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Miscibility and physical properties of chitosan and polyacrylamide blends

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ARTICLE INFO

ABSTRACT

Miscibility studies of chitosan/polyacrylamide (Ch/PAM) and chitosan/partially hydrolyzed polyacrylamide (Ch/HPAM) blends of different compositions were investigated using viscometric method. The intrinsic viscosity, ($[\eta]$), and the viscosity interaction parameters, (b_m), have been determined for the binary (solvent/polymer) and ternary (solvent/polymer A/polymer B) systems. Degree of miscibility of these polymer blends was estimated on the basis of two criteria. These studies indicate that chitosan/polyacrylamide and chitosan/partially hydrolyzed polyacrylamide are miscible at any composition in 0.1 mol·dm^{-3} CH$_3$COOH + 0.2 mol·dm^{-3} NaCl at 25 °C. The influence of blend composition on mechanical properties was also investigated in this study. Ch, PAM, HPAM and their blend films were prepared by casting technique. The mechanical properties such as ultimate tensile strength and Young modulus depend on the weight fraction of chitosan and were changed irregularly. The FTIR spectroscopy also supports the obtained results. The miscibility of polymer mixtures is related to the interactions between the functional groups of the polymeric components.

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1. Introduction

Natural polymers play an important role in food and cosmetic industries or biomedical applications. Chitosan (Ch) is the second most abundant biopolymers and is *N*-deacetylated derivative of chitin. It has a repeating structure of β-(1 → 4)-2-amino-2-deoxy-D-glucopyranose [1–3]. Chitosan is a biomaterial well known for its biocompatible and biodegradable properties, bioactivity and non-toxic for human body. The application of chitosan can be widened because of the addition of synthetic polymers and inorganic additives such as montmorillonite or hydroxyapatite [4–10]. The specific properties can be achieved without loss of characteristic features of compounds in the blends or composites. The partially hydrolyzed polyacrylamide (HPAM) is a copolymer of acrylamide and sodium acrylate [11,12] and is a water-soluble synthetic anionic polyelectrolyte. Polyacrylamide is also a synthetic, non-ionic polymer soluble in water.

The purpose of this study was to evaluate the miscibility of two chitosans, having different molecular weights, with polyacrylamide and partially hydrolyzed polyacrylamide on the basis of experimental and ideal values of the viscosity interaction parameters, which were calculated from viscosity measurements in dilute Ch/PAM and Ch/HPAM solution blends. It is well known that, viscometric study has been widely used to investigate the polymer–polymer interaction and miscibility. This technique is a simple, quick and an inexpensive method [13–17]. Finally, the influence of structural changes on mechanical properties

of Ch/PAM and Ch/HPAM blends was also studied. The present work is a continuation of our previous studies on the physico-chemical properties of chitosan with partially hydrolyzed polyacrylamide [18]. In our earlier measurements, the surface properties of thin films based on the mixture of chitosan and partially hydrolyzed polyacrylamide have shown that the wettability and the surface roughness of chitosan and its blends films have been altered by mixing.

2. Materials and methods

Chitosan samples have a degree of deacetylation of 78% with a viscosity average molecular weight of 540 000 ($\overline{M}_v/\overline{M}_n = 3.6$) for Ch I and of 1 400 000 for Ch II ($\overline{M}_v/\overline{M}_n = 2.8$). Both chitosan samples were supplied by Aldrich. Polyacrylamide, (PAM) ($\overline{\mathbf{M}}_\mathbf{v} = 2\,500\,000$, $\overline{M}_v/\overline{M}_n = 1.7$, non ionic) (Acros Organics company) and partially hydrolyzed polyacrylamide, (HPAM) ($\overline{\mathbf{M}}_\mathbf{v} = 1\,500\,000$, degree of hydrolysis DH = 1.5%, $\overline{M}_v/\overline{M}_n = 2.1$) (Aldrich) were used. The viscosity average molecular weight $\overline{\mathbf{M}}_\mathbf{v}$ of chitosan, PAM and HPAM was measured with the Ubbelohde viscometer and calculated from the viscosity of solutions according to the Mark–Houwink–Sakurada equation [19,20]:

$$[\eta] = K\overline{M}_v^a \tag{1}$$

using *K* and *a* values equal to 0.00181 and 0.93 for Ch [21] and 0.00719 and 0.77 for polyacrylamide [22] and 0.0063 and 0.82 for partially hydrolyzed polyacrylamide [22], respectively.

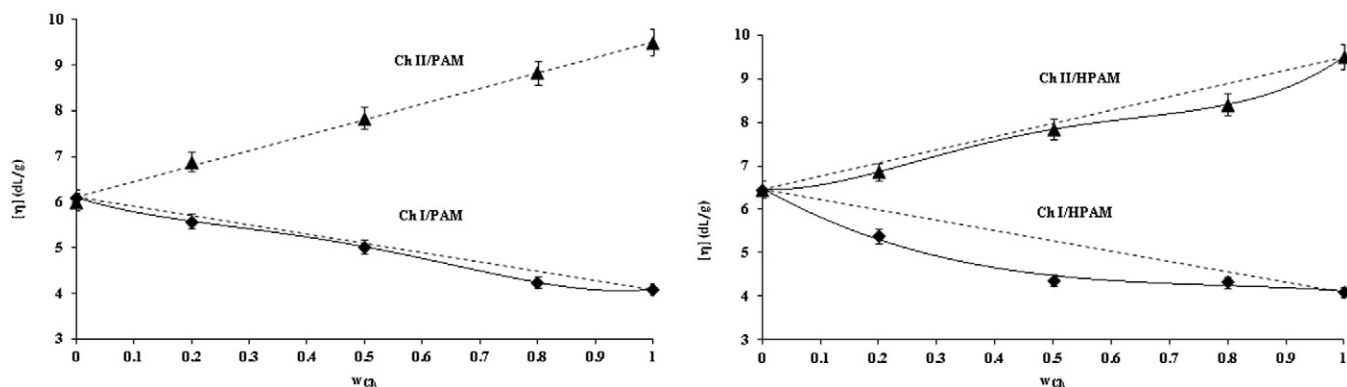*E-mail address:* reol@chem.uni.torun.pl.

Fig. 1. Intrinsic viscosity ($[\eta]$) dependence on weight fraction of chitosan (w_{Ch}) in Ch/PAM and Ch/HPAM blends. Dotted line indicates the ideal values of $[\eta]_m^{id}$ which follow the Garcia criterion [17].

The solutions of chitosan, PAM and HPAM were solubilized, separately, in aqueous $0.1 \text{ mol} \cdot \text{dm}^{-3}$ CH_3COOH + $0.2 \text{ mol} \cdot \text{dm}^{-3}$ NaCl or $0.1 \text{ mol} \cdot \text{dm}^{-3}$ CH_3COOH and then mixed at different proportions. The polymer films were obtained by solution casting method. The films were dried in a vacuum at room temperature.

Viscosity measurements of dilute polymer solution were carried out in a controlled thermostatic bath at 25 ± 0.1 °C using the Ubbelohde capillary viscometer. The flow times were recorded with an accuracy ± 0.01 s. Before measurements the solutions were filtered through G1 sintered glass filters. The intrinsic viscosity, the interaction parameter and Huggins coefficient values were determined according to Huggins equation [23] using solution of 5 concentrations. The values of experimental interaction parameter are determined from the plot of η_{sp}/c vs c (Eq. (1)) for solutions containing both polymers.

$$\left(\frac{\eta_{sp}}{c_m}\right)_m = [\eta]_m^{exp} + b_m^{exp} c_m \tag{2}$$

where:

b_m^{exp} the experimental, viscosity interaction parameter of polymer mixture;

$[\eta]_m^{exp}$ the experimental, intrinsic viscosity of the polymer blends;

c_m the total concentration of solution.

The ideal value of the interaction parameter can be defined by different equations [13–17]. In this study, we considered two different criteria to estimate the polymer–polymer miscibility in dilute solution such as: Krigbaum and Wall criterion [13] and Garcia et al. criterion

[17]. Krigbaum and Wall [13] have defined the ideal value of the interaction parameter b_m^{id} by the expression:

$$b_m^{id*} = b_A w_A^2 + b_B w_B^2 + 2b_{AB}^{id} w_A w_B \tag{3}$$

$$b_{AB}^{id} = b_A^{1/2} b_B^{1/2} \tag{4}$$

where: b_A, b_B, b_{AB} — interaction parameters of like (AA, BB) and unlike (AB) polymer molecules, respectively; $b_i = k_i [\eta]_i^2$, k_i — Huggins coefficient (i = A, B) w_A, w_B — weight fractions of polymers A and B, respectively whereas, Garcia et al. [17] defined the ideal value of the interaction parameter, b_m^{id}, as:

$$b_m^{id**} = b_A w_A^2 + b_B w_B^2. \tag{5}$$

The polymer mixture is miscible if $\Delta b_m = b_m^{exp} - b_m^{id} \rangle 0$ and immiscible if $\Delta b_m = b_m^{exp} - b_m^{id} \langle 0$.

Additionally, Garcia et al. [17] have proposed another miscibility criterion which is based on the difference between the experimental and ideal values of $[\eta]_m$. If $\Delta[\eta]_m = [\eta]_m^{exp} - [\eta]_m^{id} \langle 0$ the system is miscible, and if $\Delta[\eta]_m = [\eta]_m^{exp} - [\eta]_m^{id} \rangle 0$ the system is immiscible. The value of $[\eta]_m^{exp}$ is determined from the intercept of the plot according to Eq. (2), whereas $[\eta]_m^{id}$ is obtained from Eq. (6).

$$[\eta]_m^{id} = [\eta]_A w_A + [\eta]_B w_B \tag{6}$$

where: $[\eta]_A$, $[\eta]_B$ — intrinsic viscosity of polymers A and B, respectively, in pure solvent.

Mechanical properties of the materials were measured at room temperature using a tensile test, Zwick&Roell, Germany at a crosshead speed of 5 mm/min in accordance with the standard procedure [24]. Samples were cut with a shaper into dog-bone shapes of initial dimensions 50 mm length with a 4.2 mm width and 30 μm thickness. The thickness of the samples was determined using an ultrameter type A-91 (manufactures of Electronic Devices, Warsaw, Poland). All the film samples were cut using the same shaper. For each kind of film, at least five samples were tested.

FTIR spectra of the used polymer samples and their blends were recorded on a PerkinElmer Spectrum 2000, in the wavenumber range between 4000–400 cm^{-1}, resolution of 2 cm^{-1} and 60-times scanning.

3. Results and discussion

Using the criteria as proposed by Krigbaum et al. [13] and Garcia et al. [17] the parameters $\Delta[\eta]_m$ and Δb_m have been computed to establish the degree of miscibility in the Ch/PAM and Ch/HPAM blends. All the Huggins plots (the reduced viscosity versus polymer concentration, see in the supplementary material) show linear behavior in the range of
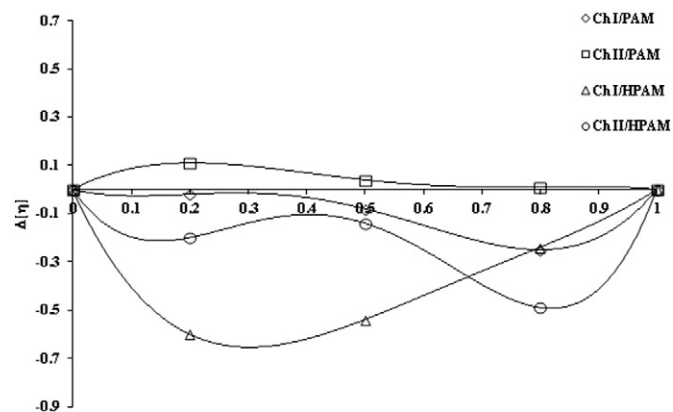

Fig. 2. Plot of criterion of $\Delta[\eta]$ versus weight fraction of chitosan (w_{Ch}) in Ch/PAM and Ch/HPAM blends.