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The influence of UV-irradiation on chitosan modified by the tannic acid addition

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ABSTRACT

The influence of UV-irradiation with the wavelength 254 nm on the properties of chitosan modified by the tannic acid addition was studied. Tannic acid was added to chitosan solution in different weight ratios and after solvent evaporation thin films were formed. The properties of the films such as thermal stability, Young modulus, ultimate tensile strength, moisture content, swelling behavior before and after UV-irradiation were measured and compared. Moreover, the surface properties were studied by contact angle measurements and by the use of atomic force microscopy.

The results showed that UV-irradiation caused both, the degradation of the specimen and its cross-linking. The surface of the films made of chitosan modified by the addition of tannic acid was altered by UV-irradiation.

1. Introduction

Chitosan, as a derivative of chitin, is biocompatible, biodegradable and nontoxic for human body [1–3]. It is commonly used as a component of materials widely applied in medicine [4–6]. Chitosan materials can be shaped into different forms such as films, 3D scaffolds or hydrogels. Biomaterials prepared as a film can be used for preparation of dressings or to coat devices which need to be incorporated into the human body. The properties of polymer networks can be modified by the cross-linking treatments. Addition of cross-linking agent is the easiest way to make any modifications of material properties [7,8]. Tannic acid is a natural compound, which is not toxic for human body [9]. It can be used in cross-linking treatments of chitosan materials, because the interactions between polymer and tannic acid are present and therefore they can modify the polymer properties [4,10,11]. Tannic acid has the ability to interact with biopolymers such as collagen, chitosan, gelatine, albumin by noncovalent interactions. Tannic acid can form ionic, hydrophobic and hydrogen interactions [11]. Addition of tannic acid to the chitosan matrix allows obtaining more stiff scaffolds because it can act as a cross-linking agent. It increases the breaking force and decreases elongation at break parameters [12]. The question is whether the addition of tannic acid can modify the photochemical stability of chitosan.

It is known that UV light destroys chitosan matrix due to the high energy of radiation. Photodegradation process occurs on the films surface an in the bulk. Main mechanism of photodegradation include formation of carboxylic groups, production the hydroxyl groups and formation of carboxylic groups in the presence of oxygen [13]. With increasing time of irradiation, degradation increases, what can be observed by FTIR or mechanical properties analysis. Non-covalent interactions are broken first because they are weaker than covalent; nevertheless, covalent bonds are also destroyed after prolonged irradiation. It results in worse properties of biomaterials made of chitosan [14–19].

UVC radiation (280–100 nm) is commonly used in biocidal lamps [20,21]. It is essential to detect the influence of UV-irradiation on biomaterials, because often they have to be irradiated by UVC light to sterilize them before the medical application [22,23].

2. Materials and methods

2.1. Materials

Chitosan powder (DD = 77% M_v = 5.4 × 10^5 g/mol) [24] and tannic acid were purchased in Sigma–Aldrich company, Poland. Chitosan solution in 0.5 M acetic acid was prepared in concentration 1 wt.%. Tannic acid was added in different weight ratios 2, 5, 10 and 20 based on chitosan. It was added during the magnetic stirring to the chitosan solution. Composites were prepared in film form, on glass plates, after solvent evaporation.

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2.2. UV-irradiation

The mercury lamp, Philips TUV-30 was used as a radiation source. The lamp emits light with 254 nm wavelength belonging to UVC. The intensity of irradiation was 27.4 μJ/cm^2. The intensity of the incident light was measured by using an IL 1400A Radiometer (International Light, USA). Irradiation experiments were carried out at a constant distance of 3 cm from the light source on the glass plates. Samples were placed directly under the lamp. Before measurement, the lamp was turned on for 15 min to warm up. The experiment was carried out in a dark room with a constant temperature and humidity. The exposure time to UV-irradiation was 2, 4 and 6 h.

2.3. FTIR spectroscopy

FTIR spectra were obtained by Genesis II FTIR spectrophotometer (Mattson, USA) for each kind of the blend. All spectra were recorded by absorption mode at 4 cm^{-1} intervals and 64-times scanning. The absorption values were obtained in the range of 600–4000 cm^{-1}.

2.4. Mechanical properties

Mechanical properties were measured by a mechanical testing machine (Z.05, Zwick/Roell, Germany). Stress–strain curves were recorded at a room temperature in the dry state. Start speed was 200 mm/min. The extension of the sample is expressed here as a percentage of elongation of the sample from the original length. The linear region of the stress extension curve gives the Young modulus (E_{mod}). The stress needed to break the sample is the breaking force (F_{max}). Samples were cut with a sharper of initial dimensions 50 mm length with a 4.5 mm width and 50 μm thickness. The thickness of the sample was measured by an ultrameter type A-91 (producer: Manufacture of Electronic Devices, Warsaw, Poland). For each kind of film, at least five samples were tested.

2.5. Differential scanning calorimetry

Differential scanning calorimetry measurements were made by DSC equipment (NETZSCH Phoenix DSC 204 F1). Heating rate was 10 °C/min, from 20 to 250 °C in nitrogen atmosphere with flow 40 ml/min. The weight of samples was 0.9–1.3 mg and the measurement pan type was aluminum pans.

2.6. Moisture content

Film moisture contents were determined by drying samples in an oven at 105 °C until constant weight. Results were expressed as grams of water in 100 g of dry sample weight.

2.7. Swelling behavior

Swelling behavior was measured by immersing the composites fragments in phosphate buffer solution (PBS) with pH = 7.3. After 1,2,3,4,5,6 and 24 h of immersion the materials were dried and weighed. Swelling after 24 h of immersion was then calculated by using Eq. (1):

$$\text{swelling} = [(m_t - m_0)/m_0] * 100\% \tag{1}$$

Such analyses were made for chitosan samples with addition of tannic acid in different ratios as well as for pure chitosan as a control sample. Then, swelling behavior of irradiated samples was measured using the same procedure.

2.8. Contact angle measurement

The contact angles of two liquids: water and diiodomethane were measured at a constant temperature using a goniometer equipped with a system of drop shape analysis (DSA 10 Control Unit, Krüss, Germany).

2.9. Atomic force microscope

Topographic images were obtained using a multimode scanning probe microscope with a Nanoscope IIIa controller (Digital Instruments, Santa Barbara, CA) operating in the tapping mode, in air, at room temperature. Surface images were acquired at fixed resolution (512 × 512 data points) using scan width 5 μm with a scan rate of 1.97 Hz. Silicon tips with spring constant 2–10 N/m were used. Roughness parameter such as the root mean square (Rq) was calculated from 1 μm × 1 μm scanned area using Nanoscope software.

3. Results and discussion

3.1. FTIR spectroscopy results

FTIR analysis of pure chitosan allows to find characteristic groups as N—H, O—H (3249 cm^{-1}), C—N, N—H (1635 cm^{-1}), C—N, N—H (1549 cm^{-1}). Such peaks are also present in the spectra for composites with addition of tannic acid (Table 1), however they are shifted to higher frequencies. It suggests, that the cross-linking process took place and complex of tannic acid and chitosan was obtained due to the presence of interactions between them. Moreover, after addition of tannic acid one more peak is observed at 1700 cm^{-1} for C=O group. Between tannic acid and O—H as well as N—H groups of chitosan the hydrogen bonds and van der Waals interactions can be formed. Exposition of the specimen to UV-irradiation results in a different wavenumber of peaks because some bonds were broken due to the degradation process and more single groups are present (Table 1).

Shifts in wavenumbers for bands observed in FTIR spectra of chitosan allow to consider that interactions between chitosan and tannic acid are present. Moreover, after UV-irradiation of the specimens the wavenumbers of these bands were changed what may suggest that the degradation process took place. For the sample with 20 wt.% of tannic acid the peak from C=O group is not observed what can suggest that tannic acid is susceptible on UV light. Moreover, peak from NH_3^+ is observed, what inform that chitosan is also degraded by UVC light. Tannic acid as smaller molecular weight component of the composite and a naturally occurring plant polyphenol with several aromatic rings is absorbing the most

Table 1
Characteristic peaks for chitosan (CTS) with addition 20 wt.% of tannic acid (CTS 20TA) before and after 4 h exposure to UV radiation (CTS 20TA 4 h).

Wavenumber (cm^{-1})	Functional group
CTS	
3249	O—H, N—H
1602	C—N, N—H
1064	C—O—C
CTS 20TA	
3305	O—H, N—H
1701	C=O
1070	C—O—C
CTS 20TA 4 h	
3318	O—H
1413	—NH_3^+
1105	C—O—C