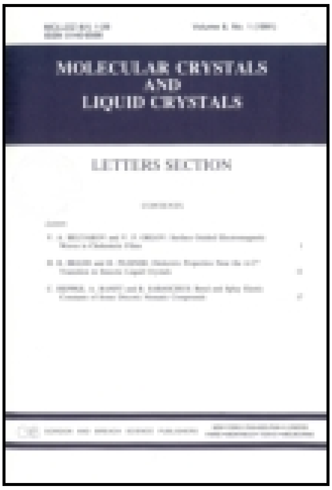

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Mechanical and Morphological Studies of Chitosan/Clay Composites

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In the present paper, the results of mechanical properties and atomic force microscopy studies of chitosan (Ch) with montmorillonite (MMT) or nano-clay are presented. The blends composed of chitosan (Ch) with montmorillonite (MMT) have been prepared as material designed for cosmetic industries and/or biomedical applications. Mechanical properties such as the ultimate tensile strength, percentage elongation and Young's modulus of films have been determined and compared. Addition of nanoclay after surface modification improved the mechanical properties more than montmorillonite without modification.
The surface properties of the chitosan and montmorillonite films and their composites have been studied by tapping-mode atomic force microscopy (AFM). The changes of topography images were considered by determining the root mean square (Rms) deviation in the image data. AFM images show differences in surface properties of chitosan films, chitosan/MMT films, and chitosan/nanoclay films. Surface roughness decreased with addition of MMT and/or nanoclay into chitosan matrix.
The obtained results suggest that the properties of chitosan and montmorillonite composites depend on the blend composition and on the way of surface modification of nano-clay.

Keywords chitosan; montmorillonite; nanoclay; composites; AFM

Introduction

Chitosan is a biopolymer obtained in deacetylation process from chitin [1,2]. Chitosan is biocompatible, biodegradable, biofunctional and non-toxic for human body [1,3]. It is miscible with several other biopolymers, such as collagen [4,5] or cellulose [6,7]. It is also miscible with several synthetic polymers, as for example poly(vinyl alcohol) [8,9] or poly(N-vinylpyrrolidone) [10]. Composites based on chitosan found application in medicine, for example as materials for tissue regeneration [11,12]. Recently hybrid materials are more and more interesting for scientists working in several fields. Special attention has been paid on hybrid materials where constituents are dispersed in nano-scale [13,14]. Such nano-scale dispersion can improve physical and mechanical properties of material

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compared to micro-scale polymer composites [15]. Nano-structured organic-inorganic materials attract significant attention as alternative for conventional materials in micro-scale. Montmorillonite is the most widely studied type of nano-clay; it is a hydrated alumina-silica layered clay [16,17]. Surface of nano-clays can be modified by octadecylamine and such a treatment can lead to different properties of material [18]. Polymers and nano-clays as a hybrid materials are nowadays in interest of many scientists, but such interest is mainly limited to synthetic polymers [19–21]. Synthetic polymer/nanoclay composites are a class of hybrid materials with good mechanical properties dependent on interface interaction. Nevertheless chitosan and nano-clay composites can be considered as interesting hybrid materials for potential application in medicine [22].

The purpose of this study was to evaluate the physico –chemical properties of new composites based on chitosan and inorganic compounds. Chitosan was blended with montmorillonite (MMT) in acetic acid solution and this solution was cast to prepare the blend film. MMT samples have been used without modification and after nanoclay surface modification. Mechanical properties such as the ultimate tensile strength, percentage elongation and Young's modulus of films have been determined and compared.

Materials and Methods

Chitosan powder (degree of deacetylation DD = 78% $M_v = 1.4\times10^6$ g/mol), and montmorillonite (MMT) were supplied by, Aldrich. Nanoclay surface was modified with octadecylamine (contain 25–30 wt.% octadecylamine, nanoclay, Aldrich).

An aqueous solution of 1.0wt.% was prepared by dissolving chitosan powder in acetic acid solution (1wt.%). Polymer films were obtained by solution casting method.

Stress-strain curves were recorded using a Zwick&Roell 0.5 testing machine. Whilst stretching the sample, it measures the amount of force (F) exerted. When we know the force being exerted on the sample, we then divide that number by the cross-sectional area (A) of our sample and calculate the stress that our sample is experiencing.

$$\frac{F}{A} = \text{stress}$$

A linear increase in force is exerted and the extension of the sample is measured until the sample fails. The extension of the sample is expressed here as a% elongation of the sample from the original length, and stress vs. elongation studied with respect to the composition of specimen. Linear region of the stress extension curve gives the Young's modulus E and gives the inherent stiffness of the material. The stress needed to break the sample is the ultimate tensile strength of the material.

Three samples were evaluated for each composition. All the samples of film were cut using the same shaper. The thickness of the samples was determined using an ultrameter type A-91 (producer: Manufacture of Electronic Devices, Warsaw, Poland). Force extension curves were obtained and used to calculate stress-strain behaviour, ultimate tensile strength (UTS), and Young's modulus. Reproducibility of the results was rather low and exhibited significant variability.

The topographic imaging was performed in air using a commercial AFM apparatus (NanoScope III Model Dimension 3100, Digital Instruments, Santa Barbara, CA) operating in tapping mode. All samples were imagined using the cantilever with spring constant of 0.06 N/m and silicon nitride tip of 10 nm radius. Surface images, using the scan widths

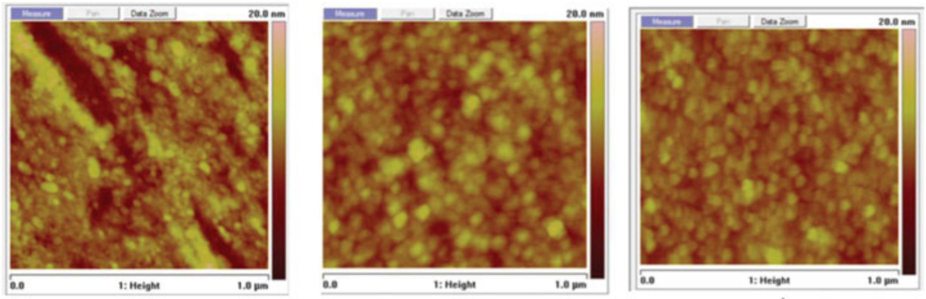

Figure 1. AFM images of the surface of chitosan films (a) and films made of chitosan/MMT composites (b) and chitosan/nanoclay composites (c).

ranging from 1 to 10 mm with scan rate of 0.7 Hz, were acquired at fixed resolution (512 × 512 data points).

Results and Discussion

Polymer films containing montmorillonite or nanoclay were obtained by solution casting method. The surface properties of chitosan/MMT composites films were observed using Atomic Force Microscopy (AFM). The examples of AFM images of chitosan/MMT and chitosan/nanoclay composites are shown in Fig. 1.

The surface morphology of films made of chitosan, chitosan/MMT and chitosan/nonaclay is different. The top layer of composites is organized in a characteristic pattern with several symptoms of surface roughness.

To compare surface properties of chitosan and chitosan/MMT as well as chitosan/nanoclay films the Atomic Force Microscopy (AFM) was used and surface roughness was evaluated. Small topographical changes in AFM images of chitosan films were observed to take place after mixing with MMT and/or nanoclay. AFM images show differences in surface properties of chitosann films, chitosan/MMT films, and chitosan/nanoclay films. The atomic force microscope is often used to obtain a reasonable measure of surface roughness on the nanometer scale. Typically, AFM users rely on root-mean-square (*Rms*) roughness. The *Rms* surface roughness of chitosan, chitosan/MMT and chitosan/nanoclay films has been shown in Table 1. *Rms* value for chitosan film (2.01 nm) is much bigger than *Rms* for chitosan/MMT and chitosan/nanoclay (1.37 nm and 1.10 nm, respectively). The surface of chitosan films has been altered by the addition of MMT and/or nanoclay. The decrease of surface roughness of chitosan/MMT and chitosan/nanoclay in comparison to chitosan films is probably due to the interaction between biopolymer and inorganic compounds.

Table 1. The roughness parameters (Rms) of chitosan and chitosan composites films

Specimen	*Rms* (nm)
Chitosan	2.01
Ch/MMT	1.37
Ch/nanoclay	1.10

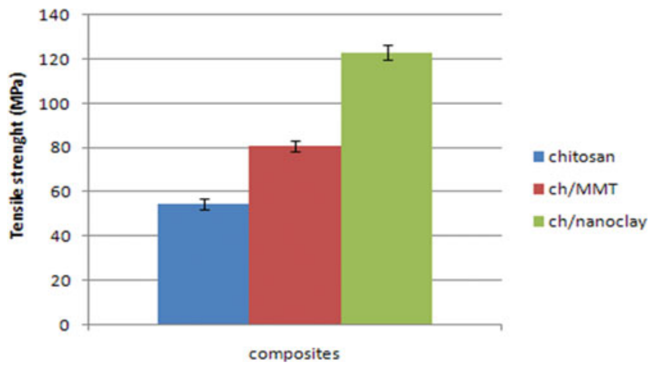

Figure 2. Tensile strenght of chitosan films and films made of chitosan/MMT and chitosan/nanoclay composites.

The characteristic stress-strain curves of chitosan films and films made of chitosan/MMT and chitosan/nanoclay were obtained by Zwick&Roell 0.5 testing machine. Stress-strain curves for chitosan films and films made of chitosan/MMT and chitosan/nanoclay show similar shape (curves not shown). Ultimate tensile strenght of chitosan films and films made of chitosan/MMT and chitosan/nanoclay composites one can see in Fig. 2. It can be noticed that chitosan/nanoclay composite film exhibits higher value of ultimate tensile strength UTS than chitosan and chitosan/MMT composite film (Fig. 2). Addition of nanoclay and MMT to chitosan is shown here to have an effect on all the mechanical parameters of the films measured in this study. The ultimate tensile strength of chitosan film increases after mixing with MMT and nanoclay. It may suggest that during the mixing of chitosan with MMT and/or nanoclay new the crosslinking reactions in chitosan film responsible for increase of UTS occur.

Young's modulus of chitosan films and films made of chitosan/MMT and chitosan/nanoclay composites is shown in Fig. 3. It can be noticed that chitosan/nanoclay composite film exhibits higher value of Young's modulus than chitosan and chitosan/MMT composite film (Fig. 3). Addition of nanoclay and MMT to chitosan is shown here to have an effect

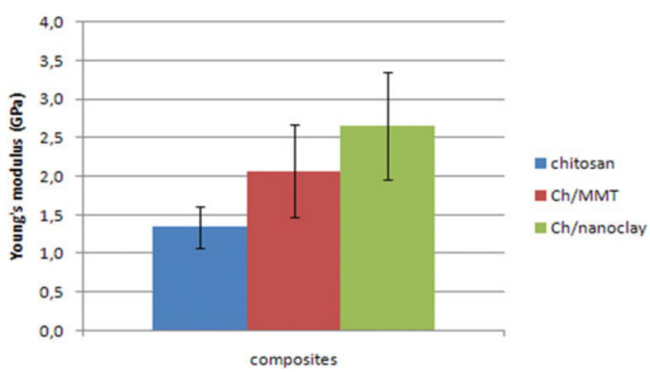

Figure 3. Young's modulus of chitosan films and films made of chitosan/MMT and chitosan/nanoclay composites.

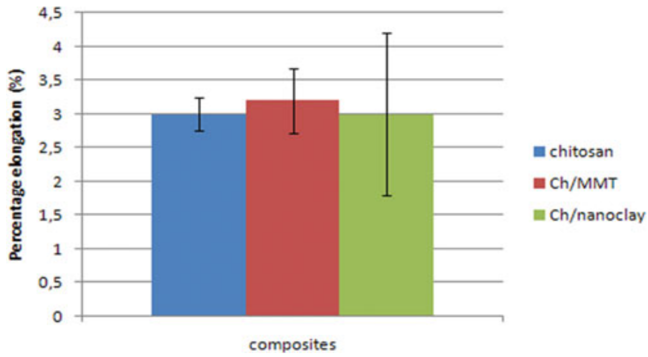

Figure 4. Percentage of elongation of chitosan films and films made of chitosan/MMT and chitosan/nanoclay composites.

on all the mechanical parameters of the films measured in this study. Young's modulus of chitosan film increases after mixing with MMT and nanoclay.

The ulimate percentage of elongation of chitosan films and films made of chitosan/MMT and chitosan/nanoclay composites is shown in Fig. 4. The ultimate percentage of elongation of chitosan was not visibly changed by the addition of MMT and/or nanoclay. It can be noticed than chitosan/MMT composite films exhibit bigger value of ultimate percentage of elongation than chitosan films. However, due to rather low reproducibility of the results of measurements of the percentage of elongation it is hard to discuss these alterations. The error bar may suggest that there are only small modification of elongation after mixing of chitosan with MMT and/or nanoclay.

All the above results suggest that modification in mechanical properties is a consequence of the interaction between chitosan and MMT and/or nanoclay. Better mechanical properties of chitosan with addition of MMT and/or nanoclay can be a result of crosslinking reactions within a chains and molecular interaction between biopolymer and MMT and/or nanoclay. It is in accordance with previously obtained data for chitosan composites [23,24].

Conclusions

All the above results suggest that modification in properties is a consequence of the interaction between chitosan and MMT and/or nanoclay. Mechanical properties such as ultimate tensile strength and ultimate percentage of elongation were much better for chitosan/MMT composite and chitosan/nanoclay composites films than for chitosan films. The improving of mechanical properties of chitosan/MMT and chitosan/nanoclay composite films can be a result of crosslinking reactions within a chains and molecular interaction between chitosan and MMT and/or nanoclay.

In the case of AFM studies, the surface morphology of films made of chitosan, chitosan/MMT and chitosan/nonaclay is different. Surface roughness decreased with addition of MMT and/or nanoclay into chitosan matrix.

Summarizing, the structure and mechanical properties of chitosan and montmorillonite composites depend on the blend composition and on the way of surface modification of nano-clay.

Acknowledgments

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