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Scientific paper

**Hydrophobic silica nanoparticles as reinforcing filler for poly (lactic acid) polymer matrix**

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## **Abstract**

Properties of poly (lactic acid) (PLA) and its nanocomposites, with silica nanoparticles ( $\text{SiO}_2$ ), as filler were investigated. Neat PLA films and PLA films with different percentage of hydrophobic fumed silica nanoparticles (0.2, 0.5, 1, 2, 3 and 5 wt. %) were prepared by solution casting method. Several tools were used to characterize the influence of different silica content on crystalline behavior, and thermal, mechanical and barrier properties of PLA/ $\text{SiO}_2$  nanocomposites. Results from scanning electron microscope (SEM) showed that the nanocomposite preparation and selection of specific hydrophobic spherical nano filler provide a good dispersion of the silica nanoparticles in the PLA matrix. Addition of silica nanoparticles improved mechanical properties, the most significant improvement being observed for lowest silica content (0.2wt. %). Barrier properties were improved for all measured gases at all loadings of silica nanoparticles. The degree of crystallinity for PLA slightly increased by adding 0.2 and 0.5 wt. % of nano filler.

Key words: Polylactic acid, silica nanoparticles, nanocomposite, food packaging

## **Introduction**

The interest in biopolymers has increasing trend due to their positive environmental impact; they are produced from renewable sources and are biodegradable, and consequently their utilization has less negative effect compared to conventional petroleum based polymers [1-9]. Biopolymers are used in variety of applications, like therapeutic aids, medicines, coatings, food products and packaging materials [10]. Poly (lactic acid), PLA, is biodegradable aliphatic polyester derived from 100% renewable resources (corn starch or sugar beet). Approximately 25-55% less energy is required to produce PLA than petroleum-based polymers [11, 12]. Popularity of PLA has significantly increased due to the ease of its processing by conventional methods (such as injection molding, film extrusion, blow molding, thermoforming, fiber spinning and film forming), which enable its utilization in diverse applications, including food packaging [13, 14]. However, due to its poor barrier and mechanical properties, utilization of PLA for food packaging is currently limited to cups, containers and films for short shelf-life products [6, 7, 15]. PLA properties can be improved by incorporation of nanoparticles into polymer matrix. Inorganic nanoparticles are added often to polymer matrix, especially for improvement of mechanical and barrier properties [6, 7, 12, 16]. Nano fillers are creating very large interfaces with polymer matrix due to their small particle size and extremely high surface area. A potential use of nanotechnology has been already identified in every segment of the food industry including food packaging [17]. Majority of the studies concerning PLA nanocomposites are related to PLA/layered nanoparticles [10, 15, 18]. Nevertheless, spherical silica nanoparticles are, due to their natural abundance, low cost, high thermal resistance and surface functionality very suitable for various applications [2]. The influence of different types of hydrophilic silica nanoparticles on PLA properties has been reported [2, 9, 13]. It was stated that direct mixing of hydrophilic silica

nanoparticles results in their aggregation [16]. The functionalization of hydrophilic silica nanoparticles is carried out in order to block reactive silanol end-groups. Surface modification results in hydrophobic product, less reactive than hydrophilic one, with better dispersion in polymer matrices. Hydrophobic fumed silica is produced by chemical treatment of hydrophilic grades with silanes or siloxanes. In the final product the treatment agent is chemically bonded to the oxide that was previously hydrophilic. These particles are characterized by a low moisture adsorption, excellent dispersion in polymer matrices (including PLA), and ability to adjust rheological behavior [13, 16]. Large surface area and smooth nonporous surface of silica nanoparticles can intensify the effect of particle-particle and/or polymer particle interaction, which could promote strong physical contact between the silica and polymer matrix causing the improvement in material properties [19]. Hydrophobic silica nanoparticles present new potential filler for enhancement of PLA polymer matrix properties. The goal of this research was to investigate the influence of different loadings of hydrophobic silica nanoparticles on thermal, mechanical and barrier properties of PLA polymer matrix.

## **Material and methods**

### ***Material***

The PLA used in this study was provided from Esun, China. Parameters of the neat PLA are: number-average molecular weight  $M_n=60520 \text{ g mol}^{-1}$ ; weight-average molecular weight  $M_w=160780 \text{ g mol}^{-1}$  and polydispersity  $Q=2.6$  (from GPC).

The hydrophobic nano silica (AEROSIL<sup>®</sup> R812) was kindly supplied by Evonik (Hanau, Germany) with specific area of  $260\pm 30 \text{ m}^2\text{g}^{-1}$  and average particle size 7 nm. They were used as received without any pre-treatment.

### ***Sample preparation***

Pure PLA film and PLA films with 0.2, 0.5, 1, 2, 3 and 5 wt. % of nano silica were prepared by solution casting method. Appropriate amounts of nano silica, was added in chloroform and stirred in an ultrasonic bath for 10 min. PLA was added to nano silica dispersion and stirring continued with magnetic bar for 4 hours at room temperature. After completely PLA dissolution, samples were poured into glass Petri dishes (10 cm diameter) and vacuum dried at room temperature. Film thickness was measured using a micrometer (Digico 1, Tesa technology, Renens, Switzerland) with sensitivity of 0.0001 mm in eight replicates for each film, from which an average value was obtained.

### ***Scanning electron microscopy (SEM) analysis***

Morphology of fractured surface of PLA and PLA/silica nanocomposite films were investigated using a PHILIPS model XL20 apparatus. The samples were frozen in liquid nitrogen and quickly broken off to obtain a random brittle-fractured surface. Before the observation, samples were coated with Au/Pd alloy using E5 150SEM coating unit.

### ***Wide angle X-ray diffraction (WAXD) analysis***

Wide angle X-ray diffraction measurements were conducted using a Philips XPW diffractometer with Cu K $\alpha$  radiation (1.542Å) filtered by nickel. The scanning rate was 0.02 °min<sup>-1</sup>, and the scanning angle was from 5 to 45 °. The ratio of the area under the crystalline peaks and the total area multiplies by 100 was taken as the degree of crystallinity.

### ***Differential scanning calorimetry (DSC)***

Thermal properties of the samples were determined using a DSC model Q20 (TA Instruments, USA). Aluminum pans containing 3-5 mg of nanocomposite films were hermetically sealed. The first heating scan (up to 170°C) was performed in order to remove all thermal history and after

cooling (with cooling rate  $20^{\circ}\text{C min}^{-1}$ ) samples were heated from 20 to  $180^{\circ}\text{C}$ . The heating rate was  $10^{\circ}\text{C min}^{-1}$ .

### ***Mechanical properties***

Tensile strength (TS) and elongation at break (EB) of prepared films were measured on Toyoseiki AT-L-118A dynamometer in accordance with ASTM D638 standard. Rectangular strips were cut from prepared films. For each data point, five samples were tested, and the average value was calculated.

### ***Permeability tests***

Determination of the gas permeability ( $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{O}_2$ ) was conducted according to the Lyssy method. This procedure is an isostatic gas-chromatographic method (DIN 53380, 1969), with the use of the Lyssy GPM-200 apparatus with the belonging Gasukuro Kogyo GC-320 gas chromatograph and the HP 3396A integrator attached. A standard Gow-Mac series 5 52 thermal conductivity detector gas chromatograph has been used as a basis for quantitative analysis. In the gas chromatograph oven a dual column system containing a 3 m Porapak QS and a 4.5 m molecular sieve column 60–80 mesh has been inserted in series, and the ratio of the beam splitting can be regulated with a restrictor valve incorporated before the Porapak column. This makes it possible to split all known permanent gases, especially oxygen and nitrogen, from air. The investigations were performed at  $23^{\circ}\text{C}$  and 1 bar pressure difference, with the volume of sample (gas) injected of 0.8 ml. The film sample was fixed and placed in the investigation chamber. Permeability of gases was determined on the base of isostatical conditions in a chamber divided by the film. The pressure at both sides of the film was equal (0.2 bars). Helium was gradually enriched due to the permeation of gases from the gaseous mixture through the film, and gas concentration in helium was recorded by the gas chromatograph and integrator. The peak area

(height) of the obtained chromatogram changes in function of time and represents the permeability of gases from the mixture. Air permeability was calculated on the basis of gases ratio in the air. The results of permeability determination are expressed in —————

## **Results and Discussion**

Figure 1 (a) shows the SEM image of neat PLA fracture surface. Figures 1 (b-g) show the SEM images of PLA filled with 0.2, 0.5, 1, 2, 3 and 5 wt. % of silica nanoparticles, respectively. In the SEM micrographs presented in Figure 1 nanoparticles are detected as white and spherical dots. PLA fracture surface (fig.1 (a)) is smooth as expected for a neat polymer. Very good and uniform dispersion of nanoparticles for samples up to 1 wt. % of silica content was noticed. The very good dispersion and distribution of nanoparticles in polymer matrix, that are key factors for improved materials, can be attributed to the specific nature of hydrophobic silica nanoparticle which causes lower inter particle interaction. With the increase of silica content (from 1 up to 3 wt.%) nanoparticles start to aggregate forming cluster, and the silica homogeneity in the matrix (distribution) drastically decreases with respect to higher silica contents. Moreover more surface irregularities and voids appear. For 5 wt. % of silica content (fig. 1(g)), material exhibits nonuniform distribution and dispersion of silica nanoparticles with a significant number of agglomerates. This result was expected as the consequence of the higher load of filler, causing higher volume- ratio in polymer matrix as well as higher inter particle interaction. Similar results were reported for both hydrophilic [2, 9] and hydrophobic silica nano fillers [16] in PLA polymer matrix.

### **<Figure 1>**

X-ray diffraction (WAXD) was used to investigate the influence of nano silica addition on the crystal structure and degree of crystallinity of PLA nanocomposite films. The X-ray diffraction



profiles of the neat PLA and PLA/silica nanocomposites films are shown in Figure 2. For comparison purposes the WAXD profile of PLA as received (pellet) is reported.

PLA can crystallise in several polymorphic forms ( $\alpha$ ,  $\beta$  and  $\gamma$  forms), depending on the preparation conditions [20]. In neat PLA, strong diffraction peaks appearing at  $16.7^\circ$  and  $19.1^\circ$ , which represent  $(200)/(110)_\alpha$  and  $(203)_\alpha$  reflections of stable  $\alpha$ -crystals, together with some weak diffraction peaks at  $14.8^\circ$  and  $22.3^\circ$  indicative of  $(010)_\alpha$  and  $(015)_\alpha$  reflections of the stable  $\alpha$ -form of PLA, are observed. The presence of silica nanoparticles does not modify the crystal structure of PLA for all the compositions studied. The degree of crystallinity by WAXD ( $C\%$ ) of pure PLA and PLA/silica nanocomposites films is reported in Table 1. These results are showing a slight increase of crystalline content of PLA for small addition of silica nanoparticles (0.2 wt. % and 0.5 wt. %). This behavior can be attributed to the well dispersed nanoparticles that act as nucleating agents, as already reported in the literature [21, 22].

<Figure 2>

<Table 1>

DSC analysis was used to determine the glass transition temperature ( $T_g$ ) of pure PLA and PLA/SiO<sub>2</sub> nanocomposite films. The effect of silica content on the  $T_g$  is shown in Figure 3. It can be seen that  $T_g$  increases from  $47.6^\circ\text{C}$  for pure PLA matrix to  $48.9^\circ\text{C}$  and  $50.6^\circ\text{C}$  for the samples filled with 0.2 and 0.5 wt. % silica, respectively. With further increase of silica content (1, 2, 3, 5 wt. %)  $T_g$  decreases with respect to neat PLA.

<Figure 3>

It is well known that polymer nanocomposite characteristics are strongly dependent on dispersion, distribution and interaction of nanoparticles and polymer matrix (adhesion between organic polymer and inorganic filler). The good dispersion and distribution of nanoparticles may

be related to: (1) sample preparation method and (2) the use of hydrophobic silica nanoparticles, preventing the agglomerate formations. Good dispersion is expected when there is a good adhesion between the polymer chains and nanoparticles [23]. Increase in  $T_g$  for PLA/SiO<sub>2</sub> nanocomposites with 0.2 and 0.5% in weight with respect to neat polymer can be ascribed to the chain mobility decreasing throughout the polymer matrix volume, in presence of nano particle filler. Many experiments show that the reduction in the mobility chain is going through the whole volume of the polymeric matrix, but affects the chains within a few nanometers from the surface of filler due to the strong interaction between the fillers and polymeric matrix [23]. For the samples with 1, 2, 3 and 5 wt. % silica content,  $T_g$  decreases in respect to the neat polymer with the increase of the silica content. The agglomerate formation and the reduction of homogeneity in the polymer matrix is affecting the chain mobility and causing a decrease in the  $T_g$  in respect that of neat polymer [23].

From the thermograms in Figure 3, it is evident that in the melting process endothermic shoulder peak prior to the dominant melting peak is present for all samples. Double peak melting endotherms are commonly present in PLA samples [24]. The multiple melting behaviour of PLA was suggested to be generated due to the melt-recrystallization mechanism, when the less perfect crystals have enough time to melt and reorganise into crystals with higher structural perfection, and re-melt at higher temperature [24]. The two crystal types that could grow upon melt crystallisation were the  $\alpha$ -form, which predominated at high crystallisation temperatures, and the  $\alpha'$ -form that grew at low crystallisation temperatures [24]. In Figure 3, the shoulder peak of  $\alpha'$ -form in PLA nanocomposites increases in the presence of silica, suggesting that the filler influences the polymorphic phase transition mechanism of PLA. Effect of silica on generation of

the multiple melting temperatures of PLA is outside the scope of this article and thus it will not be discussed in more details.

The mechanical properties are measured in order to investigate the effect of silica nanoparticles filler on PLA films. The values of the tensile strength (TS) of PLA and PLA nanocomposite films are given in Figure 4. Significant improvement of tensile strength compared to neat PLA film is recorded for the samples with silica content of 0.2, 0.5 and 1 wt. % (from 52 to 64, 63 and 60.6 MPa, respectively). The decrease of tensile strength starts with further increase of the silica contents. For the sample with 5 wt. % silica content, the value of tensile strength is below neat PLA. As the filler concentration increased, a worse dispersion and distribution of nanoparticles, higher surface irregularities and presence of voids were observed by SEM. Such defects may act as crack nucleating agents thus explaining the decrease in tensile behavior of the nanocomposite [16].

<Figure 4>

### ***Gas permeability***

Determination of the gas permeability ( $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$ ) is conducted in accordance with the Lyssy method. Gas permeability is significantly affected by hindered diffusion of gas molecules through the polymer film due to addition of silica nanoparticles. For example, addition of 0.2%  $\text{SiO}_2$  reduces permeability of all measured gasses ( $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$ ) for almost 50% compared to neat PLA (Figure 5). For example, permeability of  $\text{CO}_2$  was reduced from 8.16 to 5.45 (————) for 0.2 wt. % of silica, and to 4.45, 4.14, 4.78 (————), for 0.5, 1 and 2wt. % silica respectively. For higher loadings (3 wt. % and 5 wt. %) permeability of  $\text{CO}_2$  was a little bit higher (6.1 and 6.25 ————— respectively) but still lower than for neat PLA.

Similar trend was observed for all measured gases. This behavior can be assigned to good dispersion of filler. Silica nanoparticles with small primary particle size are evenly distributed through the polymer matrix volume even for lowest loadings, causing permeability reduction. Besides, degree of crystallinity can also influence permeability reduction. Gas transport behavior of semicrystalline polymers refers to two phase model-impermeable crystalline phase, dispersed in permeable amorphous phase [25]. Lower gas permeability values could also be assigned to increase in degree of crystallinity for 0.2 and 0.5 wt. %.

<Figure 5>

### **Conclusions**

In this article, the properties of poly (lactic acid) (PLA)/SiO<sub>2</sub> nanocomposites were investigated. Neat PLA films and PLA films with different percentage of hydrophobic fumed silica nanoparticles (0.2, 0.5, 1, 2, 3 and 5 wt. %) were prepared by solution casting method. The results of conducted investigations have shown that addition of the lowest silica content (0.2 and 0.5 wt. %) have a significant influence on polymer material behavior. In particular, PLA with 0.2 wt. % of silica nanoparticles showed an increase in degree of crystallinity, improvement in mechanical (the highest improvement in tensile strength respect to other compositions) and barrier properties of PLA, which were the drawbacks of neat polymer. The mechanical properties of the investigated nanocomposites were getting worse with respect to those of neat polymer by increasing the silica content.

### **Acknowledgments**

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Naučni rad

## **Uticaj dodatka hidrofobnih nanočestica silicijum(IV)-oksida na svojstva poli(mlečne kiseline)**

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### **Izvod**

Poli(mlečna kiselina) (PLA) predstavlja jedan od najpopularnijih komercijalnih biorazgradivih materijala. Iako može da zameni neke od najčešće korišćenih sintetskih polimera, neke njegove osobine još uvek predstavljaju prepreku u široj primeni, posebno u pakovanju hrane. Poboljšanje osobina PLA može se postići primenom nanotehnologija. U ovom radu ispitan je uticaj dodatka različitih koncentracija hidrofobnih nanočestica silicijum(IV)-oksida (od 0.2 mas.% do 5 mas.%) na toplotna, mehanička, i barijerna svojstva čiste PLA. Morfološke karakteristike uzoraka nanokompozita snimljene su pomoću skenirajuće elektronske mikroskopije (SEM). Toplotna svojstva poli(mlečne kiseline) i pripremljenih nanokompozita proučavana su primenom diferencijalnog skenirajućeg kalorimetra (DSC), dok je stepen kristaliničnosti određen pomoću širokougaone difrakcije X zracima (WAXD). Mehanička svojstva su ispitivana da bi se odredio uticaj dodatka nanočestica SiO<sub>2</sub> na PLA polimernu matricu. Disperzija nanočestica je izuzetno



dobra za koncentracije silicijum(IV)-oksida do 1%, nakon čega dolazi do stvaranja manjih aglomerata. Dalje uvećanje udela  $\text{SiO}_2$  (do 5 mas%) uzrokuje stvaranje većih aglomerata i površinskih nepravilnosti unutar polimerne matrice. Uočeno je da se dodatkom male koncentracije  $\text{SiO}_2$  postižu značajna poboljšanja mehaničkih i barijernih svojstava. Do povećanja stepena kristaliničnosti i temperature prelaska u staklasto stanje  $T_g$  dolazi samo za koncentracije od 0.2 i 0.5 mas.%  $\text{SiO}_2$  dok za ostale koncentracije dolazi do pada ovih vrednosti. Ovakvo ponašanje veovatno je uzrokovano stvaranjem aglomerata za veće udele  $\text{SiO}_2$ .

Ključne reči: Poli(mlečna kiselina), silicijum(IV)-oksid, nanočestice, pakovanje hrane

## **Figure captions**

**Figure 1** SEM micrographs of the fractured surface of the PLA and PLA nanocomposites (a) pure PLA (b) PLA+0.2 wt. % silica (c) PLA+0.5 wt. % silica (d) PLA+1 wt. % silica (e) PLA+2 wt. % silica (f) PLA+3 wt. % silica, (g) PLA+5 wt. % silica

**Figure 2** WAXD patterns of the PLA and PLA nanocomposites: PLA pellets, pure PLA film and PLA film with (0.2, 0.5, 1, 2, 3 and 5 wt. %) of silica

**Figure 3** DSC curves of pure PLA film and PLA film with (0.2, 0.5, 1, 2, 3 and 5 wt. %) of silica, respectively

**Figure 4** Tensile strength for pure PLA film and PLA film with (0.2, 0.5, 1, 2, 3 and 5 wt. %) of silica

**Figure 5** Gas permeability (CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and air) for pure PLA film and PLA film with (0.2, 0.5, 1, 2, 3 and 5 wt. %) of silica

**Table captions:**

**Table1.** Degree of crystallinity,  $C$ , for pure PLA film and PLA film with different amount of silica

**Table1.**

Sample	C, %
Pure PLA	25.1
PLA+0.2 wt. % silica	27.1
PLA+0.5 wt. % silica	27.1
PLA+1 wt. % silica	24.2
PLA+2 wt. % silica	22.0
PLA+3 wt. % silica	21.7
PLA+5 wt. % silica	24.5