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Effects of corona discharge treatment on the mechanical properties of biocomposites from polylactic acid and Algerian date palm fibres

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In this paper, biocomposites materials based on date palm fibres (untreated or treated with corona discharge) as reinforcing elements and polylactic acid matrices were prepared and characterized. The objective of this study was to evaluate the mechanical properties of these biocomposites by modification of date palm fiber by using corona discharge treatment which results in a surface oxidation. The morphology of processed biocomposites was studied by scanning electron microscopy. It was found that treated fibers of the reinforced composite showed superior mechanical properties as compared with untreated fiber reinforced composites due to the enhanced adhesion between the treated date palm fiber and the polylactic acid matrix. Changes in the surface chemistry were investigated with Fourier Transform infrared spectroscopy. Moreover, morphological studies by scanning electron microscopy demonstrated that better adhesion between the treated fiber and the matrix was achieved. Such studies are of great interest in the development of environmentally friendly composites from biodegradable polymers.

Key words: Polylactic acid, date palm fibres, biocomposites, Corona treatment, mechanical properties, surface treatments.

INTRODUCTION

The depletion of petroleum resources coupled with increase in environmental regulations have urged to put on more effort into finding new materials and products that are compatible with the environment and independent of fossil fuels. Biobased materials offer a potential solution to this complex problem.

Composites used are usually composed of synthetic polymer as the matrix and synthetic fiber such as glass, aramid or carbon fiber as the reinforcement. However, both matrix and reinforcement are the source of rising environmental problems since they do not degrade in landfills or composting environments (Huda et al., 2005b). The development of natural fiber reinforced biodegradable polymer composites promotes the use of environmentally friendly materials.

Natural fibres have many advantages compared to synthetic fibres, for example hey have low weight, and they are recyclable and biodegradable. They are also renewable and have relatively high strength. The use of green materials provides alternative way to solve the problems associated with agriculture residues.

Biopolymers offer environmental benefits such as biodegradability, greenhouse gas emissions, and renewability of the base material (Ray and Bousmina, 2005b). One of the most promising biodegradable polymers is polylactic acid (PLA).

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Figure 1. Date palm fibres.

PLA is a biodegradable thermoplastic that has been derived from 100% renewable resources such as corn starch and sugar canes, wheat and other starch-rich products (Mohanty et al., 2000; Nam et al, 2003; Meinander et al., 1997). Polylactic acid (PLA), is a linear aliphatic thermoplastic polyester, produced from renewable resources (Gupta and Kumar, 2007).PLA has properties that are comparable to many commodity polymers (for example, PP, PE, PVC, PS) such as high stiffness, clarity, gloss, and UV stability (Ray et al., 2002a). Major limitations of PLA are due to its high brittleness, low toughness and low tensile elongation (Ljungberg et al., 2005). A way to improve the mechanical properties of PLA is the addition of fibers or filler materials (Huda et al., 2005a).

Date palm is one of the oldest fiber crops in the world which is grown in n the arid regions of the Arabian Peninsula, North Africa, and the Middle East. Date palm fiber-reinforced composites have attracted increasing interest because of the advantages of date palm fibers, such as low density, relatively high toughness, high strength and stiffness, and biodegradability. Historically, date palm fiber has been used as a cordage crop to produce twine, rope (Chehma and Longo, 2001).

The incompatibility of polar cellulose fibres and non polar thermoplastic matrix leads to poor adhesion, which then results in a composite material with poor mechanical properties (Beckermann and Pickering, 2008). The adhesion between the fibres and matrix can be improved either by chemical solution (Yu et al., 2010) or free radical reaction (Bledzki et al., 2008), use of modified thermoplastic containing a compound capable of interacting with the fiber (Fung et al., 2002).

For our study, physical corona discharge treatment was selected. It is a non polluting technique based on the production of a plasma media at ambient pressure and Temperature (Ragoubi, 2009). Corona discharge treatment changes the surface characteristic of the materials (Uner, 2009).

Corona technology has a wide industrial application in the terms of polymeric products such as plastics (Krüger and Potente, 1980) but also in fibres industries (wood, textile) (Podgorski et al., 2000).

The main aim of this research is to investigate the influence of corona treatments on the mechanical properties of date palm fibres /PLA biocomposites.

MATERIALS AND METHODS

Raw materials

The date palm fibres were obtained from a local Algerian date palm. The chemical composition is 45% cellulose, 26% hemicellulose, 17 wt % of pectin, 5% lignin and 7% other compounds.

The fibres were washed in distilled water to remove field impurities and dried in a hot air oven at 50°C for 48 h. After grinding (Sieb Technik mill), date palm fibres were manually sieved to give homogeneous material with 1.5 to 2 mm granulometry (Figure 1).

Corona discharge treatment (CDT)

Fibres were treated in a CDT device designed in our laboratory and based on a dielectric barrier technique. The system consists of a horizontal cylindrically shaped glass reactor 100 mm in diameter and 300 mm length. It is fitted with three inlets and three outlets assuring the possible alimentation of inert gas or vacuum pump. In this reactor are disposed two planar rectangular (100 mm × 80 mm) electrodes positioned in the centre of the reaction chamber (distance between electrodes: 5.5 mm). The corona discharge is assured by a low frequency high voltage generator (typically 15 kV, 50 Hz). Two glass plates (130 × 110 mm^2) are used as dielectric barriers to avoid arc discharge (Figure 2). The samples are disposed between the electrodes and treated for 15 min.

Composites processing

Composites were prepared from polylactic acid PLA and date palm fibres. Polylactic acid granules were supplied by Scopus S.A (Merignac, France) and used as received. The weight-average molecular weights of the PLA were 97 000 g/mole.

Crushed sieved fibres and PLA granules were thoroughly mixed and then degassed in a stove for 1 h at 80°C. Mixtures containing different content (30 to 40 wt. %) of untreated or treated date palm fibres were manufactured by extrusion mixing using a conical mono-screw extruder. The temperatures were maintained between 175 and 200°C and the mono-screw speed to 63 rpm. At the point of delivery, the melt was collected in heated mould and the composites were quickly moulded by thermo-compression under 3 bar and 165°C. Several composites were manufactured for tensile test. Formulations of composite mixes are presented in Table 1.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) pictures were performed using a TM3000 model microscope. The morphology of the treated and untreated date palm fibers was observed. Microphotographs were also used for qualitative analysis of interfacial bonding between date palm fibres and the polymer matrix.

Figure 2. Corona treatment cell.

Table 1. Compositions of different materials.

Materials	Matrix (Wt. %)	Date palm fibres (Wt. %)
PLA	100	_
PLA/ untreated	70	30
PLA/ Treated fibres	70	30
PLA/ untreated	60	40
PLA/ Treated fibres	60	40

Table 2. The mechanical properties of PLA /date palm fibres composites.

Fibre composites	Elasticity modulus E (MPa)	Stress at yield σ (MPa)
PLA	2396 ± 67	54.5
Untreated (30%)/ PLA	2708 ± 66	48.45
Untreated (40%)/ PLA	2524 ± 95	47.6
Treated fibres (30%)/PLA	2951 ± 69	57.35
Treated fibres (40%)/PLA	2697 ± 81	53.65

Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopic analysis of untreated and treated date palm fibres was done by a spectrophotometer (Perkin Elmer Spectrum one). Fourier transform infrared spectroscopy (FTIR) was carried out to investigate the changes in chemical structure of the sample caused by the corona discharge. Grounded dried fibre and KBr (2 mg fibre per 150 mg KBr) was pressed into a disc for FT-IR measurement. The spectra of the samples were collected in the transmission mode in the range of 4000 to 400 cm^{-1}.

Mechanical analysis

Tensile tests were performed using an Instron testing machine fitted with a 10 kN load cell operating at a rate of 5 mm/min. The tensile behaviour of 20 rectangular specimens (100 * 10 * 4 mm^3) of each composite prepared was investigated to failure.

RESULTS AND DISCUSSION

Evaluation of mechanical performances

Table 2 shows the summary of the tensile values obtained for the different tested samples. The addition of date palm fibres reinforcements results in an increase of elasticity modulus compared to matrix. This tendency is

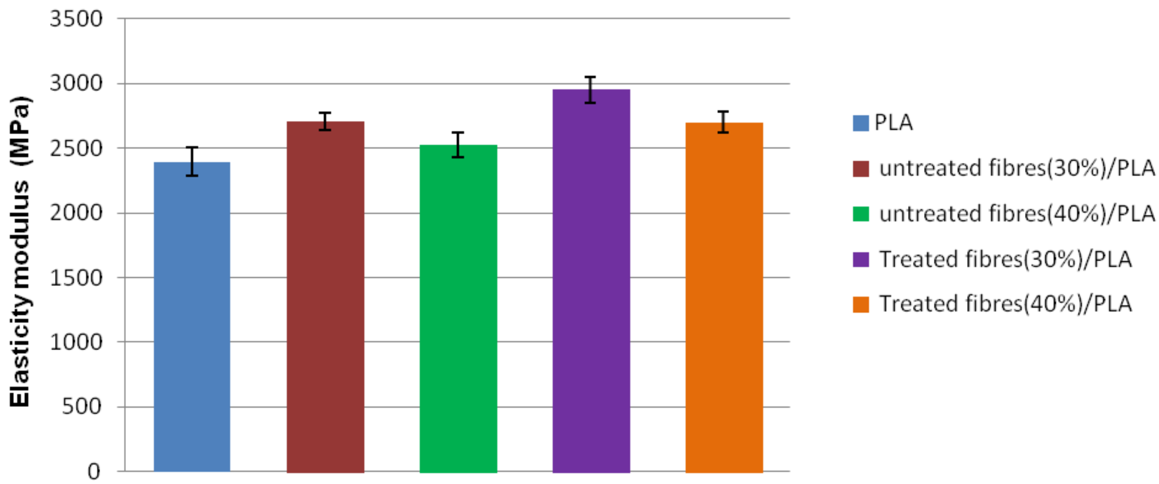

Figure 3. Elasticity modulus for composites materials with untreated and treated fibres

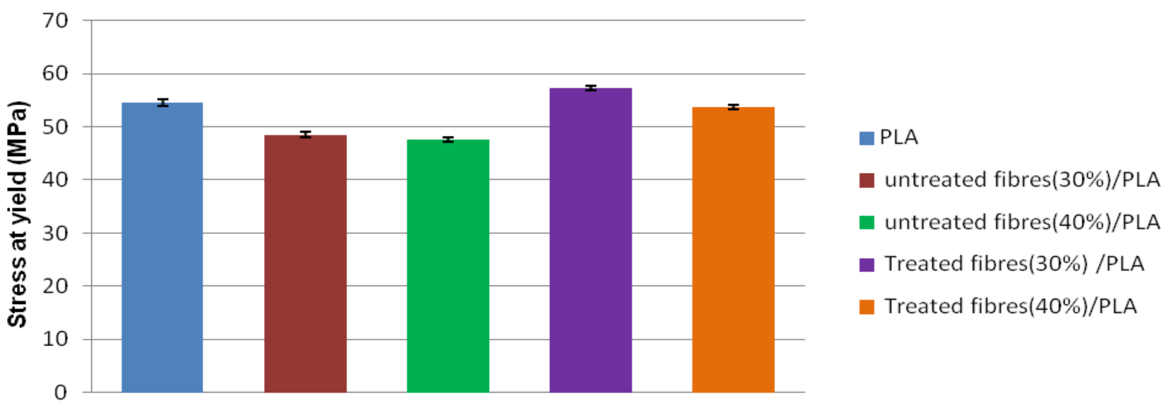

Figure 4. Stress at yield for composites materials with untreated and treated fibres.

in good agreement with Graupner (2008).

It has already been widely reported that is generally true that the values of the Young's modulus increased progressively with increasing fibre loading.

For our samples, we notice an enhancement of elastic modulus from 2396 to 2708 MPa and 2524 MPa for composites with 30% and 40 % of reinforcements respectively (Figure 3). This can be attributed to a good dispersion of fibre on PLA ensuring a better stress transfer from fibre to matrix.

For similar systems PLA/ cotton fibre, Graupner (2008) reported an increase in tensile modulus from 3820.18 MPa to 4242.3 MPa .The differences between these values can be explained by the nature of PLA used, our PLA is an industrial grade material containing several additives (Among these additives we have CESA-extend. When 2% of CESA-extend were added to PLA, the average molecular weight was raised, indicating branching extension of the polymer chains and higher molecular weights. After this modification, PLA's elastic modulus decreased) and the aspect ratio and morphology of fibres (origin, form factor, mechanical properties and chemical composition).

At higher proportion (40%) treated and untreated reinforcements, Young modulus is slightly decreased but remains much higher than the one of PLA. This lowering may be related to the formation of aggregates. During manufacturing process, we have observed that the melt becomes more viscous at this higher fillers proportion increasing the fiber–fiber friction and favouring the formation of fiber bundles (Ragoubi, 2009).

Increasing fibres proportion produces a material becoming progressively less plastic and more resistant to deformation than PLA as mentioned by Petinakis et al. (2009).

The addition of date palm fibres will not improve the tensile strength, which is an indication of poor adhesion between the date palm fibres and the PLA matrix (Figure 4).

However for composites containing treated fibres with

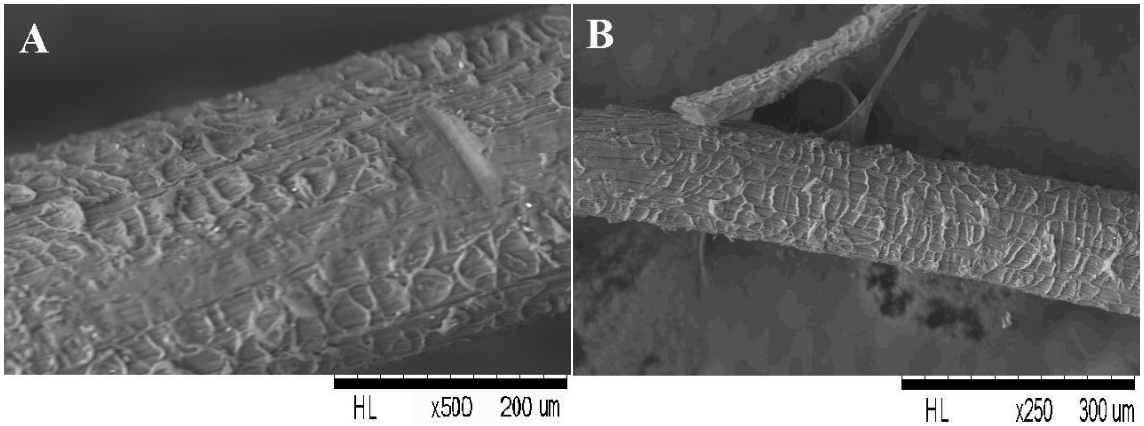

Figure 5. Effect of corona treatment on the surface of date palm fibres: (A) untreated (B) treated.

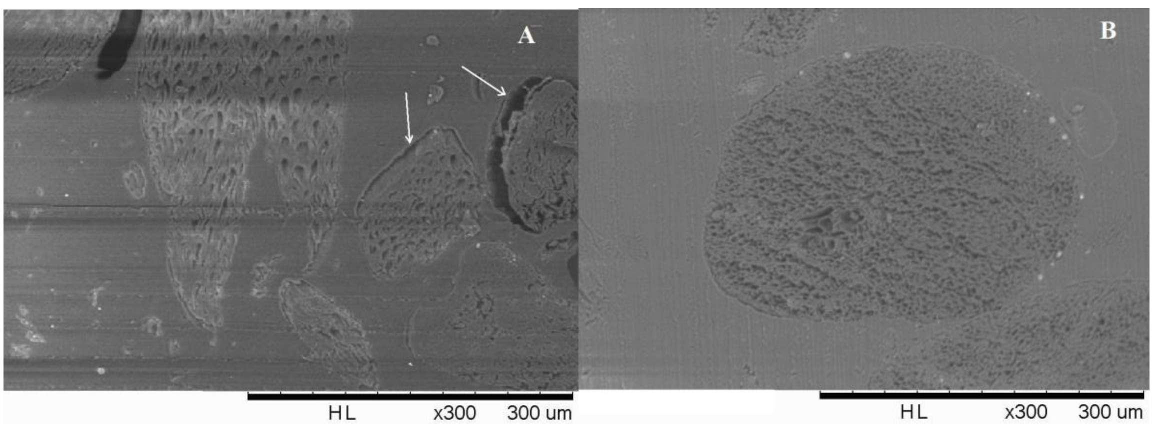

Figure 6. SEM images of PLA/ date palm fiber composites based on 30 wt% (A) untreated and (B) treated date palm fibres.

corona discharge, there was a significant increase in strength tensile and young modulus compared to the other composites which can be assumed that the interfacial contact between both components is better because of a higher mechanical anchorage enhanced as a consequence of the etching effect.

The elasticity modulus reached best values for 30% treated reinforcements (2951 MPa) with respect to the untreated reinforcements (2708 MPa) and the PLA matrix (2396 MPa) (Figure 3), which indicates improved adhesion between the date palm fibers and the PLA matrix. Therefore, good interfacial adhesion between the matrix and treated fibers is essential to improve the mechanical strength of composites.

SEM morphology study

SEM images of date palm fibres treated and untreated with corona are shown in Figure 5. The surface of treated fiber showed more roughness, and also the formation of cracks. Holes were visible on the treated date palm fibers surface.

This is attributed to the etching effect caused by the bombardment of the air plasma species on the fibers surface. As a result, the specimen surface became rougher and coarser. The size and number of these micro-pits increased with an increase of the discharge time According to Sun and Stylios (2006), this result can be attributed to the ablation effect caused by the bombardment of the oxygen plasma species on the fabric surface. It can be assumed that over the surface of the long polymeric chains, corona discharge produce many activated sites that could react with oxygen to give etching (Ragoubi et al., 2009).

Further, Figure 6 shows that the date palm fibres are in the form of single fibres and that indicates that the fibres have been separated during the extrusion process. The fibres are also very well dispersed in the PLA matrix. Good dispersion of single fibres and fibre orientation

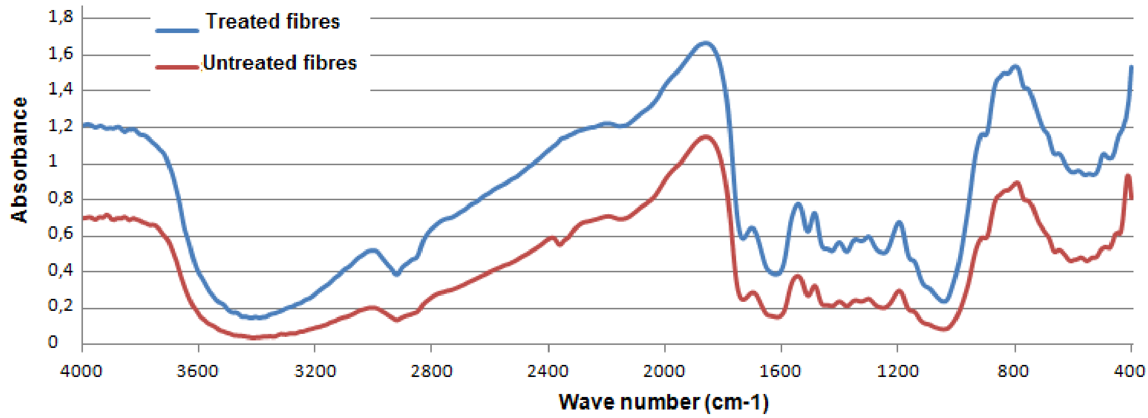

Figure 7. FT-IR spectra of untreated and corona treated fibres.

should result in very high mechanical properties.

The far majority of the fibres are well embedded by the polymer matrix, which is of importance for the strength performance of the composites.

We also observe many holes in the matrix due to sample porosity. This porosity can result from either the presence of residual air or micro bubbles of gaseous water evolved from fibres and trapped during manufacturing process.

At higher magnification we better observe hollows and gaps between the untreated fibres and the PLA matrix indicating very poor adhesion. The view of composites with treated fibres showed that the fibres were covered with PLA matrix. This suggests that the treated fibers have good interfacial adhesion with the matrix, which led to better stress transfer between the matrix and the reinforcing fibers.

Scanning electron microscopy of the composite confirms that the corona treatment improved the interfacial adhesion between date palm fibres and PLA matrix and consequently the mechanical properties.

Fourier transform infrared (FTIR) spectroscopy

Results of FT-IR study indicate that there are not any structural changes in the molecular chain of palm fibres before and after the corona treatment, but the peak intensity of the groups containing oxygen in the treated samples increased (Figure 7). The absorption between 1200 and 1000 cm^{-1} is attributed to stretching of the many C-OH and C-O-C bonds in the structure. Intensity in 1639 cm^{-1} due to C-O stretch increases. The peak at 1639 cm^{-1} shows probably the oxidation of date palm fibres. The carbonyl band at 1730 cm^{-1} can be seen in the spectrum. The band at 1730 cm^{-1} is also attributed to the C=O stretch of the acetyl groups of hemicelluloses. C-C-O stretching at 1020 cm^{-1} and C-C stretching at 993 cm^{-1} were also identified in the spectrum. C-C-O stretching and C-C shows that the changes in surface functionality of the date palm fibres.

Under corona discharge treatment, there were peak area increases for C=O, C-OH, O-C=O, whereas peak area of O-H, -C-C and C-H decreased. We can assume the formation of oxygen containing functional groups such as esters, carboxyl and carbonyl, by reaction with oxygen present in fabric surface and atmosphere (Ragoubi, 2009). So it is expected that the adhesive properties of fibres increased with the content of these groups on the surface.

Conclusions

In the present work, biocomposites were produced from treated and untreated Algerian date palm fibers and polymers as PLA to find potential applications for these materials.

An ecofriendly treatment which is the corona discharge treatment has been implemented in order to modify fibres surface and increase their compatibility with the PLA matrix.

Mechanical tests conducted showed improved values compared with untreated fibers. In addition, the SEM analysis revealed that the corona treatment improved the interfacial adhesion between date palm fibres and PLA matrix. Further study will be focused on thermal properties of the biocomposite.

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