A NOVEL APPROACH FOR QUALITATIVE DETERMINATION OF RESIDUAL TIN BASED CATALYST IN POLY(LACTIC ACID) BY X-RAY PHOTOELECTRON SPETROSCOPY

NOV NAČIN KVALITATIVNE DOLOČITVE VSEBNOSTI KATALIZATORJA KOSITRA V POLILAKTIČNI KISLINI Z RENTGENSKO FOTOELEKTRONSKO SPEKTROSKOPIJO

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This work is focused on description of qualitative determination of residual tin based catalysts in poly(lactic acid) by using X-ray photoelectron spectroscopy and fluorimetry as standard technique. Three types of poly(lactic acid) were prepared by direct melt polycondensation of lactic acid by using methanesulfonic acid ($w = 0.5$ %) or various amount of stannous 2-ethylhexanoate ($w = (0.5$ and $2)$ %). The results from both methods show that the amount of observed tin in the samples correlates with the concentration of the stannous 2-ethylhexanoate used for polycondensation. X-ray photoelectron spectroscopy was proven to be suitable for detection of tin residuals in polymer matrix.

Keywords: poly(lactic acid), catalyst residuals, tin, X-ray photoelectron spectroscopy, fluorimetry

Delo je osredinjeno na opis kvalitativne določitve katalizatorjev na osnovi kositra v polilaktični kislini z uporabo rentgenske fotoelektronske spektroskopije in fluorimetrije. Tri vrste polilaktične kisline smo pripravili z neposredno polikondenzacijo laktične kisline z uporabo metansulfonske kisline ($w = 0,5$ %) ali različne količine kositrovega 2-etilheksanoata ($w = (0,5$ in $2)$%). Rezultati obeh metod kažejo, da je vsebnost kositra v vzorcih povezana s koncentracijo kositrovega 2-etilheksanoata, ki se uporablja za polikondenzacijo. Rentgenska fotoelektronska spektroskopija se je izkazala kot primerna metoda za odkrivanje majhnih vsebnosti kositra v polimerni matrici

Ključne besede: polilaktična kislina, katalizator, kositer, rentgenska fotoelektronska spektroskopija, fluorimetrija

1 INTRODUCTION

Polymers are widely used for a variety of applications, which include packaging, adhesives, engineering materials, composites, and electronic as well as medical devices. The lastly mentioned application of polymers, production of medical devices, has gained an enormous interest in the last decades.[1–6]

Bioresorbable polymer based items are one of the most developing areas in the field of medical device production, due to necessity to introduce a material with favourable chemical, biological and mechanical properties, which would also bring a comfort with respect to traditional materials (metals or ceramics). An elimination of the second surgery after healing process could be mentioned as an example of using of an implant made of bioresorbable polymers.[7,8]

Poly(lactic acid) (PLA) is well know biodegradable polyester,[9–13] which has been already used in biomedical applications such as implant for bone fixation and tissue engineering scaffold. The synthesis techniques and its modification have been described elsewhere. However, one can find that mostly organic tin based catalysts are used for PLA preparations. It has been observed that the uptake of tin by human beings can cause acute effects (eye irritation, headache, stomach-ache, urination problems etc.) as well as long-term effects (depressions, liver and brain damage, chromosomal changes etc.).[14] In addition, Cam et al. has reported negative influence of residual metallic compounds (including tin) in the PLA matrix on a thermal stability of the polymer during its thermoplastic processing.[3] These facts must be considered during PLA based medical devices evaluation.

Tin can be analytically determined by several techniques including atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, energy-dispersive X-ray fluorescence.[15] Nevertheless, these techniques are reported for inorganic materials. On the other hand, fluorimetry has been introduced for organic samples. A disadvantage of this method is a complex procedure of sample preparation. This works is dedicated to introduction of a novel approach to tin determination in PLA matrix by using X-ray photoelectron spectroscopy, which has been already used for analysis of polymer surfaces. This approach offers fast and reliable and experimentally

undemanding way of Tin determination in polymer matrix. This method was correlated with flourimetric measurements.

2 EXPERIMENTAL

2.1 Polymer samples preparation

Three types of PLA were used for investigation in this study. The detailed characteristics of the prepared samples are shown in **Table 1**. Generally, PLA samples were prepared by direct melt polycondensation of lactic acid. A typical procedure was as follows: 50 mL lactic acid solution (80 %, LachnerNeratovice, Czech Republic) was added into a double necked flask (250 mL) equipped with a Teflon stirrer. The flask was then placed in an oil bath heated by magnetic stirrer with heating and connected to a laboratory apparatus for distillation under reduced pressure. The dehydration step followed at 160 °C, reduced pressure 15 kPa for 4 h. After that, the reactor was disconnected from the vacuum pump and the relevant amount of the catalyst (Stannous 2-ethyl-hexanoate (Sn(Oct)$_2$) or methanesulfonic acid (MSA) both Sigma Aldrich, Steinheim, Germany) was added dropwise under continuous stirring. The flask with dehydrated mixture was connected back to the source of vacuum (100 Pa) and the reaction continued for 24 h at the temperature 160 °C. The resulting product was allowed to cool down at room temperature and then dissolved in acetone. The polymer solution was precipitated in a mixture of chilled methanol/distilled water 1 : 1 (v/v). The obtained product was filtrated, washed with methanol and dried at 45 °C for 48 h. The average values of molecular weight were determined by gel permeation chromatography. Detailed procedure is shown in one of our previous works.[9]

Table 1: Characteristics of the PLA samples
Tabela 1: Karakteristike vzorcev PLA

Sample designation	Catalyst	Concentration of catalyst (w/%)*	$M_w/$ (g mol^{-1})	M_w/M_n
PLA1	MSA	0.5	17 200	1.60
PLA2	Sn(Oct)$_2$	0.5	47 000	2.08
PLA3	Sn(Oct)$_2$	2	67 700	2.06

*related to monomer

2.2 Characterization techniques

2.2.1 X-ray photoelectron spectroscopy (XPS)

Samples in powder form were analyzed with an XPS instrument TFA XPS Physical Electronics. The base pressure in the chamber was about 6×10^{-8} Pa. The samples were excited with X-rays over a 400-μm spot area with a monochromatic Al $K_{?1,2}$ radiation at 1486.6 eV. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. Survey-scan spectra were made at a pass energy of 187.85 eV and 0.4 eV energy step. An electron gun was used for surface neutralization. The concentration of elements was determined by using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer. On each sample two survey spectra were recorder on two different spots on the surface. The sensitivity of the method is 0.5 %.

2.2.2 Fluorimetric analysis

Fluorimeter FSL 920 Edinburg was used for fluorescence spectra and intensity measurements. The device was equipped with a xenon lamp. A quartz cell was used for the measurement (10 mm). A uniform resolution of 1 nm was kept in all cases. The procedure of samples treatment before the analyte determination is described in detail by Mazooriet al.[15]

3 RESULTS AND DISCUSSION

As can be noticed in **Table 1**, the expected tin concentration in the investigated samples has following trend: PLA1< PLA2 < PLA3. Moreover, it can be expected that tin concentration is equal zero in PLA1.

A method which can be used for detecting small amounts of tin in PLA samples is XPS (X-ray photoelectron spectroscopy).[16–28] The technique is particularly useful for characterization of polymer materials whose surface properties have been modified using non-equilibrium plasma treatments[29–45]Figure 1 shows XPS survey spectra of the PLA samples. The measured spectrum consists of characteristic peaks which correspond to electronic energy levels of the investigated material. Because each element has a unique set of binding energies, XPS can be used to identify and determine the concentration of the elements at the surface. XPS survey spectra shown in **Figure 1** represent characteristic peaks due to the presence of oxygen (O1s), carbon (C1s) and
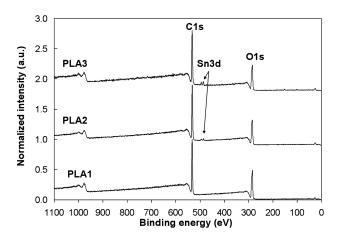

Figure 1: XPS survey spectra of PLA samples with tin additives
Slika 1: Pregledni spekter XPS površine vzorca PLA z dodatkom kositra

tin (Sn3d) elements in the examined samples. Carbon and oxygen are constituents of PLA polymer while a small peak of tin found in the samples PLA2 and PLA3 clearly shows the presence of the small amounts of catalyst.

Surface composition of the samples as determined from the XPS survey spectra (**Figure 1**) is shown in **Table 2**. Surface composition was determined from the area of the measured peaks which was correlated by taking into account special sensitivity factors, which are due to different ionization cross section. It can be noticed that no tin evidence is observed in the case of PLA1 where only carbon and oxygen was detected. On the other hand PLA2 proves a trace of tin presence in the polymer matrix. Interestingly, almost four times higher values were found for PLA3. It means that this observation directly correspond to mass of the added catalyst during PLA preparation (**Table 1**).

Table 2: Surface composition of the samples (in mole fractions, x/%) as determined from the XPS survey spectra (average ± standard deviation)
Tabela 2: Površinska sestava vzorcev (v molskih deležih, x/%) določena iz preglednih spektrov XPS

Sample designation	x(C)/%	x(O)/%	x(Sn)/%
PLA1	62.7 ± 0.8	37.4 ± 0.8	0.00 ± 0.00
PLA2	61.0 ± 0.1	38.8 ± 0.2	0.23 ± 0.05
PLA3	61.1 ± 1.4	37.8 ± 1.8	1.09 ± 0.36

The emission spectra of PLA samples show noticeable peak at 357 nm in all cases (**Figure 2**). The maximal intensities of the observed peaks for PLA
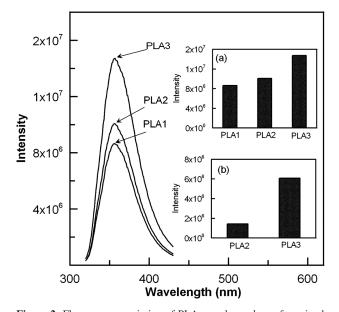

Figure 2: Fluorescence emission of PLA samples, values of maximal intensities observed for PLA samples at 257 nm (a) and intensities of polycondensates catalyzed by stannous 2-ethylhexanoate after subtraction (b)
Slika 2: Fluorescenčna emisija vzorcev PLA: vrednosti maksimalne intenzitete, določene na vzorcu PLA pri 257 nm (a) in intenziteta polikondenzatov kataliziranih s kositrovim 2-etilheksanoatom (b)

samples are presented in **Figure 2a**. It can be noticed that PLA1 emits at the given wavelength as well as tin containing samples PLA2 and PLA3. However, differences between the observed detector responses for PLA2 and PLA3 after subtraction of the signal (**Figure 2b**) of PLA1 is related with initial concentration of the catalyst used for PLA polycondensation (**Table 1**) by means of the intensities ratio PLA3/PLA2.

The results presented above reveal that both XPS and flourimetric method show similar observations in qualitative detection of tin based compounds in PLA matrix. The former method, however, consider only surface composition of a sample. That can be a limitation of the method. Practically, it brings high requirements for samples homogeneity. On the other hand, undisputed advantage of XPS technique is low demand for sample mass, which is important in the small scale productions such as medical grade PLA synthesis.

4 CONCLUSIONS

This study introduces a novel way of residual tin based catalyst determination in poly(lactic acid) by using X-ray photoelectron spectroscopy (XPS). In addition, XPS observations were correlated with fluorimetry. The results from both methods correspond with the concentration of tin based catalyst used for polymer preparation. XPS techniques can be considered as suitable for qualitative or even semi-quantitative analysis of tin based compounds in polymer matrixes providing achieving of sufficient homogeneity of the studied material.

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