

Functionalization of PLA Aerogels with TiO₂ Nanoparticles

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This study was aimed to prepare material with high porosity and photocatalytic activity by immobilization of TiO₂ nanoparticles (NPs) onto poly(lactic acid) (PLA) aerogels. PLA aerogels were prepared in three steps: (1) dissolution of polymer in chloroform at 22 °C, (2) chloroform replacement with ethanol, and (3) supercritical CO₂-drying at pressure 19 MPa and temperature 39 °C. Immobilization of TiO₂ NPs was performed by in situ and ex situ methods. Obtained samples were characterized using SEM, EDX, and FTIR analysis. Photocatalytic activity of developed material was tested by following decolorization of dye C.I. Acid Orange 7 in water solution. It was shown that the morphology of PLA aerogels was slightly affected by TiO₂ NPs immobilization. PLA aerogels with TiO₂ NPs immobilized by ex situ method sustained floatability during test period and provided a complete decolorization of dye solution after 330 minutes of illumination. High photocatalytic activity of the sample was preserved within three repeated cycles of dye decolorization.

Key words: Photocatalytic activity, poly(lactic acid) aerogel, supercritical CO₂, TiO₂ nanoparticles

1. INTRODUCTION

In the last years, poly(lactic acid) (PLA) gained significant attention as a biodegradable and biocompatible material, produced from renewable resources, which could be used in medicine and food packaging industry [1, 2]. In order to increase number of PLA applications, several methods have been explored such as chemical or thermal processing as well as addition of different organic and inorganic substances [3-6]. Functionalization of PLA films, foams or fabrics, can be performed by addition of natural bioactive components [7, 8], metal oxides [9], carbon nanotubes [3], drugs [10], proteins [11], clay [12], etc. However, this study tested functionalization of PLA aerogels by immobilization of TiO₂ nanoparticles (NPs) for application in treatment of colored wastewaters. For that purpose, PLA aerogels were prepared in three steps: (1) dissolution of PLA in appropriate solvent, (2) so-

lvent replacement with ethanol, and (3) supercritical CO₂ (scCO₂) drying.

These steps allow formation of highly porous polymer materials [13, 14]. ScCO₂ is the most appropriate medium for polymer gel drying and aerogel preparation since it has mild critical conditions, liquid like density, gas like diffusivity, GRAS status (Generally Recognized as Safe), and near zero surface tension [13].

Additionally, variation in scCO₂-assisted process pressure and temperature allows control of material morphology. TiO₂ NPs were selected for PLA aerogel functionalization due to its high photoactivity, high stability, and non-toxicity. Owing to these properties, TiO₂ NPs are appropriate for development of material that can be used for treatment of wastewater [15-17].

Through this study, we showed that the scCO₂-drying method enabled preparation of porous material and that the method of TiO₂ NPs immobilization determines material photocatalytic activity. Properties of materials were assessed by SEM, EDX, and FTIR analysis. Activity of the obtained materials was tested by following decolorization of dye C.I. Acid Orange solution under sun light illumination.

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2. MATERIALS AND METHODS

PLA beads with density of 1250 kg/m³, melting temperature 155°C, and molecular weight of 116 kg/mol were supplied by NatureWorks (USA). Beads were dissolved in chloroform (Lachema, Czech Republic) at a ratio of 1:10 (at temperature 22°C, during 4 h mixing using a magnetic stirrer). PLA solution was poured in a petri dish where absolute ethanol (p.a, Zorka Pharma, Serbia) was added for solvent replacement. After 24 h, obtained alcogels were cut into a disc shape ($V \sim 95 \text{ mm}^3$).

PLA discs were dried in a high-pressure view cell (Eurotechnica GmbH, Germany) using scCO₂ at pressure 19 MPa and temperature 39 °C [2] during 2 h and 40 min by a combination of static and dynamic mode. In this manner aerogels were obtained. The drying process was finished by release of CO₂ from the system with a rate of 2 MPa/min.

TiO₂ NPs (Degussa P25, Aeroxide, Germany) were immobilized onto prepared PLA aerogels by ex situ method. Namely, 0.5 g of PLA aerogels was immersed in 55 mL of a dispersion containing TiO₂ NPs (0.1 M) for 2 h. This method of TiO₂ NPs immobilization was also applied for PLA beads (control sample). Afterwards, samples were dried at room temperature, rinsed with deionized water, air-dried, and tested as floating photocatalysts. For comparison, TiO₂ NPs were also immobilized onto/into PLA matrix by in situ method. Namely, 20 mg of TiO₂ NPs was added into 10 mL of previously prepared PLA solution. After intensive mixing for 1 h, the obtained suspension was poured into a petri dish, and absolute ethanol was added for solvent replacement. Obtained alcogels were cut into discs shape and dried using scCO₂ (at the same conditions as previously described).

The morphology of dry PLA aerogels was analyzed by field emission scanning electron microscopy (FESEM, Tescan Mira3 FEG, Czech Republic). The samples were fractured using liquid nitrogen to preserve its morphology and coated with a thin layer of Au/Pd (85/15) prior to the analysis.

The presence of Ti on the surface of prepared material was confirmed by energy-dispersive X-Ray spectroscopy (EDX) using a JEOL JSM 5800 SEM with a SiLi X-Ray detector (Oxford Link Isis series 300, UK).

The photocatalytic activity of prepared samples with TiO₂ NPs was examined by following discoloration of acid dye C.I. Acid Orange 7 (AO7, Cassella, Germany). PLA samples with TiO₂ NPs (0.25 g) were placed in AO7 aqueous solutions (25 mL of 10 mg/L) and shaken in the water bath under sunlike illumination (ULTRA-VITALUX lamp, 300 W, Osram). Optical power was 30 mW·cm² (determined by R-752 Universal Radiometer Readout with sensor model PH-

30, DIGIRAD). The concentration of AO7 was determined using UV-vis spectrophotometer (Cary 100 Scan, Varian) by measuring absorption intensity at 484 nm. Test was repeated two times.

Fourier transform infrared (FTIR) spectra was recorded using an ATR-FTIR spectrometer Nicolet iS10 (Thermo Fisher Scientific Inc., USA).

3. RESULTS

PLA beads were transformed into disc shape alcogels (Figure 1a), which were dried using scCO₂ at 19 MPa and 39°C enabling preparation of disc-shape aerogels (Figure 1b). Compared to the volume of alcogels, the volume of obtained aerogels decreased only slightly during scCO₂-assisted drying implying that the morphology of wet gel was preserved.

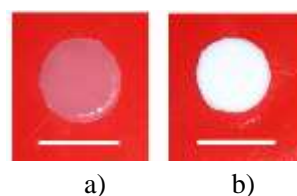


Figure 1 - Images of PLA samples: a) alcogel and b) aerogel (bar size 1 cm)

TiO₂ NPs were further immobilized onto obtained aerogels (ex situ method). Immobilization of NPs was also tested by addition of TiO₂ NPs during PLA solution preparation (in situ method). Addition of nanoparticles did not affect appearance of PLA aerogels. The same behaviour was previously reported for immobilization of TiO₂ NPs onto/into PLA aerogels prepared by using scCO₂ at 15 MPa and 35 °C [18].

Morphology of prepared PLA samples is presented in Figure 2. SEM images confirm that scCO₂-assisted drying enabled preparation of porous PLA material (Figure 2a). It can be seen that the surface of aerogels is non-uniform with pores smaller than 1 μm. On the contrary, internal pores are uniformly distributed. Aerogel interior has two size pores (around 10 μm and around 0.5 μm).

Immobilization of TiO₂ NPs by ex situ method led to formation of NPs agglomerate. Additionally, these agglomerates formed continued layer of NPs in some sections of the aerogel surface (Fig. 2b). Presence of small number of NPs in this material cross section is noticed only close to the surface. On the other hand, smaller agglomerates of TiO₂ NPs were presented through the surface and cross-section of the PLA material obtained by in situ method (Fig. 2c). In addition, it can be seen that the surface of aerogels with TiO₂ NPs immobilized by ex situ method contains larger amount of nanoparticles on its surface. Also, the size of aerogels' interior pores was not significantly affected upon nanoparticles immobilization.

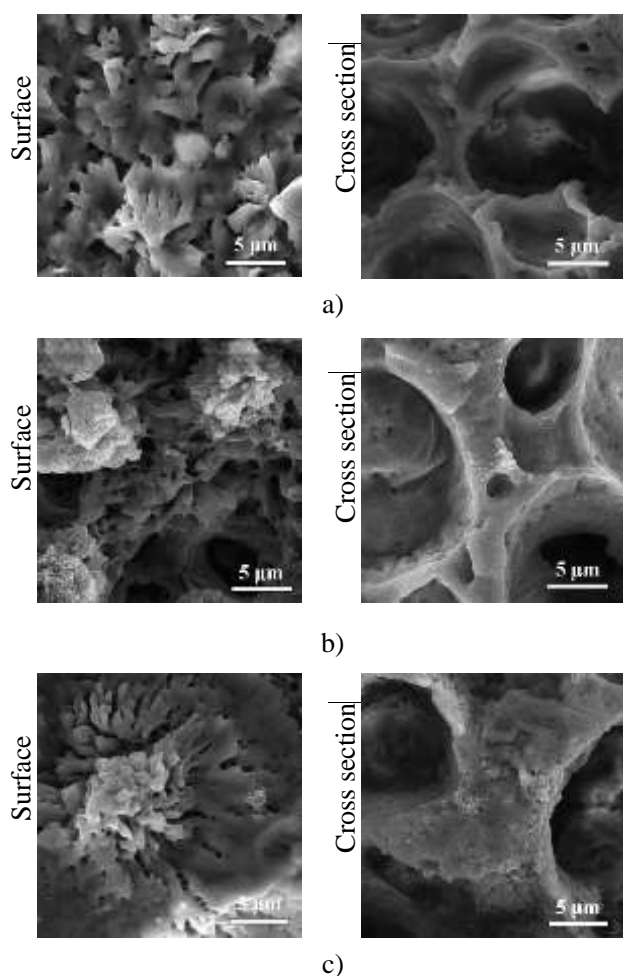


Figure 2 – SEM images of a) neat PLA aerogels, b) PLA+TiO₂ ex situ and c) PLA+TiO₂ in situ

The EDX spectra of PLA+TiO₂ aerogel samples, presented in Figure 3, revealed the presence of Ti. Picks corresponding to Ti originate from TiO₂ NPs. Additionally, it can be seen that the intensity of Ti picks is significantly larger on the surface of the sample obtained by ex situ method (Figure 3a). These results confirm findings of SEM analysis.

The photocatalytic activity of materials with NPs prepared by ex situ method (PLA aerogels and PLA beads with immobilized TiO₂ NPs), PLA aerogels with NPs prepared by in situ method, as well as neat PLA aerogels was tested in AO7 aqueous dye solution under sun-like illumination. The possible photodegradation of dye was investigated by following the decolorization of dye solution. First, it was determined that the dye AO7 was not prone to photolysis. Test revealed that neat PLA aerogels did not induce any dye sorption or dye photodegradation. The results also revealed that PLA beads with TiO₂ NPs immobilized by ex situ method as well as PLA aerogels with TiO₂ NPs immobilized by in situ method did not show any photocatalytic activity. Only PLA aerogels with TiO₂ NPs

immobilized by ex situ method enable discoloration of dye solution. The same behaviour was previously reported for PLA aerogels with TiO₂ NPs prepared using scCO₂ at 15 MPa and 35°C [18].

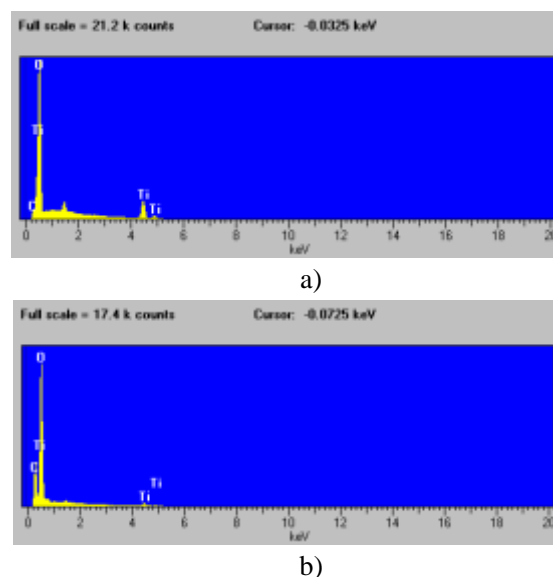


Figure 3 – EDX spectra of aerogels: a) PLA+TiO₂ ex situ and b) PLA+TiO₂ in situ

Kinetic of dye solution decolorization is presented in Figure 4. It can be seen that complete discoloration of AO7 dye solution, during first cycle, is obtained after 330 min of illumination. Hsieh et al. [19] reported that for complete discoloration of AO7 dye solution with graphene+TiO₂ composites it took more than 6 h. However, our previous publication [18] reported PLA aerogels obtained by scCO₂-drying at 15 MPa and 35 °C with immobilized TiO₂ NPs that completely discolor AO7 dye solution after 240 min of illumination.

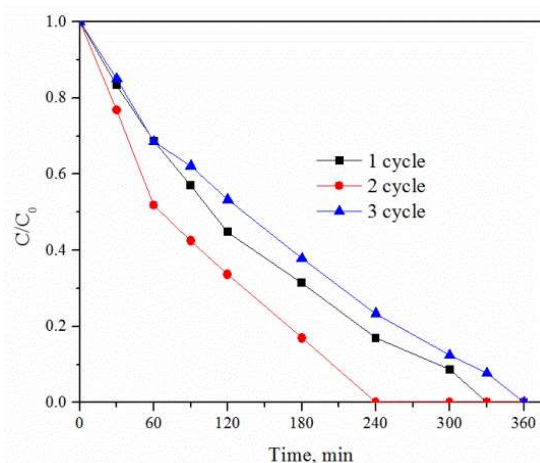


Figure 4 – The percentage of discoloration of AO7 dye solution in the presence of PLA aerogels with TiO₂ NPs immobilized by ex situ method

By comparing this result with results of current study, it can be concluded that condition of scCO₂-drying process determined aerogel morphology, which

consequently affected TiO₂ immobilization and photocatalytic activity of obtained material.

After dye solution discoloration, aerogels were separated from the liquid, dried and tested again in fresh dye solution. Reusability of aerogels was confirmed in two additional cycles. The second cycle of photodegradation resulted in dye solution decolorization after 240 min, while the third cycle resulted in dye solution discoloration after 360 min.

FTIR spectra of neat PLA aerogel, PLA with TiO₂ NPs immobilized by ex situ method (PLA+TiO₂ ex situ), and PLA with TiO₂ NPs immobilized by ex situ method after three cycles of dye solution decolorization (PLA+TiO₂ ex situ after three cycles of illumination) are presented in Figure 5.

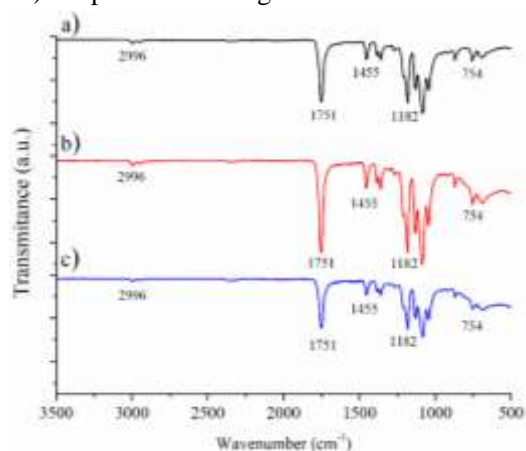


Figure 5 – FTIR spectra of: a) neat PLA aerogel, b) PLA+TiO₂ ex situ, and c) PLA+TiO₂ ex situ after three cycles of illumination

Bands observed at 2996 cm⁻¹, 1751 cm⁻¹, and 1455 cm⁻¹ are assigned to C–H from aliphatic CH₃ groups, to carbonyl stretching C=O in the ester group, and to asymmetric –CH₃ deformation vibrations, respectively [20–22]. In addition bands observed at 1182 cm⁻¹ and 754 cm⁻¹ are attributed to the symmetric C–O–C stretching of the PLA ester groups and to O–CH–CH₃ ester groups, respectively [20–22]. Namely, these bands that are characteristic for neat PLA can be seen in spectra of all samples.

Hence, it can be concluded that immobilization of TiO₂ NPs did not affect chemical stability of PLA aerogels. Figure 5c also revealed that illumination and use of samples for dye solution decolorization did not induce any change in chemical stability of PLA during tested period.

Proposed method of PLA processing enabled preparation of porous material with desired properties.

4. CONCLUSION

The results of this study indicated that scCO₂-drying process at 19 MPa and 39 °C and for 2 h 40 min led

to preparation of porous PLA material. Obtained porous PLA aerogels could be successfully used as carriers for TiO₂ NPs. It was shown that ex situ method of TiO₂ NPs immobilization was superior compared to in situ method for preparing of a floating photocatalyst. FTIR analysis indicated that TiO₂ NPs immobilization and illumination did not affect chemical stability of PLA. PLA aerogels with TiO₂ NPs immobilized by ex situ method decolorized dye AO7 solution after only 330 min of illumination. Excellent photocatalytic activity of prepared materials was retained after three illumination cycles. These results indicated that environmentally friendly material was prepared for potential use in treatment in color wastewater.

5. REMARK

The paper was presented at the International Conference on Aerogels for Biomedical and Environmental Applications, 18-20 February 2020. Santiago de Compostela (Spain).

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REZIME

FUNKCIONALIZACIJA PLA AEROGELOVA POMOĆU TiO₂ NANOČESTICA

Cilj ovog istraživanja bio je priprema materijala velike poroznosti i fotokatalitičke aktivnosti imobilizacijom nanočestica TiO₂ na aerogelove poli(mlečne kiseline) (PLA). PLA aerogelovi su pripremljeni u tri koraka: (1) rastvaranje polimera u hloroformu na 22 °C, (2) zamena hloroforma etanolom i (3) natkritično sušenje upotrebom CO₂ na pritisku 19 MPa i temperaturi 39 °C. Imobilizacija TiO₂ nanočestica izvedena je in situ i ex situ metodama. Dobijeni uzorci su okarakterisani pomoću SEM, EDX i FTIR analize. Fotokatalitička aktivnost razvijenog materijala ispitana je prateći obezbojavanje vodenog rastvora boje C.I. Acid Orange 7. Pokazano je da imobilizacija TiO₂ nanočestica ne utiče značajno na morfologiju PLA aerogelova. PLA aerogelovi sa TiO₂ nanočesticama imobilisanim ex situ metodom održavali su plutabilnost tokom isitivanja i omogućili su potpuno obezbojenje rastvora boje nakon 330 minuta osvetljenja. Velika fotokatalitička aktivnost uzorka očuvana je tokom tri ponovljena ciklusa obezbojavanja rastvora boje.

Ključne reči: Fotokatalitička aktivnost, aerogel poli(mlečne kiseline), natkritični CO₂, TiO₂ nanočestice