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# The development of antibacterial and hydrophobic functionalities in natural fibers for fiber-reinforced composite materials

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ABSTRACT

Green surface modification of coconut fibers was performed using laccase biografting of eugenol for the development of antibacterial functionalities and fiber-reinforced polymer composites. Fourier transform infrared analysis, X-ray diffraction and surface morphology of grafted fibers were utilized to confirm the biografting of eugenol. Antibacterial, hydrophobicity and thermal properties were evaluated by colony forming unit (CFU) method, moisture absorption and thermogravimetric analysis, respectively. The grafted surfaces were found to be antibacterial, hydrophobic and thermally more stable. Grafted fibers were reinforced in a poly(butylene succinate) matrix to improve the mechanical properties of the biocomposites. The mechanical properties were improved even with a low content of biografted coconut fibers.



## 1. Introduction

Natural fiber reinforced polymer composites are one of the most rapidly growing fields of research in composite science and technology [1]. Natural fibers usually display poor microbial and moisture resistance therefore biografting is utilized as a novel green method to impart antibacterial and hydrophobic properties. Enzyme-assisted surface modification of lignocellulosic fibers can be used to improve fibers for composite materials and other industrial applications [2–6]. In natural fibers, cellulose is the major constituent with a percentage of lignin varying from 0–40% of the total material [7]. Biografting of organic molecules is mainly targeted at the lignin leaving most of the surface of fibers unmodified, if the percentage of lignin is very low. Biografting a phenolic group makes natural fibers more hydrophobic and therefore more compatible with synthetic polymer matrices for the development of composite materials [8].

Attempts have been made to develop antibacterial and hydrophobic lignocellulosics through biografting methods [8–14]. Laccase-assisted coating of flax fibers with ferulic acid and hydroquinone resulted in enhanced antimicrobial activity [13]. Laccase assisted biografting of ferulic acid was also used for surface modification of sisal pulp. Effect of the laccase–ferulic acid system on the refined and unrefined pulp fibers was investigated. Increased grafting and handsheets with improved strength properties were obtained with refining before the enzyme treatment [15]. Surface functionalization of sisal and flax pulp fibers using the laccase induced grafting has been performed using simple phenols like syringaldehyde, acetosyringone, *p*-coumaric acid, coniferaldehyde, sinapaldehyde, ferulic acid and sinapic acid [16]. Dong et al. [17] used laccase catalyzed grafting of dodecyl gallate onto the jute fibers, increasing their hydrophobicity, and prepared polypropylene composites with modified jute fiber. Mechanical property enhancement was observed using the biografted jute fibers.

Coconut fibers are lignin-rich fibers and can easily be modified through laccase biografting. The main objective of this study is to investigate laccase biografting of phenolic compounds on coconut fibers and their use as a novel reinforcing material.

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## 2. Experimental

### 2.1. Materials

Coconut fibers were extracted from the skin of coconut palm (*Cocos nucifera*), which was purchased from a local market of Solan (Himachal Pradesh, India). Extracted fibers were washed with mild detergent followed by distilled water to remove the water-soluble impurities. Clean fibers were then extracted with acetone in a Soxhlet extractor for 24 h to remove other impurities. Most of the coconut fibers used in present study were 6–15 cm length with an average diameter of 0.25 mm. Laccase (from *Trametes versicolor*) (98% pure) and eugenol (EG) (99% pure) were purchased from Sigma–Aldrich. Citric acid (Himedia, extra pure), sodium citrate (Himedia, extra pure), nutrient broth (Himedia, M002), nutrient agar (Himedia, M001), and poly(butylene succinate) (PBS) (Sigma–Aldrich) were used as received.

### 2.2. Laccase biografting of eugenol

Biografting of eugenol was carried out in an Erlenmeyer flask containing 40 mM citrate buffer (pH 4), 3.5% (w/w) eugenol, 40 U laccase and coconut fibers (200 mg). This reaction mixture was incubated at 50 °C for 12 h with constant rotation at a rate of 30 rpm. A control reaction was also used under identical conditions in the absence of enzyme. Modified fibers were washed thoroughly with distilled water until a neutral pH and then Soxhlet extracted with acetone for 12 h to remove the fraction of unreacted EG. Fiber samples were then dried in a vacuum oven at 40 °C to a constant weight. Optimization of reaction conditions were determined by varying three reaction parameters such as enzyme concentration, phenol concentration and incubation period [18].

### 2.3. Quantitative analysis of biografting

Quantitative analysis of biografted coconut fibers was determined by the weighing method. The percentage of biografting was calculated by using the following equation:

$$\text{Biografting}(\%) = \frac{w_2 - w_1}{w_1} \times 100$$

where $w_2$ is the weight of biografted fibers and $w_1$ is the final weight of control sample [17,18].

### 2.4. Characterization techniques

FTIR technique was used to identify the chemical groups of unknown composition and intensity of absorption spectra associated with molecular composition of the chemical group. FTIR spectra of coconut fibers were taken with KBr pellets on a PerkinElmer RXI Spectrophotometer over a range of 400–4000 $cm^{-1}$. Surface morphology of coconut fibers was examined by using a Jeol JSM-6610LV electron microscopy machine. Thermal behavior of fibers was studied using a PerkinElmer TGA in an inert atmosphere from 50 to 800 °C at a heating rate of 10 °C/min. XRD studies were done on a Brucker $D_8$ Advance X-ray diffractometer under ambient conditions. Crystalline and amorphous material in natural fibers is represented by peak intensities at 22° and 18° respectively. Percentage crystallinity (% Cr) was calculated as follows:

$$\% \text{ Cr} = \frac{I_{22}}{I_{22} + I_{18}} \times 100$$

where $I_{22}$ and $I_{18}$ are the crystalline and amorphous intensities at $2\theta$ scale close to 22° and 18° respectively [19,20].

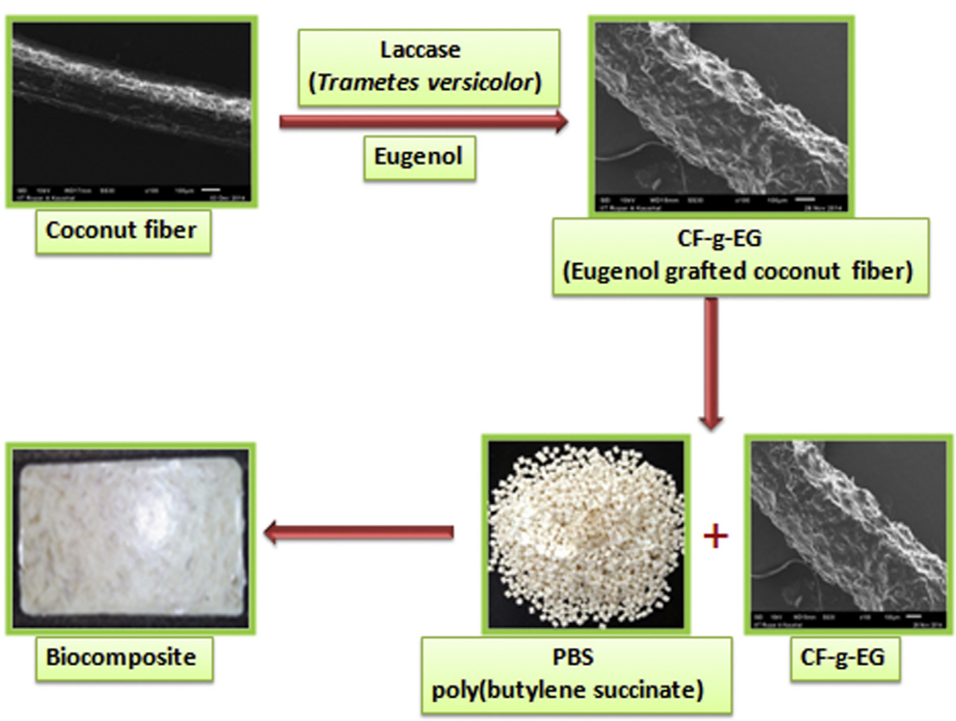


**Fig 1.** Schematic representation of preparation of biocomposites reinforced with biografted fibers.