Matrix-assisted pulsed laser evaporation of poly(D,L-lactide) for biomedical applications: effect of near infrared radiation

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Abstract. The deposition of thin films of poly(D,L-lactide) (PDLLA) by using the matrix-assisted pulsed laser evaporation (MAPLE) technique is investigated. PDLLA is a highly biocompatible and biodegradable polymer, with wide applicability in the biomedical field. The laser wavelength used in the MAPLE process is optimized to obtain a good-quality deposition. The structure of the polymer film is analyzed by Fourier transform infrared spectroscopy (FTIR). It is found that the chemical structure of PDLLA undergoes little or no damage during deposition with near-infrared laser radiation (1064 nm). It is thus confirmed that at this wavelength, the MAPLE technique can be applied for fragile biopolymer molecules, which are easily damaged by other laser radiations (UV radiation). This method allows future development of tailored polymer coatings for biomedical applications. © *2008 Society of Photo-Optical Instrumentation Engineers.* [DOI: 10.1117/1.2830660]

Keywords: matrix-assisted pulsed laser evaporation; biopolymers; coatings; poly(D,L-lactide); thin films.

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1 Introduction

Synthetic polyesters, such as polylactides and polyglycolides and their copolymers, have found a wide range of applications in the biomedical field thanks to their biocompatibility and biodegradability.[1,2] In particular, polylactides, derived from lactic acid, degrade in the human body via a hydrolytic reaction. This reaction produces first oligomers and then lactic acids, of which the L-lactic acid is a natural intermediate in carbohydrate metabolism. The monomer unit of polylactide, shown in Fig. 1, includes a chiral carbon. The mechanical properties of such a polymer depend on its stereoregularity. Optically pure poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are semicrystalline materials, while poly(D,L-lactide) (PDLLA), consisting of racemic lactate units, is amorphous. Although the mechanical properties of PLLA and PDLA are superior with respect to PDLLA, those polymers are brittle at room temperature.[3] Moreover, the degree of crystallinity of polylactides influences their degradation rate in biological fluids, i.e., amorphous PDLLA exhibits the highest degradation rate. Due to its relative high rate of degradation, and the absence of late foreign body reactions due to crystalline remnants,[4] PDLLA has been extensively studied for *in-vivo* biomedical applications, such as osteosynthesis temporary implant materials[4] and composite scaffolds,[5] controlled release of drugs,[6] proteins and antigens,[7] resorbable sutures,[8] and lately as coating for improving mechanical properties of brittle bioactive glass scaffolds for bone tissue engineering.[9]

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For some of these current or potential applications, in particular for drug delivery systems and biomedical coatings, a reliable technique for depositing biopolymer films, which allows a careful control of their thickness and structure, would be highly beneficial.

Recently, a new technique has been developed which is particularly well suited for polymer thin film deposition. The matrix-assisted pulsed laser evaporation (MAPLE) technique was first developed at the U.S. Naval Research Laboratory,[10] inspired by the pulsed laser deposition (PLD) technique. In PLD, a solid target of the material is ablated by a pulsed laser beam and the ablated material deposits onto a nearby substrate, forming a film. PLD is largely used for inorganic thin film deposition,[11,12] although some addition polymers[13,14] have been also successfully deposited. However, the ablation of addition polymers seems to proceed via a chain scission, ablation of oligomers, and repolymerization. This is clearly not possible in general for condensation polymers or other organic molecules.

Contrary to PLD, in MAPLE the target is not the bulk material itself, but a frozen solution of the molecules to be deposited in a highly volatile and light-absorbing solvent. When the laser impacts the target, a plume is formed. The mechanism of ablation is still under study, but it is thought that this highly nonlinear process proceeds through a photochemical or photothermal process[15,16] that produces phase explosion;[17,18] as the solvent evaporates, the polymer molecules attain sufficient kinetic energy through collisions with the evaporating solvent molecules to be transferred into the gas phase.

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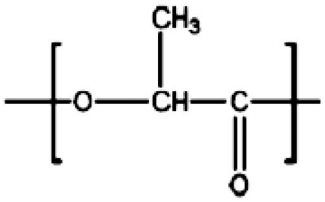

Fig. 1 Molecular structure of poly(D,L-lactide).

The plume is composed by the volatile solvent molecules and the bigger polymer solute molecules. The volatile solvent molecules are pumped away by a vacuum pump, while the heavier polymer molecules deposit onto the substrate. This technique is particularly well suited for biopolymers: in MAPLE, most of the laser radiation is absorbed by the solvent, thus hindering the photochemical damage that a direct irradiation of these fragile macromolecules is likely to produce.

The MAPLE technique allows accurate control of film thickness by varying several parameters, such as the concentration of the target solution, the laser power, and the deposition time.

For the deposition of biopolymer thin films, the MAPLE technique is a suitable alternative to solution-based processing techniques due to the following facts.

1. The MAPLE is a noncontact deposition technique, thus eliminating a major source of contamination, i.e., the solvent and its impurities, and it can be integrated with other sterile processes.

2. The accurate thickness control is beneficial to tailor the *in-vivo* degradation rate of PDLLA, being the time of degradation proportional to the thickness of the film.

3. The MAPLE technique allows multiple-layer depositions without the risk of redissolving the first deposited layer. This characteristic offers interesting perspectives for multilayer deposition of composite coatings.

Many biopolymers have already been successfully deposited by MAPLE,[19–22] including PDLLA for drug delivery system applications.[23]

This work deals with preliminary experiments for PDLLA thin film deposition by the MAPLE technique, with the ultimate objective of developing optimal coatings for biomedical applications. The main difference with the PDLLA thin films already obtained is the laser wavelength used in this investigation. Until now, following PLD trends, only UV laser light or resonant infrared (RIR)[24] laser light, in which the laser radiation is resonant with some vibrational mode of the molecule to deposit, have been utilized. The use of a different laser radiation, as near-infrared, resonant with the solvent rather than with the molecule to deposit, can be beneficial for biopolymer deposition because of pronounced decomposition of the polymer molecules induced by UV light[25] and the necessity of low absorption from the polymer. The possibility of ablating a frozen target and depositing a thin film with this wavelength radiation has been already explored by our research group.[26,27]

For a successful MAPLE deposition, a strongly light absorbing matrix should be used in combination with low absorption by the guest material. Furthermore, the solvent and concentration should be selected so that the guest material can dissolve to form a dilute, particulate-free solution. These requirements are usually difficult to fulfil completely. In our experiments, the laser wavelength of 1064 nm was chosen to minimize the damage to the polymer, which can be damaged by UV radiation. Chloroform was chosen as the solvent, since on one hand it is able to dissolve the polymer forming a clear solution, and on the other hand it can absorb the laser radiation because it has an absorption band, albeit weak, between 1050 and 1080 nm.[28]

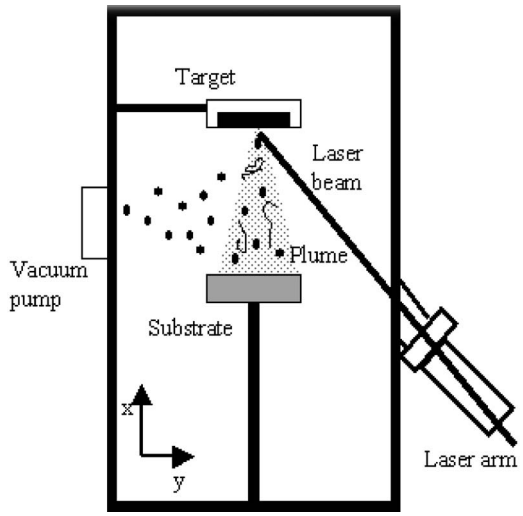

Fig. 2 MAPLE setup, top view. The target movement is in the *yz* plane, where the *z*-axis is normal to the *xy* plane.

The use of 1064-nm laser radiation should favor the deposition of the intact polymer, because the mechanism of ablation is thought to be substantially different than that observed with UV light:[16] in the latter, single or multiphoton absorption leads to electronic transitions that can cause photofragmentation. In the former, anharmonic vibrational modes are excited, generating the thermal energy required for vaporization.

2 Experimental

2.1 *Materials*

PDLLA (purasorb PDL) of inherent viscosity 1.92 dl/g was purchased from Purac Biochem (Gorinchem, The Netherlands). $CHCl_3$ (purchased from Sigma-Aldrich) of >99% purity was used as solvent.

Two sets of solutions of PDLLA in $CHCl_3$ were prepared, one set containing 0.5 wt% of PDLLA and the other set containing 2 wt%, by pouring the solvent on the weighted polymer and allowing it to dissolve for two hours. Manual stirring was not possible to dissolve the polymer, because of the high viscosity of the solvated polymer flakes.

2.2 *Matrix-Assisted Pulsed Laser Evaporation Procedure*

Our MAPLE deposition system, depicted in Fig. 2, consisted of a cylindrical vacuum deposition chamber. The target holder was a copper cup of about 2-ml capacity. It was fitted with a 2-D computer-controlled movement system, allowing the full

Table 1 Laser wavelength (λ), fluence (F), number of pulses, concentration, and visible features of the MAPLE-deposited PDLLA films.

Sample	λ (nm)	F (mJ/cm2)	nr pulses	Concentration wt%	Film
PDLLA1	1064	990	65,000	0.5	Visible
PDLLA2	532	213	120,000	0.5	Not visible
PDLLA3	355	470	63,000	0.5	Not visible
PDLLA4	1064	1140	60,000	2	Visible
PDLLA5	1064	811	120,000	2	Visible
PDLLA6	532	270	120,000	2	Not visible
PDLLA7	532	270	180,000	2	Not visible

scan of a rectangular area to avoid overheating and drilling. The target cup was in thermal contact with a liquid nitrogen tank, and the target (PDLLA in $CHCl_3$) was frozen *in situ*. The substrate holder, holding a KBr pellet for allowing Fourier Transform Infrared (FTIR) analysis, was placed parallel to the target surface at a maximum distance of 11 cm. Before filling the liquid nitrogen tank, the deposition chamber was closed and filled with helium to remove atmospheric moisture. The target temperature was then reduced up to 103 K. After the solidification of the target, the helium flux was stopped and the pressure reduced up to 10^{-5} Pa. The laser was then started and the substrate brought at the minimum distance position (1 cm) from the target. During this procedure, about 1500 laser pulses impacted the target, ablating possible impurities or residual moisture on the surface.

The laser was a common Q-switched Nd:YAG laser connected to the chamber by means of an articulated arm and passing through an optical window. The laser was operated at three different wavelengths: 1064 nm (fundamental harmonic), 532 nm (second harmonic), and 355 nm (third harmonic). The laser pulse duration was 7 ns with a repetition rate of 10 Hz. The laser spot on the target, which was elliptical because of the 45-deg laser incident angle, was 0.32 cm^2 for 1064-nm, 0.41 cm^2 for 532-nm, and 0.030 cm^2 for 355-nm laser wavelength. The laser fluence was varied between 213 and 1140 mJ/cm^2.

The films obtained, together with the deposition parameter details and the solution concentration, are reported in Table 1.

2.3 *Characterization*

To detect possible modification of the monomer unit chemical structure of PDLLA, FTIR spectroscopy analysis was carried out. FTIR spectroscopy allows the determination of a short to medium range structure of a material, thus giving information essentially on the repeat unit of a polymer. FTIR absorption spectra of the films deposited on KBr pellets were recorded, in the 4000 to 400 cm^{-1} range, using a spectrometer equipped with a deuterated triglycine sulphate with potassium bromide windows (DTGS KBr) detector. A spectral resolution of 2 cm^{-1} was chosen. The spectrum for each sample represents an average of 64 scans, which were corrected for the spectrum of the blank KBr pellet.

The microstructure of the samples was analyzed by using a LEO Gemini field emission gun scanning electron microscope (SEM), coupled with energy dispersive spectroscopy (EDS). Samples were chromium sputtered and observed at an accelerating voltage of 20 kV.

3 Results and Discussion

With both sets of solutions (see Table 1), a visible film formed only using 1064-nm laser radiation. This is not surprising for 532-nm radiation, since PDLLA and $CHCl_3$ are both optically transparent and do not absorb green light. On the other hand, the 355-nm radiation is not efficiently absorbed by $CHCl_3$, which presents its maximum UV absorption around 245 nm and only 0.003 times this value at 280 nm, as specified by the supplier. On the contrary, chloroform presents an absorption band in its NIR absorption spectrum centred at around 1064 nm.[28]

FTIR spectra of the three visible films (PDLLA1, PDLLA4, and PDLLA5) are shown in Fig. 3(a) in the 4000 to 400 cm^{-1} range. The spectrum of a film obtained by casting a drop of solution on a KBr pellet is also shown for comparison. The FTIR spectra of all the other samples did not show any peak emerging from the baseline and are not reported.

The spectra of PDLLA5 and drop cast films are normalized for the maximum intensity band at 1756 cm^{-1} to make them comparable in terms of band intensities. Furthermore, a baseline was subtracted from each spectrum.

From the spectra in Fig. 3(a), it is possible to observe that all the bands of PDLLA5 film coincide in position and relative intensity with the bands of the drop cast film, and no new bands due to decomposition appear. This means that little or no chemical modification with respect to the bulk polymer occurred during MAPLE deposition with the 1064-nm wavelength and 811-mJ/cm^2 laser radiation. PDLLA4, obtained with higher laser fluence but a smaller pulse number, shows only a very weak peak at 1756 cm^{-1} and no bands are detectable for the PDLLA1 sample, obtained at higher fluence and a lower pulse number and solution concentration, though the film is visible.

In Fig. 3(b), the spectra of drop cast PDLLA and PDLLA5 are reported alone in a smaller wavenumber range (2000 to 1000 cm^{-1}) to show the precise correspondence of all the bands in terms of wavenumber. The spectra are normalized as before, but no baseline was subtracted. To show the intensity match between the two spectra, for each spectrum the integrated peak area of each peak was calculated and divided by the peak area of the 1756-cm^{-1} band. The results are reported in Table 2, together with the band assignments.[29] The peak areas were calculated by integrating between the onset and the offset of each peak.

In spite of the inaccuracy of the method, especially in establishing the precise point of onset and offset of the peaks, the match between the peak relative intensities is surprisingly good.

It is then demonstrated that with 1064-nm radiation, the chemical structure of the biopolymer monomer unit underwent little or no modification. As shown in the literature,[23] good results were obtained for MAPLE deposition of PDLLA

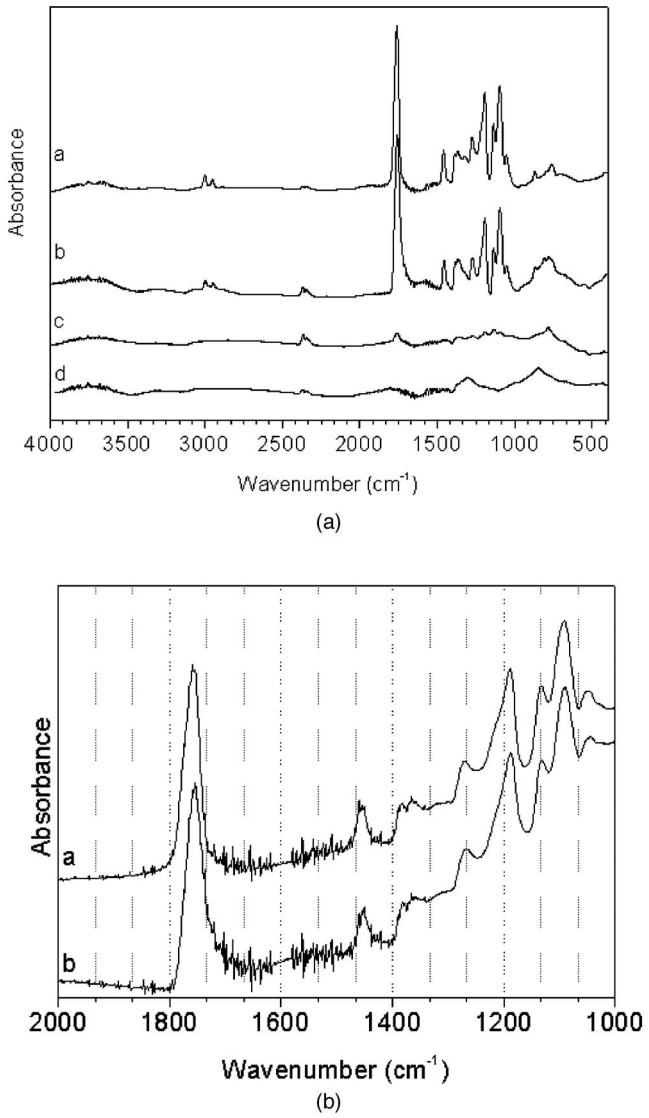

Fig. 3 (a) FTIR spectra between 4000 and 400 cm^{-1} of drop cast PDLLA (trace a), PDLLA5 (trace b), PDLLA4 (trace c), and PDLLA1 (trace d). (b) FTIR spectra of drop cast PDLLA (trace a) and PDLLA5 (trace b) between 2000 and 1000 cm^{-1}.

deposited with 193-nm radiation; the films giving FTIR spectra were well correlated with that of the drop cast PDLLA. However, some mismatch between the spectra was present, in terms of relative intensity of the low wavenumber bands. It must be pointed out that FTIR spectroscopy is a short-medium range technique, and it does not allow for determining whether the polymer remained intact in its molecular weight as well.

Figure 4 shows SEM images of PDLLA1 [Figs. 4(a) and 4(b)], PDLLA4 [Figs. 4(c) and 4(d)], and PDLLA5 [Figs. 4(e) and 4(f)] coatings at low and high magnifications. For PDLLA1, and PDLLA4, the substrate (KBr) features are visible. KBr pellets are formed by grains with roughness of 100 to 200 nm on the grain and about 1 μm on the grain border, as determined by atomic force microscopy (AFM) (not shown).

Table 2 Peak position, intensity (VS: very strong, S: strong, M: medium, W: weak, VW: very weak), and band assignment of PDLLA. Integrated areas ratio: A_0= integrated area of the 1756-cm^{-1} FTIR band of the drop cast PDLLA film; Ai= integrated area of the ith FTIR peak of the drop cast PDLLA film; A'_0= integrated area of the 1756-cm^{-1} FTIR band of PDLL5; and A'_i= integrated area of the ith FTIR peak of PDLL5.

Peak position	I	Band assignment	A_i/A_0	A'_i/A'_0
2985	W	C-H asym. stretch of -CH_3	0.04	0.033
2940	W	C-H sym. stretch of -CH_3	0.025	0.016
1880	VW	CH stretch of -CH	-	-
1756	VS	C=O stretch	1	1
1454	M	CH_3 asym. bend	0.14	0.14
1385	M	CH_3 sym. bend	0.13	0.12
1362		C-H bend of -CH+ CH_3 sym. bend		
1272	W	C-O-C stretch+ CH bend	0.076	0.086
1188	S	C-O-C asym. stretch+CH_3 asym. rocking	0.41	0.34
1133	M	CH_3 asym. rocking	0.1	0.094
1090	S	C-O-C sym. stretch	0.29	0.22
1048	W	C-CH_3 stretch	0.054	0.037
862	VW	C-COO stretch	-	-
753	VW	C=O bend	-	-

For sample PDLLA1, obtained at a lower concentration of the target, it is seen that no film was formed. This is in accordance with FTIR measurements, which show no specific band for this sample. Only a few aggregates of the polymer film can be seen on the substrate. On the contrary, sample PDLLA4 (higher concentration and laser fluence) is seen to be almost homogeneously coated by the polymer, which forms aggregates of a few microns in size. The KBr grain borders are still visible, indicating a film thickness of less than 1 μm. Finally, sample PDLLA5 appears homogeneously deposited on the substrate, forming aggregates of 1 to 10 μm. The KBr grain borders are completely hidden under the polymer coating. PDLLA5 coatings were obtained at the same target concentration used for PDLLA4, at lower laser fluence but using a double-pulse number. The more homogenous and thicker coating obtained is therefore related to the higher pulse number. It should be noted that the formation of polymer aggregates by MAPLE deposition has been already observed for polyethylene glycol (PEG),[30] another biotechnologically important polymer. MAPLE-deposited PEG showed aggregates of 5 to 10 μm in diameter, and it was demonstrated that, although it is possible that particles were transferred individually, the morphology of the film depended on the substrate temperature.[31] They concluded that uniform

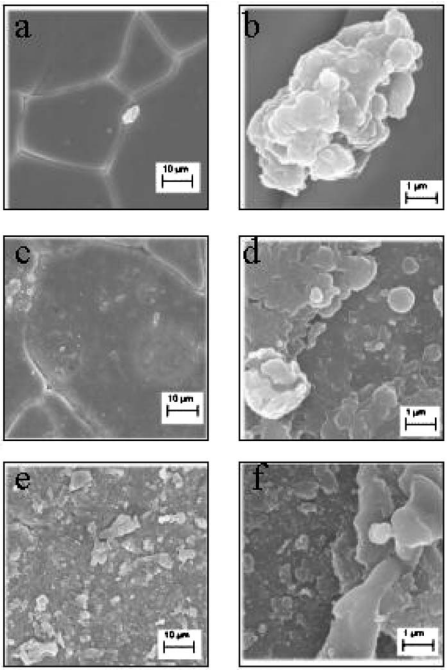

Fig. 4 SEM images of PDLLA deposits at different magnifications: (a) and (b) PDLLA1, (c) and (d) PDLLA4, (e) and (f) PDLLA5.

films of PEG could not be easily obtained by MAPLE, compared with high quality film produced by other methods.

Obtaining a rough surface formed by polymer aggregates can be a drawback, in general, when trying to develop homogeneous films. In the present case, however, the presence of a given surface roughness can be an advantage due to the potential application of the film as coating for tissue engineering scaffolds. A rough surface exhibiting topographical features is considered to favor cell adhesion.[32]

4 Conclusions

PDLLA thin films are successfully obtained by the MAPLE technique using a 1064-nm laser wavelength. We demonstrate that with this wavelength, it is possible to obtain better results than with UV radiation in the case of fragile biopolymer molecules, which are easily damaged for interaction with UV radiation. In particular, FTIR spectroscopy analysis is indicative of little or no damage of the chemical structure of the macromolecule's monomer unit. The microscopic homogeneity and surface topography of the deposited PDLLA films are investigated by SEM.

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