SURFACE PROPERTIES OF CHITOSAN COMPOSITES WITH POLY(VINYL ALCOHOL) AND HYDROXYAPATITE

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Abstract

Surface properties of composites containing chitosan (Ch), poly(vinyl alcohol) (PVA) with hydroxyapatite (HAP) were investigated by contact angle measurements and atomic force microscopy (AFM). Thin films of Ch/HAP and Ch/PVA/HAP composites have been formed by casting methods from acetic acid solutions.

Measurements of the contact angle for diiodomethane (D), and glycerol (G) on the surface of chitosan films, Ch/HAP and chitosan/PVA/HAP films were made and surface free energy was calculated. It was found that chitosan/HAP or Ch/PVA/HAP blend surface is enriched in high surface energy component i.e. chitosan. The study of composites by AFM showed a completely different morphology when compared with unmodified components. The roughness of composites increase after the addition of hydroxyapatite. This may indicates a strong interaction between the polymeric components and inorganic additive.

Key words: chitosan, poly(vinyl alcohol), hydroxyapatite, composites, AFM, surface properties.

1. Introduction

Biopolymers are widely used in the cosmetic industry as cosmetic raw materials because of their film-forming ability, controlled bioactivity, biocompatibility and biodegradability [1-4]. The aim of this study was to determine the physico-chemical properties of chitosan (Ch), poly(vinyl alcohol) (PVA) and hydroxyapatite (HAP). Increase of the practical applications for synthetic and natural polymers is associated with modification of their properties through suitable changes of molecular and chemical structures. One way is a simple blending with other inorganic and/or organic compounds [5-11]. The polymer composites used in the study are composed of a polymer matrix and dispersed therein - hydroxyapatite. In this study, methods such as the tapping-mode atomic force microscopy (AFM) and calculation of surface free energy by means of contact angle measurements, were used. It is well known that, the surfaces of blends or composites prepared from natural and synthetic polymers are important for their use in cosmetic applications.

2. Materials and Methods
2.1 Materials

Chitosan powder (degree of deacetylation DD=78% M_v= 5.4x10^5 g/mol), and hydroxyapatite (HAP) were supplied by Aldrich. Poly(vinyl alcohol) is a commercial polymer from Aldrich company with the degree of hydrolysis DH=99% and a viscosity average molecular weight of 130 000. Chitosan and poly(vinyl alcohol) were solubilized separately in aqueous acetic acid. The additive of hydroxyapatite (1% w/w on solid chitosan) was dispersed in the solvent. Then, polymer solution was added slowly to the nano-additive dispersion. These solutions were cast to prepare the films which were subsequently dried in the vacuum oven.

2.2 Methods

The measurements of 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 probe liquid (high purity, volume of 3μl) were deposited on studied surface by a micro-syringe. The drop image was recorded by video camera and digitalized. The drop shape was solved numerically and fitted by means of the mathematical functions using instrument software. Each value of contact angle is an average of 10 measurements.

AFM imaging in the tapping mode and ambient conditions was done using a multimode scanning probe microscope with a Nanoscope IIIa controller (Digital Instruments Santa Barbara, CA). Surface images, using scan widths ranging from 1μm to 5 μm, with a scan rate of 1.97 Hz were acquired at fixed resolution (512x512 data points). The roughness parameter was calculated for

scanned area (1μm x 1μm) using Nanoscope software. The AFM images and roughness calculations were obtained for different sample places and the most typical areas are presented.

3. Results and Discussion

The surface properties of chitosan composites films were observed using atomic force microscopy. The examples of AFM images of chitosan/HA, PVA/HA and chitosan/PVA/HA composites are shown in Fig. 1 and Table 1.
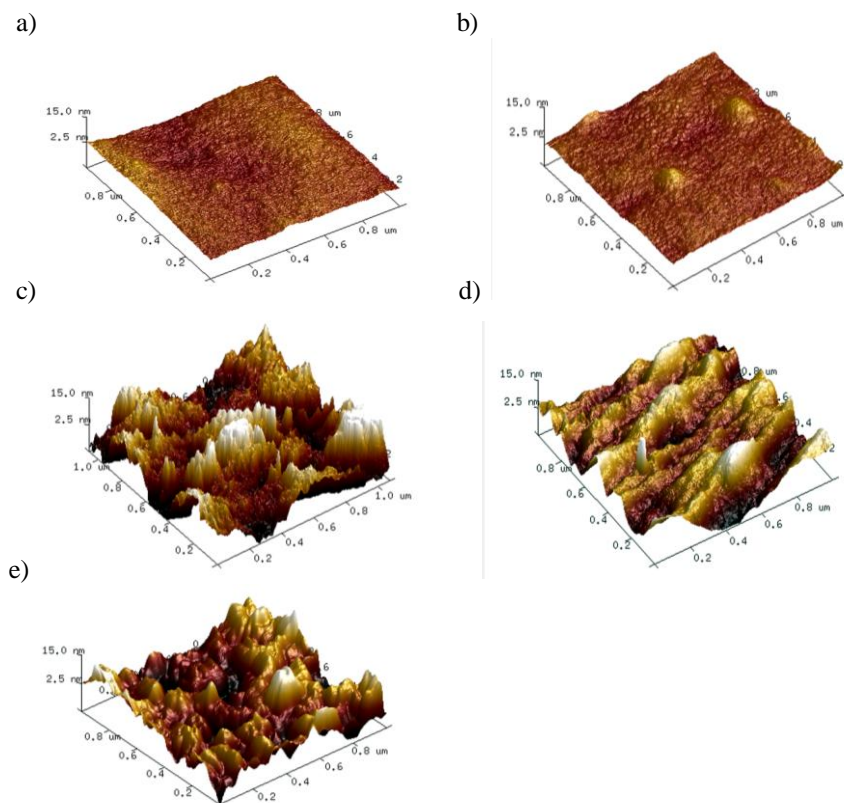
a)

b)

c)

d)

e)

Figure 1. AFM images of the surface of chitosan film and films made of chitosan composites: a) Ch, b) PVA, c) Ch/HAP, d) PVA/HAP, e) Ch/PVA/HAP.

Pure, homopolymer films have the smoothest surfaces. This agrees with the value of the roughness parameter which is about 1.0 nm for Ch and 0.7 nm for

PVA (Table 1). In the case of composites (Fig.s 1c-e), the surface topology began to alter. The surfaces of the composites have significantly more folds than the surface of chitosan and PVA films. As it can be observed, the roughness of the composites increases after the addition of hydroxyapatite. The value of the roughness of the Ch/HAP composite is the highest (Table 1). This may indicate an increase in the heterogeneity of this blend in comparison to other compositions.

The addition of PVA to the composite causes the reduction of the roughness value (Fig. 1e and Table 1).

Table 1. The roughness parameters (R_q) for films of composites of different composition.

Sample	R_q [nm]
Ch	1.02
PVA	0.68
Ch/HAP	7.03
PVA/HAP	3.74
Ch/PVA/HAP	4.41

Measurements of the contact angle for two different liquids (diiodomethane and glycerol) on the surface of chitosan, PVA and their composite films were made at room temperature using a goniometer. The surface free energy (γ_s) as well as the dispersive (γ_s^d) and polar (γ_s^p) components were calculated from contact angle values by the Owens-Wendt method using an appropriate computer program [12,13]. Table 2 gives the values of contact angles, surface free energy and its polar and dispersive components for chitosan and PVA samples and their composites. As can be observed, the surfaces of pure polymer films and their composites were rather hydrophobic as the values of glycerol contact angles were higher than the values of diiodomethane contact angles. The lowest value of glycerol contact angles is found for Ch/HAP composite, which suggests that this surface is the most hydrophilic. The values of surface free energy as well as dispersive and polar components indicate that the chitosan film has the highest polarity among the selected systems because it has the highest polar component of surface free energy. In the case of composites, the values of dispersive component are much higher than these of polar component which indicates mainly hydrophobic properties of the surface.

Table 2. Values of contact angles (deg), surface free energy (γ_s) and its polar (γ_s^d) and dispersive (γ_s^p) components for Ch , PVA and their composites.

sample	contact angle		γ_s (mJ/m^2)	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)
	(°)				
	G	D			
Ch	62.4±0.8	50.9±0.7	35.1±0.7	19.2±1.5	15.9±0.6
PVA	75.3±2.0	58.2±2.3	25.8±1.2	14.1±0.5	11.7±1.0
Ch/HAP	60.6±1.6	42.8±0.8	41.4±1.1	30.5±0.9	11.0±0.4
PVA/HAP	85.9±2.0	62.8±0.5	26.9±1.1	23.9±0.7	3.0±0.2
Ch/PVA/HAP	72.3±1.2	50.6±0.6	34.9±0.7	28.6±1.5	6.4±0.4

4. Conclusions

The results of contact angle and the surface free energy reveal that chitosan films are more polar than PVA films. In the case of chitosan composites, the value of the polar component of surface free energy is significantly reduced compared with pure polymers, especially in the composites containing PVA. This behavior indicates the rather hydrophobic character of this surface.

AFM images showed a completely different morphology of Ch/HAP and Ch/PVA/HAP composites when compared with pure components. The changes of topography images were considered by determining the root mean square (RMS) deviation in the image data. The roughness of the composites increases after the addition of hydroxyapatite, especially for the Ch/HAP composite. This may indicate a strong interaction between the polymeric components.

5. Acknowledgement

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