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Processing and nanomechanical properties of chitosan/poly(ethylene oxide) blend films

JELENA D. DJOKIĆ, ALEKSANDAR KOJOVIĆ, DUŠICA STOJANOVIĆ,
ALEKSANDAR MARINKOVIĆ[#], GORAN VUKOVIĆ, RADOSLAV ALEKSIĆ
and PETAR S. USKOKOVIĆ*

*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4,
11120 Belgrade, Serbia*

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Abstract: Chitosan-based films have found increasing implementation in a variety of fields, among which are as drug delivery carriers, in the packaging industry and as water purification filters. Therefore, in order to achieve mechanical integrity of such films while preserving processability and biocompatibility, chitosan-based films are fabricated in the forms of blends with poly(ethylene oxide) (PEO). A nano-indentation study was undertaken in order to investigate the nanomechanical properties and surface morphology of chitosan films in blends with various content of PEO. The results of differential scanning calorimetry, water uptake and nano-indentation revealed that films with an 80/20 blend ratio of chitosan/PEO showed the optimal values of reduced modulus and hardness. It appears that the incorporation of the synthetic PEO in chitosan films could lower the manufacturing costs while preserving the mechanical integrity of the films.

Keywords: chitosan; poly(ethylene oxide); polymer blend film; nano-indentation.

INTRODUCTION

The biopolymer chitosan has attracted increased interest in the past few decades due to its biodegradability and non-toxicity,¹ and containing free hydroxyl and amino groups, chitosan shows functional versatility, such as antimicrobial activity,² the ability to bind metal ions from solution,³ and as a drug release carrier.⁴ Significant work has been undertaken to fabricate multifunctional materials based on chitosan in the form of films, fibers, beads and hydrogels, which

* Corresponding author. E-mail: puskokovic@tmf.bg.ac.rs

[#] Serbian Chemical Society member.

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are designed for use in disease treatment,⁵ drug release,^{4,6,7} removal of metal ions^{3,8-10} as well as for the production of antimicrobial food packaging.^{2,11}

Widespread use of chitosan is limited mainly due to its relatively high cost compared to synthetic polymers, yellowish color that occurs over time and poor barrier properties.¹² A practical way to improve these properties and add new functionalities to chitosan-based materials is blending with low production cost synthetic polymers,¹³ such as poly(ethylene oxide) (PEO) that improves processability and mechanical properties¹⁴ and does not significantly affect the binding properties of metals from aqueous solutions and the antimicrobial properties of films, while reducing the water vapor permeability of films.^{9,10}

The synthetic polymer PEO, which is partially crystalline, biodegradable and soluble in water with the capacity to build hydrogen bonds, is widely used in the pharmaceutical and cosmetic industries, in the manufacture of paint and paper and in biomedical applications. Recently, its use in the fields of polymer membranes, solid electrolytes, hydrogels and pharmaceutical applications as drug carrier have become of interest. However, pure PEO films have relatively poor mechanical and physical properties due to the high solubility of the polymer in water, which limits their applications.¹⁵ These disadvantages are overcome by blending with other polymers, and since synthetic polymers are easy to produce at low costs, blends of natural and synthetic polymers may contribute to the feasibility of blend films. Films based on chitosan and PEO can provide additional functionality compared to the pure polymer films. Chitosan can enhance the mechanical properties and reduce the solubility of PEO in water; PEO may contribute to the formation of colorless flexible films. Conventional mechanical, metal-binding and antibacterial characterization of chitosan/PEO films was thoroughly performed in a series of studies by Zivanovic *et al.*^{9,10,15}

However, when chitosan and its blends are used in biomaterial applications, cell/tissue interactions are initiated at the nanoscale level. Nanomechanical properties of chitosan/PEO blends are not known; and as concluded by Majd *et al.*¹⁶ macroscopic mechanical properties do not necessarily convey the nanoscale properties of the material. Nano-indentation testing is used to characterize mechanical properties in fine spatial resolutions of materials such as fine-grained ceramics, polymers and composites, which found wide applications as biomedical implants.¹⁷⁻²¹ Given the wide range of applications of chitosan-based materials and its partially crystalline and amorphous composition, nanomechanical information related to chitosan films, and composites reinforced with carbon nanotubes and graphenes were studied using the nano-indentation method.²²⁻²⁶ Therefore, the aim of this study was to determine the surface nanomechanical properties and the optimal composition of chitosan and PEO blends and of the neat constituents in the form of thick films.

EXPERIMENTAL

A low molecular weight chitosan (Sigma Aldrich) with a deacetylation degree about 81 % (average value from potentiometric titration, FTIR and elemental analysis) and a molecular weight of 154 kDa (Kuhn–Mark–Houwink–Sakurada Equation) and poly(ethylene oxide) (PEO) of molecular weight 600 kDa (ACROS Organics) were used for the fabrication of the polymer blends. The solvent was 2 wt. % acetic acid (Sigma Aldrich). A phosphate buffer was used to adjust the pH value of solution in the swelling experiments. Deionized water (DI) (18 MΩ cm) was used for solution preparation. Methanol (Sigma Aldrich) was used for additional treatment of the dried films and for removal of residual monomer and acetic acid.

Films based on chitosan and PEO were prepared by the dilution technique and the film formation was completed by solvent evaporation. First, the polymers were dissolved in 2 wt. % acetic acid in a way to gain 5 wt. % polymer solutions. The solutions were prepared with different contributions of chitosan and PEO as follows: 100/0, 80/20, 70/30, 50/50, 20/80 and 0/100 (weight ratio: chitosan/PEO). The solutions of certain fractions were mixed on a magnetic stirrer for 24 h at room temperature. Homogenized solutions of the polymers, of total weight of 20 g, were poured into 50-mm diameter Petri dishes. The samples were first dried at 30 °C for 48 h, and then in a vacuum drying oven for 8 h at 40 °C. The dried films were detached from Petri dish and treated for 24 h in water and methanol sequentially to remove any remnants of acetic acid, which could affect the pH that may affect the degradation of the films in contact with water. After treatment with methanol, all the films had retained their previous form and structure. The films were then dried in a vacuum oven under the same conditions as above.

Film thickness (μm) was determined on six films each of which was measured on average five times. For these measurements, we used an electronic digital vernier caliper PRO-Max (Fowler). Thermal properties of chitosan, PEO and their blends were determined by differential scanning calorimetry (DSC Q10, TA Instruments) under a nitrogen atmosphere (50 ml min⁻¹). To determine the melting temperature (T_m), melting enthalpy (ΔH_m) and the degree of crystallinity (X_m), samples were heated to 80 °C and kept at 80 °C for 10 min. Then, they were cooled and reheated at a rate of 10 °C min⁻¹. The melting temperatures (T_m) were measured from the second cycle as the temperature at the top of the endothermic peak, $T_{m(max)}$. The melting enthalpy, ΔH_m , was determined from the area under the endothermic peak.

The static contact angles of chitosan/PEO films were measured using a DSA100 (Kruss). Samples with a circular cross-sectional diameter of 10 mm were placed on the testing board and carefully instilled with a drop of distilled water. The contact wetting angles were measured using a video camera and for each group of samples, the measurements were repeated five times. Adsorption capacity of water was determined by the degree of swelling. Specimens with mass W_0 were immersed in phosphate buffer (pH 7.4). After the desired welling time, the films were taken from the buffer, the water from the surface of the films was removed using filter paper and the weight, W_t , was recorded. The degree of swelling, Q , was calculated from the following equation:

$$Q = \left(\frac{W_t - W_0}{W_0} \right) \times 100 \quad (1)$$

The nano-indentation experiments on neat polymer films and blend films were performed using a Triboscope T950 nanomechanical testing system (Hysitron, Minneapolis, MN) equipped with Berkovich indenter type with an *in situ* imaging mode. The frequently used

power law method, developed by Oliver and Pharr,²⁷ involves the extrapolation of a tangent to the top of the unloading curve to determine the depth (a combination of elastic and plastic displacement) over which the indenter is in contact with the specimen at the maximum load. A peak load of 2 mN was applied for all samples with a load–hold–unload of 20 s for each segment. Ten indentations were made for each sample and the average values and standard deviations are reported.

RESULTS AND DISCUSSION

DSC is a particularly useful tool to study polymer–polymer miscibility and phase-separated polymer blends. The DSC method in this study was suitable for estimating the degree of phase separation and mixing of the chitosan/PEO polymer blends and determining the change in the degree of crystallinity in the blends compared to pure polymer. The degree of crystallinity of the films (X_m) can be accurately determined from DSC analysis of the samples based on the following equations:

$$\chi_{m,PEO} = \frac{\Delta H_{m,PEO}}{\Delta H_{m,PEO}^0} \quad (2)$$

$$\chi_{m,s} = \frac{\Delta H_{m,s}}{\Delta H_{m,PEO}^0 \omega_{PEO}} \quad (3)$$

where $\Delta H_{m,PEO}$ is the melting enthalpy of PEO, $\Delta H_{m,s}$ is the melting enthalpy of PEO in the blends, ω_{PEO} is the mass fraction of PEO in the blends and $\Delta H_{m,PEO}^0$ is the melting enthalpy of 100 % crystalline PEO (213.7 J g^{-1})²⁸ for PEO of 600 kDa molecular weight. The degree of crystallinity of the PEO, which was calculated according to Eq. (3), was 79 %, whereas those for the other films are given in Table I.

TABLE I. Result of the DSC analysis for chitosan/PEO blends

Sample	Melting temperature $T_m / ^\circ\text{C}$	Melting enthalpy $\Delta H_m / \text{J g}^{-1}$	Degree of crystallinity $X_m / \%$
CS/PEO–90/10	–	–	–
CS/PEO–80/20	61.99	30.97	43
CS/PEO–50/50	62.65	54.73	51
CS/PEO–20/80	65.23	73.56	72
CS/PEO–0/100	66.82	168.70	79

According to the data presented in Table I, blends with more than 10 wt. % PEO showed an increase in the degree of crystallinity and a decrease in the amount of amorphous phase. The increase of the degree crystallinity with increasing chitosan mass content could be assigned to a decrease in crystal growth because of the restriction of the molecular chain flexibility and the overall mobility of the blend. The progressive increase in the PEO content led to higher

values of T_m and ΔH_m , which is a reflection of the higher content of crystalline PEO in the polymer blend. These changes follow approximately linear trends with the PEO content and the increase of the melting enthalpy and temperature, as well as the degree of crystallinity. These findings point to a certain amount of compatibility between chitosan and PEO due to intermolecular chain formation and primary hydrogen bond formation between the polymer chains. The dependencies of the heat flow on temperature for chitosan/PEO polymer blends with various mass fractions of the starting polymers are shown in Fig. 1. If the polymer blends show a unique melting temperature instead of the individual values for the starting components, and if the melting temperatures and enthalpy shows an increase, a change in the semi-crystalline polymer could be used as proof for the qualitative degree of mixing of the polymers in the chitosan/PEO blends.

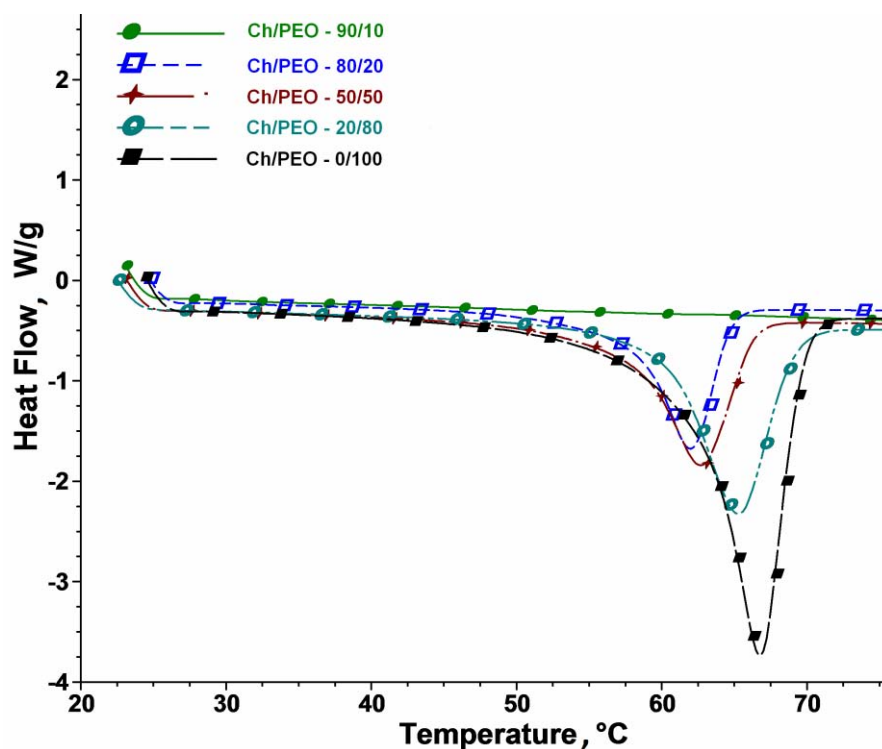


Fig. 1. Heat flow vs. temperature curves for chitosan/PEO blends.

PEO is a more hydrophilic polymer than chitosan. A higher content of chitosan in the blend led to water contact angles from 62.5 and 76.3° for 80/20 and 90/10 chitosan/PEO contents, respectively, and up to 81.2° for neat chitosan. It is interesting that the neat PEO films had a high contact angle (79.7°), probably due to their densely packed, low-dimension crystalline film structure, which is in-

soluble and make the film surface rough and hydrophobic. Zivanovic *et al.*¹⁵ revealed that the permeability of water vapor is lower for neat PEO than for films with a lower PEO content in chitosan. With an increased hydrophilic PEO content in chitosan, which in this case was more prone to hydration, the water contact angle decreased, *i.e.*, the films show more hydrophilic properties – for chitosan/PEO contents of 20/80, 50/50 and 60/40, the contact angle were 59.5, 48.7 and 55.1°, respectively. For these samples, the crystalline PEO does not prevail, but more decisive is that the water-soluble polymer is introduced that increases the hydrophilic nature of the blends. In the samples where the PEO is dominant, the crystalline structure is more decisive than its water solubility.

Water uptake tests were determined through the swelling degree after 200 min (Fig. 2) and 24 h and the results were shown to be in accordance with contact angle tests. Thus, for samples of neat chitosan and the 90/10 and 80/20 chitosan/PEO ample, swelling occurred very rapidly and equilibrium was attained in about 30 min. For 70/30 and 60/40 chitosan/PEO samples, the swelling was also at first very fast, but after 20 min, peaks in the degree of swelling were observed and equilibrium was attained in about 100 min. This could be a consequence of the dissolution of certain amount of PEO that is not bonded to the interpenetrating network and to the formation of surface layer of polymer that is not hydrophilic in the contrast to ones incorporated in the main polymer structure. Although high resistance to water uptake of polymer films may be beneficial for many applications, controlled solubility is required if films are to be used as drug and antiseptic carriers, and, in general, in membrane-like structures.

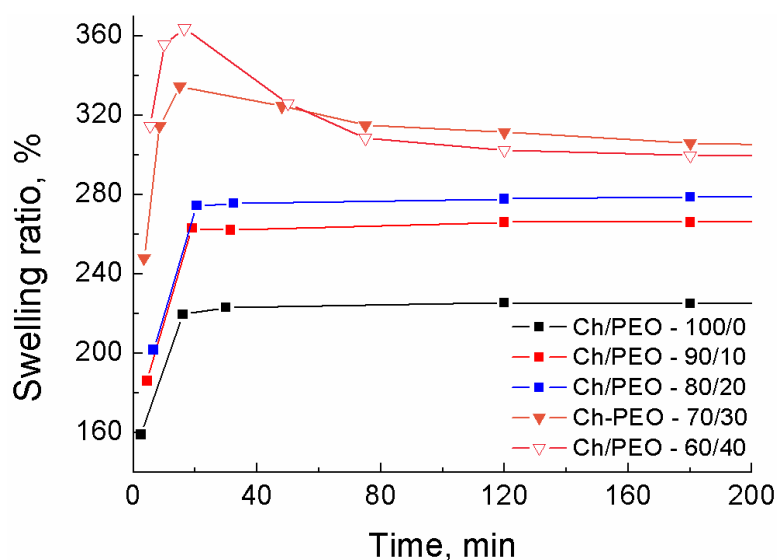


Fig. 2. Water uptake tests recorded during 200 min.

The nano-indentation method was used in this study to determine the reduced modulus and hardness of neat chitosan and PEO, as well as their blends. Typical load–depth profiles of the indents, which were recorded during the indentation of films of neat PEO and the blends with various mass content of chitosan are shown in Fig. 3, which revealed that the smallest resistance to the indentation load was shown by the neat PEO film and the largest resistance was exhibited by the blend film with 80 % of chitosan. After reaching the maximal indentation force, the plateau reveals the hold time of the indenter tip, which was predicted in order to minimize the polymer creep effect.

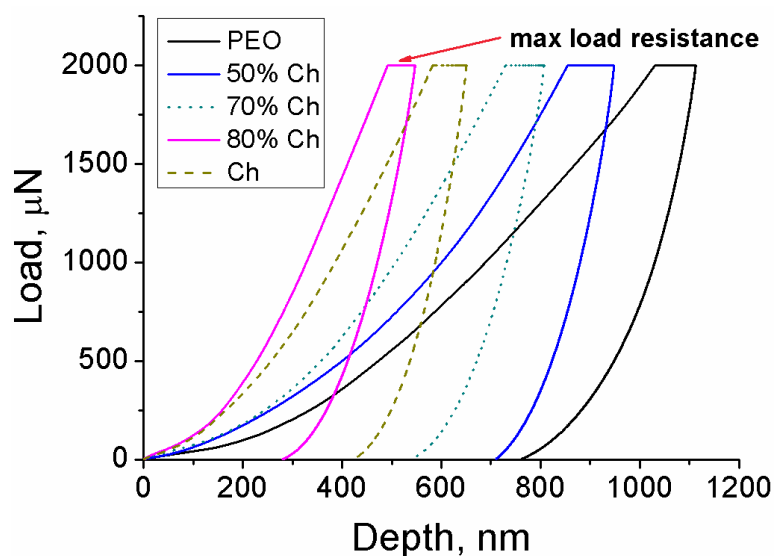


Fig. 3. Representative load–depth curves for chitosan/PEO films with various chitosan contents showing highest load resistivity of the blend film containing 80 wt. % chitosan.

The film thickness varied in the range of 353–409 μm . The indent depth did not exceed 1.1 μm ; hence, it is obvious that there was no substrate influence on nano-indentation test results. Therefore, the Oliver–Pharr method appeared suitable to calculate the reduced modulus of elasticity and the hardness values. Increasing PEO content led to a decrease in the film thicknesses. This could be explained by the contractions of the 3D film matrix due to strong interactions of the chitosan and PEO molecules, the increase in crystallinity within the PEO phase and by the fact that the addition of PEO led to a decrease in the blend viscosity.

In situ imaging scans of the indent plastic imprint with the corresponding line scan and median roughness for the blend film with 20 wt. % chitosan are shown in Fig. 4. As an insert, the 3D view of the indent imprint is included in this Figure. The tested films had median surface roughness in the range 0.09–0.14 μm whereby, the greatest roughness was measured for the neat PEO film. With addi-

tion of chitosan, a slight decreasing trend was registered. The samples were not polished prior to testing and the surface roughness was appropriate for the testing procedure. The selected imprint shown in Fig. 4 and the scans for the other samples revealed the absence of micro cracks at the indent corners. Line scans for the selected and the other tested sample show that there are no significant pile-up and sink-in formation of the material deposits at the indent edges. These findings together with the indentation curves without pop-in formations (Fig. 3) give confidence that the material properties derived from the nano-indentation testing could be considered as reliable.

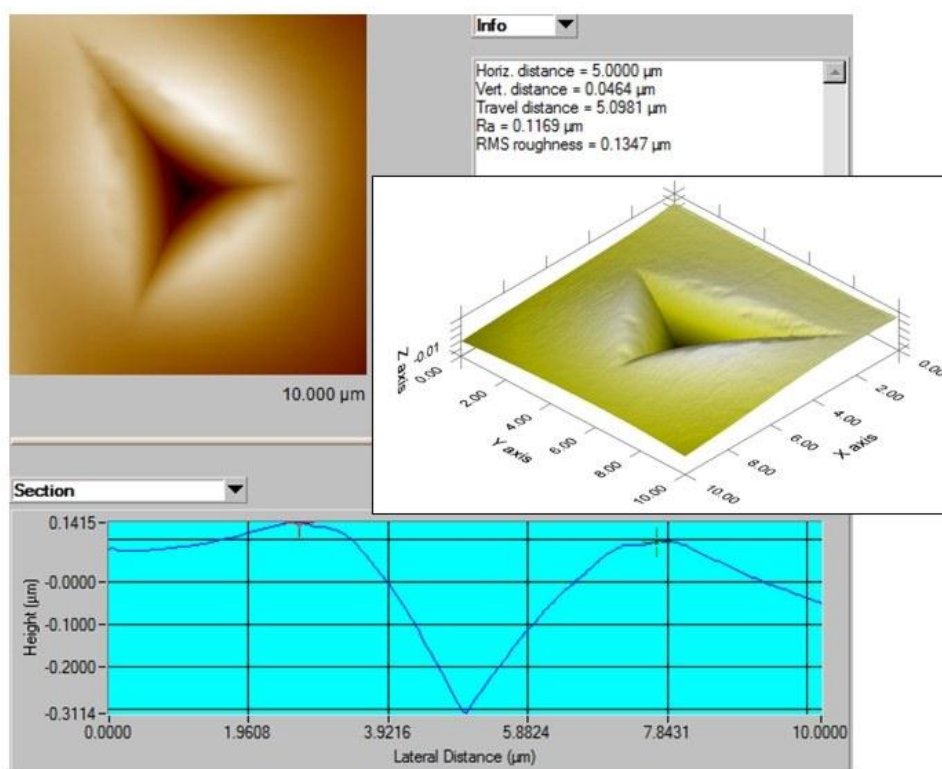
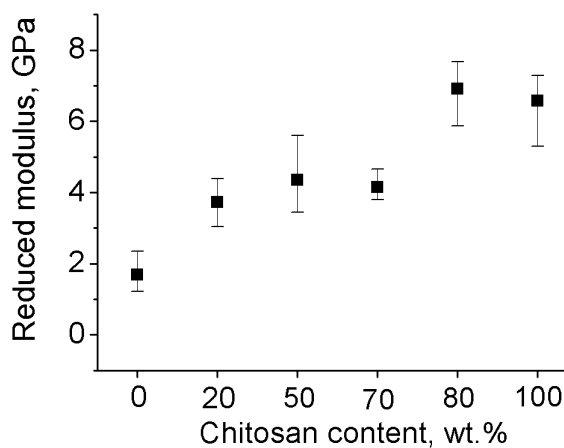


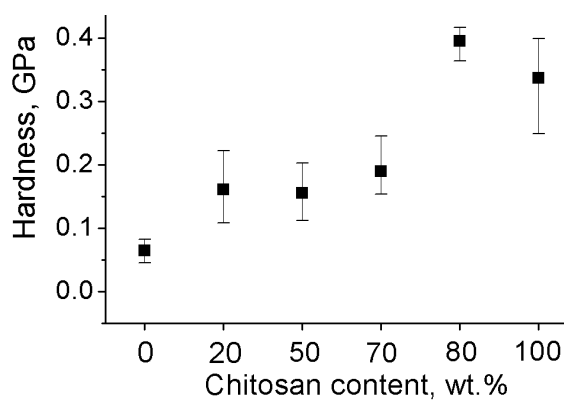
Fig. 4. 2D and 3D view (axis dimensions, μm) of the plastic nano-indentation imprint with the corresponding line scan and median roughness for the blend film with 20 wt. % of chitosan.

The average values with the range of reduced elastic modulus (E_r) and hardness (H) for PEO film samples and the appropriate blends with chitosan, the content of which was varied up to the neat chitosan sample, are shown in Fig. 5. The measured values of E_r and H of neat PEO (1.68 GPa and 0.06 GPa, respectively) are similar to the ones obtained by Nowicki *et al.*,²⁹ in a study that compared the nanomechanical properties of PEO with poly(vinyl chloride) and poly(acrylic

acid). In the present study, 20 wt. % content of chitosan in the polymer blend led to an increase in E_r and H of about 120 and 165 %, respectively. Additional increases in the chitosan content led to modest changes in the reduced modulus and hardness. The reduced modulus and hardness of the blend increased from 4.15 and 0.19 GPa, respectively, for the blend 70/30 to 6.617 and 0.385 GPa, respectively, for the 80/20 blend. Interestingly, the reduced modulus and hardness were slightly lower for the neat chitosan films (6.57 and 0.336 GPa, respectively). It appears that the optimal configuration for the optimal nanomechanical properties is with a chitosan content of 80 wt. %. The improvement in the mechanical properties with increasing chitosan content could be explained by the addition of the stiffer chitosan phase being more decisive for the mechanical properties than degree of crystallinity of the blend.



(a)



(b)

Fig. 5. Average values with error bars of a) the reduced elastic modulus and b) the hardness of blend film samples vs. chitosan content (wt. %).

Among other positive features, chitosan materials in various architectures have a significant sorption potential for environmental protection issues as well as favorable antibacterial properties. Despite this, in most material architectures, such as film-like structures, the positive effects of chitosan may be masked if the chitosan molecules are entrapped within the volume of the surrounding material. Li *et al.*⁹ argued that an increase in the surface-to-mass ratio of chitosan structures could lead to improved functionalities. In order to increase the efficiency of chitosan and maintain mechanical integrity, further work will be directed towards filters and membranes structured from chitosan nanocomposite fibers reinforced with carbonaceous structures (carbon nanotubes and graphenes) as well as natural fibers from industrial waste.

CONCLUSIONS

For certain applications, just to mention drug or antiseptic carriers and packaging materials, understanding the nanomechanical behavior of chitosan-based films should be considered when designing products. In order to enhance the production feasibility and material processability, substitution of chitosan biopolymer in certain amount by synthetic PEO could reduce the price of the blend films while still maintaining the desired functionalities. Films with 80/20 blend ratio of chitosan/PEO exhibited the best nanomechanical properties, and the trend of the overall nanomechanical results revealed that incorporation of the stiffer chitosan phase is more relevant for positive mechanical properties than the degree of crystallization of blends, which is higher when the PEO is dominant in the film composition.

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ИЗВОД

ПРОЦЕСИРАЊЕ И НАНОМЕХАНИЧКА СВОЈСТВА ФИЛМА БЛЕНДИ ХИТОЗАН/ПОЛИЕТИЛЕН-ОКСИД

ЈЕЛЕНА Д. ЂОКИЋ, АЛЕКСАНДАР КОЈОВИЋ, ДУШИЦА СТОЈАНОВИЋ, АЛЕКСАНДАР МАРИНКОВИЋ,
ГОРАН ВУКОВИЋ, РАДОСЛАВ АЛЕКСИЋ И ПЕТАР С. УСКОКОВИЋ

Технолошко-металушки факултет Универзитет у Београду, Карнегијева 4, 11120 Београд

Филмови на бази хитозана налазе све ширу примену у разним областима између осталог као носачи лекова, у индустрији амбалаже и као филтери за пречишћавање вода. Да би се постигао механички интегритет оваквих филмова и задржала процесабилност и биокompatibilност, филмови на бази хитозана припремљени су у форми бленди са полиетилен оксидом (PEO). Студија наноиндентације урађена је у циљу проучавања нано механичких својстава и површинске морфологије хитозанских филмова у блендама са различитим садржајем PEO. Резултати DSC-а, апсорпције воде и наноиндентације показали су да филмови бленди са односом 80/20 хитозана и PEO поседују оптималне вредности редукованог модула еластичности и тврдоће. Показано је да дода-

вање синтетичког РЕО у хитозанске филмове може смањити цену производње и истовремено задржати механички интегритет филмова.

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