

# VISCOMETRIC STUDIES OF MICROCRYSTALLINE CHITOSAN/POLY(VINYL ALCOHOL) MIXTURES

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## **Abstract**

*In the present paper, the results of viscosity measurements in dilute solutions of microcrystalline chitosan (MCCh) with poly(vinyl alcohol) (PVA) of different degrees of hydrolysis are presented. Microcrystalline chitosan is blended with poly(vinyl alcohol) in aqueous 0.1 M CH<sub>3</sub>COOH/0.2 M NaCl. Viscosity measurements of dilute polymer solution were carried out in an Ubbelohde capillary viscometer. The final result depends on (I) the thermodynamic goodness of the solvent, on (II) the applied extrapolation method used for determination of the interaction parameters, on (III) the assumed miscibility criteria, on (IV) the degree of hydrolysis of PVA, and on (V) the blend composition.*

**Key words:** microcrystalline chitosan, poly(vinyl alcohol), polymer blends, viscometric study.

## 1. Introduction

Viscometric study has been widely used to investigate the polymer – polymer interaction and miscibility. The studies in solid state are experimentally demanding and time-consuming techniques. They require the expensive equipment. An alternative is viscometry, which is a simple, quicker and an inexpensive method. In literature, researcher proposed many criteria to determine polymer/polymer miscibility by the viscometric method [1-5]. The viscometric evaluation of miscibility in ternary systems comprising of common low molecular weight solvent for polymers A and B, rely on comparison of the experimental interaction parameters or equivalent parameters with the ideal values. On the basis of many experimental and theoretical studies, the literature data suggested that:

- the positive deviation between experimental and ideal values indicates *the miscible system*,
- the negative deviation indicates *immiscible system*.

The aim of this study was to evaluate the miscibility of microcrystalline chitosan with vinyl polymers on the basis of experimental and ideal values of the viscosity interaction parameters:  $b_m$ ,  $[\eta]_m$ , which were calculated from viscosity measurements in dilute MCCCh/PVA solution blends.

## 2. Materials and methods

In the method of classical dilution the measurements are carried out in polymer A/polymer B solution blends, in the same low molecular weight solvent, at constant weight ratio of polymer A to B for a given composition. In this method the miscibility is estimated by comparison of the experimental and ideal values of  $b_m^{\text{exp}}$  and  $[\eta]_m^{\text{exp}}$ . The values of  $b_m^{\text{exp}}$  and  $[\eta]_m^{\text{exp}}$  are determined from the plot of  $\eta_{\text{sp}}/c$  vs  $c$  (**Equation 1**) for solutions containing both polymers.

$$\frac{(\eta_{\text{sp}})_m}{c_m} = [\eta]_m + b_m c_m \quad (1)$$

where:  $[\eta]_m$  intrinsic viscosity of the polymer blends,  $c_m$  total concentration of solution. Krigbaum and Wall [1] have defined the ideal value of the interaction parameter  $b_m^{\text{id}}$  by the expression:

$$b_m^{\text{id}} = b_A w_A^2 + b_B w_B^2 + 2b_{AB}^{\text{id}} w_A w_B \quad (2)$$

$$b_{AB}^{\text{id}} = b_A^{1/2} b_B^{1/2} \quad (3)$$

where:  $b_A$ ,  $b_B$ ,  $b_{AB}$  parameter of interaction of like (AA, BB) and unlike (AB) molecules, respectively;  
 $w_A$ ,  $w_B$  weight fractions of polymers A and B, respectively.

The polymer blend is miscible if  $\Delta b_m = b_m^{\text{exp}} - b_m^{\text{id}} > 0$  and immiscible if  $\Delta b_m = b_m^{\text{exp}} - b_m^{\text{id}} < 0$ .

Garcia et al. [4] defined the ideal value of the interaction parameter,  $b_m^{\text{id}}$ , as:

$$b_m^{\text{id}} = b_A w_A^2 + b_B w_B^2 \quad (4)$$

Additionally, Garcia et al. [4] have proposed another miscibility criterion which is based on the difference between the experimental and ideal values of  $[\eta]_m$ . If  $\Delta[\eta]_m = [\eta]_m^{\text{exp}} - [\eta]_m^{\text{id}} < 0$  the system is miscible, and if  $\Delta[\eta]_m = [\eta]_m^{\text{exp}} - [\eta]_m^{\text{id}} > 0$  the system is immiscible. The value of  $[\eta]_m^{\text{exp}}$  is determined from the intercept of the plot according to Eq. (1) whereas  $[\eta]_m^{\text{id}}$  is obtained from **Equation 5**.

$$[\eta]_m^{\text{id}} = [\eta]_A w_A + [\eta]_B w_B \quad (5)$$

Viscosity measurements of dilute polymer solution ( $c < 0.8\%$ ) were carried out in an Ubbelohde capillary viscometer. The flow times were recorded with an accuracy of  $\pm 0.01$  s, and the bath temperature was constant ( $25 \pm 0.1^\circ\text{C}$ ). The intrinsic viscosity and the Huggins coefficient values were determined according to Huggins [6 - 7] equation using solution of 5 concentrations.

The investigated blend system contained: poly(vinyl alcohol): PVA(99) {degree of hydrolysis DH = 99%,  $M_v = 1.2 \times 10^5$  g/mol}, PVA(88) {DH = 88%,  $M_v = 1.1 \times 10^5$  g/mol} with microcrystalline chitosan: MCCh {degree of deacetylation DD = 84%  $M_v = 1.0 \times 10^6$  g/mol}.

Microcrystalline chitosan were prepared by means of the original methods described in literature [8]. MCCh and PVA were solubilized separately in aqueous 0.1 M  $\text{CH}_3\text{COOH}/0.2$  M NaCl. 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.

### 3. Results and discussion

The parameters of the miscibility criteria proposed by Krigbaum et al. [1] and Garcia et al. [4] were calculated using **Equations 1 – 5** and are tabulated in **Tables 1 - 2** for MCCh/PVA blends of different degrees of hydrolysis of PVA.

It can be seen that blends MCCh/PVA(100) and MCCh/PVA(88) all give negative values of  $\Delta b_m$ . According to miscibility criteria the investigated blends are immiscible in all proportions. In the case of miscibility criterion proposed by Garcia et al. [4] the parameter  $\Delta b_m$  values are negative in the range of experimental error.

From **Tables 1** and **2** it can be seen that, the intrinsic viscosity of MCCh/PVA blends was slightly higher than calculated using **Equation 5**, indicating repulsive interaction existed between MCCh and PVA.

**Table 1.** A comparison of the experimental and ideal viscometric parameters of the MCCh/PVA(99) blends in dependence on the assumed definition of the ideal values of these parameters. **Solvent:** 0.1 mol/dm<sup>3</sup>CH<sub>3</sub>COOH/0.2 mol/dm<sup>3</sup> NaCl.

w <sub>MCCh</sub>	The criteria of Krigbaum and Wall [1]						The criteria of Garcia et al. [4]	
	$[\eta]_m^{\text{exp}},$ dl/g	$[\eta]_m^{\text{id}},$ dl/g	$\Delta[\eta]$	$b_m^{\text{exp}},$ (dl/g) <sup>2</sup>	$b_m^{\text{id}},$ (dl/g) <sup>2</sup>	$\Delta b_m$	$b_m^{\text{id}},$ (dl/g) <sup>2</sup>	$\Delta b_m$
0.2	2.15 ± 0.03	2.04 ± 0.06	<b>0.11</b>	1.013 ± 0.139	2.035 ± 0.332	<b>-1.022</b>	1.140 ± 0.185	<b>-0.127</b>
0.4	3.31 ± 0.06	3.20 ± 0.10	<b>0.11</b>	3.681 ± 0.502	5.156 ± 0.833	<b>-1.475</b>	3.814 ± 0.611	<b>-0.133</b>
0.5	3.86 ± 0.07	3.77 ± 0.12	<b>0.09</b>	5.438 ± 0.742	7.250 ± 1.168	<b>-1.812</b>	5.852 ± 0.937	<b>-0.414</b>
0.6	4.41 ± 0.08	4.35 ± 0.13	<b>0.06</b>	7.970 ± 1.086	9.702 ± 1.559	<b>-1.732</b>	8.360 ± 1.338	<b>-0.390</b>
0.8	5.61 ± 0.11	5.50 ± 0.17	<b>0.11</b>	14.28 ± 1.988	15.67 ± 2.512	<b>-1.390</b>	14.78 ± 2.36	<b>-0.498</b>

**Table 2.** A comparison of the experimental and ideal viscometric parameters of the MCCh/PVA(88) blends in dependence on the assumed definition of the ideal values of these parameters. **Solvent:** 0.1 mol/dm<sup>3</sup> CH<sub>3</sub>COOH/0.2 mol/dm<sup>3</sup> NaCl.

w <sub>MCCh</sub>	The criteria of Krigbaum and Wall [1]						The criteria of Garcia et al. [4]	
	$[\eta]_m^{\text{exp}},$ dl/g	$[\eta]_m^{\text{id}},$ dl/g	$\Delta[\eta]$	$b_m^{\text{exp}},$ (dl/g) <sup>2</sup>	$b_m^{\text{id}},$ (dl/g) <sup>2</sup>	$\Delta b_m$	$b_m^{\text{id}},$ (dl/g) <sup>2</sup>	$\Delta b_m$
0.2	2.11 ± 0.03	1.92 ± 0.06	<b>0.19</b>	1.051 ± 0.135	1.735 ± 0.270	<b>-0.684</b>	1.065 ± 0.156	<b>-0.014</b>
0.4	3.36 ± 0.05	3.08 ± 0.08	<b>0.28</b>	3.511 ± 0.456	4.868 ± 0.715	<b>-1.357</b>	3.858 ± 0.544	<b>-0.347</b>
0.5	3.83 ± 0.07	3.67 ± 0.09	<b>0.16</b>	5.392 ± 0.708	7.028 ± 1.012	<b>-1.636</b>	5.971 ± 0.839	<b>-0.579</b>
0.6	4.39 ± 0.08	4.25 ± 0.09	<b>0.14</b>	7.504 ± 0.990	9.584 ± 1.371	<b>-2.080</b>	8.561 ± 1.254	<b>-1.057</b>
0.8	5.53 ± 0.11	5.41 ± 0.11	<b>0.12</b>	13.01 ± 1.82	15.88 ± 2.24	<b>-2.870</b>	15.18 ± 2.13	<b>-2.170</b>

## 4. Conclusions

1. The studies of hydrodynamic properties of the solutions of MCCh/ PVA blends indicated that the satisfaction of the miscibility criterion depend on the definition of the ideal parameter  $b_m^{\text{id}}$  value.
2. For the miscibility criterion proposed by Krigbaum and Wall [1], the parameter  $\Delta b_m$  values are negative for all investigated systems, exceeding distinctly the range of the experimental error. It is accepted that such behaviour indicates the lack of miscibility of polymeric components.
3. In the case of the miscibility criterion proposed by Garcia [4], the parameter values are negative in the range of the experimental error for all investigated systems. Therefore can be to agree that  $b_m^{\text{exp}} \approx b_m^{\text{id}}$ . These results suggest that in the blends the components are poorly miscible.

## 5. References

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