INFLUENCE OF THE INTERMOLECULAR INTERACTION ON PHYSICO-CHEMICAL PROPERTIES OF CHITOSAN/HYALURONIC ACID BLENDS

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Abstract

In the present study, the results of viscosity measurements in dilute solutions of chitosan (Ch) with hyaluronic acid (HA) are presented. Chitosan is blended with hyaluronic acid in aqueous 0.1M CH_3COOH/0.2M NaCl and 0.3M NaCl respectively, or with the addition of HEPES. Viscosity measurements of dilute polymer solution were carried out in an Ubbelohde capillary viscometer. 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. The homogeneity and morphology of chitosan blends were ascertained from the tapping-mode atomic force microscopy. The surface roughness of chitosan, hyaluronic acid and Ch/HA blended films was altered by mixing. The obtained results suggested that there was existence of the strong interactions between chitosan and hyaluronic acid.

Key words: *chitosan, hyaluronic acid, polymer blends, viscosity interaction parameters, AFM microscopy.*

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1. Introduction

Manufacturing of new functional and structural materials from natural renewable and degradable materials has attracted much attention. Natural polysaccharides are the right candidates due to their unique structures and properties. The structure of blends obtained from polysaccharides mainly depends on the existence of intermolecular interactions. Among various interactions, hydrogen bonding and electrostatic interactions play important roles in the structure and properties of the polymer blends and composites. Chitosan and hyaluronic acid are among the most frequent natural polymers. These polysaccharides can be considered as good candidates for the preparation of new biopolymer mixtures because of their potential attractive properties such as biocompatibility, biodegradability and non toxic for human body [1-5].

In this paper, mixtures composed of chitosan with hyaluronic acid at different component ratio have been prepared as material designed for different applications e.g. in cosmetic industry or biomedical applications.

The purpose of the present work was to determine the miscibility and interactions in chitosan/hyaluronic acid blends, using viscosity measurements of dilute solution and the tapping-mode atomic force microscopy. 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 [6-12]. Atomic force microscopy (AFM) is other useful method for the study of structure and homogeneity of polymer mixtures [13-15].

2. Materials and Methods

2.1 Materials

Hyaluronic acid (HA) is a commercial polymer from Aldrich Company with a viscosity average molecular weight of 1.8×10^6. Chitosan (Ch) sample has a degree of deacetylation of 78% with a viscosity average molecular weight of 0.59×10^6. Ternary solutions for each system were prepared by mixing the appropriate quantity of polymer solutions in the weight ratios $w_A:w_B$ of 0.2:0.8, 0.5:0.5 etc.

The polymeric samples were solubilized separately in the solvent. Chitosan was blended with hyaluronic acid in aqueous 0.1MCH_3COOH/0.2M NaCl and 0.3M NaCl respectively, or with the addition of HEPES.

2.2 Methods

Viscosity measurements of dilute polymer solution (c=0.1%) were carried out in an Ubbelohde capillary viscometer. The flow times were recorded with an accuracy of □±0.01s, and the bath temperature was constant (25□±0.1°C). Before measurements the solutions were filtered through G1 sintered glass filters. The intrinsic viscosity and the Huggins coefficient values were determined according to Huggins [16-17] equation using solution of 5

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concentrations. Kinetic energy corrections were taken into account for the evaluation of the intrinsic viscosity, which was determined by extrapolation to infinite dilution (zero solute concentration).

The miscibility is estimated by comparison of the experimental and ideal values of b_m and $[\eta]_m$. The values of interaction parameters were obtained using the same methods as shown in previous papers [11,12,18].

Topographic imaging was performed in air using a multimode scanning probe microscope with a Nanoscope IIIa controller (Digital Instruments Santa Barbara, CA) operating in the tapping mode, at room temperature. Surface images, using the 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 such as the root mean square (R_q) was calculated for scanned area (1μm x 1μm) using Nanoscope software.

3. Results and Discussion

The plots of reduced viscosity (η_{sp}/c) versus concentration (c) for Ch and HA and their mixtures in different weight fraction of chitosan are shown in Fig. 1. The linear relationships are observed for the polymers and all of mixtures over whole composition range.

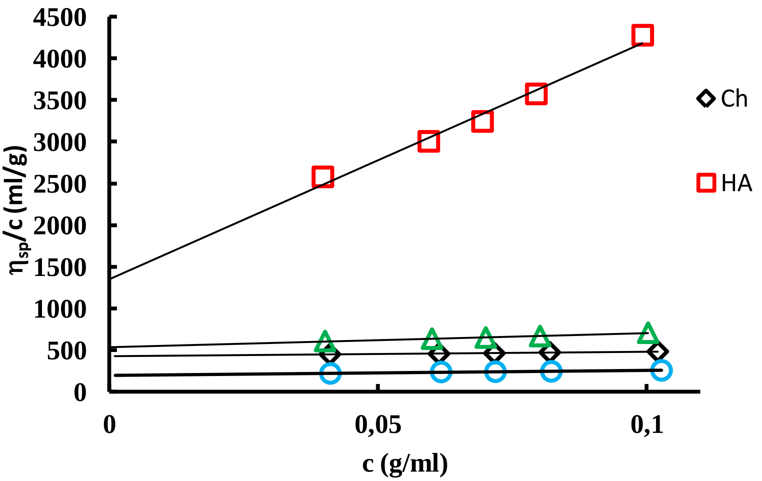

Figure 1. The reduced viscosity versus polymer concentration for Ch, HA and Ch/HA blends in 0.1 mol·dm^{-3} CH_3COOH+0.2 mol·dm^{-3} NaCl at 25°C.

The parameters of the miscibility criterion proposed by Garcia et al. [**7**] are tabulated in Tables 1. As it can be observed, for Ch/HA blend solutions, the parameters Δb_m and $\Delta[\eta]$ are negative values. The miscibility criterion is not satisfied.

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Table 1. The value of interaction parameters for Ch/HA blends.

The solutions without the addition of HEPES						
w_{Ch}	b_m^{exp} [dL/g]^2	b_m^{id} [dL/g]^2	Δb_m	$[\eta]_m^{id}$ [dL/g]	$[\eta]_m^{exp}$ [dL/g]	$\Delta[\eta]_m$
0.2	16.6	183.0	-166.4	5.38	11.68	-6.30
0.8	5.7	15.0	-9.3	1.98	6.09	-4.11
The solutions with the addition of HEPES						
0.2	9.24	137.7	-128.5	6.11	13.10	-6.99
0.8	4.84	11.58	-6.74	2.02	6.18	-4.16

w_{Ch} – the weight fraction of chitosan

The addition of HA to the mixture causes a strong interaction between the polymeric components and phase separation in the selected blend systems. These reasons could probably be responsible for the negative value of the interaction parameter. However, the addition of HEPES to the solutions decreases the negative values of the interaction parameters. This indicates the use of other solvent. It is known that the solvent plays an important role in the miscibility of polymeric compounds [12,19]. A reasonable interpretation is that in different solvents, the interactions between two different polymers are quite different. The viscosity behavior of chitosan in the presence of hyaluronic acid by using the other solvent will be presented in the subsequent papers.

The surface properties of Ch/HA blend films were observed using AFM microscopy. The examples of AFM images of Ch/HA blends are shown in Figure 2.

The AFM images show difference in surface properties films for the homopolymers and their blends. The surface morphology of pure polymer films is considerably rough, which can result from the crystalline of the sample. In the case of Ch/HA blends, the surface morphology of blend depends on its composition. For the Ch/HA blend with w_{Ch}=0.8 (Figure 2C) the surface of blend is significantly more folded than the surface of pure polymer film. This may indicate an increase in the heterogeneity of this blend in comparison to other compositions. In the case of the Ch/HA blend with w_{Ch}=0.2 the AFM image (Figure 2D) illustrates decreasing the 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.

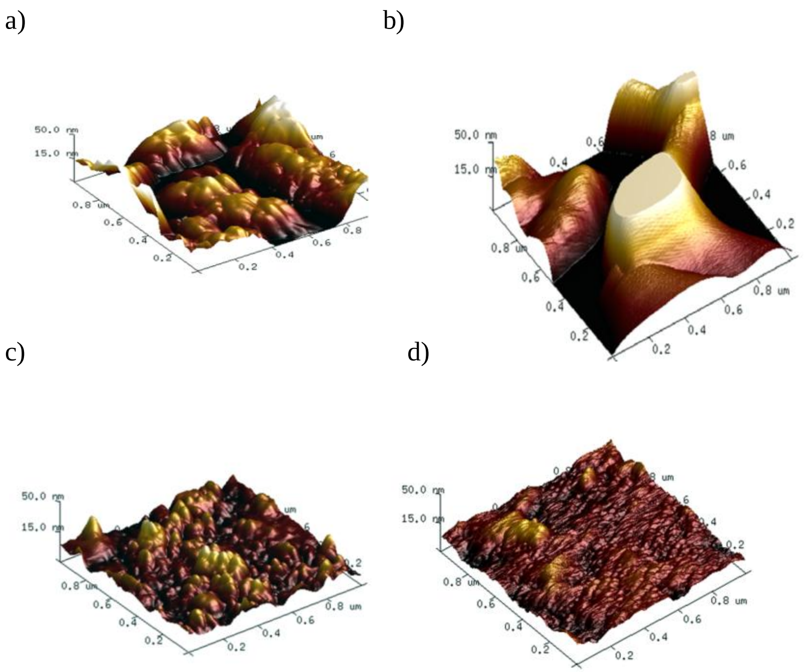

Figure 2. AFM images of the surface of Ch/HA blends: a) 100/0, b) 80/20, c) 20/80, d) 0/100.

4. Conclusions

In this paper, the miscibility of dilute aqueous Ch/HA blend solution were investigated. The studies of hydrodynamic properties of the solutions of blends indicated that the polymeric components are poorly miscible. The surface roughness of chitosan, hyaluronic acid and Ch/HA blended films was altered by mixing. The obtained results suggested that there was existence of the strong interactions between chitosan and hyaluronic acid.

5. Acknowledgement

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