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One-step enzymatic grafting of ferulic acid with cellulose to enhance matrices–fibres compatibility in bio-composites

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ABSTRACT

Bio-composites elaboration is limited by poor interfaces between cellulose and polymer matrices and the cellulose degradation. Achieving cellulose grafting with ferulic acid should enhance those resulting bio-composites mechanical properties. Therefore, a cellulose suspension was modified with ferulic acid using laccase under reaction conditions set at 60 °C, acetate buffer pH 5 for 24 h. Grafted cellulose fibrils were extruded in polypropylene-grafted maleic acid (PPgMA) for mechanical properties studies. Even if ferulic acid interacted with cellulose without any enzyme presence, the acid resilience was only detected for cellulose fibres modified with ferulic acid proving the surface grafting. Cellulose fibrillary lengths were unaffected by the enzymatic treatment suggesting a tiny coating. The resulting bio-composites had a Young modulus reduction of 12%. The elongation at maximal stress had 23% improvement, corresponding to a material mechanical resistance. This result was also confirmed by bio-composite elaboration with natural fibres under the same conditions. Ferulic acid and cellulose blends have improved the hardness properties of the resulting bio-composites with PP-PPgMA.

Introduction

Due to their intrinsic properties, cellulose fibres have been identified as potential ersatz to glass fibres in bio-composites [1]. Sustainability, biodegradability, non-abrasive behaviour, low cost and low density coupled with high mechanical resistance are the main advantage of cellulose over the glass fibres [2] in bio-composites. However, the main component of the fibres, cellulose, is hydrophilic and leads to poor cohesion with hydrophobic polymer matrices [2]. The thermal degradation of cellulose, around 310–330 °C

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[3, 4], also limits the matrices available to elaborate bio-composites.

Such problems could be overcome through physical or chemical modifications of cellulose. Both treatments tend to improve either cellulose fibres surface roughness [2] or hydrophobicity [5] for better interaction with the matrices, or thermal and mechanical resistance to explore wider composites applications. Among the physical treatments, cold plasma is widely used to enhance contact surface of the fibres [2]. This treatment aims to increase, through oxidation, functional groups available at the fibre surface. The technique involves possessing an integrated process as the plasma effect lifespan on the fibres is of a couple of hour [6]. Among the main chemical fibre modifications, alkali treatment decreases the hydrogen bonds density within the fibres and improves the surface exposure of the cellulose [7]. Silanol treatment reduces the fibres wettability by reacting with the hydroxyl groups of the cellulose [8]. Both treatments enhance some cellulose fibrils properties at the detriment of the fibre crystallinity in the case of the alkali treatment, or the use of green solvents considering silanisation [9].

Another approach is to attach amphiphilic molecules onto a cellulose fibre surface through a grafting from reaction. Thus, fibre properties should remain untouched (mechanical resistance, sustainability) while the interface with the polymer is improved for a compatibility within composites thanks to the grafted molecule.

Thermal resistance potential and hydrophobic behaviour are the top selection criteria of an ideal molecule to achieve such grafting. The commercial availability of the molecule at an affordable price is also considered when selecting the molecule. Phenolic acids are good candidates to conjunctly fulfil these multiple goals. These molecules are more hydrophobic than cellulosic fibrils and possess a natural flame retardant property, suggesting a thermal resistance [10]. Ferulic acid, a highly available commercial phenolic acid which possesses a quasi-ubiquitous presence in lignocellulosic fibres or fruit, is a good candidate to react with cellulose from the fibres. Actually, in normal plant-growing conditions, ferulic acid ensures cohesion between polysaccharides (hemicellulose and cellulose) and lignin [11].

In this study, we emphasised that an enzymatic reaction of ferulic acid with pure cellulose will enhance the cellulose surface physico-chemical properties as an analogy between lignin and cellulosic fibres. In fact, lignin naturally reacts with cellulose through enzymatic reaction [12]. Phenolic acid grafted on kraft paper pulp using laccase increases both tensile and burst strength of the paper [13]. The laccase enzyme creates radicals which react with the sugar hydroxyl leading to stable bonds [14]. However, lignol polymerisation occurs simultaneously with the grafting [15] as well as simple adsorption of either the monomer or the oligomer. Thus, an overview of the different chemical phenomenon occurring during the enzymatic reaction will also be considered in this study.

Materials and methods

All chemicals, including enzymes, were purchased from commercial suppliers and used as received.

Microcrystalline cellulose (C200) was purchased from Mikro-Technik GmbH and consists of a bleached cellulose purified from hemicelluloses and lignin, obtained from wood pulp with an average fibre size of about 200 µm in length and 30 µm diameter. The fibre density lies between 120 and 150 g/dm^3. Each reaction was triplicated except where stated otherwise.

Flax fibres were obtained from flax tow harvested in 2014 in France (Plateau de Neubourg in Le Neubourg). Flax fibres composition was 75.8% cellulose, 11.4% hemicellulose, 4.5% lignin and 8.2% extractible. Technical hemp fibres (Cannabis Sativa L. variety Santhica 27 or Fedora 17) were harvested in 2014 in France (Bar sur Aube). Hemp fibres composition was 81.0% cellulose, 11.0% hemicellulose, 2.5% lignin and 5.5% extract.

Enzymatic reactions

Laccase from Trametes versicolor (EC number: 1.10.3.2) was used at a final concentration (according to the furnisher information) of 40 U g^{-1} (E)-3-(4-hydroxy-3-methoxy-phenyl)prop-2-enoic acid (ferulic acid referred to as FA). Enzymes were allowed to re-hydrate for 20 min prior to use.

All reactions were performed in an acetate buffer pH 5, 100 mM.

Enzymatic modification of cellulose with FA was performed by suspending 200 mg of C200 in a 20 mL buffer. Two hundred and fifteen milligrams of FA

was added as well as the enzymes. The mixtures were incubated for 24 h in 100 mM pH5 acetate buffer at 60 °C. After this delay, the product was recovered by filtration (glass fibre, 1 µm) and washed three times with a 10-mL buffer. The solid was dried at 40 °C for 24 h. These samples will be referred to as C200FA. Gravimetric analyses were then performed on the dried product. Control reactions were performed under the same conditions to determine the C200 behaviour without enzyme (B.C200), the C200 and FA behaviours without enzyme (B. C200.FA), the FA behaviour without enzyme (B.FA) and the effect of the laccase on FA (PolyFA).

These conditions have been selected from a screening evaluation of ferulic acid adsorption onto cellulose with the reaction yield at pH and temperature ranging, respectively, from 5 to 9 and 20 to 60 °C. Mass reaction yield was defined as $\tau = m_{\text{initial}}/m_{\text{final}} \times 100$. Grafting was confirmed by a 7-h Soxhlet extraction (using acetone as extracting solvent) and Klason analyses according to the NREL protocol [16]. Infrared analyses were resolved from solid samples between 4000 and 400 cm^{-1} (32 scans, resolution of 4 cm^{-1}) by ATR-FTIR using a Bruker spectrometer VERTEX 70. Baseline correction and spectra vector normalisation were achieved by the OPUS 7.2 software algorithm. Solid-state CP/MAS 13C NMR was performed by a Bruker Avance III HD 400 MHz spectrometer equipped with a PH MAS VTN 400SB BL4 N-P/H probe. The CP/MAS ^{13}C NMR parameters were 300 scans and a 90° pulse length of 2.5 µs. Spinning frequency was set at 7 kHz.

Microscopy observations

Reaction products were observed under optical microscopy using a Leica DM2700P microscope equipped with a Leica MC 190HD camera. Photographs were captured and visualised on the Leica Application Suite version 4.12.0 software. Images were then analysed using ImageJ software version 1.52. Particles length was measured after systematic manual selection ($n > 85$).

Thermogravimetric analyses

The thermal behaviour of samples was evaluated by thermogravimetric analysis (TGA) performed by a Mettler Toledo TGA/DSC Stare system apparatus. Around 10 mg of the product was heated from 20 to 600 °C at a heating rate of 5 °C min^{-1} under a constant nitrogen flow during the experiments. Each analysis was duplicated.

Crystallinity

The sample crystallinity was determined by X-ray diffraction under isothermal conditions. A Bruker Twin–Twin diffractometer equipped with a variable divergence slit V12 was set with a step size 0.02 °C and step time 0.25 s/step/strip. Signals were detected with a Lynxeye XET (192 strips) detector.

Product extrusion in a polymer matrix

Bio-composites were extruded in a Haake Minilab Rheomex CTW5 equipped with counter-rotating double screw: 90% (w/w) polypropylene (PP) matrix (commercialised under the Polychim B10 FB trade name) was blended with 10% (w/w) cellulosic fibres for 45 s at 200 °C, 50 rpm. Compounds were injected into mould probes 1BA in a Haake MiniJet II at 200 °C, 100 bars. Probes were kept under controlled atmosphere for 48 h at 23 °C and 50% relative humidity.

Mechanical traction tests extension speed was set at 1 mm/min to determine the Young modulus, while the remaining mechanical parameters were determined with an extension speed set at 20 mm min^{-1}. Initial probe width was of 4.17 mm.

Statistical analyses

Minitab 18.1 software version was used to perform the ANOVA tests. Variance homogeneities were evaluated with the Fisher test. R software version 3.5.1 using the FactoMineR package was used to compute the five-dimensional principal component analyses of the data.

Results

Synthesis and chemical structure

Reaction conditions were optimised for two parameters from a one-shot reaction yield screening of the mixture C200FA, PolyFA, B.C200.FA, B.C200 and B.FA in the temperature range of 20–60 °C and pH range of 5–9 for 24 h. The reaction condition at pH 5, 60 °C was confirmed by triplicate to be the optimised

parameters according to the yields combination of the reactions. These conditions led simultaneously to reduced ferulic acid adsorption rate (measured by the B.C200.FA reaction), reduced cellulose dissolution in the buffer (checked by the B.C200 control reaction) and elevated ferulic acid dissolution (associated with the B.FA reaction yield). Optimal reaction time was also evaluated: reactions were stopped after time lapse of 5/24/72 and 168 h. Reaction yield evolved as a Gaussian-like distribution reaching its maximum after 24 h. Under these parameters, the reaction yields reached 95.8 ± 1,1% (C200FA), 61.8 ± 5.0% (B.C200.FA), 83.7 ± 4.9% (PolyFA), 96.9 ± 1.3% (B.C200) and 2.1% ± 0.0% (B.FA). Interactions between fibres and ferulic acid in the absence of laccase were highlighted as the theoretical B.C200.FA reaction yield does not correspond to the sum of the reaction yield of each component separately (B.C200 and B.FA) in the reaction proportion.

The resulting chemical composition was then determined to guaranty a chemical grafting on the fibres surface by acid analyses: cellulose with grafted ferulic acid is expected to exhibit higher acid resistant as PolyFA (resulting from the ferulic acid self-aggregation on cellulose in the presence of laccase) would possess a lignin-like structure and be acid resistant while un-grafted cellulose should be acid soluble. Pure ferulic acid was only detected as acid soluble and 19.2% of the PolyFA was acid resistant. The enzymatic reaction driven with cellulosic fibres also gained in acid resistance with 3.3% acid insoluble residues, while the cellulose FA blend without enzymes had 1% acid insoluble residues. This result was confirmed by Soxhlet extraction.

A second verification of the grafting rate was performed by measuring the extractable part. As cellulose is poorly soluble in acetone, grafted molecules should remain un-extracted while adsorbed particles in cellulose fibrils would be removed through a 7-h acetone extraction. The C200FA Soxhlet extracted sample (referred to as C200FASox) was still slightly orange coloured, while the extraction liquid in the upper part of the apparatus was totally transparent after 5 h of extraction. The extractible fraction reached 33.3 ± 0.3% for B.C200.FA and 45.9 ± 1.2% for C200FA. From the reaction yield, corresponding to 95.8 ± 1.1% (C200FA), cellulose should represent 46.7 points (according to the B.C200 reaction yield) and ferulic acid 49.1 points. The remaining 3.2 points should correspond to the un-extractable ferulic acid part. Therefore, the un-extractable fraction of ferulic acid is considered as being covalently grafted to the cellulose. Both Klason analyses and Soxhlet analyses reached this value of 3.2 point of the material reacting differently than the control. This value corresponds to the grafting rate of the ferulic acid on cellulose. For B.C200.FA Klason and Soxhlet analyses revealed exacerbated chemical resistance.

Fibres were observed under optical microscopy. The microscopic observations revealed opaque particles in the B.C200.FA and C200FA mixtures (Figure 5—Supplementary information, C and D), which are totally absent in the C200 mixture (Figure 5—Supporting information, B). These particle shapes were similar to FA particles shape (Figure 5—Supporting information, A). Based on a shapes and opacity selection, these particle sizes were analysed and compared (Fig. 1). Opaque particles sizes, in samples containing FA, were centred on 46 µm length. Measurement confirmed that C200 length was centred on 200 µm ($n > 150$). Fibrous particle size distribution was similar in all the samples containing cellulose. By measuring PolyFA particle (Fig. 1) length and the non-fibrous particle length in the C200FA samples, the particles length distribution fitted the rough size of the opaque particles detected in B.C200.FA.

Structural analyses

Infrared spectroscopy (Figure 6—Supplementary material) and CP/MAS ^{13}C NMR (Fig. 2) displayed structural variations among the treated samples. PolyFA IR spectra were clearly different to B.FA

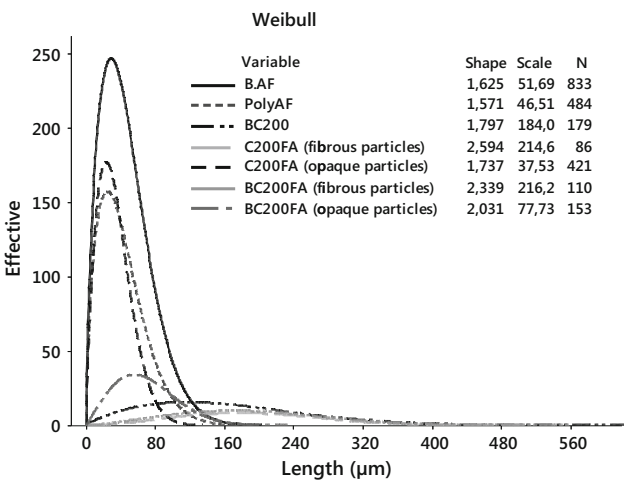

Figure 1 Particle length distribution (Weibull law).

spectra: phenolic OH signal at 3437 cm^{-1} completely disappeared and a new peak at 1745 cm^{-1} corresponding to ester appeared. The peak at 1691 cm^{-1} corresponding to carboxylic acid was still detectable. The PolyFA peaks were detected in C200FA and new peak at 1333 cm^{-1}, undetected in any of the control reaction, appeared, while a peak at 1408 cm^{-1} present in all the control reactions disappeared. The wide peak around 1000 cm^{-1} in PolyFA spectra suggested ether bond linkage which is also detected in C200.FA.

Chemical structures were also analysed by CP/MAS ^{13}C NMR (Fig. 2). B.C200.FA signals corresponded to the signals superimposition of B.FA and B.C200. C200FA and PolyFA structural determination by CP/MAS ^{13}C NMR displayed an extra peak at around 46 ppm which could correspond to a C-aromatic linkage. The multiplet signal between 109 and 127 ppm suggested that the C=C and aromatic substitution varied.

FTIR spectra confirmed ester bond while carboxylic acid was still detected.

Interactions between ferulic acid and cellulose were also investigated through DSC analyses. Endotherm corresponding to the stacked thermogram of the pure component indicates no interactions [17].

Pure FA thermogram had a unique peak at 172 °C (Fig. 3a). C200 exhibited an endotherm at 179 °C (Fig. 3a) and 350 °C. Appreciable interactions between C200 and FA are already described [17]. Peaks corresponding to these interactions are expected at 145 °C, 170 °C and 180 °C. C200FA DSC exhibited two peaks (Fig. 3b) at 134 °C and 165 °C, while PolyFA (Fig. 3b) exhibited an endotherm at 149 °C and 168 °C and an exotherm at 205 °C. C200FA thermograms were different from both the C200 thermogram and B.C200.FA or PolyFA thermograms, suggesting interactions between C200, FA and the enzyme. DSC analyses were coupled with TGA measurement. Endotherm of C200 at 350 °C and endotherm of FA at 172 °C fitted with a weight loss, i.e. the material degradation. However, the C200FA endotherm at 134 °C did not lead to a weight loss, which could suggest a molecular rearrangement. The endotherm at 165 °C corresponded to a temperature of degradation of the resulting product. The product deteriorated then massively in the temperature range [200–340] °C. PolyFA underwent two degradations: the first was endothermic and occurred at 187 °C while the second was exothermal and occurred at 205 °C, suggesting an electronic-rich bond breaking. Degradation temperature and the associated energy were plotted for each sample (Fig. 4).

PolyFA degradation required both lower temperature and less energy than the B.FA degradation. C200FA degradation occurred at temperatures lower than B.C200 but higher than those for PolyFA. Thermal gravimetric analyses were also conducted to

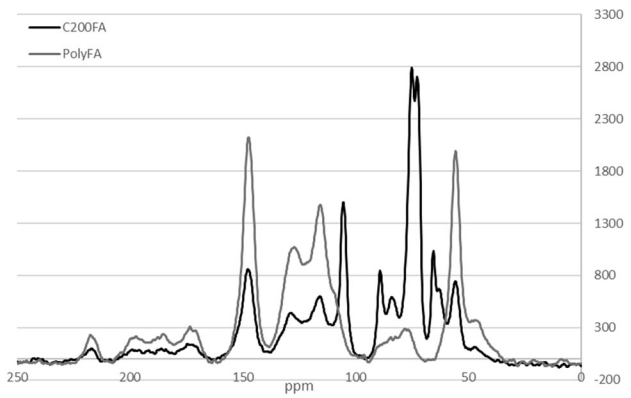

Figure 2 CP/MAS 13C NMR spectra of PolyFA and C200FA.

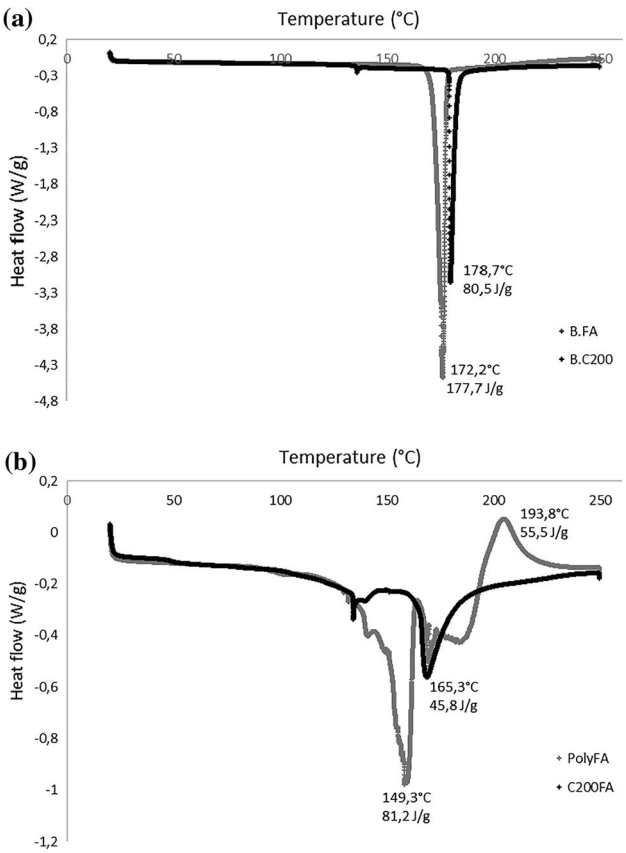

Figure 3 DSC thermograms of B.FA, B.C200 (**a**) C200FA and PolyFA (**b**).

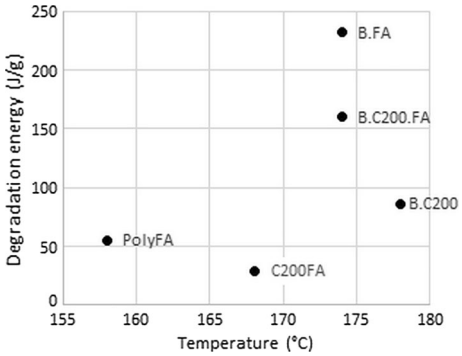

Figure 4 Temperature and energy of the main endotherm. B.C200.FA values are obtained from literature [17].

evaluate the degradation evolution (Table 1). The temperature range to reduce the sample mass by 50% was 160 °C for both C200FA and PolyFA, while B.C200 and B.FA had a temperatures of 70 °C and 49 °C, respectively. However, the degradation temperature of C200FA was lower than the pure component and PolyFA. At 600 °C, 37% of the initial mass remained for PolyFA, and C200FA had 20% remaining, while pure C200 had 10% and FA 1.6%. The exotherm detected on the TGA analyses of PolyFA suggested an electronic-rich bond presence undetected in the other samples, confirming the structural analyses.

Crystallinity

Fibres resistance determined by high cellulose crystallinity is a decisive parameter for its selection as reinforcement material in bio-composites [18]. The cellulose morphology ratio was computed considering the peak intensity at 22.7° and 20.4°, respectively, corresponding to the overall cellulose crystallinity and the cellulose II crystallinity [19]. The FA crystallinity participation at these angles was limited. The ratio varied from 67% (B.C200) to 60% (B.C200.FA). Characteristics peaks detected in ferulic acid were also present in PolyFA, but their relative intensity varied, suggesting crystalline plan modifications. The cellulose peak shape at 22.7° differed depending on the mixture. An extra peak tended to appear for the enzymatic treatment at 23.5°.

XRD measurement highlighted that the B.C200.FA blend lost 11% crystallinity compared to B.C200 (crystallinity ratio of C200FA: 45%). This effect is even more exacerbated for the enzymatic reaction with a 33% crystallinity loss. This loss may be associated with a better FA inclusion within C200 which involves disturbances in the structure of hydrogen bond network.

Composites mechanical characteristics

Composites were elaborated with C200 and C200FA. Enzymatic treatment significantly increased elastic resistance and the elongation at maximal stress, while the Young modulus significantly decreased (Table 2). The enzymatic treatments were also applied to natural flax and hemp fibres due to their high cellulose content and their usage as reinforcement material in bio-composites. Improvement in the elongation at maximal stress was verified on the natural fibres that were enzymatically treated: Elongation at maximal stress was improved of 23% for C200FA compared to C200. An improvement of 7% was detected for the treated hemp, while elongation at maximal stress was improved of 21% for treated flax. The elongation at break was also improved of 37 and 28% in composites with, respectively, treated hemp and flax-FA. Therefore, the mechanical properties variation of the modified cellulose is inherent to the biomass origin. This tendency was undetected in composites containing C200. Hemp and flax fibres contained both lignin and hemicellulose which should contribute to the enzymatic reaction and the interface with the matrix explaining the variations with pure cellulose. Lignin and hemicellulose are present in various proportions influencing then the reactivity and the final mechanical properties.

Table 1 Temperature corresponding to 5/10/25 and 50% weight loss

	B.FA	B.C200	C200FA	PolyFA
T5%	203.4 ± 0.0	275.8 ± 0.4	161.2 ± 2.3	198.6 ± 0.8
T10%	231.7 ± 0.0	303.7 ± 0.3	175.4 ± 0.4	241. ± 1.4
T25%	232.4 ± 0.2	330.3 ± 0.6	280.2 ± 2.7	292.3 ± 0.1
T50%	252.0 ± 0.0	345.6 ± 0.4	323.0 ± 0.7	360.8 ± 17.6
Δ(T50-T5%)	49 °C	70 °C	160 °C	162 °C

Table 2 Mechanical properties of the bio-composites in PP-PPgMA

	Young's modulus (MPa)	Elastic resistance (MPa)	Maximal resistance (MPa)	Elastic elongation (%)	Elongation at maximal stress (%)	Elongation at break (%)	Plastic range (%)
C200	1766.6 ± 64.7 (A)	16.3 ± 2.0 (B)	33.9 ± 0.7	1.7 ± 1.2	6.3 ± 0.4 (B)	23.0 ± 0.4	4.6 ± 0.6
C200FA	1547.3 ± 85.4 (B)	23.2 ± 0.0 (A)	34.0 ± 1.0	2.3 ± 0.7	8.2 ± 0.8 (A)	22.9 ± 1.8	5.8 ± 0.5
Hemp	1669.9 ± 61.2	15.7 ± 0.7	32.7 ± 0.8	1.7 ± 0.7	6.4 ± 0.2 (B)	14.3 ± 2.2 (B)	4.8 ± 0.9
Hemp-FA	1579.4 ± 51.6	15.2 ± 1.9	32.5 ± 0.7	1.8 ± 0.7	6.9 ± 0.1 (A)	22.8 ± 1.3 (A)	5.1 ± 0.8
Flax	1623.7 ± 34.6	14.1 ± 0.8	31.1 ± 0.7	1.6 ± 0.7	5.7 ± 0.4 (B)	9.6 ± 0.8 (B)	4.1 ± 1.1
Flax-FA	1679.6 ± 71.0	13.6 ± 0.9	35.5 ± 1.1	1.5 ± 0.8	7.2 ± 0.4 (A)	13.4 ± 0.8 (A)	5.7 ± 1.3

Values annotated with letters are significantly different. ANOVA tests were performed within each sample group

The stiffness (Young's modulus) of the resulting bio-composites significantly diminished probably due to the crystallinity loss. However, the elongation at maximal stress increases of 23% suggesting better interfaces due to a probable three-dimensional network. For bio-composites containing C200FA, a strongest stress should be applied on the material which lengthens before leaving the elastic zone. This treatment improved the material resistance.

Conclusion

Grafted cellulose fibres with ferulic acid exhibited the mechanical properties of the resulting bio-composites obtained with PP-PPgMA resin. The plastic behaviour remained intact while the material hardness was enhanced considering that the fibres crystallinity was reduced.

Elongation at maximal stress significantly increased for the natural fibres treated with ferulic acid. Only fibres lignin and hemicellulose-free (i.e. samples containing C200) possessed a Young modulus significantly decreased. This cellulose modification was attempted by enzymatic catalysis under mild conditions in respect of the green chemistry principles.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Electronic supplementary material: The online version of this article (https://doi.org/10.1007/s10853-019-03832-x) contains supplementary material, which is available to authorized users.

References

[1] Yan L, Chouw N, Jayaraman K (2014) Flax fibre and its composites – A review. Compos B Eng 56:296–317. https://doi.org/10.1016/j.compositesb.2013.08.014

[2] Ravi M, Dubey RR, Shome A et al (2018) Effect of surface treatment on natural fibers composite. IOP Conf Ser Mater Sci Eng 376:012053. https://doi.org/10.1088/1757-899X/376/1/012053

[3] Jandura P, Riedl B, Kokta BV (2000) Thermal degradation behavior of cellulose fibers partially esterified with some

long chain organic acids. Polym Degrad Stab 70:387–394. https://doi.org/10.1016/S0141-3910(00)00132-4

[4] Nada AMA, Hassan ML (2000) Thermal behavior of cellulose and some cellulose derivatives. Polym Degrad Stab 67:111–115. https://doi.org/10.1016/S0141-3910(99)00100-7

[5] Zimniewska M, Wladyka-Przybylak M, Mankowski J (2011) Cellulosic bast fibers, their structure and properties suitable for composite applications. In: Kalia S, Kaith BS, Kaur I (eds) Cellulose fibers: bio- and nano-polymer composites. Springer, Berlin, pp 97–119

[6] Temmerman E, Akishev Y, Trushkin N et al (2005) Surface modification with a remote atmospheric pressure plasma: dc glow discharge and surface streamer regime. J Phys D Appl Phys 38:505–509. https://doi.org/10.1088/0022-3727/38/4/001

[7] Burrola-Núñez H, Herrera-Franco PJ, Rodríguez-Félix DE et al (2018) Surface modification and performance of jute fibers as reinforcement on polymer matrix: an overview. J Nat Fibers 1–17. https://doi.org/10.1080/15440478.2018.1441093

[8] Agrawal R, Saxena NS, Sharma KB et al (2000) Activation energy and crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde composites. Mater Sci Eng A 277:77–82. https://doi.org/10.1016/S0921-5093(99)00556-0

[9] Li X, Tabil LG, Panigrahi S (2007) Chemical treatments of natural fiber for use in natural fiber-reinforced composites: a review. J Polym Environ 15:25–33. https://doi.org/10.1007/s10924-006-0042-3

[10] Doherty WOS, Mousavioun P, Fellows CM (2011) Value-adding to cellulosic ethanol: lignin polymers. Ind Crops Prod 33:259–276. https://doi.org/10.1016/j.indcrop.2010.10.022

[11] Marjamaa K, Kruus K (2018) Enzyme biotechnology in degradation and modification of plant cell wall polymers. Physiol Plant 164:106–118. https://doi.org/10.1111/ppl.12800

[12] Kharazipour A, Mai C, Hüttermann A (1998) Polyphenoles for compounded materials. Polym Degrad Stab 59:237–243. https://doi.org/10.1016/S0141-3910(97)00157-2

[13] Aracri E, Roncero MB, Vidal T (2011) Studying the effects of laccase-catalysed grafting of ferulic acid on sisal pulp fibers. Biores Technol 102:7555–7560. https://doi.org/10.1016/j.biortech.2011.05.046

[14] Hüttermann A, Majcherczyk A, Braun-Lüllemann A et al (2000) Enzymatic activation of lignin leads to an unexpected copolymerization with carbohydrates. Naturwissenschaften 87:539–541

[15] Slagman S, Zuilhof H, Franssen MCR (2018) Laccase-mediated grafting on biopolymers and synthetic polymers: a critical review. ChemBioChem 19:288–311. https://doi.org/10.1002/cbic.201700518

[16] Sluiter A, Hames B, Ruiz R et al (2012) Determination of structural carbohydrates and lignin in biomass. LAP 1–18

[17] Sohn YT, Oh JH (2003) Characterization of physicochemical properties of ferulic acid. Arch Pharmacal Res 26:1002–1008. https://doi.org/10.1007/BF02994749

[18] AL-Oqla FM, Sapuan SM (2014) Natural fiber reinforced polymer composites in industrial applications: feasibility of date palm fibers for sustainable automotive industry. J Clean Prod 66:347–354. https://doi.org/10.1016/j.jclepro.2013.10.050

[19] French AD (2014) Idealized powder diffraction patterns for cellulose polymorphs. Cellulose 21:885–896. https://doi.org/10.1007/s10570-013-0030-4