New strategy for grafting hydrophobization of lignocellulosic fiber materials with octadecylamine using a laccase/TEMPO system

Aixue Dong, Kidanu Masho Teklu, Weiming Wang, Xuerong Fan, Qiang Wang, Mònica Ardanuy, Zhen Dong

PII: S0141-8130(20)33321-3

DOI: https://doi.org/10.1016/j.ijbiomac.2020.05.167

Reference: BIOMAC 15650

To appear in: *International Journal of Biological Macromolecules*

Received date: 10 March 2020

Revised date: 15 May 2020

Accepted date: 20 May 2020

Please cite this article as: A. Dong, K.M. Teklu, W. Wang, et al., New strategy for grafting hydrophobization of lignocellulosic fiber materials with octadecylamine using a laccase/TEMPO system, *International Journal of Biological Macromolecules* (2020), https://doi.org/10.1016/j.ijbiomac.2020.05.167

New strategy for grafting hydrophobization of lignocellulosic fiber materials with octadecylamine using a laccase/TEMPO system

Aixue Dong[a], Kidanu Masho Teklu[a], Weiming Wang[a], Xuerong Fan[b], Qiang Wang[b,*], Mònica Ardanuy[c], Zhen Dong[d]

[a] Key Laboratory of Cleaning Dyeing and Finishing Technology of Zhejiang Province, Shaoxing University, Shaoxing, 312000, Zhejiang, China

[b] Key Laboratory of Eco-Textile, Ministry of Education, Jiangnan University, Wuxi, 214122, Jiangsu, China

[c] Textile Engineering Section, Department of Materials Science and Engineering, Universitat Politècnica de Catalunya, Spain

[d] School of Textiles and Clothing, Nantong University, Nantong, 226019, Jiangsu, China

Abstract

The enzymatic functionalization of lignocellulosic fibers using oxidoreductases was successfully achieved by targeting lignin moieties as grafting sites on the surface. In this study, a novel strategy for hydrophobization of lignocelluloses was investigated, which involved the laccase/TEMPO-mediated grafting of octadecylamine (OA) onto both lignin and cellulose components of jute fabrics. The results showed that OA monomers were successfully grafted onto jute fabric surface using the laccase/TEMPO system with the grafting percentage and efficiency values of 0.712% and 10.571%, respectively. The primary hydroxyl groups of cellulose were oxidized by laccase/TEMPO to carbonyl groups, which were then coupled with amino-contained OA monomers via Schiff base reaction. The phenolic hydroxyl groups of lignin were transformed by laccase to radicals, on which OA molecules were grafted via Michael addition reaction. Consequently, grafted jute fabrics showed a considerable increase in the surface hydrophobicity with a contact angle of 125.9° and a wetting time of at least 2 h. Furthermore, there was an acceptable decrease in the breaking strength of jute fabrics by 13.60%, and the color of fabrics turned yellowish and reddish. This eco-friendly enzymatic process provides a new strategy for grafting hydrophobization and even functionalization of lignocellulosic fiber materials using amino compounds.

Keywords: lignocellulose; laccase/TEMPO; grafting functionalization

1. Introduction

Recently, the use of enzyme technology to achieve the modification of polymer materials has received considerable attention from researchers. Enzymatic modification has incomparable advantages of high selectivity, high efficiency, mild working conditions, and environmental friendliness over conventional physical and chemical reactions. Among the six primary biological enzymes, oxidoreductases have been extensively applied to catalyze polymer synthesis and modification reactions due to their broad range of substrates and varied processing methods [1-5].

Laccases (EC 1.10.3.2, benzenediol: oxygen oxidoreductase) were first found in lacquer in the 1880s, and have since become one of the most investigated enzymes in the field. Laccases can catalyze the monoelectronic oxidation of phenols or amines to form reactive radicals in a redox reaction in which molecular oxygen is simultaneously reduced to water [6]. These radical intermediates can then undergo coupling, polymerization, cleavage of chemical bonds, or degradation of polymers. Laccase could catalyze the polymerization of low-molecular-weight compounds such as phenols and aromatic amines to produce colored substances used for the coloration of natural fibers such as cotton, flax, wool, silk [7-10], and synthetic fibers such as PET [11]. Excellent control over the reactive site of substrates and the chemical structure of polymerization products was achieved in the presence of molecular templates alone with laccase, e.g., the linear polymerization of aniline to synthesize conductive polyaniline [12-13]. The cross-linking or polymerization of lignin mediated by laccase can facilitate wet strengthening in pulp or self-gluing in fiberboard [14-15]. When phenolic or amine compounds are involved as foreign monomers, they can be grafted to lignins on the surface of wood, pulp, hemp fiber, and other lignocellulosic materials by the catalytic oxidation of laccase, thus endowing these materials with various novel functions [16-18].

In the past two decades, many studies have found that the introduction of small molecular mediators increased the range of substrates that can be oxidized via laccase. The application of laccase/mediator systems (LMS) has considerably broadened the versatility of laccase on polymers. Investigations on mediators started with the degradation of lignin in pulp by laccase for biobleaching. Due to its low redox potential, laccase could only oxidize and degrade the phenolic structure of lignins in the pulp, which resulted in the insignificant removal of lignin. However, the degradation of non-phenolic units (90% in lignins) dominated in the presence of mediators to form LMS with laccase [19]. The mediators can be synthetic such as 2,2′-azino-bis-(3-ethylthiazoline-6-sulfonate) (ABTS) and 1-hydroxybenzotriazole (HBT) [20-21], as well as natural with a higher redox potential such as syringaldehyde (SA) and acetosyringone (AS) [22-23]. Due to enzymatic delignification, the bio-bleaching of lignocellulosic pulp or textiles was achieved. Furthermore, the polymerization of lignosulfonates and the grafting of lignocellulose materials were promoted with the assistance of either natural phenolic mediators or synthetic mediators acting together with laccase [24-26].

2,2,6,6-Tetramethylpiperidine-l-oxyl (TEMPO) is a common type of selective oxidants. Recently, studies showed that the primary hydroxyl groups in the structural units of polysaccharides such as starch and cellulose can be preferentially oxidized to aldehyde groups via laccase with TEMPO as the novel mediator [27-28]. The non-enzymatic oxidation of aldehyde groups to carboxyl groups in cellulose improved the wet strength of pulp. Furthermore, the generated aldehyde groups could undergo the Schiff base reaction with amino groups in foreign compounds to form imine (-C=N-) cross-linking. Liu et al. [29] and Shi et al. [30] reported the successful grafting of amino-containing polyethyleneimine to cellulose previously oxidized using the laccase/TEMPO system. Octadecylamine (OA) has been widely utilized for hydrophobic applications due to its long alkyl chain and reactive amino group [31-33]. Although the grafting of OA onto lignocellulosic jute fabrics mediated by laccase proved to be feasible in our former study [34], the reactive sites for grafting could only be targeted at the lignin moieties on the jute surface. To increase the degree of grafting, the laccase/TEMPO combined system was introduced in this study, using which both cellulose and lignin on the surface of lignocelluloses could be grafted with amino monomers such as OA. To the best of our knowledge, no relevant attempt and analysis has been reported yet.

In this study, the novel grafting of lignocellulosic jute fabrics with OA via the laccase/TEMPO system was investigated for surface hydrophobic functionalization. First, the bulk jute fabrics were analyzed by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The surface of jute fabrics was characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). After the surface treatment, the nitrogen content of the fabrics was determined by elemental analysis, from which the grafting percentage (Gp) and grafting efficiency (GE) were calculated for grafting quantification. Finally, the surface hydrophobicity as well as the lignin content, crystallinity, mechanical properties, and chromaticity of the jute fabrics were comprehensively examined.

2. Experimental

2.1. Materials and reagents

Laccase from *Trametes versicolor* and TEMPO were purchased from Sigma-Aldrich (Shanghai, China). The 100% raw jute fabric with a 7/7 (warp/weft) cm^{-1} yarn count and a 427 g/m^2 fabric density was supplied by Longtai Weaving Co., Ltd (Changshu, China). OA (90% purity) was obtained from Aladdin Technology Co. Ltd. (Shanghai, China). All the other chemicals used in this study were commercially available and of analytical grade.

2.2. Laccase assay

The laccase activity was determined using a UV–visible spectrophotometer by monitoring the oxidation of 2,2′-azino-bis-(3-ethylthiazoline-6-sulfonate) (ABTS; $\varepsilon_{420} = 36{,}000\ M^{-1} \times cm^{-1}$) as the substrate at 420 nm in acetate buffer (0.2 M; pH 4.5) at 50 °C. The enzyme activity was expressed in units defined as micromoles of ABTS oxidized per minute [35].

2.3. Pretreatment of jute fabrics

Jute fabrics were Soxhlet-extracted using benzene/ethanol (v/v, 2:1) for 12 h to remove lipophilic extractives and then boiled in distilled water for 3 h to remove water-soluble fractions. Consequently, the enzymatic reaction of substrate molecules and analysis of modified fabrics could be performed without interference.

2.4. Enzymatic grafting of OA onto jute fabric surface

Jute fabrics (1 g) were incubated in 50 mL of acetate buffer (0.2M; pH 4.5) with 1.0 U/mL laccase, 1.4 mg/mL TEMPO, and 10 mM OA. The reaction was performed at 50 °C for 12 h with stirring at 300 r/min using magnetic bars. Then, the fabrics were washed with hot water at 80 °C for 20 min, and extracted with ethanol for 12 h to remove the absorbed OA molecules on the surface. Both control and laccase/TEMPO-treated samples were subjected to the same treatment condition as mentioned above.

2.5. Characterization of jute fabrics

2.5.1. Py-GC/MS analysis

Py-GC/MS of jute fibers was performed with a 3030 pyrolyzer (Frontier Laboratories, Japan) connected to a QP2010 GC/MS system (Shimadzu, Japan). The pyrolysis was conducted at 610°C. The chromatograph was programed from 40 to 300°C at 6 °C/min. The compounds were identified by comparing the obtained mass spectra with those of the Wiley and NIST computer libraries and those reported in the literature [36-37].

2.5.2. FT-IR analysis

FT-IR analysis of jute fabrics was performed using a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific, USA) with the ATR technique. The spectra were recorded in the range of 4000-650 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans per sample.

2.5.3. XPS analysis

The surface elemental contents of jute fabrics were assessed by XPS analysis conducted on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer, USA) with Mg-Kα radiation ($h\nu$ = 1253.6 eV). The X-ray anode was run at 250 W, and a high voltage was maintained at 14.0 kV with a detection angle of 54°. The complete spectra (0-1100 eV) and the narrow spectra of all elements with a much higher resolution were recorded using a RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. Binding energies were calibrated with the contaminant carbon (C1s = 284.6 eV).

2.5.4. SEM analysis

The surface of jute fabric samples was scanned using a JSM-6360LV SEM (JEOL, Japan) at a voltage of 20 kV at 1000×.

2.6. Quantitative estimation of grafting

The total carbon, hydrogen, and nitrogen contents of jute fabrics were determined by an EA3000 elemental analyzer (Euro vector, Italy). The Gp and GE of OA monomers onto jute fabrics were calculated from the total nitrogen contents of the samples according to Eqs. (1) and (2), respectively.

$$Gp(\%) = (N_g - N_c) / 14 \times M_{C_{18}H_{39}N} \tag{1}$$

$$GE(\%) = (N_g - N_c) \times 10^3 / (14 \times 0.05 \times C) \tag{2}$$

where N_g is the nitrogen content of the grafted jute fabric (%), N_c is the nitrogen content of the control jute fabric (%), C is the molar concentration of OA in the grafting reaction (mM), and M is the molar mass of OA (g/mol).

2.7. Performance measurements of jute fabrics

2.7.1. Surface hydrophobicity

The surface hydrophobicity of jute fabrics was assessed by contact angle and wetting time. Before measurements, the jute fabric samples were brought to moisture equilibrium in the standard atmosphere at a relative humidity of 65% ± 5% at 21 ± 1 °C. Then, the contact angle was measured on an OCA50Micro contact angle meter (Dataphysics, Germany). For each sample, five spots were measured and the results were averaged.

The wetting time was measured according to the AATCC Test Method 79-2007. A drop of water was allowed to fall from a height of 10 ± 1 mm onto the taut surface of the tested fabric. The time required for the specular reflectance of water drop to disappear was measured and recorded as the wetting time. Five readings were obtained and averaged for each sample.

2.7.2. Lignin content

The lignin content of jute fabrics was measured using Klason method [38], which involves sulfuric acid hydrolysis and solubilization of carbohydrate components. The lignin left as residue was then determined gravimetrically.

2.7.3. XRD analysis

The crystallinity of jute fabrics was analyzed using an Empyrean X-ray diffractometer (Panalytical, Netherlands) over the 2θ range of 5°-40° at a scanning speed of 4°/min. The crystalline index (C_rI) was calculated using the following equation:

$$C_rI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \qquad (3)$$

where I_{002} is the peak intensity of (002) lattice plane ($2\theta \approx 22°$) and I_{am} is the peak intensity of amorphous phase ($2\theta \approx 18°$).

2.7.4. Tensile properties

Jute fabrics were cut into pieces of 100 mm length and 20 mm width. Then, tensile tests were performed on an electronic tensile testing machine (YG (B) 026D-250; Textile Standard Instrument Co. Ltd., China). The gauge length was set at 60 mm, and the testing speed was 20 mm/min. Data of both breaking strength and elongation were recorded and each measurement was performed using at least five samples.

2.7.5. Colorimetric measurement

The colorimetric properties of the jute fabrics were evaluated using a Datacolor SF 600+ spectrophotometer (Datacolor, USA) using D_{65} illuminant and 10^{o} observer with specular component included. The chromatic parameters, i.e., *L** (lightness), *a** (red-green coordinate), *b** (yellow-blue coordinate), *C** (chroma), and *h** (hue angle) values were all determined.

3. Results and discussion

3.1. Py-GC/MS analysis of jute fabrics

Fig. 1 shows the Py-GC/MS results of laccase/TEMPO/OA-treated, laccase/TEMPO-treated, control jute fabrics, and OA monomer. The identities of characteristic peaks corresponding to OA-grafting in the chromatograms are listed in Table 1. The released compounds and mass fragments of carbohydrate and lignin moieties after Py-GC/MS of jute fabrics could be obtained from Río et al. [36-37]. In the Py-GC/MS chromatogram of OA monomer, the incremental peaks of mass fragments were observed from 112 to 238, which indicated that alkenes with different numbers of carbon atoms were the released compounds derived from OA molecules. After the laccase/TEMPO/OA treatment, the pyrogram of jute fabrics presented similar compounds as that of OA, which could not be observed in the pyrograms of laccase/TEMPO-treated and control jute fabrics. The Py-GC/MS results suggested that OA monomers were incorporated on jute fabrics assisted by the laccase/TEMPO catalytic system.

3.2. Surface analysis of jute fabrics

3.2.1. FT-IR analysis

Fig. 2 shows the ATR-IR spectra of OA monomer and laccase/TEMPO/OA-treated, laccase/TEMPO-treated, and control jute fabrics in the range of 4000-2500 cm^{-1}. The spectrum of

OA exhibited a medium peak at 3333 cm^{-1} and two strong peaks at 2918 and 2851 cm^{-1}, which corresponded to the N-H stretching vibration and the characteristic vibrations of continuous methylene groups ($C-CH_2-C$) [39], respectively. In contrast to the control samples, the spectra of laccase/TEMPO-treated and laccase/TEMPO/OA-treated jute fabrics showed weak O-H stretching vibrations at 3333 cm^{-1} because of the oxidation of both primary hydroxyl groups in cellulose and phenolic hydroxyl groups in lignin to carbonyl groups using the laccase/TEMPO system. Furthermore, the saturated C-H stretching vibration peak at 2897 cm^{-1} in the spectra of the control and laccase/TEMPO-treated jute fabrics was divided into two peaks at 2922 and 2853 cm^{-1} in the spectrum of the laccase/TEMPO/OA-treated jute fabric. The two new peaks could be attributed to the characteristic vibrations of methylene groups ($C-CH_2-C$). The spectral comparison of laccase/TEMPO/OA-treated jute fabric with the other samples and OA monomer indicated that hydroxyl groups on the jute fabric surface were oxidized as the grafting sites. Furthermore, the OA molecules with long methylene chains were grafted onto the jute fabric surface via laccase/TEMPO treatment.

3.2.2. XPS analysis

In addition to FT-IR spectroscopy, XPS was employed to better understand the changes in the surface chemistry of jute fabrics after laccase/TEMPO treatment with OA monomers. Table 2 lists the surface elemental composition of control, laccase/TEMPO-treated, and laccase/TEMPO/OA-treated jute fabrics. The surface nitrogen content of laccase/TEMPO-treated jute increased from 3.71% (control jute) to 4.24%, which could be attributed to the non-specific attachment of few laccase protein traces. Moreover, compared with control samples, the nitrogen content of laccase/TEMPO/OA-treated jute surface was higher (4.00%). The assumed grafting of amino-containing OA on jute fabrics mediated by the laccase/TEMPO system could lead to an increase in surface nitrogen content. However, the laccase/TEMPO/OA-treated samples exhibited lower surface nitrogen content than the laccase/TEMPO-treated samples. This result can be explained by the fact that the absorptive behavior of hydrophilic enzymes was weakened on a hydrophobic surface compared to a hydrophilic surface, which was also observed in our previous study [40]. Furthermore, the surface C/O ratio of the laccase/TEMPO/OA-treated jute fabrics increased from 2.78% to 4.52% because of the laccase/TEMPO-mediated grafting of OA monomers with a high carbon content of 93.9% onto the jute fabric surface.

3.2.3. SEM analysis

SEM was used to examine the surface morphologies of control, laccase/TEMPO-treated, and laccase/TEMPO/OA-treated jute fabrics. The control jute fibers had micro-sized fragments of natural impurities, such as lignin, pectin, and hemicellulose, on the surface (Fig. 3a). After the laccase/TEMPO treatment, the surface of jute fibers became clean (Fig. 3b) due to the laccase-mediated delignification in the presence of TEMPO, which acted as a mediator. The surface of the laccase/TEMPO/OA-treated jute samples was rough and covered with foreign substances, as shown in Fig. 3c. These substances can be considered as the aggregates of OA molecules incorporated by the enzymatic grafting reaction.

3.3. Quantification of OA-grafting onto jute fabrics

The total nitrogen content of jute fabrics was measured by an elemental analyzer, from which the Gp and GE of the OA-grafting reaction on the jute fabrics could be calculated. Table 2 lists the carbon, hydrogen, oxygen, and nitrogen contents of all jute fabric samples. The total nitrogen content of the laccase/TEMPO-treated jute fabric increased from 0.120% (control samples) to

0.136% because of the surface adsorption of laccase proteins. However, the laccase/TEMPO/OA-treated jute fabrics had considerably higher bulk nitrogen content of 0.194%. The tendency and magnitude of variation were different compared to the XPS data. XPS spectroscopy is useful to obtain the chemical composition information of material surfaces within 10 nm. Generally, the diameter of jute fiber is 15-25 µm, and the so-called surface area consisting of outermost middle lamella and primary cell wall is ≤1 µm wide. Therefore, a distinct change in the surface nitrogen content determined by XPS may result in a slight variation in the bulk nitrogen proportion of jute fibers. The depth of OA-grafting on the jute surface was probably larger than that of the XPS measurement and the laccase adsorption.

Furthermore, the Gp and GE of OA-grafting reaction mediated by laccase/TEMPO under certain treatment conditions were 1.42% and 10.57%, respectively, calculated according to the abovementioned Eqs. (1) and (2).

3.4. Proposed grafting mechanism of OA onto lignocelluloses via laccase/TEMPO system

Lignocellulosic materials such as jute fibers are primarily composed of cellulose, hemicellulose, and lignin. Cellulose is a polysaccharide comprising a linear chain of several hundreds to many thousands of β (1→4) linked D-glucose units, which have numerous hydroxyl functional groups. Lignin comprises three structural units, i.e., guaiacyl, syringyl, and *p*-hydroxyphenyl. Fig. 4 shows the grafting mechanism of OA onto the lignocellulose material surface mediated by the laccase/TEMPO system. For lignin on the surface, the phenolic hydroxyl groups of guaiacyl units were oxidized by laccase to phenoxyl radicals, to which amine molecules of interest could be grafted by the secondary amino linkage (-NH-) (Michael addition reaction) [34]. For cellulose on the surface, the C6 primary hydroxyl groups of glucose units were oxidized by laccase/TEMPO system to aldehyde groups. Furthermore, these reactive sites could then induce the nucleophilic addition reaction of foreign molecules with electron-donating substituents such as amino groups to form the imine bond (-C=N-) by condensation (Schiff base reaction) [41]. Consequently, OA was grafted onto both cellulose and lignin moieties of the lignocellulosic surface to endow them with excellent hydrophobicity. The new proposed strategy for the grafting hydrophobization of lignocellulosic fiber materials with aliphatic amine mediated by laccase/TEMPO system had the advantages of higher Gp compared with grafting to only lignin moieties by laccase alone. The nitrogen content of OA-grafted jute fibers mediated by laccase/TEMPO system was increased by 0.037% in contrast with those mediated by laccase. The Gp of laccase-mediated OA-grafting was only 0.71% [34]. However, the Gp of laccase/TEMPO-mediated OA-grafting doubled to 1.42%.

3.5. Effect of OA-grafting on the surface hydrophobicity of lignocellulosic jute fabrics

Table 3 lists the contact angle and wetting time of water on lignocellulosic jute fabrics. Control jute fabrics were hydrophilic with the contact angle of 99.3° and the wetting time of 18.0 s, because the pre-treatment removed the lipids and waxes on the original jute fibers by extraction using a benzene/ethanol solution. The laccase/TEMPO-treated jute fabrics exhibited minor variations in the surface hydrophobicity compared with control samples. For the laccase/TEMPO/OA-treated jute fabrics, OA monomers with nonpolar alkyl chains were grafted on the jute surface mediated by the laccase/TEMPO system. Thus, the surface hydrophobicity of lignocellulosic jute fabrics increased, as evidenced by a larger contact angle of 125.9° and a much longer wetting time of at least 2 h.

3.6. Influence of laccase/TEMPO treatment on lignocellulosic jute fabrics

3.6.1 Lignin proportion

Table 4 lists the lignin contents, crystallinity degree, and tensile properties of different treated jute fabrics. The control jute fabrics had a lignin content of 10.83%, which was determined using Klason method. After the laccase/TEMPO treatment, the lignin content decreased to 8.59% due to the oxidation and degradation of lignin macromolecular structures by the laccase and TEMPO combined system. Initially, the laccase/TEMPO system was utilized in pulp processing, as it achieved delignification and decrease in the kappa number of pulp. Xu et al. [42] reported that the primary hydroxyl groups of cellulose in pulp were converted to carboxyl groups via the laccase/TEMPO catalysis, which led to improvements in the tensile and bursting wet strength of pulp. As the laccase/TEMPO-mediated grafting of OA occurred on both the cellulose and lignin moieties of lignocellulose materials, the lignin content in the laccase/TEMPO/OA-treated jute fabrics increased to 12.12% due to coupling with OA.

3.6.2 Crystallinity

For the control jute fabrics, the degree of cellulose crystallinity was 64.07%. After the laccase/TEMPO oxidation, the crystallinity of cellulose in jute fabrics slightly decreased to 63.20%. Additional charges were introduced on the cellulose macromolecules by the formation of carboxyl groups via laccase/TEMPO, which gave rise to swelling of fibers and reduced the crystallinity degree. The OA-grafting was favorable for the crystallization behavior of jute fibers, which showed an increased crystallinity degree of 66.72%. The enhancing mechanism of crystallinity by OA-involving or OA-grafting is not clear yet and would be investigated further.

3.6.3 Mechanical properties

The breaking strength and elongation of control jute fabrics were 464.0 N and 6.33%, respectively. Although some lignin in jute fibers was removed and the crystallinity was slightly decreased after the laccase/TEMPO treatment, the breaking strength of jute fabrics was barely affected because of the construction structure of yarns and woven fabrics. The possible reason for the increase in breaking elongation (by 6.95%) was that the cohesive force between jute fibers in yarns decreased because of a smooth fiber surface after the laccase/TEMPO treatment. The OA-grafted jute fabrics mediated by laccase/TEMPO system showed a decrease in breaking strength by 13.60% compared with control samples, which was acceptable for the surface functionalization of fabrics according to relevant standards.

3.6.4. Colorimetric properties

The colorimetric properties of variously treated jute fabrics were evaluated in terms of the chromatic parameters such as *L**, *a**, *b**, *C**, and *h** values based on the CIELAB system, as shown in Table 5.

The color of control jute fabrics was yellow with the *h** value of 73.34. After the laccase/TEMPO treatment, jute fabrics turned yellower and brighter, which was demonstrated by the larger *h** value (75.38) and greater *L** value (61.80). This behavior was possibly due to the degradation of lignin and decoloration because of the laccase/TEMPO-mediated oxidation. The OA-grafted jute fabrics mediated by laccase/TEMPO system appeared reddish yellow with minimum *h** value of 70.48, and had moderate lightness with medium *L** value of 59.05, compared to the control jute fabrics and laccase/TEMPO-treated jute fabrics. Furthermore, the *a** value of grafted jute fabrics decreased to 6.21 and *b** value considerably decreased to 17.52, giving rise to a remarkable decrease in *C** value. This suggested that the color saturation of jute fabrics reduced after the laccase/TEMPO-mediated grafting with OA monomer, which indicates that the fabric color turned yellowish.

4. Conclusions

This study demonstrated the covalent grafting of lignocellulosic jute fabrics with nonpolar OA monomers using a novel laccase/TEMPO system for surface hydrophobic functionalization. The grafting reaction could be targeted at both the lignin and cellulose moieties of jute fabrics. Bulk jute fabrics were analyzed by Py-GC/MS and the jute fabric surface was characterized by FT-IR, XPS, and SEM. The results confirmed the presence of OA molecules on jute fabrics after laccase/TEMPO treatment. The Gp and GE of OA on jute fabrics were 0.712% and 10.571%, respectively, calculated from the total nitrogen content of substrates. The phenolic hydroxyl groups of lignin were transformed by laccase itself to radicals, on which the OA molecules were grafted via the Michael addition reaction. The primary hydroxyl groups of cellulose were oxidized by laccase/TEMPO to carbonyl groups, which were then coupled to amino-containing OA monomer via the Schiff base reaction. A contact angle of 125.9° and a wetting time of at least 2 h indicated that the surface hydrophobicity of jute fabrics was considerably increased after graft modification, and the jute achieved excellent water repellency. Furthermore, there was an acceptable decrease in the breaking strength of jute fabrics by 13.60%, and the color of fabrics became yellowish and reddish as a result of the treatment. To summarize, this eco-friendly enzymatic process provides a new strategy for the grafting hydrophobization and even functionalization of lignocellulosic fiber materials with amino compounds.

Acknowledgements

The work was funded by Zhejiang Provincial Natural Science Foundation of China (LGG18E030005), Fundamental Research Funds for the Central Universities (JUSRP51717A), China Postdoctoral Science Foundation (2019M652273), Jiangxi Excellent Young Talents Program (20192BCB23030), Jiangsu Key Research & Development Plan (BE2018349) and Open Project Program of Key Laboratory of Eco-textiles, Ministry of Education, Jiangnan University (KLET1703).

References

[1] S.R. Zavada, T. Battsengel, T.F. Scott, Radical-mediated enzymatic polymerizations, Intl. J. Molecular Sciences 17 (2016) 195-221. https://doi.org/10.3390/ijms17020195

[2] S. Shoda, H. Uyama, J. Kadokawa, S. Kimura, S. Kobayashi, Enzymes as green catalysts for precision macromolecular synthesis, Chemical Reviews 116 (2016) 2307-2413. https://doi.org/10.1021/acs.chemrev.5b00472

[3] S. Slagman, H.Zuilhof, M.C.R. Franssen, Laccase-mediated grafting on biopolymers and synthetic polymers: a critical review, ChemBioChem, 19 (2018) 288-231. https://doi.org/10.1002/cbic.201700518

[4] M. He, H. Hu, P. Wang, H. Fu, J. Yuan, Q. Wang, X. Fan, Preparation of a bio-composite of sericin-g-PMMA via HRP-mediated graft copolymerization, Intl. J. Biological Macromolecules 117 (2018) 323-330. https://doi.org/10.1016/j.ijbiomac.2018.05.190

[5] L. Wang, X. Zhang, J. Xu, Q. Wang, X. Fan, How starch-g-poly(acrylamide) molecular structure effect sizing properties, Intl. J. Biological Macromolecules 144 (2020) 403-409. https://doi.org/10.1016/j.ijbiomac.2019.12.143

[6] D.S. Arora, R.K. Sharma, Ligninolytic fungal laccases and their biotechnological applications, Applied Biochem. Biotech. 160 (2010) 1760-1788. https://doi.org/10.1007/s12010-009-8676-y

[7] S. Kim, C. Silva, D.V. Evtuguin, J.A.F. Gamelas, A. Cavaco-Paulo, Polyoxometalate/laccase-mediated oxidative polymerization of catechol for textile dyeing, Applied Microbiol. Biotech. 89 (2011) 981-987. https://doi.org/10.1007/s00253-010-2932-5

[8] M. Schroeder, N. Aichernig, G.M. Guebitz, V. Kokol, Enzymatic coating of lignocellulosic surfaces with polyphenols, Biotechnology J. 2 (2007) 334-341. https://doi.org/10.1002/biot.200600209

[9] R. Bai, Y. Yu, Q. Wang, X. Fan, P. Wang, J. Yuan, J. Shen, Laccase-catalyzed poly(ethylene glycol)-templated ‘zip’ polymerization of caffeic acid for functionalization of wool fabrics, J. Cleaner Production 191 (2018) 48-56. https://doi.org/10.1016/j.jclepro.2018.04.213

[10] W. Jia, Q. Wang, X. Fan, A. Dong, Y. Yu, P. Wang, Laccase-mediated in situ oxidation of dopa for bio-inspired coloration of silk fabric, RSC advances 7 (2017) 12977-12983. https://doi.org/10.1039/C6RA25533G

[11] J. Su, J. Noro, J. Fu, Q.Wang, C. Silva, A. Cavaco-Paulo, Enzymatic polymerization of catechol under high-pressure homogenization for the green coloration of textiles, J. Cleaner Production 202 (2018) 792-798. https://doi.org/10.1016/j.jclepro.2018.08.205

[12] K. Junker, R. Kissner, B. Rakvin, Z. Guo, M. Willeke, S. Busato, T. Weber, P. Walde, The use of *Trametes versicolor* laccase for the polymerization of aniline in the presence of vesicles as templates, Enzyme Microbial Tech. 55 (2014) 72-84. https://doi.org/10.1016/j.enzmictec.2013.12.008

[13] Y. Zhang, X. Fan, Q. Wang, A. Cavaco-Paulo, Preparation of functionalized cotton based on laccase-catalyzed synthesis of polyaniline in perfluorooctanesulfonate acid potassium salt (PFOS) template, RSC Advances 6 (2016) 49272-49280.

https://doi.org/10.1039/C6RA04031D

[14] M. Lund, C. Felby, Wet strength improvement of unbleached kraft pulp through laccase catalyzed oxidation, Enzyme Microbial Tech. 28 (2001) 760-765. https://doi.org/10.1016/S0141-0229(01)00339-8

[15] M. Nasir, A. Gupta, M.D.H. Beg, G.K. Chua, M. Asim, Laccase application in medium density fibreboard to prepare a bio-composite, RSC Advances 4 (2014) 11520-11527. https://doi.org/10.1039/C3RA40593A

[16] G.S. Nyanhongo, T. Kudanga, E.N. Prasetyo, G.M. Guebitz, Mechanistic insights into laccase-mediated functionalisation of lignocellulose material, Biotechnology and Genetic Engineering Reviews 27 (2010) 305-330. https://doi.org/10.1080/02648725.2010.10648155

[17] S. Kalia, K. Thakur, A. Kumar, A. Celli, Laccase-assisted surface functionalization of lignocellulosics, J. Molecular Catalysis B: Enzymatic 102 (2014) 48-58. https://doi.org/10.1016/j.molcatb.2014.01.014

[18] Q. Zhou, L. Cui, L. Ren, P. Wang, C. Deng, Q. Wang, X. Fan, Preparation of a multifunctional fibroin-based biomaterial via laccase-assisted grafting of chitooligosaccharide, Intl. J. Biological Macromolecules 113 (2018) 1062-1072. https://doi.org/10.1016/j.ijbiomac.2018.03.042

[19] J. Sealey, A.J. Ragauskas, Investigation of laccase/N-hydroxybenzotriazole delignification of kraft pulp, J. Wood Chemistry and Technology 18 (1998) 403-416. https://doi.org/10.1080/02773819809349588

[20] S. Camarero, O. García, T. Vidal, J. Colom, J.C. del Río, A.Gutiérrez, J.M. Gras, R. Monje, M.J. Martínez, Á.T. Martínez, Efficient bleaching of non-wood high-quality paper pulp using

laccase-mediator system, Enzyme Microbial Tech. 35 (2004) 113-120. https://doi.org/10.1016/j.enzmictec.2003.10.019

[21] Y. Zhang, Q. Wang, X. Fan, J. Yuan, Structural changes of lignin in the jute fiber treated by laccase and mediator system, J. Molecular Catalysis B Enzymatic 101 (2014) 133-136. https://doi.org/10.1016/j.molcatb.2013.12.010

[22] A. Fillat, J.F. Colom, T. Vidal, A new approach to the biobleaching of flax pulp with laccase using natural mediators, Bioresource Tech. 101 (2010) 4104-4110. https://doi.org/10.1016/j.biortech.2010.01.057

[23] A.G. Barneto, E. Aracri, G. Andreu, T. Vidal, Investigating the structure-effect relationships of various natural phenols used as laccase mediators in the biobleaching of kenaf and sisal pulps, Bioresource Tech. 112 (2012) 327-335. https://doi.org/10.1016/j.biortech.2012.02.136

[24] E.N. Prasetyo, T. Kudanga, L. Østergaard, J. Rencoret, A. Gutiérrez, J.C. del Río, J.I. Santos, L. Nieto, J. Jiménez-Barbero, A.T. Martínez, J. Li, G. Gellerstedt, S. Lepifre, C. Silva, S.Y. Kim, A. Cavaco-Paulo, B.S. Klausen, B.F. Lutnaes, G.S. Nyanhongo, G.M. Guebitz, Polymerization of lignosulfonates by the laccase-HBT (1-hydroxybenzotriazole) system improves dispersibility, Bioresource Tech. 101 (2010) 5054-5062. https://doi.org/10.1016/j.biortech.2010.01.048

[25] C. Silva, T. Matamá, S.Y. Kim, J. Padrão, E.N. Prasetyo, T. Kudanga, G.S. Nyanhongo, G.M. Guebitz, M. Casal, A. Cavaco-Paulo, Antimicrobial and antioxidant linen via laccase-assisted grafting, Reactive Functional Polymers 71 (2011) 713-720. https://doi.org/10.1016/j.reactfunctpolym.2011.03.011

[26] E.H. Acero, T. Kudanga, A. Ortner, I. Kaluzna, S. Wildeman, G.S. Nyanhongo, G.M. Guebitz,

Laccase functionalization of flax and coconut fibers, Polymers 6 (2014) 1676-1684. https://doi.org/10.3390/polym6061676

[27] S. Mathew, P. Adlercreutz, Mediator facilitated, laccase catalysed oxidation of granular potato starch and the physico-chemical characterisation of the oxidized products, Bioresource Tech. 100 (2009) 3576-3584. https://doi.org/10.1016/j.biortech.2009.02.035

[28] D. Jaušovec, R. Vogrinčič, V. Kokol, Introduction of aldehyde vs. carboxylic groups to cellulose nanofibers using laccase/TEMPO mediated oxidation, Carbohydrate Polymers 116 (2015) 74-85. https://doi.org/10.1016/j.carbpol.2014.03.014

[29] J. Liu, R. Pelton, J.M. Obermeyer, A. Esser, Laccase complex with polyvinylamine bearing grafted TEMPO is a cellulose adhesion primer, Biomacromolecules 14 (2013) 2953-2960. https://doi.org/10.1021/bm4009827

[30] S. Shi, R. Pelton, Q. Fu, S. Yang, Comparing polymer-supported TEMPO mediators for cellulose oxidation and subsequent polyvinylamine grafting, Industrial Eng. Chem. Res. 53 (2014) 4748-4754. https://doi.org/10.1021/ie500280e

[31] Y. Liu, Z. Liu, Y. Liu, H. Hu, Y. Li, P. Yan, B. Yu, F. Zhou, One-step modification of fabrics with bioinspired polydopamine@octadecylamine nanocapsules for robust and healable self-cleaning performance, Small 11 (2014) 426-431. https://doi.org/10.1002/smll.201402383

[32] R.K. Johnson, A. Zink-Sharp, W.G. Glasser, Preparation and characterization of hydrophobic derivatives of TEMPO-oxidized nanocelluloses, Cellulose 18 (2011) 1599-1609. https://doi.org/10.1007/s10570-011-9579-y

[33] J. Du, X. Luo, Z. Fu, C. Xu, X. Ren, W. Gao, Y. Li, Improving the hydrophobicity of nylon fabric by consecutive treatment with poly(acrylic acid), tetraethylorthosilicate, and

octadecylamine, J. Appl. Polym. Sci. 132 (2015) 42456-42459. https://doi.org/10.1002/app.42456

[34] A. Dong, X. Fan, Q. Wang, Y. Yu, A. Cavaco-Paulo, Hydrophobic surface functionalization of lignocellulosic jute fabrics by enzymatic grafting of octadecylamine, Intl. J. Biological Macromolecules 79 (2015) 353-362. https://doi.org/10.1016/j.ijbiomac.2015.05.007

[35] R.E. Childs, W.G. Bardsley, The steady-state kinetics of peroxidase with 2,2’-azino-bis-(3-ethylthiazoline-6-sulfonic acid) as chromogen, Biochemical J. 145 (1975) 93-103. https://doi.org/10.1042/bj1450093

[36] J.C. del Río, J. Rencoret, G. Marques, J. Li, G. Gellerstedt, J. Jiménez-Barbero, Á.T. Martínez, A. Gutiérrez, Structural characterization of the lignin from jute (*Corchorus capsularis*) fibers, J. Agri. Food Chem. 57 (2009) 10271-10281. https://doi.org/10.1021/jf900815x

[37] J.C. del Río, J. Rencoret, P. Prinsen, Á.T. Martínez, J. Ralph, A. Gutiérrez, Structural characterization of wheat straw lignin as revealed by analytical pyrolysis, 2D-NMR, and reductive cleavage methods, J. Agri. Food Chem. 60 (2012) 5922-5935. https://doi.org/10.1021/jf301002n

[38] A. Alves, M. Schwanninger, H. Pereira, J. Rodrigues, Analytical pyrolysis as a direct method to determine the lignin content in wood: Part 1: Comparison of pyrolysis lignin with Klason lignin, J. Anal. Appl. Pyrolysis 76 (2006) 209-213. https://doi.org/10.1016/j.jaap.2005.11.004

[39] K.M.G. Hossain, M.D. Gonzalez, G.R. Lozano, T. Tzanov, Multifunctional modification of wool using an enzymatic process in aqueous–organic media, J. Biotechnology 141 (2009) 58-63. https://doi.org/10.1016/j.jbiotec.2009.02.011

[40] A. Dong, Y. Yu, J. Yuan, Q. Wang, X. Fan, Hydrophobic modification of jute fiber used for composite reinforcement via laccase-mediated grafting, Applied Surface Science 301 (2014) 418-427. https://doi.org/10.1016/j.apsusc.2014.02.092

[41] Y. Yu, Q. Wang, J. Yuan, X. Fan, P. Wang, L. Cui, Hydrophobic modification of cotton fabric with octadecylamine via laccase/TEMPO mediated grafting, Carbohydrate Polymers 137 (2016) 549-555. https://doi.org/10.1016/j.carbpol.2015.11.026

[42] S. Xu, Z. Song, X.Qian, J. Shen, Introducing carboxyl and aldehyde groups to softwood-derived cellulosic fibers by laccase/TEMPO-catalyzed oxidation, Cellulose 20 (2013) 2371-2378. https://doi.org/10.1007/s10570-013-9985-4

Figure captions

Fig. 1. Py-GC/MS chromatograms of laccase/TEMPO/OA-treated, laccase/TEMPO-treated, control jute fabrics, and OA monomer.

Fig. 2. FT-IR spectra of control, laccase/TEMPO-treated, laccase/TEMPO/OA-treated jute fabrics, and OA monomer.

Fig. 3. SEM images of control (A), laccase/TEMPO-treated (B), and laccase/TEMPO/OA-treated (C) jute fabrics magnified at 1 k.

Fig. 4. Schematic illustration and proposed pathway of OA-grafting reaction on the jute fabric surface (targeted at both cellulose and lignin moieties) mediated by the laccase/TEMPO system.

Fig. 5. XRD spectra of laccase/TEMPO/OA-treated, laccase/TEMPO-treated, and control jute fabrics.

Table 1

Peaks and their identities in the Py-GC/MS chromatograms of laccase/TEMPO/OA-treated jute fabrics and OA monomer.

OA monomer			Laccase/TEMPO/OA-treated jute fabrics		
No.	Mass fragments	Formula	No.	Mass fragments	Formula
1	112	C_8H_{16}	1	126	C_9H_{18}
2	126	C_9H_{18}	2	140	$C_{10}H_{20}$
3	140	$C_{10}H_{20}$	3	168	$C_{12}H_{24}$
4	154	$C_{11}H_{22}$	4	170	$C_{12}H_{26}$
5	168	$C_{12}H_{24}$	5	182	$C_{13}H_{26}$
6	182	$C_{13}H_{26}$	6	184	$C_{13}H_{28}$
7	196	$C_{14}H_{28}$	7	196	$C_{14}H_{28}$
8	210	$C_{15}H_{30}$	8	198	$C_{14}H_{30}$
9	224	$C_{16}H_{32}$	9	210	$C_{15}H_{30}$
10	238	$C_{17}H_{34}$	10	212	$C_{15}H_{32}$

Table 2

XPS analysis and total elemental analysis of jute fabrics after different treatments.

Treatments	Surface elements (%)				Total elements (%)				
	C	O	N	C/O	C	H	O	N	C/O
Control	70.82	25.48	3.71	2.78	43.541	6.152	50.187	0.120	0.868
Laccase/TEMPO	68.75	27.01	4.24	2.55	43.991	6.327	49.545	0.136	0.888
Laccase/TEMPO/OA	78.63	17.38	4.00	4.52	44.192	6.430	49.186	0.194	0.898

Table 3

Contact angle and wetting time of jute fabrics after different treatments.

Jute fabric samples	Contact angle (^{o})	Wetting time
Laccase/TEMPO/OA	125.9 ± 1.7	> 2 h
Laccase/TEMPO	98.7 ± 6.5	23.7 s ± 10.0 s
Control	99.3 ± 7.8	18.0 s ± 4.2 s

Table 4

Lignin contents, crystallinity, and tensile properties of jute fabrics after different treatments.

Jute fabric samples	Lignin content (%)	Degree of crystallinity (%)	Breaking strength (N)	Breaking elongation (%)
Laccase/TEMPO/OA	12.12 ± 0.20	66.72	400.9 ± 37.3	6.67 ± 0.56
Laccase/TEMPO	8.59 ± 0.05	63.20	469.6 ± 33.3	6.77 ± 0.36
Control	10.83 ± 0.16	64.07	464.0 ± 29.1	6.33 ± 0.42

Table 5

Chromatic parameters of jute fabrics after different treatments.

Jute fabric samples	*L**	*a**	*b**	*C**	*h**
Laccase/TEMPO/OA	59.05	6.21	17.52	18.59	70.48
Laccase/TEMPO	61.80	6.87	26.34	27.22	75.38
Control	57.10	7.61	25.44	26.55	73.34

Graphical abstract

Highlights

1. Octadecylamine (OA) monomers were successfully grafted onto jute fabric surface using the laccase/TEMPO system.
2. The OA-grafting of jute fabrics was quantified in terms of grafting percentage and grafting efficiency, which were calculated from the total nitrogen content of jute fabrics.
3. Grafted jute fabrics showed a considerable increase in the surface hydrophobicity.
4. OA molecules were grafted by laccase/TEMPO onto both lignin and cellulose components of jute fabrics.
5. This eco-friendly enzymatic process provides a new strategy for grafting hydrophobization and even functionalization of lignocellulosic fiber materials using amino compounds.