

# Hydrophobic modification of jute fiber used for composite reinforcement via laccase-mediated grafting



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## ABSTRACT

Jute fiber is a lignocellulosic material which could be utilized for reinforcement of composites. To improve the compatibility of hydrophilic jute fiber with hydrophobic resin, surface hydrophobization of the fiber is often needed. In this study, the feasibility of laccase-mediated grafting dodecyl gallate (DG) on the jute fiber was investigated. First, the grafting products were characterized by FT-IR, XPS, SEM and AFM. And then the grafting percentage ( $G_p$ ) and the DG content of the modified jute were determined in terms of weighting and saponification, respectively. The parameters of the enzymatic grafting process were optimized to the target application. Lastly, the hydrophobicity of the jute fabrics was estimated by means of contact angle and wetting time. The mechanical properties and the fracture section of the jute fabric/polypropylene (PP) composites were studied. The results revealed covalently coupling of DG to the jute substrates mediated by laccase. The enzymatic process reached the maximum grafting rate of 4.16% when the jute fabric was incubated in the 80/20 (v/v, %) pH 3 0.2M acetate buffer/ethanol medium with 1.0 U/mL laccase and 5 mM DG at 50 °C for 4 h. The jute fabric modified with laccase and DG showed increased contact angle of 111.49° and wetting time of at least 30 min, indicating that the surface hydrophobicity of the jute fabric was increased after the enzymatic graft modification with hydrophobic DG. The breaking strength of the modified jute fiber/PP composite was also increased and the fracture section became neat and regular due to the laccase-assisted grafting with DG.

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## 1. Introduction

The development of biodegradable composites with high performance has become one of the hottest research areas in the world with the increased consciousness of environmental protection. Investigations into the application of some natural plant fibers such as ramie fiber, flax fiber, jute fiber, bamboo fiber and wood fiber as the fiber reinforced materials in composites are increasing in recent years [1,2]. These natural fibers have the merits of low cost, abundant, light weight and high strength. Meanwhile, the natural fiber reinforced composites can meet both the requirements of property enhancement and eco-friendly nature. However, the natural fibers have poor compatibility with hydrophobic resins owing to their high polarity and hydrophilicity, which deteriorates the mechanical properties of the composites [3]. In order to obtain high performance composites, the surface modification of natural fibers has been proved to be an important and practical method.

Two traditional approaches, i.e., physical and chemical processing technologies, have been developed for the modification of natural fibers. The reprehensive physical methods include heat treatment [4], steam explosion [5], cold plasma processing [6] and high energy ray radiation processing [7]. They could enhance the affinity and adhesion strength between the fiber and the resin matrix by altering the fiber surface structure. The chemical methods which consist of graft polymerization by chemical initiator [8] or high energy ray [9] and couplers [10] mainly change the components of the fiber by introducing some new compounds via covalent binding or electrostatic adsorption.

However, these physico-chemical means have some inherent weaknesses. The physical processes can seriously deteriorate the mechanical properties of the natural fibers such as tensile strength and are difficult to industrialize [6,7]. Although the chemical modification through grafting polymerization can increase the hydrophobicity of the fibers and improve the compatibility with hydrophobic resin matrix, it is also known that the homopolymerization of the monomers will occur inevitably. Modifications of the fibers with silicon compounds usually involve complicated and expensive multi-step processes, but such treatments are

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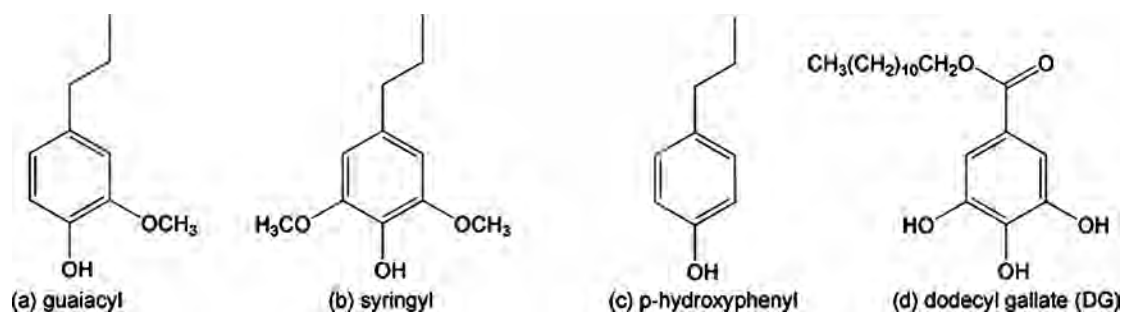


Fig. 1. The compositions of lignin (a–c) and the formula of dodecyl gallate (d).

usually recommended for fiber exposed to hazard conditions due to their high chemical and weathering stability [11].

In response to these shortcomings of these physic-chemical methods, enzymes such as laccase have emerged as important biotechnological catalysts for their eco-friendly nature and mild working conditions. The laccase (EC 1.10.3.2, *p*-diphenol: dioxygen oxidoreductase) is a multi-copper glycoprotein that catalyzes the mono-electronic oxidation of phenols and aromatic or aliphatic amines to reactive radicals in a redox reaction in which molecular oxygen is simultaneously reduced to water [12,13]. Lignin is a three-dimensional polymer composed of guaiacyl, syringyl and *p*-hydroxyphenyl units (Fig. 1) linked together in an irregular manner [14]. *p*-Hydroxyphenyl unit is a minor component of herbaceous lignins such as bast fibers. Researches show that the phenolic sites of some lignin-related substrates can be oxidized to phenoxyl radicals by laccase [15,16]. The obvious result of the lignin transformation by laccase was an increase of the molecular weight caused by the coupling of generated phenoxyl radicals regardless the radical induced degradation is simultaneous existed [16,17].

Moreover, the grafting reaction usually involves oxidation of lignin to create reactive radicals to which oxidized (radical-containing) or non-oxidized molecules of interest can be grafted to produce new engineering materials [18–22]. Investigations into the possibility of enzymatic bonding functional molecules to lignocellulosic materials using laccases to endow them with novel functions are also increasing in recent years. For instance, the laccase-mediated grafting of functional monomers to the lignin model compounds was studied by Kudanga et al. mainly by means of HPLC and MS [23–26]. Based on the similar mechanism, the functionalization of lignin-based materials including wood [25–27], bast fibers [28–30] and pulp [31–33] was also carried out.

Dodecyl gallate (DG, Fig. 1d) was first applied to the enzymatic multifunctional modification of wool by Hossain et al. [34,35]. Then the laccase-aided modifications of nanofibrillated cellulose and kraft pulp with DG were reported, respectively [36,37]. DG is

well known because of its hydrophobicity [35] and antioxidative properties [38,39]. The enzymatic grafting of DG onto lignocellulosic fibers for increasing their surface hydrophobicity provides a new approach for the modification of the fiber reinforced materials in composites. As far as our knowledge goes, none attempt has seemingly been made.

In this work, an effort using green biotechnology to increase the surface hydrophobicity of the jute fiber used as reinforced material of resin matrix composites was attempted, i.e., DG was enzymatically grafted onto the jute fabric by laccase, as presented in Fig. 2. The proposed pathway of the enzymatic reaction is shown in Fig. 3. The grafting products were characterized by FT-IR, XPS, SEM and AFM. Then the grafting rate and the DG content of the modified jute were determined. The conditions of the enzymatic grafting process where the maximum reactivity would be reached with the minimal cost were searched. Further, the hydrophobicity of the jute fabrics was estimated. And the mechanical properties as well as the tension fracture section of the jute fabric/polypropylene (PP) composites were investigated.

## 2. Experimental

### 2.1. Materials and reagents

Laccase from the *Aspergillus* species, Denilite II in graininess, was provided by Novozymes (Shanghai, China). The 100% raw jute fabric, with a 7/7 (warp/weft)  $\text{cm}^{-1}$  yarn count, was supplied by Longtai weaving limited company (Changshu, China). The polypropylene (PP) spunlace non-woven cloth was purchased from Yonghui textile technology limited company (Yangzhou, China). Dodecyl gallate (DG) with 98% purity was obtained from J&K Technology Co. Ltd. (Beijing, China). All the other chemicals used in the study were commercially available and were of analytical purity.

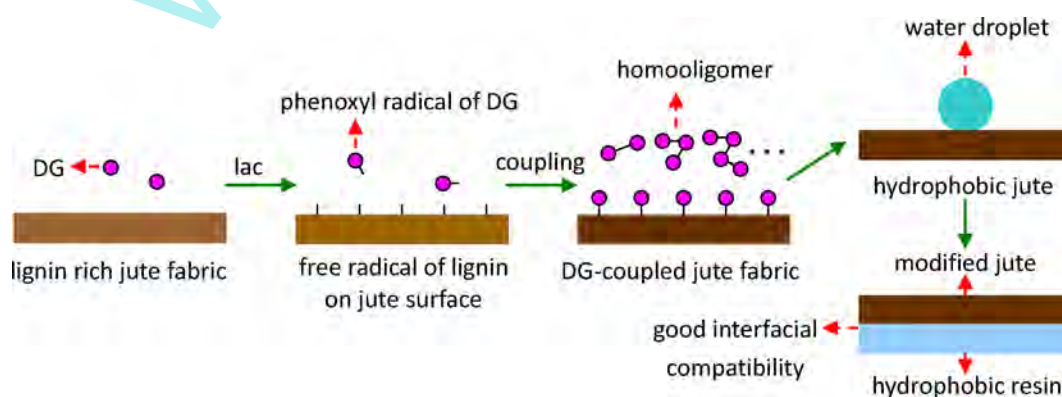


Fig. 2. Schematic illustration of the grafting reaction of dodecyl gallate (DG) on the lignin rich jute fabric catalyzed by laccase (lac).

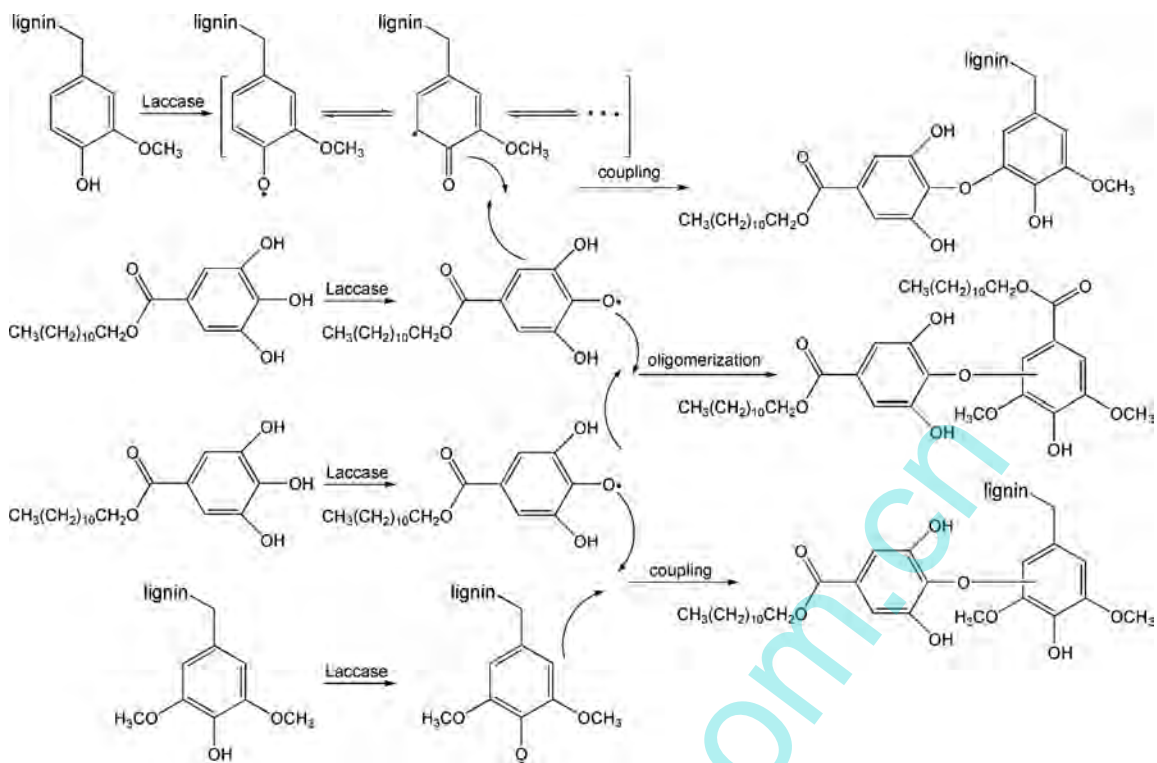


Fig. 3. The proposed pathway of the enzymatic reaction.

## 2.2. Laccase assay

The activity of laccase was measured using a UV/Vis spectrophotometer by monitoring the oxidation of 2,2'-azino-bis-(3-ethylthiazoline-6-sulfonate) (ABTS;  $\epsilon_{420} = 36,000 \text{ M}^{-1} \times \text{cm}^{-1}$ ) as substrate at 420 nm in the aqueous/organic medium (80/20, % (v/v), 0.2 M acetate buffer/EtOH). The enzyme activity was expressed in units defined as micromoles of ABTS oxidized per minute [40].

Then the pH of acetate buffer and the incubation temperature in the laccase activity were optimized. The reaction for pH optimization measurement proceeded with pH values ranged from 2 to 7 at room temperature. For each temperature studied (30, 40, 50, 60 and 70 °C), the pH of the acetate buffer was chosen as the optimum for laccase activity. The incubation procedure was the same as described in pH optimization.

## 2.3. Pretreatment of jute fabrics

The jute fabrics were Soxhlet-extracted with benzene/ethanol (v:v, 2:1) for 12 h to remove lipophilic extractives which would interfere with the oxidation of substrate molecules and affect analysis of modified surface. Then the fabrics were boiled with distilled water for 3 h, followed by the treatment using 5 g/L ammonium oxalate for 3 h to remove pectins. As a result, more lignins were exposed on the surfaces of the jute fibers.

## 2.4. Grafting of DG onto jute surface

Jute fabrics of 1 g were incubated for 4 h in 50 mL 80/20 (v/v, %) 0.2 M acetate buffer/EtOH solutions with 1.0 U/mL laccase and 5 mM DG in a shaking bath. The pH of the acetate buffer (0.2 M) and the temperature of the reaction were consistent with the optimum for the laccase activity. Control samples and the treated samples with either laccase or DG followed the same treatment condition as mentioned above.

Afterwards, the fabrics were washed with distilled water at 80 °C twice and then extracted with acetone for 12 h to remove the absorbed DG and the homooligomers of the monomers.

## 2.5. Characterization of jute fabric surface

### 2.5.1. FT-IR analysis

The FT-IR analysis 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  $\text{cm}^{-1}$  at 4  $\text{cm}^{-1}$  resolution and 16 scans per sample.

### 2.5.2. XPS analysis

Binding of DG to jute fabrics was assessed using X-ray photoelectron spectroscopy (XPS). XPS experiments were carried out at Laboratory of Surface Chemistry, Fudan University (Shanghai, China) on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg  $K\alpha$  radiation ( $h\nu = 1253.6 \text{ eV}$ ). The whole spectra (0–1100 eV) and the narrow spectra of all the elements with much high resolution were both recorded by using RBD 147 interface (RBD Enterprises, USA) through an AugerScan 3.21 software.

### 2.5.3. SEM analysis

The jute fabric samples were scanned using a SU1510 scanning electron microscope (SEM) (Hitachi, Japan) under 5.00 kV at 1.00k magnification.

### 2.5.4. AFM analysis

The three-dimensional surface topography was examined using a CSPM 4000 atomic force microscope (AFM) made by Benyuan Co., Ltd. The fibers were immobilized on magnetic AFM sample stubs by the help of a double-sided tape and the scanning was carried out in tapping mode AFM with a silicon cantilever at room temperature in atmosphere. The scanning was set at a size of 5000 nm  $\times$  5000 nm, and the scanning frequency was set at 2.0 Hz.



## 2.6. Quantitative analysis of the grafting

The grafting percentage ( $G_p$ ) of the treated jute fabric with laccase and DG was determined by the weighting method and calculated according to Eq. (1). For each treatment, triplicate samples were measured and the results were averaged.

$$G_p(\%) = \frac{(W_2 - W_1)}{W_1} \times 100 \quad (1)$$

where  $W_2$  is the weight of grafted jute fabric and  $W_1$  is the weight of initial jute fabric.

Alkali saponification of the jute fabrics including the DG-grafted sample and then titration with hydrochloric acid were carried out quantitatively. Jute fabric sample of 1 g was cut into pieces and boiled with 50 mL of 0.2 M NaOH for 2 h. The excess NaOH was titrated with 0.1 M HCl in the presence of phenolphthalein as an indicator. The volume of HCl consumed was recorded when the red color of the solution disappeared. Triplicate samples were measured per treatment and the data were averaged.

The DG content of the modified jute fabric was determined as the relative molar percentage of the ester groups regarding the hydroxyl groups consumed according to the following equation:

$$(2) \text{DG content}(\%) = \frac{[V_{\text{HCl}}(\text{control}) - V_{\text{HCl}}(\text{sample})] \times C_{\text{HCl}}}{3 \times M_{\text{C}_{19}\text{H}_{30}\text{O}_5}} \times 100$$

where  $V_{\text{HCl}}$  is the respective volume of HCl consumed (L),  $C$  is the molar concentration of HCl (mol/L) and  $M$  is the molar mass of dodecyl gallate (g/mol).

## 2.7. Optimization of the enzymatic grafting

The conditions of the enzymatic process, for instance, pH of acetate buffer, incubation temperature, laccase concentration, DG concentration and incubation period were optimized. The grafting was characterized with the grafting rate measured by the weighting method.

The enzymatic process for pH optimization was conducted with pH values of acetate buffer ranged from 2 to 7 at 50 °C for 4 h with 4.4 g/L laccase and 5 mM DG in the 0.2 M acetate buffer/ethanol medium (80/20, v/v, %). In the temperature optimization, the tested temperatures were 30, 40, 50, 60 and 70 °C. The pH of the acetate buffer was chosen as the optimum for the grafting process. The other incubation procedure was the same as described in pH optimization.

For each enzyme concentration optimized (0.4, 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6 U/mL), the jute fabric was incubated in the 80/20 (v/v, %) 0.2 M acetate buffer (optimal pH)/ethanol medium with laccase and 5 mM DG at the optimal temperature for 4 h. In the optimization of DG concentration, the tested concentrations were 2, 3, 4, 5 and 6 mM with the optimal laccase concentration. For the optimization of incubation time, periods of 1, 2, 3, 4, 5 and 6 h were tested with the optimal laccase and DG concentrations. The other incubation procedure was the same as described in the optimization of laccase concentration.

## 2.8. Hydrophobicity measurement

The contact angle was measured using a SL200B static contact angle/interfacial tension meter (Kino Industry Co, USA) after conditioning the fabric samples to equilibrium moisture content. For each sample, the water contact angle was measured until 300 s at five spots and the results were averaged. In addition, the digital photographs of water drop dissolving Methylene Blue on the surface of jute fabrics were captured by a Coolpix L320 digital camera (Nikon, Japan).

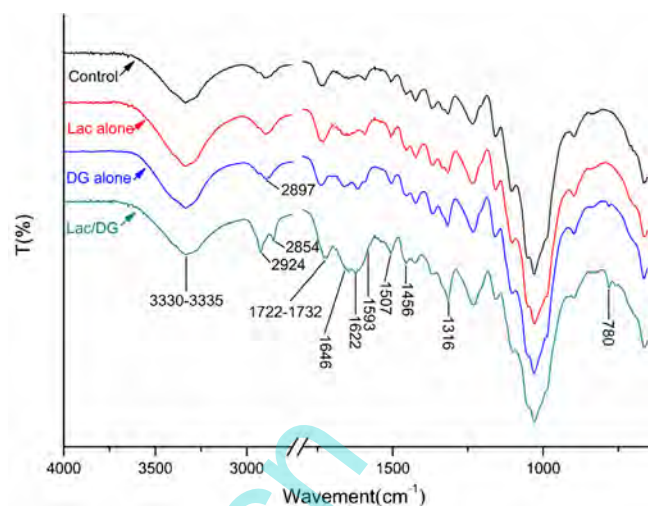


Fig. 4. FT-IR spectra of jute fabrics after different treatments: laccase/DG treatment (Lac/DG); DG alone treatment (DG alone); laccase alone treatment (Lac alone) and control.

## 2.9. Preparation of jute fabric/PP composites

Jute fabric/PP composites were prepared by hot pressing using the polypropylene (PP) spunlace non-woven cloth and the jute fabrics as raw materials. First, the jute fabrics were cut into samples of 2 cm width and 10 cm length. Then, the composite samples were prepared by successive laying of two layers of jute fabrics and three layers of PP cloth in a mass ratio of 1:1. Finally, the composite samples were compressed in the mould at 180 °C in 10 t pressure for 10 min.

## 2.10. Evaluation of mechanical properties of jute fabric/PP composites

The breaking strength of the jute fabric/PP composite was determined using a KD111-5 microcomputer-controlled electronic universal testing machine. The sample was tailored into that of 1 cm width and 10 cm length, and fixed on the shelf of the universal testing machine. Then, the testing machine began to run with a speed of 2 mm/min until the composite was pulled out. A stress–strain curve of the composite was given by the computer and the data of the breaking strength and elongation were recorded. All measurements were performed using at least five samples.

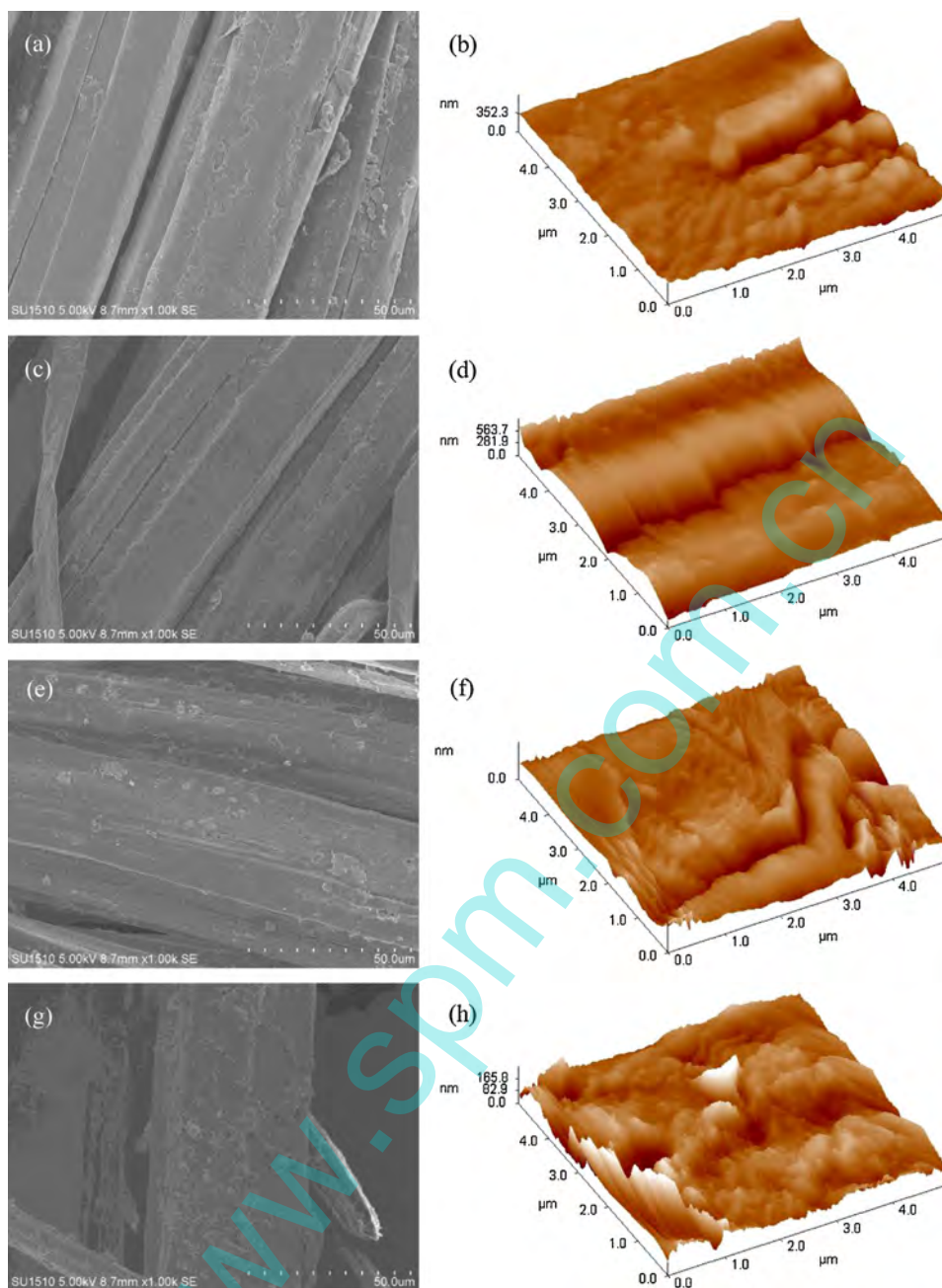
## 2.11. Analysis for fracture section of the composites by SEM

The fracture section of the jute-reinforced composites was scanned using a SU1510 scanning electron microscope (Hitachi, Japan) under 5.00 kV at 2.00k magnification.

Table 1

Assignment of wavenumbers in the FT-IR spectra of jute fabrics.

Wavenumber (cm <sup>-1</sup> )	Functional group assignment
3330–3335	O–H stretch
2897	Saturated C–H stretch
2924, 2854	C–CH <sub>2</sub> –C stretch
1722–1732	C=O stretch
1646, 1622	C=O stretch with absorbed water
1593, 1507, 1456	Aromatic skeletal vibrations
1316	CH <sub>2</sub> bending
780	CH <sub>2</sub> rocking vibration in plane



**Fig. 5.** SEM and AFM images, respectively of: control jute (a and b); laccase alone treated jute (c and d); DG alone treated jute (e and f); laccase/DG treated jute (g and h).

### 3. Results and discussion

#### 3.1. Optimization of laccase activity

Enzymatic processes are impaired mainly because of catalyst's price. The search for conditions where the maximal activity would be reached with the minimal concentration of biocatalyst is highly important and desirable. The pH of the buffer and the incubation temperature for the activity of the Denilite II laccase in the aqueous/organic medium were optimized as shown in Fig. 6.

From the graph of the pH, an optimum condition was observed at pH 2.5–3. A conclusion could be drawn that the Denilite II laccase used in this work is believed as an acid enzyme and maintains a higher activity in acidic condition. All kinds of enzymes have their most suitable temperature for catalysis in certain conditions. From the curve of the temperature, the activity of the Denilite II laccase

reached its maximum at 50 °C. The jute fabrics mentioned below for characterization and quantitative analysis were those prepared in pH 3 acetate buffer/ethanol medium at 50 °C.

#### 3.2. Surface characterization of jute fabrics

##### 3.2.1. FT-IR analysis

Attenuated total reflection (ATR) infrared spectra have been one of the most significant tools for the surface structure research of various materials, e.g., fibers, foods, surface coatings, films, etc. Fig. 4 shows the comparison among the ATR-IR spectra of the control, the laccase-treated, the DG-treated and the laccase/DG treated jute fabric samples. The spectral data were normalized with a common baseline and no smoothing functions were used. The assignment of various wavelengths in the FT-IR ATR spectra is presented in Table 1.

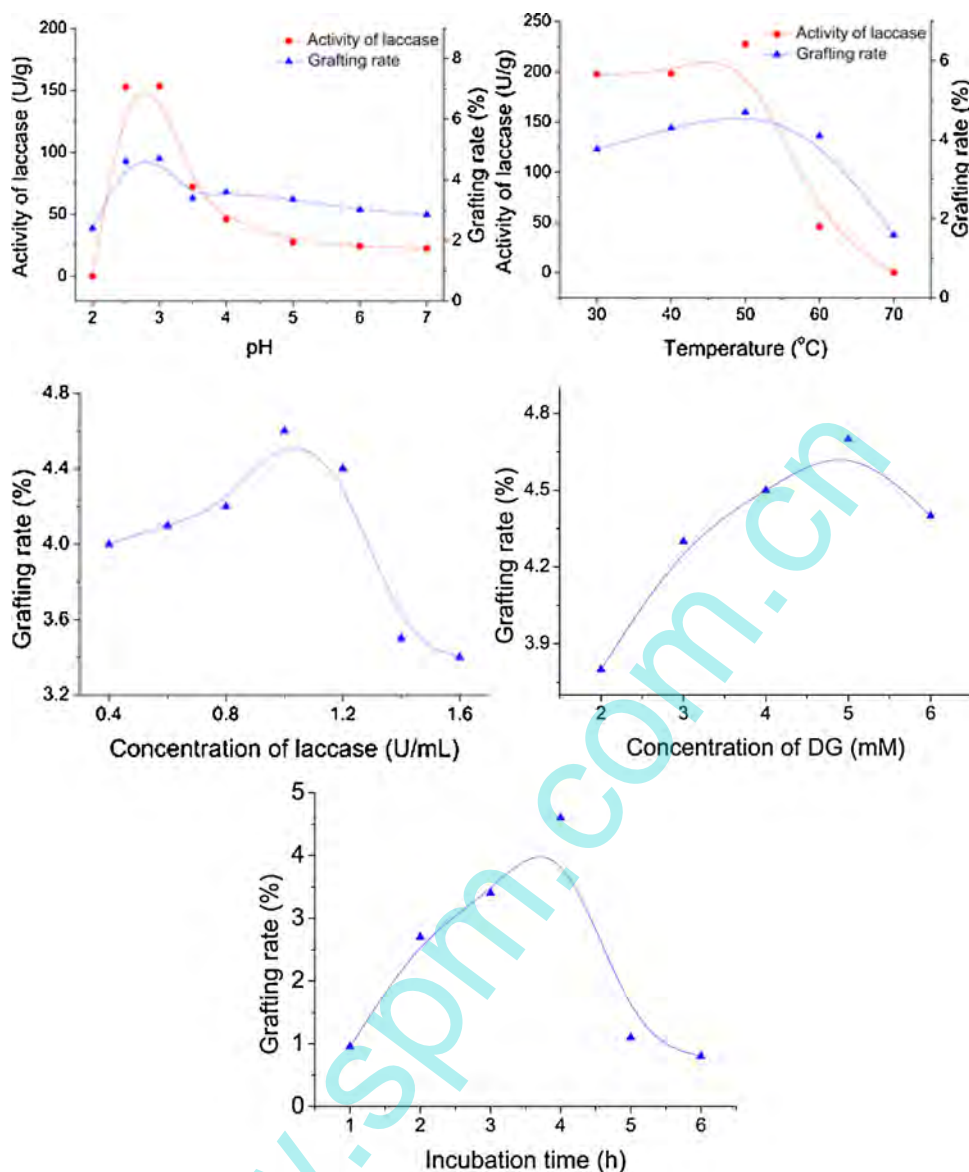


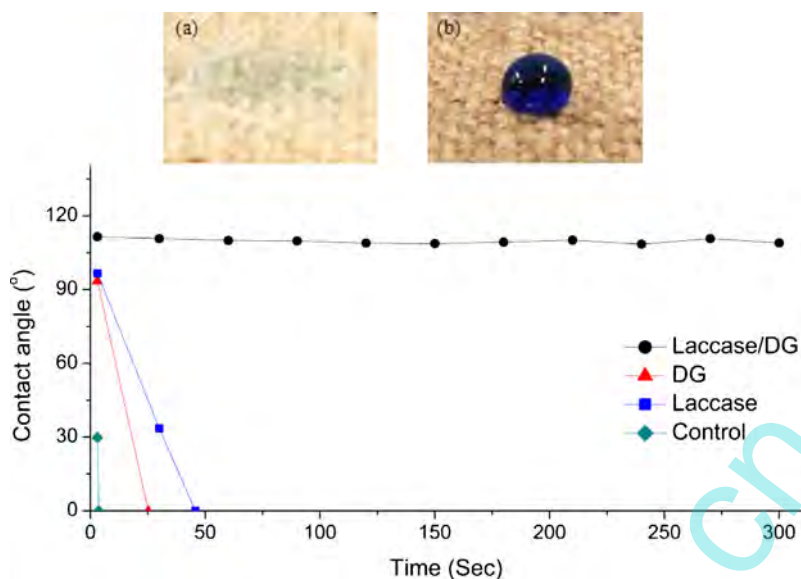
Fig. 6. Optimization of the process parameters: pH of acetate buffer, incubation temperature, laccase concentration, DG concentration and incubation time.

Compared with the control sample, the spectrum of the laccase-treated jute has several stronger peaks at  $3335\text{ cm}^{-1}$ ,  $2897\text{ cm}^{-1}$  and  $1732$ ,  $1646\text{ cm}^{-1}$ , which correspond to O–H stretching vibration, saturated C–H stretching vibration and C=O stretching vibrations, respectively. As the jute used had been pretreated to remove the wax and pectin, the surface of the jute was mainly composed of cellulose, hemicellulose and lignin. The carbonyl group was derived from the lignin only, while the hydroxyl group and the saturated carbon–hydrogen bond distributed in all the three components [41]. The increasing of the vibrations above may result from the transformation of lignin by laccase. In our former work, it was found that the hydroxyl group and the carbonyl group of the lignin on jute were increased after laccase treatment [17]. The FT-IR results of the laccase-treated jute in this study were in accordance with the previous obtained conclusions.

In contrast to the control, the DG alone treatment of jute led to a slight enhancement of IR peaks in the O–H stretching vibration at  $3335\text{ cm}^{-1}$ , the C=O stretching vibrations of ester at  $1722$ ,  $1646$ ,  $1622\text{ cm}^{-1}$  and the aromatic skeletal vibrations at  $1593$ ,  $1507$ ,  $1456\text{ cm}^{-1}$ . A stronger peak at  $1316\text{ cm}^{-1}$  corresponding to the

$\text{CH}_2$  bending vibration and a small band at  $780\text{ cm}^{-1}$  corresponding to the  $\text{CH}_2$  rocking vibration in plane were also observed. The DG molecular structure shown in Fig. 1d contains hydroxyl group, carbonyl group, phenyl group and long methylene chain. These results indicated that there was still a certain amount of residual DG nonspecifically adsorbed on the surface of jute although the DG alone treated jute had been extracted with acetone. However, these vibrations of the DG alone treated jute were far weaker than the laccase/DG treated jute. Furthermore, two new peaks corresponding to the saturated C–H stretching vibrations appeared at  $2924$  and  $2854\text{ cm}^{-1}$ , which is considered to be the consequence of long alkyl chain in the DG. The IR results of the laccase/DG treated jute suggested that the DG amount on the laccase/DG treated jute was much more than the DG alone treated jute. The extra DG should result from the enzymatic grafting by laccase. The DG attached to the surface of the jute by laccase/DG treatment can be the combination of nonspecific absorption and covalent grafting. The comparative findings above demonstrated adequately that the DG has been covalently grafted onto the surface of the jute fabrics by laccase.





**Fig. 7.** Contact angles over the time for the control jute (control), the laccase-treated jute (laccase), the DG along treated jute (DG) and the laccase/DG treated jute (laccase/DG). Insert: digital photographs of water drop captured on the surface of control jute after 5 s (a) and of treated jute with laccase and DG after 30 min (b).

### 3.2.2. XPS analysis

The XPS results (Table 2) showed an increase in C/O ratio which indicated coupling of DG onto jute fabric surfaces. The increase in the C/O ratio from 2.12 (laccase alone) to 2.65 (laccase/DG) can be attributed to the incorporation of the DG onto the jute surface as the DG has a high carbon to oxygen content ratio of 2.85. When compared with the control sample, the C/O ratio of the DG alone treated jute was also increased due to the tiny adsorption of DG. The increase in C/O ratio of the laccase/DG treated sample relative to the laccase-treated sample was far more remarkable than that of the DG-treated sample relative to the control sample. This suggested that grafting of DG onto jute surface indeed occurred and the result of the laccase/DG treated jute was the combination of absorbed DG and grafted DG on jute surface. An increase of the nitrogen content in the laccase-treated sample could result from some absorbed enzyme proteins. However, the adsorption of the hydrophilic laccases on the laccase/DG treated jute may be suppressed due to the incorporation of the hydrophobic DG onto the fiber surface, which embodied in the decrease in nitrogen content from 7.51% to 4.99%.

### 3.2.3. Surface morphology analysis

As shown in Fig. 5, the changes in the surface morphology and topography of the control, the laccase-treated, the DG-treated and the laccase/DG treated jute fabrics were studied by SEM and AFM. The surfaces of the control jute fibers were covered with some impurities in lamelleted (Fig. 3a) and natural convex under a greater magnification (Fig. 3b). Laccase-treated jute fibers became smooth (Fig. 3c and d) probably owing to enzymatic removing part of bulky lignin. The DG-treated jute fiber surface contained some small flakes (Fig. 3e and f) which were considered as the

**Table 2**  
XPS analysis of jute fabric surfaces after various treatments.

Treatment	Jute surface				DG
	C (%)	O (%)	N (%)	C/O ratio	C/O ratio
Control	62.45	30.72	3.72	2.03	–
Laccase alone	61.26	28.85	7.51	2.12	–
DG alone	65.39	29.06	3.17	2.25	–
Laccase/DG	67.75	25.57	4.99	2.65	2.85

nonspecifically absorbed DG. After the treatment of laccase and DG, the jute fiber surface became rough and irregular with some multi-spike like particulates attached (Fig. 3g and h). The materials observed on the laccase/DG treated jute could possibly be regarded as the coating of absorbed and grafted DG. The SEM and AFM microphotographs clearly demonstrated the attachment of DG on the surface of jute fibers by the laccase mediated treatment.

### 3.3. Quantitative estimation of the grafting

The weighting method was a commonly-used approach to determine grafting percentage ( $G_p$ ) for most grafting reactions. The weight gain rate (WGR) of the jute fabric sample after four treatments was measured and listed in Table 3.

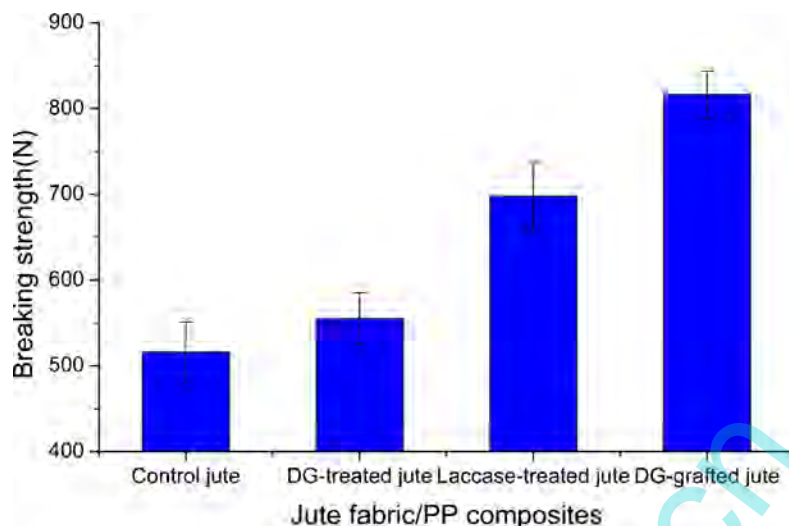
For the laccase-treated jute fabric, lignins would be partly degraded [16], but it was weight-gained probably due to the adsorption of few laccases. According to our former work [17], the effect of laccase on the weight of lignin was slight and only a little lignin of jute was degraded by laccase alone. This was partly owing to the heterogeneous catalysis and the simultaneous polymerization of lignin by laccase. The reserved lignin rich on the jute surface could provide sufficient anchors for grafting functional molecules at the catalysis of laccase. The grafting percentage of the DG-grafted jute fabric was 4.16% with an experimental error of 0.38%. The WGR values of the DG-treated and the control jute fabrics as comparative tests approximated to zero.

The method using alkali saponification and titration with acid was applied to quantitatively assess the ester content in this study. Based on the corresponding volume of hydrochloric acid consumed in Table 3, the DG content of the grafted jute fabric had been calculated according to above-mentioned Eq. (2) and the result was 3.19% with an experimental error of 0.53%.

This DG proportion is less than the grafting rate obtained from the weighting method. On one hand, the denominators in

**Table 3**  
Weight gain rate (WGR) of the jute fabric samples after various treatments and HCl volume consumed by the excess NaOH in saponification of jute fabrics.

Treatment	Control	DG alone	Laccase alone	Laccase/DG
WGR (%)	0.13 ± 0.03	0.05 ± 0.02	0.31 ± 0.10	4.16 ± 0.38
$V_{HCl}$ (mL)	86.10 ± 0.21	86.04 ± 0.17	83.26 ± 0.35	80.43 ± 0.12



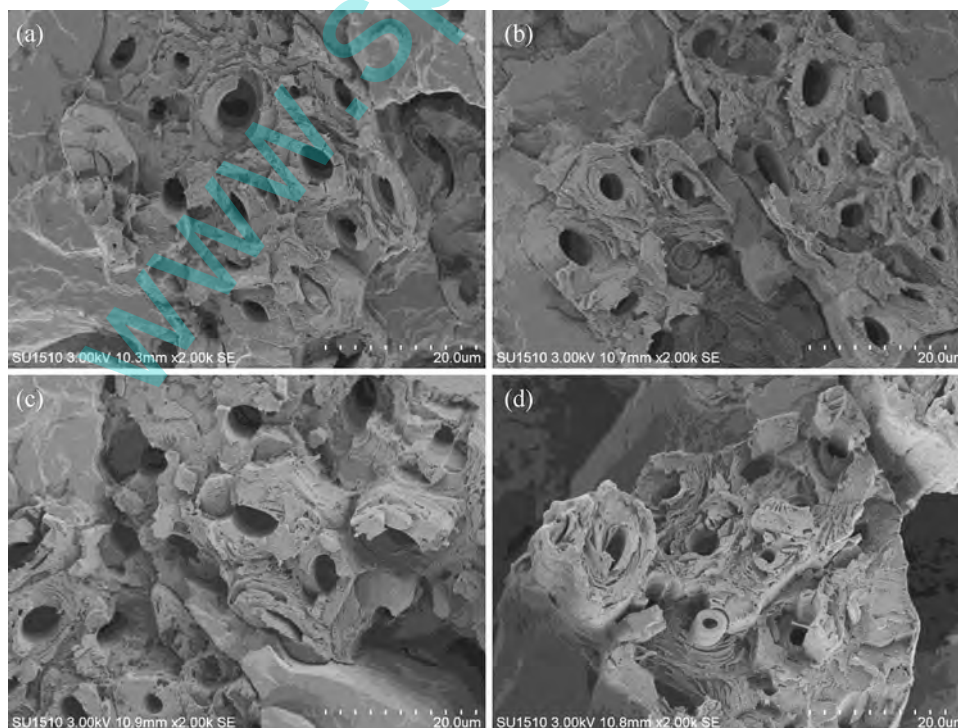
**Fig. 8.** Breaking strength of polypropylene (PP) composites reinforced by dodecyl gallate (DG)-grafted jute fabric, laccase-treated jute fabric, DG-treated jute fabric and control jute fabric.

the equations are different. The grafting rate is calculated as the weight of initial jute, while the DG content is calculated as the weight of grafted jute. On the other hand, some phenolic hydroxyl groups of lignin on the jute had been reacted in the grafting of DG. Therefore, the consumption of NaOH in the saponification was decreased and the DG content is less. Compared to the DG-treated and the control jute, the laccase-treated jute fabric consumed more NaOH for saponification. This might be attributed to the absorbed laccases which was also supported by the data of XPS and WGR.

#### 3.4. Optimization of the enzymatic grafting process

The pH of the acetate buffer, incubation temperature, laccase concentration, DG concentration and incubation time of the

grafting were optimized as shown in Fig. 6. From the graph of the pH, an optimum condition was observed at pH 2.5–3. The effect of pH on the enzymatic grafting corresponded well with that on the laccase activity. From the curves of the temperature, 50 °C is the optimal point both for the laccase activity and the grafting reaction. The two indicators reached their maximums at the same temperature. From the curve of laccase concentration, the grafting rate reached the maximum value when laccase of 1.0 U/mL was used. DG of 5 mM was observed in the curve of DG concentration as the grafting rate reached its maximum value. When the process was incubated for 4 h, the maximum value of the grafting rate was reached according to the curve of incubation time. In conclusion, the enzymatic process reached the maximum reactivity when the jute fabric was incubated in the 80/20 (v/v, %) pH 3 0.2 M



**Fig. 9.** SEM images of the fracture sections of PP composites reinforced by (a) DG-grafted jute fabric; (b) laccase-treated jute fabric; (c) DG-treated jute fabric; (d) control jute fabric.



acetate buffer/ethanol medium with 1.0 U/mL laccase and 5 mM DG at 50 °C for 4 h. The grafting rate was 4.16% and the DG content of the modified jute reached 3.19% at these conditions from Section 3.3.

### 3.5. Effect of DG grafting on hydrophobicity of jute surface

The surface hydrophilicity/hydrophobicity of materials could be evaluated by the water contact angle. The time-dependent contact angle of a water drop on jute fabric samples is shown in Fig. 7.

For the control jute fabric, the contact angle was  $29.75^\circ \pm 3.75^\circ$  at the beginning and the water droplet disappeared within 3–5 s. The laccase-treated sample showed a contact angle of  $96.67^\circ \pm 6.52^\circ$  and took 45.7 s to soak up the water droplet. The hydrophobicity increasing was possibly owing to the polymerization of lignin on the jute surface caused by the coupling of enzymatic generated phenoxyl radicals. The contact angle and the wetting time of the DG alone treated sample ( $93.48^\circ \pm 5.10^\circ$ , 25.2 s) were also higher than the control. This could be the result of some amount of absorbed DG on jute which had been demonstrated by the FT-IR, XPS and other analysis. The Laccase/DG treated sample showed larger contact angle ( $111.49^\circ \pm 2.90^\circ$ ) due to the vast hydrophobic DG grafted on the surface. And the contact angle of this sample maintained almost invariant in 300 s.

The increase of surface hydrophobicity was further confirmed by the photographs of colored water droplet on the surface of the control jute fabric after 5 s and of the modified jute fabric after 30 min (Fig. 7, insert). The enhanced hydrophobicity of the laccase/DG treated jute fabric supported the presence of DG containing long hydrocarbon chain and ester group on the surface of the fibers.

### 3.6. Analysis of jute fabric/PP composites

The mechanical properties of the jute fabric/PP composite remarkably depend on the interfacial compatibility between the jute fiber and PP. Generally, the better the compatibility, the better the mechanical properties are. In order to reveal the effect of jute fabric surface modification on the compatibility between the jute fabric and PP, the PP-based composite reinforced by DG-grafted jute fabric was prepared by hot pressing and its breaking strength was tested.

As shown in Fig. 8, compared to the control jute, the grafted jute fabric reinforced composites presented the highest breaking strength, followed by the laccase-treated jute and the DG-treated jute in order. The results are well in accordance with the hydrophobicity of the tested jute fabrics. The changes in the breaking strength indicated that the compatibility between the jute fiber and PP was enhanced after the surface hydrophobization by grafting of DG.

The fracture section of the DG grafted jute fabric/PP composite (Fig. 9a) was neat and regular, showing good interfacial compatibility between the modified jute and PP. The composites of the treated jute fabric with laccase (Fig. 9b) showed rough and irregular in fracture section while the composites reinforced by the DG-treated and the control jute fabrics (Fig. 9c and d) tended to be seriously worse. This might be attributed to the bad compatibility with the hydrophobic resins which results from the surface hydrophilicity of the original jute fabric. The interfacial compatibility can be largely influenced by the polarity of the two materials composing the interface. The more similar polarity of the materials, the better compatibility of the interface is. The surface hydrophobization of the jute fabric could fulfill the requirement of the compatibility with hydrophobic resins to prepare fiber reinforced composites of high performance.

## 4. Conclusions

The present work demonstrated that covalent attachment of DG onto jute fiber surface by using laccase combined with slight adsorption of DG resulted in an increase in hydrophobicity of the fiber. The hydrophobic fiber could be used for composite reinforcement. The grafting of DG on the jute substrate was confirmed by FT-IR, XPS, SEM and AFM. The enzymatic process of the jute reached the maximum grafting rate of 4.16% with DG content on jute of 3.19% when the grafting reaction was conducted at 50 °C for 4 h in the 80/20 (v/v, %) pH 3 0.2 M acetate buffer/ethanol medium with 1.0 U/mL laccase and 5 mM DG. The contact angle of  $111.49^\circ$  and wetting time of at least 30 min indicated that the surface hydrophobicity of the jute fiber was increased after graft modification and the jute obtained excellent water repellency. The breaking strength of the modified jute fiber/PP composite was also increased and the fracture section became neat and regular as the result of laccase-assisted grafting of the jute with DG. This eco-friendly and cost-effective process provides an attractive alternative to the current methods for improving the surface hydrophobicity of the jute fiber. Enzyme-hydrophobized jute fiber or other natural fibers containing lignins could fulfill the requirement of the compatibility with hydrophobic resins to prepare fiber reinforced composites of high performance.

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