

MISCIBILITY AND INTERACTIONS IN CHITOSAN AND POLYACRYLAMIDE MIXTURES

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Abstract

In the present work, the results of Fourier transform infrared (FTIR) and atomic force microscopy (AFM) studies of films of chitosan acetate (ChA), polyacrylamide (PAM), and their mixtures are presented. The morphology of the ChA and PAM films and their mixtures was studied by tapping-mode atomic force microscopy (AFM). The topography images were considered by determining the root mean square (RMS) deviation in the image data. The study of mixtures by AFM showed a completely different morphology when compared with pure components. The roughness of mixtures increases with the increase of ChA content but is significantly reduced after UV exposure. This may indicate a strong interaction between the polymeric components. The FTIR spectroscopy also supports the obtained results. The miscibility of polymer mixtures is related to interactions between the functional groups of the polymeric components.

Key words: chitosan, polyacrylamide, polymer blends, AFM, surface properties, FTIR analysis.

1. Introduction

Polymer mixtures with biopolymers are widely used in biomedical applications. Chitosan (Ch), a deacetylated product of chitin, is a high molecular weight polysaccharide that is mainly composed of β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucopyranose units [1 - 3]. This biopolymer has good biocompatibility, biodegradation and bioactivity. Thus, chitosan has frequently been applied in medicine, pharmacy and the food industry. Polyacrylamide (PAM) is a synthetic, non-ionic polymer that is soluble in water. This polymer is often combined with other polymers [4 - 6]. In this paper, the mixtures composed of chitosan with polyacrylamide at different component ratios have been prepared as materials for various applications. The surface properties of polymer mixtures are important for their use in further applications. UV-irradiation is a good way to modify the surface of polymeric materials, with the surface structure of the polymeric films after modification being the result of photo-oxidation processes caused by exposure to ultraviolet radiation [7, 8].

The purpose of this study was to evaluate the interaction and miscibility of chitosan acetate with polyacrylamide. The influence of UV-irradiation with a wavelength of 254 nm on the surface properties of the homopolymers and their mixtures was also studied.

2. Materials and methods

2.1 Materials

The investigated systems contained chitosan (Ch) {degree of deacetylation DD = 78%, $M_v = 1.4 \times 10^6$ g/mol, Aldrich} mixed with polyacrylamide (PAM) { $M_v = 2.5 \times 10^6$ g/mol, Aldrich}. Mixtures of chitosan with PAM samples were dissolved in 0.1 mol/dm³ acetic acid. These solutions were cast to prepare the films. The films were dried in the vacuum oven.

2.2 Methods

FTIR spectra of the used polymer samples and their blends were recorded on a Perkin Elmer Spectrum 2000, in the wavelength range between 4000 – 400 cm⁻¹, resolution of 2 cm⁻¹ and 60-times scanning.

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 μ m to 5 μ m, with a scan rate of 1.97 Hz, were acquired at fixed resolution (512 \times 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 the scanned area (1 \times 1 μ m) using Nanoscope software. The AFM images and roughness calculations were obtained for different sample places; the most typical areas are presented.

Thin polymeric films were irradiated in air at room temperature using a Philips TUV-300 mercury lamp which emits light mainly of wavelength 254 nm. Exposure time was 1 - 8 h.

3. Results and discussion

FTIR analysis has been used to identify interactions in polymer mixtures. **Figure 1** presents the FTIR spectra of pure chitosan acetate and PAM before and after UV-irradiation. The spectrum of chitosan acetate shows strong absorption bands at the frequency range 3300 - 3600 cm^{-1} , the amide I absorption peaks at 1647 cm^{-1} and amide II at 1562 cm^{-1} . For the PAM sample, the FTIR spectrum also shows strong bands in the frequency range 3300 - 3600 cm^{-1} , which are assigned to N-H stretching vibrations, and 1666 cm^{-1} (C=O

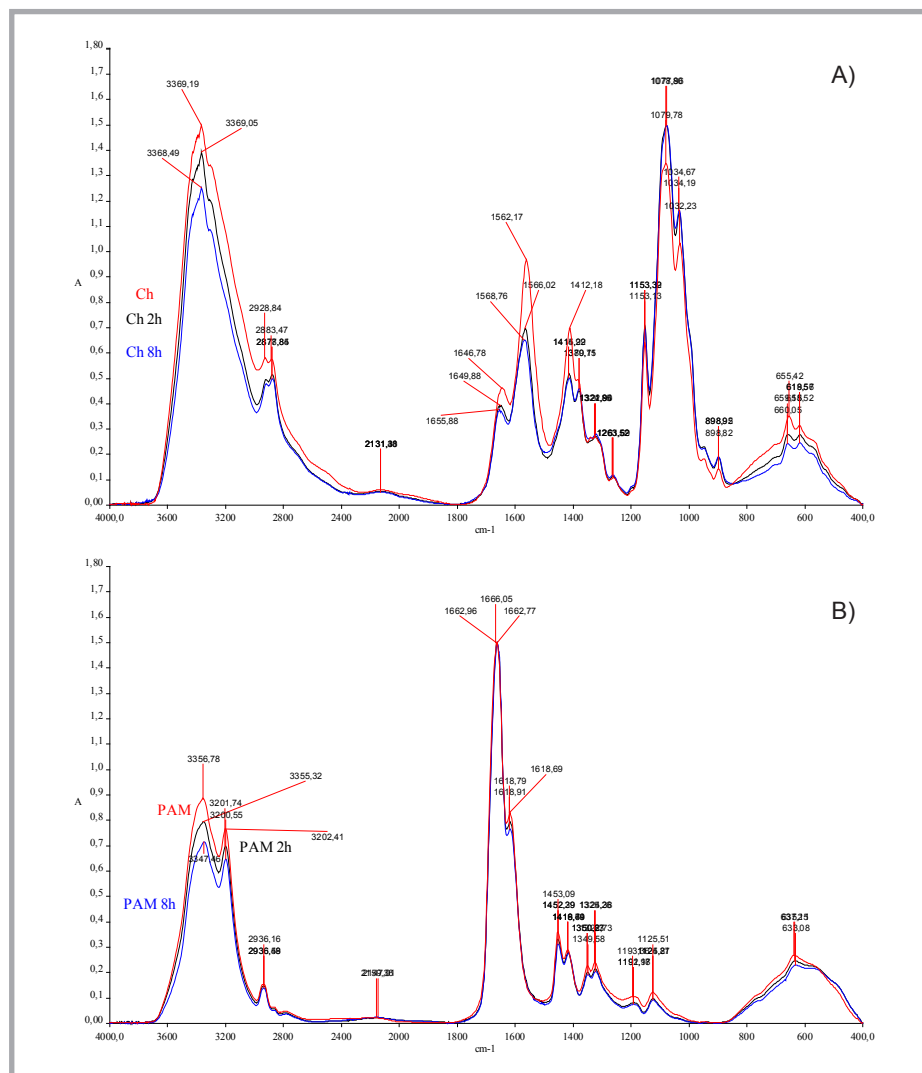


Figure 1. FTIR spectra of ChA and PAM before (A) and after (B) UV-irradiation.

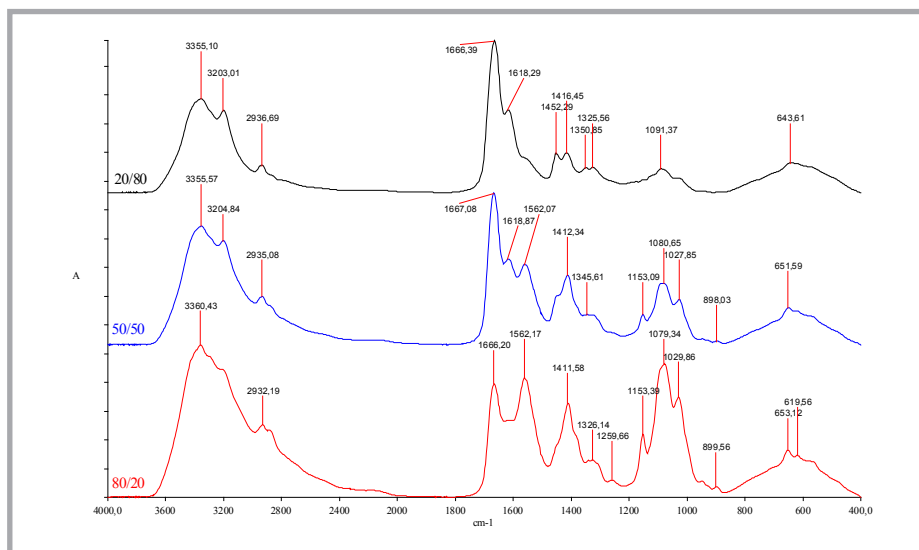


Figure 2. FTIR spectra of ChA/PAM mixtures.

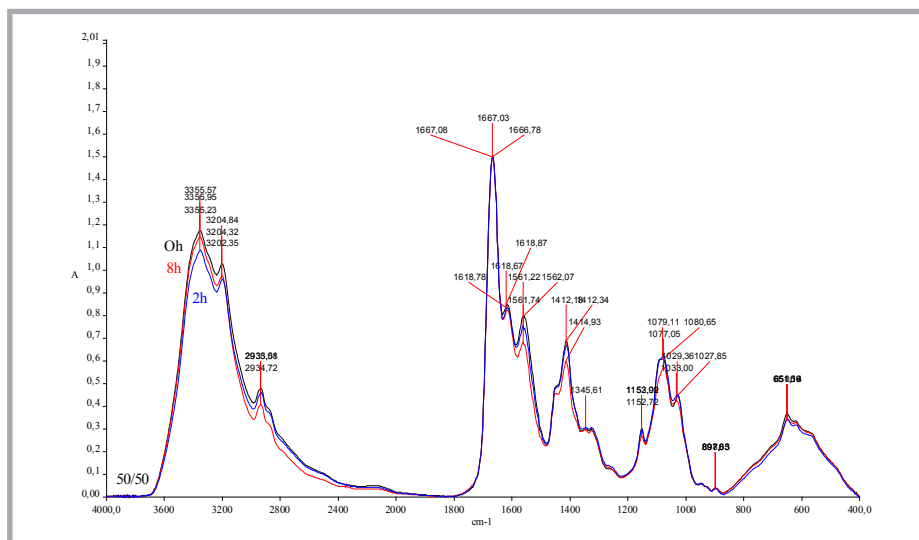


Figure 3. FTIR spectra of ChA/PAM (50/50) mixture before and after UV-irradiation.

stretching) [4]. In the film mixtures (**Figure 2**), the spectra are characterised by the presence of the absorption bands of the pure components, with intensity being approximately proportional to the weight fraction of the component. Changes in the characteristic shape of component spectra as well as small shifts in absorption peaks due to hydrogen bonding between functional groups were observed.

UV-irradiation of samples causes systematic changes in their FTIR spectra (**Figures 1** and **3**). The main changes are observed in the frequency range of 3300 - 3600 cm^{-1} in spectra of all irradiated samples. For the pure PAM and ChA/PAM mixtures, changes in the 1550 - 1700 cm^{-1} range were significantly smaller than for the ChA sample. Moreover, considering the relative changes in integral intensity bands, it can be concluded that mixtures are more photostable than pure components.

The surface morphology results of films obtained for pure components and their mixtures before and after UV-irradiation are shown in **Figures 4 - 6**. Pure, un-irradiated PAM film has the smoothest surface. This agrees with the value of the roughness parameter, which is about 0.6 nm (**Table 1**). For the pure, un-irradiated ChA film, the surface morphology is characterised by a more corrugated surface, with the roughness parameter being about 3 times higher than that for PAM film.

In the case of ChA/PAM mixtures (**Figure 6**), the surface topology began to alter. The AFM image (**Figure 6**) illustrates the decreasing number and height of peaks on the film surface. The surface becomes more flat. The observed changes in morphology are related to the interactions between polymeric compounds. UV-irradiation causes modification of all surfaces. The film surfaces become smoother after UV-irradiation and the values of the

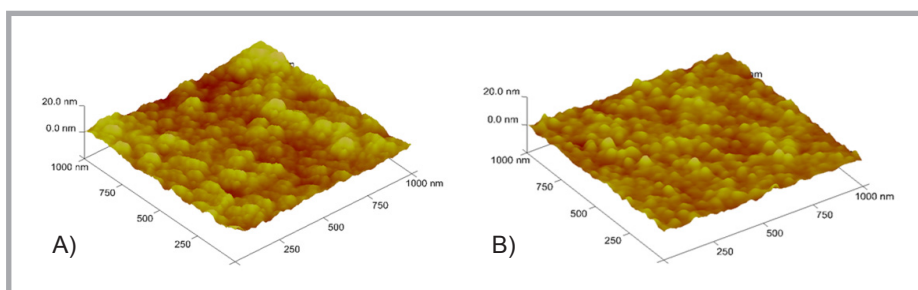


Figure 4. AFM images of the surface of chitosan films before UV irradiation (A) and after 8 h of UV irradiation (B).

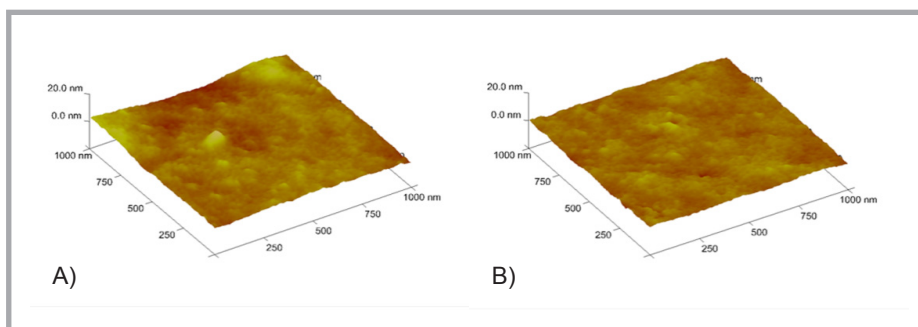


Figure 5. AFM images of the surface of PAM films before UV irradiation (A) and after 8 h of UV irradiation (B).

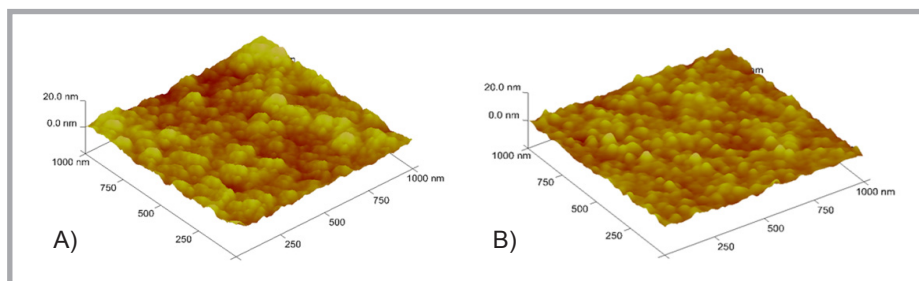


Figure 6. AFM images of the surface of ChA/PAM mixture (50/50) films before UV irradiation (A) and after 8 h of UV irradiation (B).

Table 1. The roughness parameters (R_q) for films of ChA/PAM mixtures of different composition before and after 8 h of UV irradiation. w_{ChA} – the weight fraction of chitosan.

w_{ChA}	R_q [nm]	
	0 h	8 h
0.0	0.55	0.29
0.5	1.20	0.70
1.0	1.80	1.40

roughness parameters decrease (**Table 1**). Such changes in surface morphology may result from various photo-oxidation, photodegradation and photocross-linking reactions occurring in the polymeric samples.

4. Conclusions

1. FTIR analysis showed the existence of a weak interaction of the hydroxyl or amino groups of chitosan with the amide groups of PAM.
2. The interactions between chitosan and PAM macromolecules in the mixtures, including hydrogen bonds, led to the protection of surfaces against UV-treatment.
3. The surface of PAM is flat; it has the lowest values for the roughness parameter.
4. AFM images show differences in surface properties of PAM films, and films made of mixture of chitosan and PAM.
5. The surface roughness of mixtures increases with the increase in ChA content.
6. The surface of chitosan and PAM films and their mixtures are altered by UV-irradiation.
7. The surface roughness of chitosan and ChA/PAM mixture films is reduced as a result of exposure to UV light.

5. References

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