FUNCTIONALIZATION OF CORK AGGLOMERATE COMPOSITE WITH PCM MICROCAPSULES AFTER DBD PLASMA TREATMENT

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Abstract: *This research intends to study the influence of dielectric barrier discharge (DBD) plasma treatment on the adsorption of Phase Change Materials (PCM) microcapsules applied to cork agglomerate laminated with a polymer membrane. Several experimental techniques were used to evaluate cork and membrane surface modification after plasma treatment and the influence on the microcapsules adsorption, namely, Static and Dynamic Contact Angle, Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and Tensile Strength. The plasma treatment greatly increases the hydrophilicity of both materials, justifying that more microcapsules are adsorbed on this composite. Chemical and physical characterization of the cork agglomerate and polymer membrane confirmed significant surface alteration.*

Keywords: *Microcapsules; Cork; DBD Plasma; Functionalization.*

1. Introduction

Nowadays a growing interest in materials with new properties and added value has been encouraging the industry to make greater use of microencapsulation processes. In fact, the use of microcapsules has increased in several different areas, namely in pharmaceuticals, cosmetics, fragrances, foods, paints, textiles, among other [1]. The microcapsulated products are relatively expensive and the final products must respond to clients demand and for this reason it is important that they will be able to remain fixed on the substrate, withstanding many washes and rubbing action [2].

The versatility of cork which is a vegetable tissue makes it valuable for a variety of uses in different areas, namely in fishing rods and floats, in buildings as floor tiles, for artistic purposes, in military, footwear and automobile industries among others [3]. However, the low surface energy, characteristic of this material, can be adverse for several applications. Considered as an environmentally favorable alternative, the plasma technology has been applied effectively in modifying surface properties of different substrates, improving hydrophilic characteristic [4], dyeing properties [5] adsorption and adhesion [6].

The main objective of this work is to study the adsorption of PCM microcapsules, applied by padding process, in a cork agglomerate laminated with a polymer membrane after being treated with DBD plasma. In order to analyze the effect of plasmatic treatment on the materials surface and on microcapsules adsorption, several techniques were used, such as contact angle measurements, FT-IR, EDS, DSC, SEM and tensile strength.

2. Materials and Methods

2.1 Materials

The material used was a cork agglomerate laminated with a polymer membrane (Chemical Base – Copolymer Polyamide - COPA) with 105 $g.m^{-2}$ and 0.62mm thickness.

The PCM utilized was a melamine microcapsule agent (PRETHERMO C-25). The following recipe was used: PCM microcapsules - 160 $g.L^{-1}$; Binder - 50 $g.L^{-1}$; and $MgCl_2$ – 5 $g.L^{-1}$.

2.2 Plasma Treatment

Different dosages were applied according to following parameters: Speed: 5.0 $m.min^{-1}$; Power: 750 W; Number of passages: 1, 2, 4, 8 and 16 in both sides of the sample.

2.3 Chemical and Morphological Characterization

2.3.1 Contact Angle

Dataphysics equipment using OCA software with image capturing video systems in static and dynamic modes has been used for the measurement of contact angles of the water drops in the samples.

2.3.2 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.

2.3.3 Tensile Strength

The tensile strength was measured on a Hounsfield Tensile Tester according to Norm NP EN ISO 13934-1.

2.3.4 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.

2.3.5 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.

2.3.6 Washing Fastness

To test durability of PCM bonding towards washing, the coated Cork/Membrane were treated during 1 and 5 cycles in a Linitest Original Hanau C1-20 for 30 min at 40 ºC, in accordance with ISO Standard 105-C06 A1S.

3. Results and Conclusions

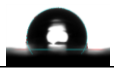
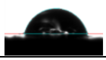
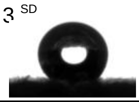
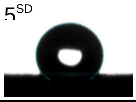
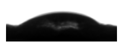
3.1 Effect of the DBD Plasma Discharge on Cork Agglomerate Composite

3.1.1 Static and Dynamic Contact Angle

The surface properties of cork and membrane samples were analyzed by static and dynamic contact angle measurements in order to evaluate the effect of different plasma dosages.

The Table 1 shows the contact angles variations using water drop of cork and membrane substrates for different dosages applied.

Table 1. Static Contact Angle(Average ^{A} and SD^{SD})

Samples Dosage	Untreated	300 W. min.m^{-2}	600 W. min.m^{-2}	1200 W. min.m^{-2}	2400 W. min.m^{-2}	4800 W. min.m^{-2}
Membrane Side	113º ^{A} 6 ^{SD} 	84º ^{A} 6 ^{SD} 	61º ^{A} 1 ^{SD} 	62º ^{A} 1 ^{SD} 	63º ^{A} 1 ^{SD} 	57º ^{A} 5 ^{SD} 
Cork Side	126º ^{A} 3 ^{SD} 	114º ^{A} 5^{SD} 	93º ^{A} 5 ^{SD} 	90º ^{A} 5 ^{SD} 	54º ^{A} 5 ^{SD} 	27º ^{A} 4 ^{SD} 

Contact angle measurements illustrate a decrease after DBD plasma treatment, which correspond to higher hydrophilicity. These results suggest that wettability of the cork and membrane are affected by cleaning or chemical changes (functionalization) induced by plasma treatment.

With plasma activation is possible to improve considerably the water adsorption velocity. When the dosage of 2400 W.min.m^{-2} is applied in the cork side the adsorption of water droplet occurs in approximately 13 seconds. The dynamic contact angle shows that the samples untreated keeps hydrophobic, even after a long period of time (Figure 1.a). Figure 1.b shows the dynamic contact angle results on the membrane side with and without plasma treatment. It can be seen that the treated mebrane has a lower contact angle from the beginning. However, this adsorption does not change over time for both samples.

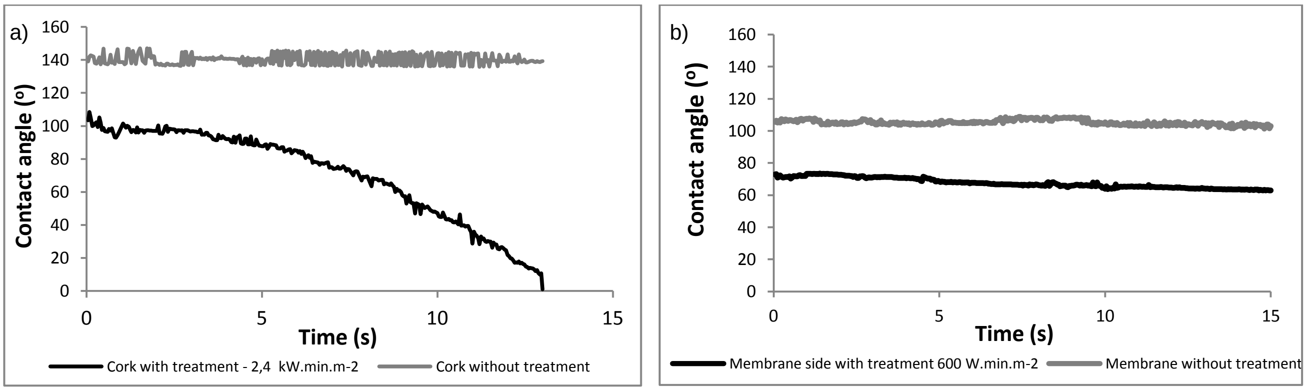


Figure 1. Dynamic Contact Angle of Cork (a) and Membrane (b) without and with plasma treatment

3.1.2 Fourier Transform Infra- Red Spectroscopy

The Figure 2 shows the characterization of the cork side composite by infra-red spectroscopy. FTIR technique confirms [7, 8] the complex nature of this material. The two largest peaks of vibration (2862 - 2916 cm^{-1}) represent the group CH_2. The presence of a strong stretching band (1697-1728 cm^{-1}) can be attributed to C = O group, these groups are present in suberin, lignin and carbohydrates components. The bands at 1049 – 1026 cm^{-1} correspond to CH, CO, in the presence of hemicellulose, cellulose and lignin. FTIR spectra shows that no major changes in the chemical structure of the samples are verified when plasma treatment was applied.

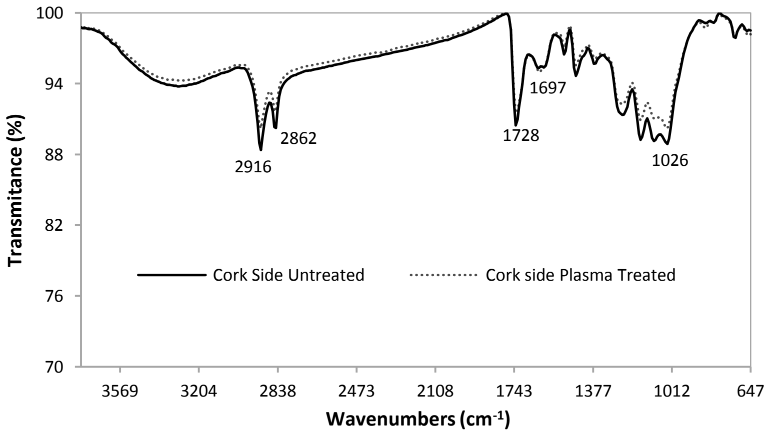


Figure 2. FTIR spectra of Cork side without and with plasma treatment

3.1.3 Energy Dispersive Spectroscopy

The increase of oxygen/carbon ratio (O/C) from 0.33 to 0.36, obtained by EDS analyse, can be responsible for the increase the content of hydrophilic functional groups on the cork and membrane surface, which can explain the decrease of water contact angle when DBD plasma treatment was applied. The table 2 shows the elemental composition of the samples with and without plasma treatment.

Table 2. Elemental Composition in Percentage (%) and Atomic Ratios of the cork side samples with and without plasma treatment

Atoms (%)	**Without treatment**	**With plasma treatment**
Carbon	75.01	73.49
Oxygen	24.71	26.3
Cl	0.29	0.20
Ratio (O/C)	0.33	0.36

3.1.4 Tensile Strength

The comparison of the tensile strength and surface morphology of untreated and plasma treated samples with dosage of 600 $W.min.m^{-2}$, showed a significant increase of tensile strength (around 20%) when plasmatic treatment has been applied passing from 4.0 N (untreated sample) to 4.7 N (treated sample). This can be explained by increase of roughness and adhesion between the membrane and the cork [9, 10].

3.1.5 Scanning Electronic Microscopy

The effect of DBD plasma treatment on the morphology of the membrane polymer surface was investigated. Figure 3 shows the SEM images of the DBD plasma-untreated (a) and plasma treated (b) samples. The surface of DBD plasma-treated is rougher than that of the untreated membrane. According to some authors the increase in the roughness of the polymers surface can be responsible for improving the wettability [11] [12].

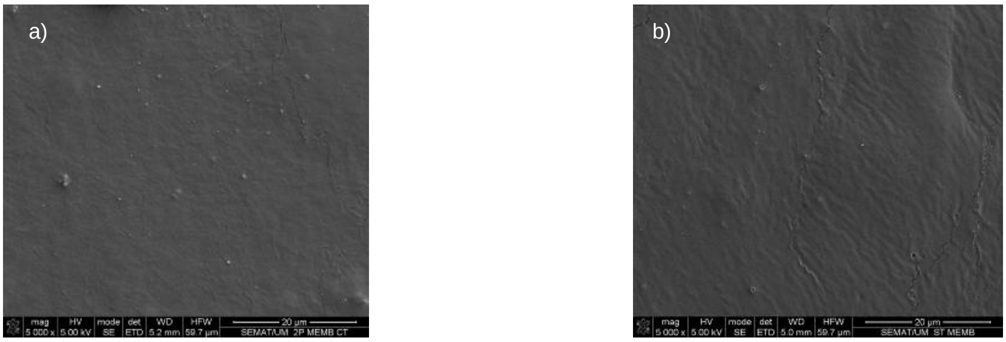


Figure 3. SEM micrographs obtained with secondary electrons of the (a) untreated and (b) DBD plasma-treated cork/membrane substrate with a dosage of 600 $W.min.m^{-2}$

3.2 Effect of the DBD Plasma Discharge on PCM Microcapsule Adsorption

3.2.1 Scanning Electronic Microscopy

Figure 4 shows the SEM images of untreated and plasma treated sample, padded with PCM microcapsules. It is possible to observe that several microcapsules are adsorbed on the surface of the both sample sides. These results confirm that DBD plasma can be used to modify the surface of this substrate (cork and membrane), leading to enhanced hydrophilicity. Due to these modifications it is possible to increase the adsorption of the PCM microcapsules on the cork surface [13,14].

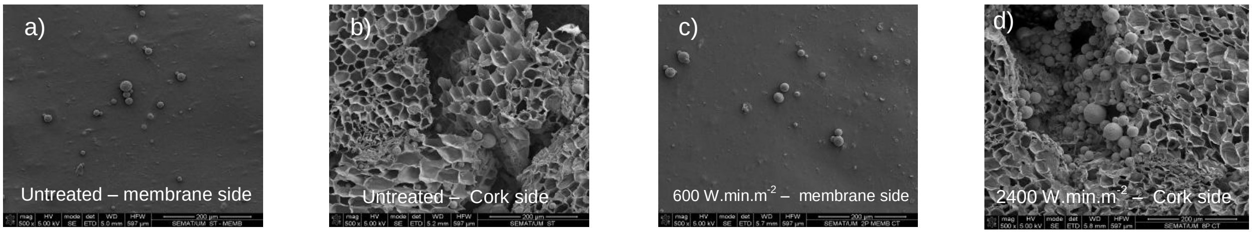


Figure 4. Images of PCM microcapsules fixed on composite (cork and membrane) untreated (a,b) and plasma treated (c,d)

3.2.2 Differential Scanning Calorimetry

Figure 5 shows the differences obtained in the energy storage capacity of the coated cork/membrane by comparison of the samples with and without plasma treatment. By means of enthalpy (Joules per gram), the evaluation of the amount of PCM microcapsules that were adsorbed to the material was done. An increase in the energy storage capacity in the samples treated with plasma was observed. This result confirmed that plasma treatment increased the adsorption capacity with regard to the PCM microcapsules.

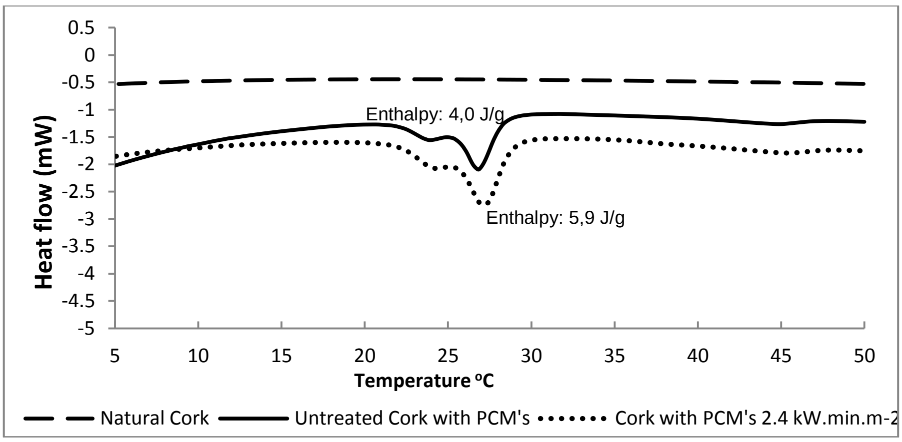


Figure 5. DSC thermograms of the untreated and plasma-treated cork material with padded PCM microcapsules

3.2.3 Fourier Transform InfraRed Spectroscopy

Oliveira et al [2] noticed the appearance of four characteristic peaks of the melamine microcapsules. These peaks were N-H stretching vibrations at about 2920 cm^{-1}, C-H stretching vibrations at about 2840, 1386 cm^{-1}, and C-O stretching vibrations at about 1160 cm^{-1}. The band at 810 cm^{-1} is also characteristic of the melamine PCM corresponding to bending vibration of triazine ring [15]. Figure 6 shows FTIR spectra of the following samples: natural cork (control), cork with PCM melamine microcapsules, and plasma-treated cork with PCM melamine microcapsules. The FTIR analysis confirms the higher amount of PCM microcapsules adsorbed on this composite material pre-treated with plasma DBD.

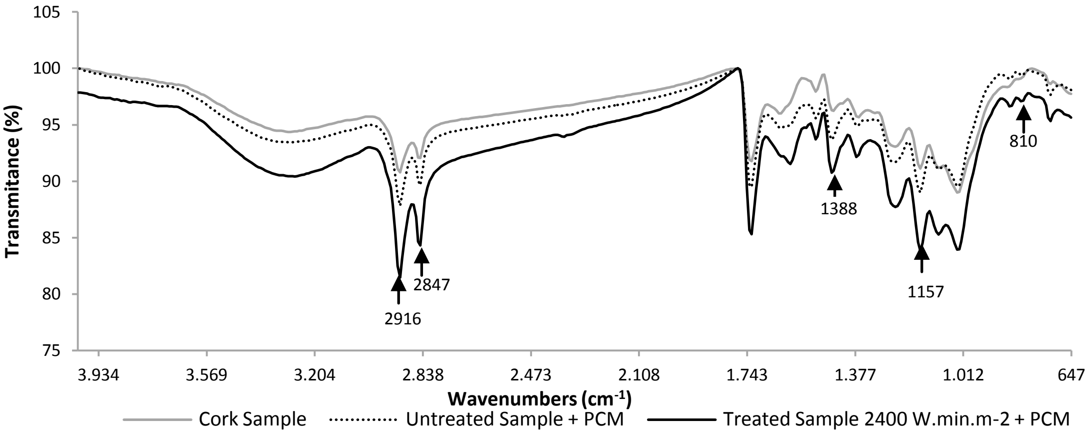


Figure 6. FTIR spectra of cork agglomerate composite (Cork Sample), cork with PCM microcapsules, and plasma treated cork with PCM microcapsules

3.3 Effect of the DBD Plasma Discharge on PCM Microcapsule Adhesion

Figure 7 shows the DSC curves of the untreated and DBD-plasma-treated cork/membrane padded with PCM microcapsules after 1 and 5 washing cycles. As can be verified, the adhesion of the PCM microcapsules in the plasma treated cork/membrane substrate increased considerably.

In the untreated substrate, the enthalpy decreased 10% and 78,5% after 1 and 5 washing cycle, respectively. On the other hand in the DBD-treated cork/membrane substrate the enthalpy only decreased 8.5% and 42.4% after 1 and 5 washing cycles. The enthalpy of the treated sample after 5 washing cycle (3,4 J/g) was approximately four times higher than the sample without treatment (0,9J/g).

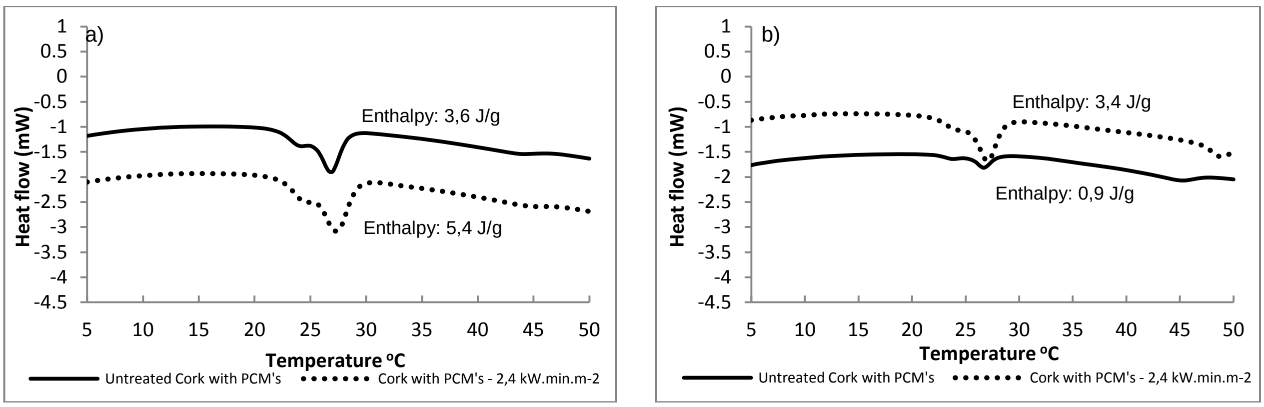


Figure 7. DSC thermograms of the untreated and plasma-treated Cork material with PCM microcapsules after 1 (a) and 5 washing cycle (b)

Activating the surface by DBD plasma treatment adding favourable functional groups, will enhance the interaction of the adhesive with the surface of the substrate and provide anchor sites for the binder+microcapsules solution.

4. Conclusions

The results prove that the surface modification of cork and membrane composite with a DBD plasma treatment lead to enhanced hydrophilicity.

The EDS analysis showed that the DBD treatment has increased the amount of oxygen in the surface of the substrates, creating more polar groups and improving the hydrophilicity/wettability of the cork/membrane. All these modifications of the cork and membrane after plasma treatment led to a remarkable increase in microcapsules adsorption and adhesion to the materials during finishing when compared to untreated samples. When DBD treatment is applied to this cork agglomerate composite the microcapsules were successfully fixed even after 5 washing cycles.

The plasma technology can be considered an excellent solution to promote the functional performance of several kinds of products, achieving more durable properties and so contributing for the sustainability of innovative textiles.

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