The application of poly(amidoamine) dendrimers for modification of jute yarns: Preparation and dyeing properties

Ali Akbar Zolriasatein a,*, Mohammad Esmail Yazdanshenas b,*, Ramin Khajavi c, Abosaeed Rashidi a

a Department of Textile Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran
b Department of Textile Engineering, Yazd Branch, Islamic Azad University, Yazd, Iran
c Department of Textile Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran

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Abstract In this study, poly(amidoamine) (PAMAM) G-2 dendrimer was used for jute yarn. Fourier transform infrared spectroscopy (FT-IR) revealed that all carbonyl groups of jute fibers reacted with amino groups of polyamidoamine dendrimers. SEM observation indicated the good dispersion of PAMAM dendrimers. Jute yarns 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 untreated jute yarn.

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1. Introduction

Colouration 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 restrict the uses of jute products is that jute suffers seriously from light induced discoloration, due to the phenolic structures of lignin (Cai et al., 2000; Callow and Speakman, 2008).

In case of dyeing of jute with reactive dyes, dyes reacts with hydroxyl group of the fiber by either substitution or addition reactions (Chattopadhyay et al., 2006). For reaction with cellulosic fibers, reactive dyes typically rely on an elevated pH (commonly over 10.5) and large amounts of electrolyte (NaCl or Na2SO4) 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. Greatest problem is dye hydrolysis or the reaction of dyes with water, since hydrolysis blocks the reactive sites so that the dyes cannot covalently bond with
fibers. The hydrolyzed dye retains 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. In addition, it results in an increase of pollution load in the environment (Burkinshaw et al., 2000).

An alternative approach to increase dye uptake and dye fixation is the modification of cellulosic fibers themselves. In essence, attention has focused on the introduction of cationic groups by means of pretreatment, commonly via quaternised 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 dyeing. In addition, if the cationic pretreatment compound also contains 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 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 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 (Blenecow et al., 2009). The nature of the outer functional groups determines the solubility and reactivity of the dendrimers. Each layer in a dendrimer is termed a single generation.

Because of their unique chemical and physical properties, dendrimers and hyperbranched polymers have received much attention over the past two decades and have been used in coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology and supramolecular science.

Dendritic polymers are typical compounds used in this aspect. With 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 with reactive dyes has become a popular topic. Most researchers focus on introducing cationic groups like amino or ammonium groups into cotton fabrics for interactions with anionic dyes. Dendrimers dyeing pretreatment enhances colour strength of cotton fabric (Burkinshaw et al., 2000; Wei et al., 2005; Jockusch et al., 1995). Amino-terminated hyperbranched polymer (HBP-NH₂) grafted cotton fiber displays markedly enhanced color strength when dyed with reactive dyes using salt-free dyeing. The washing-fastness and rubbing-fastness of the dyed hyperbranched grafted cotton fabrics are also good compared with those obtained by conventional dyeing (Zhang et al., 2008).

In the presence of citric acid, the pretreatment of cotton with the amino-terminated hyperbranched polymers as cross-linking agents can also enhance the dyeability of the cotton fiber with reactive dyes (Zhang et al., 2007).

The use of dendrimers as an antimicrobial agent can be beneficial because of their unique structures (Ghosh et al., 2010). It is 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 (Balogh et al., 2001; Aymonier et al., 2002; Mahapatra and Karak, 2008; Prosycevas et al., 2010; Dastjerdi and Montazer, 2010).

The present work aimed to understand whether the pretreatment of jute yarns with dendrimers could improve its dyeability to reactive dyes. Color strength (K/S) and light-fastness (L.F.) of treated yarns were obtained and compared to conventional dyeing method. Dendrimer of generation 2 was used to study. Since, it is less dense than water, grafting treatment was performed in alcoholic media.

2. Experimental

2.1. Materials

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

2.2. Dendrimer

Polyamidoamine (PAMAM) dendrimers of generation 2 with 16 surface groups, 3,256 molecular weight and 2.6 nm dendrimer were obtained from Institute for Color Science and Technology, Tehran, Iran (Khanafari and Ahmadi-Fakhr, 2010). The synthesis of poly(amidoamine) (PAMAM) dendrimer with ethylenediamine (EDA) core up to the second generation (G2) was performed using the divergent procedure presented by Esfland and Tomalia (2002).

2.3. Application of dendrimers

The jute yarns were first immersed into dendrimer–ethanol solution at concentration of 2.5%/omf at room temperatures for 3 h, maintaining a liquor ratio of 15:1 (w/w). Next, they were air dried at room temperature for 24 h. The samples were then treated with the dendrimer in the oven at 100 °C for 50 min.

2.4. Dyeing

To highlight differences in dye uptake between the pretreated and untreated jute samples, the dyeing process was carried out using a competitive dyeing method in which both dendrimer-treated and untreated samples are dyed competitively in the same dyebath. Dyeing with reactive dyes was performed at a liquor ratio of 50:1. Dyeing of the samples was started at 30 °C for Blue 19 and Yellow 176, and at 60 °C for Blue 66 for 50 min. The samples were left at this temperature for 30 min in the presence of sodium chloride (60 g/l). Afterwards, sodium carbonate (20 g/l) was added for dye fixation and dyeing continued at 30 °C for another 30 min.
2.5. Color strength of dyed yarns

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

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

(1)

The reflectance ($R$) of dyed samples was measured by a X-Rite Color-Eye 7000A spectrophotometer, at the wavelength of minimum reflectance, under CIE D65 standard illumination and at $d/10^\circ$ illumination/observation angle.

2.6. Assessment of covalent bonded reactive dyes

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 ($C_2$) (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, then rinsed with water and air-dried). Kubelka–Munk’s equation was used, in which the relative dyeing strength ($K/S$) is proportional to the concentration of dye in the fiber (Kamel et al., 2003; Soleimani-Gorgani and Taylor, 2006; El-Shishtawy et al., 2011). It is worth mentioning that, the fixation value was estimated based on a soaping technique.

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

(2)

where $R$ is the re-emission coefficient, $K$ is the absorption coefficient, $S$ is the reflection coefficient.

The relative degree of dye fixation was assessed by the comparison of the relative strength of dyeings (Yazdanshenas, 1983a,b).

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

(3)

2.7. Light-fastness

The light-fastness of the 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 3 h. The colour change was obtained from $\Delta E^*$ which can be calculated by the following equation.

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

(4)

where, $\Delta L^*$, $\Delta a^*$ and $\Delta b^*$ are color difference values before and after xenon arc lamp exposure.

2.8. FT-IR spectroscopy

The FTIR spectra of raw and treated jute fibers were recorded with a Bruker Tensor 27 FT-IR spectrophotometer (Bruker Corporation, Germany) using the KBr pellet technique. The dried fiber samples were crushed to a size finer than 20 mesh before pelletizing with KBr. The test KBr pellets contained about 1% powdered fiber. Comparative analysis of untreated and treated jute fibers was conducted by a FTIR spectroscopy in the range of 4000–400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.

2.9. Scanning electron microscopy (SEM)

The morphological properties of jute specimens were examined by a Scanning Electron Microscope (SEM) (Philips XL30) operated at 17.0 kV and high magnification ($>30,000\times$).

3. Results and discussion

3.1. FT-IR analysis

Unlike cellulose which only contains 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. Scheme 1 summarizes the preparation process for PAMAM dendrimer grafted jute fibers. After immersing in a dendrimer–ethanol solution, the jute yarn (containing xylose) was air-dried at room temperature. The amino groups of the dendrimer was coupled with the resulting jute yarns in the oven at 100 $^\circ$C for 50 min.
An infrared spectroscopy was utilized to monitor reaction processes. Fig. 1 shows the FT-IR spectra of the untreated and dendrimer grafted jute yarns. The characteristic absorption band of the untreated jute yarn, which clearly appeared at 1727.79 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 spectrum 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=\textit{N}–R band at the region ~1690 cm\(^{-1}\). In addition, the peak at 1632.34 cm\(^{-1}\) in the FT-IR absorption spectrum of the PAMAM dendrimer grafted jute yarn corresponded to the R–NH\(_2\) bending for the primary amines. It was found that the PAMAM dendrimers were successfully applied on the jute yarn. The yarn treated with poly(amidoamine) dendrimer showed 1530.61 cm\(^{-1}\) signals, which can be attributed 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 onto jute fibers through the reaction of the aldehyde groups of the hemi-cellulose with the amino groups of PAMAM.

3.2. SEM analysis

To check the applications of the yarn treated with PAMAM, the sample was examined with an SEM that showed good dispersion on the yarn surface, as seen in Figs. 3 and 4. The average size reported by the manufacturer is about 2–3 nm (Khanafari and Ahmadi-Fakhr, 2010). Fig. 4 represents the SEM image of PAMAM gold coated nanoparticles. In Fig. 4c and d, it can be seen that the PAMAM particles is spherical in shape, also the nano-particles increase by 34–38 nm in size due to the gold coating.

3.3. Dyeing properties of dendrimer grafted jute yarns

Fig. 5 shows the color strengths of the dendrimer grafted jute yarns and untreated jute yarns dyed at 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 dyebath.

For their reaction with cellulosic fibers, reactive dyes typically rely on large amounts of electrolyte to achieve satisfactory results. The purpose was to determine if the pretreatment of jute with the dendrimer would permit salt-free dyeing to be achieved.

Fig. 5 reveals that for untreated jute sample, a reduction in color strength occurred when alkali or electrolyte was not used. As expected, these findings clearly demonstrate the importance of using a high pH and electrolyte in the dyeing of jute with reactive dye.

Fig. 5 also indicates that an identical behavior has so far been obtained for the dyeing of pretreated jute samples as a reduction in color strength when alkali and electrolyte were not used.

However, Fig. 5 clearly shows that the color strength achieved for the dendrimer pretreated jute was much larger than those obtained for the corresponding untreated materials.

In addition, the color strength obtained for the dendrimer pretreated yarn in the absence of electrolyte 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, fixation percentage of the dyed dendrimer pretreated jute yarns and those of the untreated dyed jute yarns were tested. The results are presented in Figs. 6 and 7. Compared with the untreated jute yarns, the dendrimer pretreated yarns displayed markedly enhanced color strength.
after washed-off using salt-free or alkali-free dyeing method, and had good dye fixation. Furthermore, Fig. 7 reveals that highest dye fixation can be result in the absence of alkali.

At low pH values, the protonation of primary and tertiary amine groups within the dendrimer is occurred. 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 (Callow and Speakman, 2008). For dyeing the dendrimer treated jute yarn in the absence of alkali, the adsorption of the reactive dyes is assisted by ionic attraction between the cationic –NH\textsubscript{3}\textsuperscript{+} sites on the dendrimer treated jute yarn and the disulphonated anions on the reactive dyes.

The results were so far obtained by using one dye, i.e. C.I. Reactive Blue 19. Electrolyte-free dyeing was conducted using this same dye together with two other reactive dyes. As seen in Fig. 8 for each dyes used, dendrimer pretreatment may result in an enhanced color strength. Interestingly, the effect of pretreatment on color strength was especially marked in the case of C.I. Reactive yellow 176.

Light-fastness properties of the dyed dendrimer-treated sample and also of the untreated sample were tested by the salt-free dyeing method. Fig. 9 presents the results. Compared with the untreated jute yarn in the salt-free dyeing, the...
dendrimer-treated jute yarns had a good light-fastness. This is attributable to the increased uptake of the photostable dyes on the fibers.

Table 1 shows the effect of alcohol on dendrimer pretreatment. It is obvious that ethanol cannot change the color strength of jute yarn significantly.

Figure 4 SEM images for (a) untreated jute 1000×, (b) Dendrimer treated jute 1000×, (c) and (d) Dendrimer treated jute 30,000×.

Figure 5 Color strength of 2% owf C.I. Reactive Blue 19, dyeing produced in the absence or present of electrolyte and alkali.

Figure 6 Color strength of 2% owf C.I. Reactive Blue 19 dyeing produced in the absence or present of electrolyte and alkali, after washed off with cationic detergent.
4. Conclusions

In conclusion, an amino-terminated poly(amidoamine) dendrimer grafted jute yarn was obtained from a reaction between the aldehyde groups on the jute yarn and the amino groups of the PAMAM dendrimer. Dendrimer pretreated jute sample displayed markedly enhanced color strength, even when dyeing with reactive dyes had been carried out in the absence of electrolyte or alkali. Thus, their application as a pretreatment agent for jute fibers might provide considerable savings on electrolyte and alkali. Satisfactory light-fastness was also obtained.

References


