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Green, economic, and partially biodegradable wood plastic composites via enzymatic surface modification of lignocellulosic fibers

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Abstract

Lignocellulosic fibers, which obtained from Citrus trees trimmings, were modified with *Aspergillus flavus* (EGYPTA5) enzymes. The non-modified and the modified lignocellulosic fibers were used with low density polyethylene (LDPE) by melt blending brabender method at 170 °C with different ratio (5, 10 and 20 wt%) to obtain wood plastic composites (WPC). The prepared samples were characterized using Fourier-transformed infrared (FT-IR), Scan Electron Microscope (SEM), and Water vapor transmission rate (WVTR) as well as, the mechanical, thermal, biodegradability and swelling properties were examined. The fabricated WPC displayed good mechanical and thermal properties compare with pure LDPE. Also, the WVTR was enhanced by the addition of modified lignocellulosic fibers

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over the unmodified one. Moreover, the enzymes assay such as *cellulase* and *lignin peroxidase* enzymes were estimated and confirming the growing of fungi on the lignocellulosic fiber in solid state fermentation condition to improve lignin peroxidase production and eliminate cellulose enzymes. The fabricated WPC can be used in different environmental application such as packaging system, that it will be green, economic, and partially biodegradable.

Keywords: Natural product chemistry, Materials science, Materials chemistry

1. Introduction

Nowadays, many researchers focus to discover alternative fiber sources. One of the most consumed type of fruit over the world is citrus, due to it is inexpensive, bulk productivity, riches by vitamin and minerals, dietary fiber and many phytochemicals (flavonoids, amino acids, triterpenes.eg) (Roussos, 2011). The uses of citrus fruits have led to produce huge amounts of residue (temper, pulp, peel, and seeds) (Garcia-Castello et al., 2011). In addition, in pruning season every year, a huge amount of waste is formed, which occupies a large volume but with low weight and zero ecumenical value. The wastes obtained from citrus tree trim were considered as an agricultural waste that it was useless and contributed to the environmental pollution. Citrus by-product exhibits great potential for developing fibers which can be used (Zain et al., 2014; Hasanin et al., 2018).

Lignocellulose, which forms the plant skeletons, is the most common fibers residues which created by the nature and the main constituent of organic waste. Despite previously being considered an environmental problem it gains importance as a source of cellulosic fibers, biomaterials sectors and the energy by bio-fuel production (Mariño et al., 2015; El Sharkawi et al., 2018; Darwesh et al., 2018). Cellulose is a long chain of homopolymer with repeating units D-glucose, which are joined by ß-1-4 linkages between C-1 of one unit and the C-4 of the next unit. Each one bears three hydroxyl groups and is able to form inter and intramolecular hydrogen bonds that play a main role in formative the physical properties of cellulose (John and Thomas, 2008; Saada et al., 2018).

The woody fibers can be used as fillers and reinforcement materials, which have been blended with thermoplastic such as polyethylene, polystyrene, polypropylene, polylactic acid and polyvinyl chloride or thermosetting plastic such as polyurethanes, silicone and vinyl ester to form WPC or modified by different nanomaterials to form polymer nanocomposites (Youssef et al., 2013; Youssef and Abdel-Aziz, 2013). It used in commodity thermoplastics to reduce the cost and to improve mechanical performance as well as adding decorative shape. Nowadays, WPC have seen a large growth in the world because of rising of plastic costs and environmental portion of using renewable and biodegradable materials (Youssef et al., 2015; Youssef and El-Sayed, 2018). In addition, WPC are considered as an effective

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wherewithal of using waste wood and plastic. The advantages of using a wood component in thermoplastic composites are that wood is bio-based resource, inexpensive, excessively available, highly filling levels, high specific properties, lower density, flexible, recyclable, water resistant and biodegradable (Moustafa et al., 2017; Takatani et al., 2008).

When hydrophobic plastic and hydrophilic wood are blended, the interfacial adhesion is not good due to their poor compatibility, leading to weak mechanical properties of the composite. To enhance their compatibility and overcome the hydrophobicity and hydrophilic incompatibility, a small amount of compatibilizer such as maleic anhydride-modified polyethylene or polypropylene, which was now commercially available (Takatani et al., 2008). Additionally, the modified lignocellulose enhanced the compatibility between plastic (hydrophobic) and wood (hydrophilic). Marcovich et al. (1998) illustrated that the modified wood floor effect on the properties of unsaturated polyester composites. They establish that wood flour modified by maleic anhydride improved the mechanical properties of prepared composites. Although, the chemical treatments are more prevalent but have many environmental hazards.

Microbial enzymes play an important role in lignocellulose degradation and surface modification; also it increases the surface compatibility to hydrophobic polymers (Abdel Rehim et al., 2011; Sasikumar et al., 2014; Darwesh et al., 2015; Sharma et al., 2017). The biological treatment especially via in-suite microbial enzymes has a high capability to selectively eliminate undesirable component and lets the useful one as well as economic benefit. However the whole lignocellulose fibers is present with the fungus, the fiber induced on the fungus to produce degradation enzymes which break down cellulose which is the fiber back bone and decreasing the tensile and mechanical properties of the fiber. To overcome this problem one unique *Aspergillus flavus* (EGYPTA5) isolate was used. This strain is non-celluloytic and excellent highly peroxidase enzymes producer.

In the current work unique solid state fermentation conditions were used in which the surface of fibers were activated and modified to become suitable to contact and compactable with hydrophobic plastic surface. Since no any coupling agents were used and eco-friendly green plastic composites were produced suitable for many applications e.g. alternative wood, house hold equipment and packaging applications.

2. Materials and methods

2.1. Materials

Low density polyethylene (LDPE), 0.93 g/cm^3 density, 6.0 g/10 min Melt Index and 87.4 °C softening point was purchased from (Exxon Mobil Chemical, KSA). All

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medium and its components were purchased from modern Lab Co, India in analysis grad without any purification required.

Lignocellulosic fibers were obtained from Citrus trees trimmings, since it were collected from some local farms located in Giza, Egypt to be used as a substrate in this study. The collected raw materials were drying in air oven at 70 °C followed by mechanical grinding and sieving with mixed different fibers lengths (0.1−1.0 cm).

2.2. Methods

2.2.1. Fibers treatment with Aspergillus flavus

Fibers treatment with *Aspergillus flavus* (EGYPTA5) Lignocellulosic fibers were subjected as sole carbon source in Czapek-Dox's broth media (Atlas, 2010) under static conditions with *Aspergillus flavus* (EGYPTA5) as reported in our previous work (Hasanin et al., 2019). Additionally, the solid state fermentation (SSF) condition was applied to enhance production of lignin oxidative (lignin peroxidases) enzymes. The agriculture wastes were added to Czapek-Dox's broth media in a ratio of 1:1, sterilized, inoculated by the fungal strain and incubated under static conditions at 28 °C for 15 days. The enzymes solution was obtained by extraction of media using phosphate buffer (0.1 M, pH 7) and then assayed.

2.2.2. Enzymes assay

2.2.2.1. Cellulase enzyme assay

In order to detect ability of fungal isolate to produce cellulose enzyme, one disc of fungal growth was inoculated on MSM agar plates containing 1% cellulose as sole carbon source (Darwesh et al., 2014). After incubation at 28 °C for 3 days, formation of clear zone around fungal disc were observed as a positive result for *cellulase* enzyme using 1% iodine solution. On the other hand, for quantification of *cellulose* enzymes production, one disc of fungal strain was inoculated in cellulose-containing MSM broth medium and incubated in an incubator shaker at 28 °C with speed of 120 rpm for 3 days. *Cellulase* enzyme activity was determined using the 3, 5-dinitrosalicylic acid (DNS) method (Ghose, 1987). Data are representative of at least three experiments, till the final result read three times in the same value. This was carried out in all enzymes assay.

2.2.2.2. Hemicellulase assay

Hemicellulase activity of culture filtrate was determined spectrophotometrically at 340 nm in a reaction mixture containing 2.5 ml of 100 mM Tris HCl Buffer pH 8.6, 0.1 ml of 19 mM ß-NAD, 0.5 ml of supernatant. One unit will liberate 1.0 μ mole of D-galactose from hemicellulose in one hour at pH 5.5 at 37 °C.

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2.2.2.3. Lignin peroxidase assay

Lignin peroxidase activity of culture filtrate was determined spectrophotometrically at 420 nm in a reaction mixture containing pyrogallol and H_2O_2 as described by Darwesh et al. (2015).

2.2.2.4. Laccase enzyme assay

Spectrophotometric assay for *laccase* enzyme activity was performed at 460 nm by the oxidation of 2.6-dimethoxyphenol (DMP) in sodium acetate buffer (Darwesh et al., 2014).

2.2.2.5. Polyphenol oxidase enzyme assay

Polyphenol oxidase activity was determined for culture filtrate in a reaction mixture containing catechol in phosphate buffer. Absorbance (495 nm) measured after 3 min of incubation. The enzyme activity was expressed as changes in absorbance mg min^{-1} of protein (Darwesh et al., 2014).

2.2.3. Preparation of the wood plastic composites (WPC)

The modified and unmodified lingo cellulose were melt blending with low polyethylene density (LDPE) at 170 °C with different ratio (5, 10 and 20 wt %). The blending process was accomplished for about 5 min with the aid of a twin screw extruder with intermeshing screws of 40 cm (Haake Rheomex TW100). Sheets of the samples were prepared using a hydraulic press with two heated plates (Bucher plastics press KHL 100) at 120 bar and 150 °C. The compositions of the prepared green wood plastic composites (WPC) were displayed in Table 1.

Table 1. The sample recipe of the prepared green plastic composites.

Sample code	LDPE, %	Unmodified lignocellulosic fibers (wt. %)	Modified lignocellulosic fibers (wt. %)
LDPE	100	0.0	0.0
WPC5C	95	5.0	0.0
WPC10C	90	10.0	0.0
WPC20C	80	20.0	0.0
WPC5F	95	0.0	5.0
WPC10F	90	0.0	10.0
WPC20F	80	0.0	20.0

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2.3. Characterization

2.3.1. Natural fibers component after and before treatments

Resins and waxes content of the used oven-dried grinded plant-origin wastes were gravimetrically calculated according to (T 204 cm-97). Data are representative of at least three experiments, and the standard deviations are less than 3.0%. The method used to determine the lignin content was that of Klason lignin determination corroding to T-222 om-02 (T-222).Data are representative of at least three experiments, and the standard deviations are less than 4.0%. Hemicellulose is quantified with sodium chlorite according to the procedure of as adapted by (El-Saied et al., 2012). Data are representative of at least three experiments, and the standard deviations are less than 6.0%. Ash content was gravimetrically estimated by igniting of the waste material in muffle furnace in a porcelain crucible first at 400 °C for 30 minutes, then at 850 °C for 45 minutes (T 211 om-93). Data are representative of at least three experiments, and the standard deviations are less than 4.0%. This test was carried out according to (T256 um-91) by soak the fiber in distal water for 24 h and then centrifuged at 3500 rpm for 10 min. The WRV gravimetrically estimated according to below equation:

$$WRV = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

Where W_{wet} is the weight of the sample after centrifugation and W_{dry} is the dry weight of the sample (T-256 um-91). Data are representative of at least three experiments, and the standard deviations are less than 8.0%.

2.3.2. Characterizations of the fibers and WPC

2.3.2.1. Fourier-transformed infrared spectroscopy (FT-IR) spectral analysis

FT-IR spectra of the prepared samples were recorded in the range of 400−4000 cm^{-1} on Shimadzu 8400S FT-IR Spectrophotometer IR measurements which are including crystallity index (Cr.I = [Abs. (1430 cm^{-1})/Abs. (900 cm^{-1})]) (Nelson and O'Connor, 1964a, 1964b) and main hydrogen bond strength (MHBS = [Abs. (3400 cm^{-1})/Abs. (2920 cm^{-1})]) (Levdik et al., 1967) are calculated.

2.3.2.2. Scanning electron microscope (SEM)

The surface morphology of prepared samples were analyzed using scanning electron microscopy, (JSM 6360LV, JEOL/Noran) with accelerating voltage of 10−15 kV.

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2.3.2.3. Thermogravimetric analysis (TGA)

The thermal analysis was performed using Shimadzu TGA-50 thermogravimetric analyzer, Columbia, EUA, in a nitrogen atmosphere at 10 °C/min heating rate in the range from room temperature to 700 C.

2.3.2.4. Differential scanning calorimetry analysis (DSC)

DSC was recorded on TA Instruments DSC Q20 V24, 11 Build 124. All samples were heated with a scan rate of 10 °C/min over a temperature range of 30−700 °C under a nitrogen atmosphere.

2.3.3. Composite characterization

2.3.3.1. Mechanical properties

Prior to tested, the composite samples were conditioned for 24 h at a temperature 23 ±2 °C and a relative humidity 50 ± 5%. The mechanical properties (average of 3 replicate for each sample) of the prepared composites were subjected to the following measurements; tensile strength, Young's modulus and the elongation were tested according to the ASTM D638-91 (ASTM D638-91) standard using a universal testing machine LK10k (Hants, UK) fitted with a 1 kN load cell, and operated at a rate of 5 mm/min. The hardness tests of the composites were carried out using a Rockwell Hardness Testing Machine. The tests were conducted following ASTM D785 (ASTM D785).

2.3.3.2. Swelling test

Swelling test was carried out according to ASTM D570-99 (ASTM D570-99). The WPC samples were cut in 1 × 1 cm size and dried in vacuum at room temperature for a week. After initial weighing, they were kept in beaker with 50 ml of distilled water at room temperature for 2 h. The swelling ratio of the samples was calculated using the following equation:

$$\text{Swelling Ratio}\ (\%) = \frac{W_s - W_d}{W_d} \times 100 \qquad (2)$$

Where, W_s weight of the swollen samples, and W_d weight of the dry samples. Data were representative of at least three experiments, and the standard deviations were less than 8.0%.

2.3.3.3. Water vapor transmission rate (WVTR)

WVTR was carried out using GBI W303 (B) Water Vapor Permeability Analyzer (China) using the cup method. The water vapor permeability was measured as the

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amount of water vapor passes through the tested samples. Also, WVTR was measured as the mass of water vapor transmitted throughout a unit area in a unit time under controlled conditions of temperature (38 °C) and humidity (4%) according to the following Standards ASTM E96 (ASTM E96/E96M − 16), ISO 2528 (ISO 2528), and ASTM D1653 (ASTM D1653). Data were representative of at least three experiments, and the standard deviations were less than 7.0%.

2.3.3.4. Biodegradation of composites in soil

Biodegradation of wood plastic composite in soil was carried out as previously reported a corroding to Dalev et al. (2000). Water was sprayed once a day to sustain the moisture. The samples were weighed every week for four weeks. After each period the samples were carefully taken out, washed with distilled water, and dried at 50 °C for 24 h and then weighed. Data were representative of at least three experiments, and the standard deviations were less than 4.0%.

2.4. Statistical analysis

The experiment was arranged with three replications. The data obtained were subjected to analysis of variance (ANOVA) and analyzed for statistically significant differences using LSD test at 5% level according to the procedures reported by Snedecor and Cochran (1980).

3. Results and discussion

3.1. Lignocellulosic fibers fungal treatment and characterization

The lignocellulosic fibers were subject to two different fermentation conditions Submerged and SSF. Fig. 1 shows the plated *Aspergillus flavus* (EGYPTA5) after incubated for 7 days. The fungal enzymes production was enhanced in the SSF condition by significant change. Table 2 shows that the lignin oxidative enzymes activities were increased in peroxidase by 59%, *laccase* by 64 %, polyphenol oxidase by 60% and hemicellulase by 51%. Alternatively, the *cellulase* enzyme in both fermentation conditions was not detected. These results illustrated that the SSF fermentation condition was preferred to produce fibers surface compatible with hydrophobic plastic as well as without any attach to fibers back bone (cellulose content).

Table 3 illustrated that the fiber analysis which revealed that there was no cellulose content lose. In contrast lignin and hemicellulose were decreased by fungal treatment as well as extractive. This emphasized the increase in WRV which refer to liberation of many OH group. This reaction might be caused due to the pathway fermentation of microbial system as discussed previously (Sultan et al., 2016).

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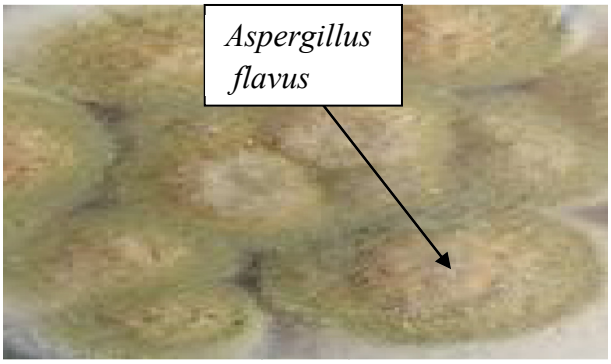

Fig. 1. After 17 days incubated *Aspergillus flavus* (EGYPTA5).

Table 2. Enzymes activity in agriculture waste medium U/ml in Submerged & SSF conditions.

Enzymes activity in agriculture waste medium U/ml					
Sample conditions	***Lignin peroxidase***	***Laccase***	***Polyphenol oxidase***	***Cellulase***	***Hemicellulase***
Submerged condition	2.43 ± 0.25	0.62 ± 0.19	0.95 ± 0.24	0.00	0.75 ± 0.22
SSF condition	3.87 ± 0.41	1.02 ± 0.3	1.54 ± 0.11	0.00	1.45 ± 0.2

Table 3. The components of modified and unmodified lignocellulosic fibers.

Components	**Components average values, % wt.**	
	Control	**Treated**
Extractive (MeOH/benzene)	2.24 ± 0.33	1.03 ± 0.14
Ash	7.21 ± 0.61	11.43 ± 0.90
Klason lignin	18.80 ± 0.70	13.00 ± 1.02
Hemicellulose	7.00 ± 0.55	1.00 ± 0.40
Cellulose	70.00 ± 2.91	79.00 ± 2.11
Water retention value	11.00 ± 0.92	16.00 ± 1.71

3.1.1. FT-IR analysis of lignocellulosic fibers

FT-IR spectra of modified and unmodified lignocellulose fiber were illustrated in Fig. 2. The carbonyl group stretching at 1700 cm^{-1} and 1600 cm^{-1} were corresponding to the ester and acetyl groups in hemicelluloses and lignin in case of unmodified lignocellulose (Mariño et al., 2015) while this peaks disappeared in case of modified lignocellulose as an indication of the effectiveness in the removal of hemicellulose by fungal enzyme.

The peak at 1700 cm^{-1} was obtained for untreated fibers, while it became faint in the treated fibers. This peak was corresponding to the C−O stretching vibration of the

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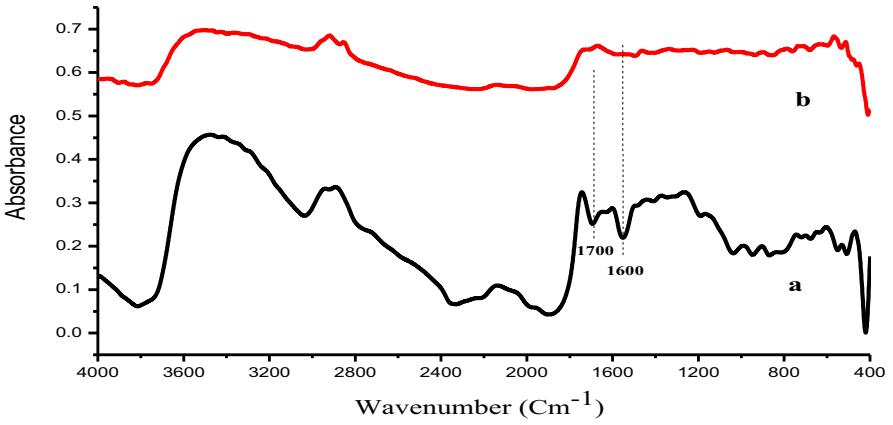

Fig. 2. FT-IR spectra of (a) unmodified lignocellulosic fibers and (b) modified lignocellulosic fibers.

acetyl groups of hemicellulose or the ester linkage between the carboxylic group of ferulic and p-coumaric acids of lignin (Mandal and Chakrabarty, 2011; Sain and Panthapulakkal, 2006; Li et al., 2014; Khalil et al., 2017). Likewise, the absorption peak at 1600 cm^{-1} was illustrated only in unmodified Lignocellulosic. This peak was associated with stretching vibration of C−C for aromatic ring of lignin (Kumar et al., 2012). The disappearance of these bands might be due to the removal of hemicellulose and lignin from fibers during the fungal treatment (Jonoobi et al., 2009; Basta et al., 2016, 2018). The absorbance peak observed in the spectra of the modified fibers in the regions 1641−1649 cm^{-1} was recognized by the O-H bending of the adsorbed water (Mandal and Chakrabarty, 2011). The increasing of moisture content may be due to the absorption of moisture in the spaces left vacant from the removal of hemicellulose and lignin.

3.1.2. The crystallinity index of the prepared WPC

The crystallinity index (Cr.I) of modified fiber showed an increase in comparative with untreated one (Table 4). Additionally, the composites which containing modified fiber showed low Cr.I value in low present of fiber content (5% and 10%) this might be related to incompatibility between untreated fiber and polymer matrix and the Cr.I value was related to polymer.

On the other hand, the treated fiber goes compatible with polymer and the interaction between fiber and matrix produced sheets like composite. This also emphasized increasing of main hydrogen bond strength (MHBS) which increased treated fiber content. Moreover, the Cr.I of modified fiber revealed an increase in comparative with untreated one from 0.53 to 0.70. Additionally, MHBS increased to 0.15 in unmodified fibers where it was 0.07 in modified fibers.

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Table 4. The crystallinity index and MHBS of the prepared composites.

	Cr.I	MHBS
LDPE	1.4311	0.5644
Fiber	0.5281	0.1541
Modified fiber	0.7043	0.0782
WPC5C	1.1988	1.0330
WPC10C	1.5294	0.2352
WPC20C	1.1234	1.0342
WPC5F	0.9764	1.0132
WPC10F	1.0982	1.0471
WPC20F	1.5647	1.9844

3.1.3. Morphological properties of modified and unmodified lignocellulose

Citrus waste fibers (source of lignocellulose) showed a closely packed structure, since their surfaces were covered with residual material (Fig. 3a). The influence of enzymatic digestion was confirmed by the complete degradation of the thinner and most vulnerable cellulosic material and germinated of many defects/holes on the fiber surface (Fig. 3b) as a results of the effect of fungal enzymes on citrus waste biomass.

3.2. Composite preparation

The main goal of the present work is to assess the WPC, as bio-composites, made from agriculture waste (citrus trees by-products) and thermoplastic (LDPE) matrix; therefore firstly, optimizing conditions was carried out. This study also performed as a trial to improve the compatibility of citrus trees by products fibers with matrix via change the fibers composition as showed in Table 1, without needing coupling agent, depending on activated fibers surface using fungal enzymes which eliminate hydrophilic impurities which made surface more hydrophobic and compatible with plastic matrix (Hasanin et al., 2018). Additionally, the mechanical and physical properties of the WPC composites produced were improved as result of increasing lignocellulosic fiber content by about 20% (El-Saied et al., 2012).

3.2.1. SEM of prepared WPC

Fig. 3e obviously established that the morphology of the surface of pure LDPE films which it was very smooth, while Fig. 3(c & d) represented the fractural morphology of partial biodegradable composites manufactured from LDPE and

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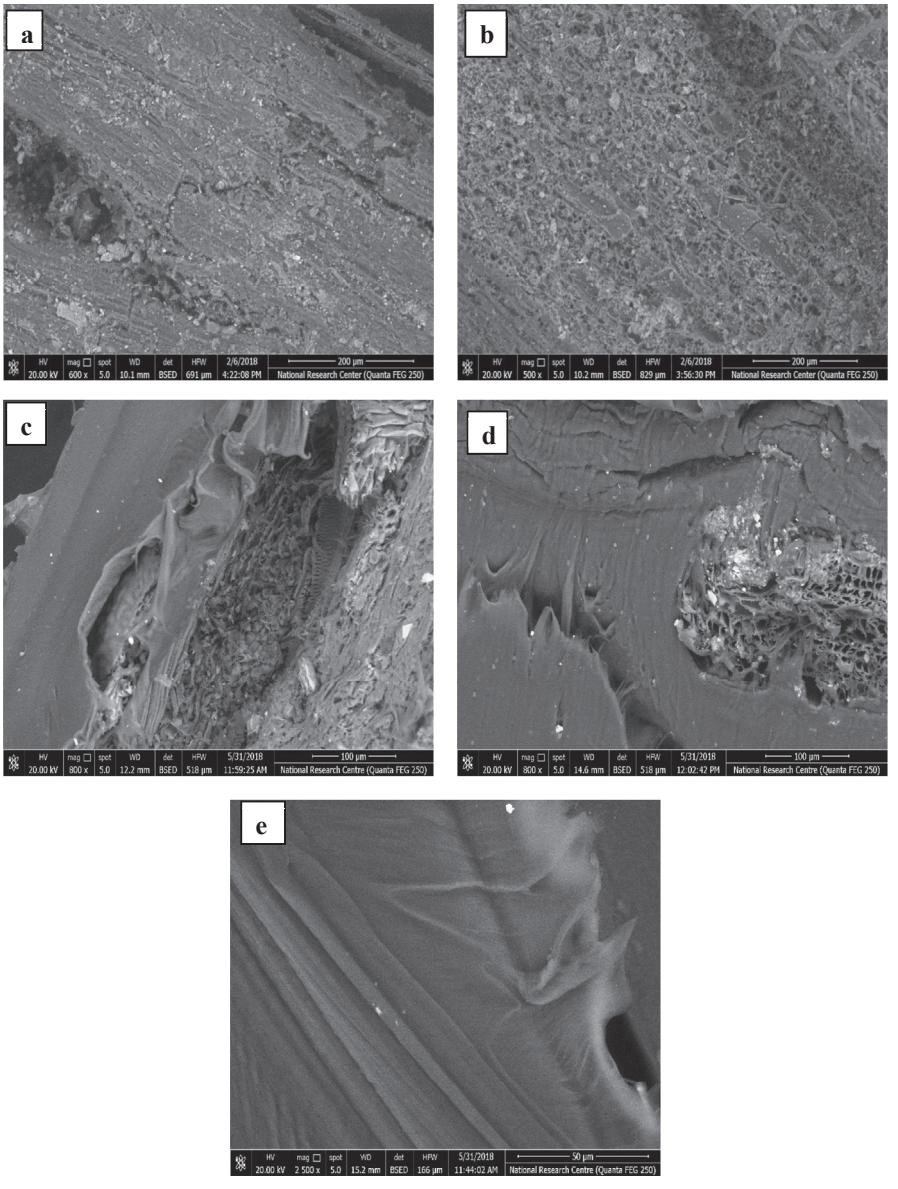

Fig. 3. SEM image of cellulose (a), modified cellulose (b), WCP20C (c), WCP20F (d) and LDPE (e).

lignocelluloses or modified lignocellulose fibers, respectively, using fiber concentration 20 % which display a smoother and a rough structure, this because of the compatibility between polymer matrix and lignocelluloses or modified lignocellulose fibers, it was clear that the composites with 20% lignocelluloses fibers less homogeneity and compatibility between fibers and polymers than 20% modified lignocelluloses fibers this because of no modification shaped not only for LDPE matrix through adding of a few modifier (e.g. plastizer), but also for lignocellulose fibers. The morphology suggested that the fiber content (%) has great effect on their internal construction.

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3.2.2. Mechanical properties of the prepared green wood composites (WPC)

Fig. 4 represents the effect of modified and unmodified lignocelluloses content in the prepared WPC on the tensile strength, elongation, Young's modulus and hardness. It was found that as the content of lignocelluloses increases the tensile strength decreasing to 11.8 MPa for WPC20C, while in case of modified lignocellulose; it increases as content of modified lignocelluloses increasing up to 14.6 MPa for WPC20F (Fig. 4a). This might be referring to the compatibility between modified lignocelluloses and the polymer more than that between unmodified one and the matrix. In addition, the elongation had inverse character with the tensile strength. Furthermore, the Young's modulus and the hardness (Fig. 4b) increased with increasing the content of modified and unmodified lignocelluloses to be for Young's modulus equal 356 and 427 MPa and hardness equal 11.68 and 12.1 (KP/mm^2) for WPC20C and WPC20F, respectively.

3.2.3. Water vapor transmission rate (WVTR) of the papered green plastic composites

WVTR is a significant technique for the suitability of the materials which used for food applications. Consistently, the passage of the vapor of water from the neighboring air into packaging food foodstuffs or the moisture losses from the foodstuff to the adjacent atmosphere is significantly influenced on the products stability and quality during storage time which may be affected in the food shelf-life (Youssef et al., 2018). Table 5 revealed the WVTR for the fabricated green WPC films which containing different loading of modified or unmodified lignocellulosic fibers. The results obtained from WVTR instrument established that the LDPE films displayed very low water vapor permeability that around 0.005 g/(m^2.day). While by adding the unmodified lignocellulosic fibers the WVTR was increased by increasing the ratios of the unmodified lignocellulosic fibers from (5−20%) to be (1.711−61.302 g/m^2.day) that means the films of green WPC became more suitable for using in packaging application due to this film could be used in application need more water vapor pass through the film. In other hand, the comparison with pure LDPE and modified lignocellulosic fibers by *Aspergillus flavus*, the WVTR increased but in very low amount compared with LDPE film but there were dramatic decreasing in the WVTR values when using modified fiber as shown in Table 5. This might be related to the modification process make the fiber more compatible with plastic materials and no more pours for water transmitted throughout the film prepared from LDPE and modified lignocellulosic fibers with *Aspergillus flavus* (EGYPTA5). Thickness swelling which tabled in Table 5 cleared that the fiber loading parent effect on WPC water up take, where the LDPE matrix is water resistance in case of (0%) of lignocellulose content. On the other hand, the lignocellulose load % increase leads to rise

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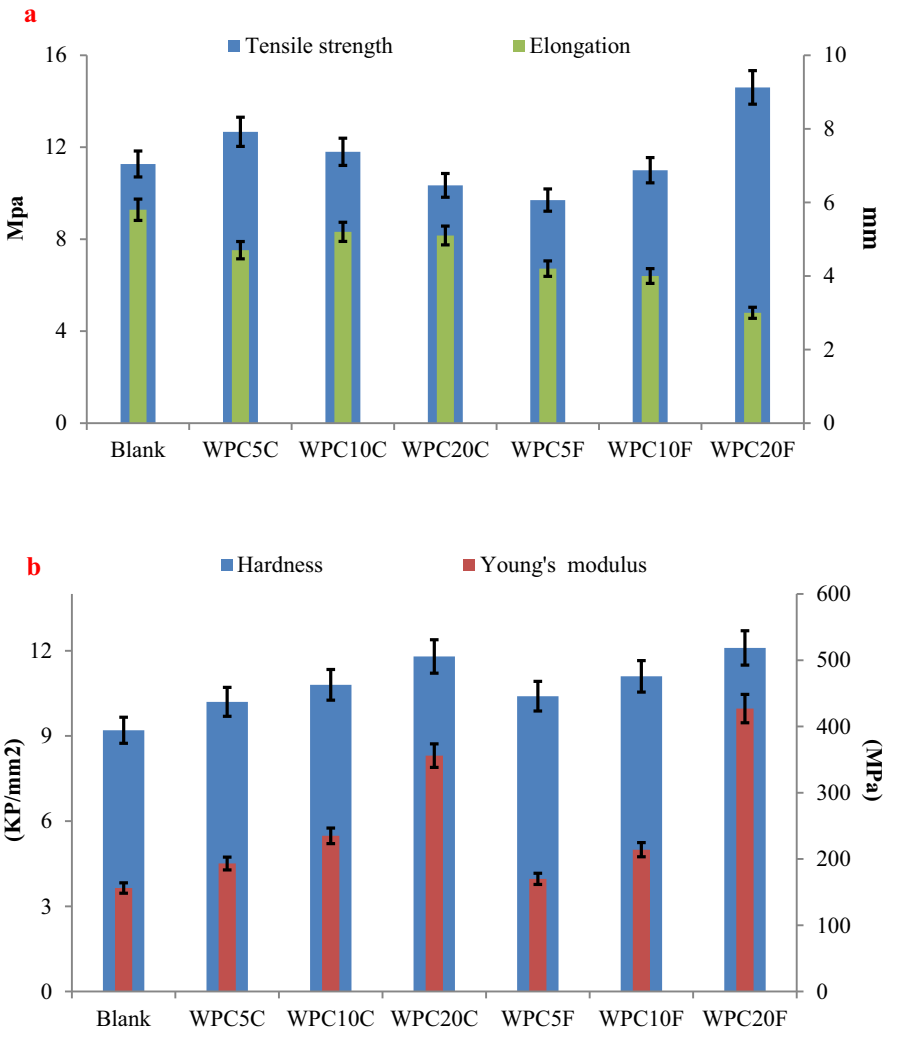

Fig. 4. The tensile strength and elongation (a) as well as the young's modulus and hardness (b) of prepared green wood composites.

Table 5. WVTR as well as the swelling of LDPE as well as the prepared WPC containing different concentration of modified and unmodified lignocellulosic fibers.

Samples	Lignocellulosic fibers, %	WVTR, g/(m^2. Day)	Thickness swelling, %
LDPE	0.0	0.005	0.20
WPC5C	5.0	1.711	0.72
WPC10C	10.0	48.322	0.87
WPC20C	20.0	61.302	1.20
WPC5F	5.0	10.204	0.69
WPC10F	10.0	12.343	0.75
WPC20F	20.0	20.818	0.95

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of water up take behavior of WPC. Additionally, the fungal treatment increase the water resistance of composite in compare with the untreated one. This might be lead to enhance of the wood polymer compatibility.

3.2.4. Thermal analysis of the green composites

Fig. 5 displayed the gravimetric thermograms of blank, WPC5C, WPC20C, WPC5F and WPC20F which revealed that the thermal stability decreased by increasing the content of lignocelluloses or modified lignocellulose fibers from 5 to 20% compare to the pure LDPE matrix. However the heat flow rises from 103 to 107 °C by using unmodified lignocellulose fiber content from 5 to 20%. Also in case of using modified lignocellulose fibers loadings % from 5 to 20% the heat flow increased from 112

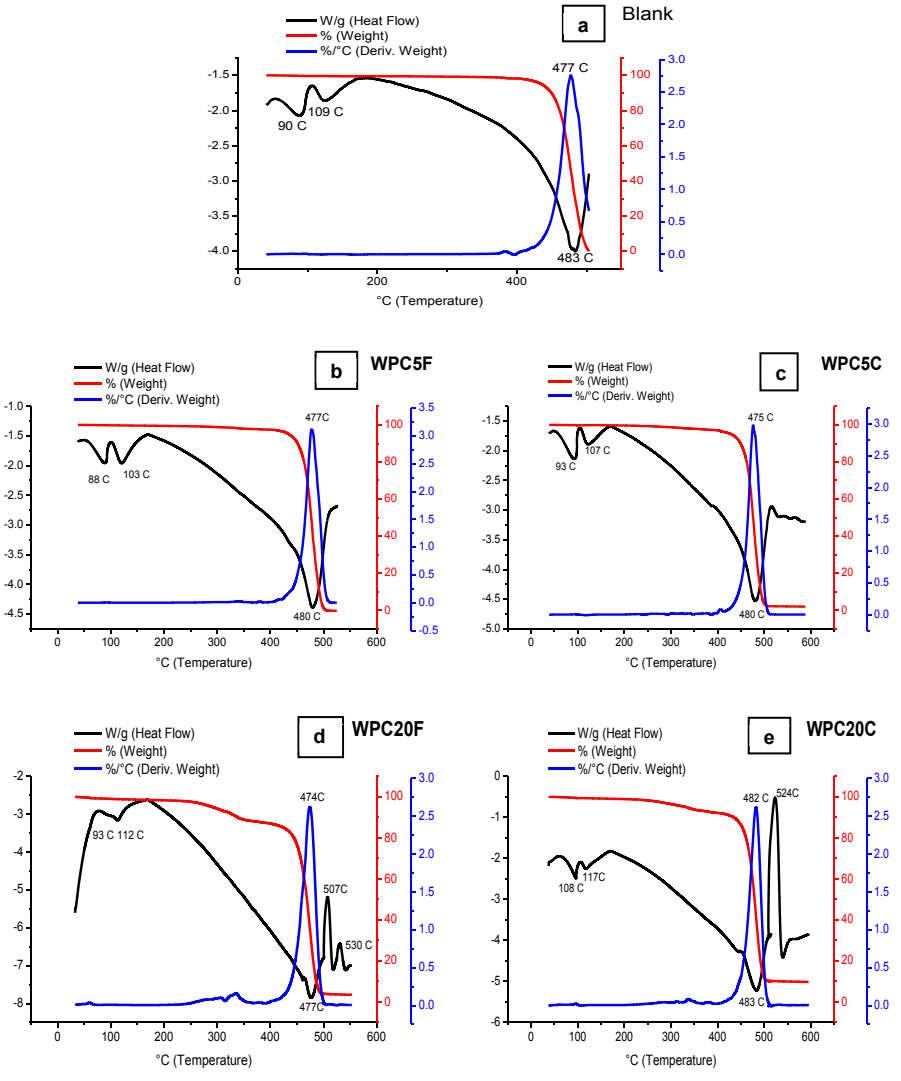

Fig. 5. The thermal properties of the prepare LDPE composites samples, A) blank LDPE, b) WPC5F, c) WPC5C, D) WPC20F, e) WPC20C.

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to 117 °C. In addition, Table 6 represented the weight loss percentage, *Tg* and Mp of the prepared samples. It illustrated that all samples were lost its weight with increasing temperature in two stages as shown from Fig. 5 and Table 6 (El-Saied et al., 2018).

Firstly, all samples lost about 3−14 wt % of their weight at first stage at the temperature up to 400 °C due to the evaporation of the moisture and crystalline water adhere to composites. Then, they misplaced about 80−90 wt % of their weight at second stage due to the decomposition of the polymer and the cellulose (Ibrahim et al., 2018).

3.2.5. Biodegradation of composites in soil

Biodegradation ability was carried out according to (Bras et al., 2012; Barakat et al., 2017) via impeded the tested samples into soil for four weeks. The standard method was applied in collecting soil and spreading with water. The microbial soil population decomposed the tested samples with helping of humidity and temperature as well as duration (Zhang and Liu, 1996).

The effect of lignocellulose fibers on biodegradability percentage of the composite in soil was presented in Fig. 6. The composite lost about 0.18 % of its weight after being buried in soil for 4 weeks where this result is refer to non-biodegradability of the blank (LDPE). Additionally, additive of natural lignocellulosic fiber enhanced the composite biodegradability where WPC containing 5%, 10 and 20 wt% of untreated lignocellulosic fiber lost about 4.2, 5.2 and 10.1%, respectively, after the same period buried in soil. In addition, the treated fiber by fungal enzymes were showed slightly decrease in biodegradability however WPC containing 5%, 10 and 20 wt% of treated lignocellulosic fiber lost about 3.9, 4.9 and 9.1%, respectively, after the same period buried in soil. The decrease in biodegradability of treated fibers composite in soil as a result of remove of undesirable lignocellulosic fibers constituent this made the fiber more compatible with the polymer and reduced the surface of fiber which subjected to microorganisms included the soil. These results were in agreement with previous findings (Bras et al., 2010), that the presence of degradable fiber into non-degredable

Table 6. The weight loss percentage, glass transition (T_g) and melting point (Mp) of the prepared composites.

Sample	Wt% 1st stage	Wt% 2nd stage	T_g	Mp
LDPE	2.9	96.9	90.3	109.5
WPC5C	3.8	94.2	93.1	107.3
WPC20C	8.2	82.1	108.3	117.9
WPC5F	3.4	96.5	88.0	103.0
WPC20F	14.2	82.3	93.5	112.0

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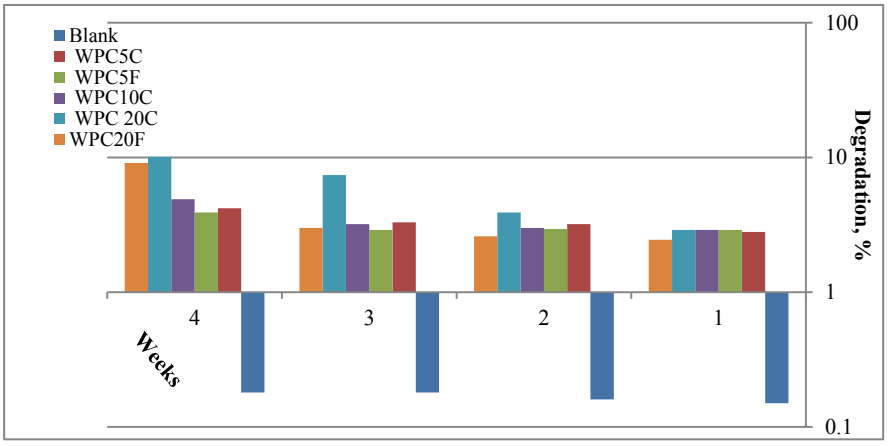

Fig. 6. Biodegradability of prepared WPC and pure LDPE as blank.

polymer leads to improve the biodegradability feature of the produced composite. Since, the degradable fibers after degradation make holes into polymer which makes polymer easy to be digested in environment by the different environmental factors. In addition, the prepared composite could be considered as partially biodegradable.

4. Conclusions

This study achieved the compatibility of citrus trees by products fibers with LDPE matrix through alteration the fibers composition without requiring coupling agent, depending on activated fibers surface using fungal enzymes which eliminate hydrophilic impurities which made surface more hydrophobic more compatible with LDPE matrix. Correspondingly, the mechanical, thermal and swelling properties were examined and the prepared WPC demonstrated good mechanical and thermal properties compare with pure LDPE. Correspondingly, the WVTR was enhanced by rising the loading of lignocellulosic fibers in the polymer matrix. Furthermore, the enzymes assay such as *cellulose* and *lignin peroxidase* were evaluated and approving the developing of fungi on the lignocellulosic fiber in solid state fermentation condition increasing lignin peroxidase production and reducing cellulolytic enzymes. Finally, the biodegradation of the prepared WPC were estimated. Finally, we can say that WPC can be used in many applications as green, economic, and partially biodegradable plastic composite.

Declarations

Author contribution statement

Ahmed M. Youssef: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Mohamed S. Hasanin, Mahmoud E. A. El-Aziz: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Osama M. Darwesh: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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