



# The influence of UV-irradiation on thermal and mechanical properties of chitosan and silk fibroin mixtures



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## ABSTRACT

In the present paper the results regarding the influence of UV-irradiation with 254 nm wavelength on the thermal and mechanical properties and the intrinsic viscosity of chitosan/silk fibroin mixtures are presented.

The mixture of chitosan and silk fibroin in solution and thin films made of chitosan/silk fibroin mixture obtained by solvent evaporation were submitted to the treatment with UV irradiation (wavelength 254 nm) for different time intervals. Mechanical properties of thin films made of chitosan/silk fibroin blends before and after UV-irradiation have been investigated by mechanical testing machine and compared with mechanical properties of chitosan films. The changes in such mechanical properties as ultimate breaking strength, percentage of elongation at break and Young Modulus have been investigated.

The results have shown, that the mechanical properties of the blends were greatly affected by time of exposure to UV irradiation. Ultimate tensile strength and ultimate percentage of elongation decreased after UV irradiation of the blend. Increasing UV irradiation led to the decrease in Young's Modulus of the chitosan/silk fibroin blend. Viscosity of chitosan/silk fibroin mixtures decreased after UV-irradiation. Thermal properties of the mixtures have been only slightly altered by UV-irradiation.

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## 1. Introduction

Thermal and mechanical properties of materials are very important from the point of view of their potential applications. Natural polymers are widely applied in several fields, such as biomedical and cosmetic ones. They are also widely used in packaging and textile industry. Products made of natural polymer for biomedical applications need to be sterilized. For the sterilization of materials made of polymers both, UV radiation and high temperature can be used.

Silk is a biopolymer widely used in textile production and as biomaterial in medicine [1–3]. Raw silk consists of 75–83 wt% of silk fibroin, 17–25 wt% of glue-like coating sericine, wax and fats (1.5%), colorants and mineral components (1%), depending on the species, origin and culture conditions [4,5]. Photochemical stability of silk fibroin was studied previously [6]. It was found that the absorption of silk fibroin in solution increased during UV-irradiation of the sample (most notably between 250 and 400 nm) and a wide peak emerged between 290 and 340 nm with maximum at about 305 nm. The new peak suggested that new photoproducts

were formed during UV irradiation of regenerated silk fibroin [6]. SDS-PAGE chromatography showed the alterations of molecular weight of silk after UV exposure.

Chitosan is a natural polymer derived from chitin. Chitin is a polysaccharide, a homopolymer comprised of 2-acetamido-2-deoxy- $\beta$ -D-glucopyranose units. Chitosan can be obtained from chitin by the deacetylation process. Some units in chitosan chains exist in the deacetylated form as 2-amino-2-deoxy- $\beta$ -D-glucopyranose. Chitosan is a biodegradable natural polymer with great potential for pharmaceutical applications and cosmetic industry due to its biocompatibility, high charge density, non-toxicity and mucoadhesion [7–12]. Chitosan itself is a very good material for biomedical applications, but after several modifications of its properties one can obtain versatile biomaterial for cell therapy, tissue engineering and gene therapy [13–15]. Covalent and ionic cross-linking of chitosan leads to formation of hydrogels which can be used as drug delivery system under pH-controlled conditions [16]. Chitosan derivatives can also be applied in various tissue engineering applications namely, skin, bone, cartilage, liver, nerve and blood vessel [17–22]. In the scientific literature one can find information about blending of chitosan with other natural polymers and/or synthetic polymers. There are several methods of preparing polymer blends of cellulose, chitin and chitosan with natural and synthetic polymers [23]. Chitosan was blended with

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other proteins such as soy protein, collagen and silk fibroin [24–30]. From such the blends mainly biomaterials for applications in wound healing and skin tissue engineering scaffolding have been considered [30,31].

The formation of scaffolds from chitosan/fibroin blends from aqueous solution is possible but it depends on the pH value [26,27]. By electrospinning of the silk fibroin/chitosan blends with a chitosan content of up to 30% the continuous fibrous structure of material can be obtained [29].

Chitosan and silk fibroin due to the specific properties of each one may be used to produce synthetic mixture that confer unique structural properties [30,31].

The aim of our work was to study the mechanical and thermal properties of chitosan and silk fibroin mixtures after treatment with UV-irradiation. We previously studied the influence of UV light on surface properties of thin films obtained by solvent evaporation from chitosan/silk fibroin mixture [31,32]. Both, the contact angle measurements and the AFM investigations have proved that the surface of chitosan/silk fibroin blend is enriched in silk fibroin component. The contact angle measurements and values of surface free energy have shown that the wettability of chitosan/silk fibroin blended films was changed by UV-irradiation due to photooxidation process [32]. UV-irradiation caused the decrease of surface roughness of chitosan film, silk fibroin film and film made of the blend of chitosan and silk fibroin [32]. For our best knowledge the influence of UV light on the thermal and mechanical properties of chitosan/silk fibroin films has not been studied yet.

## 2. Materials and methods

Chitosan powder (CTS) (degree of deacetylation DD = 80%  $\bar{M}_v = 1.9 \times 10^5$  g/mol) was obtained from Aldrich and used without further purification. The viscosity average molecular weight  $\bar{M}_v$  of chitosan was measured with the Ubbelohde viscometer using 0.2 M sodium acetate and 2% acetic acid as a solvent [33] and calculated from the viscosity of solutions according to the Mark–Houwink–Sakurada equation [34]. The degree of deacetylation (DD) of chitosan was estimated by the conductometric of titration method [35]. Silk fibroin (SF) was prepared in our laboratory from *Bombyx mori* cocoons (Jedwab Polski Sp. z o.o. company). Cocoons were boiled for 1 h in aqueous solution of 0.5%  $\text{Na}_2\text{CO}_3$  according to the procedure found in literature [36] and then rinsed thoroughly with distilled water to extract the sericin proteins. The subsequent procedure was the same as described earlier [31,32]. The SF solution with a concentration of 5% was obtained.

The solutions of chitosan and silk fibroin were prepared separately, in aqueous 0.1 mol  $\text{dm}^{-3}$   $\text{CH}_3\text{COOH}$ , and then mixed at different proportions. The polymer films were obtained by solution casting method. The films were dried in vacuum at room temperature. To the treatment with UV-irradiation were submitted both, the solutions and thin films based on the mixture of chitosan and silk fibroin. UV-irradiation of solution was carried out directly in quartz viscometer. Polymeric films and solutions were irradiated in air at room temperature using a mercury lamp Philips TUV – 300 which emits light mainly 254 nm. Time of exposure was 2–8 h.

Thermogravimetric analysis (TGA) was carried out using Thermal Analysis SDT 2960 Simultaneous TGA–DTA analyser of TA Instruments in the temperature range of 20–600 °C at heating rate 10 °C/min in nitrogen. From thermogravimetric curves the characteristic temperatures of decomposition such as: temperature of initial decomposition ( $T_{di}$ ) and temperature at maximum decomposition rate ( $T_{max}$ ) of the investigated samples were determined.

Mechanical properties of the materials were measured at room temperature using a tensile tests Zwick&Roell at a crosshead speed of 5 mm/min in accordance with the Polish Norm PN-81/C-89034 (ISO 527-1 i 527-2) standard procedure. Samples were cut with a shaper into dog-bone shapes of initial dimensions 50 mm length with a 4.1 mm width and 30  $\mu\text{m}$  thickness. The thickness of the samples was determined using an ultrameter type A-91 (producer: Manufacture of Electronic Devices, Warsaw, Poland). All the samples of film were cut using the same shaper. For each kind of film, at least five samples were tested.

Viscosity measurements of diluted polymer solution were carried out in a controlled thermostatic bath at  $20 \pm 0.1$  °C using the quartz Ubbelohde capillary viscometer. The flow times were recorded with an accuracy  $\pm 0.01$  s. Before measurements the solutions were filtered through G1 sintered glass filters. The intrinsic viscosity was determined according to Solomon–Ciuta equation [37,38].

Images by optical microscope were made in ambient conditions using Biological Microscope XSP-44 ENLARGEMENT with a magnification  $40\times$  to  $1024\times$ . Films surface were analyzed by computer program Ulead Video Studio 7 SE VCD with 4 and 40-times of magnification.

## 3. Results and discussion

Thermal properties of polymeric materials can be studied by means of thermogravimetric analysis and by differential scanning calorimetry. Thermogravimetric analysis is widely used for characterization of thermal stability of different polymeric materials. Thermal properties of polymers and their composites and/or blends provide valuable information regarding stiffness, toughness, stability and miscibility with other compounds [39,40]. Miscibility investigations of chitosan (CTS) with silk fibroin (SF) mixtures with different weight percentage composition were studied previously in diluted solution using viscometric method [41]. It was found that system are miscible in solution at the weight fraction of chitosan in the mixtures  $W_{CTS} \leq 0.5$ . The results of thermogravimetric analysis of chitosan, silk fibroin and their mixture films are shown in Table 1. TG and DTG curves for chitosan/silk fibroin mixture in film are shown in Fig. 1. TGA curve of the film made of chitosan/silk fibroin mixture shows a weight loss in three stages (Table 1). The first stage (97–143 °C) is associated with the loss of absorbed and bound water and residue of acetic acid and shows about 6% loss in weight for non-irradiated chitosan and chitosan/silk fibroin samples. The second stage with  $T_{max}$  for chitosan at 281 °C is due to the degradation of chitosan with loss in weight 39%. The second stage for specimens based on the blends of chitosan/silk fibroin was observed at lower temperature: 188 °C for the blend with ratio 50/50. After UV-irradia-

**Table 1**  
The weight loss ( $\Delta m$ ) and temperature at maximum decomposition rate ( $T_{max}$ ) of CTS/SF mixtures before and after UV-irradiation.

$W_{CTS}$	Time of UV irradiation (h)	$\Delta m$ (%)			$T_{max}$ (°C)		
		I	II	III	I	II	III
1.0	0	6	39	12	143	281	399
	2	7	41	13	92	295	399
	8	6	40	14	89	282	395
0.5	0	6	5	47	123	188	260
	2	5	11	44	98	174	273
	8	6	7	45	107	208	265
0.0	0	6	8	47	97	168	265
	2	7	8	45	93	179	270
	8	5	6	6	92	179	270

$W_{CTS}$  – the weight fraction of chitosan in the mixtures.

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