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Influence of Low Pressure Plasma Treatment on the Durability of Thermoplastic Composites LDPE-flax/coconut under Thermal and Humidity Conditions

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Abstract: The aim of this work is to study the influence of low pressure plasma (LPP) treatment on the durability of thermoplastic composites using flax and coconut fibers as reinforcement. Two different aging conditions were evaluated, high temperature (73 °C) and high temperature plus water immersion. In both cases five aging times (1, 2, 8, 30 and 60 days) were evaluated. Composite materials were prepared with treated and untreated flax and coconut fibers with 30 % of fiber content and a low density polyethylene (LDPE) matrix. Composites were manufactured using a rotor mixer and a hot plates press. The influence of the aging conditions on each type of fiber, flax or coconut, as well as the plasma treatment effect in all composite materials were studied by determining water absorption and mechanical properties. Mechanical properties were assessed by three point bending tests and the water uptake was determined by weight measurements. Thermal properties were also studied by Differential Scanning Calorimetric (DSC) technique. Finally, the liquids where the specimens were submerged in were evaluated by ultraviolet spectroscopy to analyse cellulose or lignin amounts dissolved. In all cases, durability was mainly affected by the humidity but not so much by high temperatures, obtaining better bending strength and Young's modulus in the LPP treated materials, especially those with flax fiber reinforcement.

Keywords: Natural fibers composites, Durability, Fiber/polymer bond, Surface treatment, Plasma

Introduction

Currently, polymeric composite materials are essential in many different sectors and applications being used as the main reinforcement synthetic fibers such as glass, carbon or aramid. But from the point of view of biodegradability or renewable materials they have a very strong competitor, which are the natural fibers. Natural fibers represent a green solution with excellent mechanical properties, low cost, high availability and low density [1], which also improves weight matters. Natural fibers are mainly composed of cellulose, hemicelluloses and lignin. Lignin and hemicelluloses act as a matrix of microfibrils made up of cellulose molecules [2].

Flax fibers come from the flax plant and grow in those places where the temperature is below 30 °C. The life cycle of a flax plant is around 100 days and the stem height is about 80 cm [3], 75 % of which can be used to produce fiber. Flax fibers are bast fibers, they are contained within the stalk, surrounded by a fine layer of bast. They are formed according to a complex process, and their composition and architecture confer its properties to the flax. The flax fiber has a mass composition of cellulose around 71-81 %, hemicellulose, 18.6-20.6 % and lignin, 2.2-3.0 % [4].

Coconut is a fiber found between the hard inner shell and the outer coat of coconuts, which grows in tropic and subtropic regions [5]. Although this fiber is considered as a poor reinforcing fiber due to its low strength and modulus, it has been found of interest because of its low density, low thermal conductivity and high elongation [6]. The main composition of coconut fiber is 32-47 % of cellulose, 0.3-20 % of hemicellulose and 31-45 % of lignin [4], much less cellulose percentage as it can be observed.

Flax and coconut main mechanical properties [7,8] are shown in Table 1.

On the other hand, some drawbacks should be solved in order to extend the range of application of this kind of materials. These include weak interaction between cellulose fibers and polymer matrices, poor moisture resistance, lower fire resistance and limited processing temperatures [9]. Natural fibers hydrophilicity generates incompatibility with the hydrophobic polymer matrices, and it also produces high moisture absorption of the fibers which is the main reason of the poor adhesion between matrix and natural fiber [9,10]. Natural fiber/polymer composites are able to absorb moisture in humid atmosphere or when they are immersed in water. In some studies [11] it was observed that the more cellulose it contents the more tensile strength and thermal degradation occurs at lower temperature [12]. Moreover, if hemicelluloses content is higher, moisture uptake is also bigger [13].

Table 1. Fibres mechanical properties

Fibre	Density (g/cm^3)	Strength (MPa)	Modulus (GPa)	Elongation at break (%)
Flax	1.50-1.54	450-1500	27.6-38.0	1.5-3.2
Coconut	1.15-1.45	95-174	2.5-4.5	13.7-41.0

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This problem can be solved by surface treatments that improve adhesion between fiber and matrix. Sodium or potassium hydroxide alkali treatments [10], silane treatment, maleic anhydride coupling agent or other chemical treatments [14] are the most commonly used. This work evaluates the influence of Low Pressure Plasma treatment on the thermal and moisture durability by improving fiber/matrix bonding.

Plasma technology consists in an ionized gas created by applying enough energy to reorganize the electronic structure of the species present in the gas [15]. Plasma sources represent a fast, environmentally friendly, nontoxic and dry process which acts on the surface material without affecting bulk properties [16,17]. This kind of treatment is useful to activate the surface and enhance the adhesion of several materials [18]. Additionally, plasma treatments can be used for other applications such as coating or cleaning surfaces without producing a hazardous effect on the substrates [19]. On flax fibers, it has a cleaning effect that enhances adhesion between matrix and fiber improving mechanical properties [20].

Experimental

Materials and Sample Preparation

Low density polyethylene (LDPE), DOW 780E, was used as the composite matrix. It was supplied by Dow Chemical Company (Madrid, España). Short flax fibers (10 mm in length) and short coconut fibers (5 mm in length) provided by Procotex (Dottignies, Belgium) were used as reinforcement in a 30 wt % content.

The mixtures were prepared in a rotor mixer, Haake Rheomix 252P (Massachusetts, USA), at 150 °C for 40 min. When the torque exerted by the rotors of the mixer has been stabilized it is considered that mixture of LDPE and flax or coconut fibers is homogeneous. A good random dispersion is obtained, thus, mixture can be extracted from the mixer. Afterwards, they were pressed in a hot plate press using a framework to obtain a controlled thickness of 5 mm. The dimensions of each sheet were 240×240×5 mm.

Plasma Device

Before mixing them, flax and coconut fibers were treated with LPP in a Harrick Plasma Cleaner chamber (Ithaca, NY, USA) like the one shown in Figure 1, using air as the gas to produce plasma at a pressure of 300 mtorr. Once vacuum is made in the chamber, fibers remain there for 1 min at 30 W [20]. Fibers were placed on a plane surface in a very small amount in order to make sure that all fibers surfaces were completely covered by LPP treatment.

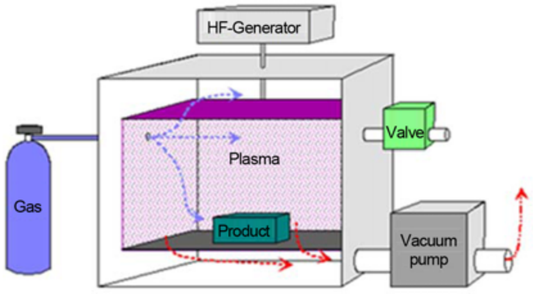

Figure 1. LPP treatment scheme.

Water Absorption Tests

Specimens were immersed into a water bath at high temperature, 73 °C, inside of an oven during different periods. After removing them from the water, surfaces were dried with absorbent papers and weighed immediately. After each aging time, water absorption was evaluated by the relative uptake of weight, M_t, according to the following equation:

$$M_t = \frac{W_t - W_0}{W_0} \times 100 \tag{1}$$

where W_0 is the weight of dry specimen and W_t is the weight of wet specimen at each aging time.

Different models have been developed in order to describe the moisture absorption behavior of composite materials. The most simple and common are the Fickian laws of diffusion [21]. For a plane sheet of thickness h with uniform initial distribution and equal initial surface concentration, Fick's laws follow the next equation [22]:

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \pi^2 Dt}{h^2}\right] \tag{2}$$

where M_t is the moisture uptake at time t, M_m, is its maximum moisture uptake, at equilibrium state, D is the diffusivity and h is the thickness of the specimen.

Depending on M_t/M_m values, some approximations are reported [23]. When M_t/M_m is lower than 0.6, the initial part of the curve can be correlated by:

$$\frac{M_t}{M_m} = \frac{4}{h}\sqrt{\frac{Dt}{\pi}} \tag{3}$$

For M_t/M_m values upper than 0.6 a good approximation is shown in following equation:

$$\frac{M_t}{M_m} = 1 - \exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right] \tag{4}$$

Diffusion coefficient, D, is the most important parameter and should be calculated with equations (3) or (4) for each case depending on M_t/M_m values.

Mechanical Properties

Three point bending tests were performed after each aging time in all composite materials in an electromechanical universal testing machine Microtest EM2/FR (Madrid, Spain) according to EN ISO 178:2001 standard. Dimensions of the sample and length of span between supports are

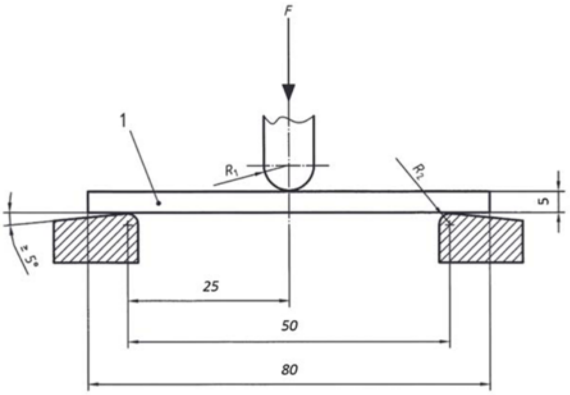

Figure 2. Bending test specimen dimensions.

shown in Figure 2. The test speed was 10 mm/min. After tests, bending strength and Young's modulus were evaluated.

Morphology Study

Fracture surface of the tensile tests specimens were analysed using a Philips XL-33 FEI EUROPE SEM microscope (Eindhoven, Holland) to observe the effect of the LPP treatment. To obtain an electron conductor media and enough contrast in the SEM micrographs, the samples were prepared using a gold coating in a Polaron high-resolution sputter coater.

Differential Scanning Calorimetric (DSC) Technique

The DSC instrument was supplied by Mettler Toledo GmbH (Greifensee, Switzerland). Aluminium crucibles of 40 µ*l* were used and filled with approximately 9 mg of composite for each test. Nitrogen (80 ml/min flow) was used as purge gas. The program procedure conducted dynamic ramps from 20 to 180 °C with a heating rate of 5 °Cmin^{-1}.

Visible Ultraviolet Spectroscopy (UV)

In order to know which substance was dissolved and its concentration in the water where composites were submerged, ultraviolet spectrums were carried out in all liquids after long aging time, 30 and 60 days by UV-vis spectroscopy using a Cary 4000 UV-vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). Additionally, lonely natural fibers were submerged into water to also evaluate UV spectrums of these liquids after aging time. For the determination of the lignin concentrations, the corresponding UV calibration curve was previously performed by the preparation of different standard solutions of Lignosulfonic acid, sugared sodium salt from Sigma Aldrich in water, at different concentrations.

Results and Discussion

Mechanical Properties

Influence of Fiber Type

Due to the difference on the main composition between flax and coconut fibers, it is important to analyse how their behaviour against aging conditions is, in order to evaluate which fiber is better from the point of view of the mechanical properties. Some authors assert that the more cellulose content, the better mechanical properties [21,22], and flax fibers have around double content of cellulose than coconut fibers.

As it can be observed in Figure 3, when composite materials are only exposed to high temperature both reinforcements considerably improve LDPE bend strength and Young's modulus (E). When aging time increases, the difference between LDPE and natural fibers composites resistance is smaller if it is compared with the existing difference at time zero. This is due to the increase in the resistance of LDPE, around 50 %, with aging time, because of a plasticization

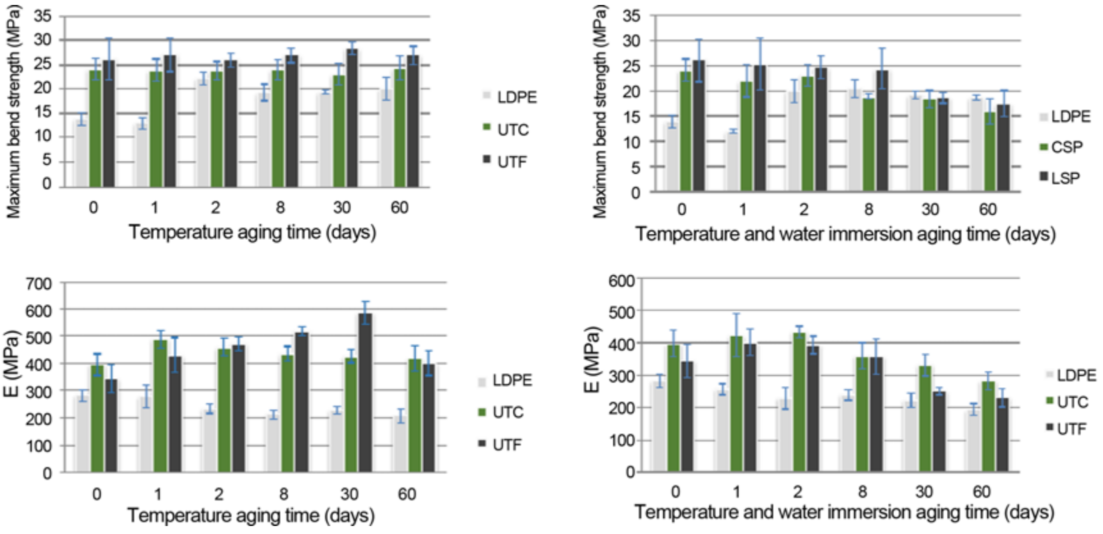

Figure 3. Mechanical properties of flax and coconut composites at different aging conditions.

effect, decreasing its Young's modulus. However, in practically all cases, flax composites (UTF) provide better results than coconut composites (UTC).

If materials are also under high humidity conditions, the damage occurs before, and the difference between LDPE and composites is null at 8 days for coconut composites and at 30 days for flax composites. In fact, at 30 and 60 days, LDPE bend strength is higher than both natural fibers composites due to the greater water absorption by natural fibers. Therefore, composite materials become weak after long aging time of humidity exposure.

Influence of LPP Treatment

First of all, and as it was already detailed above, natural fibers presence causes the water uptake in composites materials [26]. It is very important to know how the LPP treatment affects in this way and what type of fiber has the bigger tendency to absorb water. Figure 4 shows the weight gain of each type of fiber composite, flax or coconut (UTF and UTC), and its comparison with the LPP treated counterpart (PTF and PTC) under high temperature and water immersion conditions.

LPP treatment on flax fibers causes an increment of its wettability [20] so it is lawful to think that after plasma treatment, natural fibers composites will absorb more water than untreated materials and the durability of treated materials would be compromised. However, contrary to what was expected, for all treated materials the obtained amount of absorbed water is lower or similar to the homologous without LPP treatment. This can be explained because of the better adhesion between matrix and fiber reinforcement due to the LPP treatment which acts as a barrier against moisture. Figure 5 shows micrographs of tensile samples of the fracture surface. It can be clearly seen that untreated fibers (a) flax and c) coconut) were not bonded to the matrix, whereas LPP treated fibers (b) flax and d) coconut) are totally embedded presenting many anchor points.

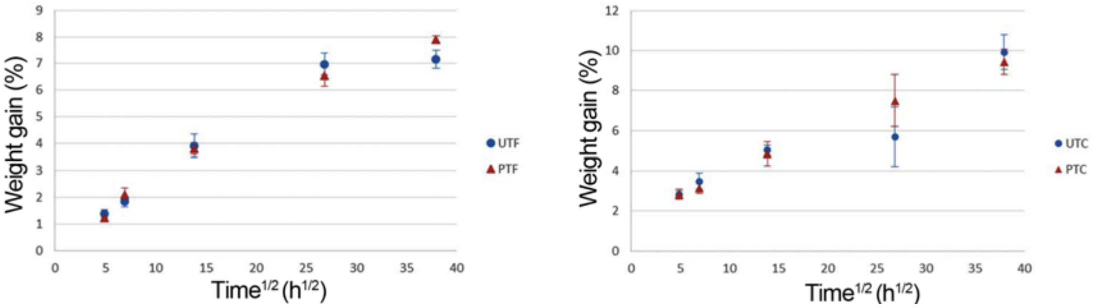

Figure 4. Weight gain of flax and coconut untreated and LPP treated composites at different aging times.

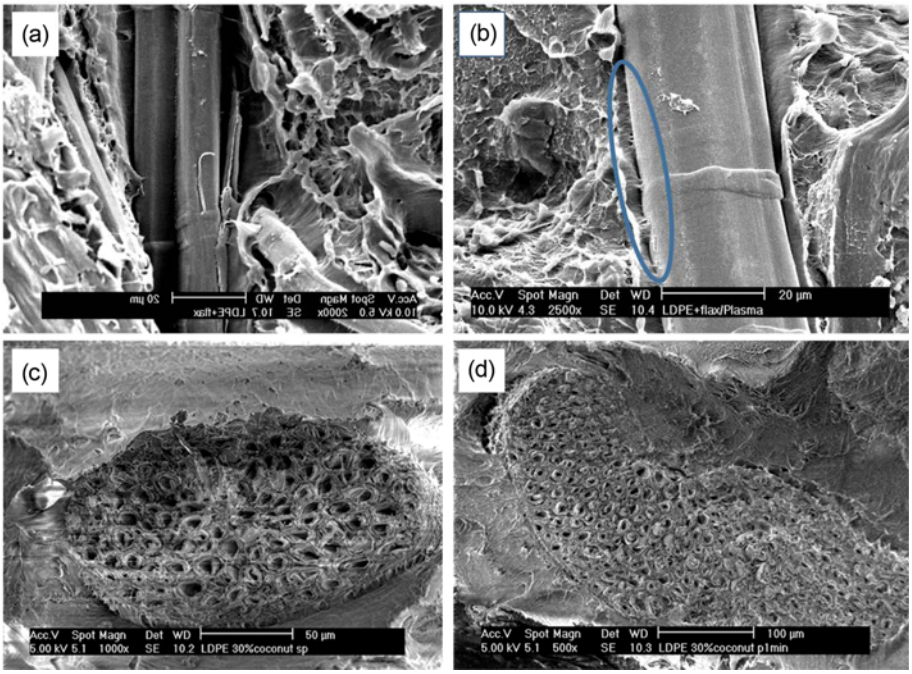

Figure 5. SEM micrographs of (a) an (c) untreated flax and coconut fibers and (b) and (d) LPP treated flax and coconut fibers.

Table 2. Diffusion coefficient for treated (PTF) and untreated (UTF) flax composites

	$M_{m\,(\%)}$	$D\times10^9$ (cm^2/s)
UTF	7.2	9.35
PTF	8	9.23

Regarding Figure 4, can be also concluded that coconut composites absorb more water than flax composites for all aging time conditions. Finally, as expected, LDPE without any type of reinforcement does not absorb water, even after 60 days of aging time.

According to Fick's laws, diffusion coefficient was calculated in the cases of flax fibers composite materials. Coconut composites, do not seem to have a Fickian behavior. As others authors claim [27], coconut fibers follow Fick's laws at room temperature but not at high temperatures, as in this case, so equilibrium uptake value, $M_{m,}$ cannot be obtained. Equilibrium uptake value for flax composites can be obtained from Figure 4, however, it is not completely clear that materials have reached saturation after two months, especially LPP treated materials. Some authors reported that M_m value for flax-PP composite with 30 wt % of fiber is around 6 % [28], which is in line with what is obtained in this work, around 7 %. For other studies with other matrices, such as epoxy, this value is increased due to the bigger absorption by the matrix [22]. Table 2 shows equilibrium uptake selected values and diffusion coefficients for both LPP treated and untreated flax composites.

These results confirm the same as concluded regarding weight gain. LPP treatment on flax fibers does not cause bigger water absorption. Equilibrium uptake values were considered as the maximum relative uptake of weight, M_t. For PTF materials this value is probably higher than the one considered (8 %) because saturation condition will occur after 60 days of aging time. Therefore, diffusion coefficient will be lower than the one obtained and it would be verified that water diffusion of treated flax composites is lower than in those reinforced with untreated flax fibers.

Regarding mechanical properties bend strength and Young's Modulus were also studied in order to evaluate the effect of LPP treatment. In Figure 6 it can be appreciated that under high temperature conditions, bend strength do not presents a significant variation in both flax and coconut composite materials. But in both cases, LPP treatment improves resistance values, although in a slightly way.

When composites are also submerged in water, bend strength decreases with the aging time due to the water absorption. Coconut composites absorb more water than flax, so the effect of LPP treatment becomes more important in coconut materials and has a more significant role. This is reflected in Figure 6, where plasma treatment improves the resistance of coconut materials at all aging times.

In the case of flax reinforcement, plasma treatment also improves the durability of the composites but this improvement is not much relevant.

As well as the bend strength, Young's Modulus does not suffer great variations when the composites are only subjected to high temperature. Therefore, in Figure 7, the results obtained for the Young's modulus when the materials are under high temperature and water immersion are shown. As it can be observed, during the first days, the variations are not very marked. But from the eighth day onwards, Young's modulus decreases in both materials. Regarding the influence of the treatment, and taking into account the dispersion of the results, it can be affirmed that improvements are

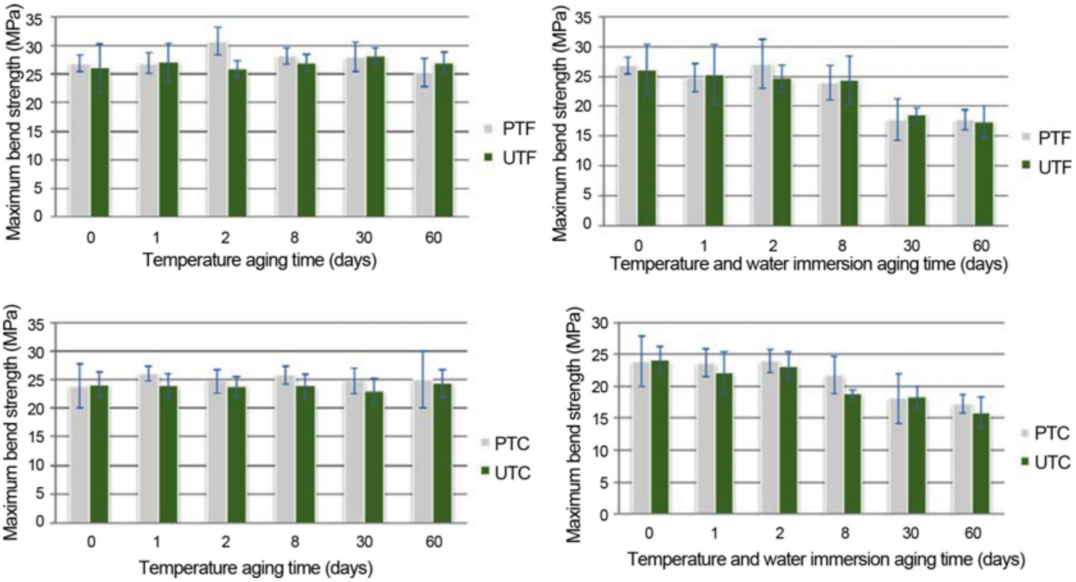

Figure 6. Maximum bend strength of flax and coconut untreated and LPP treated composites at different aging times.

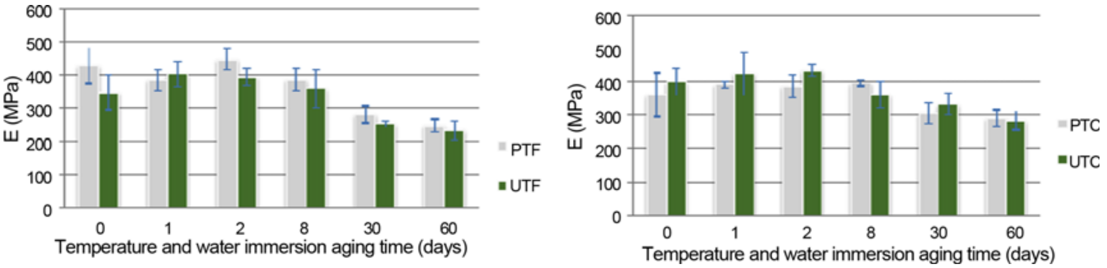

Figure 7. Young's Modulus of flax and coconut untreated and LPP treated composites at different aging times.

obtained again with the LPP treatment for both materials, although they are not very outstanding.

Thermal Properties

All plasma sources only change surface properties without affecting any other. In this work, it is important to consider if main thermal properties suffer any variation due to the LPP treatment and how these properties evolve with aging time. Melting point was measured by DSC in all treated and untreated composite materials when they were subjected to water immersion and high temperature [29]. Crystallinity was measured without aging conditions in a previous work [20] on flax fibers/LDPE composites and it was confirmed that crystallinity decreased with natural fibers addition, but not due to plasma treatment. Hence, in this research only one heating ramp was carried out to measure melting point variations, because in a second ramp aging effect will be lost. Error margin of melting temperature is ±3 °C. Table 3 shows melting point values for all specimens. As it can be remarked for all materials, differences between treated and untreated composites, comparing homologous materials, are insignificant and within the margin error. Therefore, it can be confirmed that LPP treatment only affects the material surface properties but not the thermal ones.

Table 3. Melting point variation with aging time (water immersion and high temperature)

Aging time (days)	T_m (ºC)		
	0	30	60
LDPE	113.20	112.27	111.71
UTF	113.25	113.78	116.69
PTF	111.48	111.51	115.14
UTC	113.18	112.66	112.63
PTC	112.62	114.96	113.57

UV

After 60 days, water where specimens were submerged changed its color to a yellow hue. Lonely natural fibers were also submerged in water in order to provide more information and to verify which natural fiber component yellowed water (FFUT, FFT, untreated flax fiber and plasma treated flax fiber and FCUT, FCT, untreated and plasma treated coconut fiber, respectively). First of all, water pH was measured after 60 days in all liquids and it was compared with the tap water pH value prior to aging conditions. The initial value of tap water pH was 7.5 and, as it can be observed in Table 4, when natural fibers or composites were submerged, the pH becomes more acid. Coconut fiber reduces water pH more than flax fiber. So it could be thought that the substance which is dissolved in water could be the main component of coconut and the one in less amount of flax fiber: lignin. Moreover, lignin color could yellowed water [30,31] and not cellulose, which is commonly white.

The used commercial lignin, with a pH of 3.5 and soluble in water, was diluted in water until achieving a similar color to tap water after aging (60 days). Three solutions were prepared at three different concentrations of lignin, 0.1, 0.05 and 0.025 %wt, to see what value of wavelength corresponds to lignin absorbance. In Figure 8 the UV spectrum is shown

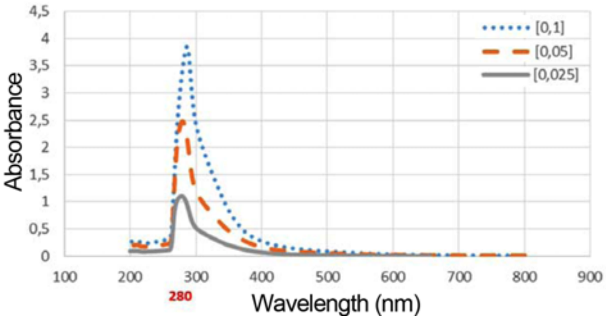

Figure 8. UV spectrums for lignin solutions.

Table 4. Water pH after 60 days of composites and lonely natural fibres immersion

Aging time (days)	Water pH								
	LDPE	UTF	PTF	FFUT	FFT	UTC	PTC	FCUT	FCT
60	9.86	5.64	5.06	7.03	6.87	4.26	4.26	4.73	4.14

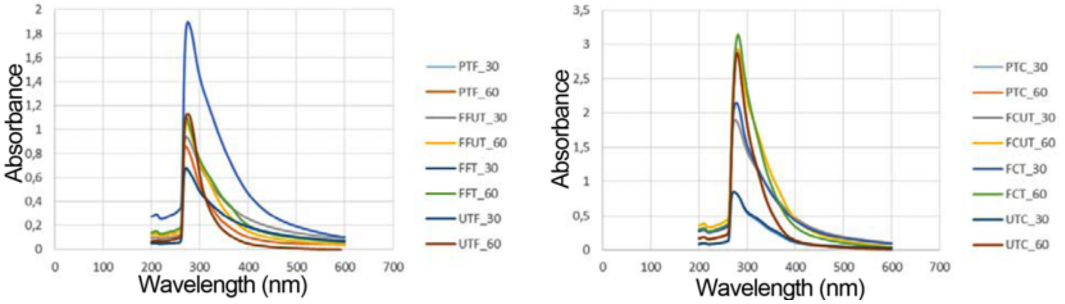

Figure 9. UV spectrums for liquids where composites or fibres were submerge (flax left and coconut right).

Table 5. Lignin concentration in each liquid after aging time

Aging time (days)	Lignin concentration (mg/m*l*)								
	LDPE	UTF	PTF	FFUT	FFT	UTC	PTC	FCUT	FCT
30	0	0.12	0.15	0.19	0.20	0.17	0.18	0.47	0.54
60	0	0.25	0.18	0.23	0.23	0.30	0.76	0.80	0.83

for each lignin solution, and it can be concluded that the maximum absorption occurs at a wavelength about 280 nm. It is reported that this can be originated from phenolic hydroxyls conjugated to α-carbonyl, carbon-carbon double bonds or biphenyl groups presents in lignin [32].

Calibration curve for lignin was, hence, performance at 280 nm. The spectrum of all others liquids, where composites or natural fibers were submerge, were also carried out. The maximum absorbance peak at 280 nm in all aging liquids represented in Figure 9, confirms that, indeed lignin was the mainly substance dissolved during aging time [33].

Lignin concentration of each liquid was calculated using the calibration curve and the results obtained are shown in Table 5. As a substantiation that the dissolved substance comes from the natural fibers, the lignin measure of the concentration for the liquid where LDPE were submerged is zero. It can be highlighted that coconut materials lose much more lignin than flax materials and, as expected, lonely fibers also more than composites. Regarding Table 5, it can also be extracted that LPP treatment practically does not affect to the flax materials lignin loss. But in case of coconut materials because of the better cleaning of the fibers, due to the LPP treatment, lignin loss is slightly favored. Therefore, it can be concluded that coconut materials lose more lignin than flax materials and as a consequence, delignification can occur. Lignin gives mechanical strength to the cell wall and to the whole fiber [34,35], so delignification causes materials deterioration and mechanical properties loss.

Conclusion

In the present work, a comparison of two different types of natural fibers composites, flax and coconut, and the influence of a low pressure plasma treatment were carried out against different aging conditions.

Comparing both types of natural fibers composites, it can be concluded that, without aging, flax fibers present better mechanical properties than coconut fibers due to the greater cellulose amount in their composition. When composites are under aging conditions, also coconut composites lose mechanical properties before than flax composites, mainly in presence of very high humidity, which is the worst condition. Mechanical properties are very affected by the water absorption and coconut composites have bigger water uptake than flax.

Low pressure plasma treatment (LPP) improves adhesion between LDPE matrix and natural fibers reinforcement. This better interaction acts as a barrier against moisture and the water absorption from the composite materials is slightly lower. This effect is more remarkable in the case of coconut composites because of the bigger water absorption by coconut fibers. According to this, mechanical properties were improved due to the plasma treatment, without affecting other properties such as thermal ones, as it was proven by DSC technique.

Finally, by UV spectroscopy it was observed that coconut composites lose more lignin than those of flax, so delignification of the coconut fiber reinforcement can occur, and accordingly the loss of mechanical properties.

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