CHARACTERIZATION OF NATURAL CORK AGGLOMERATE FUNCTIONALISED BY PLASMA TREATMENT

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ABSTRACT

This work intends to study the chemical and physical modifications of natural cork agglomerate after plasma treatment using dielectric barrier discharge (DBD). Different experimental techniques were used to evaluate the surface alterations of the substrate pre-treated with DBD plasma, namely, static and dynamic contact angle, surface energy, Fourier transform infrared spectroscopy (FTIR), energy dispersive spectroscopy (EDS), scanning electronic microscopy (SEM) and differential scanning calorimetry (DSC). Plasma discharge greatly increases the wettability and surface energy of the samples. Chemical and physical analyses of the cork agglomerate confirmed considerable surface modification.

INTRODUCTION

Over the last decades several different materials and technologies have been widely used to new applications. The number and volume of composite materials have grown steadily, penetrating and conquering new areas of engineering. In fact, everyday modern composite products are created to be applied in sophisticated niche markets.

Cork is a natural material with an immense potential to be used in different applications, such as: cork stoppers, fishing rods and floats, buildings, military, footwear, automobile industries among others (Pereira, 1998). Portugal is the world's largest manufacturer of cork, been responsible alone, for approximately 50% of the total production of this substrate. However, cork has a low surface energy, which can be adverse for several applications.

Chemical treatments to change the surface properties of different materials have been sometimes successful in improving the interfacial bonding (Oliveira, 2012). Nevertheless, problems related to the high cost of the treatment, the disposal of the chemical products in addition with increasing concern about environmental pollution has limited extensive industrial application of chemical surface treatments (Yoldas, 2010). Plasma technology is considered as a dry and clean process with an enormous potential environmental (Carneiro, 2001; Oliveira 2012) to modify the surface of several materials without affect its bulk properties. In plasma processing, it is well established that exposure to plasmas generated in inert and reactive gases can clean the surface of materials and change their properties, particularly their surface energy (Oliveira, 2013).

This work presents a study of plasma treatment of agglomerate cork, using a dielectric barrier discharge (DBD) run in different dosages. The experiments were conducted to determine the effects of the plasma treatments on the measured changes to surface, wettability, morphology and chemical composition.

MATERIALS AND METHODS

The material used was cork agglomerate laminated with a polymer membrane (CM) with 105 $g.m^{-2}$ and 0.62 mm thickness.

Plasma Treatment

Plasma treatment of cork agglomerate material was carried out at atmospheric pressure with the dielectric barrier discharge plasma (DBD) (Softal/University of Minho patented prototype). The machine has a metallic electrode coated with ceramic; a metallic counter electrode coated with silicone; an electric generator, and a high tension transformer. The velocity (v) and power (P) are variable and the fabric passages through the electrodes continuously. The plasma dosage can be defined according to the equation (1) (Carneiro, 2004):

$$dosage = \frac{N \cdot P}{v \cdot w} \quad (1)$$

Where: N (number of passages), P (power, W), v (velocity, m min^{-1}), w (width, 0.5 m). For the treatment of cork agglomerate material, velocity and power were maintained constant and the number of passages was varied. Table 1 shows the parameters employed for the treatments.

Table 1. Parameters and plasma dosages applied to cork agglomerate material.

Samples	Velocity (m min^{-1})	Power (W)	Number of passages	Dosage (W min m^{-2})
1	5	750	1	300
2	5	750	2	600
3	5	750	4	1200
4	5	750	8	2400
5	5	750	16	4800

Chemical and Morphological Characterization

Contact Angle, Work of adhesion and Surface Energy

Dataphysics equipment using OCA software with video system for the caption of images has been used for the measurement of static and dynamic contact angles and for calculation of the cork agglomerate surface free energy.

The work adhesion (WAdh) equation (2), was calculated by means of water contact angle evaluation - average values - (Baley, 2006).

$$W_{Adh} = \gamma_l(1 + cos\,\theta) \quad (2)$$

For polar solids or liquids the total surface energy is a sum of the always existing London dispersion forces (γ^D) with intermolecular interactions that depend on the chemical nature of the material, compiled as polar forces (γ^P) (3) (Papakonstantinou, 2007)

$$\gamma = \gamma^D + \gamma^P \quad (3)$$

The polar and dispersive components of the surface energy were calculated using the Wu method (harmonic-mean), by the equation (4) (Kim, 1999).

$$\gamma_{sl} = \gamma_s + \gamma_l - 4\left[\frac{\gamma_s^D \gamma_l^D}{\gamma_s^D + \gamma_l^D} + \frac{\gamma_s^P \gamma_l^P}{\gamma_s^P + \gamma_l^P}\right] \quad (4)$$

Since it is necessary at least two liquids for the calculation of surface energy, three liquids with known surface energy and surface energy components were used in this study: distilled water (Y: 72.8; Y^D: 29.1; Y^P: 43.7), polyethylene glycol 200 (PEG) (Y: 43.5; Y^D: 29.9; Y^P: 13.6) and glycerol (Y: 63.4; Y^D: 37.4; Y^P: 26.0) (Oliveira, 2013).

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Fourier Transform Infra-Red and Energy Dispersive Spectroscopy

A Nicolet Avatar 360 FT-IR spectrophotometer using an attenuated total reflectance accessory (ATR) was employed to record the FTIR spectra of the cork/membrane samples. The surface chemical composition of CM, before and after plasma modification, was determined by EDS using an EDAX Si(Li) detector and an acceleration voltage of 15 kV.

Scanning Electronic Microscopy

Surfaces of the plasma treated and the PCM coated samples were observed with an ultra-high resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company.

Differential Scanning Calorimetry

Mettler Toledo DSC822 equipment was used in order to analyze the plasma treated and untreated substrates and to quantify the PCM energy absorption of these samples.

RESULTS AND CONCLUSIONS

Static and Dynamic Contact Angle

The static and dynamic contact angle results, using water drop, showed a significant difference when compared the samples with and without plasma treatment (Fig. 1-a). These results suggest that wettability of the cork is significantly affected by plasma treatment. With plasma activation is possible to improve considerably the water adsorption velocity in the cork substrate as can be seen in Fig. 1-b.

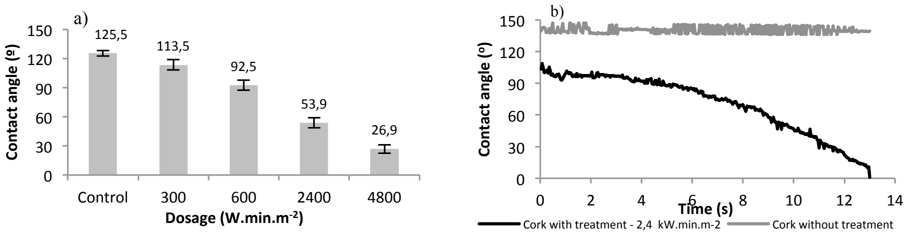

Fig. 1 Static (a) and dynamic (b) contact angle of cork agglomerate.

Surface Energy and Work of Adhesion

Double Barrier Dielectric plasma is very effective regarding the increase of the surface energy of different materials including textiles, not only by chemical conversion of the surface but often simply through plasma cleaning process. In a cleaning process, inert and oxygen plasmas are used. Plasma is able to remove, via ablation, organic contaminants, either natural or added, on the materials, increasing surface energy and improving the wettability of the substrate (Oliveira, 2013; Keller, 2005).

Using water, PEG and glycerol contact angle values, the total surface energy (γ), dispersive component (γD) and polar component (γP) were calculated and the results are shown in Table 2.

Table 2 – Surface energy and Work of adhesion (ºdistilled water) in the cork samples with and without plasma treatment

	θ_{water}(º)	θ_{PEG}(º)	$\theta_{glycerol}$(º)	γ $mJ.m^{-2}$	γ^D $mJ.m^{-2}$	γ^P $mJ.m^{-2}$	W_{adh} $mJ.m^{-2}$
Untreated	125.5	100.2	137.2	10.9	7.4	3.5	30.52
600 W.min.m^{-2}	92.5	70.6	132.9	17.1	4.4	12.7	69.62
2400W.min.m^{-2}	53.9	70.8	116.0	26.9	2.5	24.4	115.69
4800W.min.m^{-2}	26.9	65.4	117.2	35.5	10.0	25.5	137.72

Total surface energy significantly increases after DBD plasma treatment. Initially the dispersive and polar components of the cork agglomerate without treatment were 7.4 $mJ.m^{-2}$ and 3.5 $mJ.m^{-2}$ respectively. For the dosage of 4800 $W.min.m^{-2}$, the dispersive component has increased to 10.0 $mJ.m^{-2}$ and the polar component has a huge increase up to 25.5 $mJ.m^{-2}$.

These results can be explained by partial decomposition of the hydrophobic layer after DBD plasma treatment caused by etching process and the formation of new polar groups on the cork agglomerate surface (Cheng, 2010).

Furthermore, the work of adhesion of the cork substrate after plasma treatment is significantly increased. The polar functional groups formed by means of plasmatic treatment can become the external substances more easily to attach on the cork agglomerate material. Moreover, in the table 2 can be also observed that the work of adhesion enhanced with the increase of plasmatic dosage applied from 30.5 $mJ.m^{-2}$ (untreated sample) to 137.7 $mJ.m^{-2}$ (4800 $W.min.m^{-2}$) . In this way, DBD plasma treatment can be considered an interesting solution to promote the functional performance of different materials (Oliveira, 2013; Cheng, 2010).

Fourier Transform Infra-Red and Energy Dispersive Spectroscopy

Figure 2(a) presents the infrared spectra of cork agglomerate substrate in which some of the most prominent band were assigned: 3348 cm-1 can be attributed to the O-H stretching, 2926 and 2850 cm^{-1}, nCH of mostly suberin aliphatic chains;1735 cm^{-1}, nCO of suberin ester groups; 1635 and 723 cm^{-1}, suberin $R_1CH=CHR_2$ groups; 1607 and 1513 cm^{-1}, nC=C of lignin aromatics (Carmo, 1997; Lopes, 2000) .

FTIR results also provided the evidence of changes in the chemical constituents with plasma treatment. Mainly in the bands at 2926 and 2850 cm^{-1}, which presents a lower intensity to the

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treated samples, 1735 cm^{-1} (carbonyl bonds), 1357 cm^{-1}(C-N) and 1010-1300 cm^{-1} bands (carbohydrate and lignin C-O bond) which present higher intensity peak after plasmatic dosage applied. The interaction between DBD plasma species and cork agglomerate leads to increase of amount of the polar oxygen and nitrogen groups onto the surface (Bozaci, 2009). The effect of plasma treatment on functional groups of cork agglomerate material was also observed by EDS analysis. The results show an increase of oxygen/carbon ratio (O/C) from 0.33 to 0.36, which can be responsible to enhance the content of hydrophilic functional groups on the cork surface. Fig. 2(b) shows the elemental composition of the samples untreated and plasma treated (2400 W.min.m^{-2}).

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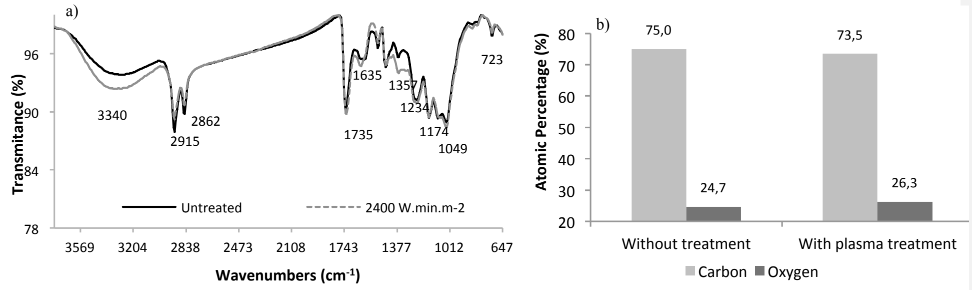

Fig. 2. FTIR-ATR spectra (a) and atomic percentage by EDS (b) of the cork agglomerate samples untreated and plasma treated (2400 W.min.m^{-2})

The results obtained by differential scanning calorimetry and scanning electronic microscopy techniques showed no major structural changing in the cork material after plasma application. These results prove that DBD plasma treatment can modify the surface of cork agglomerate material without changing its bulk properties or appearance.

CONCLUSIONS

This study proved that the surface modification of cork agglomerate caused by DBD plasma treatment can create more polar groups, increasing the surface energy, wettability and work of adhesion of the samples, which can be responsible to improve the interaction of this substrate with finishing products and polymeric resins.

Plasma technology can be considered an excellent solution to provide certain material surface characteristics without sacrificing the primary manufacturing qualities of the material. This technology is capable of altering the surface of a material only a few molecules deep and promote the functional performance of several types of finishing products, achieving more absorption and durable properties contributing for the sustainability of the innovative materials.

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REFERENCES

Baley C, Busnel F, Grohens Y, Sire O. Influence of chemical treatments on surface properties and adhesion of flax fibre-polyester resin. Composites Part A: Applied Science and Manufacturing, 2006, Vol.37, p. 1626-1637.

Bozaci E, Sever K, Demir A, Seiki Y, Sarikanat M, Ozdogan, E. Effect of the atmospheric plasma treatment parameters on surface and mechanical properties of jute fabric. Fibers and Polymers, Vol.10, No.6, p.781-786, 2009.

Carmo, S. R. Ph.D. dissertation, University of Aveiro, Portugal, 1997; pp 173–176.

Carneiro N, Souto AP, Silva E, Marimba A, Tena B, Ferreira H, Magalhães V. Dyeability of corona-treated fabrics. Journal of Society of Dyers and Colouristic. 2001, Vol.117, p. 298-302.

Carneiro N, Souto AP, Forster F, Prinz E. Continuous and semicontinuous treatment of textile materials integrating corona discharge. Patent in internationalization phase (2004) /patent number PCT/PT2004/000008 (2004).

Cheng SY, Yuen CWM, Kan CW, Cheuk KKL, Daoud WA, Lam PL, Tsoi WY (2010), Influence of atmospheric pressure plasma treatment on various fibrous materials: performance properties and surface adhesion analysis. Vacuum, 84, 1466-1470.

Keller M, Ritter A, Reimann P, Thommen V, Ficher A, Hegemann D. Comparative study of plasma-induced and wet-chemical cleaning of synthetic fibers. Surface & Coatings Technology vol. 200 issue 1-4 October 1, 2005. p. 1045-1050.

Kim, JS, Friend RH, Cacialli F. Improved operational stability of polyfluorene-based organic light-emitting diodes with plasma-treated indium–tin–oxide anodes. Journal of Applied Physics, 1999, p.86.

Lopes MH, Pascoal NC, Barros AS, Rutledge D, Delgadillo I, Gil AM. Quantitation of aliphatic suberin in quercus suber L. cork by FTIR spectroscopy and solid-state (13)C-NMR Spectroscopy. Biopolymers (Biospectroscopy), Vol. 57, p.344–351, 2000.

Oliveira FR, Erkens L, Fangueiro R, Souto AP. Surface modification of banana fibers by DBD plasma treatment. Plasma Chemistry and Plasma Processing, 2012, Vol.32, p.259-273.

Oliveira FR, Fernandes M, Carneiro N, Souto AP. Functionalization of wool fabric with phase-change materials microcapsules. Journal of Applied Polymer Science, 2013, Vol.128, p.2638–2647.

Papakonstantinou D, Amanatides E, Mataras D, Ioannidis V, Nikolopoulos, P. Improved surface energy analysis for plasma treated PET films. Plasma Process. Polym.2007, 1057-1062, 4.

Pereira H, Costa A. Evolução recente da indústria de cortiça. Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade Técnica de Lisboa, Lisboa, 2002.

Souto AP, Oliveira FR, Carneiro N. Polyamide 6.6 modified by dbd plasma treatment for anionic dyeing processes, in textile dyeing. Intech Open Access, ISBN 978-953-307-565-5, Croatia, 2011, p. 241-260.

Yoldas S, Mehmet S, Kutlay S, Seckin E, Ali G. Effect of the low and radio frequency oxygen plasma treatment of jute fiber on mechanical properties of jute fiber/polyester composite, Fiber and Polymers, 2010, Vol. 11(8), p.1159–1164.