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Dedicated to Professor Valer Farcasan on the occasion of his 95th anniversary

POLYLACTIC ACID CONTAINING SILVER PARTICLES

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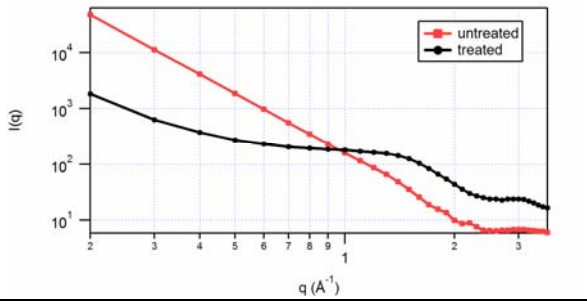
Nowadays one of the most widely used biomaterials is the polylactic acid (PLLA) which degrades into non-toxic components with a well-described degradation rate in vivo. This paper reports on a study concerning argon plasma followed by silver nitrate treatments on polylactic acid (PLLA) in order to obtain antimicrobial proprieties. Characterization methods like scanning electron microscopy, Fourier transform infrared spectroscopy and small angle X-ray scattering were used to study the modification induced by the two-step treatment in the polymer.



INTRODUCTION

A material which ensures the interface with biological systems to enhance, treat or replace any organ, tissue or function of the body is considered to be a biomaterial.[1] PLLA the US Food and Drug Administration approval for clinical use, [2,3] have been used as degradable surgical sutures for a long time.

The study of the materials surface plays a crucial role in determining the overall biocompatibility because it comes first in contact with biological environment. [4] A major influence on the attachment of cells, on the cell topology, on the spatial orientation of cell's cytoskeleton components and on many other important parameters is gained by surface morphology and its physiochemical properties.[5-7] PLLA is chemically inert and has no reactive side-chain groups, which makes it challenging in modifying its surface and bulk. PLLA is hydrophobic, with a static water contact angle of about 80◦ which leads to low cell affinity and can provoke anti-inflammatory response from the living host upon direct contact with biological fluids.[8-9] Non-thermal plasma treatments (plasma corona discharge, dielectric barrier discharge, etc.) are often used for inserting chemically reactive functional groups on polymeric substrates to increase the biocompatibility.[10] While non-thermal plasma surface treatments are preferred for simplicity, modification of PLLA under thermal plasma conditions remain less popular owing to inherent difficulties associated with identifying appropriate plasma conditions for a specific(bio)-material surface treatment.[11] Radio-frequency (RF) plasma is a common way to create high biocompatible surfaces and biostable polymeric materials.[10-12]

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The silver-ion treated polymers in reducing infections are included in the most actual attempts, but the methods of obtaining silver ions at the polymer surfaces differ and the antimicrobial activity time differs.

The aim of the present work was to obtain silver-treated polymer in order to reduce infections in patients. Silver-containing polymers surfaces were obtained by using a method in two steps: argon plasma treatments followed by silver nitrate chemical modification.[13-18]

EXPERIMENTAL

The two steps experimental method of PLLA assures the optimal content of silver at the polymer surface. The first step is the plasma treatment, performed in an EMITECH RF plasma device at a power of 40 W for 1 min. As background gas was used argon at a pressure $p = 10^{-3}$ mbar, the polymer being immersed into the plasma that fills the gas vessel. For the second step, the plasma-treated polymer was immersed for 7 days at room temperature in a 0.1 m solution of $AgNO_3$, protected from light. Then the samples were rinsed with deionized water and analyzed by the different characterization techniques.

FTIR analyses were performed in the range 600-4000 cm^{-1}. The spectra were recorded on a BRUKER VERTEX 70 spectrometer at a resolution of 2 cm^{-1} at incidence angle of 45°. The signal-to noise ratio was improved by coadding 128 scans per spectrum.

Scanning electron microscopy (SEM) was used to analyze the surface morphology and topography. Prior to SEM analysis untreated and modified PLLA substrates were sputter-coated with an ultra-thin layer of gold (JEOL-JFC) for 30s at 20mA. Afterwards samples were analyzed by SEM (JEOL-JSM- 6400F) at an accelerating voltage of 15kV.

Small angle X-ray scattering (SAXS) experiments were performed on a Bruker Nanostar instrument by using a Cu sealed tube fine-focus X-ray source (Kα = 1.54184Å with a potential of 40 kV and a current of 35 mA). The detector was set at 107 mm from the sample and the sample chamber and x-ray paths were evacuated. The instrument was controlled with the SAXS software suite and the data was collected in the still (add) mode.

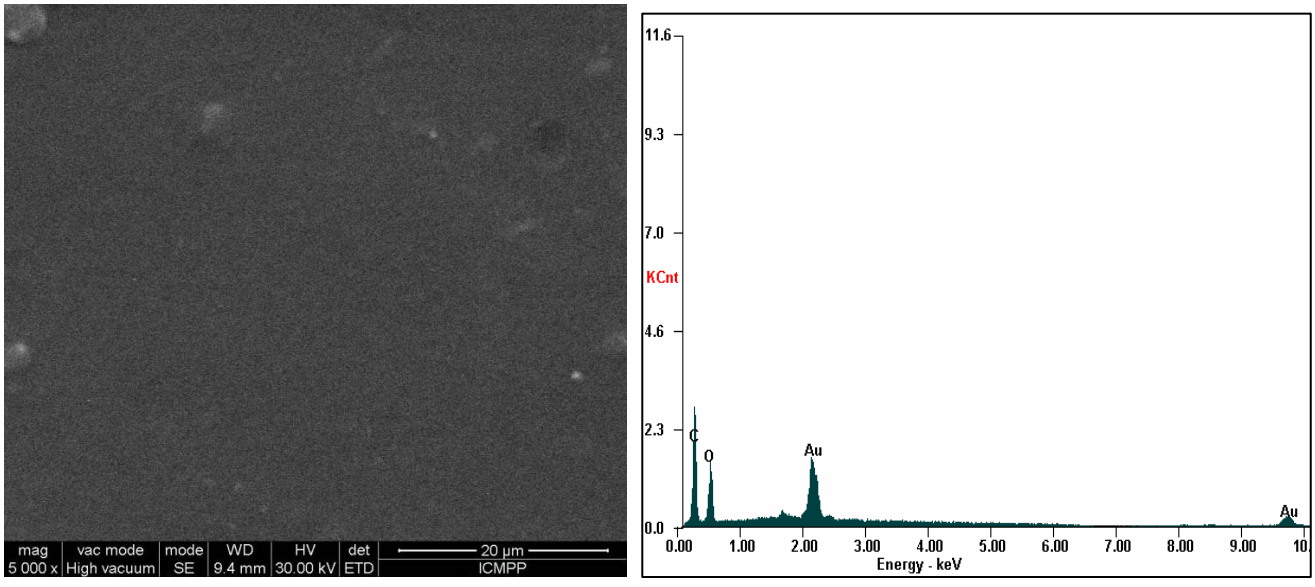
RESULTS AND DISCUSSIONS

SEM image for pristine material form Fig. 1a) revealed a uniform surface without any important imperfections. SEM images of treated PLLA from Fig. 2a show a surface with small "grains" of different dimensions as a result of plasma treatment and silver ions presence. From SEM-EDAX measurements a slightly decreasing of carbon concentration after the two step treatment can be observed, as well as the presence of silver in a 3.24% concentration (Table 1 and Figs. 1 and 2b).

Table 1

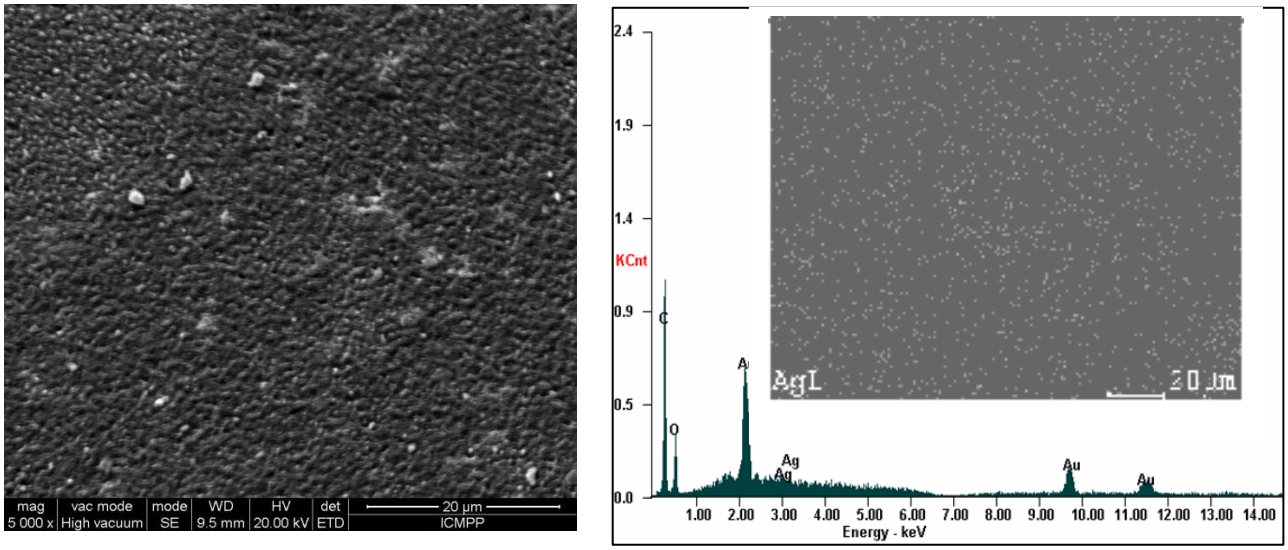
Composition of studied samples

Element (%)	***CK***	***OK***	***AgL***	***AuL***
untreated	58.37	28.13	-	13.50
treated	53.31	29.43	03.24	14.02



(a) (b)

Fig. 1 – SEM results for pristine PLLA: (a) SEM image; (b) EDAX measurements.



(a) (b)

Fig. 2 – SEM results for treated PLLA: (a) SEM image; (b) EDAX measurements.

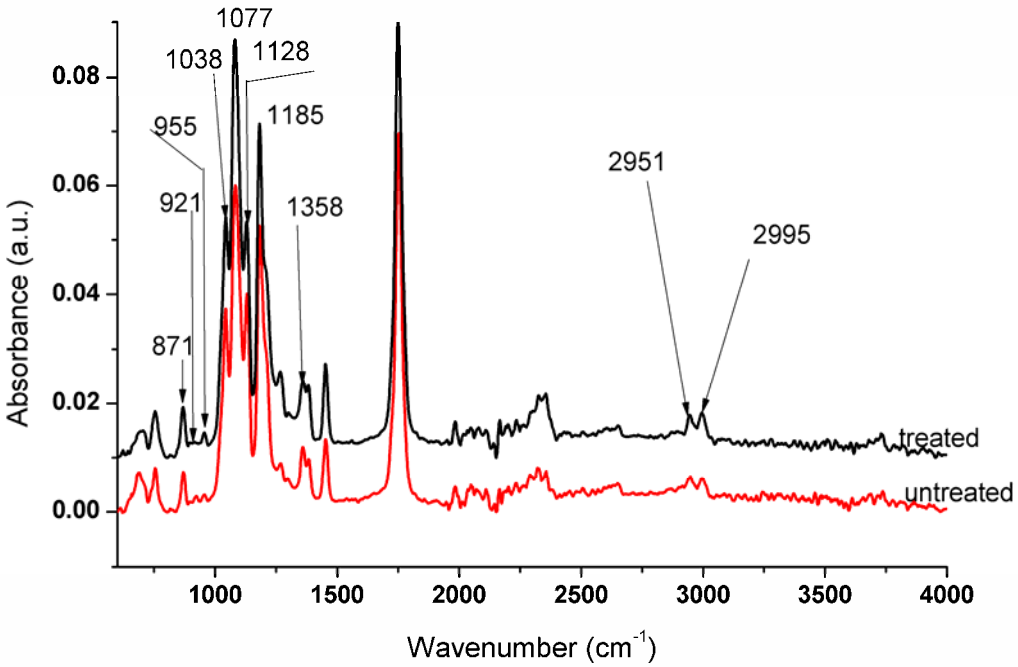
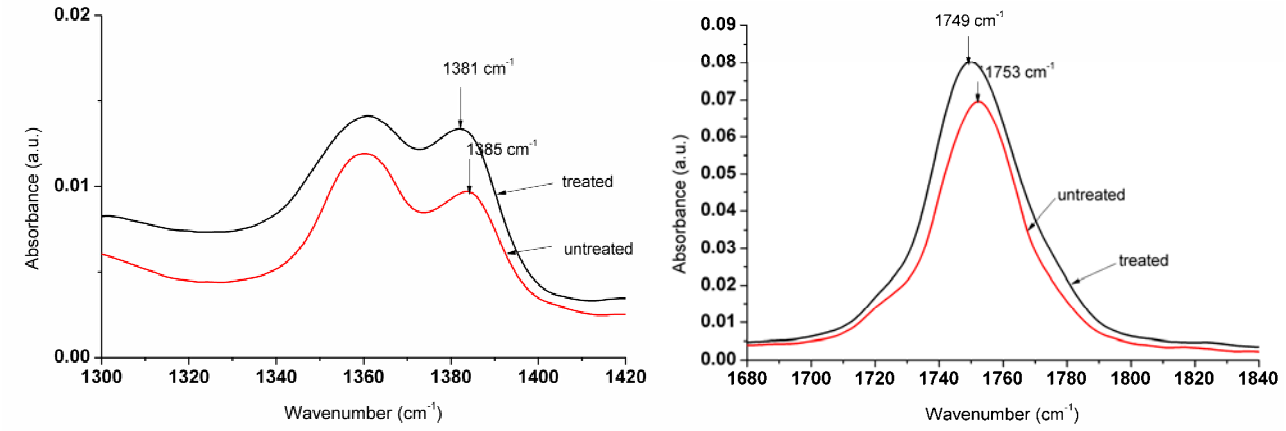


Fig. 3 – FTIR spectra of the studied samples.

Fig. 3 shows the IR spectra of the studied samples. The typical spectrum of PLLA: peak at 1749 cm^{-1} is given by the stretching of C = O; the 1185 and 1077 cm^{-1} bands are attributable to C–O–C asymmetric and symmetric stretchings, respectively. The peak at 1128 cm^{-1} is ascribable to the C–H (of CH_3 groups) rocking mode, while the peak at 1038 cm^{-1} is caused by C–CH_3 stretching. After the treatment we can observe an increase in the degree of PLLA crystallinity. There is an increase in 1381 cm^{-1} (Fig. 4a) and in the 1749 cm^{-1} (the 1810–1710 cm^{-1} region) band intensities (Fig. 4b). A shift with 4 cm^{-1} to lower wavenumbers of those bands can be observed. Those bands are assigned to the carboxylic groups and demonstrate an increase of those functional groups quantity after plasma treatments and the presence of silver ions at the polymer surface. It is known that the crystal modification of PLLA is easily formed from the melt,[19,20] therefore the increase in the intensity of the absorption bands characteristic for the crystal structure of PLLA is an indication that the process of PLLA crystallization is caused by heating of the polymer

surface as a result of the interaction with high-energy plasma particles.

Fig. 5 representing the SAXS measurements shows a significantly changes in the treated polymer pattern compared with the pristine, indicating the presence of Ag structures in the treated samples. From the Guinier analysis which refers to the analysis of the SAXS scattering curve at very small scattering angles, the direct estimation of the radius-of-gyration, Rg was obtained. From Bruker NanoFit software, the fitting of the obtained SAXS profiles with spherical models gives the size distribution profiles for Ag structures in the case of treated polymer (Rg = 80 nm).



(a) (b)

Fig. 4 – FTIR bands of the carboxylic group.

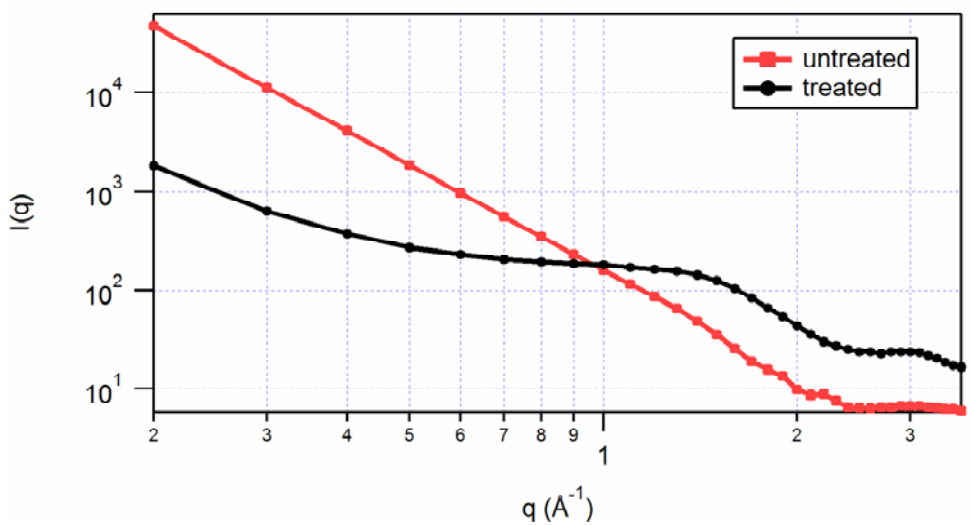


Fig. 5 – SAXS measurements.

CONCLUSIONS

This work demonstrates that the argon plasma followed by silver nitrate treatment is an appropriate method for obtaining silver-containing PLLA. The EDAX-SEM, FTIR and SAXS methods confirm the presence of silver particles in the treated PLLA. This surface modification can therefore enhance PLLA usability as a biomaterial without the risk of infection in patients.

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