

# RHEOLOGICAL AND MECHANICAL STUDIES OF CHITOSAN BLENDS WITH THE ADDITION OF AN IONIC LIQUID

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## **Abstract**

*In the present paper, results from rheological measurements and tensile tests of polymer blends containing chitosan and poly(vinyl alcohol) with different additions of an ionic liquid are presented. Flow measurements were carried out using solutions of pure polymers and their blends with and without the addition of an ionic liquid. It has been observed that the polymer solutions and their blends exhibited non-Newtonian behaviour. Rheological parameters from the power law and activation energy of viscous flow were determined and discussed. Mechanical properties, such as the tensile strength and ultimate percentage of elongation of films, have been determined and compared. This study thus shows that the addition of an ionic liquid is an effective method for improving the flexibility of chitosan blends.*

**Key words:** *chitosan, poly(vinyl alcohol), polymer blends, ionic liquid, rheological properties, mechanical properties*

**Received:** 24.01.2019

**Accepted:** 06.05.2019

## 1. Introduction

Biopolymers and selected synthetic polymers are widely used in the cosmetics industry, in food processing, and in medicine as raw materials and thickening agents because of their unique properties, such as their solubility in an aqueous solution, ability to form complexes, bioactivity, biocompatibility, biodegradability, and non-toxicity to humans. Chitosan and poly(vinyl alcohol) constitute examples of hydrophilic polymers with great potential for biomedical applications, as well as applications in the cosmetics industry and food processing [1–3]. The drawbacks of using chitosan and its blends as a material are its rapid degradation and its poor mechanical stability and brittleness. An usual way of increasing the ductility of polymers or blends is through the addition of plasticizers. Plasticizers are low molecular weight compounds, such as glycerol, sorbitol, and some organic acids, that reduce the polymer–polymer chain bonding [4]. Recently, ionic liquids have been reported as efficient plasticizers for chitosan and its composites [4–7]. Therefore, the purpose of this study was to compare the properties of chitosan, poly(vinyl alcohol), and their blends before and after the addition of an ionic liquid to the polymers and polymer blends. The properties of chitosan (Ch), poly(vinyl alcohol) (PVA), and the Ch/PVA blends were investigated by rheological measurements and tensile tests. These studies are important for various applications, such as applications in cosmetics, food, and packaging.

## 2. Materials and Methods

### 2.1 Materials

Chitosan (Ch) has a degree of deacetylation of 79%, with a viscosity average molecular weight of 590 000. Poly(vinyl alcohol) (PVA) is a commercial polymer with a degree of hydrolysis (DH) of 88% and a viscosity average molecular weight of 136 000. The viscosity average molecular weight of the polymers ( $\overline{M}_v$ ) was determined by their intrinsic viscosity  $[\eta]$  in the solutions using the Mark–Houwink–Sakurada equation [8], as follows:

$$[\eta] = K\overline{M}_v^a \quad (1)$$

The Mark–Houwink constants for chitosan were obtained from the literature [9] with values of  $K=0.00181\text{cm}^3/\text{g}$  and  $a=0.93$  at  $25^\circ\text{C}$  in  $0.1\text{mol/l CH}_3\text{COOH}/0.2\text{mol/l NaCl}$ . For poly(vinyl alcohol) in water, the values of constants are:  $K=0.08\text{cm}^3/\text{g}$  and  $a=0.58$  at  $25^\circ\text{C}$  [10]. The intrinsic viscosity of the samples was measured from dilute solution viscometry using an Ubbelohde capillary viscometer.

The degree of deacetylation (DD) of Ch was determined by the 1DUV method [11]. The degree of hydrolysis of PVA refers to the content of residual vinyl acetate groups. It was measured titrimetrically according to the Japan Industrial Standard [12].

1-butyl-3-methyl-imidazolium chloride (ionic liquid) was used as received and hereafter is referred to as IL. Chitosan and PVA were separately solubilized in aqueous acetic acid ( $0.1\text{ mol/dm}^3$ ) and then mixed at different weight ratios. The composition of Ch/PVA was 80/20, 50/50, and 20/80. IL was added to the polymer solution at 1% and 5% relative to the polymer mass. Polymer films were obtained by the solution casting method.

### 2.2 Methods

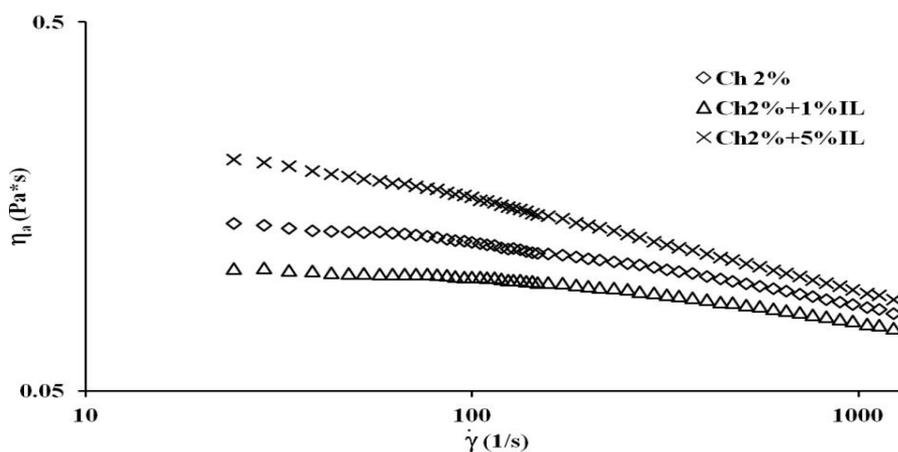
Flow measurements were carried out using a rotary viscometer (Bohlin Visco 88) with a concentric cylinder at different temperatures ( $25\text{--}40^\circ\text{C}$ ) and shear rates ( $19\text{--}1230$

$s^{-1}$ ). The rheological parameters from the power law (Ostwald de Waele model) and activation energy of viscous flow ( $E_a$ ) were calculated using the same methods as shown in previous papers [13,14].

The mechanical properties of the polymer films were measured at room temperature using tensile tests. The equipment used for carrying out the test was Zwick Roell (Germany) at a crosshead speed of 200 mm/min in accordance with the standard procedure [15]. Samples were cut into dog-bone shapes, with initial dimensions that were 50 mm in length, 4.2 mm wide, and 30  $\mu$ m thick. The sample thickness was determined using an ultrameter type A-91 (Manufacture of Electronic Devices, Warsaw, Poland). All of the film samples were cut using the same shaper. For each type of film, a minimum of five samples were tested.

### 3. Results and Discussion

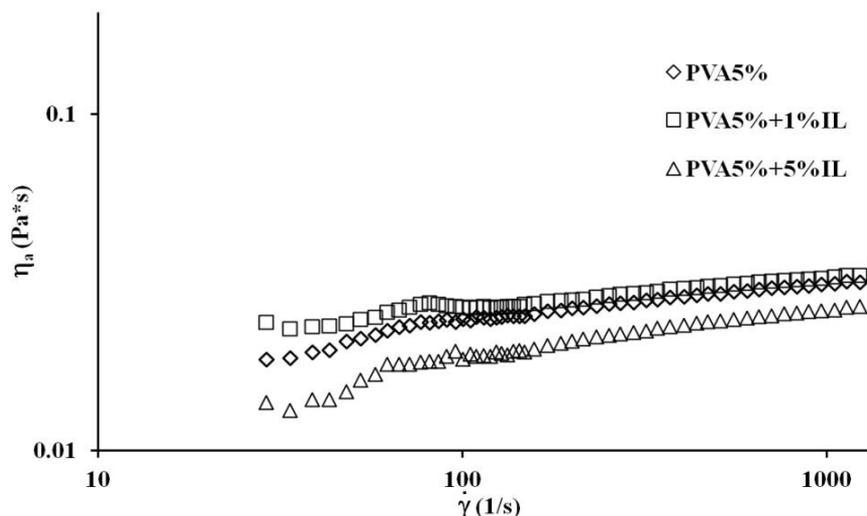
In the flow measurements, the values of apparent viscosity ( $\eta_a$ ), the rheological parameters from the power law model ( $n$  and  $k$ ), and the activation energy of viscous flow ( $E_a$ ) for the solutions of Ch, PVA, and their blends were determined. The viscosity curves for the solutions of Ch and PVA with different additions of IL are presented in Figure 1 and Figure 2. The solutions of pure polymers and their blends behave as non-Newtonian fluids. In the case of chitosan solutions (Figure 1), the shear-thinning effect is observed. It is in accordance with previously reported data [13,16].



**Figure 1.** Apparent shear viscosity versus shear rate of chitosan (Ch) solutions with different additions of ionic liquid (IL) ( $T=298$  K)

As can be observed, an aqueous acidic solution of chitosan has a higher apparent viscosity than the chitosan solution with 1% addition of IL. In the aqueous acidic solution of a polyelectrolyte, the macromolecules are stretched due to the electrostatic repulsive force between the positive charges on the amine groups. The addition of IL to the solution induces an increase in the solution ionic strength and screens the electrostatic charges. Then, the macromolecule conformation reduces to the statistical coil conformation. As a consequence, a decrease in apparent viscosity in the chitosan solution with 1% addition of IL is observed (Figure 1). However, the higher concentration of IL (5%) causes a marked increase in the apparent viscosity. This may

be attributed to the strongest ionic interactions and hydrogen bonds between chitosan macromolecules and ion pairs with the IL ( $\text{Cl}^-/\text{BMIM}^+$ ).



**Figure 2.** Apparent shear viscosity versus shear rate of poly(vinyl alcohol) (PVA) solutions with different additions of ionic liquid (IL) ( $T=298\text{ K}$ )

For the solution of PVA (Figure 2), the apparent viscosity increases with the increase in the shear rate, indicating shear-thickening behaviour. The phenomenon of shear-thickening may be related to a change in macromolecular conformation induced by flow, as well as deformation and associations of macromolecules. Moreover, no significant difference in the apparent viscosity was observed, depending on different additions of IL to the polymer solution. Similar directions of changes were also observed for the blended solutions (curves not shown).

Table 1 presents the values of rheological parameters of pure polymers and their blends with different additions of IL. For all the studied solutions (polymers and their blends), the power law model provides a good fit to the data over the range of shear rate used.

Generally, the addition of IL to polymer solution causes the less pronounced non-Newtonian behaviour (e.g.,  $n$  increases from 0.77 to 0.85 for the Ch solution). In the case of the chitosan solution and blends with  $w_{\text{Ch}} \geq 0.5$ , the  $n$  values are less than 1, which indicates shear-thinning behaviour. For the PVA solution where the shear thickening behaviour is observed, the  $n$  parameter is more than 1. The values of the  $n$  parameter indicate Newtonian flow behaviour ( $n = 1$ ) for the Ch/PVA blend solution with  $w_{\text{Ch}}=0.2$ .

The activation energy of viscous flow of Ch/PVA blends are tabulated in **Table 2**. After the addition of IL to the polymer and blend solutions, we observed an increase in the activation energy values for the PVA solution and blends with  $w_{\text{Ch}} \leq 0.5$ . It can be observed that the values of  $E_a$  for Ch and the blend with  $w_{\text{Ch}} = 0.8$  are practically stable and do not change after the addition of IL. In case of the PVA solution, the activation energy is higher than those for the solution before the addition of IL. The highest value of  $E_a$  is found for the Ch/PVA blend solution with  $w_{\text{Ch}} = 0.2$ .

**Table 1.** Rheological parameters of Ch, PVA, and their blends with different additions of ionic liquid (IL) (T=298 K.)

Before the addition of IL (0%)			
w <sub>Ch</sub>	n	k (Pa*s) <sup>n</sup>	R <sup>2</sup>
0.0	1.16	5.6×10 <sup>-3</sup>	0.999
0.2	1.05	0.013	0.999
0.5	0.97	0.040	0.999
0.8	0.88	0.16	0.998
1.0	0.85	0.25	0.999
After the addition of IL (5%)			
w <sub>Ch</sub>	n	k (Pa*s) <sup>n</sup>	R <sup>2</sup>
0.0	1.15	9.3×10 <sup>-3</sup>	1.000
0.2	1.00	0.044	0.999
0.5	0.91	0.14	0.999
0.8	0.83	0.27	0.999
1.0	0.77	0.47	0.999

w<sub>Ch</sub>=weight fraction of Ch

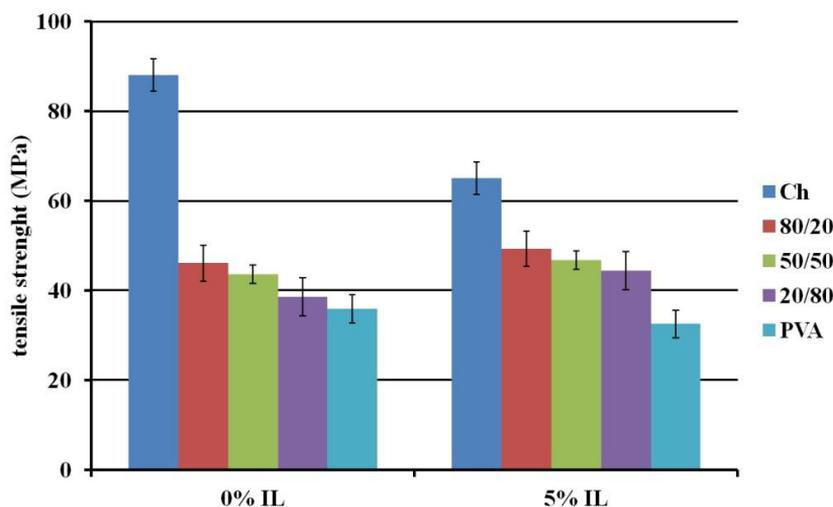
**Table 2.** Activation energy of viscous flow of Ch, PVA, and their blends with different additions of ionic liquid (IL) ( $\dot{\gamma} = 400 \text{ s}^{-1}$ )

before addition of IL (0%)		
w <sub>Ch</sub>	E <sub>a</sub> (kJ/mol)	R <sup>2</sup>
0.0	25.9	0.984
0.2	23.2	0.987
0.5	24.9	0.963
0.8	26.1	0.997
1.0	27.0	0.942
After the addition of IL (5%)		
w <sub>Ch</sub>	E <sub>a</sub> (kJ/mol)	R <sup>2</sup>
0.0	30.1	0.998
0.2	36.7	0.998
0.5	27.7	0.997
0.8	26.7	0.999
1.0	25.3	0.998

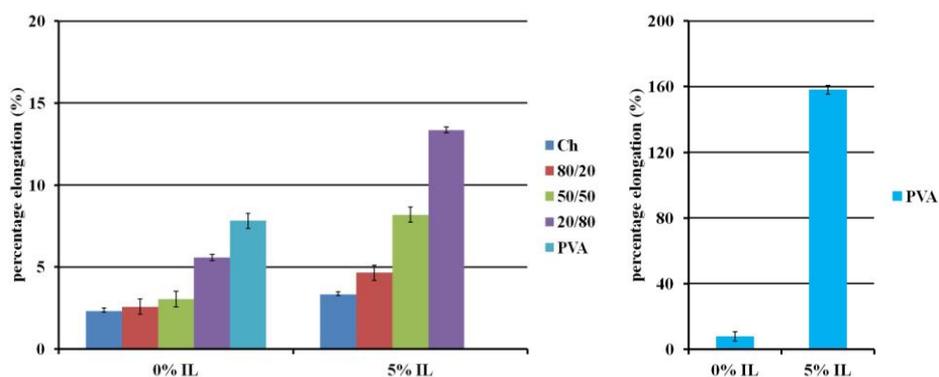
w<sub>Ch</sub>=weight fraction of Ch

The effect of the addition of ionic liquid (IL) in Ch/PVA blends on the mechanical properties are shown in Figure 3 and Figure 4. It can be observed that Ch/PVA blend films exhibited lower values of tensile strength than the pure chitosan film, but it is higher than for the PVA film. The lowest value of tensile strength is characteristic for the PVA film. All of the investigated blend films exhibited higher values of ultimate percentage of elongation compared to chitosan. The value of ultimate percentage of

elongation of PVA film is the highest. Ultimate percentage of elongation of Ch/PVA blend films increased after mixing with PVA. The blended films exhibited a large percentage of elongation because of their flexibility. After the addition of IL to the blend solutions, all the specimens led to an increase of both tensile strength and ultimate percentage of elongation. Thus, the addition of IL to the blend solutions is effective in inducing significant changes in the mechanical properties of blended films. The interactions between polymeric compounds and the IL could change the polymer macromolecular networks and interactions between polymer molecular chains, which may be the reason for improvement of the mechanical properties of the films.



**Figure 3.** Effect of addition of ionic liquids (IL) in Ch/PVA blends on tensile strength



**Figure 4.** Effect of addition of ionic liquids (IL) in Ch/PVA blends on ultimate percentage of elongation.

#### 4. Conclusions

The solutions of pure polymers and their blends behave as non-Newtonian fluids. The  $n$  values are less than 1, indicating shear-thinning behaviour of the chitosan solution and Ch/PVA blends with  $w_{\text{Ch}} \geq 0.5$ . In the case of PVA solutions, the  $n$  values are higher than 1, which indicates shear-thickening behaviour. For the Ch/PVA blend solution with

$w_{Ch}=0.2$ , the values of the  $n$  parameter indicate Newtonian flow behaviour ( $n=1$ ). The highest  $E_a$  value is obtained for the blend solution with  $w_{Ch}=0.2$  after the addition of IL.

Mechanical properties of Ch/PVA blend films, such as tensile strength and ultimate percentage of elongation, are sensitive to the addition of IL. The tensile strength and ultimate percentage of elongation of Ch/PVA blend films showed a pronounced increase after the addition of IL.

The observed changes in rheological and mechanical properties are related to the ionic interactions and hydrogen bond between polymeric compounds and IL. The addition of IL is beneficial to the formation of intermolecular forces and the network structure of the Ch/PVA blend films, which leads to an improvement in the mechanical properties of chitosan blends.

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