

## Modification of Jute Fabric via Laccase/*t*-BHP-Mediated Graft Polymerization with Acrylamide

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**ABSTRACT:** Enzymatic processes provide new perspectives for the modification of lignocellulose materials. Lignin is an excellent substrate for laccase, and the modification of lignin-rich jute fabric via graft polymerization with acrylamide (AAM) mediated by laccase and *tert*-butyl hydroperoxide (*t*-BHP) was investigated in this study. The products obtained were characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. The grafting rate was determined in terms of elemental analysis. The hydrophilicity and thermal and dyeing properties of the modified jute fabric were studied. The results supported the conclusion that the polyacrylamide was grafted on the lignin of the jute fiber by laccase in coordination with *t*-BHP, representing a grafting rate of 2.87%. The hydrophilicity, thermostability, dye uptake, and dyeing depth of the jute fiber were increased after the enzymatic graft modification with AAM. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40387.

**KEYWORDS:** fibers; grafting; radical polymerization; surfaces and interfaces; textiles

Received 2 July 2013; accepted 2 January 2014

DOI: 10.1002/app.40387

### INTRODUCTION

Natural jute fiber is a common textile material in home and industry and has broad development prospects owing to the merits of low cost, abundance, antibiosis, UV protection, thermal-wet comfortability, and biodegradability. However, it has some shortcomings such as stiffness, tickle, poor crease resistance, and being difficult to dye deeply or brightly. These disadvantages of the jute fiber limit its application in textiles. To improve the properties of the jute, the graft modification with vinyl monomers has been proved to be an important and feasible method.<sup>1</sup>

The two traditional approaches, that is, chemical initiation reaction and irradiation by high energy ray, have been applied to initiate the graft copolymerization in a free radical reaction. However, these processes are becoming increasingly unpopular because of their inherent weaknesses. Irradiation processing can seriously deteriorate the mechanical properties of the fiber and is difficult to industrialize.<sup>2,3</sup> Chemical grafting is able to create radicals at different sites on the fiber molecule resulting in graft copolymerization; however, the homopolymerization of the monomers will usually occur.<sup>4</sup> The formation of numerous homopolymers will decrease the grafting efficiency and cause the waste of the monomers. Therefore, it has important practical significance to explore new graft modification methods for the jute fiber.

In response to the shortcomings of chemical and irradiation methods, enzymatic graft modification with some biotechnological catalysts such as tyrosinase<sup>5,6</sup> and microbial transglutaminase<sup>7,8</sup> has emerged because of their ecofriendly nature and mild application conditions. Laccases (EC 1.10.3.2, *p*-diphenol : dioxygen oxidoreductase) are multicopper glycoproteins that catalyze the monoelectronic oxidation of phenols and aromatic or aliphatic amines to produce reactive radicals in a redox reaction in which molecular oxygen is simultaneously reduced to water.<sup>9,10</sup> Researches show that lignin is an excellent substrate for laccase,<sup>11–13</sup> and its grafting reaction usually involves oxidation of lignin moieties to produce reactive radicals that could initiate the grafting of foreign molecules to produce new engineering materials.<sup>14–16</sup> Based on the similar mechanism, investigations into the possibility of using laccases to covalently attach functional compounds to lignocellulosic materials such as wood, pulp, and bast fibers to endow them with novel functions are also increasing.<sup>17–21</sup> These functional monomers include phenols and aromatic or aliphatic amines, but rarely involve vinyl or acrylic compounds. Mai et al.<sup>22,23</sup> first reported the graft copolymerization of lignin and acrylamide (AAM) initiated by the combination of laccase and some peroxides in a homogeneous system. However, as far as our knowledge, no attempt has been made for the heterogeneous modification of lignocellulose materials by grafting acrylic monomers with laccase in the presence of *tert*-butyl hydroperoxide (*t*-BHP).

In this work, a laccase/*t*-BHP-assisted method of covalently grafting AAm onto the jute fabrics was studied, and the schematic illustration of the reaction has been presented in Figure 1. The products were analyzed in terms of elemental analysis, grafting rate, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) analyses. Furthermore, the hydrophilicity and thermal and dyeing properties of the modified jute fabrics were also measured.

## EXPERIMENTAL

### Materials and Reagents

Laccase Denilite II from the *Aspergillus* species (EC1.10.3.2) was provided by Novozymes (Shanghai, China). The 100% raw jute fabric, with a 7/7 (warp/weft)  $\text{cm}^{-1}$  yarn count, was supplied by Longtai Weaving Company (Changshu, China). All the other chemicals used in the study including AAm and *t*-BHP (70%) were commercially available and were of analytical purity.

### Laccase Assay

The activity of laccase was measured spectrophotometrically by monitoring the oxidation of 2,2'-azino-bis-(3-ethylthiazoline-6-sulfonate) (ABTS;  $\epsilon_{420} = 36,000 \text{ M}^{-1} \times \text{cm}^{-1}$ ) as substrate at 420 nm in 50 mM acetate buffer (pH 5) at 50°C. The enzymatic activity was expressed in units defined as micromoles of ABTS oxidized per minute.<sup>24</sup>

### Pretreatment of Jute Fabrics

The jute fabric samples were desized by boiling with distilled water for 2 h. Iodine–potassium iodine method was used to examine whether the starch or PVA sizes were dislodged completely or not.

### Grafting of AAm onto Jute Surfaces

Jute fabric sample of 1 g was incubated with 30 mL of 50 mM acetate buffer (pH 5), which contained 200% of AAm and 2 U/mL laccase in a shaking bath. Subsequently, the reaction was started by the addition of 170  $\mu\text{L}$  *t*-BHP (70%) and allowed to proceed at 50°C for 24 h. After that, the resulting sample was washed twice with distilled water at 50°C for 30 min to obtain the polyacrylamide (PAM)-grafted jute fabric. The control samples were treated under the same condition as laccase treatment, except no laccase was used.

### Elemental Analysis

The carbon, hydrogen, and nitrogen contents of the jute fabric samples were determined in an elemental analyzer (Elementar Vario EL III, Germany).

### Determination of Grafting Percentage

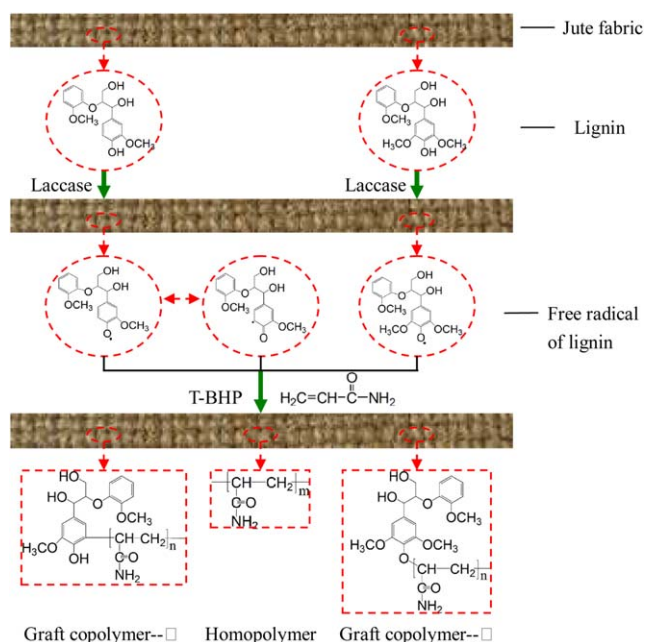
The proportion of AAm on the grafted jute was calculated from the total nitrogen content of the samples, and the grafting percentage ( $G_p$ ) was calculated by the following equation:

$$G_p (\%) = \frac{N_p - N_c}{N_a} \times 100 \quad (1)$$

where  $N_p$  is the nitrogen content on the grafted jute,  $N_c$  is the nitrogen content on the control jute, and  $N_a$  is the nitrogen content on the initial AAm monomer.

### FTIR Analysis

The FTIR analysis was performed using a Nicolet iS10 FTIR spectrometer (Thermo Fisher Scientific) with the ATR



**Figure 1.** Schematic illustration of the reaction to graft acrylamide on the lignin of jute fabrics catalyzed by laccase and *t*-BHP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

technique. The spectra were recorded in the range of 4000–650  $\text{cm}^{-1}$  at 4  $\text{cm}^{-1}$  resolution and 32 scans per sample.

### SEM Analysis

The control and grafted jute fabric samples were scanned using a SU1510 electron microscope (Hitachi, Japan) under 5 kV voltage at 2000 $\times$  magnification.

### Hydrophilicity Measurement

The hydrophilicity of the jute samples was evaluated using wetting time and contact angle. The wetting time was measured according to AATCC Test Method 79–2007. The fabric swatch was mounted in a plate to be spread tightly so that the surface is free of wrinkles and without distorting the structure of the material. The plate was placed about 10 mm  $\pm$  1 mm below the tip of a burette. A drop of distilled water was allowed to fall onto the taut surface of the test specimen. The time required for the specular reflectance of the water drop to disappear was measured using a stopwatch. Five readings were averaged as the wetting time.

The contact angle was measured in 5 s after drop deposition using a SL200B static contact angle/interfacial tension meter (Kino Industry) after conditioning to equilibrium moisture content. For each sample, the water contact angle was measured at five spots, and then the results were averaged.

### Thermal Analysis

The differential scanning calorimetry (DSC) analysis of the jute samples was performed using a Q200 DSC (TA Instruments). The curves were recorded in the range of 30–400°C with a heating rate of 20°C/min.

The thermogravimetric analysis (TGA) was conducted on a TGA/SDTA851 thermoanalysis system (Mettler Toledo Instrument,

**Table I.** Element Composition and Grafting Rate of Jute Fabrics After Different Treatments

Treatment	Element content (wt %)			C/N ratio	Grafting rate (%)
	C	N	H		
Control	46.270	0.137	5.839	394	-
Laccase	45.250	0.189	5.948	279	0.26
Laccase/ <i>t</i> -BHP	45.840	0.683	6.001	78	2.78

Switzerland) in the range of 30–700°C with a heating rate of 20°C/min.

### Evaluation of Dyeing Properties

The jute fabrics were dyed with 2% of Direct Scarlet 4BS with a liquid-to-fabric ratio of 50 : 1. This process involved dyeing at 40°C, rising to 70–90°C in 15 min, dyeing for 45 min under the constant temperature during which sodium chloride was added batchwise in twice, and final washing with distilled water.

The washing solutions containing unbound dyestuff were pooled and analyzed using a UV-2802S spectrophotometer at the maximum absorbance of the Direct Scarlet 4BS ( $\lambda_{\max} = 506$  nm). The dyeing exhaustion was calculated according to the following equation:

$$E(\%) = \frac{A_0 - A_1}{A_0} \times 100\% \quad (2)$$

where  $E$  (%) is dye uptake,  $A_0$  is the absorbance of solution before dyeing, and  $A_1$  is the absorbance of solution after dyeing.

The  $K/S$  values of the fabrics were measured by a ColorEye-7000A spectrophotometer (CretagMacbeth) with D65, a visual angle of 10° and CIE-Lab color measuring system. The fabrics were folded in four layers and measured in triplicate.

## RESULTS AND DISCUSSION

### Estimation of Grafting Percentage via Elemental Analysis

The carbon, hydrogen, and nitrogen contents of the jute fabric samples treated with laccase/*t*-BHP, laccase only, and neither in the presence of AAm are shown in Table I. The grafting rates of AAm were also calculated according to the nitrogen contents. The nitrogen contents of the jute fabrics grafting AAm by laccase in the presence and absence of *t*-BHP were 0.683% and 0.189%, respectively, in comparison with 0.137% for the corresponding value of the control jute fabric. The grafting rate of AAm on the jute fabric in the free radical graft copolymerization initiated by laccase and *t*-BHP reached 2.78% in contrast to 0.26% obtained by laccase alone.

The study by Mai et al.<sup>22,23,25</sup> on grafting AAm to organosolv lignin has shown that although the laccase in the reaction medium is essential for the initiation of the polymerization process, its catalysis alone is insufficient to produce a significant yield of the copolymerizates; a combination of laccase and proper organic peroxides could cause an abundant copolymer production. The slight increases in the nitrogen content and grafting rate of the laccase-treated jute fabrics may result from the residuals of laccase or AAm. The laccase/*t*-BHP-initiated

system could start the graft copolymerization of AAm onto the lignins in the jute fibers to endow them with desired properties such as hydrophilicity, feeble tickle, thermoresistance, and easy dyeing.

### FTIR Analysis

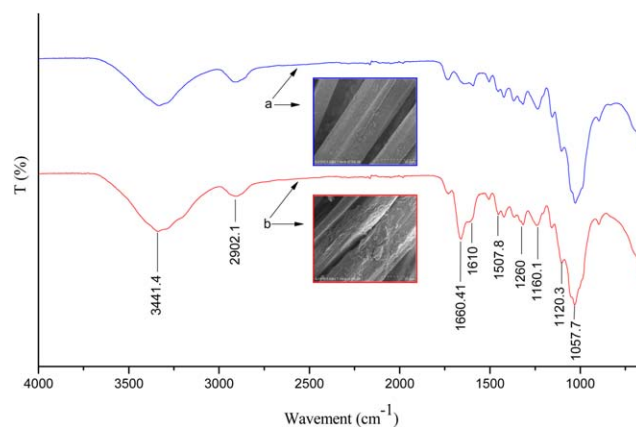
Figure 2 shows the IR spectra of the pretreated and grafted jute fabric samples. A broad peak corresponding to the —OH stretching vibration is observed at 3441.4  $\text{cm}^{-1}$ , and the C—H vibrations of methyl and methylene appears at 2902.1  $\text{cm}^{-1}$ . The peaks at 1160.1, 1120.3, and 1057.7  $\text{cm}^{-1}$  represent the C—O— vibrations of cellulose, and the peak at 1507.8  $\text{cm}^{-1}$  shows the aromatic skeletal vibration of lignin.<sup>26</sup> When compared with the control jute, the spectrum of the grafted jute fabric has three stronger peaks at 1660.41, 1610, and 1260  $\text{cm}^{-1}$ , which correspond to the C=O vibration, the N—H vibration, and the C—N vibration of —CONH<sub>2</sub>, respectively.<sup>27</sup> The distinctions of the two spectra indicated that PAM has been grafted onto the jute fabrics in the presence of laccase and *t*-BHP.

### SEM Analysis

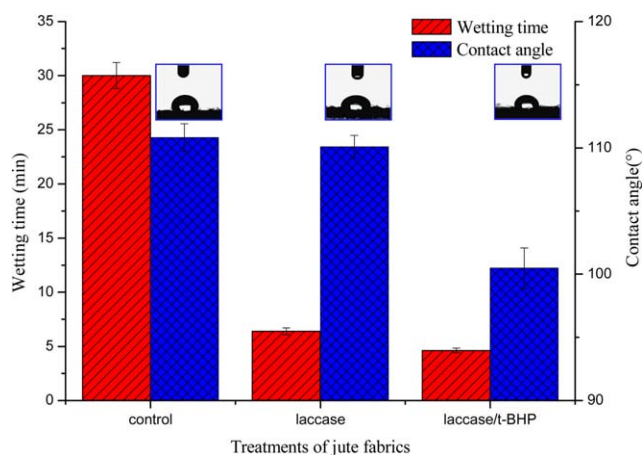
As shown in Figure 2, the surfaces of the ungrafted jute fibers were neatly arranged with few particles of impurities existing on the surface [Figure 2(a)]. The water boiling process removed the starch or PVA sizes, but was unable to dislodge pectins on jute. After grafting modification, the surface morphology of the jute fiber became rough and irregular [Figure 2(b)]. The materials observed on the fiber surface were considered as the graft copolymers of AAm. The SEM microphotographs clearly represented the grafting of AAm on the surface of the jute fiber.

### Effect of the Grafting of AAm on the Hydrophilicity of Jute

The effect of the incorporation of PAMs to the jute fabrics on their hydrophilicity was investigated in terms of the wetting time and the contact angle. As shown in Figure 3, laccase treatment alone caused just a slight decrease in the contact angle in contrast to the control treatment (110.82°). However, the laccase/*t*-BHP-mediated jute fabric showed a contact angle of



**Figure 2.** FTIR spectra and SEM images of the pretreated jute fabric sample (a) and the one pretreated and then grafted by laccase and *t*-BHP (b). The images of SEM were both amplified at  $\times 2000$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** The wetting time and contact angle of control, laccase-treated jute fabrics, and laccase/*t*-BHP-treated jute fabrics in the presence of acrylamide. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

100.47°, representing a 9.61° decrease when compared with the laccase-treated jute fabric without *t*-BHP.

The wetting time of the jute fabrics grafted with AAmS catalyzed by the combination of laccase and *t*-BHP was also lower than that treated with laccase alone or neither, which corresponded well with the contact angle. It is obvious that the introduction of  $-\text{CONH}_2$  by AAmS grafting could enhance the hydrophilicity of the jute fabrics.

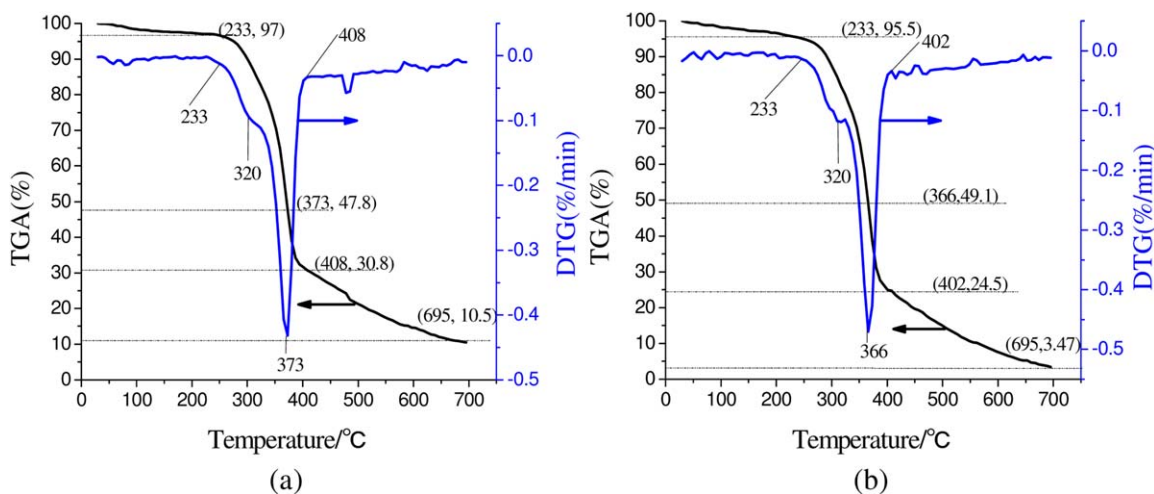
### Thermal Analysis

The pyrolysis characteristics, both TGA (in wt %) and DTG (in wt %/°C) curves of the control and grafted jute fabrics, are shown in Figure 4. Some differences in the pyrolysis behavior of the control and grafted jute fabrics were found. These fabrics started their decomposition at the same temperature (233°C); however, the main weight loss of the grafted jute was terminated at 408°C, representing an increase of 6°C when compared with that of the control jute (402°C). The grafted jute got the

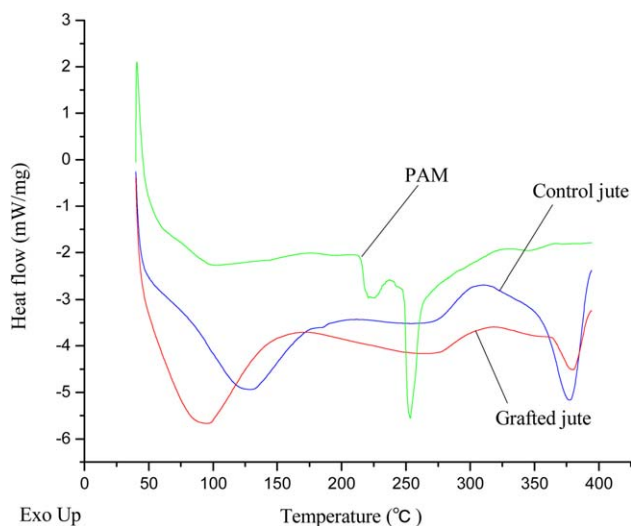
maximum mass loss rate ( $-0.43 \text{ wt \%}/^\circ\text{C}$ ) at 373°C, and there was still 10.5% solid residue left even at 695°C. The control jute attained its maximum mass loss rate ( $-0.47 \text{ wt \%}/^\circ\text{C}$ ) at 366°C, and most jute was pyrolyzed with a lower solid residue (3.47%) left. All these changes indicated that the heat resistance of the jute fiber was enhanced by the grafting of AAm.

Besides the TGA and DTG curves of the fibers that were used to reveal the degradation behavior of the jute fibers, the DSC curves showing the energy consumption property in pyrolysis were also measured. The results are plotted in Figure 5. From the DSC curve of PAM, a drastic endothermic peak at 253.5°C could be observed. The DSC curves of the control and grafted jute fabrics showed a similar tendency. The reactions that occurred below 200°C were all endothermic, which mainly contributed to the removal of moisture when the sample was heated up. The peak of the grafted jute was found at 95°C, which was lower than that of control jute (129°C), indicating that the grafted jute got more free moisture resulting from the hydrophilic PAM chain on it. The DSC profiles showed a broad exothermic peak at about 320°C and a sharp endothermic peak from 370 to 390°C with the further increase in temperature ( $>200^\circ\text{C}$ ). Ball et al.<sup>28</sup> pointed out that the charring process was highly exothermic, whereas volatilization was endothermic. The exothermic peaks could be attributed to the charring of hemicellulose and lignin, whereas the sharp endothermic peaks might be ascribed to the quick devolatilization reactions of cellulose decomposition. The endothermic peak of the grafted jute had a slightly higher temperature (380°C) than the control jute (377°C), and the areas of the two peaks were also lower than that of the control jute, indicating that the thermostability of the jute fiber was increased via the grafting reaction.

It seems that the DSC curves corresponded well with the DTG curves. The DSC curves of the control and grafted jute got the peaks at about 320°C for the primary pyrolysis of hemicellulose or lignin, and the peak at 380°C represented the depolymerized volatilization of cellulose. The two peaks were also found in the DTG curves at almost the same temperatures (Figure 4).



**Figure 4.** TGA and DTG curves for the grafted jute (a) and the pretreated control jute (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



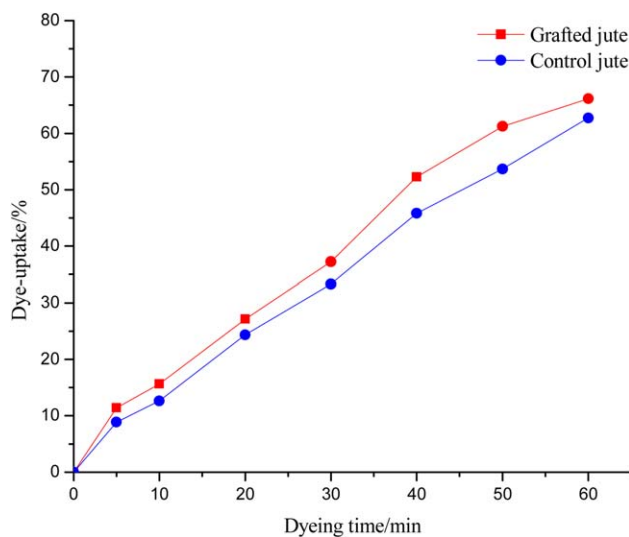
**Figure 5.** DSC curves for the pretreated control jute, grafted jute, and PAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Manfredi et al.<sup>29</sup> reported that the flax fibers were the most commonly used fire-resistant materials among the natural fibers and that the jute fiber showed a short duration but a quick growing fire with the lowest smoke emission. As the graft copolymer of jute with AAm has higher decomposition temperature than the natural jute, its application as the natural fire-resistant material is of great significance.

### Dyeing Properties Analysis

The variations in the dyeing properties of jute fabrics pregrafting and postgrafting were analyzed. The uptake of Direct Scarlet 4BS on the jute fabrics is shown in Figure 6. It can be seen that the grafting of AAm on the jute fabric led to an increase in dye uptake. The grafted jute showed a 3.3% increase when compared with the control jute. The increase in dye uptake indicated that the modification could increase the adsorption of direct dyes on jute fibers. This phenomenon was ascribed to the formation of hydrogen bonding between the direct dye and acrylamide, which was introduced on the surface of jute fiber by the grafting of AAm.

The *K/S* values of the two jute fabrics dyed at three incremental temperatures are shown in Table II. Both control jute and grafted jute showed a certain increase in the dyeing depth with the temperature. At the same time, the *K/S* values of the grafted jutes at the three dyeing temperatures were all higher than those of the control jutes. The grafted jute had just a slight increase in *K/S* value at 70°C, whereas the *K/S* value of the grafted jute reached 23.34 when compared with 21.53 of the control jute at 90°C. In the LAB color model, the luminance, redness, and chroma values



**Figure 6.** The dyeing rate curves of Direct Scarlet 4BS on jute fabrics. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of the grafted jute dyed at 90°C were also improved when compared with the control jute as shown in Table II. The variations of the dyeing properties indicated that the AAm-grafted jute could combine better with direct dyes and obtain deeper dyeing effect.

### CONCLUSIONS

The initiated system of laccase and *t*-BHP could start the graft copolymerization of AAm onto lignin in jute fiber. The grafting rate of AAm on the jute fabric is 2.87%, which is calculated from the nitrogen contents of the grafted jute (0.683%) and the control jute (0.137%). The laccase in the reaction medium is essential for the initiation of the polymerization process, but its catalysis alone is insufficient to produce a significant yield of the grafting copolymers. The new peaks of C=O vibration, N—H vibration, and C—N vibration of —CONH<sub>2</sub> in the FTIR spectra and the rough surface of the grafted jute shown in SEM images are also powerful evidences to show that AAm has been grafted on the surface of the jute fabric. The introduction of —CONH<sub>2</sub> to the jute fiber by grafting AAm caused improvements of its applied properties such as hydrophilicity, thermostability, dye uptake, and dyeing depth. It should be noted that the graft modification occurred only on the surface of the jute fiber, whereas the interior of the jute fiber was weakly influenced. Thus, the thermostability and the dyeing properties of the modified jute fiber changed less when compared with the change of the surface hydrophilicity characterized with wetting time and contact angle. In addition, the grafting reaction was proved for having a low

**Table II.** *K/S* Values of Jute Fabrics Dyed at Different Temperatures and Chromatic Values of Jute Fabrics Dyed at 90°C

	<i>K/S</i>			Valuation indicator at 90°C		
	70°C	80°C	90°C	Luminance (L)	Redness (A)	Chroma (C)
Control jute	20.15	20.56	21.53	31.220	33.830	41.185
Grafted jute	20.65	21.74	23.34	32.748	39.366	47.626

grafting rate unfortunately owing to the heterogeneous catalysis when compared with the chemical grafting or coating by couplers. In our subsequent study, the enhancement of grafting by exposing more lignins on jute surface and assisting with calcium ion in the reaction is being investigated.

#### ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (51173071), the Program for New Century Excellent Talents in University (NCET-12-0883), the Program for Changjiang Scholars and Innovative Research Team in University (IRT1135), the Natural Science Foundation of Jiangsu Province (BK2011157), the Ph.D. Programs Foundation of the Ministry of Education of China (20110093110003), the Fundamental Research Funds for the Central Universities (JUSRP51312B), the Graduate Student Innovation Plan of Jiangsu Province of China (CXZZ13\_07), and the Doctor Candidate Foundation of Jiangnan University of China (JUDCF13023).

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