EXPLORING CONTINUOUS GRAFTING OF ACRYLIC ACID ONTO COTTON FABRIC

JAVED SHEIKH* and M. D. TELI**

*Department of Textile Technology, Indian Institute of Technology, Delhi, India
**Department of Fibres and Textile Processing Technology, Institute of Chemical Technology, Mumbai, India
✉Corresponding author: J. Sheikh, javedtexttech@gmail.com

*Received September 6, 2015

Graft copolymerization is generally carried out by the exhaust method, which is a batch process with limitations in its application. In the current study, acrylic acid was grafted onto cotton fabric using potassium persulfate (KPS) as an initiator, employing different padding techniques in order to explore the potential to make this operation continuous. The graft copolymerization parameters for the padding techniques were optimized in terms of temperature, time and concentration of initiator and monomer. The grafted product was characterized using FTIR, TGA and SEM, and further evaluated regarding properties such as moisture regain and yellowness index. The unmodified and grafted fabrics were then dyed using cationic dyes. Promising results were obtained, indicating the suitability of the pad-cure technique for such a modification as part of continuous operation, especially for lower levels of graft add-on with higher efficiency of the process. The grafted material showed improved dyeability towards cationic dyes with enhanced fastness properties, confirming the attachment of cationic dyes to the grafted cotton by ionic bonding.

Keywords: cotton, acrylic acid, continuous grafting, cationic dyeing

INTRODUCTION

Textile coloration and finishing are aimed at improving the aesthetics and serviceability of textile materials. Grafting of textile substrates is one of the routes to achieve chemical modifications that are essential to attaining desired performance properties. Among various fibres, cellulosic materials are also subjected to such modification processes. However, most of these processes involve exhaust techniques, and thus, even though a very good enhancement in performance has been reported in some of these cases, commercial application still remains a challenge in the textile processing field. Alternatively, by employing a padding technique, although there is a potential to make such a modification as part of continuous operation, very little research has been reported in this direction.

Franklin et al. carried out combined acrylic polymerization and methylol crosslinking to make durable press cotton fabrics. This process is based on continuous grafting using low cost commercial reagents. Rowland and Mason studied the simultaneous finishing of cotton with DMDHEU and a polymerizable zinc monomer (zinc salt of acrylic, methacrylic and itaconic acid). Hebeish et al. graft copolymerized polyester/cotton blend fabric to different levels with poly(acrylic acid) and poly(methacrylic acid), using the mutual γ-irradiation technique and Fe²⁺·H₂O₂ redox system. Hebeish et al. carried out concurrent grafting of acrylic acid and crosslinking of DMDHEU with cotton fabric in the presence of ammonium persulphate, magnesium chloride and ammonium chloride catalyst using the pad-dry-cure method. Ghosh and Das carried out the modification of jute and cotton fabric using acrylic acid as a finishing agent, in the presence of K₂S₂O₈ and Na₃PO₄ separately and in combinations employing the pad-dry-cure technique. They claimed simultaneous esterification, radical polymerization, along with crosslinking with free acrylic acid to take place in the reaction. Yen et al. treated cotton fabric with DMDHEU and acrylic acid using the pad-dry-plasma-cure process. They found lower rate constants and structural diffusion for the pad-dry-plasma-cure process than for the pad-dry-cure process.
Researchers also prepared antimicrobial textiles using the continuous grafting process.\textsuperscript{12-14}

Thus, very limited, but diverse attempts have been made to graft copolymerize different textile fibres, such as jute, polyester, cellulose, etc., with vinyl monomers by employing different techniques, such as gamma ray irradiation, chemical initiation and/or plasma or thermal curing. Traditionally, free radical grafting reactions were carried out using radical initiators, vinyl monomers, and textile fibres in the reaction bath coexisting in a solution. However, in such systems, the grafting reaction of the monomer on the fibre is a minor reaction, while the homopolymerization is the dominating one.

Since grafting is majorly taking place on the surface, there is very little damage to the strength of the fabrics. In addition, by the introduction of carboxylic groups as a result of grafting of acrylic acid onto cotton fabric, many interesting properties could be imparted to such modified fibres. The present paper explores this possibility of continuous grafting of acrylic acid onto cotton fabric using padding techniques and reports additional enhancement in dyeability with cationic dyes.

**EXPERIMENTAL**

**Materials**

Cotton fabric (EPI-69, PPI-88, GSM-122.95) was supplied by Century Mills Ltd. (Mumbai). All chemicals used were of laboratory grade. Cationic dyes were supplied by Clariant India Ltd.

**Methods**

**Grafting of acrylic acid onto cotton**

Cotton fabric was padded with a solution (in water) containing the required concentration of monomer and initiator with 75 ± 1\% expression, using a two bowl vertical padding mangle, and then dried and/or cured. Various processes were selected, namely, pad-dry, pad-cure and pad-dry-cure, and the parameters were varied in order to optimize them. After completion of the grafting process by padding, the grafted fabric was washed with hot water several times, to remove the homopolymers, until constant weight was reached (after complete drying at 105 °C). The graft add-on was calculated using the formula:

\[
\text{Graft add on (\%)} = \frac{W_2 - W_1}{W_1} \times 100
\]

where \(W_1\) and \(W_2\) are the bone dry weights of ungrafted and grafted fabric, respectively.

**Characterization of grafted cotton**

The grafted cotton was characterized by the following methods: FTIR analysis, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

FTIR spectra of original and grafted cotton samples were recorded using an FTIR spectrophotometer (Shimadzu 8400s, Japan), by the ATR sampling technique, recording 45 scans in %T mode in the range of 4000-600 cm\(^{-1}\).

Thermograms of grafted and ungrafted cotton fabric samples were recorded using an aluminum pan in the temperature range from 30 to 500 °C, and under inert atmosphere of N\(_2\) at a flow rate of 50 ml/min (Shimadzu, Japan).

The morphology of ungrafted and grafted cotton fabric was analyzed using scanning electron microscopy (FEI Quanta 200, Netherlands).

**Measurement of textile properties**

**Moisture regain**

The moisture regain was determined by the vacuum dessicator method with sodium nitrite to give 65\% RH at 21 ± 1 °C.\textsuperscript{15} The samples were treated with 1\% NaOH for 3 h and then the moisture regain was determined.

**Yellowness index**

Samples were evaluated for yellowness by determining the E-313 yellowness index, using a Spectraflash SF 300 (Datacolor International, U.S.A.).

**Crease recovery angle (CRA)**

To estimate the wrinkle resistance of the finished fabric, its crease recovery angle was measured using the ASTM D-1296 method by Shirley’s Crease Recovery Tester.\textsuperscript{16}

**Bending length**

In order to estimate the stiffness of the fabric, its bending length was measured in accordance with ASTM D-1388 on Shirley’s stiffness tester.\textsuperscript{16}

**Tensile strength**

The tensile strength of the finished fabric was evaluated in accordance with ASTM D-5035, ravelled strip test method.\textsuperscript{16}

**Tearing strength**

The tearing strength of the finished fabric was measured following ASTM D 1424-09 on an Elmendorf tear strength tester.\textsuperscript{16}

**Dyeing with cationic dyes**

The ungrafted and grafted cotton fabrics were dyed with cationic dyes, namely Bismark Brown G and Rhodamine B. The dyebath was set with 2\% (owf) acetic acid and 0.5\% (owf) dye solution, maintaining a material to liquor ratio of 1:30. It was heated up to 90 °C with a heating rate of 2.5 °C/min and dyeing was continued at 90 °C for 30 min. The fabric samples were then washed with cold water, followed by soaping.
treatment using Auxipon NP (non-ionic soap), 2 gpl at 60 ºC for 10 min. Finally, the samples were washed again with cold water and dried.

**Analysis of dyed fabrics**

*Colour value by reflectance method*

The dyed samples were evaluated for the depth of colour by the reflectance method, using a 10 degree observer. The absorbance of the dyed samples was measured on a Spectraflash SF 300 (Datacolor International, U.S.A.), equipped with reflectance accessories. The K/S values were determined using the expression:

\[
\frac{K}{S} = \frac{(1-R)^2}{2R}
\]

where \( R \) is the reflectance at complete opacity, \( K \) is the absorption coefficient and \( S \) is the scattering coefficient.

**Colour fastness**

Evaluation of colour fastness to washing was carried out using ISO II methods.\textsuperscript{17} Also, colour fastness to rubbing (dry and wet) was tested using a “crock-meter” with 10 strokes of rubbing. In addition, colour fastness to light was determined using ISO 105/B02 test methods.

**RESULTS AND DISCUSSION**

The cotton fabric was padded with a solution containing potassium persulfate and acrylic acid, where potassium persulfate, being a radical initiator, initiated radical sites by H-abstraction from cellulose and the acrylic acid would be grafted at these sites. As the curing temperatures were higher (140 ºC), the grafting reaction was expected to be faster and completed in a short time of curing. Even though the grafting reaction was in the continuous mode (i.e. pad-cure), the mechanism of grafting was expected to be the same as that in the batch mode, i.e. radical initiation by potassium persulfate.

**Evidence of grafting**

The cotton fabric grafted with acrylic acid (AA-g-Cotton) was characterized in order to validate the grafting.

The FTIR spectrum of the grafted fabric (Fig. 1), when compared with that of the ungrafted fabric, clearly indicates a peak at 1710 cm\(^{-1}\), which corresponds to the C=O stretching vibration in acrylic acid.

![FTIR spectra of ungrafted cotton and AA-g-Cotton](image1)

![TGA of ungrafted cotton and AA-g-Cotton](image2)
This confirms the introduction of the polyacrylic acid graft onto the cotton backbone.

Figure 2 shows the thermograms of the ungrafted and grafted cotton samples. In the initial stage, the weight loss values of both samples were of 6.27% and 5.89% at 250 °C, respectively. Between 250 °C and 400 °C, drastic decomposition of the samples resulted in a significant weight loss, which was of 84.90% for the ungrafted and 81.26% for the grafted cotton fabric at 400 °C. However, beyond 400 °C, the loss in weight slowed down and finally, at 500 °C, the weight loss values observed were of 96.75% for the ungrafted and 91.70% for the grafted cotton, respectively. This clearly indicates relatively higher thermal stability of the grafted sample, as compared to that of the ungrafted one. This could be attributed to the formation of a polyacrylic side chain network as a result of grafting acrylic acid onto the cellulose backbone, increasing its molecular weight.

The SEM images in Figure 3 A and B indicate surface deposition on AA-g-cotton, which is absent in the unmodified substrate. This further confirms the presence of grafted acrylic acid on the cellulose backbone. Striations can be seen on cotton, but are less visible in the grafted fabric. However, no distinct changes, except surface deposition, in the morphology of cotton were observed.

The results in Table 2 show the carboxyl content values of representative samples, which increased as a result of grafting. This further confirms the grafting of acrylic acid onto cotton fabric.

**Optimization of grafting parameters**

The initial attempt was to select a process for optimum grafting using padding techniques, hence the three commonly used padding techniques, namely pad-dry, pad-cure and pad-dry-cure, were applied and the results of grafting are presented in Table 1. The pad-cure method gave the maximum level of grafting, when compared with that of the other two methods. In the pad-cure process, the monomer was padded onto cotton and cured at a high temperature, where the probability of grafting was the highest due to the presence of initiator and monomer in the wetted fabric. The pad-dry involved drying the fabric at much lower temperature (80 °C) after padding and the rate of reaction was quite lower than that at higher temperature in the pad-cure processes. In the pad-dry-cure process, grafting occurred during drying and even though curing was carried out, the fabric was not in the wetted state to allow the movement of monomers, facilitating grafting. The curing process (after padding and drying) is advantageous in the cases where crosslinking is supposed to happen during curing. However, in comparison with the pad-cure process required for continuous grafting, this pad-dry-cure process does not seem to be advantageous.

The pad-cure process was subjected to further optimization (Fig. 4). With an increase in curing temperature from 100 °C to 140 °C, graft add-on increased, while beyond 140 °C, further increase in temperature resulted in a decrease in the graft add-on. The increase in the graft add-on with temperature is due to the higher rate of dissociation of the initiator, as well as the diffusion and mobility of the monomer from the aqueous phase to the cellulose fibre phase. With an increase in temperature beyond 140 °C, the radical termination reaction might be accelerated, leading to a decrease in graft add-on (%) and also an increase in the extent of homopolymerization. This may be possibly due to a recombination of growing homopolymer chain radicals, which is possible at high temperatures. Even when such a process was used for continuous grafting, since
the grafting took place at elevated temperature and in a short time, the effect of grafting temperature on the graft add-on was found to be much more pronounced.

An increase in the graft add-on was observed with the increase in time of curing from 1 min to 5 min. It may be attributed to the increase in the number of grafting sites in the initial stages of the reaction due to a higher amount of initiator participating in the formation of reactive sites at the cellulose backbone. However, after 5 min, there was no further significant increase in graft add-on. Higher curing time, however, can result in loss of mechanical properties of the cotton fabric and, hence, a curing time of 5 min was taken as the optimum.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Process</th>
<th>Temperature (Drying/Curing) (ºC)</th>
<th>Time (Drying/Curing) (min)</th>
<th>Initiator conc. (g/L)</th>
<th>Monomer conc. (g/L)</th>
<th>Graft add-on (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pad-Dry</td>
<td>80</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>1.45</td>
</tr>
<tr>
<td>B</td>
<td>Pad-Cure</td>
<td>140</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>2.65</td>
</tr>
<tr>
<td>C</td>
<td>Pad-Dry-Cure</td>
<td>80/140</td>
<td>5/5</td>
<td>15</td>
<td>100</td>
<td>2.29</td>
</tr>
</tbody>
</table>

* represents the average value of three measurements

![Figure 4: Optimization of parameters for AA grafting onto cotton](image)

It was observed that graft add-on increased with the increase in potassium persulphate concentration from 5 gpl to 15 gpl, which may be due to an increase in the number of radicals generated. A further increase beyond this concentration of initiator decreased the graft add-on, possibly because of homopolymer formation, which occurs simultaneously during grafting causing a reduction in the concentration of monomer available for grafting. It is well known that high initiator concentrations lead to short side chain polymers and thus, at higher concentration of KPS, the decrease in graft add-on could be justified.

The graft add-on (%) was found to increase significantly initially with the increase in monomer concentration from 50 to 100 gpl. Then the increase slowed down for monomer concentrations in the range of 100 to 200 gpl. This is explained by higher availability of monomer for grafting initially, while at higher concentration, homopolymer formation becomes a
dominant phenomenon, compared to grafting, causing only a slight increase in graft add-on. However, the efficiency of grafting decreased at higher concentration of AA. Since overall graft add-on values were quite small, the continuous grafting of acrylic acid onto cotton seems, however, to be advantageous in the cases when lower graft add-on is desired with better efficiency.

**Effect of grafting on textile properties**

Even though graft add-on varied with the parameters of grafting, as presented in Table 2, it was not the only factor affecting the textile properties, especially in the case of mechanical properties, which were greatly affected by parameters such as high temperature, increased reaction time and higher concentration of initiator, causing degradation of cellulose chains, and higher concentration of acrylic acid reacting with the hydroxyl groups of cellulose rather than participating in grafting. In order to study the effect of all these parameters on the mechanical properties, the grafted samples were evaluated for their mechanical properties and the results are summarized in Table 2.

In order to study the increased hydrophilicity, moisture regain and carboxyl content, some representative samples with different graft add-on were evaluated (Table 2). Results indicate an increase in moisture regain with the increase in graft add-on, giving 6.67% moisture regain for the optimum grafted sample (with a graft add-on of 2.65%). This was around 7.01% enhancement in moisture regain, when compared with the moisture regain of the ungrafted sample. The enhancement in moisture regain was due to the introduction of polyacrylic acid into the molecular structure of the cellulose substrate during grafting. The carboxyl content was also increased with the increase in graft add-on, resulting in increased hydrophilicity of the grafted sample. The moisture regain of the grafted product was found to be further increased to 7.68% after the treatment with sodium hydroxide, which forms the corresponding salt, showing 22.39% enhancement for the sample with the optimum graft add-on, over that of the ungrafted sample. The sodium carboxylate group has much higher moisture absorption capacity than did the carboxylic group and hence there was an enhancement in the moisture regain of the grafted cotton.\(^1\)

The whiteness index decreased with the increase in graft add-on, which may be due to an increase in the carboxyl content of the product and also ester group formation between the free acrylic acid and hydroxyl groups of the cellulose. The whiteness index decreased with reaction temperature, irrespective of the increase or decrease in graft add-on levels, indicating the negative effect of higher curing temperatures on whiteness. In the case of the time parameter, the whiteness decreased with the increase in reaction time, keeping all other reaction parameters constant. However, the effect of time on the whiteness seems to be less significant as compared to that of reaction temperature. The whiteness index also decreased with the increase in initiator concentration, irrespective of graft add-on. The increase in the concentration of acrylic acid also resulted in decreased whiteness, mainly because of the increase in graft add-on, since all other parameters were constant.

Tensile strength and tearing strength were found to be negatively influenced by the grafting reaction, the individual extent of which depended on the combination of various parameters of grafting. Tensile strength decreased with increased curing temperature, increased reaction time, increased initiator concentration and increased acrylic acid concentration. A similar trend was found in the case of tearing strength.

In general, tensile strength depends on the distribution of the force throughout the fabric, when it is pulled between the jaws during testing. The grafting reaction resulted in the deposition of side chains on the cellulose backbone, consuming the hydroxyl groups and preventing the H-bond formation between them. Grafting also resulted in increased stiffness of the fabric, facilitating failure at lower load. The degradation of the cellulose chains during grafting can be also another possible reason, as the treatment with acrylic acid is followed by curing at high temperature.

The crease recovery angle, which is the measure of the ability of the fabric to recover from creases, increased with the increase in graft add-on, independently of the reaction parameters. The addition of side chains prevents the H-bond formation among the hydroxyl groups and hence increases the ability of the fabric to recover from creases. Polymer deposition, which is considered to be one of the possible mechanisms occurring, also resulted in increased CRA. However, the bending length increased with the increase in graft add-on, indicating increased stiffness after grafting.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Graft add-on (%)</th>
<th>Whiteness index</th>
<th>Carboxyl content (meq/100 g)</th>
<th>Moisture regain (%)</th>
<th>Tensile strength (Kg)</th>
<th>Tearing strength (g)</th>
<th>CRA (°)</th>
<th>Bending length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UG</td>
<td>0.0</td>
<td>70.05</td>
<td>4.40</td>
<td>6.23(6.28)</td>
<td>36.34</td>
<td>1920</td>
<td>106</td>
<td>1.10</td>
</tr>
<tr>
<td>2A</td>
<td>1.30</td>
<td>59.90</td>
<td>18.44</td>
<td>6.444(6.94)</td>
<td>28.76</td>
<td>1472</td>
<td>144</td>
<td>1.15</td>
</tr>
<tr>
<td>2B</td>
<td>1.88</td>
<td>48.35</td>
<td>27.616</td>
<td>6.540(7.234)</td>
<td>26.76</td>
<td>1440</td>
<td>155</td>
<td>1.20</td>
</tr>
<tr>
<td>2C</td>
<td>2.63</td>
<td>35.51</td>
<td>38.361</td>
<td>6.653(7.61)</td>
<td>26.51</td>
<td>1440</td>
<td>175</td>
<td>1.25</td>
</tr>
<tr>
<td>2D</td>
<td>2.65</td>
<td>33.37</td>
<td>39.035</td>
<td>6.667(7.625)</td>
<td>23.22</td>
<td>1408</td>
<td>175</td>
<td>1.30</td>
</tr>
<tr>
<td>2E</td>
<td>2.50</td>
<td>24.02</td>
<td>35.853</td>
<td>6.633(7.54)</td>
<td>22.51</td>
<td>1152</td>
<td>173</td>
<td>1.37</td>
</tr>
<tr>
<td>2F</td>
<td>1.50</td>
<td>18.22</td>
<td>23.766</td>
<td>6.477(7.04)</td>
<td>17.31</td>
<td>960</td>
<td>145</td>
<td>1.47</td>
</tr>
<tr>
<td>3A</td>
<td>2.18</td>
<td>42.65</td>
<td></td>
<td></td>
<td>26.19</td>
<td>1472</td>
<td>160</td>
<td>1.20</td>
</tr>
<tr>
<td>3B</td>
<td>2.21</td>
<td>37.94</td>
<td></td>
<td></td>
<td>25.94</td>
<td>1472</td>
<td>163</td>
<td>1.20</td>
</tr>
<tr>
<td>3C</td>
<td>2.33</td>
<td>35.93</td>
<td></td>
<td></td>
<td>23.84</td>
<td>1440</td>
<td>165</td>
<td>1.25</td>
</tr>
<tr>
<td>3D</td>
<td>2.45</td>
<td>33.48</td>
<td></td>
<td></td>
<td>22.87</td>
<td>1408</td>
<td>170</td>
<td>1.25</td>
</tr>
<tr>
<td>3E</td>
<td>2.65</td>
<td>33.37</td>
<td></td>
<td></td>
<td>23.22</td>
<td>1408</td>
<td>175</td>
<td>1.30</td>
</tr>
<tr>
<td>3F</td>
<td>2.67</td>
<td>27.70</td>
<td></td>
<td></td>
<td>20.52</td>
<td>1120</td>
<td>176</td>
<td>1.37</td>
</tr>
<tr>
<td>3G</td>
<td>2.67</td>
<td>26.82</td>
<td></td>
<td></td>
<td>19.17</td>
<td>992</td>
<td>176</td>
<td>1.40</td>
</tr>
<tr>
<td>4A</td>
<td>2.22</td>
<td>46.00</td>
<td></td>
<td></td>
<td>26.72</td>
<td>1440</td>
<td>162</td>
<td>1.20</td>
</tr>
<tr>
<td>4B</td>
<td>2.39</td>
<td>34.60</td>
<td></td>
<td></td>
<td>24.56</td>
<td>1408</td>
<td>167</td>
<td>1.30</td>
</tr>
<tr>
<td>4C</td>
<td>2.65</td>
<td>33.37</td>
<td></td>
<td></td>
<td>23.22</td>
<td>1408</td>
<td>175</td>
<td>1.30</td>
</tr>
<tr>
<td>4D</td>
<td>2.12</td>
<td>25.55</td>
<td></td>
<td></td>
<td>17.04</td>
<td>1088</td>
<td>159</td>
<td>1.45</td>
</tr>
<tr>
<td>4E</td>
<td>1.73</td>
<td>26.58</td>
<td></td>
<td></td>
<td>12.16</td>
<td>928</td>
<td>153</td>
<td>1.40</td>
</tr>
<tr>
<td>5A</td>
<td>1.40</td>
<td>52.76</td>
<td></td>
<td></td>
<td>24.07</td>
<td>1408</td>
<td>144</td>
<td>1.20</td>
</tr>
<tr>
<td>5B</td>
<td>2.65</td>
<td>33.37</td>
<td></td>
<td></td>
<td>23.22</td>
<td>1408</td>
<td>175</td>
<td>1.30</td>
</tr>
<tr>
<td>5C</td>
<td>3.61</td>
<td>24.36</td>
<td></td>
<td></td>
<td>19.14</td>
<td>1216</td>
<td>177</td>
<td>1.60</td>
</tr>
<tr>
<td>5D</td>
<td>3.79</td>
<td>16.89</td>
<td></td>
<td></td>
<td>17.89</td>
<td>960</td>
<td>180</td>
<td>1.70</td>
</tr>
</tbody>
</table>

*CRA – crease recovery angle, †represents average value of three determinations*
Table 3
Effect of AA grafting on cationic dyeing properties

<table>
<thead>
<tr>
<th>Graft add-on (%)</th>
<th>K/S $^\dagger$</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>Washing fastness</th>
<th>Rubbing fastness</th>
<th>Light fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C/S Dry Wet</td>
<td>Dry Wet</td>
<td></td>
</tr>
<tr>
<td>Bismark Brown G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>1.20</td>
<td>72.71</td>
<td>11.76</td>
<td>27.32</td>
<td>1-2 3 3 3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1.3028</td>
<td>1.98</td>
<td>63.70</td>
<td>17.90</td>
<td>22.67</td>
<td>4 3-4 4 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1.45</td>
<td>2.20</td>
<td>65.06</td>
<td>17.54</td>
<td>27.47</td>
<td>4 3-4 4 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>2.48</td>
<td>61.09</td>
<td>10.77</td>
<td>23.95</td>
<td>4 3-4 4 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1.8819</td>
<td>2.95</td>
<td>60.82</td>
<td>17.49</td>
<td>28.09</td>
<td>4 3-4 4 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2.2974</td>
<td>3.62</td>
<td>59.15</td>
<td>18.30</td>
<td>30.46</td>
<td>4 3-4 4 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2.5034</td>
<td>4.99</td>
<td>56.66</td>
<td>23.18</td>
<td>34.19</td>
<td>4 3-4 4 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2.6306</td>
<td>5.10</td>
<td>53.03</td>
<td>14.80</td>
<td>28.61</td>
<td>4 3-4 4 3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>2.65</td>
<td>5.23</td>
<td>55.03</td>
<td>19.07</td>
<td>32.45</td>
<td>4 3-4 4 3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Methylene Blue G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>0.88</td>
<td>74.24</td>
<td>-12.47</td>
<td>-15.26</td>
<td>1-2 3 3 3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1.3028</td>
<td>6.77</td>
<td>52.51</td>
<td>-11.56</td>
<td>-34.59</td>
<td>3 3 3 2-3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1.45</td>
<td>6.95</td>
<td>52.77</td>
<td>-11.93</td>
<td>-34.84</td>
<td>3 3 3 2-3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>8.26</td>
<td>50.75</td>
<td>-10.81</td>
<td>-36.15</td>
<td>3 3 3 2-3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1.8819</td>
<td>9.70</td>
<td>50.03</td>
<td>-11.53</td>
<td>-35.13</td>
<td>3 3 3 2-3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2.2974</td>
<td>12.40</td>
<td>46.82</td>
<td>-10.27</td>
<td>-36.53</td>
<td>3-4 3 3 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2.5034</td>
<td>13.12</td>
<td>43.21</td>
<td>-7.77</td>
<td>-37.47</td>
<td>3-4 3 4 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2.6306</td>
<td>13.44</td>
<td>43.91</td>
<td>-8.23</td>
<td>-37.15</td>
<td>3-4 3 4 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2.65</td>
<td>13.52</td>
<td>43.55</td>
<td>-8.32</td>
<td>-36.64</td>
<td>3-4 3 4 3</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

C – Change in shade, S – Staining, $^\dagger$ represents average value of three determinations

Effect of acrylic acid grafting on cationic dyeing of cotton

The acrylic acid grafted cotton was studied as to its dyeability towards cationic dyes and the results are summarized in Table 3.

Colour strength increased with the increase in graft add-on for both cationic dyes. The increase in graft add-on resulted in an increase in the carboxyl content of the cotton fabric (Table 2), hence providing more attachment points for the cationic dye molecules, which explains the enhanced colour values. The grafted sample (with a graft add-on of 2.65%) showed an increase in colour strength, compared to that of the ungrafted sample, by 334.04% for Bismark Brown and 1436.77% for Methylene Blue dyes. Since, in this case, the grafted cotton is in fabric form, by using the padding method, the grafting is more or less controlled by the mangle pressure and expected to be uniform along the length and width of the fabric. The fabrics dyed using cationic dyes showed such an even dyeing along the fabric.

The fastness properties of the dyed samples were improved for both dyes. Cationic dyes are known for inferior fastness properties on cellulose and hence an improvement in fastness properties for the grafted product may be attributed to the increase in carboxyl groups, which provided better attachment to the sites for the dye molecules, hence offering resistance to removal during washing or rubbing.

The improvement in light fastness is due to a larger amount of dye being adsorbed onto the fibre, as compared to the case when the graft copolymer was absent. The samples with optimum graft add-on exhibited not only cationic dyeability (which would not be otherwise possible without the use of mordant), but also a 3 grade improvement in light fastness and 1 to 2 grade improvement in rubbing fastness.

CONCLUSION

Grafting of acrylic acid onto cotton fabric was successfully carried out by padding techniques and, among all, the pad-cure technique was found to be the most suitable. Various parameters of the grafting reaction were optimized. The grafted cotton fabrics showed increased thermal stability. The mechanical properties, such as tensile strength and tearing strength decreased to some extent, whereas there was an improvement in crease recovery angles. The grafted fabric showed significant enhancement in dyeability towards cationic dyes with improved fastness properties.
The findings of the present study clearly indicate that, in order to achieve modification of textile fabrics, continuous grafting should be considered as a potential operator-friendly process, yielding efficient and uniform results.

REFERENCES