Note from the field

Maleic acid crosslinking of C-6 fluorocarbon as oil and water repellent finish on cellulosic fabrics

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ABSTRACT

Tencel, viscose from bamboo, organic cotton and its blends are getting importance due to its biodegradability but they exhibit deficiency in oil and water repellency performance. In this research an effort has been made to enhance the oil and water repellency as well as washing durability of the tencel-organic cotton blends and viscose from bamboo-organic cotton blends by using environmentally friendly cross linker. C6 based short chain environmentally friendly fluorocarbon successfully incorporate oil and water repellency in the fabrics. However, addition of maleic acid as zero formaldehyde cross-linker with fluorocarbon not only significantly enhanced the washing durability of the oil and water repellency finish but crease recovery and antimicrobial performance were also enriched. Surface of the fabric was examined by using Scanning Electron Microscope.

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1. Introduction

Regenerated cellulosic fibers like tencel and viscose from bamboo are gaining importance due to their superior performances like comfort, softness, biodegradability, ease of dyeability and good appearance. These fibres combine the advantages of natural and synthetic fibres (Emam et al., 2013) and provide unique properties with respect to their intended application (Gun et al., 2008). In addition, organic cotton is also gaining more popularity as it is more eco-friendly as compared to normal cotton where large amount of pesticide and chemicals are used. Despite numerous advantages, cellulosic based fibers like tencel, viscose from bamboo and organic cotton lack oil and water repellency. Oil and water repellency is essential for end uses like workwear, rainwear, military uniforms, upholstery fabrics and curtains (Heywood, 2003). However, fabric can be made oil and water repellent by using various chemical treatments. Unfortunately, most of the chemical like aluminium and zirconium compounds, paraffin wax (Abo-Shosha et al., 2008), glue, pyridinium compounds, chromium and aluminium organo—metallic complexes and silicone compounds used in past only impart water repellency with no oil repellency (Mohsin et al., 2013a). In addition, most of the chemicals exhibited low washing durability and some of them are not environment friendly. Introduction of fluorocarbon in the oil and water repellency market was the major step forward as fluorocarbon significantly lowers the surface energy of the treated fabric. Consequently, treated fabric exhibited both oil and water repellency.

Typically, C8 chemistry based fluorocarbons were used as oil and water repellent finish. However, toxic perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are released from such finishes. PFOS and PFOA are linked with damage to children immune system (Phillipe et al., 2012), lower female fertility (Fei et al., 2009) and cancer (Jorgensen et al., 2011). Accordingly, fluorocarbon producers agreed to withdraw PFOS and PFOA and their precursors from the market. C6 based fluorocarbon have been developed which are PFOS and PFOA free but their oil and water repellency rating and washing durability is much lower than C8 based fluorocarbons.
Cross-linkers have been reported to enhance the performance and durability of various finishes like fire retardants (Mohsin et al., 2013b), nano titanium dioxide particles (Mohsin et al., 2013c), softeners (Mohsin et al., 2013d) as well as dyes (Mohsin et al., 2013e). However, most of the research work in case of oil and water repellent was on the use of formaldehyde based cross-linker (Sato et al., 1994) with C8 based fluorocarbon (Cerne and Simoncic, 2004). Formaldehyde based cross-linkers are very effective but they are toxic (Mohsin et al., 2014) and human carcinogen (International Agency for Research on Cancer, 2006). Butanetetracarboxylic acid (BTCA) is formaldehyde free cross-linker and has been reported with C8 fluorocarbon (Xu and Shyr, 2001) but it is very expensive and cause severe damage to the physical properties of the treated fabric.

Keeping in view the above scenario, the aim of this study was to increase functional performance of tencel and viscose from bamboo blend fabrics by the application of oil and water repellent with zero formaldehyde based cross-linker.

2. Materials and methods

Lab grade maleic acid and sodium dihydrogen phosphate (SDP) were purchased from Sigma–Aldrich. Oleophobol based on C6 chemistry was kindly supplied by Huntsman Chemicals. Fabric samples of different materials and constructions which are commonly used were selected to compare impact of density and nature of material. Fabrics used in this experiment were the blend of cellulosic fibers. Viscose from bamboo is viscose derived from bamboo pulp. Construction and composition of fabrics are given in Table 1.

Each fabric cover factor was calculated by using below mentioned formula and described in Table 2:

\[
\text{Cover Factor (CF)} = \frac{\text{Ends per inch}}{\sqrt{\text{warp count}}} + \frac{\text{Picks per inch}}{\sqrt{\text{weft count}}} \quad (1)
\]

The percentages of the chemicals described below are in w/w of solution. 1% of the Oleophobol was used as oil and water repellent finish as suggested by supplier. Maleic acid amount of 5% was used as zero formaldehyde cross-linker and 5% sodium dihydrogen phosphate was used as catalyst, whenever cross-linker was incorporated into the recipe. Padding is performed by using paddler at wet pick up of 80%. Pad-Dry-Cure method was used for application and fixation of chemicals. After padding with desired recipe samples were dried at the temperature of 100 °C for 4 min and then cured at 180 °C for 2 min in oven. All samples were conditioned before performing any testing.

BS EN 22313 (1992) was used to measure the dry and wet crease recovery angle of the samples. Twenty reading for each fabric is taken both in warp and weft direction and final angle is the addition of warp and weft values. Oil repellency of the treated fabric was assessed using AATCC-118. Standard Kaydol test liquid was used to assess the oil repellency. Five drops of Kaydol test liquid were placed onto the cotton fabric and standard time of 30 s were allowed before giving the judgment. If more than two oil drops out of five were penetrated into the fabric and made the fabric wet rather than roll off then fabric was considered wet. Oil repellency was assessed after each washing cycle and was continued until more than two drops were penetrated and fabric was considered wet. Water repellency was tested by AATCC 193–2004 water repellency test. Distilled water was used in water repellency test. Five drops of the distilled water were placed onto the fabric and standard time of 10 s was allowed before making the judgment. If more than two distilled water drops were penetrated and made the fabric wet then fabric is considered wet. Water repellency was also assessed after each wash cycle and washing was continued until more than two drops were penetrated into the fabric. The wash cycle value mentioned in the Table 3 is representing the last wash cycle where no more than two drops of oil and water respectively penetrated into the fabric. After this wash cycle value fabric was made wet by at least more than two drops. ISO 105-C10:2006 method was used to assess the washing durability of the treated fabric. ASTM-1424-07 method was used to assess the tear strength. AATCC 147 was used to evaluate the antimicrobial activity of the fabrics. Escherichia coli (E. coli) was used as bacterial strain. E. coli was stored at four degrees and refreshed weekly. Strains were streaked on nutrient agar plates and incubated for 24 h at thirty seven degrees. A single colony was transferred to nutrient broth for 48 h. The cells were collected by centrifugation at 10,000 rpm at four degrees for 15 min, washed with normal saline and re-suspended to an absorbance of 0.7 at 600 nm. These cell suspensions were used as inocula for antibacterial testing. The sample fabric was cut into 6-mm diameter discs and tested using the modified agar diffusion assay. The plated were examined for possible clear zones after incubation at thirty degrees for overnight. The presence of a clear zone around the circular disc on the plate medium was recorded as inhibition against the microbial species. The width of clear zone was determined using the formula:

\[
\text{Width of clear zone of inhibition} = \frac{[\text{Total Dia. of test sample} \times \text{Clear zone} - \text{Dia. of test sample}]}{2} \quad (2)
\]

Table 1 Details of the fabrics used in the research.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fabric description (warp count × weft count/Ends per inch × picks per inch)</th>
<th>Fabric ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 × 16/68 × 40 Twill (50% Viscose from bamboo, 50% Organic Cotton)</td>
<td>BC1</td>
</tr>
<tr>
<td>2</td>
<td>20 × 22/73 × 32 Twill (50% Viscose from bamboo, 50% Organic Cotton)</td>
<td>BC2</td>
</tr>
<tr>
<td>3</td>
<td>10 × 10/108 × 50 Twill (50% Tencel, 50% Organic Cotton)</td>
<td>TC1</td>
</tr>
<tr>
<td>4</td>
<td>20 × 20/94 × 60 Twill (50% Tencel, 50% Organic Cotton)</td>
<td>TC2</td>
</tr>
</tbody>
</table>

Table 2 Cover factor of the fabrics. Symbol σ represents standard deviation; values of σ are expressed in parentheses.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fabric ID</th>
<th>Cover factor (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BC1</td>
<td>25.2(0.1)</td>
</tr>
<tr>
<td>2</td>
<td>BC2</td>
<td>22.2(0.1)</td>
</tr>
<tr>
<td>3</td>
<td>TC1</td>
<td>50.0(0.2)</td>
</tr>
<tr>
<td>4</td>
<td>TC2</td>
<td>34.4(0.1)</td>
</tr>
</tbody>
</table>
3. Results and discussions

3.1. Oil and water repellency

All four control untreated fabrics exhibited no oil and water repellency, reflecting the need to apply oil and water repellent finish on the fabrics. In addition, application of C6 based fluorocarbon successfully incorporated oil and water repellency properties in all fabric blends. It was observed that the maximum numbers of washes were determined before each fabric became wet and at that stage the oil and water rating was one. Application of 1% of fluorocarbon on TC1 & TC2 fabrics exhibited oil and water repellency rating to greater number of washes, Table 3. Cover factor (CF) of TC1 fabric is 50.0 while cover factor of TC2 fabric is 34.4. Cover factor is related to area occupied by the yarns in relation to the air space between the yarns. Lower the value of cover factor less dense will be fabric and consequently there will be better penetration and application of the finish resulting in the improved repellency performance. Therefore, maximum oil and water repellency of TC2 fabric is much higher as compared to TC1 fabric due to their significant difference in cover factor. On the other hand BC1 fabric showed repellency rating up to 30 and 25 washes for water and oil respectively, while for BC2 fabric it was 40 and 25 washes. However, significant increase in performance rating of all fabrics was observed when same concentration of fluorocarbon was used in combination with maleic acid and sodium dihydrogen phosphate.

There was at least 10 rating and maximum of 30 rating improvement in the maximum number of washes before fabric became wet, when cross-linker was incorporated in the recipe as compared to without cross-linker. Therefore, it can be concluded that C6 based fluorocarbon perform well in combination with maleic acid.

3.2. Crease recovery angle

All four cellulosic based untreated fabrics exhibited poor crease recovery angle due to poor fiber bonding in amorphous region and more swelling in wet state. However, in case of organic cotton-tencel blends when treated with alone fluorocarbon, 9° increase in crease recovery angle was observed in TC1 fabric while in case of TC2 fabric, 10° improvement was observed, Table 4.

Similarly, in case of viscose from bamboo-organic cotton blends, both fabrics demonstrated improvement in crease recovery angle. So it can be concluded that fluorocarbon finish imparted beneficial effect on crease recovery performance. Mainly, it is due to the bonding and coating of fluorocarbon on the fabric surface. Fluorocarbons are based on acrylates which are capable of forming links between cellulose chains as shown in Fig. 1, which resulted in slight improvement in crease recovery performance of the treated fabric.

However, significant improvement in crease recovery angle was observed in fabrics when same amount of fluorocarbon was applied in combination with maleic acid cross-linker. Tencel-organic cotton blend fabric TC1 exhibited crease recovery angle of 175° and angle for BC2 fabric was 196°. In addition, viscose from bamboo-cotton blend fabric BC1 exhibited crease recovery angle of 169° and angle for BC2 fabric was 192°. There was improvement of 31° in crease recovery angle of both TC2 and BC2 fabrics. This increase in the crease recovery angle of the cellulosic fabrics in the presence of maleic acid cross-linker and fluorocarbon is partly due to the ability of maleic acid to link the cellulose chain and fluorocarbon as shown in Fig. 2. In addition, maleic acid is a dicarboxylic acid and capable of forming efficient bonding directly with cellulose as shown in Fig. 3. Therefore, greater improvement in crease recovery angle when maleic acid was also present in the recipe was due to better bonding and enhanced cross-linking of cellulosic chains.

In addition, fabric with less cover factor demonstrated better improvement in crease recovery performance. Crease recovery angle of TC2 and BC2 fabric is higher due to the low cover factor value of TC2 and BC2 fabrics as compared to TC1 and BC1 respectively. Cover factor is related to fabric compactness, as lower the cover factor value less dense will be the fabric, which will surely facilitate easy penetration and application of finish resulting in

![Table 3: Oil and water repellency performance durability against washing.](https://example.com/table3)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>BC1</th>
<th>BC2</th>
<th>TC1</th>
<th>TC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (untreated)</td>
<td>0(0.0)</td>
<td>0(0.0)</td>
<td>0(0.0)</td>
<td>0(0.0)</td>
</tr>
<tr>
<td>Oleophobol 1%</td>
<td>20(1.0)</td>
<td>30(1.0)</td>
<td>25(1.0)</td>
<td>40(1.0)</td>
</tr>
<tr>
<td>Maleic acid-5%, SDP-5%, Oleophobol 1%</td>
<td>35(1.0)</td>
<td>50(1.0)</td>
<td>50(1.0)</td>
<td>60(1.0)</td>
</tr>
</tbody>
</table>

![Table 4: Effect of treatment on the crease recovery angle of the cellulosic blend fabric.](https://example.com/table4)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Dry crease recovery angle, degree (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BC1</td>
</tr>
<tr>
<td>Control (untreated)</td>
<td>156(1.0)</td>
</tr>
<tr>
<td>Oleophobol-1%</td>
<td>159(0.5)</td>
</tr>
<tr>
<td>Maleic acid-5%, SDP-5%, Oleophobol-1%</td>
<td>169(0.5)</td>
</tr>
</tbody>
</table>
better improvement in crease recovery performance of less dense fabrics.

Cellulosic fabrics and its blends exhibited relatively low wet crease recovery angle as compared to dry one due to more swelling and breakage of chains in water. There was only slight improvement of 5–14° in wet crease recovery angle when fluorocarbon was applied onto the fabrics. Table 5. However, there was improvement of 30, 36, 28, 38° for BC1, BC2, TC1 and TC2 fabrics respectively when they are treated with fluorocarbon and cross-linker as compared to the respective control fabrics. This improvement in the wet crease recovery angle is due to the enhanced bonding as shown in Fig. 2. In addition, TC2 and BC2 fabrics have less cover factor values and hence exhibited better wet crease recovery angle as compared to TC1 and BC2 fabrics.

It is bit surprising that the ratio of wet to dry crease recovery angles is lower for BC2 and TC2 as compared to BC1 and TC1 respectively. One possibility is that BC2 and TC2 may contain more of the finish due to their comparatively open structure. However, BC2 and TC2 at the same time may be slightly more prone to water diffusion as well due to open structure as compared to BC1 and TC1 and consequently leading to lower wet CRA.

### 3.3. Tear strength

Strength properties of the fabric are among the key performance parameters. Therefore, tear strength of the fabric was assessed. In case of alone fluorocarbon highest tear strength loss of only 1.9% was observed for BC2 fabric, Table 6. Fluorocarbon finish was applied to the fabrics in acidic pH, which is responsible for acidic degradation of cellulosic linkage resulting in decrease of fabric strength. In all treated fabrics tear strength loss was minimal. However, there was slightly more tear strength loss when maleic acid was also present in the recipe of fluorocarbon as compared to alone fluorocarbon. It is due to the acidic conditions, and more cross-linking in the fabric resulting in the less uniform distribution of the applied stress. Highest tear strength loss of only 2.9% was observed for BC2 fabric. Therefore, it can be concluded that there was no drastic effect on tear strength due to the application of cross linkers along with fluorocarbon.

### 3.4. Antimicrobial performance

Typically, natural fibers are attacked by microbes, so effect of the finish on the antimicrobial properties of the treated fabric was also assessed. In case of all four fabrics when treated with alone fluorocarbon then there was almost no antimicrobial activity was observed, Table 7 & Fig. 4A. When combination of maleic acid along with fluorocarbon was applied on TC1 and TC2 fabrics, then they demonstrated good antimicrobial performance and both fabric surface was not attacked by the microbes. It is not surprising as maleic acid has been reported as antimicrobial agent in the literature. However, when this combination was assessed on BC1 and BC2 fabric both fabrics demonstrated better antimicrobial activity than tencel-organic cotton blend. More amorphous region in viscose from bamboo fibers, facilitate deep penetration of the finish, and responsible for better antimicrobial performance of cotton-viscose from bamboo blends over cotton-tencel blends.

### 3.5. Scanning electron microscope and energy dispersive spectroscopy analysis

TC2 fabric exhibited best result in terms of oil and water repellency and crease recovery angle among all four fabrics. Therefore, scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analysis were performed on TC2 fabric. Smooth and clean surface image of untreated TC2 fabric by SEM showed that there was no coating and hence did not exhibit any repellency, Fig. 5A. However, SEM image of fabric treated with fluorocarbon exhibited coating on the fabric surface, Fig. 5B, which is responsible for improved oil and water repellency and crease recovery angle of the treated fabric. In addition, strong coating is observed, Table 7 & Fig. 4A. When combination of maleic acid along with fluorocarbon was applied on TC1 and TC2 fabrics, then they demonstrated good antimicrobial performance and both fabric surface was not attacked by the microbes. It is not surprising as maleic acid has been reported as antimicrobial agent in the literature. However, when this combination was assessed on BC1 and BC2 fabric both fabrics demonstrated better antimicrobial activity than tencel-organic cotton blend. More amorphous region in viscose from bamboo fibers, facilitate deep penetration of the finish, and responsible for better antimicrobial performance of cotton-viscose from bamboo blends over cotton-tencel blends.

### Table 5

Wet crease recovery performance of the fabric.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Wet crease recovery angle, Degree(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (untreated)</td>
<td>124(0.5) 126(0.5) 131(0.5) 129(0.5)</td>
</tr>
<tr>
<td>Oleophobol-1%</td>
<td>130(1.0) 134(0.5) 136(0.5) 143(1.0)</td>
</tr>
<tr>
<td>Maleic acid-5%, SDP-5%, Oleophobol-1%</td>
<td>154(0.5) 162(1.0) 159(1.0) 167(0.5)</td>
</tr>
</tbody>
</table>

Fig. 2. Reaction between cellulose, maleic acid and fluorocarbon.

Fig. 3. Reaction between cellulose and maleic acid.

### Fig. 2

Reaction between cellulose, maleic acid and fluorocarbon.

### Fig. 3

Reaction between cellulose and maleic acid.
The presence of fluorine was assessed by the EDS analysis. No peak of fluorine was observed in the TC2 control fabric, Fig. 6A. However, clear fluorine peak was detected in the fluorocarbon and maleic acid treated fabric, Fig. 6B, thus confirming the successful coating of fluorocarbon on to the TC2 fabric. In addition, higher peaks of carbon and oxygen for the fluorocarbon and maleic acid treated fabric as compared to control fabric also indicate the high level of carbon and oxygen due to the presence of both chemicals.

4. Conclusion

C6 based fluorocarbon successfully imparted oil and water repellency to all four fabric blends. However, incorporation of
maleic acid as zero formaldehyde cross-linker with fluorocarbon enhanced the washing durability of the oil and water repellent finished fabric. Cross-linker imparted minimum of 10 and maximum of 30 rating improvement in the number of washes before fabric is wet. In addition, highest washing durability of 100 washes for water and up to 90 washes for oil was exhibited by TC2 fabric. All fabric blends exhibited improvement in crease recovery when fluorocarbon or combination of fluorocarbon and cross-linker was incorporated in the recipe. Highest value of crease recovery angle of 196° was demonstrated by BC2 fabric when combination of fluorocarbon and cross-linker was used. There was negligible tear strength loss for the treated fabric and maximum tear strength loss of only 3.7% was observed in case of BC1 fabric when fluorocarbon and maleic acid was used. All four fabrics exhibited antimicrobial properties only when treated with combination of fluorocarbon and maleic acid. In short, it can be concluded that combination of C6 based fluorocarbon with maleic acid exhibited excellent wash durability for oil and water repellency, good crease recovery and good antimicrobial performance. Therefore, this combination can give environment friendly replacement for C8 based oil and water repellent finishes with additional performance benefits.

References


