



Characterization of chitosan composites with synthetic polymers and inorganic additives



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ABSTRACT

In the present study, the results from thermogravimetric analysis (TGA), contact angle measurements, tensile tests, scanning electron microscopy (SEM) and atomic force microscopy (AFM) of polymer composites containing chitosan (Ch) and montmorillonite (MMT) with and without poly(vinyl alcohol) (PVA) are presented.

Measurements of the contact angles for diiodomethane (D) and glycerol (G) on the surfaces of chitosan films, Ch/MMT and Ch/PVA/MMT, were made and surface free energies were calculated. It was found that the wettability of the chitosan/MMT or Ch/PVA/MMT composite films decreased relative to the wettability of chitosan. The microstructure of unmodified polymers and their composites, as observed by SEM and AFM, showed particles that are relatively well dispersed in the polymer matrix. The TGA thermograms and mass loss percentages at different decomposition temperatures showed that the thermal stability of the binary composite slightly decreases upon the addition of PVA. The film mechanical properties such as tensile strength, Young's modulus and tensile strain at break depend on the composition and varied non-uniformly. Both composites possessed a tensile strength and Young's modulus of 27.6–94.3 MPa and 1.5–3.5 GPa, respectively. The addition of PVA to the composite led to a reduction in tensile strength by approximately 40%.

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1. Introduction

Natural polysaccharides are widely used in the cosmetic industry as raw materials and hold promise for biomedical applications because of their film-forming ability, controlled bioactivity, biocompatibility and biodegradability [1,2]. Chitosan (Ch; poly[β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucopyranose]) is a polysaccharide that is obtained by the deacetylation of chitin. Chitin, after cellulose, is the most widespread polymer in nature; however, its general insolubility makes further processing impossible. Chitin occurs in animals, particularly in crustaceans, mollusks and insects [1]. Chitosan also occurs naturally in some fungi; however, its occurrence in these materials is much less than that of chitin. Chitin is a copolymer of poly[β -(1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucopyranose] and residual 2-amino-2-deoxy-D-glucopyranose units. Chitosan is chemically defined as a copolymer of two residues: 2-amino-2-deoxy-D-glucopyranose (D-glucosamine) and 2-acetamido-2-deoxy-D-glucopyranose (N-acetyl-D-glucosamine) [1,2], where the proportion of D-glucosamine is larger than

N-acetyl-D-glucosamine. The physico-chemical properties of chitosan and chitin mainly depend on their degrees of deacetylation and molecular weights. These parameters influence the viscosity and the solubility of chitosan. It is well known that chitosan can be dissolved in dilute aqueous inorganic and organic acids as a polycation at a DD of 50% or more. In the solid state, chitosan is a semi-crystalline polymer. Five crystalline polymorphs of chitosan have been described, the adoption of which depends on the degree of deacetylation, on the distribution of functional groups, and on the chitosan preparation procedure [3–6]. The specific properties of chitosan, such as its bioactivity, biocompatibility, biodegradability, solubility in an aqueous solution, and ability to form complexes and non-toxicity for humans, have resulted in increased interest in the material's potential biomedical applications, e.g., in bone substitutes, drug delivery systems, delivery of proteins/peptides and genes, artificial skins, and wound dressings, as well as carriers for contrast agents [7–14]. Moreover, chitosan has been used in such diverse areas, such as the food, cosmetic and packaging industries [2,8]. The increasing breadth of practical applications for this biopolymer is related to the modification of its physico-chemical properties. A simple approach involves blending with additional inorganic and/or organic compounds, such as synthetic polymers, montmorillonite, hydroxylapatite, titanium

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dioxide, bioactive glasses, tannic acid (as a crosslinker), and glycerol (as a plasticizer) [15–29].

In the last decade, an extensive amount of work has been devoted to the modification of chitosan with montmorillonite (MMT) to produce nanocomposite materials for biomedical applications [30–41]. Chitosan composites have included various types of nanofillers, such as unmodified MMT and surface-modified clays, and nanofillers of different dimensions. Additionally, the influence of changing different composite production parameters, such as the polymer concentration, the molecular weight of chitosan, the filler/polymer weight ratio, and the addition of a plasticizer have been studied [14,15,18,20,25,31]. For cases of chitosan with unmodified MMT (chitosan/MMT), it has been shown that the mechanical properties of these composites increased significantly with increasing clay concentrations [17,18,34]. Thermal properties and FTIR analysis proved that molecular interactions were present between the chitosan and MMT [14,15,30,35]. AFM images indicated well-distributed nanoparticles at the surface of the chitosan matrix [14,39,40]. Moreover, raising the loading of nano-dispersed clay improves the thermal stability of the material [30,32,33,35].

Poly(vinyl alcohol) (PVA) is a non-ionic synthetic polymer that is soluble in water. The properties of PVA mainly depend on its molecular weight and degree of hydrolysis [21,42,43]. In addition, PVA displays several advantageous properties, such as biodegradability, non-toxicity, biocompatibility, and hydrophilicity; the polymer is also miscible with high and low-molecular-weight compounds. PVA is widely used in food processing, cosmetics, and in drug delivery systems. This polymer is often combined with other polymers and/or in inorganic additives, for example, PVP [44–46], starch [47–49], chitosan acetate [50–53], and montmorillonite [54–57]. The present work is a continuation of our previous studies on the physico-chemical properties of chitosan with poly(vinyl alcohol) [21,52,53]. A previous study [52] has shown that the thermal properties of thin films produced by blending Ch and PVA depend on the PVA degree of hydrolysis and on the molecular weight of Ch. These results revealed that chitosan is miscible in PVA for weight fractions of chitosan $w_{\text{Ch}} > 0.2$ [53]. Characterization of films made of chitosan with poly(vinyl alcohol) and montmorillonite has been reported [58–62]. The composite mechanical properties and thermal stability have been shown to increase with chitosan oligosaccharide and montmorillonite contents [58]. XRD results confirmed that these improvements were related to the MMT exfoliation and strong interaction between the PVA/chitosan blend and MMT [58,60–62].

The purpose of the present work was the preparation and evaluation of the physico-chemical properties of new composites of biopolymers and inorganic additives. The characterization methods that were employed in this study include tapping-mode atomic force microscopy (AFM), thermogravimetric analysis (TGA), tensile tests and contact angle measurements. The surface properties of blends or composites, which are prepared from natural and synthetic polymers, are important for their use in cosmetics.

2. Materials and methods

Poly(vinyl alcohol) is a commercial polymer from the Aldrich company with a degree of hydrolysis $DH = 99\%$ and a viscosity average molecular weight of 130,000. Chitosan powder (a degree of deacetylation of 78% and a viscosity average molecular weight of 540,000) and montmorillonite were supplied by Aldrich, Poland. Glycerol and diiodomethane (POCh, Poland and Aldrich, Poland, respectively; analytical grade) were used as test liquids for contact angle measurements.

Chitosan and PVA were separately solubilized in aqueous acetic acid (0.1 mol dm^{-3}) and water, respectively. The additive montmorillonite (1 wt% with respect to the polymer) was dispersed in the

Table 1

The roughness parameters (R_q) for films of different compositions.

Sample	R_q [nm]
Ch	10.6
PVA	15.8
Ch/MMT*	3.6
Ch/MMT*	12.9
PVA/MMT	8.1
Ch/PVA/MMT	19.0

* Montmorillonite was dispersed in aqueous acetic acid.

** Montmorillonite was dispersed in water.

same solvent, after which a polymer solution was added slowly to the clay dispersion. Composite films were produced from cast solutions, followed by drying in a vacuum oven.

Thermogravimetric analysis (TGA) was carried out using a Thermal Analysis SDT 2960 Simultaneous TGA-DTA analyser from TA Instruments in the temperature range of 20–650 °C at a heating rate of 20 °C/min in nitrogen. From the thermogravimetric curves we obtained the characteristic temperatures of decomposition: temperature of initial decomposition (T_{di}) and temperature at maximum decomposition rate (T_{max}).

The morphology of the samples was studied using Scanning Electron Microscopy (SEM) LEO Electron Microscopy Ltd. England.

Atomic force microscopy (AFM) was used to study the surface roughness and morphology of thin films in air. AFM topographic images were obtained at room temperature using a multimode AFM with a Nanoscope III controller (Digital Instruments, Veeco Metrology Group, Santa Barbara, CA); data were obtained in the tapping mode. The scan size was $5 \mu\text{m}^2$, and the scan rate was 1.97 Hz with 512 pixels collected per line. The root-mean-square (R_q) roughness of the surface was determined using Nanoscope software.

Measurements of the contact angles (Θ) by the sessile drop method were performed at room temperature using the DSA10 goniometer of Krüss GmbH (Germany), equipped with software for the drop shape analysis. The droplets of the probe liquid (high purity, volume of 3 μL) were deposited using a micro-syringe; the drop image was recorded with a video camera and then digitalized. Using the instrument's software, the drop shape was fitted to obtain the contact angle between the solvent and the surface. Each contact angle represents an average of 10 measurements.

The mechanical properties of the materials were measured at room temperature using tensile tests, Zwick Roell (Germany), at a crosshead speed of 5 mm/min in accordance with the standard procedure [63]. Samples were cut into dog-bone shapes of initial dimensions of a 50-mm length, 4.2-mm width and 30 μm thickness. Sample thickness was determined using an ultrameter type A-91 (Manufacture of Electronic Devices, Warsaw, Poland). All of the film samples were cut using the same shaper. For each type of film, a minimum of five samples were tested.

3. Results and discussion

The surface properties of the chitosan composite films were observed using atomic force microscopy and scanning electron microscopy. Examples of AFM images for chitosan/MMT, PVA/MMT and chitosan/PVA/MMT composites are shown in Fig. 1. The corresponding roughness values are presented in Table 1.

The AFM images show differences in the surface properties of films for the homopolymers and their composites. The surface morphologies of unmodified polymer films are considerably rough, which can result from the crystallinity of the samples (Fig. 1a and b); the roughness parameters are approximately 10.6 nm for Ch and 15.8 nm for PVA (Table 1). With respect to the composites (Fig. 1c–f), the surface topology began to alter after the addition of MMT. For the Ch/MMT and PVA/MMT composites, the surfaces

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