# INFLUENCE OF CHITOSAN-BASED COMPOSITES ON THE PROPERTIES OF CHEMICALLY MODIFIED POLY-LACTIC ACID FILMS

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## ABSTRACT

*The presented paper investigates the creation of chitosan-based composites on the surface of chemically modified poly-D-lactic acid (PDLA). PDLA was dissolved in chloroform and cast into a glass dish until the complete evaporation of the solvent. The surface of the created PDLA films was modified with 1,6-hexanediamine and glutaraldehyde for the creation of free aldehyde side groups. Composite layers of chitosan (CH) were deposited on the surface of the modified films. The mechanical properties of the composite films were investigated using a dynamometer. The surface morphology of the created composite films was studied with Scanning electron microscopy (SEM). Sessile drop method was used to determine the surface free energy of the created chitosan-based composite layers.*

*Keywords: chitosan-based composites, 1,6-hexanediamine, poly-lactic acid, mechanical properties.*

## INTRODUCTION

The production of biodegradable alternatives of the most common synthetic polymers has been one of the major focuses of the polymer industry in the last decade. One biopolymer that has demonstrated significant potential in that field is poly-lactic acid (PLA). With its high biocompatibility and sustainability PLA has become one of the main eco-friendly alternatives of many petroleum-based products, but its poor mechanical properties and hydrophobicity has limited its potential applications [1]. To improve its properties, poly-lactic acid is often chemically modified by adding other polymers in its structure [2]. Materials such as chitosan [3 - 5] have all been utilized for the improvement of different properties of PLA. Additionally, studies of different chitosan composites have demonstrated its suitability for a variety of medical applications [6 - 8]. In this paper we aim to investigate the effect of different chitosan composites on the physical properties of chemically modified poly-lactic acid.

## EXPERIMENTAL

### Materials

Poly (D-lactic acid) (PDLA), chitosan (high molecular mass, degree of deacetylation > 75 %), 1,6-hexanediamine and glutaraldehyde were delivered from Sigma-Aldrich and were used without further purification.

### Methods

***Composite films preparation***

Polylactic acid films were prepared by dissolving 3 g of PDLA in 100 mL of chloroform. The solution was then poured into glass dishes and left to dry for 24 h until the complete evaporation of the solvent. The chemical modification was performed by dissolving 1,6-hexanediamine in 15 mL of isopropanol at a concentration of 6 mg $mL^{-1}$. The solution was then poured onto the dried PDLA films and left for 2 min at room temperature. The modified films were rinsed in ethanol and deionized water five times and left in an ethanol/water solution overnight to remove any traces of the hexanediamine. The surface of the films was then modified with 1 % solution of glutaraldehyde for 3 h. This was done to transform the amino side groups created from the hexanediamine treatment into aldehyde groups. The films were rinsed again with deionized water and left to dry. 50 mL of 0.2 % chitosan solution was poured onto the films and left to dry for 24 h. This modification procedure is a modified version of the procedure used in Z. Lai et al [9]. This procedure was chosen from a number of similar ones due to the relative mildness of its conditions. However preliminary tests demonstrated the degradation of the used films after the first 2 min, which lead to further modification of the conditions. The modified films were compared to others described in literature and were found to be comparable to them visually and mechanically. Additionally, a ninhydrin reaction was performed, which confirmed the existence of amino side groups in the modified PDLA. In total 3 different films were created: pure PDLA (Pure), chemically modified PDLA (CM) and chemically modified PDLA with added chitosan (PDLA + CM + CH).

### *Mechanical properties*

The mechanical (tensile) properties of the films were examined in tensile mode using an LS1 universal testing machine (Lloyd Instruments) according to ASTM D882-91 standard [10]. The stripped (wideness 10 mm, length 100 mm, gap 50 mm) and fasten by rubber sealed pneumatic clumps films were loaded with deformation rate 1 mm $s^{-1}$ up to break.

### *Scanning electron microscopy (SEM)*

The general morphology of the obtained composite films was revealed by means of SEM. A scanning electron microscope Lyra 3 XMU (Tescan) was employed. The working voltage was 8.1 kV. Prior to the measurements, the samples were covered with a thin film of gold (about 30 nm).

### *Water Contact Angle Measurement*

All water contact angle measurements were performed under standard conditions (at room temperature and normal air pressure). Five measurements were performed for each type of modification on different places of the surface of the multilayer films. The average of those five results was used for determination of the hydrophobicity of the modified samples. Tiny droplets of 2 μL were used to reduce the effect of surface roughness on the water contact angle. The drops were deposited on the surface with the use of a precise 10 μL micro syringe (Innovative Labor System GmbH, Germany). Contact angles were obtained by using the tangent of the drop profile from pictures captured with an USB microscope. Image processing was performed using public domain ImageJ software (ImageJ v1.51k software).

## RESULTS AND DISCUSSION

### Mechanical properties

The most important properties in the context of applicability of the polymer films are their Young's modulus, determining their hardness, and their rupture point, given by stress at break and strain at break. These parameters for all investigated samples are given in Table 1.

It is seen from the experimental data, that the chemical modification of PDLA film with 1,6-hexanediamine drastically changes its mechanical properties. From viscoelastic, the film becomes highly hard and brittle. The Young's modulus changes from (62.34 ± 8.60) MPa to (1024.5 ± 71.85) MPa. At the

Table 1. Mechanical parameters of Pure, CM, PDLA + CM + CH films*.

| Type of film | Stress at break, MPa | Strain at break | Young's modulus, MPa |
|---|---|---|---|
| Pure | $17.72 \pm 1.86^{a}$ | $4.61 \pm 0.60^{c}$ | $62.34 \pm 8.60^{a}$ |
| CM | $26.04 \pm 3.40^{c}$ | $2.05 \pm 0.32^{a}$ | $1024.5 \pm 71.85^{d}$ |
| PDLA + CM + CH | $35.27 \pm 7.06^{d}$ | $3.35 \pm 0.69^{b}$ | $928.15 \pm 53.68^{c}$ |

** Values are presented as mean ± SD. Values with different superscripts within the same column (a, b, c, d) are statistically significantly different ($P < 0.05$).*

same time the strain at break changes from (4.61 ± 0.60) to (2.05 ± 0.32).

The addition of second chitosan–based composite layer on the modified PDLA film did not change sufficiently its mechanical properties.

**Scanning electron microscopy (SEM)**

The surface morphology of the pure PDLA, chemically modified PDLA (CM) and chemically modified PDLA with added chitosan (PDLA + CM + CH) are presented in Fig. 1.

The results presented in Fig. 1. show that the pure PDLA (Fig. 1a) is characterized by homogeneous and smooth structure. It was observed separate morphological entities generated during the solvent evaporation process. After aminolysis (chemical modification - Fig. 1b and Fig. 1c) the surface of PDLA became rougher. It was observed pores with size of about several microns. The existence of these pores also provided the probability that hexanediamine molecules could penetrate the PDLA film [11].

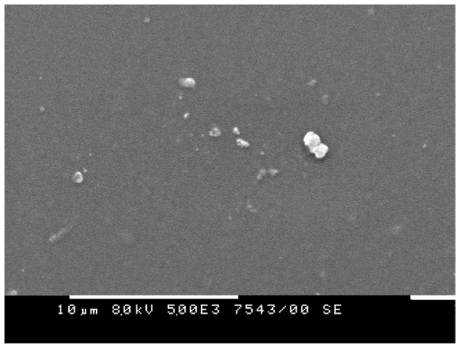
**Water contact angle measurements**

Contact angle values of the pure PDLA, chemically modified PDLA (CM) and chemically modified PDLA with added chitosan (PDLA + CM +CH) were measured.

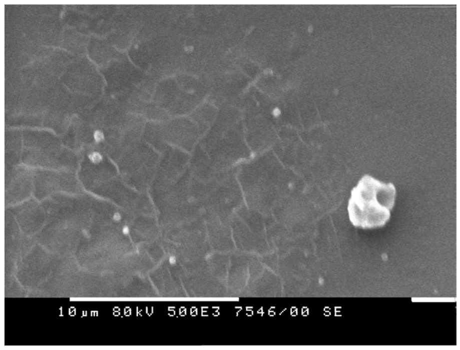
The results presented in Fig. 2 shows the surface wettability alteration before and after PDLA films was chemically modified and further immobilized by chitosan. Water contact angles measured by the sessile drop method decreased slightly after the PDLA films was chemically modified but decreased obviously after immobilization of chitosan. That is, the hydrophilicity of PDLA films increase after it was modified. On the other hand, this wettability alteration also confirmed the occurrence of the aminolysis reaction and the immobilization of chitosan [11, 12].

The surface free energy was determined based on the contact angle measurements of two different standard liquids: ultrapure water and diiodomethane at room temperature, using Owens and Wendt method [13]. The values of the total surface free energy are presented in Fig. 3.

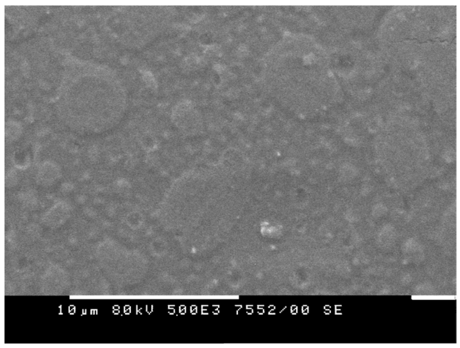
The results obtained show that the values of the surface free energy of CM and PDLA + CM + CH films are higher than those of the pure PDLA. The chemical modification of the films and the implementation of




(a)




(b)




(c)

Fig. 1. SEM images of different PDLA films (a) Pure (b) CM (c) PDLA + CM + CH.

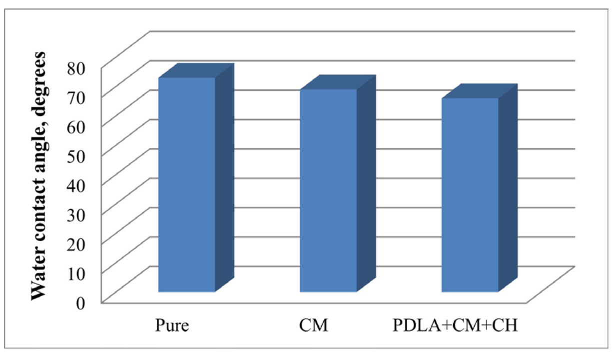



Fig. 2. Water contact angle of all investigated samples.

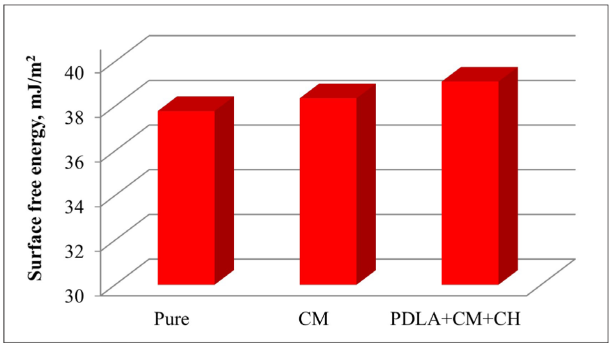



Fig. 3. Surface free energy of all investigated films.

chitosan lead to increasing of surface free energy. Then the hydrophilicity of chitosan-based composite films increases. A higher surface free energy will cause good wetting and has respectively a lower contact angle.

## CONCLUSIONS

The presented results demonstrate that the chemical modification of PDLA with hexanediamine creates a significant change in its mechanical properties. The addition of chitosan in the composite structure does not produce a significant change in the mechanical properties of the modified film and combined with the increase in roughness of the surface after modification, show that this method can be utilized for the creation of more suitable bases for the creation of different multilayer structures. The produced composites can be used for further developments in the field of composite polymer structures.

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