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Weathering of chitosan films in the presence of low- and high-molecular weight additives

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ABSTRACT

The effects of artificial solar radiation from an Accelerated Weathering Chamber (Weatherometer) on thin chitosan films were studied by UV–Vis and FTIR spectroscopy, contact angle measurements, microscopy methods and mechanical properties investigation. Chitosan films were prepared through a solution casting method. Several films were prepared with low- and high-molecular weight additives, such as camphorquinone, glutathione, tyrosine, phenylalanine and collagen. It was found that UV–Vis spectra, which characterize chitosan, were significantly altered by artificial solar radiation. The thermal properties and polarity of the surface were also altered by artificial solar light. Mechanical properties such as the ultimate tensile strength, percentage elongation and Young's modulus of chitosan films were changed irregularly according to irradiation time. The deterioration of the mechanical properties of chitosan films after irradiation results mainly from photochemical changes such as cross-linking and chain scission. The contact angle and the surface free energy of chitosan films were altered by artificial solar UV irradiation. The influence of low- and high-molecular weight additives on photodegradation of chitosan has also been discussed.

1. Introduction

Chitosan is a natural polymer (polysaccharide) prepared from chitin by deacetylation. One of the most promising features of chitosan is its excellent ability to be processed into porous structures and thin films for use in cell transplantation and tissue regeneration. Chitosan is also widely applied in cosmetics such as body creams and/or hair conditioners. Chitosan is sensitive to various types of degradation such as oxidative, hydrolytic, thermo-, photo- and ultrasonic degradation (Casimiro, Botelho, Leal, & Gil, 2005; Sionkowska, Wisniewski, Skopinska, Kennedy, & Wess, 2004; Sionkowska, Wisniewski, Skopinska, Marsano, & Vicini, 2005; Wang, Huang, & Wang, 2005; Wasikiewicz, Yoshi, Nagasawa, Wach, & Mitumo, 2005). Due to the fact that chitosan is commonly used in the production of cosmetics such as hair conditioners, it is often exposed to solar light after it is applied to the surface of the hair (Rinaudo, 2006).

Naturally occurring polymers absorb solar radiation and undergo photolytic, photo-oxidative and thermal-oxidative reactions that result in the degradation of the material (Andrady, Hamid, Hu, & Torikai, 1998; Rabek, 1995). The degradation suffered by bio-polymeric materials can lead to a loss of mechanical properties which limit their performance. In particular, in sunlight, the ultraviolet radiation determines the useful lifetime of many materials. Any increase in the UV content of terrestrial solar radiation due to a partial depletion of the stratospheric ozone layer is therefore expected to have an impact on biopolymers. Moreover, for biopolymers the humidity and air temperature during exposure have a large influence on photo-degradation. For synthetic polymers it was found that the specimens kept at lower temperatures deteriorated much more slowly than those at ambient temperature although both were exposed to the same dose of solar radiation (Rabek, 1995).

At the first stage the photochemical reactions usually occur on the surface (Kaczmarek, Kowalonek, Szalla, & Sionkowska, 2002; Sionkowska, 2007). Later on, the alterations occur in the bulk of the material. The aim of our work was to study the properties of chitosan film after weathering using an artificial source of light similar to solar radiation in an Accelerated Weathering Chamber (Weatherometer). To the best of our knowledge this is the first time such studies have been carried out. The photochemical degradation of chitosan was studied after exposure to 254 nm wavelength (Sionkowska et al., 2004, 2005; Wang et al., 2005; Wasikiewicz et al., 2005). It was found that chitosan is an accelerating agent for the photochemical reaction in collagen solution after exposure to 254 nm wavelength (Sionkowska et al., 2004). Moreover, it was found that the wettability of chitosan films was changed by UV irradiation (Sionkowska et al., 2006a). The increase of polarity of the samples indicated an efficient photooxidation on the surface following UV irradiation. UV laser treatment of chitosan films leads

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to damage of the surface of chitosan film as well as foaming of the surface (Sionkowska et al., 2006a).

Chitosan films were prepared by solution casting method. Several films were prepared with low- and high-molecular weight additives, which contain chromophores. We added the following additives: camphorquinone, glutathione, tyrosine, phenylalanine or collagen. In fact in many cosmetic products amino acids from hydrolysed protein and chitosan exist together in one formulation. Camphorquinone, glutathione, tyrosine and phenylalanine are considered to be low-molecular weight additives, whereas collagen is a high molecular weight additive.

The surface alterations of chitosan films were observed using a scanning electron microscopy (SEM) and an atomic force microscopy (AFM). Moreover the surface properties of chitosan films were investigated by the means of contact angle measurement to observe the wettability of the film. In order to study the chemical and structural changes during UV irradiation, FTIR spectra and UV–Vis spectra were recorded. The mechanical properties were studied using a Zwick&Roell testing machine.

2. Materials and methods

Chitosan was obtained from Fluka, Switzerland. The molecular weight of chitosan was investigated using the viscometry method and it was found to be 750 kDa, while the deacetylation degree was 91.22. After having been dissolved in 0.4 M acetic acid solution, the chitosan films were prepared by casting the chitosan solutions onto glass plates. After solvent evaporation, the samples were dried in air at room temperature. Collagen was obtained in our laboratory from the tail tendons of young albino rats (Medical Academy, Poznan, Poland). The tendons were washed in deionized water and placed in 0.1 M of acetic acid for 72 h at 8 °C. The impurities and insoluble parts were separated by centrifugation at 10,000 rpm in an Eppendorf Centrifuge. The method used was the same as was previously employed (Sionkowska et al., 2004, 2005). The molecular weight of collagen was 300 kDa. Camphorquinone (CQ) (bornanedione, 1,7,7-trimethyl bicyclo [2,2,1] heptane-2,3-dione), glutathione, tyrosine and phenylalanine were purchased from the Sigma Chemical Company.

Biopolymer films were exposed to radiation in the Accelerated Weathering Chamber's (Weatherometer) Suntest which produces artificial sunlight (Xenon lamp, 300–800 nm). The intensity of artificial solar light was 0.1542 J/(s^2 m) (25.7 W/m^2). The specimens were irradiated with increasing irradiation time.

The UV–Vis absorption spectra of chitosan films, before and immediately after irradiation were recorded using a Shimadzu spectrophotometer (Model UV-1601PC). Data was collected and plotted using the *UVPC* program and a computer data station supplied by the manufacturer. UV–Vis spectra were also recorded for the chitosan solution. The changes in the chemical structure of chitosan were evaluated by attenuated total reflection infrared spectroscopy using a Genesis II FTIR spectrophotometer (Mattson, USA) equipped in ATR device (MIRacle^{TM} PIKE Technologies) with zinc selenide (ZnSe) crystal. All spectra were recorded in absorption mode at 4 cm^{-1} intervals and 64 scans.

The morphology of chitosan films before and after irradiation was studied using a scanning electron microscopy (SEM) (LEO Electron Microscopy Ltd., England). The measuring of all of the specimens was repeated at different locations. The samples in the form of films were also observed using an atomic force microscope (AFM). Topographic imaging was performed in air using a commercial AFM a MultiMode Scanning Probe Microscope Nanoscope IIIa (Digital Instruments Veeco Metrology Group, Santa Barbara, CA) operating in the tapping mode in air. Surface images, using scan widths ranging from 4 to 20 μm with a scan rate of 0.7 Hz, were acquired at fixed resolution (512 × 512 data points).

The contact angles of two liquids: diiodomethane (D) and glycerol (G) on chitosan films were measured at a constant temperature (22 °C) using a goniometer equipped with a system of drop shape analysis (DSA 10 produced by Krüss, Germany). Each contact angle was the average of a maximum of 10 measurements; the precision was 0.2°. The surface free energy was calculated using the Owen–Wendt method (Adamson, 1990). Thermogravimetric analysis (TG) was performed using a TA Instruments SDT 2960 Simultaneous TGA–DTA in nitrogen, at a heating rate of 10 °C/min using heating programme 25–600 °C. The mechanical properties of the materials have been measured by a Zwick&Roell testing machine.

3. Results and discussion

The molecular weight of chitosan before irradiation was 750 kDa. The deacetylation degree was 91.22. After 120 h of irradiation by artificial UV–Vis solar light the molecular weight decreased to the value 21.5 kDa. This fact clearly highlights the photodegradation of chitosan in a solution under artificial solar radiation.

The alterations of UV–Vis spectra of chitosan films after weathering are presented in Fig. 1. We can see that absorbance increases after weathering mainly in the region of 260–330 nm. In the presence of additives, such as collagen, glutathione, camphorquinone and tyrosine we can see that the absorbance increases more quickly with weathering time than for pure chitosan (for comparison we have chosen the absorbance at 320 nm, Fig. 1).

The FTIR spectra of chitosan (Fig. 2) depict characteristic absorption bands at 3362, 2932, and 2887, 1635 and 1384 cm^{-1} which represent the presence of –OH group, $-CH_2$ and $-CH_3$ group (aliphatic group), –C=O group and C–O stretching of primary alcoholic group ($-CH_2-OH$, are considered to be a potential site for cross-linking), respectively (Brugnerotto et al., 2001; Raghu, Gadaginamath, Mathew, Halligudi, & Aminabhavi, 2007). The NH_2 amino groups have a characteristic absorption band in the region of 3400–3500 cm^{-1}, which is overlapping by the absorption band due to the –OH group. The presence of significant peaks at 1635 cm^{-1} (due to $CH_3-C=O$ group denoting the presence of acetyl group) and 3362 cm^{-1} (representing the presence of $-NH_2$ group), confirms that chitosan is a partially deacetylated product, unlike its parent molecule chitin which is a completely acetylated moiety. In Fig. 3 one can see changes of integral absorbance at 1520–1800 cm^{-1} (carbonyl group) in FTIR spectra of chitosan irradiated by a Xenon lamp (300–800 nm) in a Weatherometer. After 50 h of exposure we observe a decrease of the amount of carbonyl groups due to the fact that they were probably turned into carboxyl groups via the photooxidation process. After 120 h of irradiation we observed an increase in the amount of carbonyl groups. This fact suggests that photooxidation processes occur on the surface (a part of OH groups can be oxidized to carbonyl). After 200 h of irradiation carbonyl groups were destroyed, probably due to the degradation of chitosan to low-molecular weight products. In the presence of 5% of collagen, 0.1% of glutathione, 0.1% of camphorquinone or 0.1% of tyrosine we can see that the integral absorbance of carbonyl groups undergoes greater alterations with increasing weathering time than for pure chitosan (Fig. 3). We can conclude that the above additives act as accelerators for the photodegradation of chitosan.

Camphorquinone (CQ) absorbs UV radiation in the region of 200–300 nm due to the π,π^* transition. CQ also absorbs visible light 400–500 nm (responsible for its yellow color) due to the n,π^* transition of the α-dicarbonyl chromophore (Sionkowska, Kaczmarek, Pedemonte, Vicini, & Wisniewski, 2002; Sionkowska, Kaminska, Linden, & Rabek, 1999). The energy absorbed by CQ can

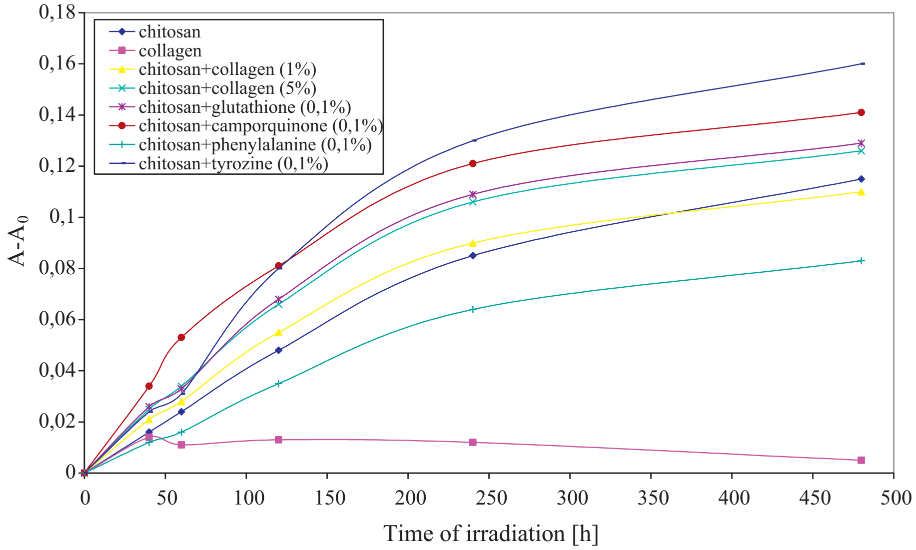


Fig. 1. Changes of absorbance at 320 nm in UV–Vis spectra of chitosan irradiated by Xenon lamp (300–800 nm) in Weatherometer.

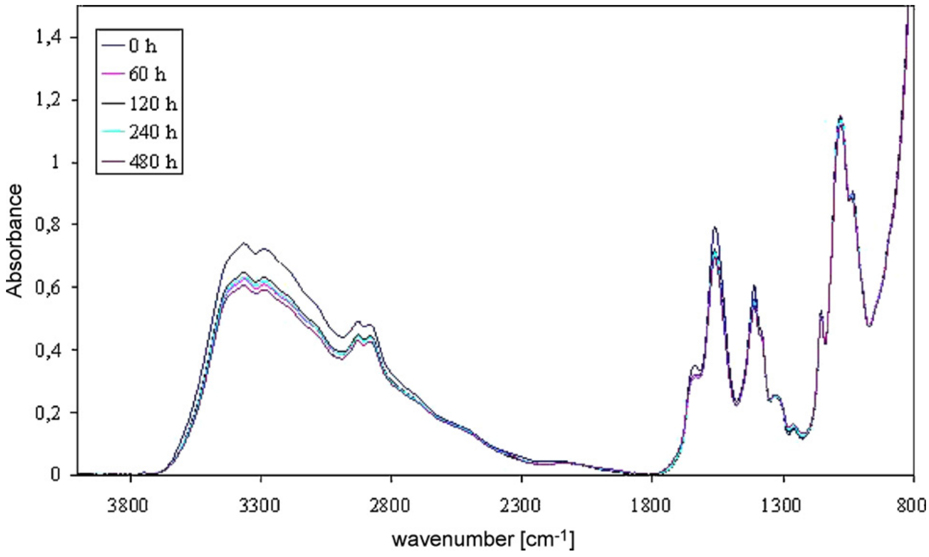


Fig. 2. FTIR spectra of chitosan irradiated by Xenon lamp (300–800 nm) in Weatherometer.

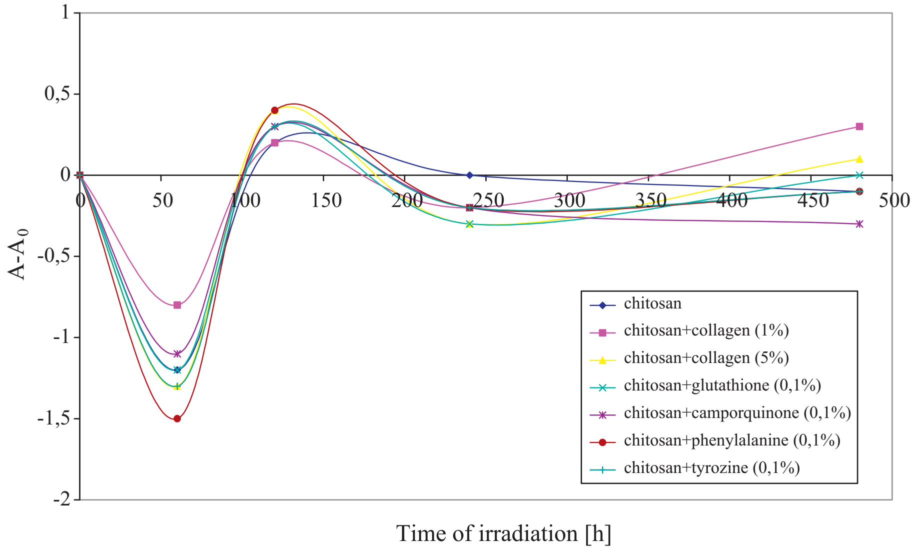
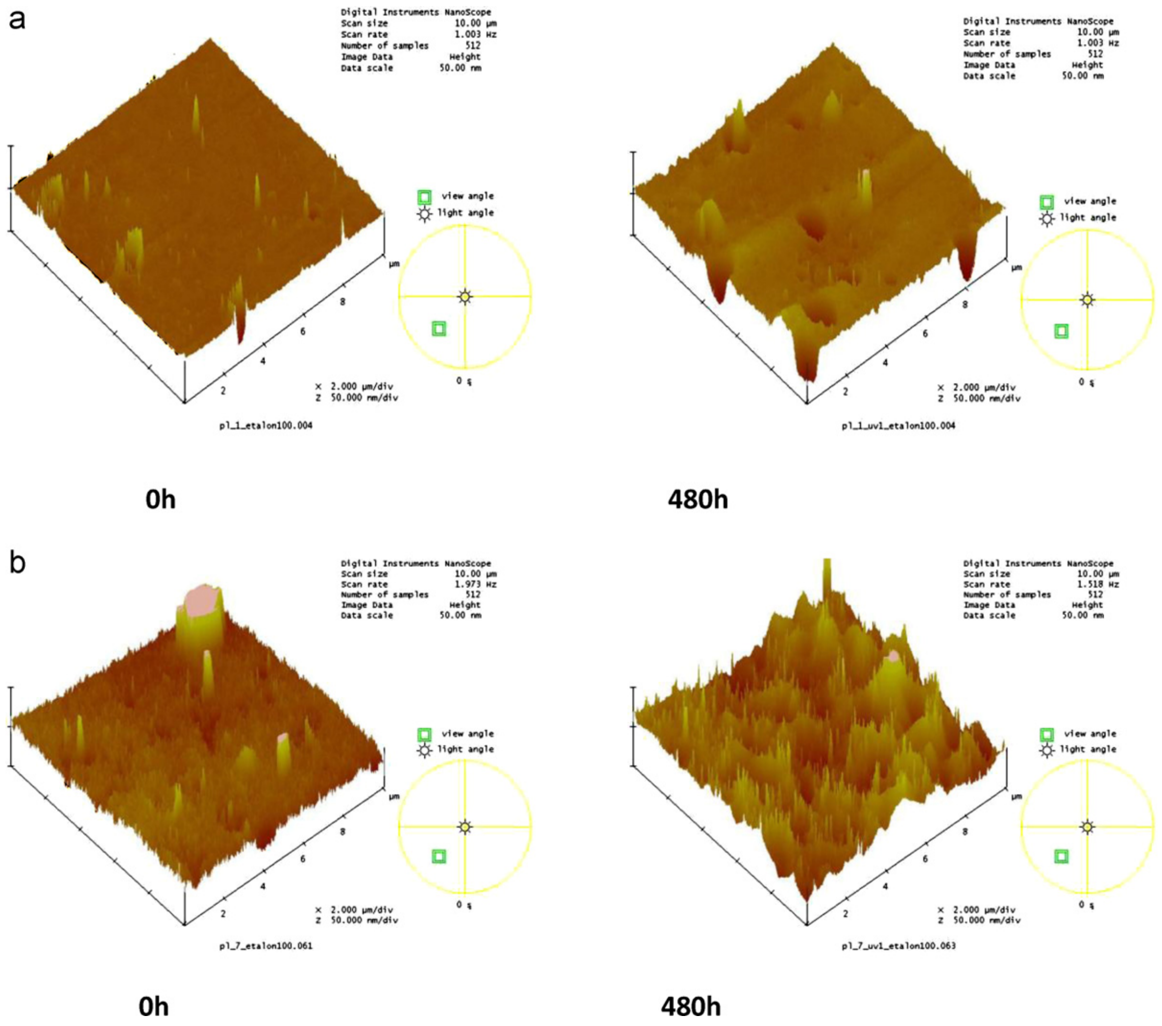


Fig. 3. Changes of integral absorbance at 1520–1800 cm^{-1} (carbonyl group) in FTIR spectra of chitosan irradiated by Xenon lamp (300–800 nm) in Weatherometer.



0h 480h

0h 480h

Fig. 4. AFM images of the surface of chitosan film (a) and chitosan film containing phenylalanine (b) before and after irradiation by Xenon lamp (300–800 nm) in Weatherometer.

be transferred to chitosan and leads to its efficient photodegradation. Glutathione (GSH) is a tripeptide, which plays a pivotal role in protecting the eye lens against photooxidative damage. This photostabilizer can scavenge and quench the reactive free radicals (Kamińska, Kowalska, & Balter, 1999; Sionkowska, 2001). In our study, GSH acts as a photosensibilizer of the photochemical reaction in chitosan. It seems that thinyl radicals formed in GSH after irradiation enhance the photooxidation process in chitosan (Kamińska et al., 1999).

The absorption spectra of tyrosine and phenylalanine in solution showed a wide peak in the region of 250–280 nm (Davidson, 1996; Sionkowska, Kaminska, Miles, & Bailey, 2001; Sionkowska, Skopinska, Wisniewski, Leznicki, & Fisz, 2006b). Artificial solar light does not contain wavelengths lower than 300 nm, but the absorption tail of aromatic amino acids can be found in the region above 300 nm. The energy absorbed by tyrosine and phenylalanine can be transferred to chitosan molecules and enhance photodegradation of this biopolymer. Collagen as a high molecular weight additive, contains in its chain aromatic amino acids, so it can also absorb an additional portion of energy, that can be used for the photodegradation of chitosan (Rabek, 1995; Sionkowska et al., 2004).

The microscopic images of chitosan films before and after treatment by artificial solar radiation showed that the surface morphology of chitosan before and after irradiation is similar (Fig. 4a). The chitosan top layer before and after irradiation has a relatively smooth and flat surface. AFM images of the surface of the chitosan film containing phenylalanine before and after irradiation by a Xenon lamp (300–800 nm) in the Weatherometer has been shown in Fig. 4b. The value of R_q for all the specimens before and after irradiation can be seen in Table 1. The surface roughness of chitosan films after weathering during 480 h was greater than before

Table 1
Roughness parameters R_q for chitosan films irradiated in the presence of additives for 480 h in weatherometer (apparatus Suntest emitting 300–800 nm). $\Delta R_q = R_q$ after exposure – R_q before exposure.

Specimen	Time of irradiation (h)	Roughness R_q (nm)	ΔR_q (nm)
Chitosan (CT)	0	3.07	
	480	8.97	5.90
Collagen	0	40.38	
	480	38.98	–1.92
Chitosan + collagen (1%)	0	6.35	
	480	3.85	–2.5
Chitosan + collagen (5%)	0	17.68	
	480	25.63	7.95
Chitosan + glutathione (0.1%)	0	9.02	
	480	3.73	–5.29
Chitosan + camphorquinone (0.1%)	0	23.93	
	480	6.91	–17.02
Chitosan + phenylalanine (0.1%)	0	22.44	
	480	12.20	–10.24
Chitosan + tyrosine (0.1%)	0	11.34	
	480	9.06	–2.28

Table 2
The influence of artificial solar radiation (300–800 nm) on ultimate tensile strength UTS of chitosan containing additives.

Specimen	UTS (MPa) after irradiation		
	0 h	120 h	480 h
Chitosan	84	110	60
Collagen	96	40	44
Chitosan + collagen (1%)	99	11	65
Chitosan + collagen (5%)	96	41	49
Chitosan + glutathione (0.1%)	103	146	92
Chitozan + camphorquinone (0.1%)	83	117	50
Chitosan + phenylalanine (0.1%)	140	107	71
Chitosan + tyrosine (0.1%)	97	56	33

Table 4
The influence of artificial solar radiation (300–800 nm) on Young's modulus (E) of chitosan containing additives.

Specimen	Young's Modulus (N/m^2) after irradiation		
	0 h	120 h	480 h
Chitosan	4246	6852	3346
Collagen	2764	2278	3328
Chitosan + collagen (1%)	2738	6088	1308
Chitosan + collagen (5%)	3782	3916	2150
Chitosan + glutathione (0.1%)	5374	7912	5584
Chitozan + camphorquinone (0.1%)	5384	7536	3618
Chitosan + phenylalanine (0.1%)	6832	6319	5772
Chitosan + tyrosine (0.1%)	4430	1353	2000

weathering. The surface roughness also increases with weathering time for chitosan films containing 5% of collagen. Whereas the surface roughness of chitosan films containing 1% of collagen, 0.1% of glutathione, camphorquinone, phenylalanine or tyrosine decreases after weathering. However, the starting value of R_q for chitosan containing the above additives was greater than that for pure chitosan films.

The mechanical properties of chitosan films were changed irregularly with increasing doses of artificial solar light. Ultimate tensile strength UTS (Table 2) of chitosan films increases after 120 h of irradiation, but after 480 h of irradiation it decreases. It may suggest that, after short time of weathering, chitosan undergoes photo cross-linking reactions, but after a long time of weathering the main process in chitosan under solar light is photodegradation. The same behaviour was observed for chitosan containing glutathione and camphorquinone. UTS for chitosan containing collagen, phenylalanine and tyrosine decreases after weathering. It seems that in the presence of tyrosine, phenylalanine and collagen the photodegradation of chitosan is very effective. The ultimate percentage of elongation (UPE) of chitosan films after weathering is presented in Table 3. The UPE for chitosan films after weathering is smaller than for untreated ones. The UPE of chitosan films containing collagen, glutathione, camphorquinone, phenylalanine and tyrosine after weathering is less than for those before weathering. Young's modulus for chitosan films containing collagen, glutathione and camphorquinone increases after 120 h of weathering, whereas after 480 h of weathering it decreases. Young's modulus for chitosan films containing tyrosine and phenylalanine decreases after 120 h and 480 h of weathering (Table 4).

The thermal behaviour of chitosan as a biopolymer has been studied widely (de Britto & Campana-Filho, 2007; López, Mercê, Alguacil, & López-Delgado, 2008; Mucha & Pawlak, 2005; Nam, Park, Ihm, & Hudson, 2010; Sionkowska et al., 2006c; Zotkin, Vikhoreva, Smotrina, & Derbenev, 2004). Thermal stability of chitosan depends on many factors, such as the degree of deacetylation, humidity of the sample, the shape of the specimen and molecular weight of chitosan (Nam et al., 2010). TG and DTG plots of the chitosan films (thermograms not shown) point out the three stages of thermal decomposition of the chitosan films. From TG curves we determined the mass decrement during the heating process. From DTG we determined the temperature of the starting point of decomposition taking the initial reaction as the point at which the DTG curve begins to deviate from its base line. The temperature of the maximum speed of the process (T_{max}) was determined from the maximum on the DTG curve. In Table 5 the thermal parameters for the chitosan after exposure in the Accelerated Weathering Chamber have been presented. The three peaks in the characteristic DTG curve for chitosan in nitrogen are representative of the three-stage sample destruction due to the temperature. The first stage (between 50 and 100 °C) is connected to the evaporation of water absorbed to chitosan. From the second stage (between 170 and 210 °C) the glass transition temperature can be read. At the third stage (between 250 and 350 °C) water bound to chitosan is released and small molecular products of thermal degradation of chitosan are liberated. The T_{max} of chitosan for the first stage is smaller after weathering. The T_{max} in the second and third stages increases slightly after weathering. The T_{max} for second and third stages was significantly altered for chitosan films containing additives. When chitosan contains 0.1% of glutathione, phenylalanine or tyrosine, the T_{max} of the first stage increases with increasing exposure time. The T_{max} for the third stage of thermal degradation is slightly smaller for chitosan irradiated in the presence of additives than for pure irradiated chitosan.

Table 3
The influence of artificial solar radiation (300–800 nm) on ultimate percentage of elongation of chitosan containing additives.

Specimen	Ultimate percentage of elongation (%) after irradiation		
	0 h	120 h	480 h
Chitosan	6.2	2.1	1.8
Collagen	9.7	1.3	1.4
Chitosan + collagen (1%)	3.3	2.2	2.1
Chitosan + collagen (5%)	2.5	1.8	1.7
Chitosan + glutathione (0.1%)	7.3	2.6	2.0
Chitozan + camphorquinone (0.1%)	2.5	1.7	1.6
Chitosan + phenylalanine (0.1%)	3.0	1.8	1.5
Chitosan + tyrosine (0.1%)	2.5	2.0	1.5

The weight loss at the first stage for the chitosan film is 9.12% before the exposure and 11.70% after exposure to artificial solar light for 480 h. For chitosan containing 1% of collagen we observed a greater weight loss than for pure chitosan after 480 h of exposure. For chitosan containing low-molecular weight additives the weight loss in the first stage is similar before and after 480 h of exposure. The second peak on the DTG curve appears with a maximum at 181 °C for the chitosan film and it is accompanied by a mass decrement of 7.64%. After 480 h of exposure of the chitosan films experience the second peak on the DTG curve and appears with a maximum at 183.3 °C while the weight loss of this process is 8.47%. The results suggest that exposure of chitosan to artificial solar light does not significantly change the glass transition temperature of chitosan. The third peak on the DTG curve appears with a maximum at 283.2 °C for the chitosan film and it is accompanied by a mass decrement of 49.4%. After 480 h of exposure of chitosan films the third peak on DTG curve appears with a maximum at 279.6 °C and the weight loss of this process is 53.62%. For chitosan films containing collagen, glutathione, phenylalanine or camphorquinone we did not observe a significant alteration of weight loss in comparison to pure irradiated chitosan. However, for chitosan containing 1% of tyrosine the weight loss before exposure was 58.27% whereas after 480 h of exposure it was 48.09%. The results suggest that chi-

Table 5
The mass decrement (Δm) and maximum speed of the thermal decomposition of chitosan films process (T_{max}) containing additives before and after weathering.

Specimen	Time of irradiation [h]	T_{max} (°C)				Δm	(%)
		I	II	III	I	II	III
Chitosan	0	75.9	181.0	283.2	9.12	7.64	49.04
	120	78.1	182.1	284.7	9.69	9.91	58.36
	480	66.8	183.3	286.7	11.70	8.47	53.62
Chitosan + collagen (1%)	0	97.3	181.0	279.6	9.05	8.04	50.83
	120	98.5	186.7	275.1	9.98	7.76	47.16
	480	99.6	205.9	275.5	12.07	6.88	47.91
Chitosan + collagen (5%)	0	95.1	177.6	280.1	11.18	9.48	46.18
	120	100.7	183.7	275.9	9.74	8.78	47.32
	480	81.5	196.8	282.9	11.71	5.98	45.88
Chitosan + glutathione (0.1%)	0	65.7	184.4	286.4	7.55	6.98	52.80
	120	71.3	187.8	284.8	8.65	7.08	50.96
	480	69.1	186.7	284.7	10.19	7.70	52.82
Chitosan + camphorquinone (0,1%)	0	91.7	187.8	277.5	9.32	5.95	52.81
	120	82.6	178.7	281.9	8.45	8.03	49.92
	480	79.3	182.1	283.2	8.89	8.17	49.39
Chitosan + phenylala (0.1%)	0	55.5	190.0	287.1	10.26	3.49	48.88
	120	82.6	183.3	282.0	8.96	6.64	49.92
	480	83.8	182.1	282.2	9.00	6.93	47.18
Chitosan + tyrosine (0.1%)	0	69.1	176.5	284.7	8.05	1.27	58.27
	120	90.6	176.5	281,7	8.48	9.24	49.71
	480	82.6	173.1	283.9	9.23	10.36	48.03

tosan containing 1% of tyrosine is more thermally stable than pure chitosan irradiated over 480 h by artificial solar light. It is probably the cause of the cross-linking reaction of chitosan in the presence of tyrosine, which can absorb UV light and turn to radicals capable of further cross-linking.

The contact angle values of two different liquids (diiodomethane – D, and glycerol – G) on chitosan films after weathering were measured and the surface free energy was calculated. The results have been presented in Table 6. The contact angle measured for chitosan films containing additives gave very similar results to those obtained for pure chitosan films with all the liquids used. After irradiation we observed a drop in the contact angle for glycerol and only a small drop for diiodomethane. The surface free energy of chitosan films containing 0.1% of glutathione, camphorquinone or phenylalanine increases after irradiation time. The polar component of surface free energy (γ_s^p) also reveals a much greater value after irradiation. The alterations of these parameters are the biggest in the case of chitosan with 0.1% of glutathione. The increase of polarity of the films indicates that photooxidation reactions take place on their surface.

Table 6
The surface free energy for chitosan films containing additives before and after weathering.

Specimen	Time of irradiation (h)	Total surface free energy (mN/m)	Dispersive part	Polar part
Chitosan	0	28.36	27.83	0.53
	480	40.90	27.71	13.19
Chitosan + glutathione (0.1%)	0	25.94	25.11	0.83
	480	65.99	21.65	44.33
Chitosan + camphorquinone (0.1%)	0	29.12	27.81	1.30
	480	40.69	26.36	14.33
Chitosan + phenylalanine (0.1%)	0	25.98	24.93	1.04
	480	37.79	16.05	21.74
Chitosan + tyrosine (0.1%)	0	25.77	24.91	0.87
	480	20.69	17.99	2.70
Chitosan + collagen	0	27.66	25.50	2.16
(5%)	480	30.52	15.50	15.02

4. Conclusions

The deterioration of the mechanical properties of the chitosan films after exposure to artificial solar light results mainly from photochemical alterations such as cross-linking and chains scission. The alteration of the amount of carbonyl groups and increase of the amount of polar groups on the surface after irradiation time point out both the photooxidation of chitosan and changes of its structure. Photooxidation of the surface of the chitosan films leads to the formation of oxidized groups such as OH, OOH, CO. The values of polar and dispersive components of surface free energy showed that irradiated chitosan films containing glutathione or phenylalanine were more polar than pure chitosan films. Artificial solar radiation causes the increase of surface roughness of pure chitosan, but when chitosan contains glutathione, camphorquinone or phenylalanine the decrease of the surface roughness of chitosan films was observed after irradiation. Although photodegradation of chitosan by solar light is undesirable when we consider the final cosmetic formulation and its application on the skin or hair, it can be very useful in the preparation process of a soluble form of chitosan. Photochemically degraded chitosan has a lower molecular weight than the native one, and, as a result, such chitosan possesses greater solubility. Chitosan with a high molecular weight is soluble only in an aqueous solution of organic acids, whereas partially degraded chitosan can be soluble in water. More soluble chitosan can be used in cosmetics formulations in a wide range of pH. Chitosan is more sensitive to the action of artificial solar light in the presence of additives, such as collagen, glutathione, camphorquinone, and tyrosine. In cosmetic formulation one has to take this fact into account when in one product both protein hydrolysates which contain aromatic amino acids and chitosan are present.

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