

INFLUENCE OF NANOSILVER ON THERMAL STABILITY OF CHITOSAN

Sylwia Białas, Maria Mucha

Lodz University of Technology,
Faculty of Process and Environmental Engineering,
ul. Wolczańska 213, 90-924 Łódź, Poland
E-mail: syl.bialas@gmail.com

Abstract

Nanoadditives for polymers have many valuable features: e.g. the ability to change the properties of polymers: mechanical strength, stability and heat resistance and resistance to radiation. These properties make them an interest in recent years. Studies of polymer composites with nanoadditives leads to discovering more, unique types of nanoadditive interactions on a structure and properties of the polymer. One of the most widely used nanoadditive is nanosilver, which have antibacterial and antifungal properties. An important aspect is thus to investigate the effect of this additive on thermal stability of the polymer composite. The aim of this study was to investigate the effect of nanosilver on the thermal stability and properties of chitosan. Chitosan composites with nanosilver in the form of films with a thickness of 10 - 30 μm and the content of silver 0.5 and 1% was obtained by casting. In order to study the thermal stability samples were subjected to a temperature of 120 °C (time 0 - 90 h). Studies on influence of nanosilver on the thermal stability of the polymer was performed using infrared spectroscopy (FTIR). This allows to observe changes in the chemical structure of polymer. The changes in the major functional groups was observed: 1420 cm^{-1} (bending vibration of -C-H group), 1577 cm^{-1} (bending vibrations of the amine group -NH₂), 1655 cm^{-1} (vibrations of C=O in amide group). Mechanical strength test of chitosan composites subjected to high temperature was also performed. Tensile tests (using the Instron 5325 apparatus) were conducted to determine changes in values of Young's modulus, maximum stress and elongation at break. The study showed an effect of the presence of nanosilver on the structural and mechanical properties of chitosan. Nanosilver improves the thermal stability of studied functional groups of chitosan.

Key words: *thermal degradation, chitosan, nanosilver.*

1. Introduction

Chitosan as a natural biopolymer with exceptional properties (antimicrobial, chelating, film-forming) is used in many fields of medicine, agriculture and food industry. Depending on the application, it is exposed to various environmental factors such as temperature and radiation, which cause changes in its properties due to degradation. Thermal degradation leads to breaking and destruction of chain side groups, in particular amino groups (decreases deacetylation degree), and the cross-linking chains, thereby increasing the compaction of the structure and reduction of sorption capacity of the polymer. There are a number of publications on the mechanism of thermal degradation of chitosan [1 - 6].

Properties of chitosan can be significantly improved by the use of different types of chemical modifications (acylation, sulfation, enzymatic substitution, metal chelation, nitration, phosphorylation). This is possible due to the free amino groups occurring in the chitosan [7].

Nanosilver is used as an additive for polymers mainly by its antibacterial properties. Silver nanoparticles by attaching to the bacterial cell wall causes disruption of the cell-wall permeability and cellular respiration. They can also penetrate into the bacterial cell, and due to the interaction of phosphorus and sulfur (present in DNA and bacterial cell proteins) cause cell destruction. For example, Wei et al. [8] have shown an increase in antimicrobial resistance of chitosan by the addition of nanoparticles to the polymer matrix.

Thus, nanosilver is used to modify the plastics in various forms (eg. catheters, dental materials, medical devices and implants) to prevent microbial contamination. Silver is used also in textiles.

Modification of polymers by using nanoadditives is a very effective and simple way to change their properties. Therefore, in presenting study the difference between degradation of pure chitosan, and chitosan in the composite material was determined. The effect of nanosilver on mechanical properties of chitosan was also investigated.

2. Materials and methods

Chitosan from crab and shrimp shells (grey powder, DD = 85%, Viscosity 800 mPas) were purchased from Hepe Biomaterial GmbH i.G. Silver, nanopowder, particles size < 100 nm, has been obtained from Aldrich Chemistry.

Chitosan was dissolved in 1% acetic acid water solution. The samples for studies have been prepared by vigorous mixing of 1%(wt) polymer solution with proper amount of nanosilver previously dispersed in 1% acetic acid water solution. Thin chitosan films and its mixtures with nanosilver were obtained by casting. The weight fraction of nanosilver in chitosan was: 0.5 and 1%.

The samples of pure chitosan and chitosan/Ag composites have been exposed to temperature 120 °C. Maximum time of exposure was 90 h. After defined period of exposure time, the polymeric films were systematically analyzed by FTIR spectroscopy and mechanical strength test.

Infrared spectra were recorded by Genesis II FTIR spectrometer (Mattson, USA). The absorbances of selected bands have been measured and their relative change has been calculated.

Stress-strain curves were recorded using Instron 5325 apparatus. During stretching of the sample, the stress was measured (force F divided by cross sectional area A).

Increase of the stress versus strain, until the sample break was drawn. The extension of the sample is expressed here as an elongation at break (EB) in mm/mm. The linear region of the stress-strain curve gives the Young's modulus E and reflects an inherent stiffness of the material. Ultimate tensile strength (UTS) is the stress needed to break the sample.

Dried films were tested using 5 samples for each measurement. The test was carried out at ambient temperature and at a cross-head speed of 10 mm/min. The thickness of the film sample was the same (20 μm). Composites were tested before and after different times of thermal degradation.

3. Results and discussion

3.1. FTIR spectroscopy

FTIR spectroscopic studies allowed to estimate molecular changes induced by high temperature in samples studied and to obtain reliable kinetic data. The main bands observed are typical for chitosan: 1040 - 1150 cm^{-1} (-C-O-C- vibration), 1415 cm^{-1} (bending vibration of -C-H group), 1577 cm^{-1} (bending vibrations of the amine group-NH₂), 1655 cm^{-1} (vibrations of C=O in amide group), 2880 - 2920 cm^{-1} (vibration of CH₂), 3380 - 2450 cm^{-1} (-OH vibration).

The films containing up to 1% of nanosilver do not show any significant changes in FTIR spectrum.

Figure 1 displays the infrared spectra of chitosan before ageing and after specific exposure times. The main change observed was a decrease of the amine group (-NH₂) at 1577 cm^{-1} and the formation of an amide group at 1655 cm^{-1} . It was also observed a decrease of absorbance at 1415 cm^{-1} (vibration of C-H band in CH₂ group). **Figures 2.a, 2.b** and **2.c** present the kinetic curves of processes occurring in chitosan and its nanocomposites obtained on the basis of the relative absorbance changes (A_t/A_0) of selected bands.

To connect degradation criteria from the microscopic scale to the macroscopic, phenomenological model for description of the kinetic process of degradation [9] was used:

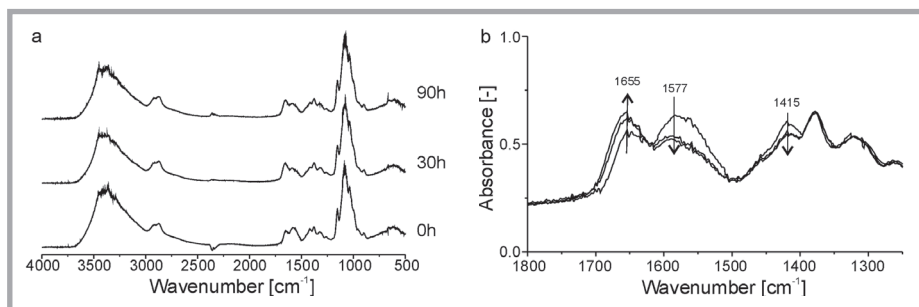


Figure 1. FTIR spectra of chitosan before ageing and after specific exposure times (a) and the main changes in the functional groups (b).

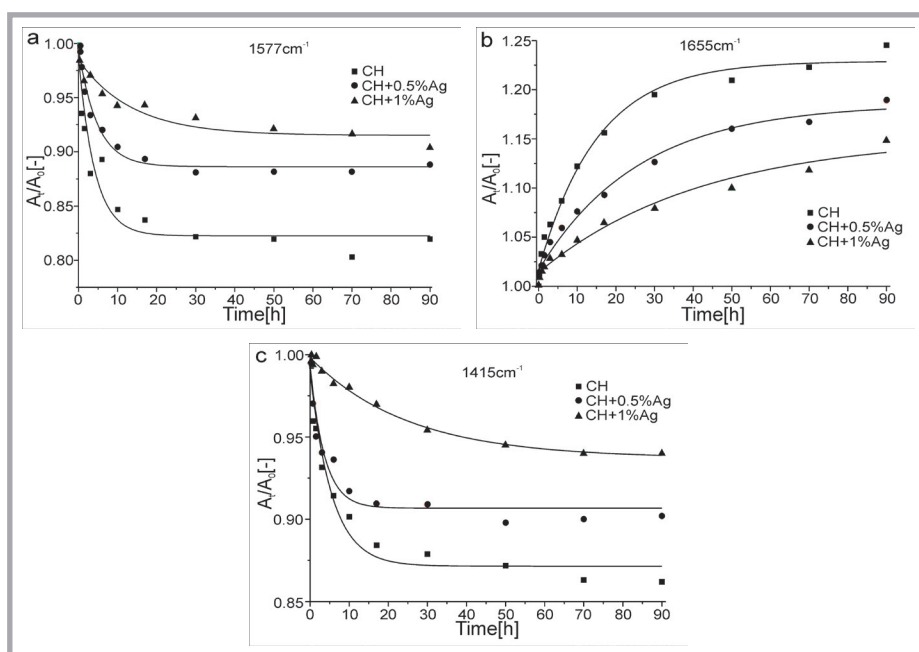


Figure 2. Relative changes of absorbance (A_t/A_0) of selected bands from FTIR spectra of chitosan and its composites with 0.5 and 1% content of nanosilver: (a) $-NH_2$ (at 1577 cm^{-1}), (b) C=O (at 1650 cm^{-1}) and (c) $-CH_2$ (at 1415 cm^{-1}) versus degradation time; A_0 and A_t are absorbances of non-degraded specimen and after t -time exposure, respectively. Points-experimental data, curves- fitted equation (2).

$$\frac{dX}{dt} = Ae^{-E_a/RT} (X_\infty - X)^n \quad (1)$$

$$k = Ae^{-E_a/RT}$$

For $n = 1$, integration of **Equation 1** gives form **Equation 2**.

Table 1. Degradation rate k of selected functional groups in chitosan and its blends with nanosilver.

Parameters		Wavelength		
		1577 cm ⁻¹	1650 cm ⁻¹	1415 cm ⁻¹
CH	k, h ⁻¹	0.240	0.066	0.179
	C. coeff R ²	0.944	0.987	0.966
CH + 0.5% Ag	k, h ⁻¹	0.209	0.039	0.151
	C. coeff R ²	0.985	0.985	0.923
CH + 1% Ag	k, h ⁻¹	0.073	0.024	0.040
	C. coeff R ²	0.925	0.962	0.992

$$\left(\frac{A_t}{A_0}\right) = \left(\frac{A_t}{A_0}\right)_\infty + \left[\left(\frac{A_t}{A_0}\right)_0 - \left(\frac{A_t}{A_0}\right)_\infty\right] e^{-kt} \quad (2)$$

In our case, the X parameter is the relative changes of absorbance (A_t/A_0) which evolved with the time. $\left(\frac{A_t}{A_0}\right)_\infty$ is the parameter when $t \rightarrow \infty$, $\left(\frac{A_t}{A_0}\right)_0$ is the parameter value at $t = 0$ (it is equal to 1) and k is the Arrhenius-type kinetic constant.

As shown in **Figures 2.a, 2.b** and **2.c** first order model ($n = 1$) perfectly fit the experimental data. Degradation rate constant k of selected functional groups of chitosan and nanosilver additive effect on the value is presented in **Table 1**.

It is clearly seen that the degradation rate constant (k) depends on the amount of nanosilver content in chitosan film. Already 0.5% Ag significantly retards chitosan degradation and 1% Ag content further enhances this effect. The thermal stability of chitosan improved by the presence of nanosilver.

3.2. Mechanical properties

The characteristic stress-strain curves of chitosan and chitosan/nanosilver films before and after several time of exposure at 120 °C are reported in **Figure 3**.

Results show, that pure chitosan films exhibit lower value of elongation at break (EB, mm/mm), ultimate tensile strength (UTS, MPa) and higher value of Young's Modulus (MPa), than films containing 0.5 and 1% of nanosilver. Nanosilver particles improve plasticity of chitosan.

High temperature (120 °C) has also an effect on the values of all the mechanical parameters of the films under study. The general trend of stress-strain curves of chitosan and chitosan/nanosilver films after thermal exposure is very similar to that of the non-exposed control specimens.

As a result of thermal degradation, there was a decrease of elongation at break (EB) and increase of Young's Modulus and ultimate tensile strength (UTS) of chitosan and chitosan/

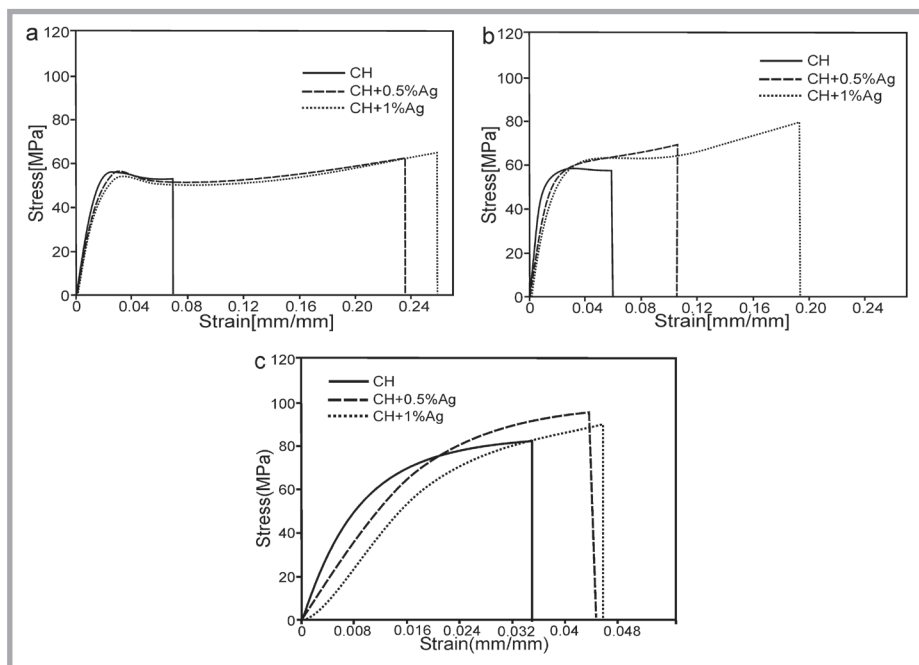


Figure 3. Stress-strain curves recorded for chitosan and chitosan/ nanosilver films before (a) and after 20 h (b) and 40 h (c) of thermal degradation.

nanosilver composites. This allows to formulate a conclusion that as a result of thermal degradation increased stiffness and brittleness of chitosan. Effect of nanosilver is pronounced.

4. Conclusions

Properties and thermal stability of chitosan/nanosilver composites depend on Ag content in the films.

Small amount (0.5 and 1%) of nanosilver in composites with chitosan improved thermal stability of chitosan (resulting in FTIR spectrum). It is probably caused by a complexation of chitosan through amine groups with nanosilver ions.

Mechanical properties, such as elongation at break EB, ultimate tensile strength UTS, and Young's Modulus are modified for chitosan/nanosilver films and are sensitive to thermal degradation. Nanosilver particles act as plasticizer of chitosan (decrease of Young's modulus, increase of EB and UTS).

5. Acknowledgments

Presented research was financially supported by the National Centre of Science under Grant no. UMO-2011/01/B/ST8/06679.

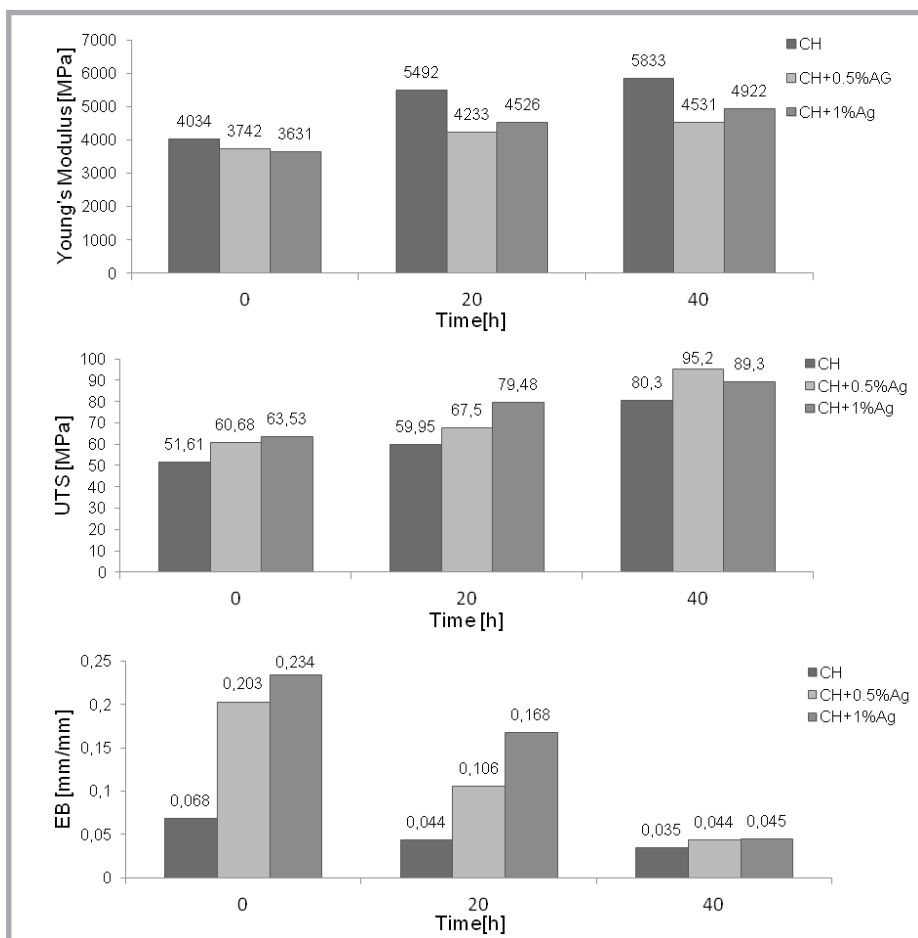


Figure 4. Changes in mechanical properties: a) Young's Modulus, b) Ultimate Tensile Strength, c) Elongation at Break of chitosan and chitosan/nanosilver films before and after thermal degradation.

6. References

1. Toffey A., Samanarayake G., Frazier C.E. et al.: Chitin derivatives I. Kinetics of heat-induced conversion of chitosan to chitin. *J.Appl. Polym. Sci.*, 1996,60,78-85.
2. Lim L.Y., Khor E., Thenmozhiyal J.C.: Heat-induced physicochemical changes in highly deacetylated chitosan. *Adv.Chitin Sci. Vol IV. Red.: M.G. Peter, A.Domard, R.A.A. Muzzarelli (2000) 445 (Euchis 99).*
3. Wanjun T., Cunxin W., Donghua Ch.: Kinetic study on the pyrolysis of chitin and chitosan, *Polym. Degr. Stab.* 2005, 87, 389-394.
4. Mucha M., Bratkowska M., Woszczalski D., Thermal and UV degradation of chitosan. *Adv. Chitin Sci. Vol IV. Red.: M.G. Peter, A.Domard, R.A.A. Muzarelli (2000) 436-444 (Euchis 99).*
5. Mucha M., Pawlak A., Complex study of chitosan degradability. *Polymer.* 2002, 47, 43-51.

6. Mucha M., Chitosan, Versatile Polymer from Renewable Sources, WNT, Warsaw, 2010.
7. M.A. Diab, A.Z. El-Sonbati, D.M.D. Bader.: Thermal stability and degradation of chitosan modified by benzophenone, *Spectrochimica Acta Part A* 79 (2011) 1057– 1062.
8. Dongwei Wei, Wuyong Sun, Weiping Qian, The synthesis of chitosan-based silver nanoparticles and their antibacterial activity, *Carbohydrate Research*, 344 (2009), 2375-2382.
9. J.-F. Larche, P.-O. Bussiere, S. Therias, J.-L. Gardette; photooxidation of polymers: Relating material properties to chemical changes; *Polymer Degr. And Stab.* 97 (2012) 25-34.