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Hydrophobic functionalization of jute fabrics by enzymatic-assisted grafting of vinyl copolymers

Huimin Wu,^a Carla Silva,^b Yuanyuan Yu,^a Aixue Dong,^a Qiang Wang,^a  *^{ac}
Xuerong Fan,^a Ping Wang,^a Jiugang Yuan^a and Artur Cavaco-Paulo  ^{bc}

We report an eco-friendly approach to improve the hydrophobicity of jute fabrics *via* horseradish peroxidase (HRP)-catalyzed covalent grafting of butyl acrylate (BA) and 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA). Hydrophobic vinyl monomers were grafted onto the exposed lignin molecules of the jute surface by free-radical polymerization in the presence of a HRP/H₂O₂/acetylacetone (ACAC) system. Coupling onto the lignin–jute surface was demonstrated by attenuated total reflection–Fourier transform infrared spectroscopy (ATR–FTIR), solid-state nuclear magnetic resonance (solid-state ¹⁹F NMR), elemental analyses, X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS), matrix-assisted laser desorption/ionization mass spectrometry (MALDI–TOF MS) and scanning electron microscopy (SEM). The hydrophobicity and oleophobicity of modified jute fabrics was estimated in terms of contact angle and wetting time. The results indicated that it was essential to attain vinyl monomers grafting polymerization onto jute surfaces in a HRP/H₂O₂/ACAC system. Moreover, the grafting of vinyl monomers led to hydrophobicity increases of 53.86% and 61.03% in the contact angle of grafted jute fabrics with BA and HFBMA when compared with unmodified jute fabrics, respectively. Both vinyl monomers demonstrated high propensity to be polymerized by HRP in the presence of H₂O₂, and acquired the ability to act as high-performance composites with hydrophobic resins.

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Introduction

Jute fiber is one of the cheapest natural fibers (ranking second to cotton in terms of planting) and has been used by humans for a long time. Jute fiber has luster, biodegradability as well as excellent moisture absorption and air permeability. It is mainly used for making sacks, rope, woven carpets, and curtains. Nowadays, its application has expanded from home textiles to industrial products, including nonwovens, geotextiles, and fiber-reinforced composites.^{1–3} In spite of their wide application, these fibers have strong rigidity, low elongation at break, poor hydrophobicity and low spinnability, which seriously hinders their industrial application. For instance, hydrophilic jute fabrics have poor compatibility with hydrophobic resins and so are being discarded as fiber-reinforcing materials in composites. Thus, the hydrophobicity of jute fabrics needs to be improved to impart a good interfacial compatibility with hydrophobic resins.

These resins can form high-performance composites with modified jute using chemical, physical or radiation approaches.^{4–6} For example, Mohanty *et al.* grafted copolymers of acrylonitrile and methyl methacrylate on jute surfaces to improve the performance of biodegradable jute-fabric/biopolymer composites.⁴ Mwaikambo *et al.* used mercerization and acetylation to reduce the hydrophilic tendency of hemp, jute and kapok for resin bonding in natural composite materials.⁵

To lower the use of toxic chemical reagents and reduce the environmental impact, enzymes have become important biocatalysts due to their high efficiency and eco-friendly nature.^{7,8} Horseradish peroxidase (HRP, EC.1.11.1.7) is a heme-containing enzyme and has been applied widely due to its high activity, high stability, low molecular weight and convenient storage. Lalot *et al.* reported that the HRP/H₂O₂/acetylacetonate (ACAC) system can catalyze free radical-polymerization of acrylamide in water.⁹ Derango *et al.* reported the polymerization of vinyl monomers catalyzed by HRP, such as acrylamide and methyl methacrylate.^{9–11} It was assumed that the enzyme in an oxidation state could be directly used as an initiator. In addition, HRP-mediated oxidative coupling of phenol⁹ and aromatic amines using β-diketones as initiators has been studied.^{12,13} HRP can also initiate one-electron oxidation of the phenolic sites of lignin by generating free radicals as intermediates.⁶ Above all, HRP has been shown to be an excellent alternative to conventional chemical catalysts.

^a Key Laboratory of Science and Technology of Eco-Textiles, Ministry of Education, Jiangnan University, Wuxi 214122, Jiangsu, P. R. China.
E-mail: qiang_wang@163.com; Fax: +86-51085912009; Tel: +86-51085912007

^b Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal. E-mail: artur@deb.uminho.pt; Tel: +351-253-604409, +351-93-3263158

^c International Joint Research Laboratory for Textile and Fiber Bioprocesses, Jiangnan University, Wuxi, 214122 Jiangsu, China

In view of the 16% of lignin in jute fabrics that can be oxidized by enzymes because of syringyl- and guaiacyl-units, scholars have attempted to graft vinyl monomers onto the exposed lignins of jute fabrics *via* enzymatic polymerization.^{14–16} In the present work, butyl acrylate (BA) and 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA) were covalently grafted onto exposed lignins of jute surfaces by HRP. The hydrophobicity of grafted jute was enhanced due to the ester groups as well as special groups (C–F) of polymers. The structures of both BA and HFBMA monomers are similar (–C=C– and –C=O).

The characterization of copolymers obtained and the hydrophobicity of grafted jute were tested using physical and chemical analyses. The coupling reaction between lignin and vinyl monomers was estimated by Fourier transform (FT-IR) spectroscopy, scanning electron microscopy (SEM), solid-state ¹⁹F nuclear magnetic resonance (NMR) and matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS). The hydrophobic/oleophobic behavior of modified jute was recorded using measurements of the contact angle and wetting time.

Experimental

Materials and reagents

HRP from horseradish, having an activity of > 300 U mg⁻¹, was produced by Aladdin Industrial (Beijing, China). A 100% raw jute fabric with a yarn density of 7/7 (warp/weft) cm⁻¹ was supplied by Longtai Weaving (Changshu, China). Dimethyl sulfoxide (DMSO), trichloromethane, H₂O₂ (30 wt%), BA, HFBMA, and ACAC were obtained from Sinopharm Chemical Reagents (Shanghai, China). 2-Methoxy-4-propylphenol (MP) was purchased from Sigma-Aldrich (Saint Louis, MO, USA). Water was distilled and all chemicals were reagent grade.

Pretreatment of jute fabrics

Jute fabrics were extracted with benzene/ethanol (v:v, 2:1) for 12 h using a Soxhlet extractor to eliminate the textile-sizing agent and waxiness on jute fabrics. Then, the fabrics were boiled with distilled water for 3 h to remove water-soluble material and pectins. Finally, a larger amount of lignin was exposed upon the surface of jute fabrics.

Grafting copolymerization

HRP-catalyzed covalent grafting of BA onto the surface of jute fabrics. The dried jute fabric (1 g) was incubated in 20/80 (v/v, %) ethanol/phosphate buffer (0.1 M, pH 7.0) with 10 mM of BA and 200 μl of ACAC using three-necked flasks under agitation and continuous bubbling of nitrogen for 30 min. The three-necked flasks were shaken and bubbled with nitrogen for 30 min. After 30 min, HRP (1 mg mL⁻¹) and 40 μl of H₂O₂ (30 wt%) were added to the reaction tank. The reaction was carried out at 30 °C for up to 4 h.

HRP-catalyzed covalent grafting of HFBMA onto the surface of jute fabrics. HFBMA (10 mM) was incubated in phosphate buffer (0.1 M, pH 7.0) with 50 μl of Triton X-100 under vigorous stirring (10 000 rpm) for 3 min. Jute (1 g) and 200 μl of ACAC

were added to the solution under continuous shaking and bubbling with nitrogen for 30 min. After 30 min, HRP (1 mg mL⁻¹) and 40 μl of H₂O₂ (30 wt%) were introduced in the reaction tank. The reaction was carried out at 30 °C for up to 4 h.

Finally, treated samples were washed twice with distilled water and Soxhlet-extracted with trichloromethane/acetone for 12 h to remove homopolymers and other oligomeric compounds. Several samples were treated in different conditions as well as their corresponding controls: untreated jute fabric; jute fabric incubated only with HRP/BA; jute fabric incubated only with H₂O₂/BA; jute fabric incubated with HRP/H₂O₂/BA; and jute fabric incubated with HRP/H₂O₂/HFBMA.

Attenuated total reflectance (ATR)-FTIR spectroscopy

ATR-FTIR spectra were applied to reveal the functional groups of the modified jute fabrics.^{17,18} Differently treated jute fabrics were scanned using a Nicolet iS10 Fourier transform infrared spectrometer (Thermo Scientific, Waltham, MA, USA). Spectra were recorded at 4000–650 cm⁻¹ at 4 cm⁻¹ resolution and scan times up to 16 times.

Copolymer structures of BA-grafted jute and HFBMA-grafted jute

MALDI-TOF MS analyses of BA-grafted lignin model compound.

MALDI-TOF MS was used to evaluate the formation of new structures after modification. This method was not feasible for the solid state, so we confirmed the covalent grafting of BA onto jute using a lignin model compound (MP). The complicated and ambiguous structure of lignin had led to a difficulty to extract lignin from jute. Therefore, 2-methoxy-4-propylphenol was chosen as a lignin model compound to react with BA (which has a similar structure to the lignin in jute). 2,5-Dihydroxybenzoic acid (DHB) was chosen as the matrix due to its good results with regard to lignin analyses. The experiment was performed in a specific fashion. Briefly, the reacting mixture was dissolved in DMSO at 1 mL mL⁻¹. A droplet of DHB was infiltrated into the electrically conducting target (*e.g.*, a stainless-steel plate). Then the mixed solution was added dropwise and allowed to dry at room temperature.^{19–22} Positive-ion mass spectra were acquired from the dried sample spots in reflective mode.

Solid-state ¹⁹F NMR analyses of HFBMA-grafted jute. The covalent grafting of HFBMA onto jute fabrics was performed differently from BA. We expected a high level of attachment, so solid-state NMR was tested using the functionalized jute fabrics.²³ ¹⁹F magic angle spinning (MAS) spectra were recorded on an AVANCE III 400 WB spectrometer (Bruker, Billerica, MA, USA) equipped with a 2.5 mm standard-bore CP MAS probe head whose X channel was tuned to 376.55 MHz for ¹⁹F using a magnetic field of 9.39 T at 297 K. The dried and finely powdered samples were packed in a ZrO₂ rotor closed with Kel-F caps which were spun at 20 kHz. A total of 500 scans was recorded with 3 s recycle delay for each sample. All ¹⁹F MAS chemical shifts were referenced to the resonances of the trichlorofluoromethane (CFCl₃) standard (*d* = 0.00).

X-ray photoelectron spectroscopy (XPS) analyses. XPS was recorded for the surface chemical composition of different-treated

jute using a PHI-5000C ESCA system equipped with an Mg-K α X-ray source (Laboratory of Surface Chemistry, Fudan University, Shanghai, China).

Elemental analyses. Modified jute with BA did not have special groups like HFBMA-grafted jute. Furthermore, the integral elemental test was carried out of modified jute with BA. The carbon, hydrogen, and oxygen contents in the jute fabrics were determined using an elemental analyzer (Vario ZLIII; Elementar, Berlin, Germany).

SEM and energy-dispersive spectroscopy (EDS) analyses. Surface morphology of the grafted jute fabrics was evaluated by SEM. Scanning electron micrographs were recorded using an SU1510 system (Hitachi, Tokyo, Japan) under 3.00 or 5.00 kV at magnifications of 1.00–3.00k. The surface of the jute fabrics was coated with gold by vacuum evaporation. The distribution of elements in the grafted jute fabric was determined by EDS^{24,25} using IXR EDS 2008 software at a sufficient beam energy.

Quantification of copolymer grafting. The grafting percentage of the treated jute fabric was calculated by an automatic potentiometer. A jute fabric sample of 0.5 g was cut into pieces and placed in a conical flask with 0.1 M NaOH and incubation at 90 °C for 2 h. Excess NaOH was titrated with 0.1 M hydrochloric acid solution to neutralize residual NaOH. The volume of HCl consumed was recorded when the curve appeared to change suddenly in the computer, and the data were averaged. Each sample was measured at least thrice, and the results of treated jute were averaged.

Hydrophobicity and oleophobicity measurement. The contact angle was recorded using a SL200B static contact angle/interfacial tension meter (USA Kino Industry, Norcross, GA, USA). The fabric was placed on the instrument platform. The needle of a syringe was at a distance of 5 mm and pictures were taken when the water droplet (2 μ l) fell on the jute surface. Unlike the contact angle of water, the dosage of oil was 10 μ l per drop, so that the oil droplet was dropped automatically and vertically. Each sample was tested at least five spots and the data were averaged.

The wetting time was measured according to AATCC 79-2007. A drop of water was allowed to fall from a height of 10 \pm 1 mm onto the jute surface. The wetting time was recorded until specular reflectance of water drop completely disappeared.^{26–28} Each sample was measured five times and the data presented as the average of these measurements.

Results and discussion

ATR-FTIR analyses of BA/HFBMA-grafted jute

Cotton contains cellulose without lignin. Therefore, cotton fiber was used as a control to test if cellulose could be grafted by a polymer synthesized with vinyl monomers. The ATR-FTIR spectra of untreated cotton and BA/HRP/H₂O₂-treated cotton are shown in Fig. 1a. The control sample and BA/HRP/H₂O₂-treated sample had identical adsorption peaks, which confirmed that BA could not be grafted onto cotton. That is, the cellulose of jute would not participate in the reaction of the HRP/H₂O₂/ACAC system.

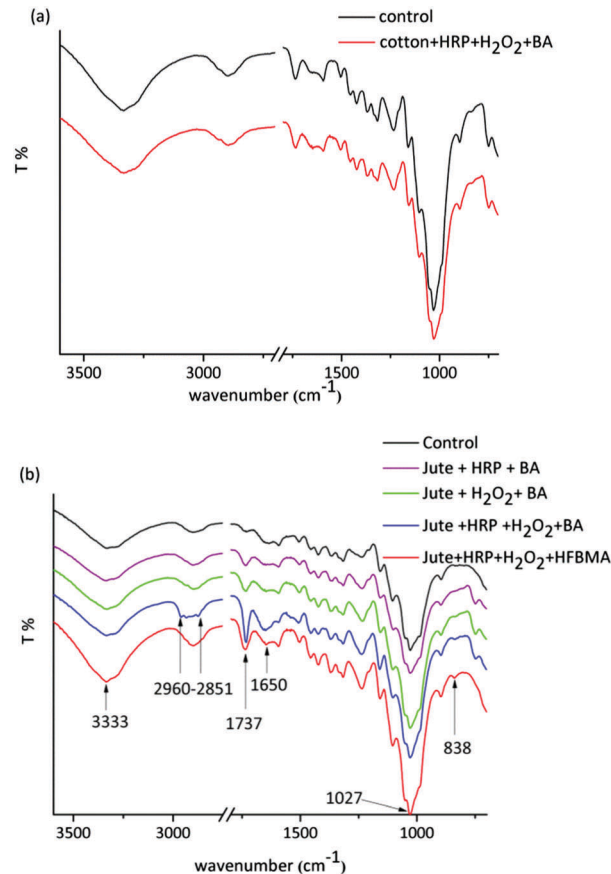


Fig. 1 (a) ATR-FTIR spectra of untreated cotton and BA/HRP/H₂O₂-treated cotton samples; (b) ATR-FTIR spectra of jute fabrics after different treatments: untreated jute; jute + HRP + BA; jute + H₂O₂ + BA; jute + BA + H₂O₂ + HRP; and jute + HFBMA + H₂O₂ + HRP.

The ATR-FTIR spectra of different jute samples with BA/HFBMA covalently attached to their surface are shown in Fig. 1b. The O–H stretching vibration was visible at 3333 cm⁻¹. It identified the saturated C–H stretching vibration²⁹ at around 2965 cm⁻¹ and of the C=O stretch of ester at 1737 cm⁻¹ and also of the C=C stretch of olefin in the ATR spectra between 1680 and 1610 cm⁻¹. Comparison of all the spectra in Fig. 1 it confirmed that the control sample, sample incubated only with HRP/BA, and sample incubated only with H₂O₂/BA had the same behavior, in contrast with the spectra of BA/HRP/H₂O₂-grafted fabric, which had a stronger peak at 1737 cm⁻¹ owing to some of the ester groups of BA. It seemed that the vinyl groups of monomers were fragmented and formed new groups (–CH₂–: ~2925, ~2850 cm⁻¹; –CH: 2890 cm⁻¹) in grafted jute fabrics. Therefore, the spectrum of the BA-grafted sample had a slight “saw-toothed” peak at around 2900 cm⁻¹ compared with the other three spectra. Furthermore, the peak of the C–O stretching vibration in the ATR spectra of the BA-grafted sample had a small increase at 1016 cm⁻¹ due to the ester groups of BA. Based on ATR-FTIR analyses, it could be preliminarily concluded that poly-(butyl acrylate) was grafted onto the surface of jute fabrics using a HRP/H₂O₂/ACAC system. In addition, the obvious absorption at 838 cm⁻¹ was due to the C–F bond of HFBMA-grafted jute when compared with other treated

jute fabrics. These FTIR-ATR results confirmed that vinyl monomers could be grafted onto the jute surface *via* enzymatic polymerization.

Copolymer structures of BA-grafted jute and HFBMA-grafted jute

MALDI-TOF MS of BA-grafted jute. MP, a lignin model compound soluble in DMSO, was used to covalently attach poly-(butyl acrylate) and confirm the new structures formed by HRP oxidation. The MALDI-TOF mass spectrum of the BA-grafted lignin model compound is shown in Fig. 2, and the corresponding mass-to-charge ratio (m/z) is reported in Table 1. The molecular-weight distribution of the different species formed was in the range of 200–1000 Da, as evidenced by the formation of dimers and oligomers between BA and MP. For example, the m/z of 294.39, 317.39 or 332.39 Da corresponded to the dimer formed between the lignin model compound and BA with the addition of H^+ , Na^+ or K^+ to the molecule, respectively. The trimer (482.829 Da), tetramer (615.253 Da) and pentamer (779.331 Da) were predominant from the sequences of signals. The spectrum revealed that BA could be polymerized *via* the HRP/ H_2O_2 /ACAC system and that new vinyl copolymers were formed between poly-(butyl acrylate) and the lignin model compound.

Solid-state ^{19}F NMR of HFBMA-grafted jute. Fig. 3 shows the solid-state ^{19}F NMR spectrum of HFBMA-grafted jute fabric. Solid-state ^{19}F NMR had a clear signal in the range of -150 to -100 ppm, which revealed the existence of fluorine in the HFBMA-grafted jute fabric. The existence of an amount of fluorine on small organic molecules was demonstrated by a very sharp peak in the solid-state ^{19}F NMR (Fig. 3a). The broad peak observed in the NMR spectrum demonstrated copolymers

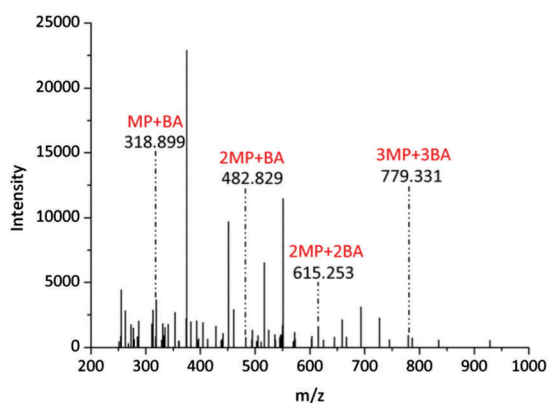


Fig. 2 MALDI-TOF mass spectra of the BA-grafted lignin model compound.

Table 1 The possible molecular mass (m/z) assignments of different copolymers formed between BA (butyl acrylate) and MP (2-Methoxy-4-propylphenol) by HRP polymerization

m/z (Da)	BA-grafted jute
318.899	MP + BA
353.128	2M
374.952	2M
404.793	3BA
482.829	2MP + BA
550.975	3M
615.253	2MP + 2BA
779.331	3MP + 2BA

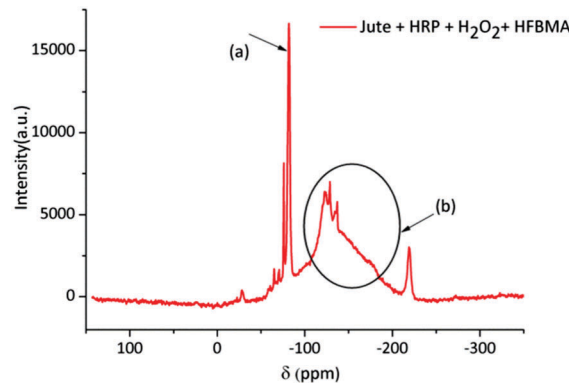


Fig. 3 Solid-state ^{19}F nuclear magnetic resonance spectra of jute + HRP + H_2O_2 + HFBMA sample (HFBMA-grafted jute). (a) The sharp peak of -80 to -85 ppm; (b) The broad peak of -100 to -150 ppm.

containing fluorine (Fig. 3b). The solid-state ^{19}F NMR indicated the formation of copolymers between HFBMA/poly-(2,2,3,4,4,4-hexafluorobutyl methacrylate) and lignin in the corresponding condition.

Surface characterization of BA/HFBMA-grafted jute by XPS.

XPS showed the surface chemical composition using the atomic percentage of elements. Different functional carbon groups were classified based on the C1s XPS signal as identified by the relative peak position (binding energy (BE)).³⁰ The most intense peak component of the C1s signal was between 294.2 and 284.4 eV, and C–C (284.54 eV), C–O/C–O–C (286.05 eV) and C=O (288.45 eV) on the untreated jute sample (Fig. 4a). Compared with untreated jute, the C–C, C–O/C–O–C and C=O peaks appeared at around 284.47, 285.67 and 288.34 eV on BA-grafted jute (Fig. 4b). The CF_2 and CF_3 peak appeared at 291.72 and 293.89 eV on the HFBMA-grafted jute sample, indicating the grafting of the monomer onto the exposed lignin of jute fabrics (Fig. 4c).

Carbon, oxygen, nitrogen and fluorine contents at the surfaces of jute fabrics after enzymatic polymerization are shown in Table 2. Covalent grafting of the jute fabric with BA promoted an increase in the carbon content from 59.50% to 67.69% (Table 2) that may have resulted from the formation of poly-(butyl acrylate). Compared with untreated jute, the reduction in the C/O ratio from 1.55 to 2.39 in HRP/ H_2O_2 -treated jute could be attributed to the formation of copolymers between poly-(butyl acrylate) and the available lignin. In addition, it was only possible to quantify fluorine (29.41%) when jute was functionalized with poly-(2,2,3,4,4,4-hexafluorobutyl methacrylate). This confirmed the ability of HRP to polymerize the vinyl monomer and its copolymerization within the lignin available at the jute surface.

Elemental analyses of BA-grafted jute. The results of the elemental test revealed the variations in carbon, hydrogen, and oxygen contents as well as the C/O ratio in the integral jute fabrics (surface and interior) after different treatments (Table 3). First, each element did not show an apparent increase in HRP alone-treated jute or H_2O -treated jute by comparison of untreated jute fabric. Second, compared with the other three samples, the increase in carbon content in HRP/ H_2O_2 -treated jute from 39.76% to 44.35% was due to the high carbon content of BA or

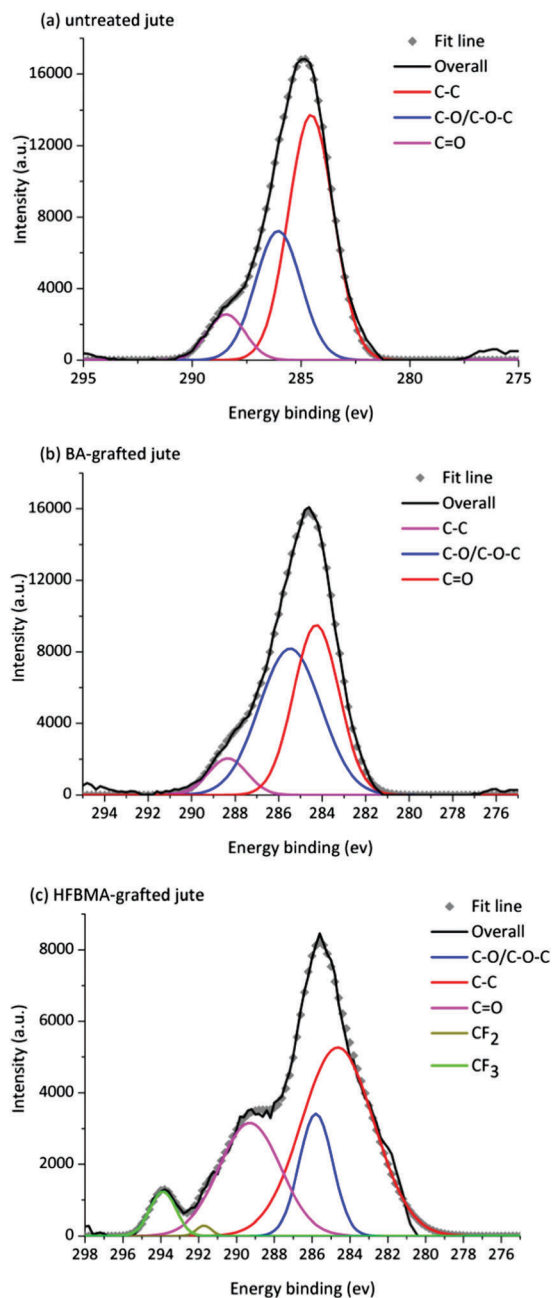


Fig. 4 XPS high-resolution C1s spectra of jute samples: (a) untreated jute; (b) BA-grafted jute; (c) HFBMA-grafted jute.

Table 2 XPS analyses of the surface of the jute fabric after different incubation conditions

Treatment	Jute surface			
	C (%)	O (%)	N (%)	F (%)
Untreated jute	59.50	38.36	2.13	—
Jute + HRP + BA	60.64	37.13	2.40	—
Jute + H ₂ O ₂ + BA	58.04	37.64	4.32	—
Jute + HRP + H ₂ O ₂ + BA	67.69	28.37	3.94	—
Jute + HRP + H ₂ O ₂ + HFBMA	45.57	23.52	1.50	29.41

poly-(butyl acrylate). In addition, the C/O ratio of BA-grafted jute increased from 0.736 to 0.907.

Table 3 Elemental analyses of jute fabric after grafting with butyl acrylate (BA)

Treatment	C (%)	H (%)	O (%)	C/O ratio
Untreated jute	39.76	6.20	54.04	0.736
Jute + HRP + BA	40.15	6.44	53.41	0.752
Jute + H ₂ O ₂ + BA	39.91	6.46	53.63	0.744
Jute + HRP + H ₂ O ₂ + BA	44.35	6.75	48.90	0.907

Hence, vinyl monomers could undergo grafting polymerization with lignin only in the presence of HRP, ACAC, and H₂O₂ simultaneously.

SEM and EDS analyses of BA/HFBMA-grafted jute. The surface morphology of jute fabrics after modification was confirmed by SEM. Untreated jute fabrics had a smooth surface with few impurities (Fig. 5a). The surface of fabrics incubated only with HRP/BA (Fig. 5b) presented a morphology that was similar to that of untreated jute. Instead, the sample incubated only with H₂O₂/BA (Fig. 5c) had a slightly rough surface with small granules. Compared with untreated jute fibers, the HRP/H₂O₂/BA-treated jute fabrics exhibited a rougher and irregular surface (Fig. 5d) that seemed to denote film coverage. Compared with untreated fabrics, HFBMA-grafted jute fabrics also exhibited an irregular surface with many particles covering their surface (Fig. 5e), which was due to the formation of copolymers between vinyl monomers and exposed lignin.

On the basis of SEM, EDS of HFBMA-grafted jute fabric is shown in Fig. 6. Elemental X-ray maps showed that carbon, oxygen, and fluorine were distributed homogeneously on the HFBMA-grafted jute surface. The fluorine content was less than

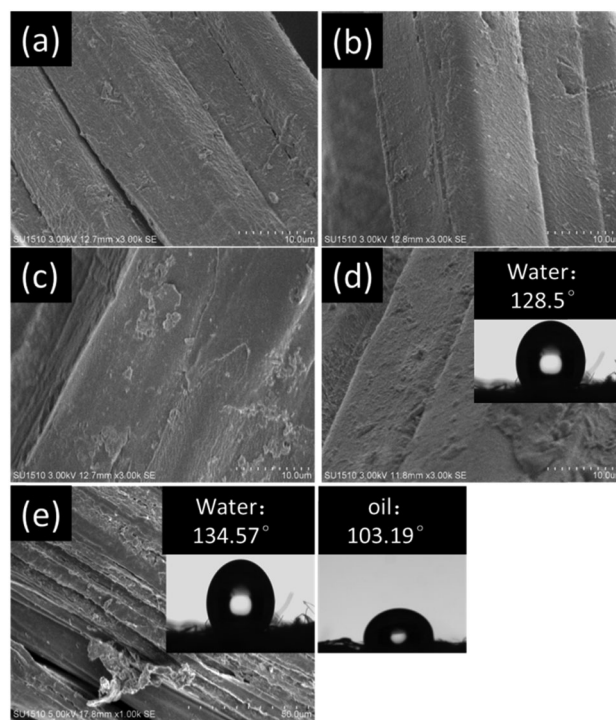


Fig. 5 Surface morphology (10 μ m of image size) of jute-grafted samples: (a) untreated jute, (b) jute + HRP + BA, (c) jute + H₂O₂ + BA, (d) jute + HRP + H₂O₂ + HRP + BA; (e) jute + HRP + H₂O₂ + HRP + HFBMA.

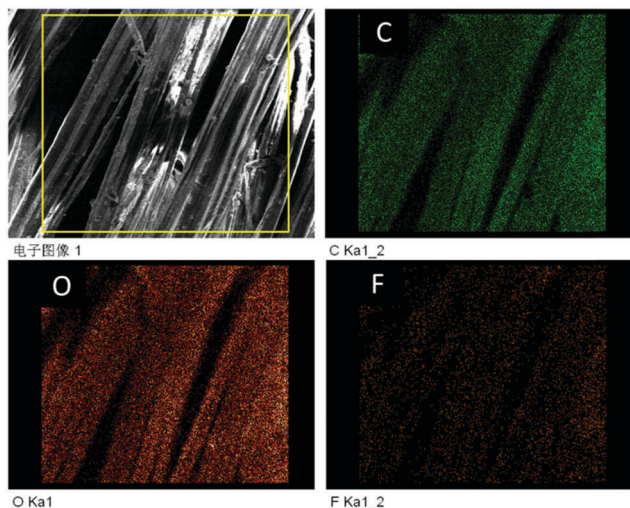


Fig. 6 Energy-dispersive spectroscopy of a jute + HRP + H₂O₂ + HFBMA sample.

that of carbon and oxygen. This was due to the plentiful cellulose as well as few lignin molecules at the surface of jute fabrics. Simultaneously, the existence of fluorine on the HFBMA-grafted jute surface indicated that HFBMA was successfully grafted onto jute fibers *via* enzymatic polymerization.

Grafting percentages of BA and HFBMA copolymers onto jute fabrics. The grafting percentages of both BA and HFBMA copolymers grafted onto jute fabrics were evaluated in terms of a reverse saponification titration (Table 4). The volume of HCl consumed by excess NaOH was almost identical to that of untreated samples, as well as for the samples incubated only with HRP/monomer or only with H₂O₂/monomer. These results showed non-grafting onto jute fabrics. On the other hand, grafting was quantifiable only if BA was incubated in the presence of both HRP and H₂O₂. Table 4 also demonstrated that the grafting rate of HFBMA onto jute surface (7.99%) was higher than that of BA (3.09%). The grafting percentages of both copolymers were low, possibly due to the low level of lignin content available at the surface of the fabrics. Moreover, the covalent attachment of vinyl monomers onto lignin was limited by mass transfer phenomena in the solid-liquid system.

Hydrophobic and oleophobic behavior of functionalized jute fabrics. The hydrophobicity and oleophobicity of jute fabrics after modification was evaluated by measurements of contact angle and wetting time. The static contact angle of grafted jute fabrics was determined as a function of time to evaluate their hydrophobic and oleophobic behaviour.³¹

Table 4 Grafting percentages of BA and HFBMA copolymers grafted onto jute fabrics

Treatment	V _{HCl} (mL)	Grafting percentage (%)
Control jute	16.62 ± 0.10	—
Jute + HRP + BA	16.38 ± 0.24	—
Jute + H ₂ O ₂ + BA	16.53 ± 0.11	—
Jute + HRP + H ₂ O ₂ + BA	15.41 ± 0.08	3.09
Jute + HRP + H ₂ O ₂ + HFBMA	15.02 ± 0.12	7.99

Water droplets were almost immediately absorbed on untreated jute, demonstrating that the jute surface was initially hydrophilic. The contact angle of the control sample was 83.75° at the beginning, and the water droplet disappeared within 3 s (Table 5). The water contact angle and the wetting time of the samples incubated only with HRP/monomer and only with H₂O₂/monomer were nearly similar to those of untreated jute. In contrast, BA-grafted and HFBMA-grafted jute fabrics showed good hydrophobic behavior with water contact angles of 128.58° and 134.57° at the beginning of the measurement test, respectively (Table 5 and Fig. 7). The surface hydrophobicity of grafted jute was remarkably enhanced owing to the copolymers grafted onto lignin molecules at the jute surface. The wetting time (> 30 min) of HFBMA-grafted jute was higher than that of BA-grafted jute fabric (23 min). This could be explained by a higher grafting percentage of HFBMA onto jute fabrics and by the hydrophobic groups formed after HFBMA polymerization, which endowed the modified jute fabric with excellent hydrophobic properties. Furthermore, the very high fluorine content of HFBMA resulted in the excellent oleophobicity of HFBMA-grafted jute when compared with BA-grafted jute as well as the other treated jute (Table 6). The contact angle and wetting time of paraffin oil were 103.19° and >6 min, respectively.

The new jute surfaces had not only remarkable hydrophobic/oleophobic behavior but also had high compatibility with hydrophobic resins which are usually employed for production of high-performance composite materials.

Table 5 Contact angle at time zero and the wetting time of water after grafting monomers

Treatment	Water contact angle (°) at 0 s	Wetting time of water
Control jute	83.57 ± 4.79	2.1 ± 0.42 s
Jute + HRP + BA	98.32 ± 3.23	2.3 ± 0.52 s
Jute + H ₂ O ₂ + BA	84.65 ± 3.09	3.0 ± 0.63 s
Jute + HRP + H ₂ O ₂ + BA	128.58 ± 2.57	23 ± 1.55 min
Jute + HRP + H ₂ O ₂ + HFBMA	134.57 ± 1.65	> 30 min

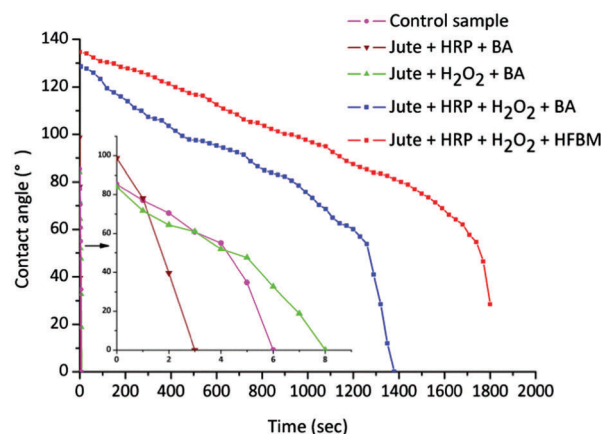


Fig. 7 Water contact angles of jute-grafted samples: untreated jute; jute + HRP + BA; jute + H₂O₂ + BA; jute + HRP + H₂O₂ + BA; jute + HRP + H₂O₂ + HFBMA.

Table 6 Contact angle at time zero and oil wetting time of paraffin oil after grafting monomers

Treatment	Oil contact angle (°) at 0 s	Wetting time of oil
Control jute	72.07 ± 3.23	0 s
Jute + HRP + BA	76.32 ± 2.16	0 s
Jute + H ₂ O ₂ + BA	74.55 ± 3.59	0 s
Jute + HRP + H ₂ O ₂ + BA	82.46 ± 4.38	1.3 ± 0.52 s
Jute + HRP + H ₂ O ₂ + HFBMA	103.19 ± 3.98	6.1 ± 0.57 min

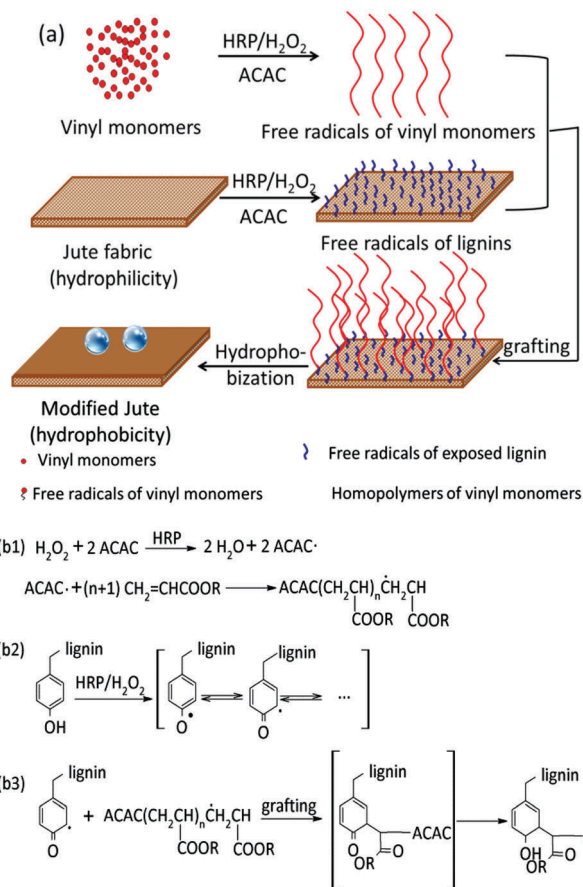


Fig. 8 (a) Schematic diagram and (b) mechanism of HRP-catalyzed grafting of vinyl monomers onto the lignins of jute fabrics.

HRP-assisted covalent grafting of vinyl monomers onto jute surfaces: proposed mechanism. The grafting mechanism of the vinyl monomers onto the lignin molecules of jute fabrics is proposed tentatively in Fig. 8. First, the carbonyl group of ACAC was catalyzed in the HRP/H₂O₂/ACAC system *via* an oxidation reaction to form free radicals.^{32–35} Then, these radicals transferred electrons to the vinyl groups of monomers as well as to the phenolic groups of lignin molecules, producing copolymers of BA/HFBMA and lignins at the surface of jute fabrics.

Conclusions

The results presented here indicated the feasibility of the hydrophobic modification of jute fabrics *via* covalent grafting

polymerization of vinyl monomers mediated by HRP. The carbonyl group of ACAC was catalyzed enzymatically to form free radicals. These free radicals transferred electrons to the vinyl groups of monomers as well as for the phenolic groups of lignin, producing copolymers between BA/HFBMA and the exposed lignin molecules at jute fabrics.

Alternatively to old methods, enzymatic grafting polymerization provided an eco-friendly approach for the modification of jute fibers. These are promising results for the assessment of hydrophobic jute fabrics as fiber reinforcements for high-performance composites.

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