

Surface Modification of Polylactic Acid Films by Atmospheric Pressure Plasma Treatment

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Abstract. A new approach for the modification of polylactic acid (PLA) materials using atmospheric pressure plasma (APP) is described. PLA films plasma exposure time was 20, 60, 120 s. The surface morphology and wettability of the obtained PLA films were investigated by atomic force microscopy (AFM) and the sitting drop method. The atmospheric pressure plasma increased the roughness and surface energy of PLA film. The wettability of PLA has been improved with the application of an atmospheric plasma surface treatment. It was shown that it is possible to obtain PLA films with various surface relief and tunable wettability. Additionally, we demonstrated that the use of cold atmospheric pressure plasma for surface activation allows for the immobilization of bioactive compounds like hyaluronic acid (HA) on the surface of obtained films. It was shown that composite PLA-HA films have an increased long-term hydrophilicity of the films surface.

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable thermoplastic polyester [1, 2] derived from renewable resources such as corn that could be used in a variety of applications. Due to its biocompatibility PLA is one of the most extensively used polymer in the biomedical field [3]. As PLA is bioresorbable polymer with minimum irritant effect on contacting tissues and degrades on non-toxic monomers, it is approved for medical applications and approved by FDA (US Food and Drug Administration) for clinical usage [4]. However, such disadvantages as hydrophobicity and low surface energy limit its application as a material for tissue engineering. In order to improve its surface properties a lot of approaches have been employed including physical and chemical treatment [5–7]. One of the promising strategies for the surface modification is a non-thermal atmospheric pressure plasma assisted immobilization of biomolecules. Non-thermal plasmas have garnered significant attention owing to the easy formation of stable plasmas, low operation cost and high productivity [8]. Depending on the used discharge gas, a variety of surface functional groups can be created on different polymers materials, thereby improving such surface properties as wettability, adhesion and biocompatibility [9–13]. Moreover, the surface activation and increased wettability of plasma treated polymers make it possible to conduct the surface immobilization of water-soluble biomolecules such as hyaluronic acid (HA). HA is hydrophilic biomolecule widely distributed in the body. As a major component of extracellular matrix (ECM), HA has been shown to play a vital role in tissue regeneration and cell migration and proliferation [14].

Thus, atmospheric pressure plasma assisted HA immobilization on the surface of PLA films might be a promising approach, which allows increasing in PLA-based materials surface hydrophilicity and regeneration properties.

MATERIALS AND METHODS

Poly-L-lactic acid PL38 (PURAC, Netherlands) solution in a mixture of chloroform (Fisher Chemical, USA) with a concentration of 1 wt % was prepared. Solution homogenization time was 12 h. Then 15 ± 1 g of solution was

poured into a dry Petri dish 10 cm in diameter, sealed and dried in solvent vapor for 72 h. The thickness of the obtained films was $35 \pm 3 \mu\text{m}$.

Films modification was performed by the non-thermal plasma, which was generated by self-sustained volume discharge in atmospheric pressure air with high pulse repetition [13, 15]. The following parameters were used: pulse frequency—500 Hz, pulse voltage—20 kV, pulse duration on the matched load—120 ns, pulse energy—0.32 J. The samples were placed on anode and PLA films plasma exposure time was 20, 60, 120 s. The materials are assigned as PLA-20, PLA-60 and PLA-120 respectively. Then the samples were stored at the normal room conditions before the analysis.

After non-thermal atmospheric pressure plasma treatment PLA-120 samples were placed in 0.6 wt % aqueous solutions of HA ($M_w = 2 \times 10^6$ g/mol, Sinopharm Chemical Reagent Co., China) for 30 min. Then the samples were washed with distilled water and dried at room temperature. The produced material is assigned as PLA-HA.

The wettability of the samples was characterized by depositing of 3 μl drops of polar (water and glycerine) liquids using Krüss Easy Drop contact angle measurement system. The droplets were placed at different positions on the samples and the images were captured after the 1 min disposition of each drop. All the data were obtained from an average made from the measurements taken at five different spots on the surface of the respective sample, with the standard deviations all shown. The total surface energy, its polar and dispersion components were calculated with the Owens-Wendt method.

Atomic force microscopy (AFM) measurements were carried out to observe the surface topography of the samples before and after plasma treatment. The measurements were carried out on an AFM “Solver HV” (NT-MDT, Russia). Measurements of the surface’s relief were performed in the semi-contact scanning mode with parallel investigation of phase contrast. The NSG11 cantilevers with needle tip curvature radius of 10 nm and dopant concentration of $5 \times 10^{20} \text{ cm}^{-3}$ were used for experiments. The AFM images were processed using the Gwiddion 2.31 and ImageJ 1.45 software packages.

RESULTS AND DISCUSSION

The effect of the plasma treatment and HA immobilization on the wettability of the PLA nonwoven material has been examined using contact angle measurements. The untreated sample showed hydrophobic properties and has a water contact angle equal to $71.1^\circ \pm 1.68^\circ$ (Table 1). Plasma treatment leads to higher hydrophilicity (the contact angle reduces to $40.2^\circ \pm 2.25^\circ$) and surface energy. It might be explained by the hydrogen abstraction and surface oxidation resulting in the formation of polar groups after the plasma treatment. The decrease in dispersive component and increase in polar component of surface energy is shown in Table 1.

AFM results show the changes in surface relief and consequently the changes in roughness of films surface.

The images of the surface topography of the original PLA film surface and modified PLA films surface are shown in Fig. 1. The untreated PLA film has a smooth surface with the mean roughness of the surface profile equal to (0.00067 ± 0.0004) nm. Table 2 presents the results of measurement of surface roughness of the samples obtained using the software package Gwiddion 2.31. 1. It is clear that the roughness increased with increasing in the treatment time.

It is known that the plasma treatment leads to the degradation of the polymer material due to thermal and photochemical destruction and ion etching. The crystalline regions of the polymer are more stable to degradation in comparison with the amorphous ones.

Plasma treatment of the polymer films leads to a change in the surface topography so that the surface roughness increases. The longer period of treatment leads to the higher roughness of the films surface. The periodic cone-like structures appearing on the samples would be most likely due to the aforementioned etching effect of applied plasma (Fig. 1).

TABLE 1. The wettability of PLA film surface.

Sample	Contact angle (water)	Surface energy, mJ/m^2	Dispersive component, mJ/m^2	Polar component, mJ/m^2
PLA	$71.1^\circ \pm 1.68^\circ$	33.93 ± 1.09	18.16 ± 0.61	15.76 ± 0.48
PLA-20	$54.23^\circ \pm 1.28^\circ$	45.34 ± 0.99	14.70 ± 0.46	30.64 ± 0.53
PLA-60	$50.73^\circ \pm 1.35^\circ$	46.40 ± 0.70	8.97 ± 0.24	37.43 ± 0.46
PLA-120	$43.5^\circ \pm 3.21^\circ$	58.32 ± 2.54	5.30 ± 0.72	53.03 ± 1.82
PLA-HA	$40.2^\circ \pm 2.25^\circ$	61.20 ± 1.87	4.10 ± 0.81	57.10 ± 1.07

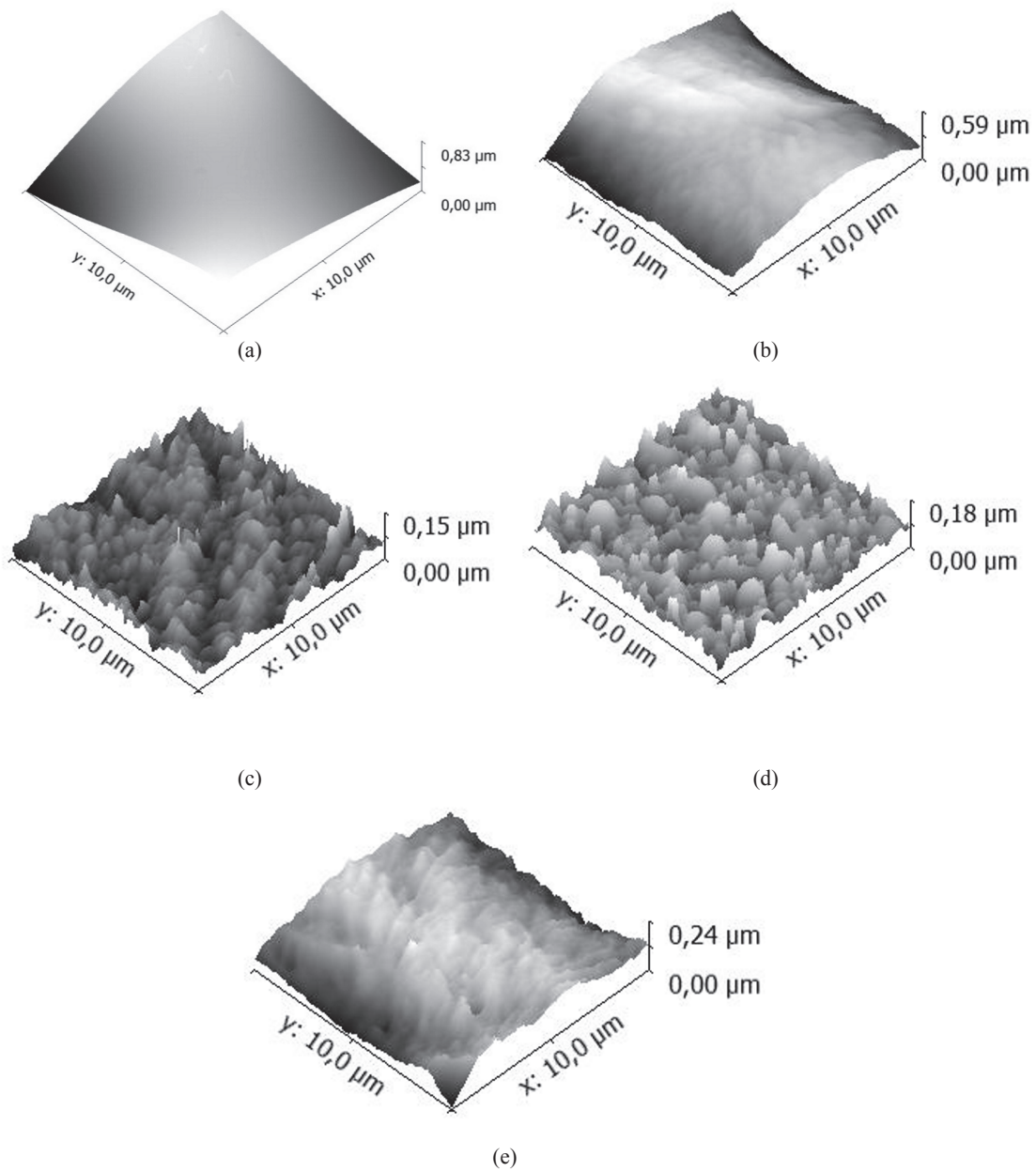


FIGURE 1. AFM images of the surface of (a) untreated and PLA films treated with plasma for (b) 20 s, (c) 60 s, (d) 120 s, (e) 120 s and HA

These structures presented a typical feature size and spacing at the order of few nanometers or smaller. The area of flat surface was reduced and the grooves appeared at higher heights, as shown by the data of the highest peak and the lowest groove. Similar types of topographical features upon air-plasma treatment were also observed by [11, 16]. The appearing of smoother surface of sample after HA immobilization would be most likely due to thin HA layer.

TABLE 2. The roughness of PLA film surface.

Sample	R_a , nm	R_{peak} , nm	$R_{grooves}$, nm
PLA	0.00067 ± 0.0004	0.0030 ± 0.0005	0.0020 ± 0.0003
PLA-20	3.27 ± 0.73	16.77 ± 1.07	7.87 ± 1.58
PLA-60	4.80 ± 0.87	25.90 ± 2.73	13.73 ± 1.18
PLA-120	5.43 ± 0.44	30.47 ± 3.49	15.23 ± 2.84
PLA-HA	1.16 ± 0.15	7.07 ± 0.44	3.60 ± 0.15

SUMMARY

Non-thermal atmospheric plasma treatment of PLA films with different duration provides an ability to design PLA films with diverse surface relief.

The modified materials have improved hydrophilicity that differs among the films obtained at various time of treatment. The most hydrophilic ones are obtained after the PLA treatment for 120 s and after HA immobilization. Thus, composites with tunable wettability could be produced.

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