

PREPARATION OF TITANIUM-SILICA BINARY MIXED OXIDE TO USE AS A FILLER IN POLY (LACTIC ACID)

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Abstract

Poly(lactic acid) (PLA), a biodegradable polyester, derived from renewable resources has been widely used in biomedical and packaging applications due to its good strength and high stiffness. However, one of the main drawbacks of PLA is its slow crystallization rate leading to several problems during large-scale production. Titanium-silica binary mixed oxide (TiO₂-SiO₂) is an environmentally benign and antimicrobial biomaterial. In addition, it has good chemical resistance, high chemical stability, and non-toxicity which is suitable for biomedical applications such as wound dressing and drug delivery. In this study, TiO₂-SiO₂ mixed oxide was prepared for use as a nucleating agent for PLA. The TiO₂-SiO₂ was synthesized via the sol-gel method using tetraethyl orthosilicate and tetraisopropoxide as silicon and titanium precursors, respectively. The structural and chemical properties of the TiO₂-SiO₂ mixed oxide were characterized by powder X-ray diffraction, X-ray fluorescence, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy with energy dispersive X-Ray spectroscopy. The FTIR spectra showed 2 strong bands at 1,052 and 801 cm⁻¹ associated with asymmetric and symmetric Si-O-Si stretching vibrations. Moreover, the band at 949 cm⁻¹ of the TiO₂-SiO₂ mixed oxide associated with Ti-O-Si vibration indicated the forming of a chemical bond between the TiO₂ and SiO₂.

Keywords: Mixed oxide, sol-gel method, titania, silica

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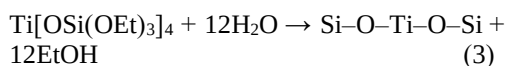
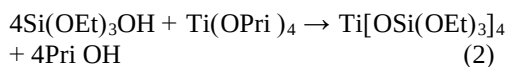
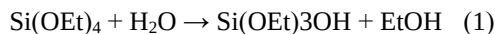
Introduction

Titanium dioxide (TiO₂) or titania, is an important substance. It is well recognized as a valuable material used in applications such as paints or as a filler in paper, polymer, textiles or photocatalysis, etc. Nano- TiO₂ particles hold many positive properties such as good chemical resistance, high chemical stability (Zapata *et al.*, 2013), attractive photocatalytic activity, excellent photostability, biocompatibility, and antimicrobial activity (Fonseca *et al.*, 2015).

Silicon dioxide (SiO₂) or silica, is a chemical compound that contains oxygen and silicon. It has a good thermal stability, low cost, and high density of silanol groups (Si-OH) on the surface. As a result, it has been widely used in many applications. For example, poly(lactic acid)/SiO₂ hybrid microspheres (PLAHs) have been used in the controlled release of drugs by embedding the drugs in the holes of the PLAHs. The drug loading amount can be controlled by the size and number of holes in the PLAHs (Wang *et al.*, 2006). Moreover, the crystallization properties of PLA can be improved by SiO₂ (Ge *et al.*, 2014).

Titanium-silicon binary mixed oxide (TiO₂-SiO₂) represents a novel class of materials that has attracted much attention in recent years. The mixed oxide can be generated via a sol-gel process to obtain a controllable combination of the beneficial mixed oxide (Kim *et al.*, 2000). This is due to the interaction of TiO₂ with SiO₂ and chemical bonds between the 2 materials. The sol-gel process is an adaptable method that has been successfully used in commercial applications because of its ability to form pure and homogenous products in mild conditions. The synthesis usually includes the hydrolysis of titania and silica alkoxide precursors and their condensation processes that leads to branched polymeric gels. The most common procedure was proposed by Yoldas (1980) in which Si-alkoxide was pre-hydrolyzed in an alcohol solution of concentrated acid and water under magnetic stirring to create silanol groups (Ismail and Vejayakumaran, 2012). The Ti-alkoxide was

added dropwise to the solution to prevent instant precipitation of the TiO₂ species. The reactions are shown as follows (Kibombo *et al.*, 2012):



The goal of this work is to determine the synthesis and structural characterization with different molar ratios of the Ti and Si. In addition, the effect of pre-hydrolysis of tetraethyl orthosilicate (TEOS) was investigated. The mixed oxide was characterized by powder X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS). The mixed oxide will be used as a filler in a PLA composite in our future work.

Materials and Methods

Materials

Tetraethyl orthosilicate (TEOS, 98%, AR grade) and titanium (IV) isopropoxide (TTIP, 98%, AR grade) were purchased from Acros Organics BVBA, Geel, Belgium. Absolute ethanol (C₂H₅OH, AR grade) and hydrochloric acid (HCl, AR grade) were supplied from Carlo Erba Reagents S.A.S., Val de Reuil, France.

Experimental Procedures

Titania-silica mixed oxide was prepared using the sol-gel method (Kim *et al.*, 2000). The TEOS and TTIP were used without purification. Hydrochloric acid was added to the alkoxide (TEOS and TTIP) solution to catalyze the sol-gel process. The mixture of 0.11 mole of alkoxides and 25 cm³ ethanol was added into a reactor containing 75 cm³ ethanol. A condenser was attached to prevent the

solvent from vaporizing. The reactor temperature was increased to 75°C while stirring. A solution of HCl was slowly added to the reactor drop by drop for 1 h. An additional 0.22 mole of distilled water was added into the sol and aged at 80°C for 24 h in an oven. During this period, ethanol was removed and the aged gel was almost dry in appearance. The aged gel was further dried under a reduced pressure in a rotary evaporator at 80°C for 2 h and calcined in the reactor at 550°C for 4 h. The compositions of the sol-gel liquid solution used for the preparation of TiO₂-SiO₂ are shown in Table 1.

Characterization Techniques

The crystal structures of the SiO₂ and TiO₂-SiO₂ were determined by XRD using a Model D2 phaser (Bruker Corporation, Billerica, MA, USA), with CuK α radiations scanning from 10-60° at a rate of 0.05°/s with the current at 35 mA. The chemical compositions were analyzed by XRF using an ED 2000 EDS analyser (Oxford Instruments, Abingdon, UK)

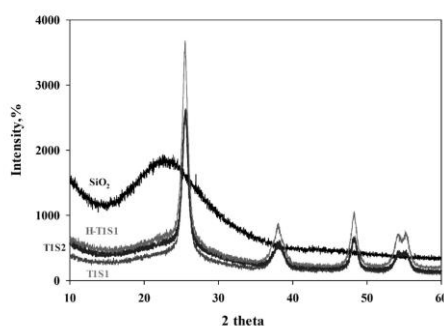


Figure 1. XRD pattern of SiO₂, T1S1, T1S2, and H-T1S1

with a Rh X-ray tube and a vacuum medium. The infrared spectra of the TiO₂-SiO₂ were determined by FTIR spectroscopy using attenuated total reflectance (FTIR-ATR) with a TENSOR 27 spectrometer (Bruker Corporation, Billerica, MA, USA). The spectra were recorded within the wavenumber of 400-4,000 cm⁻¹ with 4 cm⁻¹ resolution through the accumulation of 64 scans. A JSM-6380LV scanning electron microscope (JEOL Ltd., Tokyo, Japan) and an EDAX Genesis 2000 energy dispersive spectrometer (AMETEK, Inc., Berwyn, PA, USA) were applied to determine the morphology and composition of the SiO₂ and TiO₂-SiO₂.

Results and Discussion

The X-ray diffraction patterns of the synthesized SiO₂ and TiO₂-SiO₂ mixed oxides are shown in Figure 1. The SiO₂ showed the only diffraction peak at 23° attributed to a typical pattern of amorphous silica (Pabón *et al.*, 2007). The TiO₂-SiO₂ nanoparticles showed the diffraction peaks at 25° (101) and 48° (200) corresponding to the crystalline phase (anatase) of the TiO₂ (Yamashita *et al.*, 1998; Sahu *et al.*, 2009). The crystal structure of the TiO₂ was tetragonal; a = b = 3.782 Å, c = 9.502 Å (Etacheri *et al.*, 2015). However, no rutile phase was detected in any case according to the absence of the (110) diffraction peak at 27.4°. The crystal structures of the anatase and rutile are shown in Figure 2. The molar content of the metal oxides of the SiO₂ and TiO₂-SiO₂ mixed oxides by XRF are shown in Table 2. From the XRF analysis, pre-hydrolyzed TiO₂-SiO₂ mixed oxides (H-T1S1) showed a higher content of SiO₂ (32.64%) than the T1S1 (24.36%) because TTIP can be hydrolyzed faster than the TEOS.

Table 1. Compositions of sol-gel liquid solution used for the preparation of TiO₂-SiO₂ mixed oxide

Compound	TTIP (mol)	TEOS (mol)	HCl (mol)	Mole ratio of Ti:Si
SiO ₂	-	0.11	0.055	0:1
T1S1	0.055	0.055	0.055	1:1
T1S2	0.037	0.073	0.055	1:2
*H-T1S1	0.055	0.055	0.055	1:1

*Hydrolysis TEOS for 1h before reaction

Moreover, the content of the SiO_2 in the T1S2 increased with increasing the molar ratio of the Ti/Si (43.72%). The FTIR technique was utilized to analyze the stretching and bending vibration frequencies in the mixed oxide materials. The FTIR spectrum of the TiO_2 - SiO_2 mixed oxides showed 3 main peaks with the wavenumbers of 801, 949, and 1052 cm^{-1} as depicted in Figure 3. The peaks at the wavenumbers of 1,052 and 801 cm^{-1} were assigned to the symmetric and asymmetric stretching vibration of the Si-O-Si of silica, respectively (Sahu *et al.*, 2009). The peak with the wavenumber of 949 cm^{-1} was commonly attributed to the Ti-O-Si vibrations. Thus, the appearance can be used to infer the presence of Ti-O-Si linkages (Yamashita *et al.*, 1998). In addition, the Ti-O-Ti bond of the mixed oxides was too weak to be detected at $1,400\text{ cm}^{-1}$ (Huang *et al.*, 2012).

The images of the SEM, the corresponding EDS spectra, and the mapping of the synthesized SiO_2 and TiO_2 - SiO_2 mixed oxide

for the Si, Ti, and O elements are shown in Figure 4. The mixed oxide exhibited a morphology containing a flat surface without porosity in the magnification used ($\times 5000$), together with a uniform dispersion of mixed oxides. Maps of different elements over the same area showed the absence of the phase's segregation or islands on the sample. In addition, the element maps showed the spatial distribution of the Si, Ti, and O elements in a T1S1 sample, as shown in Figure 5. The distribution of Si and Ti in the particles was relatively uniform in the case of the T1S1.

Conclusions

In this study, TiO_2 - SiO_2 mixed oxide was synthesized using TTIP and TEOS as precursors. The XRD pattern showed the diffraction peaks at 25° and 48° , which were attributed to the crystalline phase (anatase) of TiO_2 . The FTIR spectra showed 2 strong bands

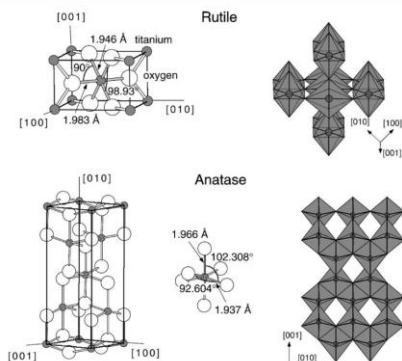


Figure 2. Crystal structures of rutile and anatase phases (Diebold, 2003)

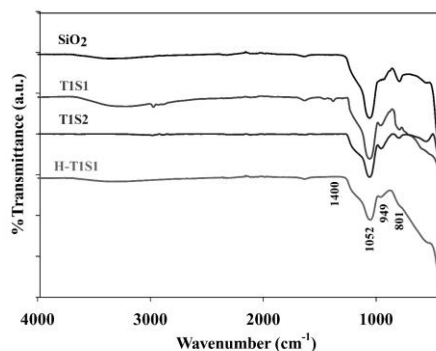


Figure 3. FTIR transmission spectra of SiO_2 , T1S1, T1S2, and H-T1S1

Table 2. Molar content of metal oxides of SiO_2 and TiO_2 - SiO_2 mixed oxides by XRF

Compound	TiO_2 (mol.%)	SiO_2 (mol.%)
SiO_2	-	99.94
T1S1	75.64	24.36
T1S2	56.28	43.72
H-T1S1	67.36	32.64

at 1,052 and 801 cm^{-1} associated with asymmetric and symmetric Si-O-Si stretching vibrations. Additionally, the Ti-O-Si vibration of the TiO_2 - SiO_2 mixed oxide was confirmed by the band at 949 cm^{-1} indicating the forming of a chemical bond between the TiO_2 and SiO_2 . Furthermore, SEM images exhibited a morphology containing a flat surface and a uniform dispersion of mixed oxides without porosity. Additionally, the absence of the phase's

segregation or islands was demonstrated in the EDS elemental mapping.

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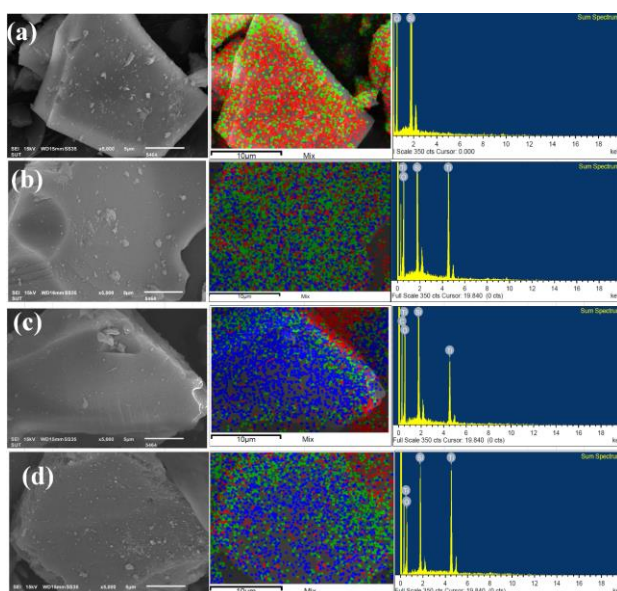


Figure 4. SEM images (x5000, 15 kV), EDS spectra, and mapping of SiO_2 and TiO_2 - SiO_2 mixed oxides; (a) SiO_2 , (b) T1S1, (c) T1S2, and (d) H-T1S1

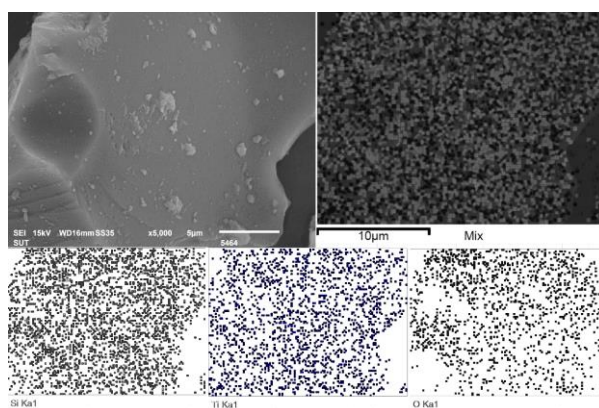


Figure. 5 EDS mapping of T1S1

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