Graft Copolymerization of Methylacrylonitrile Monomer onto Sulfonated Jute-Cotton Blended Fabric

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ABSTRACT

Graft copolymerization of methylacrylonitrile monomer onto bleached sulfonated jute-cotton blended fabric was carried out in an aqueous medium using potassium permanganate as an initiator under the catalytic influence of sulfuric acid in a nitrogen atmosphere. The effect of concentrations of monomer, permanganate, sulfuric acid, reaction time, and reaction temperature on the percent graft yield was studied. The polymerization reaction was studied with the respect of graft yield and graft efficiency. Optimization of various parameter of grafting viz. time, temp., monomer, initiator and sulfuric acid concentration was carried out. As evidence of polymer grafting, some instrumental analyses, such as thermogravimetric analysis, infrared spectroscopy, and X-ray diffractometry were carried out. Grafting improved the thermal stability, protected from photo-oxidative degradation, affected dyeability, and had a positive impact on color fastness.

Keywords: grafting, methylacrylonitrile monomer; sulfonation; jute; cotton; blended fabric

Introduction

Chemical modification through grafting of vinyl monomers onto jute and cotton fibers has been receiving considerable interest in recent years. Although jute fiber possesses high dimensional stability, certain unfavorable textile properties such as high stiffness, very low elasticity, and susceptibility toward sunlight have tremendously limited their use. Therefore, to minimize their undesirability and to enhance their effectiveness for intensified textile uses, graft copolymerization of vinyl monomers onto jute fiber has been attempted during recent years using chemical (Haque, 2003; Patnaik, 2003; Ghosh, 1994; Moharan, 2003; Sikdar, 2003), photochemical (Gitisudha, 2003), and radiation-induced (Majumdar, 1964; Mubarak, 2003; Khan, 2005; Imrisova, 2003), methods of initiation where the grafted fiber show improved tenacity, dyeability and tensile properties. Furthermore, among the methods of initiation, chemical method of initiation of grafting involving oxidizing agents such as KMnO₄, Na₂S₂O₃, K₂S₂O₈, and KHSO₅ are promising from the economic point of view and are quite selective in nature. Among the chemical initiators, permanganate has an identity of its own. Permanganate ions are known to act as strong oxidizing agents in an aqueous solution, and alone or in the presence of an activator they have been used to initiate graft copolymerization onto various...
In the present investigation, an effort was made to modify bleached sulfonated jute-cotton blended fabric with methylacrylonitrile monomer, initiated by a KMnO$_4$/$H_2$SO$_4$ redox system. To make the modification process more economical, an attempt also was made to find out the optimum modification conditions depending on concentrations of monomer, initiator, catalyst, reaction time, and temperature. Graft yield and graft efficiency were determined on the basis of the weight increase of the fabric treated. Some instrumental analyses such as infrared spectroscopy, X-ray diffractometry, and thermogravimetric analysis (TGA) were done to identify graft on fabric.

**EXPERIMENTAL**

**Materials**

Loomstate bleached sulfonated jute-cotton blended (BSJCB) fabric (Rajshahi-Bangladesh) was used as a material for the investigation. Methylacrylonitrile (Ridel-dehaen) was used fresh after distillation under a reduced pressure. All other chemicals used were of C.P. grade and were used as such without further purification.

**Production of fabric**

Jute fiber was sulfonated with sodium sulfite (Janson, 1966). Sulfonated jute fiber was blended with 40% cotton for the production of 60 × 60 plain woven fabric. Sulfonated jute-cotton blended fabric was bleached with hydrogen peroxide in a high-pressure rapid lab dip machine (Salam, 1978; Ibrahim, 2004).

**Graft copolymerization**

The treatment of BSJCB fabric was carried out in a 100-mL stoppered Erlenmeyer flask. Polymerization was done with 20%-70% monomer, 0.0%-1.25% permanganate as initiator, and 0.25%-1.5% sulfuric acid as catalyst based on the weight of fabric at 30°C-80°C for 0.5-3.0 h in the fabric: liquor ratio of 1 : 50. At the end of the desired reaction period, the BSJCB fabric was thoroughly washed with boiling soap solution (1.5%) to removed the loosely adhering polymer, washed, and dried (Sikdar, 2003; Abou-Zeid, 2003; Eromosele, 1998).

Percent graft yield and graft efficiency were calculated according to:

\[
\% \text{ graft yield} = \frac{B - A}{A} \times 100
\]

\[
\% \text{ graft efficiency} = \frac{B - A}{C} \times 100
\]

where A is the weight of ungrafted BSJCB fabric before treatment, B is the weight of the grafted BSJCB fabric after treatment, and C is the total weight of monomer.

**Thermogravimetric analysis**

The thermogravimetric analysis (TGA) of the fabric sample was done using a Mettle TG-50 (Shimadzu, Kyoto, Japan). The heating rate throughout the study was 10°C/min. The measurement was made under a constant flow rate (20 mL/min) of nitrogen (Ibrahim, 2004).

**IR spectroscopy**

Fabric sample was mixed with KBr in the ratio 1:100, and a pellet was prepared. Then, the IR spectra of this KBr pellet was recorded with IR-470 infrared spectrometer (Shimadzu, Kyoto, Japan) (Singh, 2003).

**X-ray diffractometry**

X-ray diffraction of the fabric sample was measured using a Phillips diffractometer. The dried isotropic sample was compressed as a pellet into the pore of a disk with a diameter of 2 mm and a thickness of 1 mm, and its X-ray diagrams were made with Ni-filtered Cu k$_\alpha$ radiation at 30 kV and 20 mA. Crystallinity of the fabric sample was determined by Segal et al (Segal, 1959).
Measurement of breaking strength

The breaking strength of the fabric sample was measured by the tensile strength tester (Torsee's Schopper type OS-100) (ISO 5081-1977E).

RESULTS AND DISCUSSION

Effect of monomer

The effect of MAN concentrations on its polymerization with BSJCB fabric using KMnO₄/H₂SO₄ redox system is shown in Figure 1. From Figure 1 it can be seen that the percent graft yield increased with the increase of monomer concentration, and with more than 60% monomer, the percent graft yield decreased. But the percentage of graft efficiency decreases with the increase of monomer concentration. This may be because of the higher availability of monomer molecules in the vicinity of immobile cellulose macroradicals as well as a higher monomer concentration in the polymerization medium. The greater availability of the monomer in the polymerization medium acted in favor of molecular collision (Sikdar, 2003; Hebeish, 1981), thereby enhancing polymerization in general or homopolymer formation in particular. The decreased percent graft yield of more than 60% suggests that homopolymerization prevails over grafting at a higher monomer concentration.

![Fig.1](image)

Fig. 1. Effect of monomer concentration on percent graft yield and graft efficiency of methacrylonitrile monomers onto BSJCB fabric (↑: graft yield, □: graft efficiency).

Effect of initiator

The effect of variation of initiator, that is, KMnO₄ concentration on the percent graft yield and graft efficiency are shown in Figure 2. It can be observed from Figure 2 that percent graft yield, graft efficiency and homopolymer were 0 when BSJCB fabric was grafted with MAN in the absence of KMnO₄. This is because in the absence of KMnO₄ in the polymerization medium, cellulose as well as monomer were not converted to their radicals. However, the percent graft yield and graft efficiency...
increased with the increase of permanganate concentration up to 0.9% and beyond this range, the graft yield and graft efficiency decreased. A similar behavior was true for homopolymer. The increasing trend of percent graft yield and graft efficiency might be a result of the formation of a great number of grafting sites on the fiber backbone of BSJCB fabrics through a reduction of KMnO₄ to Mn(III) or Mn(II). The grafting sites, that is, cellulose macroradicals in the presence of vinyl monomers, induced grafting (Sikdar, 2003; Samal, 1986). Another explanation is that a significant amount of graft formation occurred in the presence of KMnO₄ because a certain amount of MnO₂ deposited on the BSJCB fabric.

![Fig. 2](image)

**Fig. 2.** Effect of initiator concentration on percent graft yield and graft efficiency of methacrylonitrile monomers onto BSJCB fabric (▲: graft yield, □: graft efficiency)

Again, the decrease of percent graft yield and graft efficiency observed at above 0.9% KMnO₄ concentration could be interpreted in terms of retardation of monomer diffusion and faster rate of their termination. Besides impeding monomer diffusion at higher KMnO₄, the deposited MnO₂ colloidal particles on the fabric act as a source of excess Mn(IV) which may contribute to oxidation of BSJCB fiber macroradicals, and termination of growing poly-MAN chain. However, abundance of primary free radicals may also lead to termination by coupling, thereby decreasing the overall polymerization yield.

**Effect of temperature**

The effect of the rise of reaction temperature on percent graft yield and graft efficiency are shown in Figure 3. From Figure 3 it can be seen that the percent graft yield and graft efficiency increased with the increase of the temperature up to 60°C and
beyond which it decreased. The increase in percent graft yield and graft efficiency at high temperature may be a result of the increase in the rate of production of active free radicals, which increased the number of grafting sites at a higher rate. In addition, the rate of graft initiation and the increase in temperature also increased the rate of diffusion of monomer into the fiber matrix, where grafting was also initiated by complexed monomer. The decrease in percent graft yield and graft efficiency beyond 60°C, may be the result of an increase in the formation of homopolymer and the premature termination of growing grafted chains by excess Mn(III) or Mn(II) ions produced on oxidation of Mn(IV) ions.

![Fig. 3](image)

**Fig. 3.** Effect of reaction temperature on percent graft yield and graft efficiency of methacrylonitrile monomers onto BSJCB fabric (○: graft yield, □: graft efficiency)

**Effect of catalyst**

The effect of catalyst, that is, H$_2$SO$_4$ concentration, on the percent graft yield and graft efficiency of BSJCB fabric is shown in Figure 4. The percent graft yield and graft efficiency increased with the increase of sulfuric acid concentration up to 1.0% and then it decreased gradually as the acid concentration was increased. The plausible explanation of such behavior is that sulfuric acid in the grafting medium assisted the grafting, both by causing inter- and intracrystalline swelling of the substrate and by acting as a catalyst in the hydrolysis of cellulose, leading to uncoiling of the chains and improvement of the monomer accessibility. On the other hand, the experiment showed that homopolymer formation was also enhanced in the presence of acid. A higher concentration of acid, however, may cause degradation of the backbone chain of cellulose as well as of the graft chains. Thus, with the increase in the amount of sulfuric acid in the polymerization medium, the percent graft yield was decreased.
Fig. 4. Effect of catalyst concentration on percent graft yield and graft efficiency of methacrylonitrile monomers onto BSJC fabirc (▲: graft yield, ■: graft efficiency)

Effect of time

The effect of the rise of reaction time on percent graft yield and graft efficiency are shown in Figure 5. From Figure 5 it can be seen that the percent graft yield and graft efficiency increased with the increase of the temperature up to 2.0hr and beyond which it decreased. This tendency of graft to first increase, attain a maximum value and then decrease may be accounted for by the increasing extents of initiation and propagation of the reaction initially with time (Merlin, 2003). The decrease in grafting after a particular time is due to the detrimental effect of the high temperature onto the grafted side chain of MAN (Misra, 2001). The excess monomer is used to form homopolymerization (Salam, 2002).
Fig. 5. Effect of reaction time on percent graft yield and graft efficiency of methyacrylonitrilemonomers onto BSJCB fabric (▲: graft yield, ▌: graft efficiency).

**Thermogravimetric analysis**

The thermal behavior of BSJCB and its MMA-grafted fabrics was examined by a study of their TGA thermograms. From the results, listed in Table I, it can be observed that the loss in weight up to 289°C in the TGA curves was 8.2%-11.0%, which is a result of the desorption of adsorbed water and volatile matters. The actual pyrolysis started at around 285°C and ends at around 392°C. The blended fabric that lost its weight at 384°C was at 66.0%. The char residue at 600°C of blended fabric was lower (7.22%) than that of grafted fabric (17.2%). The grafted fabric's moisture content, which was lower than that of the ungrafted fabric, and char residue, which was higher than its grafted counterpart, are related to the monomer that pertains to the grafting. The TGAs of grafted and ungrafted BSJCB fabrics suggest that the thermal stability of grafted fabric is higher than that of ungrafted fabric.

<table>
<thead>
<tr>
<th>Fabric sample</th>
<th>Initial weight loss region (°C)</th>
<th>Weight loss (%)</th>
<th>Actual pyrolysis region (°C)</th>
<th>Weight loss at end of pyrolysis (%)</th>
<th>Char decomposition region (°C)</th>
<th>Decomposed char (%)</th>
<th>Residual char (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ungrafted</td>
<td>25-289</td>
<td>11.0</td>
<td>289-384</td>
<td>66.00</td>
<td>384-600</td>
<td>10.5</td>
<td>7.22</td>
</tr>
<tr>
<td>MAN- grafted</td>
<td>25-285</td>
<td>8.2</td>
<td>285-384</td>
<td>64.80</td>
<td>384-600</td>
<td>11.2</td>
<td>17.20</td>
</tr>
</tbody>
</table>
IR spectroscopy

The infrared spectra of the BSJCB fabric (control) and grafted BSJCB fabrics are shown in Figure 6. Figure 6 shows that the absorption bands of hydroxyl and carboxyl groups are around 3315-3455 and 1639-1725 cm\(^{-1}\), respectively. However, an additional peak obtained for MAN-grafted fabrics at 2235 cm\(^{-1}\) was observed. This peak is characteristic of the nitrite group corresponding to MAN-grafted onto BSJCB fabric. This ultimately shows that BSJCB fabric is being grafted with metylacrylonitrile monomer.

X-ray diffractometry

To define the crystalline structure of MAN-grafted BSJCB fabrics before and after grafting, X-ray diffraction patterns were analyzed. The degree of crystallinity of BSJCB fabric and their MAN-grafted fabrics was 70% and 60.2%, respectively. This may be explained by the grafting with metylacrylonitrile, which reduces the crystallinity of the BSJCB fabric because of the incorporation of amorphous copolymers. This may mechanically bind the cellulosic chains, confirming the additional strength to the fabric.

Characteristics

The breaking strength of grafted BSJCB fabric is higher than that of ungrafted fabric. Again, the loss in breaking strength of grafted BSJCB fabric on exposure to sunlight in air for 300 h was 10.0% lower than that of BSJCB fabric (results are listed in the Table 2). This means that the grafting of BSJCB fabric with metylacrylonitrile decreases the loss in breaking strength by photo-oxidative degradation. The incorporation of monomer through grafting increases breaking strength as well as decreasing the photo-oxidation degradation that occurs by sunlight.
Table 2: Effect of sun-light on breaking strength of grafted and ungrafted bleached sulfonated jute-cotton blended fabrics

<table>
<thead>
<tr>
<th>Exposure Period (hr.)</th>
<th>Breaking Strength (kg/f)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafted bleached sulfonated jute-cotton blended fabrics</td>
</tr>
<tr>
<td>0</td>
<td>20.56</td>
</tr>
<tr>
<td>300</td>
<td>18.7</td>
</tr>
<tr>
<td><strong>Loss in breaking strength (%)</strong></td>
<td><strong>9.04</strong></td>
</tr>
</tbody>
</table>

The BSJCB and their modified fabrics were dyed (2.5% dye) with Reactive Red M8B and Reactive Orange M2R at 70°C for 60 min in the fabric : liquor ratio of 1 : 30. The dye absorption of the grafted fabric was 9.0% lower than that of ungrafted fabric, meaning that grafting increased the hydrophobicity of the grafted fabric. The graft copolymerization had a positive impact on colorfastness to sunlight in air, on wash fastness to a soap medium up to 100°C, and on colorfastness to some common acids and alkalis.

Conclusion

Bleached sulfonated jute-cotton blended fabrics were graft-copolymerization at five varying conditions e.g. concentrations of monomer, initiator, catalyst, reaction time, and reaction temperature. During graft-copolymerization keeping all other variables constant, better graft yield and graft efficiency were obtained at 60°C, 2 hr, 60% monomer, 0.9% initiator and 1% catalyst. Grafting improved the thermal stability protected from photo-oxidative degradation affected dye ability crystallinity. It had a positive impact on color fastness such as light, wash, and acids and alkalis spotting (results are listed in the Table 3, 4, 5 and 6).

Table 3: Light fastness of grafted and ungrafted bleached sulfonated jute-cotton blended dyed fabrics on exposure to sunlight

<table>
<thead>
<tr>
<th>Exposure Period (hr.)</th>
<th>Fastness grade</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dyes used</td>
</tr>
<tr>
<td></td>
<td>Reactive Orange ME2R</td>
</tr>
<tr>
<td>Grafted bleached sulfonated jute-cotton blended fabrics</td>
<td>Ungrafted bleached sulfonated jute-cotton blended fabrics</td>
</tr>
<tr>
<td>300</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 4: Color fastness on washing of grafted and ungrafted bleached sulfonated jute-cotton blended dyed fabrics with soap solution

<table>
<thead>
<tr>
<th>Washing Temp. (°C)</th>
<th>Fastness grade</th>
<th>Dyes used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactive Orange ME2R</td>
<td>Reactive Red ME8B</td>
</tr>
<tr>
<td></td>
<td>Grafted bleached sulfonated jute-cotton blended fabrics</td>
<td>Ungrafted bleached sulfonated jute-cotton blended fabrics</td>
</tr>
<tr>
<td></td>
<td>Grafted bleached sulfonated jute-cotton blended fabrics</td>
<td>Ungrafted bleached sulfonated jute-cotton blended fabrics</td>
</tr>
<tr>
<td>40</td>
<td>4-5</td>
<td>4</td>
</tr>
<tr>
<td>70</td>
<td>4</td>
<td>3-4</td>
</tr>
<tr>
<td>100</td>
<td>3-4</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 5: Color fastness of grafted and ungrafted bleached sulfonated jute-cotton blended dyed fabrics to acid spotting

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Fastness grade</th>
<th>Dyes used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactive Orange ME2R</td>
<td>Reactive Red ME8B</td>
</tr>
<tr>
<td></td>
<td>Grafted bleached sulfonated jute-cotton blended fabrics</td>
<td>Ungrafted bleached sulfonated jute-cotton blended fabrics</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>4-5</td>
<td>3-4</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 6: Color fastness of grafted and ungrafted bleached sulfonated jute-cotton blended dyed fabrics to alkali spotting

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Fastness grade</th>
<th>Dyes used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactive Orange ME2R</td>
<td>Reactive Red ME8B</td>
</tr>
<tr>
<td></td>
<td>Grafted bleached sulfonated jute-cotton blended fabrics</td>
<td>Ungrafted bleached sulfonated jute-cotton blended fabrics</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>4</td>
<td>3-4</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>5</td>
<td>4-5</td>
</tr>
</tbody>
</table>
References


International Standard ISO 5081-1977(E) (Stip method) International Standardization for Organization, Switzerland.


Acrylonitrile on Chemically Modified Sisal Fibers. Journal of Macromolecular Materials and Engineering, 286(2), 107.”


