

STUDY OF THE INFLUENCE OF UV RADIATION ON BIODEGRADABLE BLENDS BASED ON CHITOSAN AND STARCH

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Abstract

The biodegradable blends of chitosan and starch with different component ratios were prepared by casting method. Obtained thin films were UV-irradiated ($\lambda = 254$ nm) and changes in chemical structure were monitored using FTIR and UV-Vis spectroscopies. It was found that the chitosan-starch blends were more susceptible to UV irradiation comparing to pure starch specimen. FTIR spectra of blends suggest partial interactions between chitosan and starch macrochains.

Key words: *chitosan, starch, polymeric blends, UV-irradiation.*

1. Introduction

Chitosan and starch belongs to the group of biodegradable, natural polymers applied in practice [1 - 3].

Starch is renewable polysaccharide, which usually contains about 30% amylose, 70% amylopectin and less than 1% lipids or proteins from plants. Biodegradable starch-based plastics, such as blends of starch with polyolefines or poly(vinyl alcohol) have recently been widely investigated due to the great market demands for agricultural foils, composting bags, food packaging as well as materials for biomedicine, pharmacy and cosmetics [4, 5].

Chitosan, N-deacetylated derivative of chitin, which consists of 2-deoxy-2-amino anhydroglucose residues, is the second most abundant biopolymer occurring in nature after cellulose. The unique properties of chitosan - antibacterial and antifungal activities as well as ability to bind various chemical compounds have been especially followed with great deal of interest [6 - 9]. Moreover, chitosan is soluble in acidic water solutions, so it is easy to process and modificate. Studies on functionalized blend films containing chitozan, for example, poly(vinyl alcohol)/chitosan, collagen/chitosan, poly(vinyl pyrrolidone)/chitosan, gelatine/chitosan) have been also recently reported [10 - 13].

Properties of pure polymers are well known, but the possibility of practical application of polymeric blends requires careful analysis of their properties, with particular emphasis on the interactions between the two components and the resulting surface susceptibility of materials to external factors such as heat, mechanical stresses or UV radiation.

It is known that mixing of polymers is an effective and convenient method to improve the performance of polymeric materials, so the blends of chitosan/starch were the object of this study. The aim of our work was to investigate the changes in chemical structure of these blends induced by UV radiation. Although the photochemical reactions of pure chitosan and pure starch were studied [13 - 20] there is a lack of information on the behavior of chitosan/starch upon UV action.

2. Materials and methods

Chitosan of the deacetylation degree of 75% and molecular weight $M = 1.5 \times 10^5$ g/mol and starch (potato flour Emix, Poland) were used in this study. Chitosan solution in 1M acetic acid was prepared. Then starch powder was added and such solutions were heated in 80 °C until starch was dissolved. The obtained mixtures were cast onto flat CaF₂ plates (for FTIR spectroscopy) or quartz plates (for UV-VIS studies) and left at room temperature for drying for at least 3 days. The following blend compositions with weight ratio of chitosan to starch were prepared: 25:75; 50:50; 75:25; 100:0 (pure chitosan) and 0:100 (pure starch).

Radiation source was a low pressure mercury lamp emitting light with a wavelength of 254 nm. All the samples were UV irradiated from 0 – 13 h.

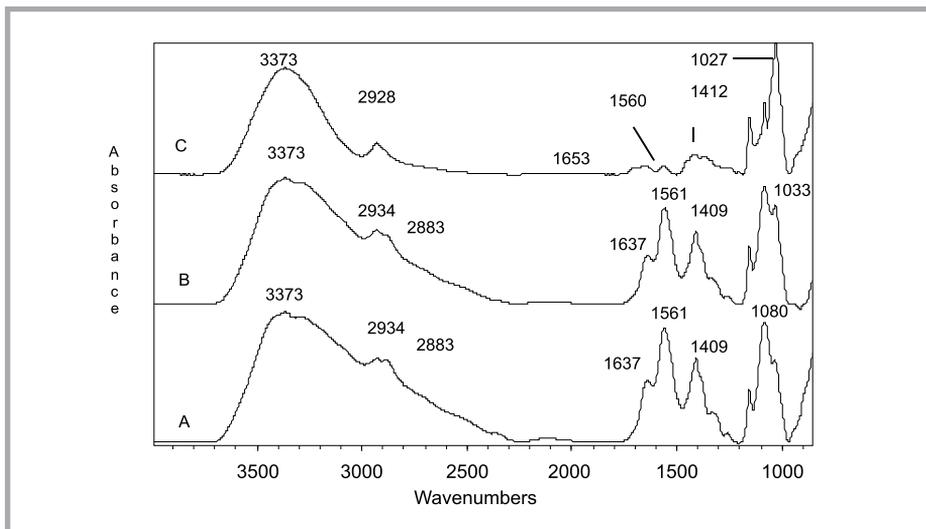


Figure 1. FTIR spectra of chitosan (A), starch (B) and 50:50 chitosan/starch blend (C) before UV-irradiation.

FTIR spectra of the films were recorded using an FTIR spectrophotometer Genesis II, Mattson, USA. For each spectrum, 64 consecutive scans at 4 cm^{-1} resolutions were averaged.

UV-Vis analysis was performed using a spectrophotometer UV-1601 PC (Shimadzu Corporation, Japan).

All experiments were conducted at room temperature and in air atmosphere.

3. Results and discussion

FTIR spectroscopic studies allowed to estimate the surface changes induced by UV irradiation in samples studied. The results obtained for chitosan/starch blends were compared with data received for reference specimens, which were pure chitosan and pure starch. The regions of the characteristic bands corresponding to vibrations of the hydroxyl-, methyl- and methylene-, carbonyl-, and amide groups were analyzed. FTIR spectra also provide data about some interactions between polymeric components in the blends.

The comparison of FTIR spectra of unirradiated chitosan, starch, and chitosan/starch (50:50) composite film are presented in **Figure 1**. The spectra of pure components are similar to published elsewhere [13, 20].

The broad band at $3000\text{--}3600\text{ cm}^{-1}$ range in spectra of all samples is attributed to the OH stretching, which overlaps the NH stretching in the same region. The characteristic chitosan absorption band at 2928 and 2883 cm^{-1} represent $>\text{CH}_2$ and $-\text{CH}_3$ aliphatic

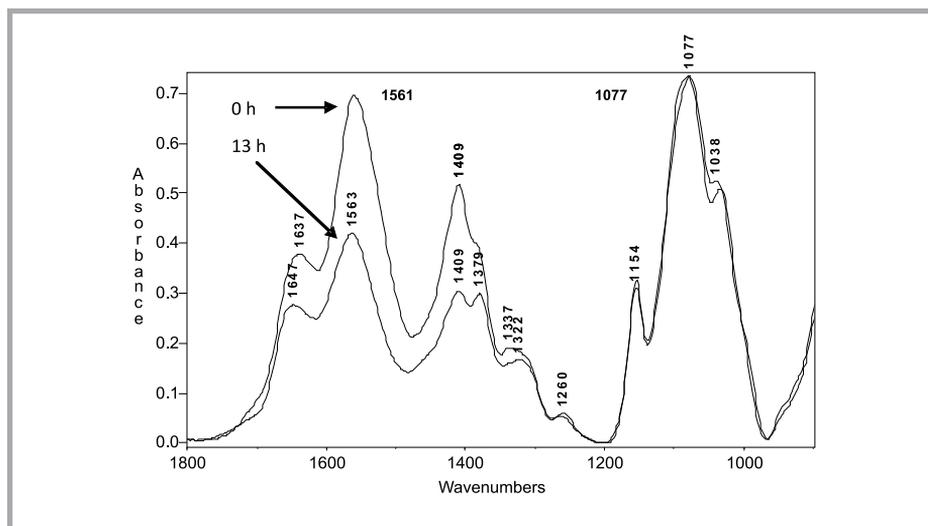


Figure 2. FTIR spectra of chitosan before and after 13 hours of UV-irradiation.

groups, respectively. The band at 1561 cm^{-1} is the NH bending vibration. A small peak near 1637 cm^{-1} (amide I) is due to the vibrations of C=O groups, which is an evidence of not completed chitosan deacetylation. An intensive peak at 1409 cm^{-1} corresponds to deformation vibrations of OH and CH groups whereas 1080 cm^{-1} peak is due to glycosidic bonds.

In FTIR spectrum of starch film, besides of absorption in hydroxyl and aliphatic ranges, the intensive bands at 1027 cm^{-1} assigned to C-O-C appeared. Moreover, weak peak at 1708 cm^{-1} suggests that some carbonyl impurities are present in starch film.

In the blend spectra, the significant decrease of the amine peak intensity at 1563 cm^{-1} and also at 1409 cm^{-1} (-OH primary alcoholic group) was noticed, which is connected with smaller content of chitosan in the sample of mixed polymers. However, small shifts of absorption bands (**Figure 1**) suggests some interactions between macrochains from both polysaccharides, besides of hydrogen bonds in starch and chitosan alone.

FTIR spectra recorded after UV irradiation of samples show noticeable changes in the intensities of characteristic bands in the case of pure chitosan and its blends with starch. An example of FTIR spectra of chitosan before and after 13 h UV-irradiation is shown in **Figure 2**. Only small insignificant changes were found for starch sample exposed separately at the same conditions.

After 13 hours of UV irradiation of pure chitosan sample, amino- and carbonyl bands (1561 cm^{-1} , 1637 cm^{-1}) in FTIR spectrum were shifted to higher wavenumbers and lost much of their intensities. It indicates that intermolecular and intramolecular hydrogen bonds in chitosan were partially broken or became weaker what can reduce the polymer

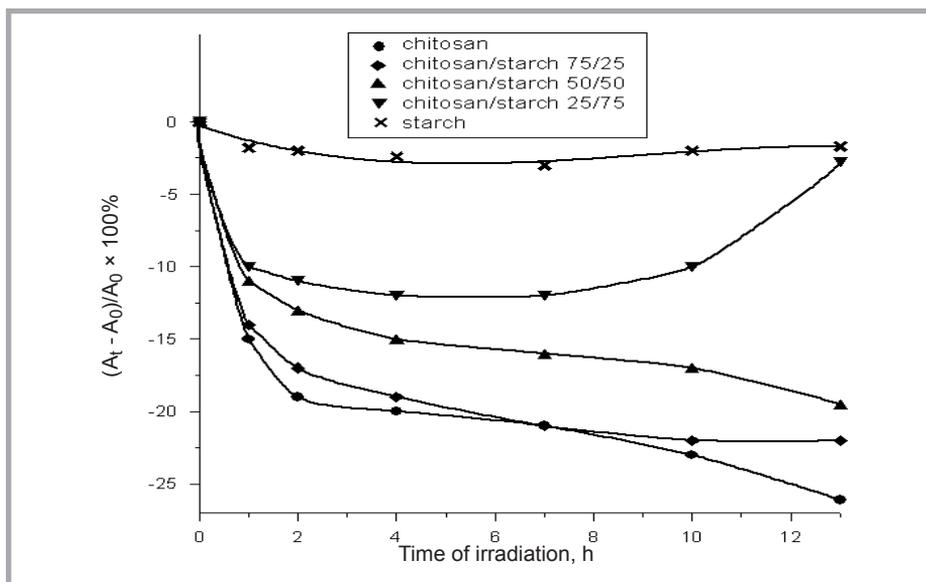


Figure 3. Changes in relative hydroxyl group concentration in pure chitosan, pure starch and their blends after UV irradiation (0-13h); A_t and A_0 – integral intensities of hydroxyl band at spectrum of sample after t irradiation time and before irradiation, respectively.

crystallinity. Hydroxyl band at 1409 cm^{-1} decreased and the small new maximum at 1379 cm^{-1} appeared. Band at 1077 cm^{-1} , which corresponds to $-\text{C}-\text{O}-\text{C}-$ glycosidic linkage in pyranose ring, stayed unchanged after 13 hours of irradiation (**Figure 2**). Analogous changes were observed for all studied chitosan/starch blends.

The significant drop of the amount of hydroxyl ($-\text{OH}$), methylene ($-\text{CH}_2$) and carbonyl ($\text{C}=\text{O}$) groups after the first two hours of exposure to UV in chitosan/starch samples was found. Further irradiation resulted in only minor fluctuations in absorption of these characteristic groups, thus demonstrating the relative stabilization of samples. **Figures 3** and **4** present the kinetics curves obtained as a dependence of relative content of hydroxyl and amido groups versus irradiation time. Decrease of the concentration of amide groups in irradiated chitosan is associated with its photodestruction i.e. detachment of the side substituents upon UV.

Because starch is relatively stable in these conditions, we can conclude that changes observed in chitosan/starch concerned mainly one ingredient of analyzed blend i.e. chitosan.

Additional information on changes in chemical structure of UV-irradiated samples supplied UV-Vis spectroscopy (**Figure 5**). New band with maximum at about 300 nm appeared in UV-Vis spectra of pure chitosan and its mixtures with starch as a result of exposure to UV radiation. Intensity of this band increased with time of irradiation and with

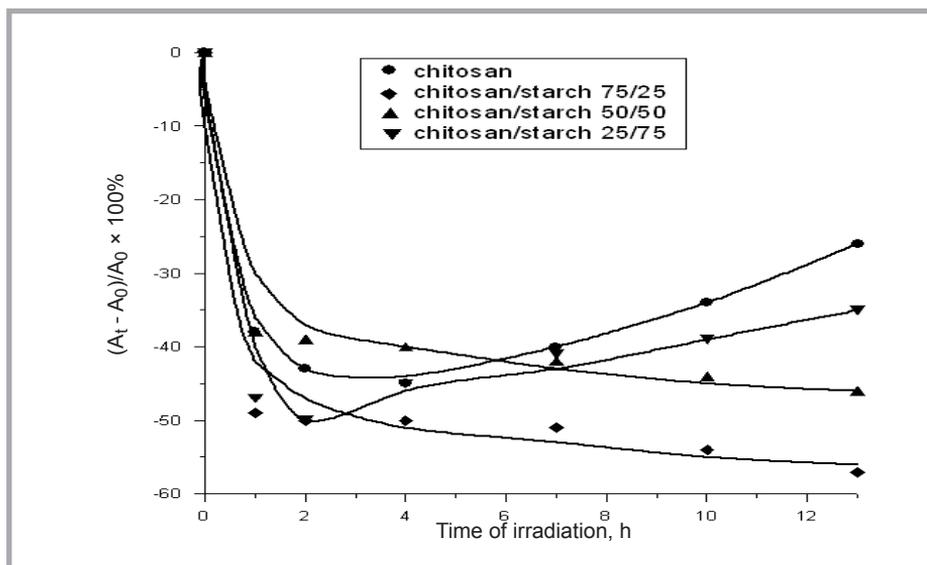


Figure 4. Changes in relative amido group concentration in chitosan/starch blends after UV irradiation (0-13h); A_t and A_0 – integral intensities of amido band at spectrum of sample after t irradiation time and before irradiation, respectively.

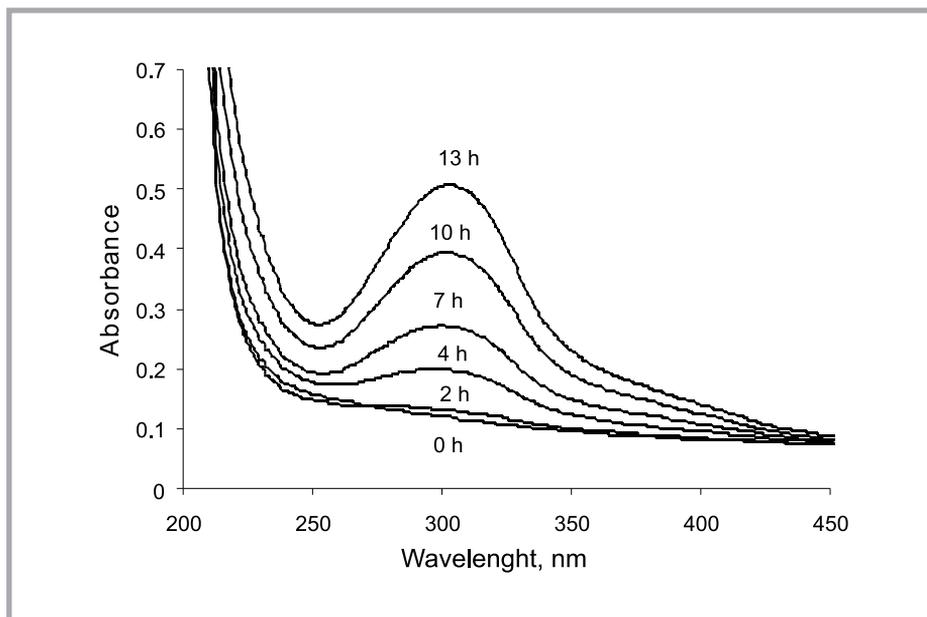


Figure 5. Changes in UV-Vis spectra of chitosan/starch blends (75:25) after UV irradiation (0 - 13 h).

increase of chitosan content in the sample. In previous works such band was also observed and interpreted as $n \rightarrow \pi^*$ transition in carbonyl groups formed resulting of chitosan photooxidation [13, 14, 20]. The formation of C=O has to be preceded by the breaking of glycosidic bonds with chain scission and formation of free radicals. Such macroradicals react with atmospheric oxygen giving peroxyradicals. Secondary reactions lead to creation of oxidation products containing ketone, aldehyde and carboxylic functionalities. It is very difficult to detect these products on the base of FTIR spectra because most of characteristic absorption bands overlap in the same region. It is necessary to remember that competitive photochemical reactions: destruction of existing and formation of new carbonyl groups take place simultaneously. Thus, in FTIR spectra of UV-irradiated samples we observe total effect and final complex product.

4. Conclusions

The results indicate that chitosan and its blends with starch are characterized by considerably lower resistance to UV radiation than pure starch. The observed changes in the photochemical properties of chitosan/starch blends are not additive, suggesting the presence of intermolecular interactions of the two polysaccharides. A new product absorbing radiation around 300 nm appeared in chitosan and its mixtures with starch during UV irradiation, which can cause UV-sensitization of materials in further steps of degradation.

Owing to complete biodegradability of both components, the studied chitosan/starch blends seem to be promising candidates for future materials.

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