



HRP-mediated polyacrylamide graft modification of raw jute fabric



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ARTICLE INFO

Article history:

Received 17 December 2014

Received in revised form 27 February 2015

Accepted 7 March 2015

Available online 14 March 2015

Keywords:

Horseradish peroxidase

Acrylamide

Hydrophilicity

Graft polymerization

Jute fabric

ABSTRACT

The horseradish peroxidase (HRP)/hydrogen peroxide system can catalyze the free-radical polymerization of aromatic compounds such as lignins. In this study, to improve the hydrophilicity of lignin-rich jute fabrics, acrylamide (AM) was grafted onto their surface by HRP-mediated oxidative polymerization. The resulting AM-lignin graft polymer in jute fibers, from which the lignin was removed by extracting with dioxane, was characterized by gel permeation chromatography, elemental analysis, matrix-assisted laser desorption/ionization mass spectrometry, nuclear magnetic resonance, scanning electron microscopy, and Fourier transform infrared spectroscopy. The results show that AM was grafted to the jute fiber by HRP. Furthermore, the hydrophilicity of the fabrics was determined in terms of wetting time, balance moisture regain, and static contact angle. Compared to the control sample, the wetting time, balance moisture regain, and static contact angle of the grafted fabrics varied from 11.62 min to 7.45 min, from 9.78% to 10.40%, and from 122.30° to 92.84°, respectively, indicating that the hydrophilicity of the raw jute fabric improved. The modification conditions of the HRP-catalyzed AM-grafting reaction were optimized in terms of the nitrogen content of the jute fabrics.

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1. Introduction

As a widely-used household and industrial textile material [1,2], raw jute fiber has some shortcomings such as rigidity, scratchiness, poor hydrophilicity and dyeing property due to the high content of lignin (approximately 16%), which is a complex three-dimensional amorphous polymer consisting of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units [3]. These shortages of jute fiber seriously affect the quality of its products, making them merely usable for low-grade goods such as packaging fabrics and bags. Two traditional grafting modifications, i.e., chemical initiation [4] and high-energy irradiation initiation [5,6], could improve the properties of jute fibers, but some deficiencies like the homopolymerization of monomers and severe damage to fibers limit their application. To date, enzymatic grafting modification has been proved to be an important and feasible method as an alternative to traditional approaches because of their eco-friendly nature and mild reaction conditions [7,8].

Horseradish peroxidase (HRP, EC1.11.1.7) is a plant peroxidase obtained from the roots of horseradish. It readily combines with hydrogen peroxide (H₂O₂) and the resultant HRP–H₂O₂ complex can oxidize a wide variety of hydrogen donors like aromatic compounds [9]. Recently, HRP-catalyzed free-radical polymerization has been used for the synthesis of polymers from varied monomers [10]. Sgalla et al. [11] obtained a novel 4-phenylphenol ortho dimer and revealed the reactivity of HRP with water insoluble phenolic compounds in ionic liquid/water mixtures. Chul and Young [12] studied the free-radical polymerization of aniline initiated by the HRP–H₂O₂ system in a nonaqueous phase and obtained a polyaniline product directly connected to benzene. Moreover, Lv et al. [13] reported the copolymerization of starch and different monomers such as dimethyl diallyl ammonium chloride initiated by HRP. In addition, the HRP-mediated vinyl polymerizations in the presence of H₂O₂ and β-diketone [14] have been also carried out using hydrophilic monomers such as acrylamide (AM) [15] and hydrophobic monomers such as methyl methacrylate [16], styrene derivatives [17,18] and 2-vinylnaphthalene [17]. The homopolymerization of AM [19,20], copolymerization of lignin and phenols [21] and polymerization of lignosulfonates [22] catalyzed by HRP have provided theoretical and experimental foundation for the grafting polymerization of AM onto the surfaces of jute fibers.

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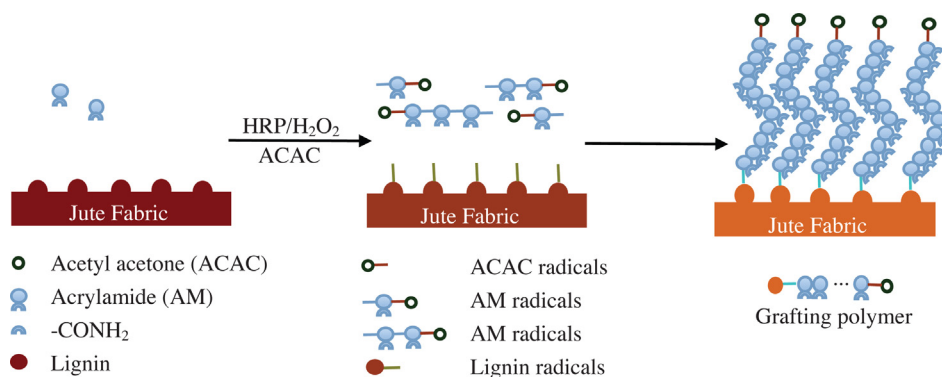


Fig. 1. Schematic illustration of HRP-catalyzed grafting reaction of acrylamide (AM) onto the jute fabric.

In the present work, HRP was used to catalyze the free-radical copolymerization of AM and lignin on the surface of jute fibers, thus grafting AM onto the jute fiber surface and improving the moisture absorption, wettability, etc. of the resulting jute fiber. AM was enzymatically grafted onto the jute fabric surface by HRP, as illustrated in Fig. 1. The proposed pathway of the enzymatic reaction is shown in Fig. 2. As far as our knowledge goes, this is not only the first attempt for the functional modification of jute fabric using HRP, which is efficient, environmentally friendly, and does not damage the material, but also a new application of HRP in textile processing.

2. Experimental

2.1. Materials and reagents

The 100% raw jute fabric, with a 7/7 (warp/weft) cm⁻¹ yarn density, was supplied by Longtai Weaving Company (Changshu, China). Plant HRP stored at -20 °C, and AM were obtained from Aladdin Reagent Ltd. (Shanghai, China). The HRP was used directly as received without further purification. All the other chemicals used in this study were commercially available and of analytical grade.

2.2. HRP assay

First, an HRP solution was prepared by dissolving 25 mg HRP in 25 mL of distilled water at 4 °C. The enzymatic activity of HRP at 30 °C was measured spectrophotometrically by monitoring the oxidation of gallic acid, as the substrate, at 420 nm in 0.1 M phosphate buffer (pH 7.0) with diethyl ether, as the extraction agent. The enzymatic activity was expressed as milligrams of oxidized gallic acid extracted with 100 mL diethyl ether per minute [23]. The enzymatic activity was 332 U/mg, calculated as follows:

$$\text{HRP (U/mg)} = E_{420} \times 8.5 \times E_w \quad (1)$$

where E_{420} is the absorbance at the wavelength of 420 nm, E_w is the weight of the enzyme, and 8.5 was derived from the unit definition and principle that the absorbance at the wavelength of 420 nm is 1.000 when 8.5 mg of oxidized gallic acid is extracted with 100 mL diethyl ether.

2.3. Isolation of lignin from jute fibers

The lignin in jute fibers was extracted using a method described by Evtuguin et al. [24–26].

2.4. Copolymerization of AM and lignin catalyzed by HRP

First, 0.2 g of lignin, 100% of AM, and 0.1 mL of acetylacetone (ACAC) were dissolved in 30 mL phosphate buffer (0.1 M, pH 7.0) in a reaction vessel, and the incubation was started by adding 0.2 mL H₂O₂ and 0.1 mg HRP. The reaction was maintained at 30 °C for 4 h. Then, the lignin was centrifuged with a certain volume of ethanol/water (3:7) (v/v) and collected by freeze-drying [19,20]. The control sample, sample treated with inactivated HRP, and sample treated with either HRP or AM followed the same treatment conditions, as mentioned above.

2.5. Pretreatment of jute fabrics

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

2.6. HRP-mediated grafting of AM onto jute fiber surfaces

The jute fabric sample (1 g) was incubated with 50 mL of phosphate buffer (0.1 M, pH 7.0), containing 100% of AM, a certain volume of ACAC, and HRP in 250 mL three-neck round-bottom flask under shaking. Then, H₂O₂ (30 wt%) was added dropwise after the mixture was degassed for 30 min. Next, the reaction was carried out at 50 °C for 6 h. The resulting sample was washed twice with a certain volume of ethanol/water (30:70) (v/v, %) at 80 °C for 30 min to obtain the polyacrylamide (PAM)-grafted jute fabric. The control sample and sample treated with either HRP or H₂O₂ followed the same condition as the HRP treatment [7,20].

2.7. Characterization of lignin

2.7.1. Gel permeation chromatography (GPC) analysis

The relative molecular weight and polydispersity of the lignin, which was soluble in *N,N*-dimethyl formamide (DMF), were measured using a Waters 1515 gel permeation chromatograph and Waters 2414 refractive index detector. The measurements were performed at 35 °C, and DMF was used as the mobile phase at a flow rate of 1.5 mL/min, using polystyrene as the standard sample.

2.7.2. Elemental analysis

The carbon, hydrogen, and nitrogen contents in the lignin samples were determined using an elemental analyzer (Elementar Vario ZLIII, Germany).

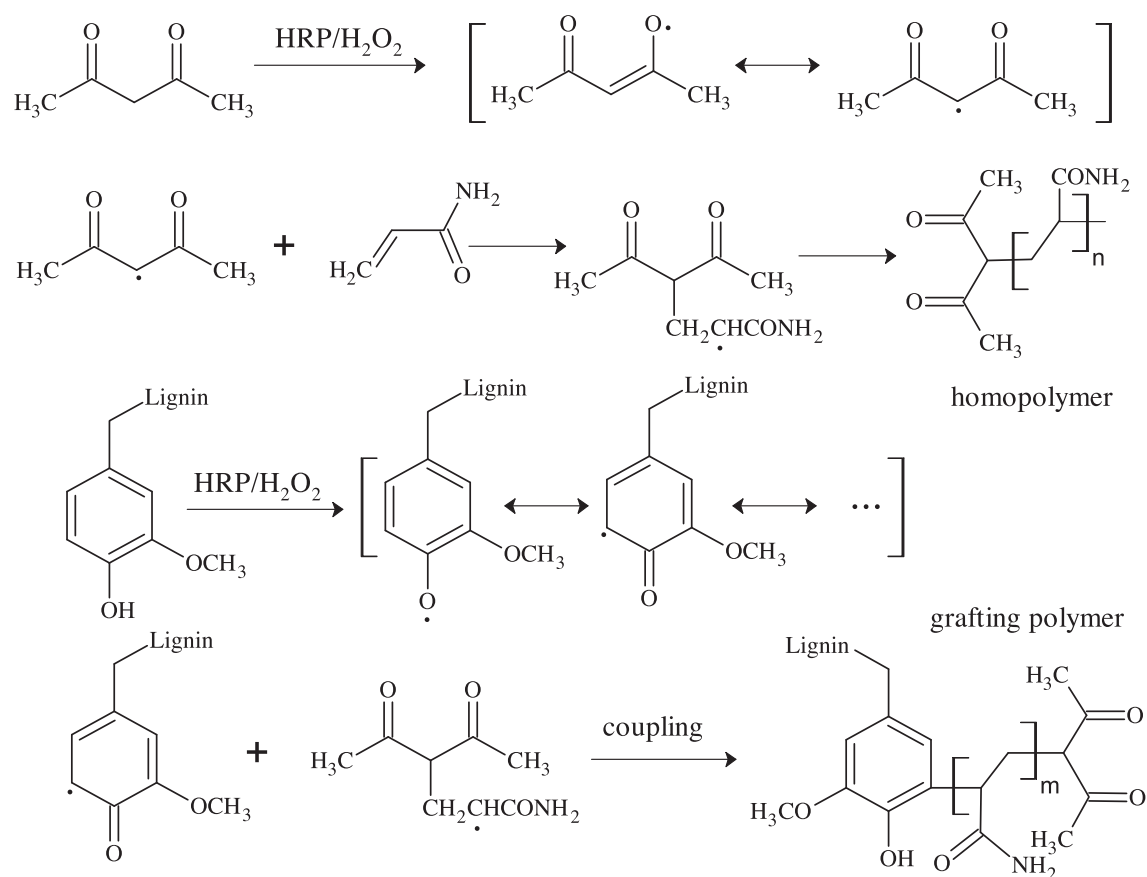


Fig. 2. Hypothetical mechanism of lignin and acrylamide polymerization catalyzed by HRP.

2.7.3. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF MS) analysis

Formations of lignin treated with different chemicals were studied with a Bruker ultrafleXtreme MALDI-TOF/TOF MS (Bremen, Germany). For the MALDI-TOF MS analysis, the lignins were dissolved in N,N-dimethyl formamide (DMF). Sinapinic acid comparing to other matrices was found to give the best results for lignin analysis [27]. A volume of 2 μL of the sample-matrix mixture was dried onto the MALDI target plate at room temperature. The positive ion mass spectra were acquired from the dried sample spots in reflector mode.

2.7.4. Nuclear magnetic resonance (NMR) analysis

The ^1H NMR spectra of 20 mg acetylated lignins solved in 0.5 mL chloroform (CDCl_3) were recorded, using tetramethylsilane (TMS) as the internal standard in a Bruker Avance 400 spectrometer with an operating frequency at 400 MHz.

2.8. Characterization of jute fabric surface

2.8.1. Fourier transform infrared (FT-IR) analysis

The FTIR spectra were recorded using a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific, USA) with the attenuated total reflection (ATR) technique. The scan range was from 4000 cm^{-1} to 650 cm^{-1} at 4 cm^{-1} resolution and 32 scans per sample.

2.8.2. Scanning electron microscopy (SEM) analysis

The SEM micrographs were recorded using a SU1510 SEM (Hitachi, Japan) under 5.00 kV at 3.00 K magnification. The surface of the jute fiber was coated with gold by vacuum evaporation.

2.9. Hydrophilicity measurement

The hydrophilicity of the jute samples was evaluated by wetting time, water contact angle, and equilibrium moisture regain. The wetting time was measured according to the AATCC Test Method 79-2007. The jute fabric swatch was planished under a standard atmospheric pressure for 24 h and then mounted on a plate, which was placed $\sim 10 \pm 1$ mm below the tip of a buret, with a filter paper spread tightly to make sure that the surface was free of wrinkles and without distorting the structure of the material. A drop of distilled water was allowed to fall from a height of 2 cm onto the taut surface of the test specimen, and the time taken for the specular reflectance of the water drop to completely disappear was recorded using a stopwatch. Five readings were averaged as the wetting time.

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

The equilibrium moisture regain was measured using the weighing method, in which the dry jute samples were placed under a standard atmospheric pressure for 24 h before weighing. The water absorption of the jute samples was calculated as follows:

$$\text{Water absorption (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (2)$$

where W_1 and W_2 are the weights of the dry and wet jute fibers, respectively.

Table 1
The average molecular weight and polydispersity of lignin.

Sample	Mn	Mw	Mw/Mn
Lc	25,769	44,429	1.724
Lt ₁	27,898	52,263	1.873
Lt ₂	27,483	48,705	1.772
Lt ₃	25,422	43,803	1.723
Lt ₄	25,724	43,833	1.704

2.10. Determination of nitrogen content and grafting percentage (GP)

According to the current standard of Determination of Protein Content in Food GB/T5009.5-2010 in China, the nitrogen content of jute-AM graft copolymer was measured with the micro-Kjeldahl method. The GP was calculated as follows:

$$GP(\%) = \frac{N_p - N_c}{N_a} \times 100 \quad (3)$$

where N_p , N_c , and N_a are the nitrogen contents on the grafting jute, control jute, and initial AM monomer, respectively.

2.11. Effect of process parameters on the grafting percentage

The HRP-mediated polyacrylamide graft modification of raw jute fabric was carried out as a function of different enzymatic reaction variables such as dosages of AM (0.5, 1.0, 1.5, 2.0 and 2.5 g), HRP (0.5, 1.0, 1.5, 2.0 and 2.5 mg) and H₂O₂ (0.25, 0.5, 1.0, 1.5 and 2.0 mL), pH of phosphate buffer (5,6,7,8,9), incubation temperature (20, 30, 40, 50 and 60 °C), and incubation period (3, 4, 5, 6 and 7 h). The grafting was characterized by the grafting percentage (GP) measured by the nitrogen content of jute-AM graft copolymer as mentioned above.

3. Results and discussion

3.1. Characterization of lignin

3.1.1. GPC analysis

The molecular weight distribution curves of various treated lignins are shown in Fig. 3. The values of the number-average (M_n) and weight-average (M_w) molecular weights of the lignins were calculated from the curves (Table 1).

As shown in Table 1, the results of the control groups, the M_n and M_w of Lc, Lt₃, and Lt₄ and the polydispersity value (M_w/M_n) were smaller than the grafting group. The M_n and M_w values of Lt₁ were 27898 and 52263, respectively, and the polydispersity value was 1.873. Compared to the results of other treated lignins, the M_w , M_n , and polydispersity values of Lt₁ increased. Similar result was also obtained by Zhou et al. [22].

Compared to Lt₃, the M_n and M_w values of Lt₂ increased by 8.11% and 11.19%, respectively. This indicates that HRP played an important role in the polymerization of the lignins of jute fabrics. Moreover, unlike Lt₃, the M_n and M_w values of Lt₁ increased by 9.74% and 19.31%, respectively. Thus, the lignins in the jute fibers could be polymerized by the HRP/H₂O₂ system. Compared to Lt₃, the polydispersity value of Lt₁ increased from 1.723 to 1.873, while it increased by 0.049 for Lt₂, indicating that the HRP/H₂O₂-treated lignin had a wider distribution range of relative molecular mass than the ungrafted lignin.

3.1.2. Elemental analysis

The elemental analysis results of the lignins treated with different reagents showed an increase in the nitrogen content, indicating that AM was successfully grafted onto lignins (Table 2). The increase

Table 2
The element content of lignin.

Sample	N (%)	C (%)	H (%)
Lc	0.363	57.09	5.673
Lt ₁	0.463	58.34	5.654
Lt ₂	0.418	58.64	5.577
Lt ₃	0.399	53.82	5.540
Lt ₄	0.408	58.72	5.436

Table 3
The m/z of MALDI-TOF mass spectrum of lignins and the substance construction.

m/z (Da)		Element
Grated sample	Control sample	
351.197	351.151	2M
434.558	434.491	2M
469.172	469.120	2M
471.192	471.137	2M
534.065	–	2M + 2AM
649.295	649.225	3M
677.293	677.222	3M
695.307	695.233	3M
711.293	711.210	3M
749.254	–	3M + 1AM
887.383	887.286	4M
917.389	917.295	4M
933.377	933.267	4M
935.390	935.287	4M
957.382	957.276	4M
979.382	–	3M + 4AM
995.365	–	3M + 4AM
1141.496	1141.370	5M
1197.460	–	5M
1365.611	1365.447	6M
1421.568	–	6M

in the nitrogen content from 0.418 (Lt₂) to 0.463 (Lt₁) can be attributed to the high nitrogen content of AM (C₃H₅NO).

Moreover, compared to other samples, the rates of change in the nitrogen content of the lignins were 27.55% (from Lt₁ to Lc), 10.76% (from Lt₁ to Lt₂), 16.04% (from Lt₁ to Lt₃), and 13.48% (from Lt₁ to Lt₄). Moreover, an increase in the nitrogen content of the HRP/H₂O₂-treated sample may result from the absorbed enzyme proteins on lignins. However, the increase in the nitrogen content of the HRP/H₂O₂/AM-treated sample may be suppressed due to the incorporation of AM to lignins, which achieved the same effect in the study on grafting AM to jute fibers by laccase [7].

3.1.3. MALDI-TOF MS analysis

The MALDI-TOF mass spectra of the control and grafted lignins were shown in Fig. 4. A molecular weight distribution from two hundred to more than one thousand Da is evident. The spectra have pronounced fine structure which may be assigned to the different groups of oligomers, from ca. 400 Da for the dimers to 1400 Da for the heptamers. These mass spectra show a similar structure to those obtained by Bocchini et al. [27]. According to the study of Bocchini et al., sequences of signals, with $\Delta m = 14$ –18 mass units for the dimers (m/z 351, 393, 434, 455 and 469 related to non-methylated GG and SS units), the trimers (m/z 649, 677 and 695) and the tetramers (m/z 887, 917 and 933) were confirmed in natural and synthetic lignins. In Fig. 4 and Table 3, the MALDI-TOF mass spectrum ions of grafted lignin show some differences compared to the control sample at molar mass 534 Da, 749 Da, 979 Da, and 995 Da, which were the peaks of the polymer of lignins and polyacrylamide or acrylamide. In addition, another two points at 1197 Da and 1421 Da showing the molecular weight of grated lignin was more than that of control lignin, which revealed that HRP can

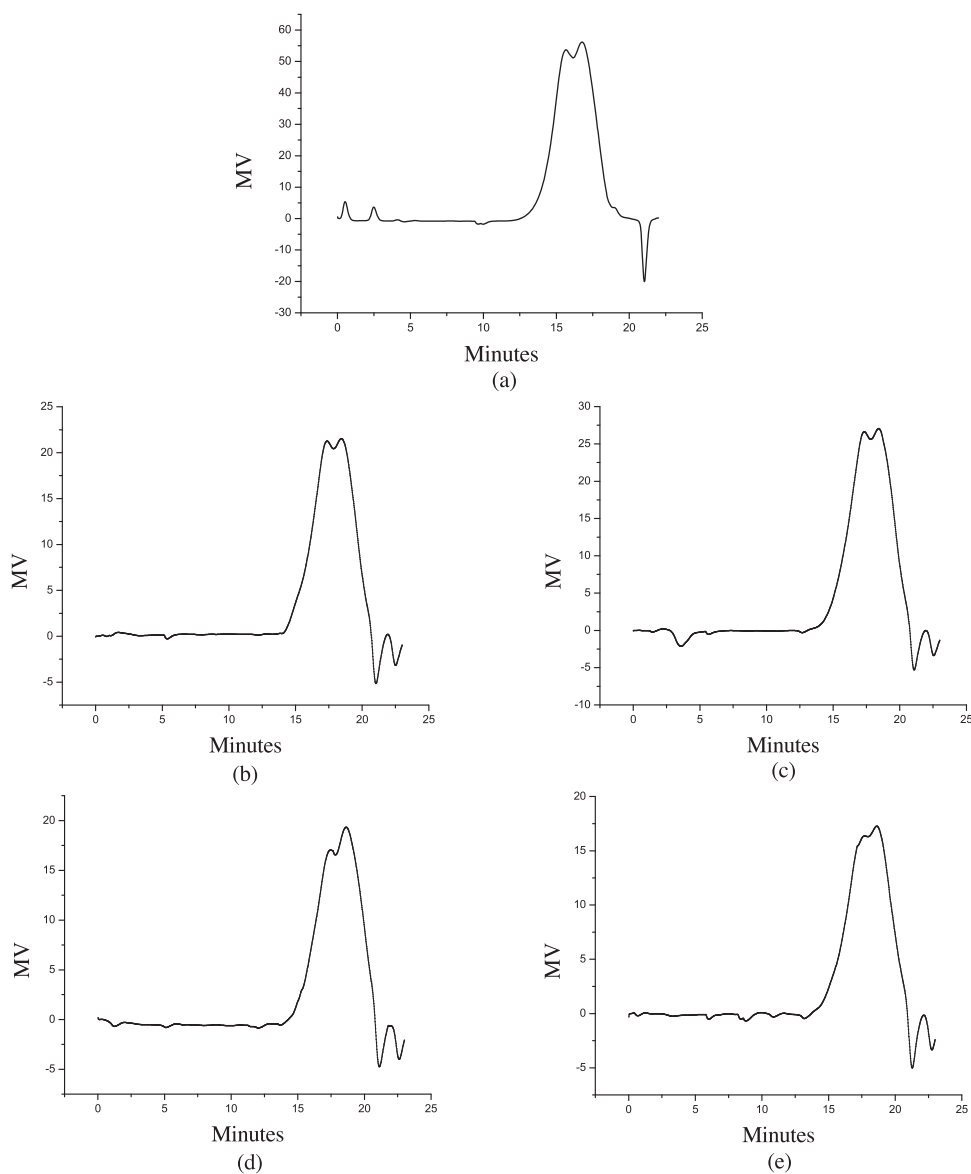


Fig. 3. The molecular weight distribution of lignin. (a) Control (butter) (Lc), (b) HRP/H₂O₂/AM treated lignin (Lt₁), (c) HRP/H₂O₂ treated lignin (Lt₂), (d) inactivation HRP/H₂O₂/AM treated lignin (Lt₃), (e) H₂O₂/AM treated lignin (Lt₄).

make the polymerization of lignins as the same result in above GPC analysis.

3.1.4. ¹H NMR analysis

The ¹H NMR spectra obtained for the grafted and control lignins were shown in Fig. 5, and Table 4 listed the position of signals assigned by Sarwar Jahan et al. [28,29]. The position of lignin in the present samples was almost the same. The main assignments such as aromatic protons (two peaks in the aromatic proton region, which correspond to guaiacyl units (δ 6.971) and syringyl units (δ 6.616)), β -O-4 structure (δ 6.014), β -5 structure (where there is no noticeable signal in range number 4 between ppm δ 5.20 and δ 5.75 indicating low amount of phenylcoumaran units in the lignin structure.), β -1 and β - β structures were similar in Fig. 5a and b. While, a noticeable and different signal was shown in Fig. 5b, i.e., ppm δ 1.20 (H _{β} in the chain CH₂ of the ends of PAM (–CH₂–CH₂–CH₂–CONH₂)). In addition, the signal H of amide group structure (δ 6.0) may be covered by that of H _{α} of β -O-4 and β -1 structures. H _{α} of main chain CH of PAM (–CHCONH₂CH₂–) and

H _{β} of β - β structures (between δ 2.50 and δ 3.10) might have a same ppm [30].

3.2. FT-IR analysis of jute fabrics

FT-IR spectroscopy is a powerful technique to reveal the changes in the hydroxyl, carbonyl, and other functional groups in a polymer. The FTIR-ATR spectra of the untreated jute fiber (A) and jute fiber grafted with AM (B) are shown in Fig. 6; some differences between the two fibers were observed. The O–H stretching vibration peak in the FTIR-ATR spectra appeared at 3337 cm⁻¹; the C–H vibrations of methyl and methylene groups appeared at 2884 cm⁻¹. The peaks at 1233, 1099, and 1035 cm⁻¹ represent the C–O vibrations of cellulose, and the absorbance bands at 1451 cm⁻¹ show the aromatic skeletal vibration of lignin [31]. Compared to the control jute sample, the spectrum of the grafted jute fabric showed three strong peaks at 1660 cm⁻¹ (C=O group), 1590 cm⁻¹ (N–H group), and 1312 cm⁻¹ (C–N group) [32]. The differences in the two spectra indicate that AM was grafted onto the jute fabrics in

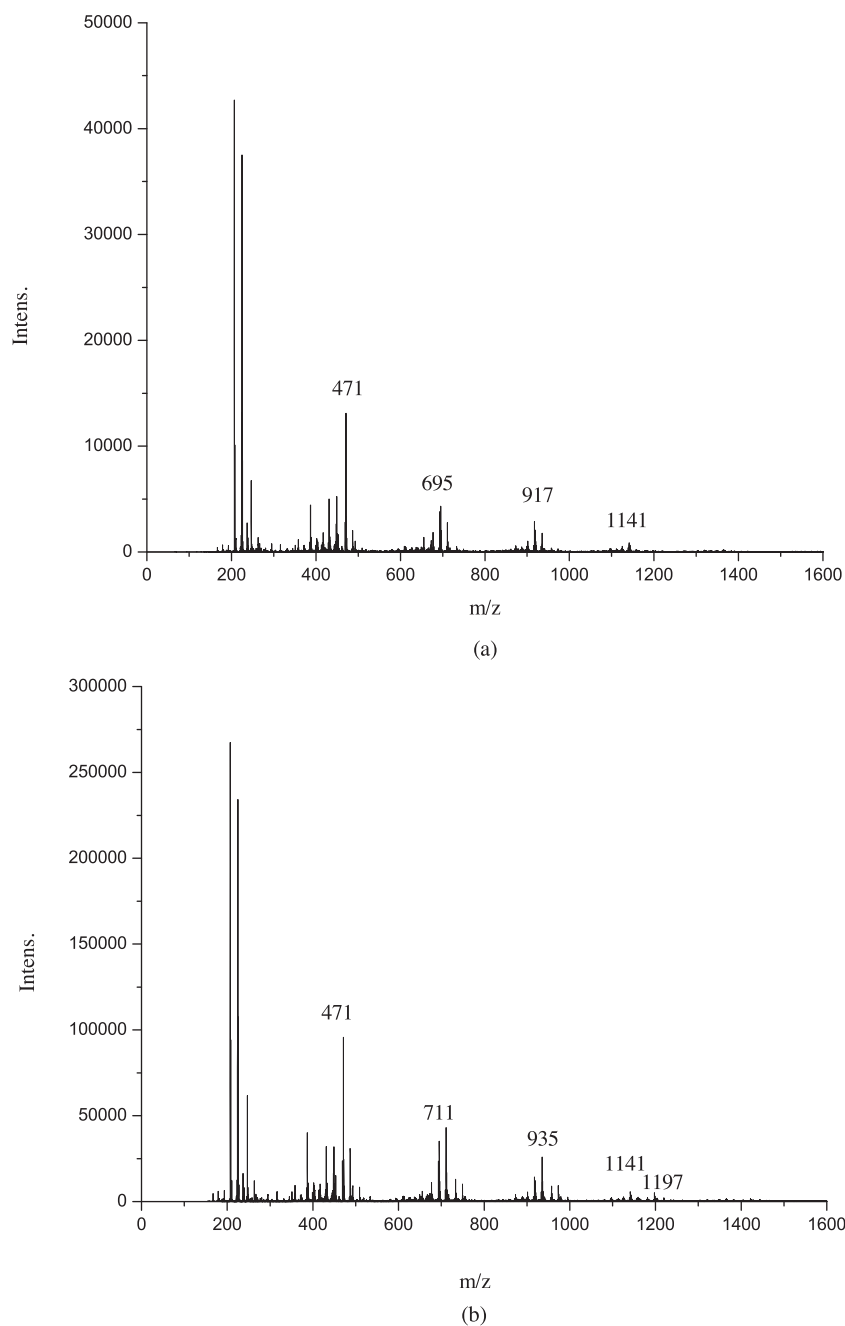


Fig. 4. Expanded section of MALDI-TOF mass spectra of the control (a) and grafted (b) lignins.

Table 4

Assignment of signals in the ^1H NMR spectra of the control and grafted lignins.

Range number	Range (ppm)	ppm of the maximum	Main assignments
	7.30	7.272	Chloroform (solvent)
1	7.25–6.80	6.971	Aromatic proton in guaiacyl units
2	6.80–6.25	6.616	Aromatic proton in guaiacyl units
3	6.25–5.75	6.014	H_α of β -O-4 and β -1 structures, H of amide group structure
4	5.75–5.20	5.434	H_α of β -5 structure
5	5.20–4.90	5.092	H of xylan residue
6	4.90–4.30	4.439	H_α and H_β of β -O-4 structures
7	4.30–4.00	4.173	H_α of β - β structures, H of xylan residue
8	4.00–3.48	3.757	H of methoxyl groups
9	3.10–2.50	2.619	H_β of β - β structures, H_α of main chain CH of PAM
10	2.50–2.22	2.292	H of aromatic acetates
11	2.22–1.60	2.011	H of aliphatic acetates
12	1.60–1.30	1.391	Hydrocarbon protons
13	1.20	1.208	H_β of main chain CH_2 of PAM

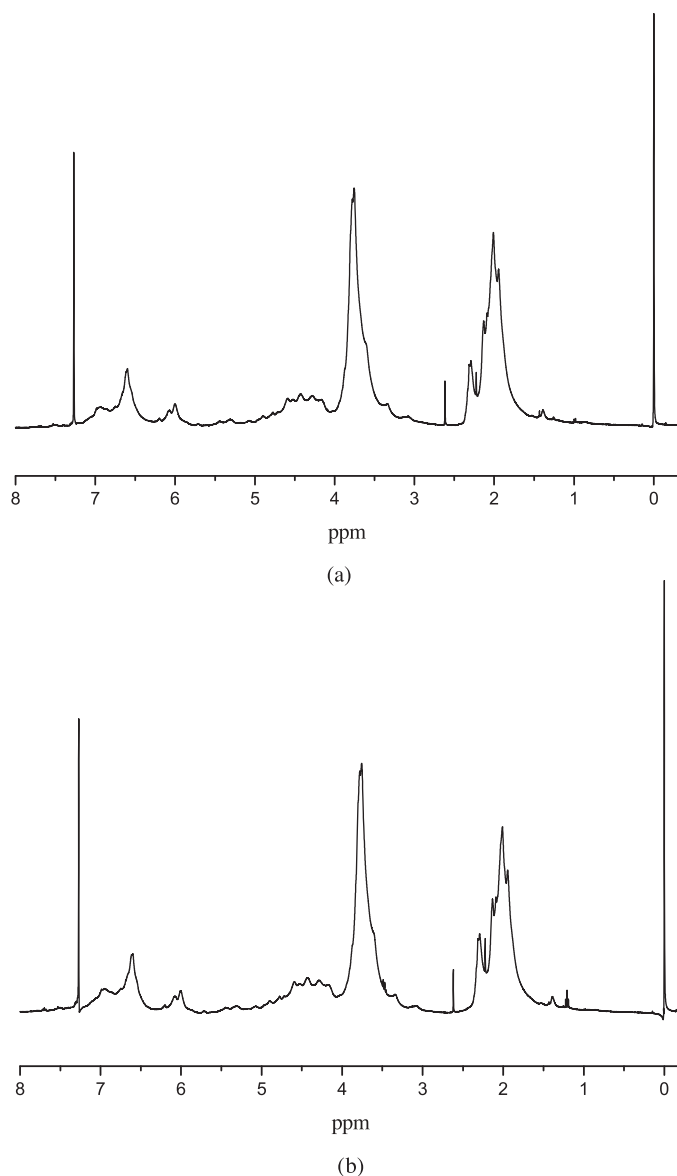


Fig. 5. ^1H NMR spectra of the control (a) and grafted (b) lignins.

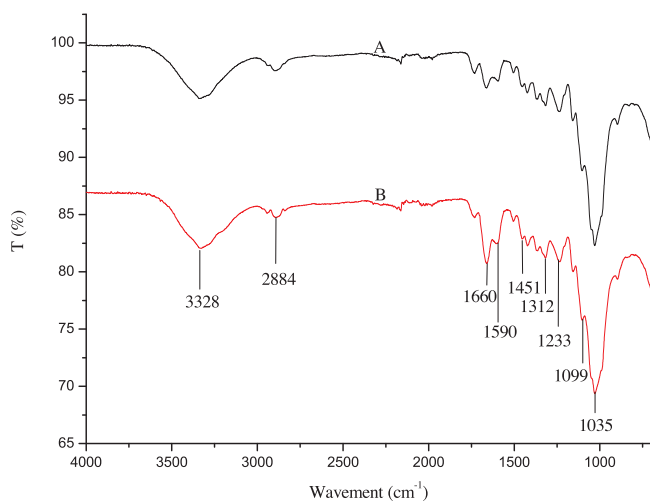


Fig. 6. FTIR-ATR spectra of the untreated jute fiber (A) and the AM-grafted jute fiber (B).

the presence of HRP and H_2O_2 . Therefore, the surface properties such as the hydrophilicity of jute fiber could be improved.

Other than lignin, cellulose is also present in jute fabrics. Therefore, to verify that lignin was the only substrate for the HRP catalysis, the cellulose was investigated. A bleached cotton fabric with AM-grafted cellulose was investigated, which would demonstrate whether or not AM was grafted onto cellulose structure by HRP. The peaks at 1660 cm^{-1} in the FTIR-ATR spectra of the bleached cotton fibers, treated with HRP, inactivated HRP, or phosphate buffer (0.1 M, pH 7.0) instead of HRP were very similar (data not shown), suggesting that no AM was grafted onto the cellulose of the fibers by HRP catalysis.

The probable mechanism of the HRP/ H_2O_2 system has been studied [10,33,34]. In this paper, a probable mechanism of HRP-catalyzed grafting modification of lignin on the surface of jute fibers in the presence of H_2O_2 is proposed based on our investigation, as shown in Fig. 2. The carbonyl group of ACAC first undergoes an oxidation reaction catalyzed by HRP in the presence of HRP/ H_2O_2 , forming the corresponding radicals. Then, the radicals transfer electrons to the phenolic hydroxyl group of lignin and AM, forming the reactive radicals for grafting AM onto the lignin of jute fabrics and modifying the jute fabric surface. The side reaction is the homopolymerization of AM. The reaction is terminated by the copolymerization between lignin and AM radicals, polymerization of AM, and crosslinking or degradation of lignins.

3.3. SEM analysis of jute fabrics

The morphology of various treated jute fibers was observed by SEM. As shown in Fig. 7, the four types of jute fibers exhibited different structures. The surfaces of the ungrafted jute fibers were smooth, tidy, and neatly arranged with few impurities on the surface (Fig. 7a, b, and d). The 2 h water reflux removed the starch and PVA sizes, but was unable to dislodge the pectins on jute fabrics. Compared to the untreated jute fibers, the surface of the grafted jute fibers was rough and irregular (Fig. 7c), probably because of the graft copolymers of PAM. Moreover, the grafted jute fibers exhibited damaged-like porous structures. For instance, the surface of the H_2O_2 -untreated fibers had a smooth, complete, and compact structure (Fig. 7a and b). In contrast, the surface of the H_2O_2 -treated fibers had a rough, damaged-like, and slightly loose structure with small pores (Fig. 7c and d). The damaged-like porous structure of the grafted jute fibers was probably influenced by the H_2O_2 concentration.

3.4. Determination of nitrogen content and grafting percentage

The results of the nitrogen content of jute fibers are shown in Table 5. The nitrogen contents of the AM-grafted and control (only HRP-treated) jute fibers were 0.3902% and 0.1730%, respectively. Compared to the grafting rate of the control (0.1949%), the grafted jute fibers catalyzed by the HRP/ H_2O_2 system with a grafting rate of 2.29% achieved the same effect as the result shown in Table 2 and provided another evidence for the grafting of AM onto the jute surface. Moreover, the nitrogen contents of the jute fibers treated with HRP alone, H_2O_2 alone, and neither in the presence of AM were almost identical. It was shown that, without HRP or H_2O_2 , the graft copolymerization of AM onto the lignins in the jute fibers did not occur with the desired properties such as hydrophilicity and feeble tickle. The results are different from those obtained from the studies by Mai et al. [35–37] and Dong et al. [7], which showed that the catalysis by laccase alone was able but insufficient to produce copolymerizates.

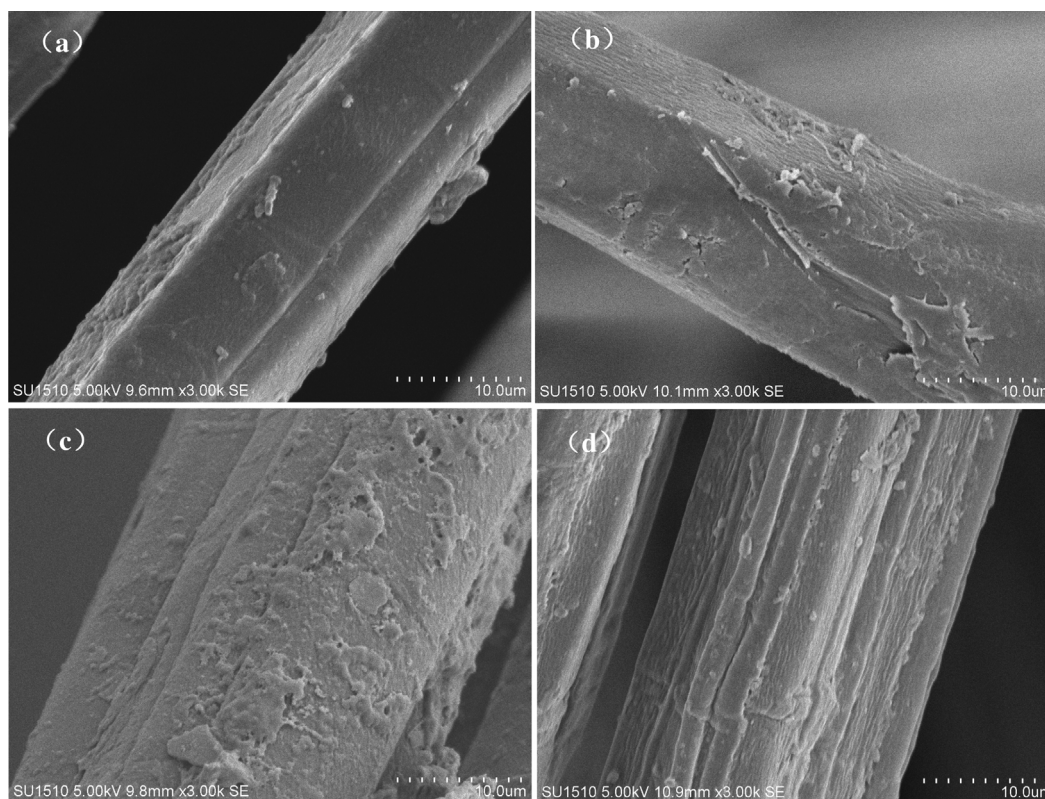


Fig. 7. Surface morphology change of treated and untreated jute fibers. (a) Control, (b) the HRP alone treated jute, (c) the HRP/H₂O₂ treated jute, (d) the H₂O₂ alone treated jute.

Table 5
The nitrogen content of the jute fiber.

Treatment	HRP/H ₂ O ₂	HRP alone	H ₂ O ₂ alone	Control
N (%)	0.6529	0.1730	0.1840	0.1949
V _{HCl} (mL)	1.8842	0.6464	0.5975	0.5689
GP (%)	2.29	–	–	–

3.5. Effect of process parameters on the grafting percentage

The effect of enzymatic reaction conditions including AM dosage, HRP dosage, H₂O₂ dosage, pH of phosphate buffer, incubation temperature, and incubation period on the grafting percentage were shown in Fig. 8. Fig. 8a and b indicated that the grafting percentage increased greatly with the addition of AM or HRP until reached its maximum value and then decreased. This revealed that the increase in monomer or HRP concentration might accelerate the homopolymerization reaction rather than grafting after a certain limit, thus decreasing the grafting yield. According to the curve of H₂O₂ dosage (Fig. 8c), the grafting percentage decreased with increasing H₂O₂ dosage due to the degradation of HRP by H₂O₂, which canceled out the catalytic activity of the enzyme [38]. The effect of pH and temperature on the enzymatic grafting (Fig. 8d and e) corresponded roughly with that on the HRP activity (data not shown). The grafting percentage remarkably increased with increasing of incubation period and then decreased slowly (Fig. 8f). This phenomenon may be explained by the slow decay of the enzyme activity [39].

3.6. Effect of AM grafting on hydrophilicity of jute fabric

The surface hydrophilicity of the jute fabric was investigated in terms of water contact angle, wetting time, and balance moisture regain. As shown in Table 6, the HRP treatment alone (121.68°) and

Table 6
The hydrophilicity of the jute fiber.

Treatment	Wetting time (min)	Contact angle (°)	Balance moisture regain (%)
Control	11.62 ± 0.59	122.30 ± 1.86	9.78 ± 0.36
HRP/H ₂ O ₂	7.45 ± 0.79	92.84 ± 2.23	10.40 ± 0.40
HRP alone	11.38 ± 0.69	121.68 ± 3.45	10.06 ± 0.38
H ₂ O ₂ alone	13.24 ± 0.83	118.65 ± 4.47	9.87 ± 0.29

H₂O₂ treatment alone (118.65°) merely caused a slight decrease in the water contact angle in contrast to the control treatment (122.30°). However, the jute fabric grafted with AM catalyzed by the HRP/H₂O₂ system showed a water contact angle of 92.84°, representing a decrease of 29.46° compared to the control jute fabrics.

The wetting time of the grafted jute fabrics catalyzed by the HRP/H₂O₂ system was also lower than the other three samples, consistent with the water contact angle. Moreover, the balance moisture regain of the grafted jute was higher than the other samples.

In conclusion, the wetting time, contact angle, and balance moisture regain of the grafted jute fiber were 7.45 min, 92.84°, and 10.40%, respectively, which were clearly much better than the others and indicated that the hydrophilicity of the jute fibers was enhanced after grafting PAM and introducing the amide hydrophilic group (CONH₂).

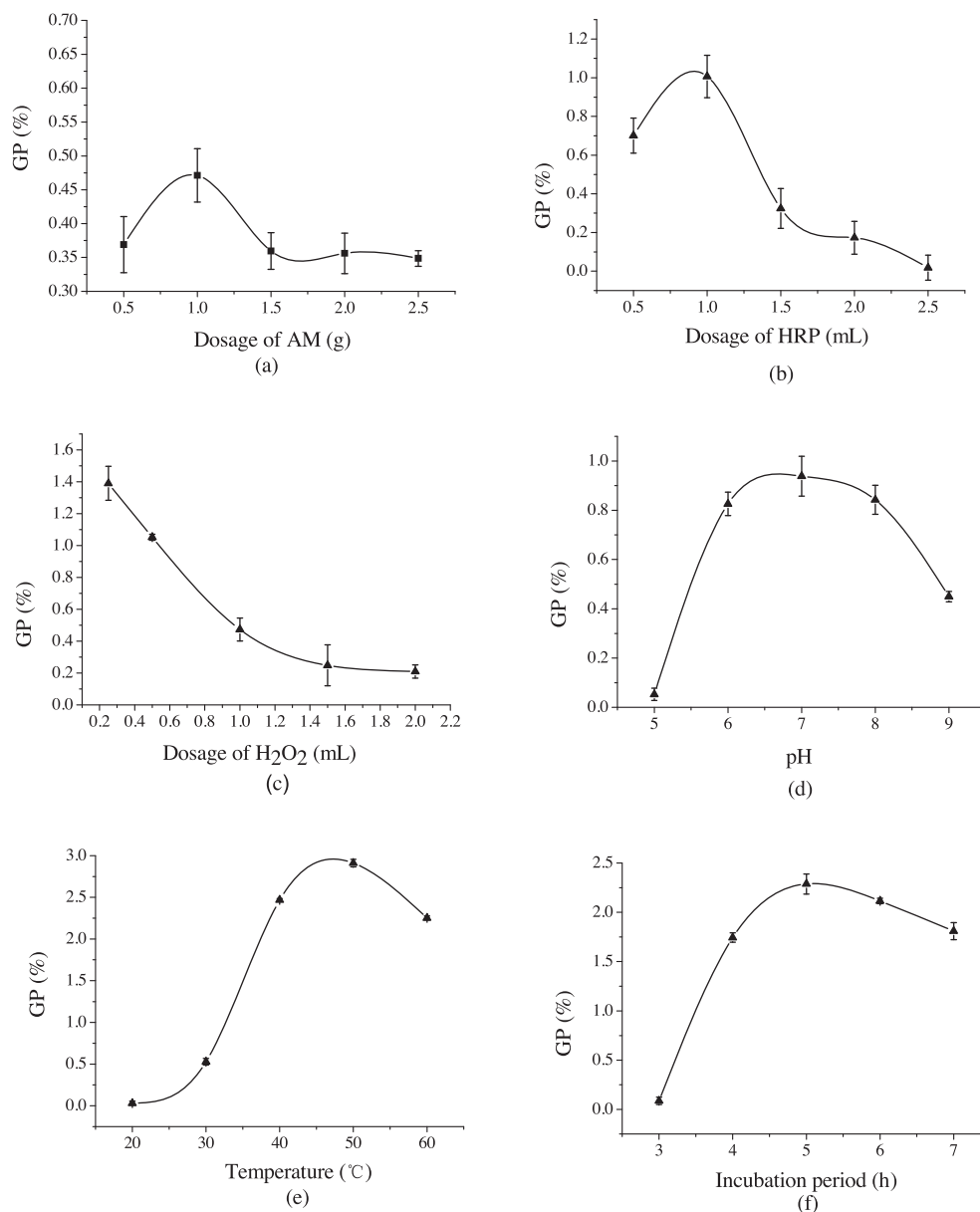


Fig. 8. Effect of process parameters on the grafting percentage. (a) Dosage of AM, (b) dosage of HRP, (c) dosage of H₂O₂, (d) pH of phosphate buffer, (e) incubation temperature and (f) incubation period.

4. Conclusions

In this study, the grafting modification of jute fabrics was performed with AM monomer using HRP as the catalyst. The initial system of HRP/H₂O₂/ACAC could start the graft copolymerization of AM onto the lignin in jute fibers which was proved by GPC, elemental analysis, MALDI-TOF MS and ¹H NMR. The HRP in the reaction medium was essential for the initiation of the free-radical polymerization process, but the catalysis alone was ineffective to produce the grafting copolymers. The characteristic absorption peaks of the C=O vibration, N–H vibration, and C–N vibration of the –CONH₂ group shown in the FTIR-ATR spectra and the rough surface of the grafted jute fibers in the SEM image also confirm that AM was grafted onto the jute fibers, introducing the –CONH₂ group, and that the grafting mechanism was free-radical grafting mechanism. The introduced –CONH₂ group improved the desired property, hydrophilicity, as characterized by the wetting time, water contact angle, and balance moisture regain. Moreover, the grafting reaction had a low grafting rate, unfortunately because of the heterogeneous

catalysis compared to the chemical grafting or coating by couplers. In the future, the enhancement of AM grafting by adding transition monomers in the reaction will be 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 Fundamental Research Funds for the Central Universities (JUSRP51312B) and the Graduate Student Innovation Plan of Jiangsu Province of China (SJLX.0527).

References

- [1] K.E. Achyuthan, A.M. Achyuthan, P.D. Adams, S.M. Dirk, J.C. Harper, B.A. Simmons, A.K. Singh, *Molecules* 15 (2010) 8641–8688.

- [2] R.M. Isroi, S. Syamsiah, C. Niklasson, M.N. Cahyanto, K. Lundquist, M.J. Taherzadeh, *BioResources* 6 (2011) 5224–5259.
- [3] J.C. del Río, J. Rencoret, G. Marques, J. Li, G. Gellerstedt, J. Jiménez-Barbero, A.T. Martínez, A. Gutiérrez, *J. Agric. Food Chem.* 57 (2009) 10271–10281.
- [4] R.L. Chen, B.V. Kokta, C. Daneault, J.L. Valade, *J. Appl. Polym. Sci.* 32 (1986) 4815–4826.
- [5] S. Marais, F. Gouanve, A. Bonnesoeur, J. Greneta, F. Poncin-Epaillardb, C. Morvanc, M. Métayer, *Compos. Part A* 36 (2005) 975–986.
- [6] C. Albanoa, J. Reyes, M. Ichazo, J. Gonzálezc, M. Britob, D. Moronta, *Polym. Degrad. Stab.* 76 (2002) 191–203.
- [7] A.X. Dong, J.G. Yuan, Q. Wang, X.R. Fan, *J. Appl. Polym. Sci.* 131 (2014) 40387–40392.
- [8] E. Aracri, A. Fillat, J.F. Colom, A. Gutiérrez, J.C. Del Río, A.T. Martínez, T. Vidal, *Bioresour. Technol.* 101 (2010) 8211–8216.
- [9] (a) M. Kohri, H. Fukushima, T. Taniguchi, T. Nakahira, *Polym. J.* 42 (2010) 952–955;
(b) H. Uyama, in: K. Loos (Ed.), *Biocatalysis on Polymer Chemistry*, 1st ed., Wiley-VCH Verlag & Co. KGaA, Weinheim, 2011, p. 165.
- [10] F. Hollmann, I.W.C.E. Arends, *Polymers* 4 (2012) 759–766.
- [11] S. Sgalla, G. Fabrizi, S. Cacchi, A. Macone, A. Bonamore, A. Boffi, *J. Mol. Catal. B: Enzym.* 44 (2007) 144–148.
- [12] H.L. Chul, J.Y. Young, *Process Biochem.* 36 (2000) 233–241.
- [13] S.H. Lv, T. Sun, Q.F. Zhou, J.J. Liu, H.D. Ding, *Carbohydr. Polym.* 103 (2014) 285–293.
- [14] F. Hollmann, in: K. Loos (Ed.), *Biocatalysis on Polymer Chemistry*, 1st ed., Wiley-VCH Verlag & Co. KGaA, Weinheim, 2011, p. 143.
- [15] (a) A. Durand, T. Lalot, M. Brigodiot, E. Maréchal, *Polymer* 41 (2000) 8183–8192;
(b) B. Kalra, R.A. Gross, *Green Chem.* 4 (2002) 174–178.
- [16] B. Kalra, R.A. Gross, *Biomacromolecules* 1 (2000) 501–505.
- [17] A. Singh, D. Ma, D.L. Kaplan, *Biomacromolecules* 1 (2000) 592–596.
- [18] G. Qi, C.W. Jones, F.J. Schork, *Biomacromolecules* 7 (2006) 2927–2930.
- [19] R.L. Shogren, J.L. Willett, A. Biswas, *Carbohydr. Polym.* 75 (2009) 189–191.
- [20] G.N. Fan, J.C. Zhao, Y.K. Zhang, Z.A. Guo, *Polym. Bull.* 56 (2006) 507–515.
- [21] H. Liu, F.K. Yang, L.H. Qiu, *Sci. Eng. Polym. Mater.* 17 (2001) 173–175.
- [22] H.F. Zhou, D.J. Yang, X.Q. Qiu, X.L. Wu, Y. Li, *Biotechnol. Products Process Eng.* 97 (2013) 10309–10320.
- [23] B. Stellmach, *Bestimmungsmethoden Enzyme Für Pharmazie, Lebensmittelchemie, Technik, Biochemie, Biologie, Medizin*, Steinkopff-Verlag, Darmstadt, 1988, pp. 217–223.
- [24] D.V. Evtuguin, C.P. Neto, A.M. Silva, P.M. Domingues, F.M. Amado, D. Robert, O. Faix, *J. Agric. Food Chem.* 49 (2001) 4252–4261.
- [25] Y.B. Zhang, Q. Wang, X.R. Fan, J.G. Yuan, *J. Mol. Catal. B: Enzym.* 101 (2014) 133–136.
- [26] K. Lundquist, B. Ohlsson, R. Simonson, *Svensk papperstidning* 80 (1977) 143–144.
- [27] P. Bocchini, G.C. Galletti, R. Seraglia, P. Traldi, S. Camarero, A.T. Martinez, *Rapid Commun. Mass Spectrom.* 10 (1996) 1144–1147.
- [28] M. Sarwar Jahan, S.P. Mun, *J. Sci. Ind. Res.* 44 (2009) 271–280.
- [29] T.T. Yan, Y.Q. Xu, C.W. Yu, *J. Appl. Polym. Sci.* 114 (2009) 1896–1901.
- [30] S.H. Lv, Y.F. Ma, D. Li, *Adv. Mater. Res.* 455–456 (2012) 582–588.
- [31] F. Chen, J.X. Chen, *Trans. China Pulp Pap.* 9 (1994) 80.
- [32] H.L. Zheng, P. Zhang, G.C. Zhu, C.J. Zhu, J.J. Wang, S.J. Jiang, *Spectrosc. Spectral Anal.* 11 (2011) 2944–2947.
- [33] O. Emery, T. Lalot, M. Brigodiot, E. Marechal, *J. Polym. Sci.: Part A: Polym. Chem.* 35 (1997) 3331–3333.
- [34] G.S. Nyanhongo, E. Nugroho Prasetyo, E. Herrero Acero, G.M. Guebitz, *Chem. Eng. Technol.* 35 (2012) 1359–1372.
- [35] C. Mai, A. Majcherczyk, A. Hüttermann, *Enzyme Microb. Technol.* 27 (2000) 167–175.
- [36] C. Mai, O. Milstein, A. Hüttermann, *J. Biotechnol.* 79 (2000) 173–183.
- [37] C. Mai, O. Milstein, A. Hüttermann, *Appl. Microbiol. Biotechnol.* 51 (1999) 527–531.
- [38] A. Durand, T. Lalot, M. Brigodiot, E. Maréchal, *Polymer* 41 (2000) 8183–8192.
- [39] E. Battistel, M. Morra, M. Marinetti, *Appl. Surf. Sci.* 177 (2001) 32–41.