

## The Use of Poly(amidoamine) Dendrimer in Modification of Jute for Improving Dyeing Properties of Reactive Dyes

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**ABSTRACT:** In this study, the poly(amidoamine) (PAMAM) G-2 dendrimer was applied to the jute yarn. Fourier transform infrared spectrophotometry (FTIR) of the dendrimer-treated jute yarn indicated that all carbonyl groups of the jute fiber have reacted with amino groups of the PAMAM dendrimer. Jute yarns which had been pretreated with PAMAM dendrimer displayed markedly enhanced color strength with reactive dyes, even when dyeing had been carried out in the absence of electrolyte or alkali. Dendrimer-treated jute yarn showed much better light-fastness than that of untreated jute yarn. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** dendrimers; polyamidoamine; jute; dyeing; reactive dyes

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### INTRODUCTION

Coloration of jute fabric has become essential for all sorts of fabric starting from decorative value added fabrics to attractive packaging material. Due to the eco-friendly and biodegradable nature of jute fiber, the demand for jute fabric is rising worldwide day by day. One of the major problems that restricts the application of jute products is that jute suffers seriously from light-induced discoloration (i.e., due to phenolic structure of lignin).<sup>1,2</sup>

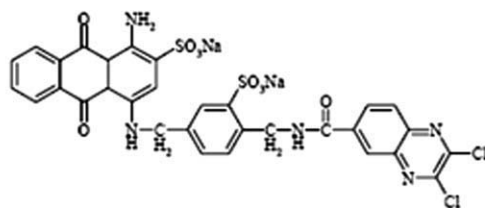
In case of reactive dyes, the dyes reacts with hydroxyl group of the fiber by either substitution or addition reaction.<sup>3</sup> For their reaction with cellulosic fibers, reactive dyes typically rely on an elevated pH (commonly over 10.5) and large amounts of electrolyte (NaCl or Na<sub>2</sub>SO<sub>4</sub>) to overcome the static repulsion between cotton fibers and reactive dyes in order to promote dyeability. During their application, along with dye absorption, dye hydrolysis also takes place. The greatest problem is dye hydrolysis or the reaction of dyes with water, since hydrolysis blocks the reactive sites so that the dyes cannot form covalent bond with fibers. The hydrolyzed dye retained on the fabric and is removed by severe washing. This results in

wastage of dye. Hydrolysis of the dye by water is more rapid at higher pH values. The application of reactive dyes to cellulosic fibers continues to be costly for the dye house in terms of dye wasted, electrolyte, and alkali used and, in addition, presents a large pollution load for the environment.<sup>4</sup>

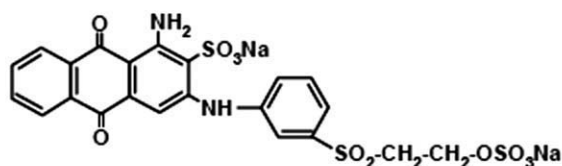
An alternative approach to increase dye uptake and dye fixation is by the modification of cellulosic fibers themselves. In essence, attention has focused on the introduction of cationic groups by means of pretreatment, commonly via quaternized amino groups, to which the anionic reactive dyes are attracted and so enhance dye-fiber substantivity. Such enhanced dye-fiber substantivity can result in reduced electrolyte usage and, potentially at least, lead to salt-free dyeings. In addition, if the cationic pretreatment compound also contained nucleophilic groups, such as primary amine or thiol, it is possible that the reactive dye could react with such added nucleophiles at lower pH values than are normally needed for cellulosic fiber dyeing; this, in turn, could, theoretically, lead to reduced dye hydrolysis.

Dendritic polymers can be divided into two classes: dendrimers (branched uniform structure) and hyperbranched

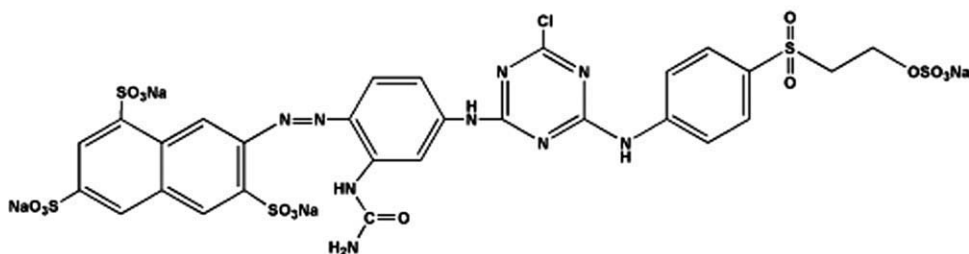
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C.I Reactive Blue 66 (Levafix Brilliant Blue PRL)



C.I. Reactive Blue 19



C.I Reactive Yellow 176

Figure 1. The chemical structure of reactive dyes.<sup>6</sup>

polymers (more random fashion). Dendrimers are a class of low-molecular weight highly branched polymers with several functional groups that have a central core and terminal end groups. They are generally prepared using either a divergent method or a convergent method. In the divergent method, dendrimers grow outward from multifunctional core molecules, whereas, in the convergent method, the dendrimer is constructed stepwise starting from the end group and moving inward.<sup>5</sup> The nature of the outer functional groups determines the solubility and reactivity of the dendrimers. Each layer in a dendrimer makes up a single generation.

Due to the unique chemical and physical properties, dendrimers and hyperbranched polymers have received much attention over the past two decades and have been applied to coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science.

Synthetic dendritic polymers are typical compounds used in this aspect. Due to the smaller molecular size, these compounds present good penetrability in fiber, and the exhaustion and fixation of reactive dyes on the modified fiber have improved.

Salt-free/low-salt dyeing technology using reactive dyes has become a popular topic. Most researchers focus on introduc-

ing cationic groups like amino or ammonium groups into cotton fabrics for interactions with anionic dyes. Dendrimer pretreatment enhanced color strength of cotton fabric.<sup>4,7</sup> Amino terminated hyperbranched polymer (HBP-NH<sub>2</sub>) grafted cotton fiber markedly enhanced color strength when dyed with reactive dyes using salt-free dyeing. The washing and rubbing fastness of the dyed hyperbranched grafted cotton fabrics were also good compared with those obtained by conventional dyeing.<sup>8</sup>

The pretreatment of cotton with the amino-terminated hyperbranched polymers in the presence of citric acid as crosslinking agents can also enhance the dyeability of the cotton fiber with reactive dyes.<sup>9</sup>

The use of dendrimers as an antimicrobial agent could be beneficial because of their unique structures.<sup>10</sup> It was believed that dendrimers with amine functional groups could be converted to effective antimicrobial agents due to their dense primary amine functional groups. Dendrimers have some unique properties because of their globular shape and tunable cavities. It has also been shown that dendrimers are able to form complexes with a variety of ions and compounds and act as a template to fabricate metal nanoparticles.<sup>11–15</sup>

The purpose of the present work was to determine whether the pretreatment of jute with a dendrimer could enhance the

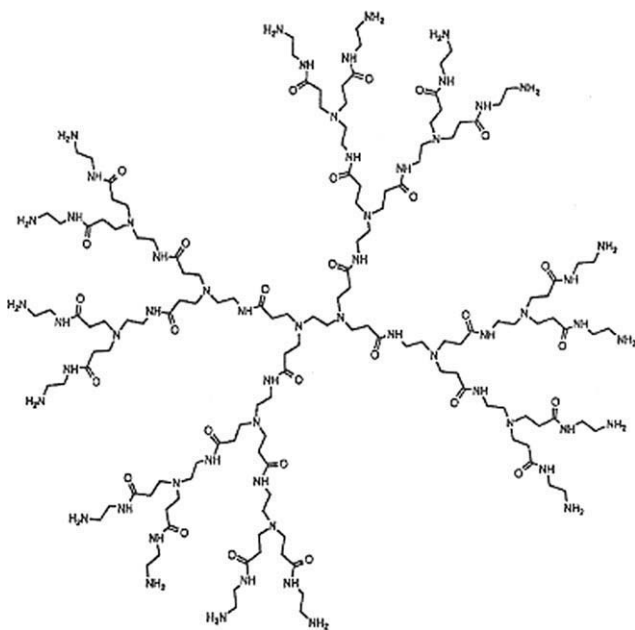


Figure 2. Structure of poly(amidoamine) PAMAM.

dyeability of the fiber with reactive dyes.  $K/S$  values, light-fastness of the treated yarns were tested and compared with those properties in conventional dyeing. Dendrimer Generation 2 was used in this study. Since, it is lighter than water (in density), grafting treatment was performed in alcoholic media.

## EXPERIMENTAL

### Materials

C.I Reactive Blue 19 and Reactive Yellow 176 were purchased from the Nordex International D.Z.E Dye., UK. Levogen WRD-T (cationic detergent) manufactured by Bayer, Germany. All chemicals were used without any purification. Commercially available tossa jute yarn with a twist of 308 t/m and yarn count of 4118 dTex was used throughout the study.

### Dendrimer

Poly(amidoamine) (PAMAM) dendrimer Generation 2 with 16 surface groups (Figure 2), 3.256 molecular weights, and 2.6

nm dendrimer were obtained from Institute for Color science and Technology, Tehran, Iran.<sup>16</sup> The synthesis of PAMAM dendrimer with ethylenediamine (EDA) core up to the second generation (G2) was performed using the divergent procedure described by Esfand et al.<sup>17</sup>

### Application of Dendrimer

The jute yarns were immersed in dendrimer–ethanol solution at concentrations 2.5% omf for 3 h at room temperatures, using a 15 : 1 liquor ratio. Next, the resulting jute yarn was air-dried at ambient temperature for 24 h. The samples of jute were cured with the dendrimer at 100°C in oven for 50 min.

### Dyeing

To highlight differences in dye uptake between the pretreated and untreated jute samples, the dyeings process was carried out using a competitive dyeing method in which a sample of dendrimer-treated jute and a sample of untreated jute were dyed competitively in the same dyebath. Dyeing with reactive dyes was carried out at a liquor ratio of 50 : 1. Dyeing of the samples was commenced at 30°C for Blue 19 and Yellow 176, and at 60°C for Blue 66 for 50 min, and kept at this temperature for 30 min in the presence of sodium chloride (60 g/L). Afterwards, sodium carbonate (20 g/L) was also added for dye fixation and dyeing continued for 30 min at 30°C.

### Color Strength of Dyed Yarns

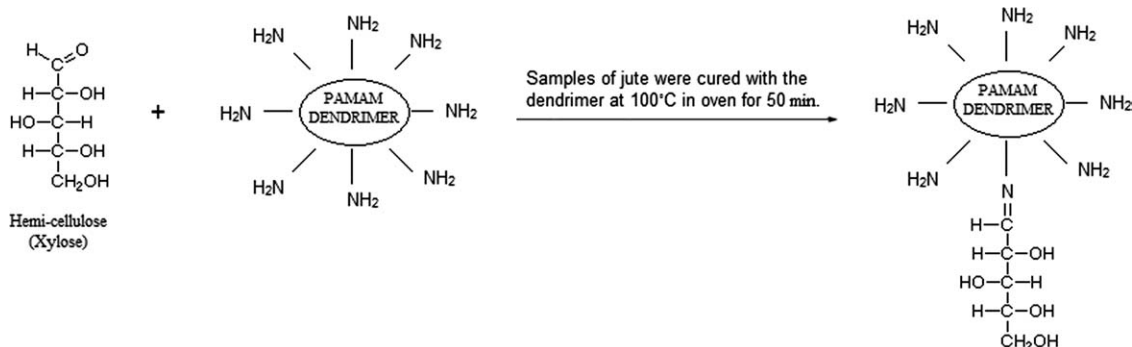
The color strength of dyed samples was determined from the values  $K/S$  calculated from the sample reflectance ( $R$ ):

$$K/S = (1 - R)^2 / 2R \quad (1)$$

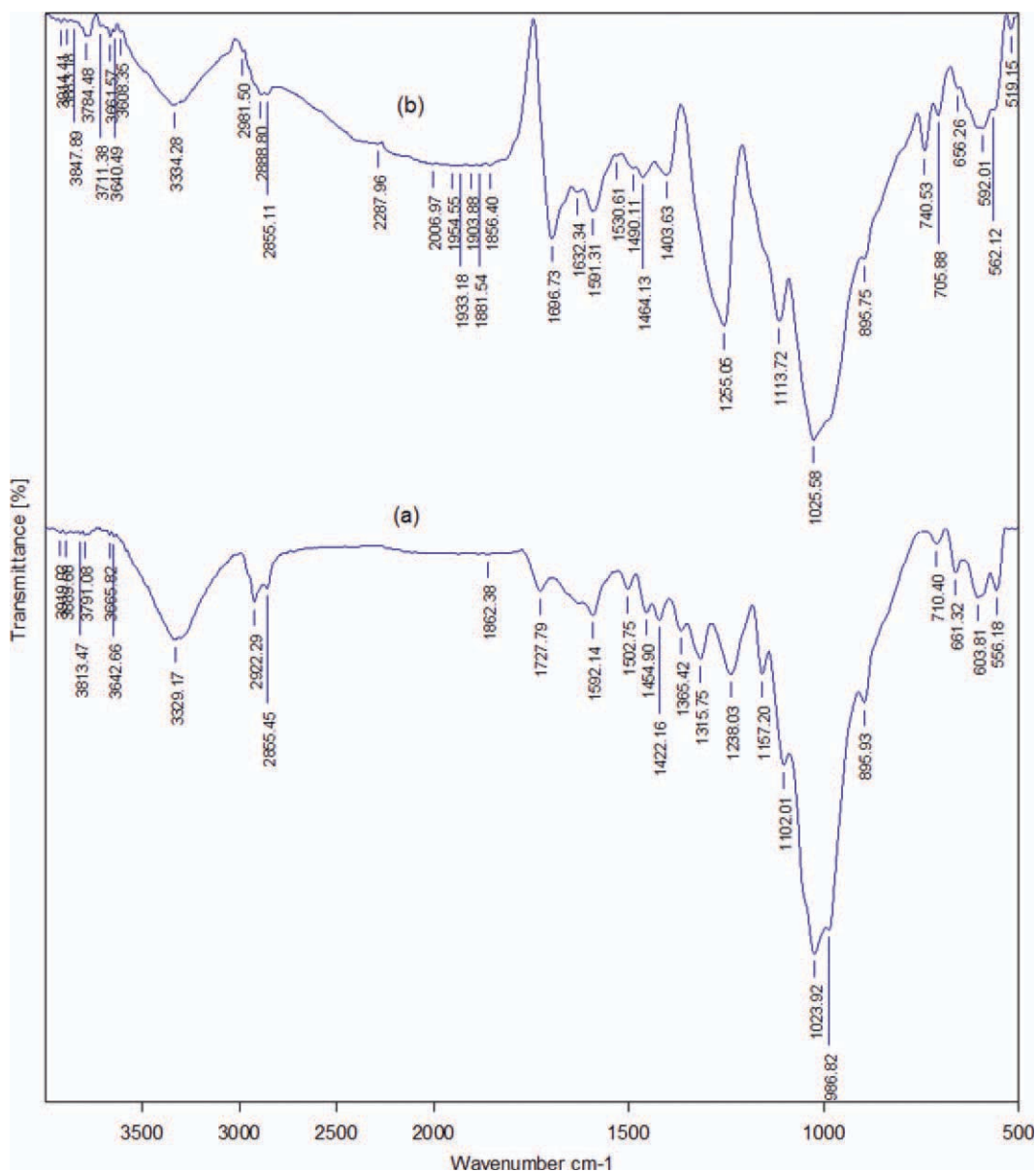
The reflectance  $R$  of dyed samples was measured on a X-Rite Color Eye 7000 A spectrophotometer measurement system, at the wavelength of minimum reflectance, under CIE Illumination D65 and d/10° illumination/observation.

### Covalent Bonded Reactive Dyes Assessment

The degree of dye fixation on the fiber ( $F$ ) was estimated by spectrophotometric comparison of the dye concentration in the dyed fabric before ( $C_1$ ) and after washing (the sample was washed with a solution containing 5 g/L cationic detergent at a liquor to goods ratio of 50 : 1, boiled for 30 min, rinsed with



Scheme 1. Schematic representation of the method of jute fiber modification.



**Figure 3.** FTIR spectra of: (a) untreated jute yarn; (b) dendrimer-treated jute yarn. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

water and air-dried) ( $C_2$ ). Kubelka–Munk's equation was used, in which the relative dyeing strength ( $K/S$ ) is proportional to the concentration of dye in the fiber.<sup>18–20</sup> It is worth mentioning that the fixation value was estimated based on a soaping technique.

$$(K/S)_1 = (1 - R)^2 / (2R) = kC_1 \quad (2)$$

where:  $R$ —the reemission coefficient,  $K$ —the absorption coefficient,  $S$ —the reflection coefficient.

The relative degree of dye fixation was assessed by the comparison of the relative strength of dyeing.<sup>21,22</sup>

$$F(\%) = C_2/C_1 \times 100\% = (K/S)_2 / (K/S)_1 \times 100(\%) \quad (3)$$

### Light-Fastness

The light-fastness of treated and untreated samples was tested on fad-o-meter (Sima Nassaj co. Iran) after partially exposing the samples to the Xenon arc lamp for 2 h. The color change was estimated by calculating  $\Delta E^*$ , which is defined by the following equation.

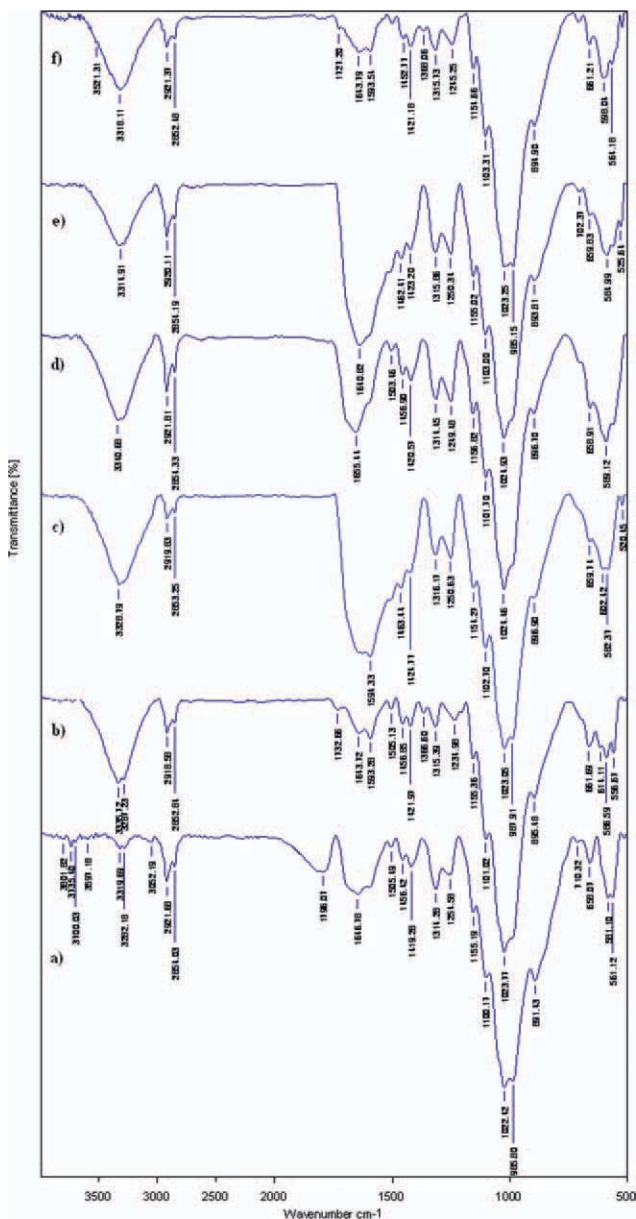
$$\Delta E^* = \sqrt{[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]} \quad (4)$$

where  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  are color difference between before and after exposing the sample to the xenon arc lamp.

### FTIR Spectroscopy

The FTIR spectra of raw and surface-treated jute fibers were recorded with Bruker Tensor 27 spectrophotometer (Bruker Corporation, Germany) using KBr pellet technique. The dried fiber



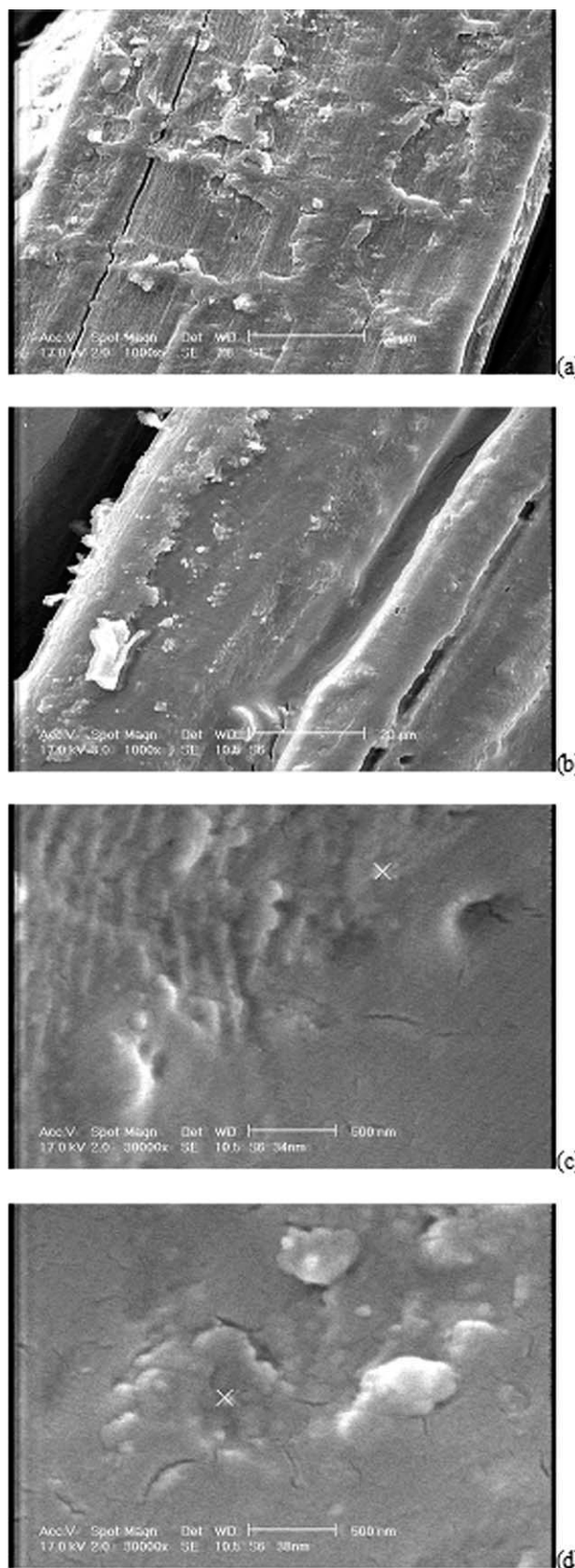


**Figure 4.** FTIR spectra of dyed samples: (a) Untreated jute yarn dyed with C.I. Reactive Blue 66; (b) dendrimer-treated jute yarn dyed with C.I. Reactive Blue 66; (c) untreated jute yarn dyed with C.I. Reactive Blue 19; (d) dendrimer-treated jute yarn dyed with C.I. Reactive Blue 66; (e) untreated jute yarn dyed with C.I. Reactive Yellow 176; and (f) dendrimer-treated jute yarn dyed with C.I. Reactive Yellow 176. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

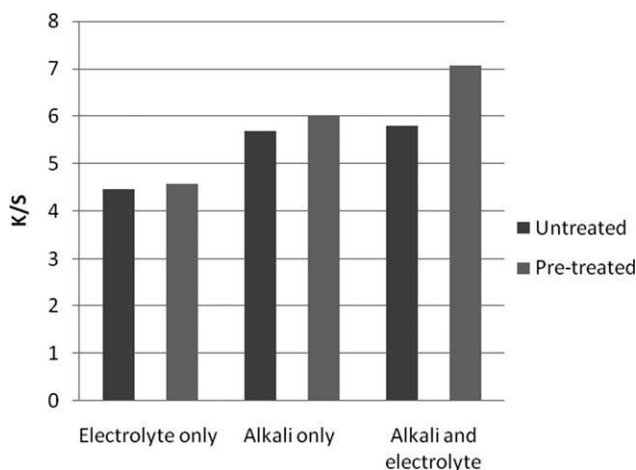
samples were crushed to a size that was finer than 20 meshes before pelleting with KBr. The test KBr pellet contained about 1% powdered fiber. Untreated and treated jute fibers were analyzed by FTIR spectroscopy with a resolution of  $4\text{ cm}^{-1}$  and a scanning range from  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ .

### Scanning Electron Microscopy

The surface morphology of jute specimens was examined by a Philips XL30 Scanning Electron Microscope (SEM) with an



**Figure 5.** SEM image of (a) untreated jute 1000 $\times$ . (b) Dendrimer-treated jute 1000 $\times$ . (c, d) Dendrimer-treated jute 30,000 $\times$ .



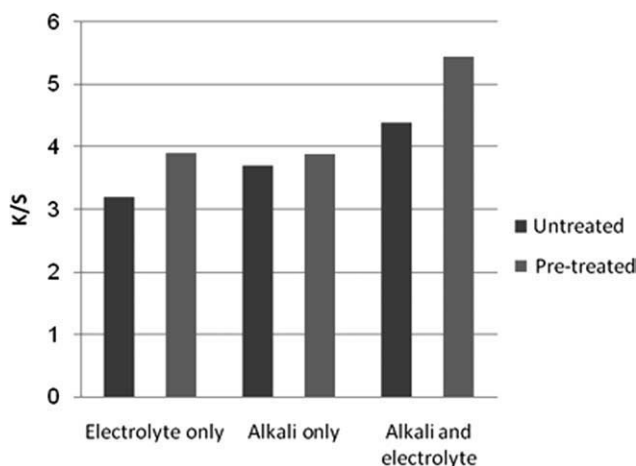
**Figure 6.** Color strength of 2% owf C.I. Reactive Blue 19 dyeing produced in the absence or present of electrolyte and alkali.

accelerating voltage of 17.0 kV and a high magnification power up to  $\times 30,000$ .

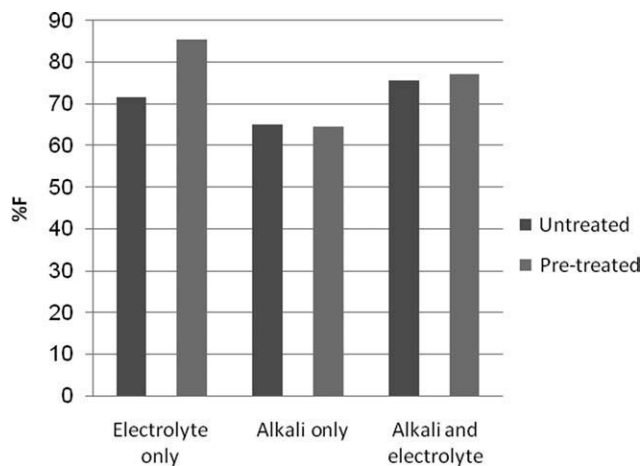
## RESULTS AND DISCUSSION

### FTIR Analysis

In contrast, cellulose contains only anhydrous glucose, hemicellulose contains many different sugar monomers. For instance, besides glucose, sugar monomers in hemicellulose can include xylose, mannose, galactose, rhamnose, and arabinose. Hemicelluloses contain most of the D-pentose sugars, and occasionally small amounts of L-sugars as well. Xylose is always the sugar monomer present in the largest amount, but mannuronic acid and galacturonic acid also tend to be present. The preparation process of PAMAM dendrimer grafted jute fibers is summarized in Scheme 1. The jute yarn (containing xylose) was immersed in a dendrimer-ethanol solution, and the resulting jute yarn was air-dried at ambient temperature. The resulting jute yarn



**Figure 7.** Color strength of 2% owf C.I. Reactive Blue 19 dyeing produced in the absence or present of electrolyte and alkali, after wash off with cationic detergent.

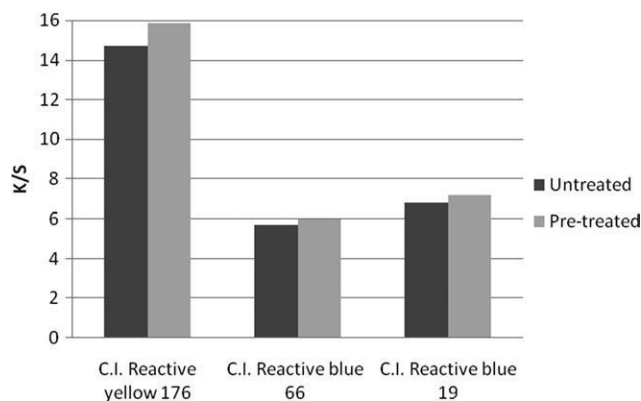


**Figure 8.** Effect of dendrimer pretreatment on fixation of reactive dyes measured by cationic detergent.

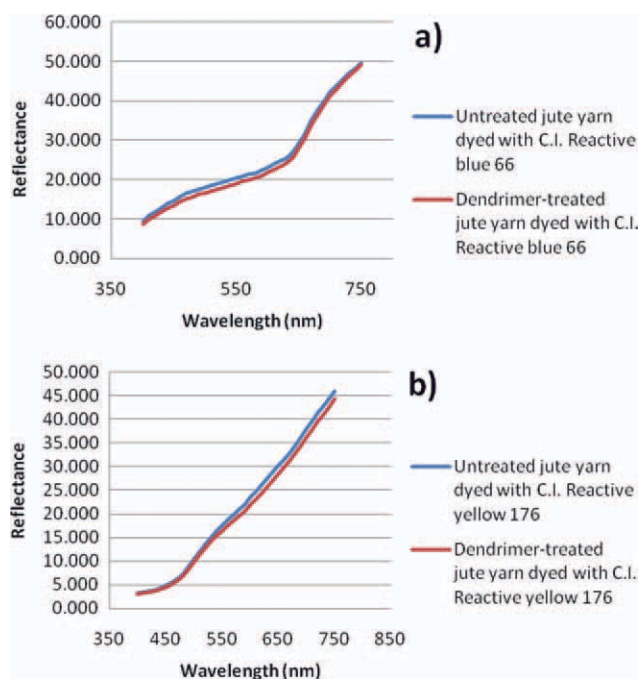
would be coupled with the amino groups of the dendrimer at 100°C in oven for 50 min.

The reaction process was monitored by infrared spectroscopy. Figure 3 shows the spectra of the untreated jute yarn and the dendrimer-grafted jute yarn. The characteristic absorption band of the untreated jute yarn, which clearly appeared at 1727.79  $\text{cm}^{-1}$  due to the stretching vibration of the C=O double bond of the aldehyde group, disappeared after the graft reaction with PAMAM dendrimer. This peak completely disappears from the spectra of PAMAM dendrimer grafted jute yarn as a result of the imination reaction. In this step, the imine group was produced, corresponding to the appearance of the absorption intensity of the R-CH=N-R band in the region of  $\sim 1690 \text{ cm}^{-1}$ .

In addition, the absorption peak at 1632.34  $\text{cm}^{-1}$  in the IR spectrum of the PAMAM dendrimer-grafted jute yarn corresponds to the R-NH<sub>2</sub> bending of the primary amine. It was found that the PAMAM-based dendrimer was successfully applied to the jute yarn. The yarn treated with PAMAM dendrimer showed signal at 1530.61  $\text{cm}^{-1}$ , which can be attributed



**Figure 9.** Comparison of color strength of untreated and dendrimer-treated jute yarns in salt-free dyeing (all dye concentrations were 2% owf).

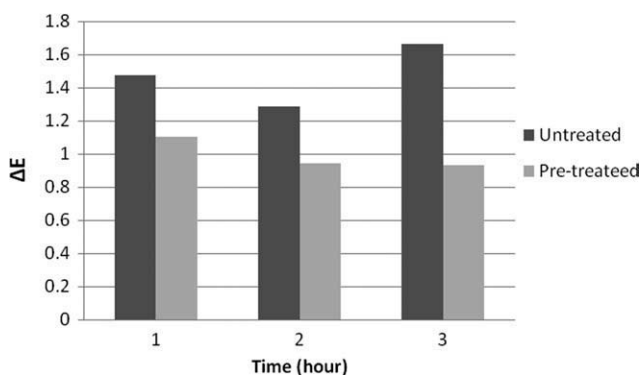


**Figure 10.** The UV-spectra of dyed samples: (a) dyed with C.I. Reactive Blue 66, (b) dyed with C.I. Reactive Yellow 176. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

to amide II (NH) modes on the basis of the dendrimeric structure of this chemical. This finding led us to the conclusion that PAMAM dendrimer can be grafted to the jute fiber by the reaction of the aldehyde groups of the hemi-cellulose with the amino groups of PAMAM. The result of this analysis was also confirmed by the FTIR spectra of both untreated and dendrimer-treated jute yarns dyed with the three reactive dyes (Figure 4).

### SEM Analysis

To check the applications of the yarn treated with PAMAM, the sample was examined with an SEM that exhibited good dispersion on the yarn surface, as seen in Figure 4. The average size reported by the manufacturer is about 2–3 nm.<sup>16</sup> Figure 5 rep-



**Figure 11.** Effect of dendrimer treatment on light fastness (expressed as  $\Delta E$ ) of the yarns dyed with C.I. Reactive Blue 19.

**Table I.** Effect of Alcohol and Dendrimer on the Color Strength of 2% owf C.I. Reactive Blue 19

Pretreatment	Alkali and electrolyte K/S	Alkali only K/S
Untreated	5.798	5.686
Untreated	5.798	5.686
Ethanol	5.66	5.761
Ethanol + dendrimer	7.065	6.008

resents the SEM image of gold-coated PAMAM nanoparticles. It can be seen from the Figure 5(c, d) that the shape of PAMAM particles is spherical and the size of nanoparticle increased by 34–38 nm due to the gold coating.

### Dyeing Properties of the Dendrimer Grafted Jute Yarns

Figure 6 shows the color strength of the dendrimer-grafted jute yarns and untreated jute yarn dyed with 2% owf C.I. Reactive Blue 19 in the absence or the presence of electrolyte and alkali, using a competitive dyeing method in which the dendrimer-grafted jute yarns and the untreated jute yarns were dyed in the same dye bath.

Reactive dyes typically rely on large amounts of electrolyte to achieve satisfactory results for their reaction with cellulosic fibers. It was decided to determine whether the pretreatment of jute with the dendrimer would permit salt-free dyeing to be achieved.

Figure 6 reveals that for untreated jute, a reduction in color strength occurred when alkali or electrolyte was not used. These findings were expected and clearly demonstrate the importance of using a high pH and electrolyte in the dyeing of jute with the reactive dye used.

Figure 6 also shows that an identical behavior was obtained for the dyeing of pretreated jute insofar as a reduction in color strength occurred when alkali or electrolyte was not used.

However, Figure 6 clearly shows that the color strength achieved for the dendrimer pretreated jute was much larger than that obtained for the corresponding dyeing of untreated material.

In addition, the color strength gained for the dendrimer pretreated yarn with electrolyte absent was much higher than that obtained for the untreated jute yarns in the presence of both electrolyte and alkali.

K/S values after washing off with cationic detergent, and fixation percentage of the dyed dendrimer pretreated jute yarns and those properties of the untreated dyed jute yarns were tested. The results are shown in Figures 7 and 8. Compared with the untreated jute yarns, the dendrimer pretreated yarns displayed markedly enhanced color strength after washing off when using salt-free or alkali-free dyeing and had good dye fixation. Figure 8 also reveals that dyeing in absence of alkali produced highest dye fixation.

At low pH, the primary and tertiary amine groups of the dendrimer are protonated. The ensuing local high positive charge density should act as a primary point of attraction for the



anionic dye molecules. When the pH is subsequently increased during the dyeing process, the amines are deprotonated and the liberated primary amine groups can serve as highly reactive nucleophilic sites for the dyes.<sup>2</sup> In the dyeing of the dendrimer-treated jute yarn in the absence of alkali, the adsorption of the reactive dyes is assisted by ionic attraction between the cationic  $-\text{NH}_3^+$  sites on the dendrimer-treated jute yarn and the disulfonated anions on the reactive dyes.

The results so far were obtained using one dye, namely C.I. Reactive Blue 19. Electrolyte-free dyeing was conducted using this same dye together with two other reactive dyes. Figure 9 shows that for each of the three dyes used, dendrimer pretreatment resulted in enhanced color strength. The result of this analysis was also confirmed by the UV-spectra of both untreated and dendrimer-treated jute yarns dyed with the reactive dyes (Figure 10).

Light-fastness of the dyed dendrimer-treated jute yarn in salt-free dyeing and this property of the untreated jute yarn were tested. The results are shown in Figure 11. Compared with the untreated jute yarn in salt-free dyeing, the dendrimer-treated jute yarns had a good light-fastness. This is attributable to the increased uptake of the photostable dye on the fibers.

Table I shows the effect of alcohol in dendrimer pretreatment. It is obvious that ethanol cannot significantly alter the color strength of jute yarn.

## CONCLUSIONS

In conclusion, an amino-terminated PAMAM dendrimer-grafted jute was obtained by the reaction between the aldehyde groups on the jute yarn and the amino groups of the PAMAM dendrimer. Dendrimer-pretreated jute displayed markedly enhanced color strength, even when dyeing with reactive dyes had been carried out in the absence of electrolyte or alkali. Their use as a pretreatment of jute fibers might thus offer considerable savings of electrolyte and alkali. Satisfactory light-fastness was also obtained.

## REFERENCES

- Cai, Y.; David, S. K.; Pailthorpe, M. T. *Dyes Pigm.* **2000**, *45*, 161.
- Callow, H. J.; Speakman, J. B. *J. Soc. Dyers Colourists* **2008**, *65*, 758.
- Chattopadhyay, S. N.; Pan, N. C.; Da, A. *Bioresour. Technol.* **2006**, *97*, 77.
- Burkinshaw, S. M.; Mignanelli, M.; Froehling, P. E.; Bide, M. J. *Dyes Pigm.* **2000**, *47*, 259.
- Blencowe, A.; Tan, J. F.; Goh, T. K.; Qiao, G. G. *Polymer* **2009**, *50*, 5.
- Jockusch S.; Turro N. J.; Donald A.; Tomalia D.A. *Macromolecules* **1995**, *28*, 7416.
- Pelegri, R.; Peralta-Zamorab, P.; de Andrade, A. R.; Reyes, J.; Durán, J. N. *Appl. Catal. B: Environ.* **1999**, *22*, 83.
- Zhang, F.; Chen, Y.; Lin, H.; Wang, H.; Zhao, B. *Carbohydr. Polym.* **2008**, *74*, 250.
- Zhang, F.; Chen, Y. Y.; Lin, H.; Lu, Y. H. *Color. Technol.* **2007**, *123*, 351.
- Ghosh, S.; Yadav, S.; Vasanthan, N.; Sekosan, G. J. *Appl. Polym. Sci.* **2010**, *115*, 716.
- Balogh, L.; Swanson, D. R.; Tomalia, D. A.; Hagnauer, G. L.; McManus, A. T. *Nano Lett.* **2001**, *1*, 18.
- Aymonier, C.; Schlotterbeck, U.; Antonietti, L.; Zacharias, P.; Thomann, R.; Tiller, J. C.; Mecking, S. *Chem. Commun.* **2002**, 3018.
- Mahapatra, S. S.; Karak, N. *Mater. Chem. Phys.* **2008**, *112*, 1114.
- Prosycevas, I.; Tamuleviciene, A.; Guobiene, A.; Adliene, D.; Puiso, J.; Abdrakhmanov, O. *Mater. Sci. (MEDŽIAGOTYRA)* **2010**, *16*.
- Dastjerdi, R.; Montazer, M. *Colloids and Surfaces B: Biointerfaces* **2010**, *79*, 5.
- Khanafari, A.; Ahmadi-Fakhr, F. J. *Toxicol. Sci.* **2010**, *2*, 203.
- Esfand, R.; Tomalia, D. A. In *Dendrimers and Other Dendritic Polymers*; Frechet, J.M. J., Tomalia D. A., Eds.; Wiley: Baffins Lane, Chichester, **2002**; p 587.
- Kamel, M. M.; El-Shishtawy, R. M.; Hanna, H. L.; Ahmed, N. S. *E. Polym. Int.* **2003**, *52*, 373.
- Soleimani-Gorgani, A.; Taylor, J. A. *Dyes Pigm.* **2006**, *68*, 109.
- El-Shishtawy, R. M.; El-Zawahry, M. M.; Ahmed, N. S. *E. Color. Technol.* **2011**, *127*, 28.
- Yazdanshenas, M. E. Thesis (Ph.D.), Leicester Polytechnic, Leicester, UK, **1983**.
- Yazdanshenas, M. E. Instability of Reactive Dyeing to Oxidation. Council for National Academic Awards: London, UK, **1983**.