SURFACE MODIFICATION OF POLYLACTIC ACID FABRICS USING AMBIENT AIR PLASMA

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Abstract

The aim of this work is to study the changes in the properties of Polylactic acid (PLA) fabrics after plasma treatment at atmospheric pressure. Volume dielectric barrier discharge (VDBD) and diffuse coplanar surface barrier discharge (DCSBD) were applied to modify the PLA surface in ambient air using exposure times 1 - 10s. Various PLA fabrics in the weight range of 18 – 50 gsm were studied. The change in wettability and its aging were evaluated using the contact angle measurement by the Washburn method. A scanning electron microscope was used to measure the morphology changes.

Keywords: Polylactic acid nonwoven textile, DCSBD, Volume DBD, wettability, SEM

1. INTRODUCTION

Polylactic acid (PLA) represents an interesting biopolymer that successfully replaces synthetic polymers in many industrial applications. Lactic acid can be sourced from renewable resources, such as cornstarch or sugarcane. This sustainable approach aligns with the growing demand for eco-friendly materials and solutions. The production of PLA showcases the potential for reducing reliance on fossil fuels, a crucial step toward more sustainable manufacturing practices. Due to its biocompatible, bioabsorbable, biodegradable properties and easy production process from renewable resources, PLA has become an intensively investigated material.

Also, the unique combination of high strength and high modulus sets it apart as a material of great promise for an array of applications in agriculture, electronics, engineering, and various consumer products. The high tensile strength makes PLA material robust and reliable under varying conditions [1-4]. The biocompatible nature of PLA is a key feature that underpins its extensive use in biomedical applications. When used in medical devices or implants, PLA interacts harmoniously with the human body, minimizing adverse reactions. PLA's bioabsorbable characteristics mean that over time, it gradually breaks down into non-toxic byproducts without causing harm, making it an excellent choice for materials designed to be implanted and eventually absorbed by the body [5].

However, the surface properties, such as wettability, printability, and liquid sorption, are poor in the case of PLA materials, and prior surface treatments are needed before further processing to improve the wetting and activate the surface [6-8]. Plasma treatment is one of the interesting alternatives that lead to surface activation, improvement of surface wettability and adhesion properties.

The aim of this study was to investigate the effect of plasma treatment on the surface properties of PLA nonwoven fabrics. Plasma treatment was realized using two different plasma sources: Diffuse coplanar surface barrier discharge (DCSBD) [9-12] and Volume dielectric barrier discharge (VDBD) operated in ambient air at atmospheric pressure. The change in surface wettability and surface morphology after plasma treatment were studied. The surface wettability of the modified PLA nonwoven fabrics was analyzed by Washburn method measurement. The surface morphology was evaluated using scanning electron microscopy (SEM).

2. EXPERIMENTAL

2.1 Materials

Three different nonwoven fabrics with basis weights ranging from 18 gsm to 50 gsm were investigated. The PLA nonwoven fabrics with an areal density of 18 gsm were supplied by FloraSeft, as a commercially available fabric usually used in agriculture. The PLA nonwoven fabrics with an areal density of 30 gsm and 50 gsm were purchased by Shenzhen Esun Industrial Co.,Ltd., China. N-Hexane (CAS 110-54-3) was provided by MACH CHEMIKÁLIE s.r.o. and distilled water was prepared by Direct - Q® 3 UV.

2.2 Plasma treatment

DCSBD [13] represents dielectric barrier discharge in coplanar geometry. Applying sinusoidal high-frequency high voltage (14 kHz), the large thin layer of uniform visually diffuse cold plasma with high non-isothermicity is generated (**Figure 1a**). The thickness of DCSBD plasma layer is ~0.33 mm and the plasma can be generated in any working gas, including ambient air or hydrogen. For better contact with plasma, the flax fabrics were pressed to the ceramics by a glass plate as a pusher.

A commercial device AHLBRANDT Industrial Corona System GmbH company (Lauterbach, Germany) is roll-to-roll system using a volume configuration of electrodes isolated by a ceramic layer (**Figure 1b**). Plasma is generated between a rotating cylinder and a detachable electrode with gaps, which serve as an air outlet. The input power was set of 375 W corresponding to the same square power density (2.56 $W.cm^{-2}$) as in the case of DCSBD. The distance between the sample and electrodes was 1 mm. The plasma was generated in ambient air at atmospheric pressure, at room temperature.

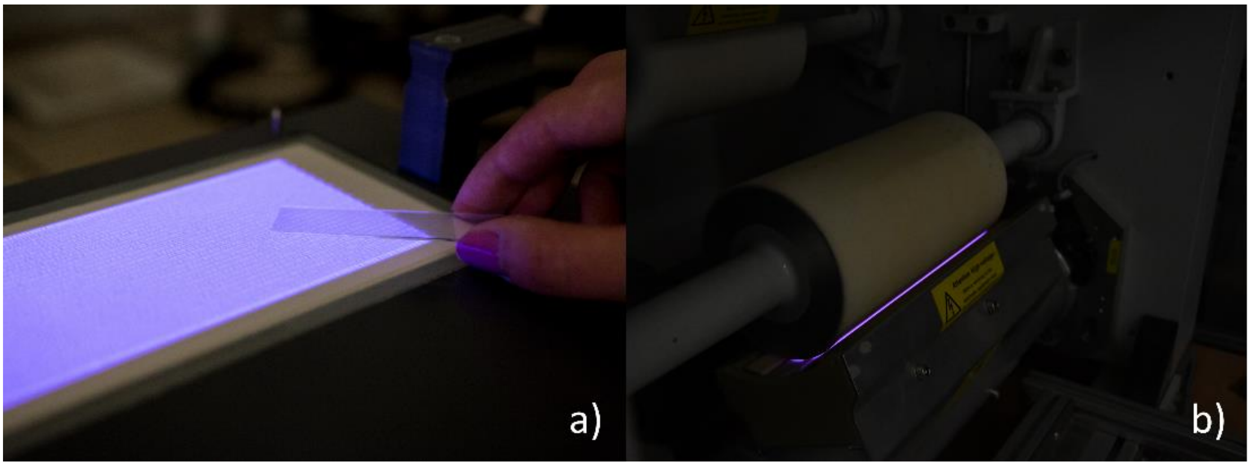

Figure 1 The photography of plasma sources. a) Diffuse coplanar surface barrier discharge, and b) Volume dielectric barrier discharge operated in ambient air at atmospheric pressure.

2.3 Wicking measurement

The dynamic water contact angle was measured by a modified Washburn method. The flax fabrics were cut into 2 cm wide and 5 cm long strips. The strips were held vertically upwardly direction and connected to precise microbalance RadWag AS 310.R2 with the precision of 0.1 mg. Each strip was slowly moved downward into the tested liquid. When contact with the liquid level, the mass change was recorded 10 times per second as a function of time. The average of five tests was measured in each condition.

We studied the capillary flow of demineralized water and n-Hexane in flax fabric strips. n-Hexane is a totally dispersive liquid, the contact angle is supposed to be zero, therefore it completely wets the fibers. The properties of used liquids are summarized in **Table 1**.

Table 1 Liquid properties

Liquid	Density (kg/m3)	Surface tension (N/m)	Dynamic viscosity (Pa.s)
Water	660	17.9E-3	3.0E-4
n-Hexan	997	72.2E-3	8.9E-4

The WCA of PLA fabrics was calculated from „equation (1)":

$$\cos(\alpha) = \frac{\eta \cdot A}{\sigma \cdot \rho^2 \cdot C} \tag{1}$$

where:

α - contact angle (°)

η - dynamic viscosity (Pa.s)

A – slope of interpolated curve (kg/(s.m^3))

σ - surface tension (N/m)

ρ - liquid density (kg/m^3)

C – material constant (m^2)

The material constant is determined by measuring with a perfectly wetting liquid, usually n-hexane, and slope A is determined from the measured time dependence curve of the penetrated liquid into the PLA.

2.4 Scanning electron microscopy

The surface morphology was observed by SEM (TESCAN Mira 3) equipped with a Schottky Field Emission electron gun, secondary electron detector, and back-scattered electron detectors. The maximal resolution is 1.0 nm by 30 kV. To avoid the sample charging, the surfaces were coated with 20 nm of AuPd layer.

3. RESULTS

3.1 Wetting properties

The water contact angles obtained by the Washburn method measurement were carried out to investigate the wettability and soaking improvement of PLA fabrics' wettability and soaking improvement of PLA fabrics after plasma treatment. **Figure 2** shows the water contact angle of all types of investigated PLA fabrics modified in DCSBD and VDBD for various exposure times. As-received, untreated PLA textiles are naturally non-wettable (WCA ≥ 90°), therefore it was not possible to measure the contact angle of their surfaces using the Washburn method. After treatment in DCSBD and VDBD plasma, the WCAs decreased. During 1 s and 3 s in the plasma, there was a slight decrease in the contact angle. The great difference in the wetting improvement was observed after 10 s treatment time. While the VDBD treatment again resulted in only a slight reduction of the WCA, after the 10 s modification in DCSBD plasma, complete wettability was achieved for all three PLA textiles. The significant difference in wettability of PLA treated for 10 s in DCSBD and VDBD is probably due to the different filament arrangements in the two plasma source geometries and the different nature of the plasma. In DCSBD, the filaments burn parallel to the sample surface and the plasma is more diffuse, compared to DBD. Therefore, the treated fabric is in better contact with the plasma, the plasma is uniform and has a more intense effect in the bulk. In contrast, by using DBD geometry, the filaments burn perpendicular to the treated sample and the plasma is strongly filamentary. It is possible that in the case of PLA fabric, which has a very sparse structure (depending on the areal density), the filaments burn between the individual PLA fibers and the resulting fabric is not in as intense contact with the plasma as in the case of DCSBD.

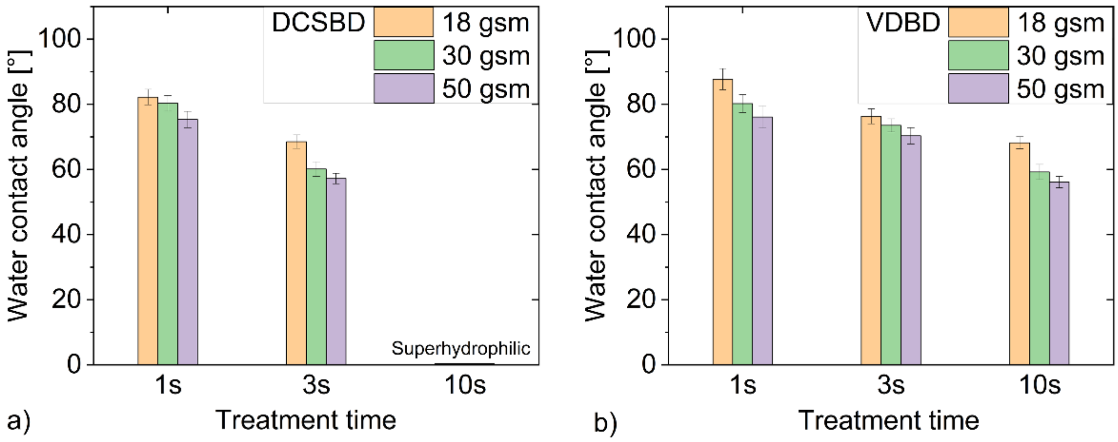

Figure 2 Water contact angle of PLA textile surface modified in DCSBD and VDBD for 1 s, 3 s and 10 s in ambient air

3.2 Surface morphology

The surface morphology of untreated, as-received individual PLA fibers from 18gsm, 30 gsm and 50 gsm fabrics are shown in **Figure 3**. Evidently, the untreated PLA fibers were smooth, with residual random contaminations, however without any visible cracks, surface structure, or roughness. Significant changes in the surface morphology of PLA fibers after plasma treatment were observed. **Figure 4** and **Figure 5** clearly summarize photographs of PLA filaments of different areal fabric densities and treatment times of 1 s, 3 s, and 10 s in DSCBD and VDBD plasma, respectively. Obviously, the effect of plasma treatment on the fiber surface morphology increased with increasing treatment time and with increasing areal fabric density.

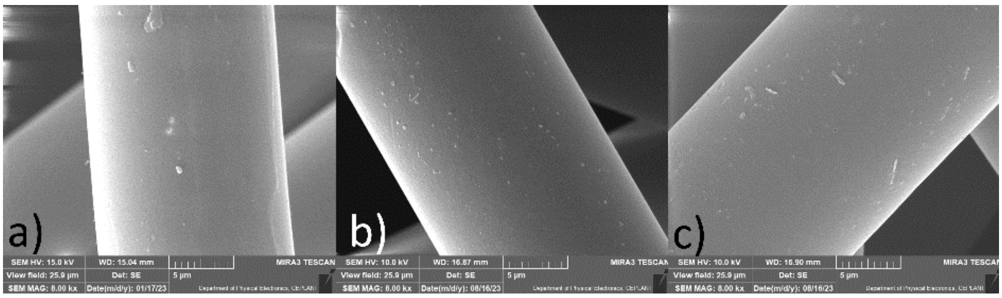

Figure 3 SEM images of untreated, as-received individual fibers of a) 18 gsm, b) 30 gsm and c) 50 gsm PLA nonwoven fabrics

There was no significant change in morphology during the short treatment times in both DCSBD (**Figure 4a – Figure 4d)** and VDBD (**Figure 5a – Figure 5d**). In the case of VDBD, even the 18 gsm fabric was without any observed surface change during 10 s treatment time (**Figure 5g**). This result corresponds closely with the WCA measurements (**Figure 2b**), where the wetting effect was also weaker for these conditions. With increasing treatment time in DCSBD (**Figure 4h – Figure 4i**) and in VDBD (**Figure 5e – Figure 5i**), changes in morphology can be observed on the surface of the PLA fibers. After 10s treatment time, the strong micro-bubble structure on the surface was observed. These surface changes can be attributed to the thermal effect of plasma because the PLA fibers are characterized by low thermal resistivity, approx. 50 °C [15].

According to the WCA measurement, shown in **Figure 2**, plasma treatment in DCSBD led to a more uniform, homogeneous surface modification, which resulted in an increase of wettability. On the other hand, apparently, plasma treatment in VDBD led to a non-uniform effect on the fibers, caused by filamentation of the discharge, which resulted also in only slight increase of wettability of the PLA fabrics.

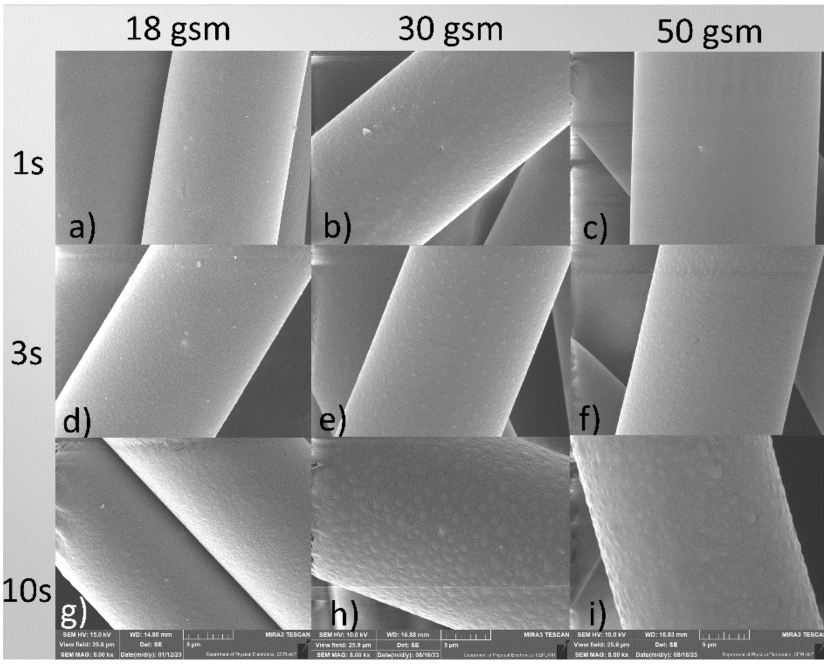

Figure 4 SEM images of individual fibers from PLA nonwoven fabrics after plasma treatment in DCSBD

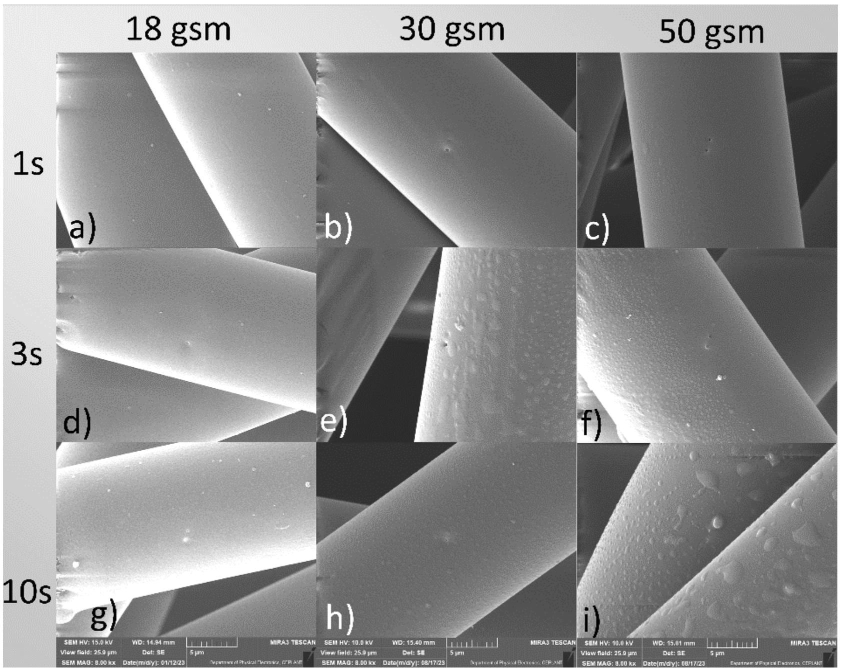

Figure 5 SEM images of individual fibers from PLA nonwoven fabrics after plasma treatment in VDBD

4. CONCLUSION

The effect of plasma treatment on the wettability and on the surface morphology of PLA fabric was studied. Plasma treatment was realized using two different plasma sources: DCSBD and VDBD. It was found that the wetting properties of PLA fabrics can be effectively improved using atmospheric pressure plasma. A significant effect of morphology change was observed only at high plasma treatment times of 10 s. At short plasma treatment times of 1 s and 3 s, the wettability increased, but the morphology of individual fibers was not significantly changed. The areal density of the PLA fabric also had an effect on the wettability and surface morphology.

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