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Abstract. In this study, a novel simple and fast method was developed of immobilizing a natural polysaccharide (chitosan) on a polylactide (PLA) surface. In order to overcome the lack of surface adhesion between the chitosan and the PLA due to incompatibility issues, atmospheric pressure plasma was used. The plasma activation was able to modify the PLA surface by generating surface chemistry proper for stabilizing the chitosan layer. The activation of the surface was monitored through water contact angle (WCA) measurements and X-ray photoelectron spectroscopy (XPS). Indeed, the introduction of new functionalities lowers the hydrophobicity of the PLA surface allowing an effective spreading and immobilization of the chitosan layer. The presence of chitosan on the polyester's surface was proven by Fourier transform infrared spectroscopy (FTIR).

1. Introduction

Tissue engineering (TE) is a multidisciplinary field of science focused on the regeneration of damaged living tissues [1]. Knowledge in chemistry, physics, engineering, and clinical sciences is combined to solve the problems related to tissue loss and organ failure via the design of a 3D scaffold with specific properties, allowing the cells to reproduce and form a natural implant. As the materials used for the 3D scaffold design have to combine multiple properties, finding a single material component that can fulfill all the requirements is highly improbable [2]. Thus, multiple combinations between polymers (inert, biodegradable, bioactive) and particles (metallic, ceramic, polymeric) are often studied. In terms of polymers, for example, polyesters are widely used in 3D scaffold preparation due to their biocompatibility and biodegradability. More particularly, the polylactic acid (PLA) has a long history of uses and has gained the US Food and Drug Administration (FDA) approval for clinical use. Despite the polymer biocompatibility, biodegradability, and bioresorbability, the adhesion of cells to the surface of the hydrophobic PLA remains a major challenge.[3], which limits the polyester uses in the biomedical field [4].

Many ways to improve the surface-cell compatibility can be found in the literature [4–7]. One of them relies on the introduction of bio(macro)molecules onto the surface of the polyester. In this respect, chitosan gains interest for its outstanding biological properties related with cell adhesion and antimicrobial and wound dressing properties. However, the incompatibility between the PLA and the chitosan chemistries implies the use of a prior chemical modification of one or both polymers to allow efficient coating or grafting. Usually, chitosan modification or covalent crosslinking is used to anchor the biopolymer onto the PLA surface. However, this significantly alters chitosan's biological activity and limits the success of the final scaffolds. Modifying the PLA seems more appropriate, but when performed in the polymer bulk this might alter the PLA functions. Therefore, other methods limited to surface modification are under extensive development. Amongst all, atmospheric plasma has already demonstrated its capability of modifying the surface chemistry of polymers and preserving their bulk properties [8].

In this work, a microwave atmospheric plasma torch was used to improve the adhesion of chitosan to the PLA surface. The plasma creates new functionalities for interacting with chitosan and an interface for its adhesion. The activation of a PLA surface was investigated by WCA and XPS. The presence of chitosan was also investigated by FTIR and WCA.

2. Experimental

2.1 Materials
The polyester used in this work is an amorphous PLA from INGEO (PLA 4060D). It possesses a T_g around $55\,°C$ and no melting temperature. The PLA pellets were dried under reduced pressure overnight before thermo-compression at $180\,°C$ to obtain a square sample of 4 cm² and a thickness of 500 µm. The chitosan is commercially available (Sigma) from shrimp with a deacetylation degree of 75% and a molar mass of 300 kg/mol. Acetic acid (ACS reagent, 99.7% purity) was supplied by Sigma and used as received. The chitosan was used as received and solubilized in an aqueous medium with the help of acetic acid (1 wt%). The final concentration of chitosan was 1 mg/ml.

2.2 Samples preparation
The plasma treatment was realized using an IONJET (a microwave plasma torch from IONICS, Belgium) with a generator set at a frequency of 2.5 GHz and a power of 30 W. Ar (99.9% purity, Air Liquide) was used as a carrier gas at a flow of 2 L/min. The torch was placed vertically at 1 cm off the sample surface fixed on an XY table moving at a speed of 8 mm/sec. A single cycle was performed and the samples were then dip-coated for 10 s in the chitosan solution. The as-prepared samples were dried in ambient air overnight.
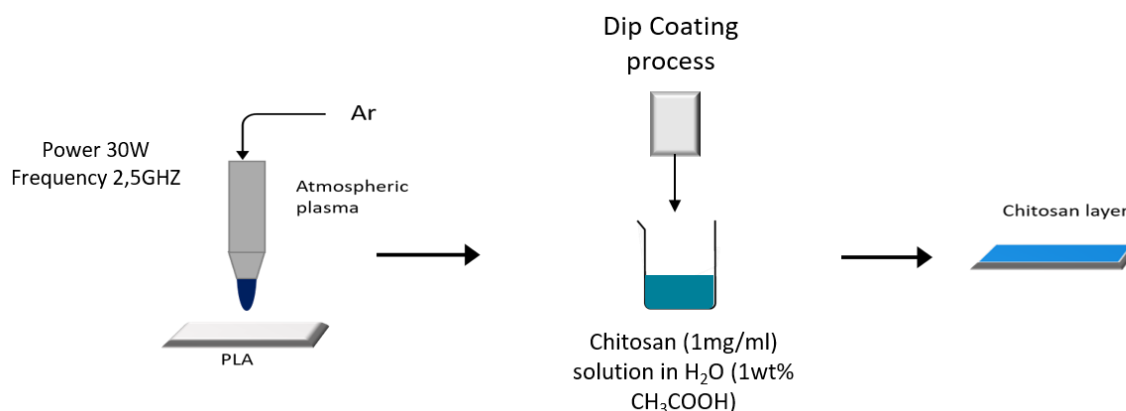
Figure 1 Schematic representation of the PLA surface modification and chitosan deposition.

2.3 Analyses

The FTIR spectra were recorded on a Bruker Tensor 27 spectrometer in attenuated total reflectance mode with a 4-cm^{-1} resolution. The background and sample spectra were obtained in the wavenumber range 600 – 4000 cm^{-1}. The water contact angle (WCA) measurements were implemented using a DSA Mk2 drop shape analysis system in a static mode at 25 °C by a sessile drop method. For each sample, at least five measurements on different surface locations were averaged. The XPS analyses of all samples were performed using an ESCA-5000 (Physical Electronics) Versa Probe system. The following X-ray settings were used: beam-size diameter 200 μm; beam power 50 W; voltage 15 kV. The pressure in the analysis chamber was typically 2×10^{-6} Pa. The XPS data were collected using monochromatic Al Kα radiation at 1486.6 eV. The photoelectrons were collected at a take-off angle of 45° (normal detection) to the surface normal. Survey (general) spectra were taken with a 187.85 eV pass energy, a 0.5 eV step and 40 ms/step, and the high-resolution spectra, with a 23.5 eV pass energy, a 0.2 eV step and 50 ms/step. The atomic compositions were derived from the high-resolution peak areas using the photoionization cross-sections calculated by Scofield, corrected for the dependence of the escape depth on the kinetic energy of the electrons and for the analyzer transmission function of our spectrometer. The atomic compositions were derived from the peak areas after a Shirley background subtraction.

3. Results and discussion

In order to fully assess the different steps of the process (Figure 1), *(i)* the plasma conditions were defined to prevent any modification of the PLA bulk or over-degradation of the polyester surface; *(ii)* the surface chemistry of the PLA was completely studied; and *(iii)* the chitosan layer deposition was investigated.

The change of the water contact angle (WCA) is a clear indication of a change in a polymer surface chemistry [9]. When applied to the untreated and the plasma-activated PLA surfaces, this easily accessible and well-known technique showed a sharp decrease of about 30° in WCA (Figure 2). Indeed, while the WCA of PLA was close to the typical value of 85° [10], after plasma activation it dropped to 55°. This result attests to a decrease in the surface hydrophobicity [7] and is related to imparting oxidized functions onto a polyester surface [11]. These newly formed reactive species form hydrophilic groups (hydroxyl or carboxylic) that will be finally used to interact with chitosan [12].
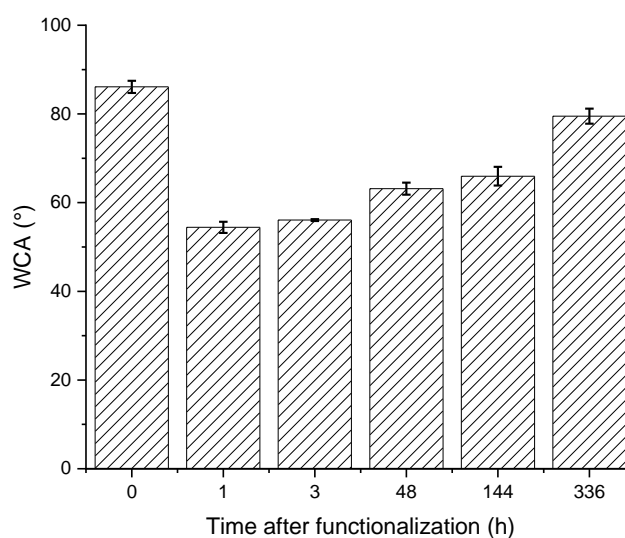

Figure 2 Evolution of the water contact angle with time after Ar treatment.

However, this change in the surface hydrophobicity was not permanent, as an increase of the WCA was observed with time within two weeks. This phenomenon is due to a relaxation process of the surface known as hydrophobic recovery [13]. The period for effective chitosan deposition was then defined to be of several hours and the coating process was realized directly after the plasma activation.
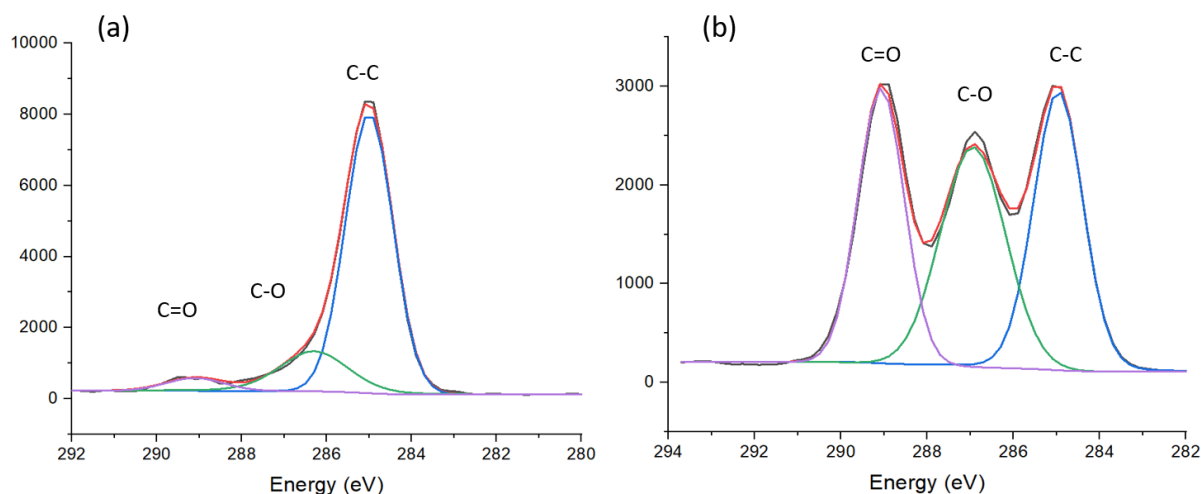

Figure 3 C1s analysis of (a) neat PLA and (b) activated PLA

To confirm and determine the plasma-created chemistry, the surface composition of the samples was studied by XPS. Figure 3 (a)-(b) shows the deconvoluted C1s core-level spectra of the pristine and the activated PLA, respectively. The C1s spectrum of the pristine PLA surface contained three peaks: 285 eV (-C-H/C-C) (80%), 286.3 eV (C-O-C/C-OH) (16%), and 289.2 eV (O-C=O) (4%) [14]. However, the proportion of C-O to C=O increased when the sample was subjected to plasma activation. The surface was highly enriched in oxygen, the oxygen content rising from 10 to 40 atomic %. These results are associated with the formation of oxidized functions on the surface as concluded from the WCA results [15]. The presence of these new hydrophilic functions will have two purposes. They will allow obtaining a better spreading of the chitosan solution during the dip-coating process[16] and stabilization of the chitosan coating on the PLA surface.

At the next step, chitosan layer deposition was performed by short-time dip-coating to prevent any possible PLA surface alterations. The chitosan presence at the surface was then studied by FTIR (Figure 4). The characteristic bands of polyester can be seen on the reference (black curve), the CH_2 and CH_3 vibrations around 2800 cm^{-1}, and the carbonyl around 1700 cm^{-1}. As a control, one sample was dip-coated without any plasma activation (red curve). Its spectrum is almost overlapping the reference curve highlighting the necessity of the plasma activation process in the stabilization of this chitosan layer. For the plasma-activated and dip-coated sample (act+dpc), two major observations can be made. First, the peaks of the polyester are still present on the curve, which means that the layer of chitosan is thinner than the depth of analysis (i.e., 2 µm) or discontinuous. As several spots of the sample showed this behavior, the first hypothesis seems more plausible. Second, three new peaks appear on the spectrum, two relatively sharp bands of amide I and II respectively at 1650 cm^{-1} (stretching of the C=O group hydrogen bonded to N–H of the neighboring intra-sheet chain) and 1580 cm^{-1} (NH_2 bending), and a wide peak corresponding to the amine and hydroxyl functions around 3300 cm^{-1} [17] attributed to the presence of chitosan. These groups can be assigned to the OH of the sugar unit and the amine of the lateral group of the D-glucosamine unit of the chitosan.
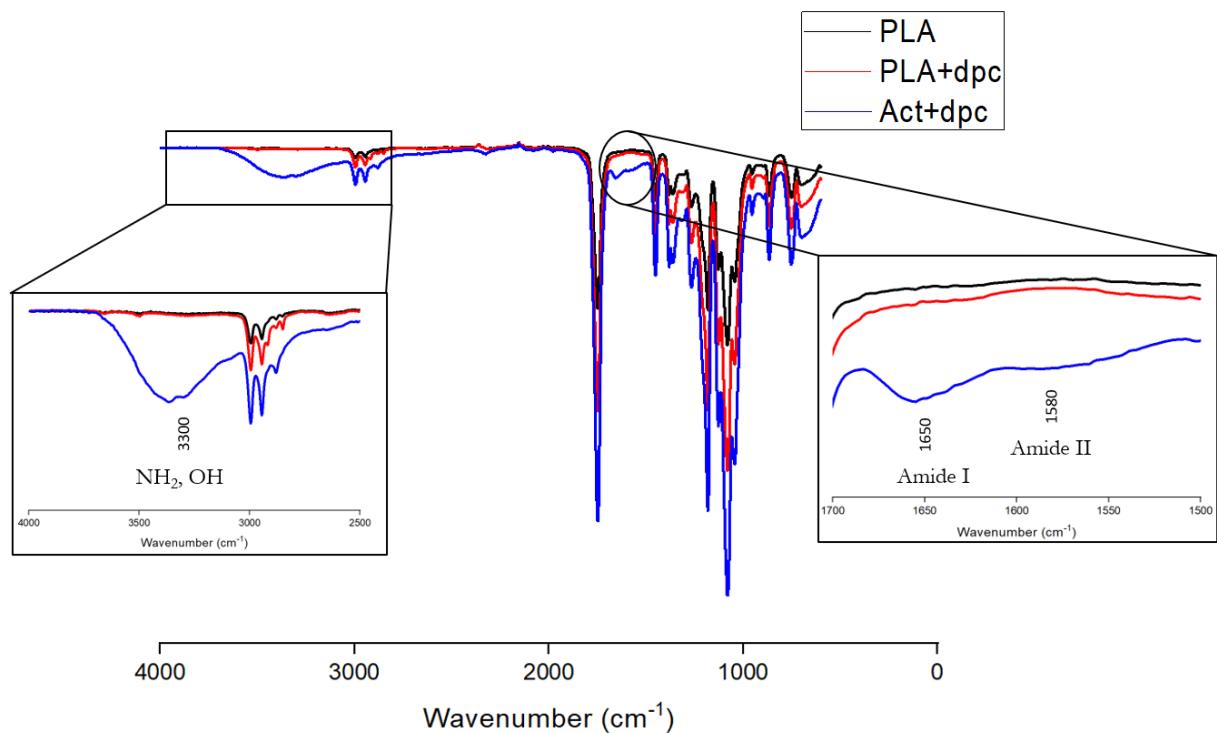
Figure 4 FTIR spectra of neat PLA (black), a dip-coated PLA (dpc, red) and a plasma-activated + dip-coated PLA (act+ dpc, blue)

4. Conclusions

In this work, a new technique of improving the immobilization of a polysaccharide, chitosan, on a polyester surface was developed. Thanks to the plasma technology employed, the polyester surface could be modified to possess enough functions to allow the immobilization of the chitosan as proved by FTIR, contact angle measurements and XPS. This technique exhibits several advantages, as it is fast, efficient, and could be easily adapted to treat 3D objects in reduced time compared to the usual chemical methods [18]. However, several issues are still to be dealt with. The morphology changes of the surface during the process and a chemical investigation of the final layer to assess the interactions involved in the stabilization will be part of a future publication.

5. Acknowledges

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