

## PLA-PMMA blends: A study by XPS and ToF-SIMS

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### Abstract

This paper reports which are the possibilities of quantification by time of flight secondary ion mass spectrometry (ToF-SIMS) for some polymer blends. In order to assess the composition of the mixtures, we studied first different poly(L-lactide)/polymethylmethacrylate (PLA/PMMA) blends by X-ray photoelectron spectroscopy (XPS), this technique being quantitative. By XPS fitting of the C 1s level, we found a very good agreement of the measured concentrations with the initial compositions. Concerning ToF-SIMS data treatment, we used principal component analysis (PCA) on negative spectra allowing to discriminate one polymer from the other one. By partial least square regression (PLS), we found also a good agreement between the ToF-SIMS predicted and initial compositions. This shows that ToF-SIMS, in a similar way to XPS, can lead to quantitative results. In addition, the observed agreement between XPS (60–100 Å depth analyzed) and ToF-SIMS (10 Å depth analyzed) measurements show that there is no segregation of one of the two polymers onto the surface.

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### 1. Introduction

Nowadays organic polymers and their derivatives are one of the most important class of material constituting the surrounding objects in our life, like computer, refrigerators, plastic packaging, . . . They are characterized by a wide range of chemical and mechanical properties (resistance, . . .), and by a low cost in general. One way to obtain new material properties, is to associate polymers into copolymers, or in polymer blends. It seems that blending pristine polymers is more interesting, because it is an easier and more economic way to get new polymer materials.

This work aims at applying ToF-SIMS for the surface quantification of PLA/PMMA blends. Such kinds of polymer blends are characterized by interesting bulk and surface properties, like their biodegradability, biocompatibility, and the possibility of using such materials for in vitro drug agent release materials [1–4]. The literature references also the hydrolytic degradation kinetics of PLLA [5]. First of all, we studied these mixtures by XPS, which is quantitative, and

then compared these results with ToF-SIMS measurements [6].

### 2. Experimental

#### 2.1. Chemicals and materials

Poly(L-lactide) (PLA) was synthesized by the SMPC laboratory (D, L-LA, Mn = 20,000 – Mw/Mn = 1.36). Polymethylmethacrylate (PMMA) was purchased from Polysciences Inc. (MW 75,000), chloroform >99.9% HPLC grade was bought from Aldrich and methanol >99% from Chem Lab. The substrates used were 1 cm<sup>2</sup> square coupons taken from silicon wafers.

#### 2.2. Sample preparation

PLA/PMMA blend samples were prepared from corresponding solutions formed by dissolving a total amount of polymer of 10 mg in chloroform. Silicon pieces were previously rinsed with methanol, and then spin-casted with the polymer solutions, and were allowed to dry in ambient atmosphere during 24 h. After that time, the polymer samples were studied by XPS and ToF-SIMS. The final compositions studied were, as expressed

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in terms of % of PLA: 100%, 80%, 50%, 20% and 0% (=100% PMMA).

### 2.3. Sample characterization and data treatment

XPS was used to control the elemental composition of the polymer blend surfaces. All reported spectra were recorded at a 90° take-off angle relative to the substrate with a VG ESCALAB 220iXL spectrometer using the monochromatised Al K $\alpha$  radiation (1486.6 eV). The core level lines analyzed (C 1s and O 1s) were referenced with respect to the C 1s binding energy conventionally set here at 285.0 eV and characteristic of aliphatic moieties. XPS results were analyzed by curve-fitting of the C 1s signal by using mixed Gaussian–Lorentzian curves after a linear background subtraction.

ToF-SIMS measurements were carried out on an ION TOF IV spectrometer equipped with an argon analysis ion gun. The analysis conditions were 10 keV, 1 pA, pulsed Ar<sup>+</sup> beam at a 45° incidence, rastered over 300  $\mu\text{m}$   $\times$  300  $\mu\text{m}$ , during 100 s, insuring in this way analysis under quasi-static conditions. All secondary ion signals were normalized by the total ion intensity recorded in the whole spectrum. We took six spectra per sample, and the corresponding ToF-SIMS results were analyzed by principal component analysis (PCA). The peaks in the negative spectra considered were for PLA:  $m/z = 71$  (C<sub>3</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>), 87 (C<sub>3</sub>H<sub>5</sub>O<sub>3</sub><sup>-</sup>), 89 (C<sub>3</sub>H<sub>5</sub>O<sub>3</sub><sup>-</sup>), 143 (C<sub>6</sub>H<sub>7</sub>O<sub>4</sub><sup>-</sup>), 145 (C<sub>6</sub>H<sub>9</sub>O<sub>4</sub><sup>-</sup>), 159 (C<sub>7</sub>H<sub>11</sub>O<sub>4</sub><sup>-</sup>), 215 (C<sub>9</sub>H<sub>11</sub>O<sub>6</sub><sup>-</sup>) and 217 (C<sub>9</sub>H<sub>13</sub>O<sub>6</sub><sup>-</sup>). For PMMA, the peaks studied were:  $m/z = 55$  (C<sub>3</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>), 85 (C<sub>4</sub>H<sub>5</sub>O<sub>2</sub><sup>-</sup>), 141 (C<sub>8</sub>H<sub>13</sub>O<sub>2</sub><sup>-</sup>) and 185 (C<sub>9</sub>H<sub>13</sub>O<sub>4</sub><sup>-</sup>) [7–9]. The corresponding data were mean-centered and scaled, and then partial least square (PLS) modeling was used to predict compositions of the polymer blends. The software that we used was SIMCA-P from Umetrics AB.

## 3. Results

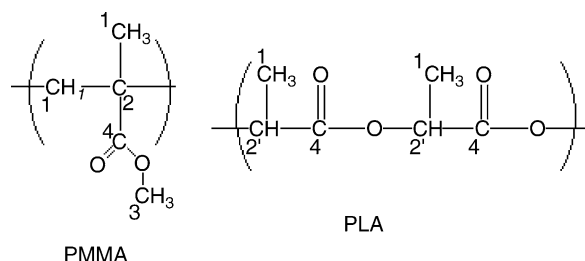
We will present in the sequel first XPS results to quantify the different PLA/PMMA blends, and then we will expose the ToF-SIMS results to evaluate the possibilities of quantification by this technique.

### 3.1. XPS measurements

First, we studied atomic relative percentages of the different compositions blends, as cited in Section 2. From the results presented in Table 1, we can observe that the experimental and

Table 1  
Relative atomic concentrations (%), experimental and theoretical C/O ratio, for 100% PLA, 80% PLA, 50% PLA, 20% PLA and 0% PLA samples

Polymer sample (% PLA)	C 1s (%)	O 1s (%)	C/O experimental	C/O theoretical
0	73.54	26.46	2.78	2.5
20	72.61	27.39	2.65	2.3
50	69.88	30.12	2.32	2.0
80	67.83	32.17	2.11	1.7
100	64.69	35.31	1.83	1.5



Scheme 1.

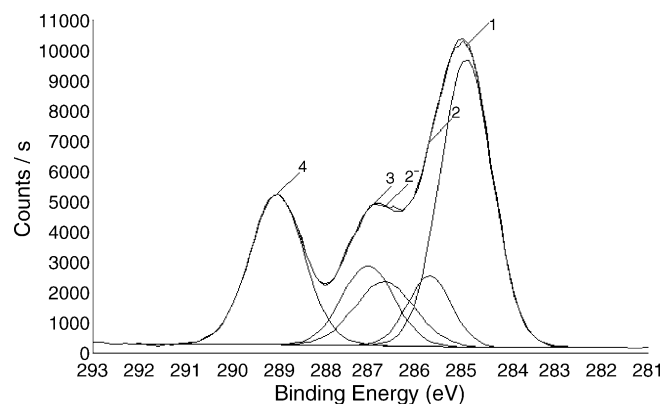


Fig. 1. XPS C 1s spectrum of 50% PLA sample.

theoretical C/O ratios are approximately equal, the slight discrepancy being due to adventitious hydrocarbon contamination coming from the contact of the samples with the ambient atmosphere.

Second, we analyzed by curve-fitting the C 1s line of the polymer blends. For such analysis, we deconvoluted the C 1s spectrum of 0% PLA and 100% PLA in order to determine the components characteristic of each compound (Scheme 1; Fig. 1). In this way, we found four components in the C 1s spectrum of pure PMMA sample (“0% PLA sample”), and three for pure PLA sample. More precisely, the carbon atom labeled 2 (in pure PMMA) is located at 286.7 eV, and the one labeled 2' (in pure PLA) is located at 287.0 eV. We based our calculations on these components in each blend, to determine the surface composition (Table 2).

We can observe from Table 2 that there is a good agreement between theoretical and experimental compositions. XPS analyzing 60–100 Å depth, these results mean that there is no segregation of one of the components over this depth.

Table 2  
Relative atomic concentrations (%), experimental and theoretical C/O ratio, for 100% PLA, 80% PLA, 50% PLA, 20% PLA and 0% PLA samples

Theoretical composition (% PLA)	Experimental composition (% PLA)
0	0
20	22.2
50	48.1
80	75.8
100	100

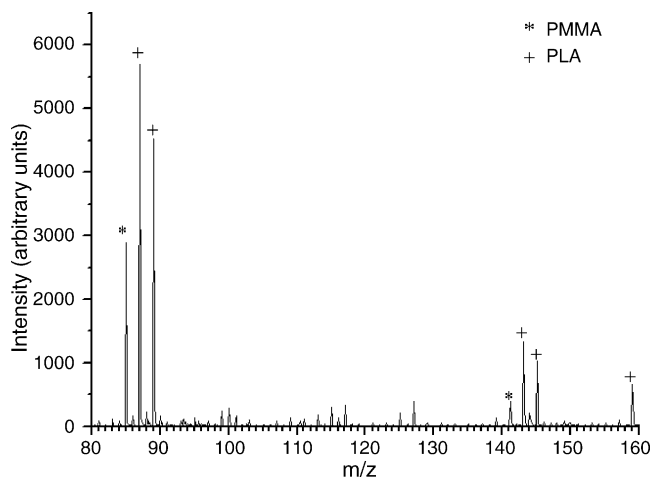


Fig. 2. ToF-SIMS spectrum from  $m/z = 80$  to 160 of a 50% PLA sample.

### 3.2. ToF-SIMS measurements

As shown in the peak list previously exposed (cf. Section 2), PLA/PMMA blends are characterized by a complex ToF-SIMS spectrum, with fragments of similar nature, because namely these two compounds are both hydrocarbonated polyester. A typical spectrum of a 50% PLA–50% PMMA sample is shown in Fig. 2. The peaks mentioned therein are single component (most probably oligomer fragments) whose formula are listed in Section 2 of this paper. In Fig. 3 is represented the evolution, as a function of PLA composition, of  $C_3H_3O_2$  peak (characteristic of PLA) and of  $C_4H_5O_2$  peak (characteristic of PMMA), which are the most intense ones. We can observe from this figure that at intermediate compositions, both ion intensities are lower than the line binding 0% and 100% PLA. For this reason, we introduced the peaks cited in Section 2 into a partial least squares (PLS) model, allowing to integrate the contribution of overall peaks characteristic of each compound.

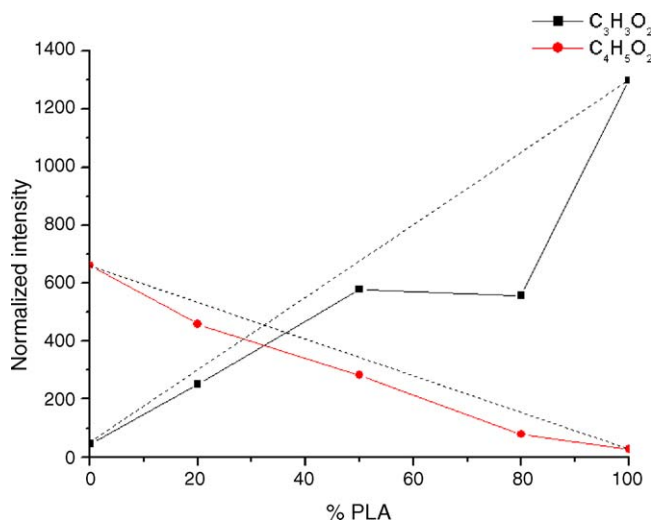


Fig. 3. Evolution of  $C_3H_3O_2$  (PLA) and  $C_4H_5O_2$  (PMMA) as a function of PLA composition.

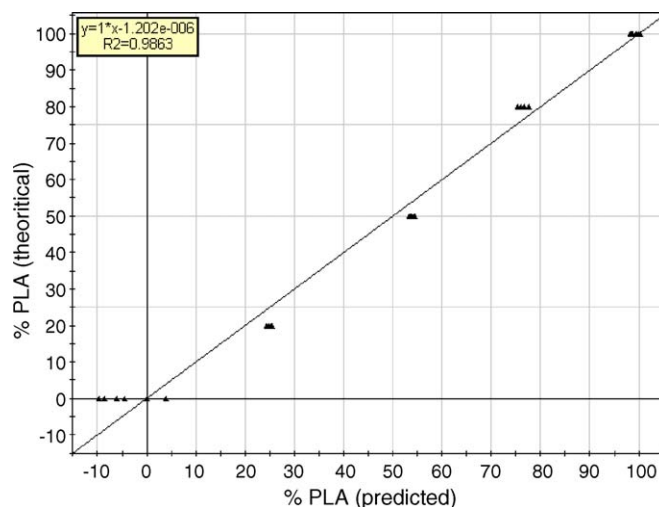


Fig. 4. PLS regression curve for different polymer blends.

By PLS, we predicted the surface composition of the polymer mixtures. In Fig. 4, we can observe that there is, like in XPS, a good correlation between predicted and theoretical compositions. The error is within  $\pm 5\%$  around the theoretical value (i.e. 50% PLA sample predicted as 53% in average).

These results indicate that ToF-SIMS, using PLS modeling, is quantitative in the case of PLA/PMMA blends.

### 4. Conclusions

In this work, we studied different PLA/PMMA blends by XPS and ToF-SIMS. XPS was first used to quantify the composition of the blends, and a very good agreement was found between the XPS-measured concentrations and the theoretical concentrations. Then negative ToF-SIMS spectra were recorded for the different polymer mixtures, and by introducing, into a PLS model, peaks which are characteristic for each of the polymer, we found like also a good agreement between the ToF-SIMS predicted compositions and theoretical concentrations.

These results indicate that ToF-SIMS data analyzed by PLS allowing to make a quantification in the case of PLA/PMMA blends [10]. In addition, ToF-SIMS and XPS are surface-sensitive techniques for different depths, i.e. 10 and 60–100 Å, respectively. These two techniques are in good complement to each other to indicate that at the outermost surface, there is no segregation of any of the two polymers.

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