

PHYSICO-CHEMICAL PROPERTIES OF CHITOSAN COMPOSITES WITH SYNTHETIC POLYMERS AND INORGANIC ADDITIVES

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Abstract

In the present study the results of rheological measurements and atomic force microscopy (AFM) of polymer composites with montmorillonite (MMT) are presented. Chitosan is blended with synthetic polymers and inorganic additives in acetic acid solution and this solution is cast to prepare the mixture film. Flow measurements were made on a Bohlin Visco 88 rotary viscometer in the temperature range 25°C-40°C. The apparent shear viscosity and rheological parameters of the unmodified components and their composites were determined and discussed. Polymer films were examined using a Scanning Probe Microscopy SPM production Veeco.

The obtained results suggest that the modification of several properties of polymer composites is a consequence of the interaction between the polymeric components and inorganic additives.

Key words: *chitosan, poly(vinyl alcohol), polyvinylpyrrolidone composites, AFM, rheological properties.*

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1. Introduction

Blends composed of chitosan (Ch), poly(vinyl alcohol) (PVA) and polyvinyl-pyrrolidone (PVP) and their composites containing inorganic particles, have been prepared as materials designed for biomedical applications or/and cosmetic industries.

The purpose of the present work was the preparation and evaluation of the physico –chemical properties of new composites of biopolymers and inorganic additives. It is well known that natural polymers present good biocompatibility, biodegradability and non-toxic for human body but their mechanical and rheological properties are often poor. The application of chitosan can be widened because of the addition of synthetic polymers and inorganic additives such as montmorillonite or hydroxyapatite [1-6]. The specific properties can be achieved without loss of characteristic features of compounds in the composites. In this study, atomic force microscopy (AFM) and rheological measurements were used. The rheological properties are important for cosmetic applications. Almost all concentrated polymer solutions show non-Newtonian behavior. The shear viscosity will be not constant but rather will depend upon the time, shear rate, temperature etc.

Flow properties of the polymers used and their composites solutions obey the power law relationship of the Ostwald de Waele model [7-13]:

$$\tau = k \dot{\gamma}^n \quad (1)$$

where: τ is shear stress; $\dot{\gamma}$ is shear rate; n and k are constants, known as the non – Newtonian index and the consistency index, respectively.

From equation (1) it follows that if n is unity, then k is identical to η and eq. (1) appears as Newton's law. The rheological parameters n and k are derived from the curve of logarithm shear stress versus logarithm shear rate.

Analysis of polymer films was performed by Tapping Mode, one of the most dynamic techniques, which allows the examination of the sample surface topography and the surface roughness at high resolution without damaging the surface of the sample.

2. Materials and Methods

2.1 Materials

Poly(vinyl alcohol) and polyvinylpyrrolidone are commercial polymers and were obtained from the Aldrich company and had viscosity average molecular weight of 130 000 and 630 000, respectively. The degree of hydrolysis was DH=99% for PVA while the chitosan sample had a degree of deacetylation of 78% and a viscosity average molecular weight of 540 000.

Chitosan, PVA and PVP were solubilized separately in aqueous acetic acid (0.1M) or water. The nanoclay additive (1% with respect to chitosan) was dispersed in the same solvent, after which a polymer solution was added slowly

to the nanoclay dispersion. These solutions were cast to prepare the films. The films were dried in the vacuum oven.

2.2 Methods

Flow measurements were made on a Bohlin Visco 88 rotary viscometer at different temperatures (25–40°C) and shear rates (20–1230 s⁻¹). It has a cylindrical configuration, consisting of a cylinder and a corresponding piston.

Atomic force microscopy (AFM) was used to study the surface roughness and morphology of thin films in air. AFM topographic images were obtained at room temperature using a multimode AFM with a Nanoscope III controller (Digital Instruments Veeco Metrology Group, Santa Barbara, CA) in tapping mode. The scan size was 1 μm² and the scan rate was 1.97 Hz with 512 pixels collected per line. The roughness of the surface was determined by measuring the root-mean-square (R_q) roughness parameter using Nanoscope software.

3. Results and Discussion

Based on the dependence of the shear viscosity on the shear rate the type of solutions was determined. The viscosity curves for solutions of polymers and their composites are presented in Figures 1–3. The solutions of investigated samples behave as non-Newtonian fluids. It could be seen that the chitosan solution and Ch/MMT composites solution had a pseudoplastic behavior (Figs. 1a and 2a). It is in accordance with previously reported data for the solutions of chitosan [8,10,11]. In the case of the synthetic polymer solutions and their composites (Figs. 1b,c and 2b,c), the shear thickening behavior is observed.

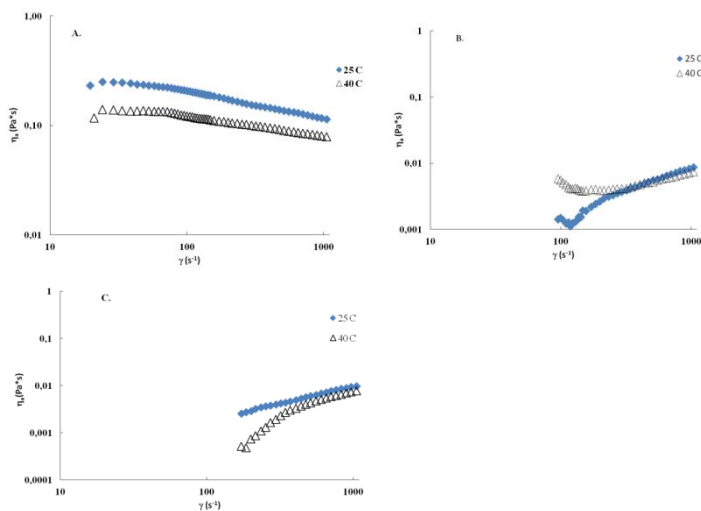


Figure 1. Apparent shear viscosity dependence on shear rate in the 2% polymer solution at various temperatures. A.: Ch, B. PVA, C. PVP.

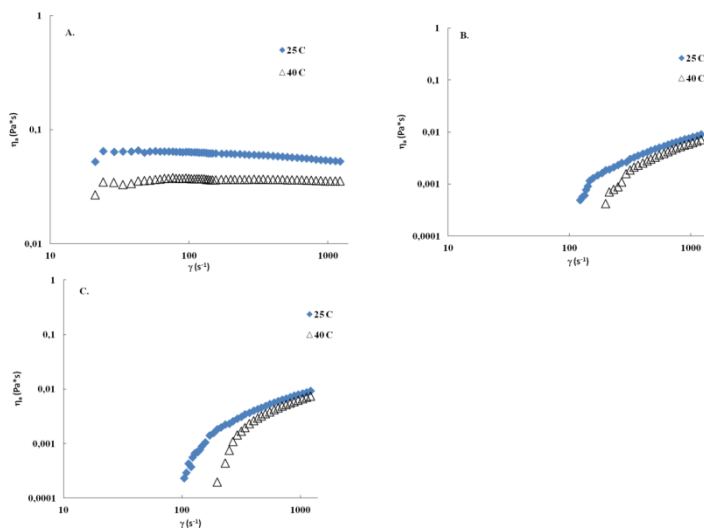


Figure 2. Apparent shear viscosity dependence on shear rate in the 2% solution of composites at various temperatures. A. Ch/MMT, B. PVA/MMT, C. PVP/MMT.

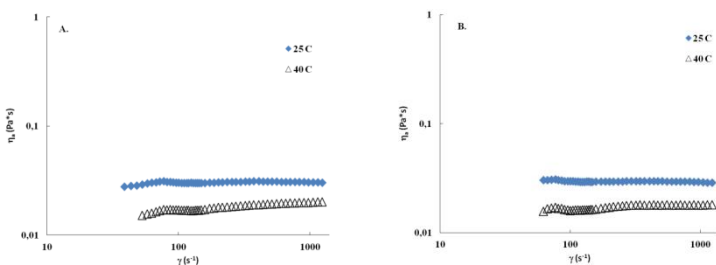


Figure 3. Apparent shear viscosity dependence on shear rate in the 2% solution of composites at various temperatures. A. Ch/PVA/MMT, B. Ch/PVP/MMT.

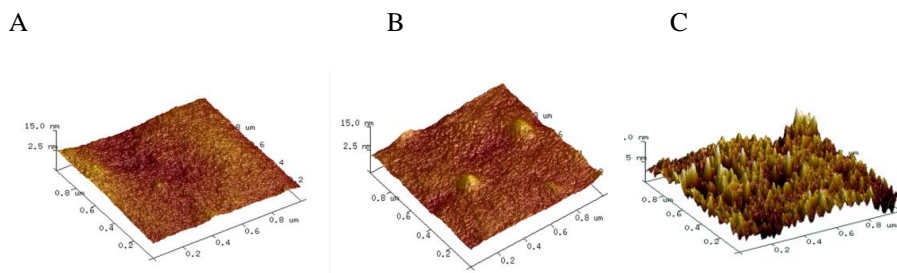
It can be observed, for the ternary composites (Fig. 3), showed the flow pattern close to the Newtonian behavior. The experimental data has been fitted with the power law model (Eq. 1) and the rheological parameters have been calculated using linearized equation. The obtained results are listed in Table 1. The power law model fits the experimental data satisfactorily.

As can be observed, the values of the parameter n was less than 1, indicating pseudoplastic behavior for the chitosan solution and the Ch/MMT composite solution. For the PVA and PVP solutions and their composites, where the shear thickening effect was observed, the parameter n was more than 1. In the case of the ternary composites, the values of the parameter n approximate to 1 (Newtonian flow).

Table 1. Values of rheological parameters of polymers and their composites at 298 K.

Sample	n	k	R ²
Ch	0.76	1.45	0.999
PVA	1.63	2.46x10 ⁻⁴	0.999
PVP	1.62	3.10x10 ⁻⁴	0.996
Ch/MMT	0.88	0.34	1.000
PVA/MMT	1.73	1.53x10 ⁻⁴	0.995
PVP/MMT	1.75	1.23x10 ⁻⁵	0.999
Ch/PVA/MMT	1.03	0.06	1.000
Ch/PVP/MMT	0.98	0.09	0.999

The surface morphology of films obtained for unmodified components and their composites are shown in Figures 4-5. Unmodified Ch and PVA films have the smoothest surfaces. This agrees with the value of the roughness parameter which is about 1 nm (Table 2). For unmodified PVP film, the surface morphology is characterized by a more corrugated surface, with the roughness parameter being about 3 times higher than that for Ch film. This may be related to the presence of residual solvent on the film surface. It is well known that a networked structure can be formed, where cross-links by water molecules between polymeric chains via hydrogen bonds appeared [3,14]. Thus the existence of such effects may cause a more corrugated surface of PVP film.

**Figure 4.** AFM images of the surface of polymer films: (A) Ch, (B) PVA, (C) PVP.

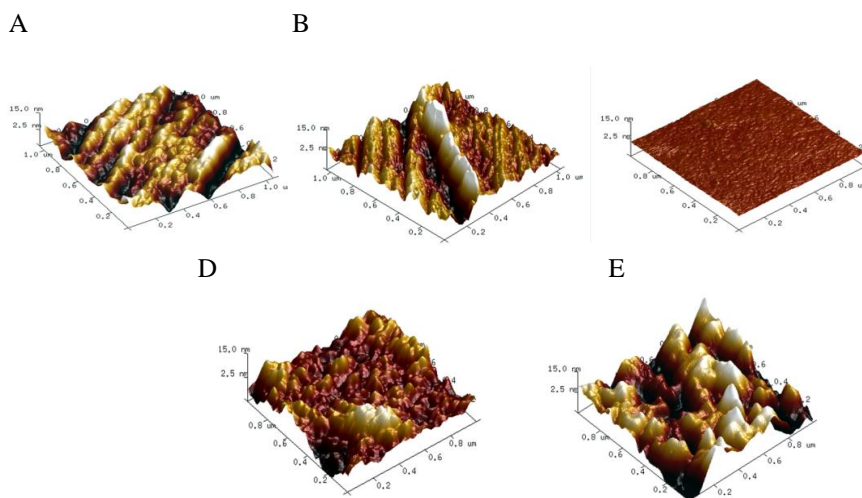


Figure 5. AFM images of the surface of composite films (A) Ch/MMT, (B) PVA/MMT, (C) PVP/MMT, (D) Ch/PVA/MMT, (E) Ch/PVP/MMT.

Table 2. The roughness parameters (R_q) for films of composites of different composition.

sample	R_q [nm]
Ch	1.02
PVA	0.68
PVP	3.55
Ch/MMT	3.49
PVA/MMT	3.96
PVP/MMT	0.57
Ch/PVA/MMT	5.14
Ch/PVP/MMT	3.07

In the case of composites (Fig. 5), the surface topology began to alter after the addition of MMT. The observed changes in morphology are related to the interactions between polymeric compounds. The film surfaces become rougher than before the addition of MMT and the values of the roughness parameters increase (Table 2). This may indicate an increase in the heterogeneity of these composites in comparison to unmodified polymer films. The exception is the PVP/MMT composite film. The observed change in morphology is related to an increase in the homogeneity of the PVP sample with MMT in comparison to other compositions. The attractive force between the PVP and MMT in the composite may cause the increase of homogeneity composite.

4. Conclusions

1. The solutions of chitosan, PVP and PVA samples as well as their solution two-component composites behave as non-Newtonian fluids. In the case of the ternary composite solutions, Newtonian flow was observed.
2. Both increase of temperature and the presence of montmorillonite produce an important decrease in the viscosity magnitude as well as an approximation to Newtonian behavior in relation to its rheology, especially for chitosan.
3. The n value is less than 1, indicating the pseudoplastic behavior of the chitosan solution (Table 1). In the case of the synthetic polymers and their binary composites, the n value is higher than 1, which indicates shear-thickening behavior.
4. AFM images show differences in surface properties between chitosan, PVA, PVP films and films made of mixture of Ch and MMT and/or the synthetic polymers.
5. The surface roughness of composites increases after the addition of montmorillonite. The exception is the PVP/MMT composite.
6. The change of the surface roughness of composites can be a result of the interaction between polymeric compounds and inorganic additive.

5. References

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