a).

3.4.2 FTIR Analysis

The ATR-FTIR spectra of intact, control and PVA treated PET fabrics are shown in Fig. 3. The high peaks from 1700 cm\(^{-1}\) to 600 cm\(^{-1}\) indicate the original signals, such as characteristic spectra of stretching vibration band of C=O at 1730 cm\(^{-1}\) and C-O-C stretching vibration band at 1097 cm\(^{-1}\) and 1240 cm\(^{-1}\). All these peaks confirm the existence of ester linkage. Sodium hydroxide treated control fabric shows an additional peak at 2359 cm\(^{-1}\). This is attributed to carboxylic group (–COOH), introduced on the surface due to hydrolysis of the ester linkage. The PVA treated PET fabric shows a broad band in the region 3435 cm\(^{-1}\) which shows the presence of hydroxyl groups and the peak at 2359 cm\(^{-1}\) is absent in this fabric. This confirms the adsorption of PVA onto the PET surface. This can be due to the attachment of PVA on PET fabric surface by base catalyzed transesterification reaction.

3.5 Thermal Analysis of Polyester Fabric

Thermo-physical properties of the PET fabric samples are studied using differential scanning calorimeter. Thermal curves of intact, control and PVA treated PET fabrics are given in Fig. 4. The data are given in Table 2. Melting temperature of PVA attached PET fabric exhibits a drop of 7°C compared to intact fabric. The average heat of fusion of PVA treated fabric is found to be 29.617 J/g, whereas that of intact fabric is 81.327 J/g. Heat of fusion is the energy involved in formation and melting of crystalline regions. It is proportional to % crystallinity. The heat of fusion decreases after treatment of fabric with PVA, indicating a loss in the degree of crystallinity of the fabric, and loosening of compact structure of PET.

3.6 Dyeability of Polyester Fabric

The PET fabric samples (intact, control and PVA treated) were dyed using basic dye para-rosaniline.

Fig. 3—FTIR spectra of (a) untreated fabric, (b) control PET fabric, and (c) PVA treated PET fabric

Fig. 4—DSC of (a) untreated fabric, (b) control PET fabric, and (c) PVA treated PET fabrics
hydrochloride, and the $K/S$ values obtained are 1.579, 2.218 and 1.956 respectively. The basic dye binds well with carboxylic group present in the textile fabric. $K/S$ value can be taken as an indication of the amount of carboxylic groups present in the PET fabric. Of the three samples, the NaOH treated polyester fabric (control) shows the highest $K/S$ value due to the improved dye uptake by the reaction between basic dye and carboxyl group in control PET fabric. PVA treated PET fabric shows a lower $K/S$ value as the carboxylic acid group in PET fabric for the linkage (dye uptake) with basic dye is negligible.

4 Conclusion
The wetting behavior of PVA treated PET fabric increases considerably due to the good linkage between PET and PVA. The presence of PVA in the treated PET fabric after ten washes is confirmed by spot test. The water contact angle of PVA treated PET fabric is found to be much less than the intact and control PET fabrics, which reveals its hydrophilic character. The presence of PVA and the hydroxyl groups is also confirmed by SEM and FTIR studies. DSC traces of PVA attached PET fabric exhibit a lower melting temperature and lesser value of heat of fusion compared to intact PET fabric. PVA treated PET fabric exhibits lesser basic dye uptake compared to the control fabric due to lack of carboxylic groups which is also confirmed by FTIR interpretation.

References