SURFACE PROPERTIES OF CHITOSAN ACETATE, POLYACRYLAMIDE AND THEIR MIXTURES

Katarzyna Lewandowska

Nicolaus Copernicus University,
Faculty of Chemistry,
Chair of Chemistry and Photochemistry of Polymers,
ul. Gagarina 7, 87-100 Toruń, Poland
E-mail: reol@chem.umk.pl

Abstract
The surface properties of chitosan acetate (ChA), polyacrylamide (PAM) and ChA/PAM mixtures have been investigated by the tapping-mode atomic force microscopy (AFM) and monitored by contact angle measurements. Chitosan is blended with polyacrylamide in acetic acid solution and this solution is cast to prepare the mixture film. Measurements of the contact angle for two different liquids (diiodomethane and glycerol) on the surface of chitosan acetate. The surface free energy (γs) as well as dispersive (γ_s^d) and polar (γ_s^p) components were calculated from contact angle values by Owens-Wendt methods using an appropriate computer program. The values of polar and dispersive components of surface free energy show that PAM films are more polar than chitosan acetate films. In the case of ChA/PAM mixtures, the values of surface free energy and polar component are reduced significantly compared with pure polymers. This behavior indicates rather hydrophobic character of this surface. The changes of topography images were considered by determining the root mean square (RMS) deviation in the image data. The study of blends by AFM showed a completely different morphology when compared with pure components. The roughness of blends increases with the increase of ChA content. This may indicates a strong interaction between the polymeric components.

Key words: *chitosan acetate, polyacrylamide, polymer blends, AFM, contact angle, surface properties.*

1. Introduction

Polymer-polymer miscibility continues to attract the interest of many researchers. Blending of polymers with good miscibility is considered to be a very convenient method to meet new requirements in material properties. It is known that the surfaces of blends prepared from natural and synthetic polymers are important for their use in biomedical applications. The following paper is a continuation of our studies on the miscibility of chitosan with polyacrylamide. In our earlier measurements, the rheological properties of ChA/PAM solution blends were used to deduce the miscibility of ChA with PAM [**1**]. The purpose of this work was to study the surface properties of chitosan acetate with polyacrylamide by means of atomic force microscopy studies (AFM) and contact angle measurements.

2. Materials and methods

2.1 Materials

The blend system contained partially hydrolyzed polyacrylamide (PAM) {degree of hydrolysis DH = 1%, $\overline{M}_v = 1.1\times10^6$ g/mol, Aldrich} with chitosan (Ch) {degree of deacetylation DD = 86%, $\overline{M}_v = 4.7\times10^5$ g/mol, Aldrich}. Chitosan and PAM were solubilized separately in 0.1 M aqueous acid. The blends of different component ratios were obtained by mixing calculated volumes of both solutions. Polymer films were obtained by casting solutions onto glass plates.

Glycerol (glycerin, propane-1,2,3-triol) and diiodomethane (POCh and Aldrich, respectively, analytical grade) were used as test liquids for contact angle measurements

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 microsyringe. 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.

Topographic imaging was performed using a multimode scanning probe microscope with a Nanoscope IIIa controller (Digital Instruments Santa Barbara, CA) operating in the tapping mode, in air, at room temperature. Surface images, using scan widths ranging from 1 μm to 5 μm, with a scan rate of 1.97 Hz were acquired at fixed resolution (512 × 512 data points). Commercial silicon tips with spring constant 2 - 10 N/m were used. The roughness parameter such as the root mean square (R_q) was calculated for scanned area (5 × 5 μm) 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

Table 1 shows the values of contact angles of chitosan acetate, PAM and their blends. As can be observed, the surfaces of chitosan acetate and blend films were rather hydrophobic as the values of glycerol contact angles were higher than the values of diiodomethane contact angles. Glycerol interacts with surfaces by polar forces but diiodomethane interacts with surfaces by dispersion forces [**2**]. The lowest value of glycerol contact angle is found for PAM film, which suggests that the surface is the most hydrophilic.

The surface free energy (γ_s) as well as dispersive (γ_s^d) and polar (γ_s^p) components were calculated from contact angle values by Owens-Wendt methods [**2, 3**]. The surface free energy as well as its polar and dispersive components indicate that the PAM film has the highest polarity among the investigated systems because it has the highest polar component of surface free energy. The lowest polarity are characteristic for ChA/PAM blend films. This behaviour indicates some interaction between the polymer components in the blend films.

The morphology of four of the investigated films is presented in ***Figure 1*** (see page 40). The AFM images show differences in the film surface properties of the homopolymers and their blends. The surface morphology of pure ChA film is considerably rougher than PAM or the blends. In the case of the PAM sample the film has a relatively flat and smooth surface, which is a consequence of its amorphous state. For the ChA/PAM blends, the surface is smoother than that of ChA itself, with visible areas of crystalline phase of ChA (***Figure 1.A*** and ***1.B***). In the case of blend containing 20% chitosan acetate (***Figure 1.C***), it is clearly visible changes in character of the surface of the blend as compared to the pure PAM film. This may indicates an increase in the heterogeneity of this blend in comparison to other compositions. ***Table 2*** gives the values of the roughness parameters for the investigated samples. As can be observed the roughness of the blends increases with increase in ChA content. The exception is the ChA/PAM blend with $w_{ChA} = 0.5$. Similar direction of changes were also observed for other chitosan blends [**4 - 7**]

Table 1. *Values of contact angles (deg), surface free energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) components for ChA, PAM and their blends (w_{ChA} – ChA weight fraction).*

w_{ChA}	contact angle, °		γ_s, mJ/m^2	γ_s^d, mJ/m^2	γ_s^p, mJ/m^2
	Glycerol	Diiodomethane			
0.0	46.4 ± 0.4	59.4 ± 0.1	45.0 ± 0.3	18.2 ± 0.1	26.7 ± 0.3
0.2	69.0 ± 0.7	54.1 ± 2.7	36.6 ± 1.2	25.6 ± 1.5	9.0 ± 0.3
0.5	67.3 ± 1.6	53.3 ± 0.2	35.5 ± 0.6	25.7 ± 0.5	9.8 ± 1.0
0.8	69.8 ± 1.1	54.3 ± 1.4	33.9 ± 0.6	26.0 ± 1.3	7.9 ± 1.7
1.0	61.3 ± 1.4	52.7 ± 0.4	38.2 ± 1.1	24.8 ± 0.7	10.4 ± 0.2

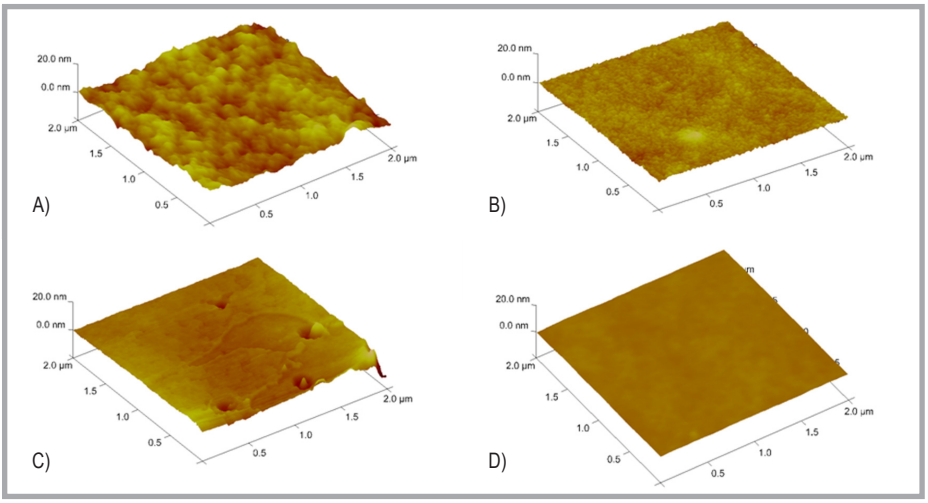

Figure1. *AFM images: A) chitosan acetate, B) 50/50 blend, C) 20/80, D) HPAM.*

Table 2. *The roughness parameters (R_q) for films of ChA/PAM blends of different composition.*

w_{ChA}	R_q, nm
0.0	0.2 ± 0.04
0.2	1.3 ± 0.2
0.5	0.6 ± 0.1
0.8	1.2 ± 0.2
1.0	1.6 ± 0.2

4. Conclusions

1. The surfaces of chitosan acetate and ChA/PAM blends have similar values of surface free energy.
2. The highest polarity of surface is characteristic of polyacrylamide film.
3. The mixtures have significantly less polarity of surface.
4. In the case of ChA/PAM blends, the surface free energy and its polar component decreases with the increase of ChA content which indicates that between functional groups of ChA and PAM are interactions particularly in the bulk of the blend.
5. The surface of PAM is flat, it has the lowest value for the roughness parameter.
6. AFM images show differences in surface properties of PAM films and films made of blends of chitosan acetate and PAM.
7. The surface roughness of blends increases with the increase of ChA content.

5. References

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