

RHEOLOGICAL PROPERTIES OF CHITOSAN BLENDS WITH PARTIALLY HYDROLYZED POLYACRYLAMIDE IN DIFFERENT SOLVENTS

Katarzyna Lewandowska

*Faculty of Chemistry,
Chair of Chemistry and Photochemistry of Polymers,
Nicolaus Copernicus University,
ul. Gagarin 7, 87-100 Toruń, Poland
E-mail: reol@chem.umk.pl*

Abstract

In the present paper; the results of rheological measurements in solutions of chitosan (Ch) with partially hydrolyzed polyacrylamide (HPAM) are presented. Aqueous acetic acid, lactic acid and aqueous acetic acid/NaCl were used as solvents for chitosan, HPAM and Ch/HPAM solution blends. The criterion of miscibility of solution blends, based on the additivity rule of apparent shear viscosity (η_a) has been discussed. The rheological parameters from power law (Ostwald de Waele model) and activation energy of viscous flow (E_a) have been calculated from the flow curves and Arrhenius plots, respectively. It was found that studied polymer solutions exhibited the non-Newtonian behaviour with shear-thinning and/or shear-thickening areas. The final result depends on the thermodynamic goodness of the solvent and on the blend composition.

Key words: *chitosan, polyacrylamide, polymer blends, apparent shear viscosity, rheological properties.*

1. Introduction

Natural and synthetic high molecular weight compounds are used as thickening agents in paper industry, cosmetics, food processing etc. Partially hydrolyzed polyacrylamide (HPAM) is a synthetic, water-soluble polymer, showing unique shear-thickening properties [1]. HPAM is a copolymer of acrylamide and sodium acrylate. The degree of hydrolysis is defined as the number Y of carboxyl residues (COO^-) replacing the amide groups (CONH_2) X over total number of the macromolecular residues $Y/(X+Y)$. HPAM is an anionic polyelectrolyte, and in aqueous solution, the electrostatic interactions are weakly screened, hence, the polyelectrolytic effect of HPAM is observed. Chitosan has unique properties including bioactivity, biocompatibility and biodegradability favorable for a broad variety of its industrial applications. Chitosan is readily soluble in dilute inorganic and organic acids. In an aqueous acid medium, the amine group of chitosan is easily protonated, and the polymer behaves like cationic polyelectrolyte [2].

The aim of this study was to evaluate the miscibility of blends of hydrophilic high molecular weight compounds.

2. Materials and methods

2.1 Materials

Aqueous acetic acid, lactic acid and aqueous acetic acid/NaCl were used as solvents for chitosan, HPAM and Ch/HPAM solution blends. The investigated blend system contained partially hydrolyzed polyacrylamide (HPAM) (degree of hydrolysis $\text{DH} = 1\%$, $M_v = 5 \times 10^6$ g/mol) with chitosan (Ch) (degree of deacetylation $\text{DD} = 81\%$, $M_v = 5.7 \times 10^5$ g/mol). Chitosan and HPAM were solubilized separately in 0.1 M aqueous acid and 0.1 M aqueous acetic acid/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. The obtained solutions were transparent and stable, as the reproducibility of the flow curves was very high.

2.2 Methods

Flow measurements were carried out using a rotary viscometer Bohlin Visco 88 with concentric cylinder at different temperatures (25 - 40 °C) and shear rates (20 - 1230 s^{-1}).

2.3 Data analysis

Flow properties of the used Ch, HPAM and their blend solutions obey the power law relationship of the Ostwald de Waele model [1-6]:

$$\tau = k \dot{\gamma}^n \quad \text{and} \quad \eta = \tau/\dot{\gamma} = k \dot{\gamma}^{n-1} \quad (1)$$

where τ is shear stress, $\dot{\gamma}$ is shear rate, η is shear viscosity, n and k are constants, known as the non-Newtonian index and the consistency index, respectively. From the equation it follows that if n is unity, then k is identical to η and **Equation 1** appears as Newton's law. The rheological parameters n and k derived from the curve logarithm shear stress versus logarithm shear rate. The value of $n < 1$ indicates the shear-thinning effect, and the value of $n > 1$ implies the shear-thickening behaviour.

Activation energy of viscous flow (E_a) was calculated with Arrhenius equation [1,5]:

$$\eta_a = A_0 \exp(E_a/RT) \quad (2)$$

where A_0 is a preexponential parameter and E_a is the activation energy of viscous flow.

3. Results and discussion

The criterion of miscibility of solution blends [3 - 6], based on the additivity rule of apparent shear viscosity (η_a) has been discussed. The viscosity curves for solutions of Ch in different aqueous solvent are presented in **Figure 1**. The solutions behave as non-Newtonian fluids. The lower viscosity for chitosan in 0.1 M $\text{CH}_3\text{COOH}/0.2 \text{ NaCl}$ can mean a better screening of the charges than in the formation aqueous acid.

In the case of HPAM solutions (**Figure 2**), no significant difference of viscosity was observed among the solvent used.

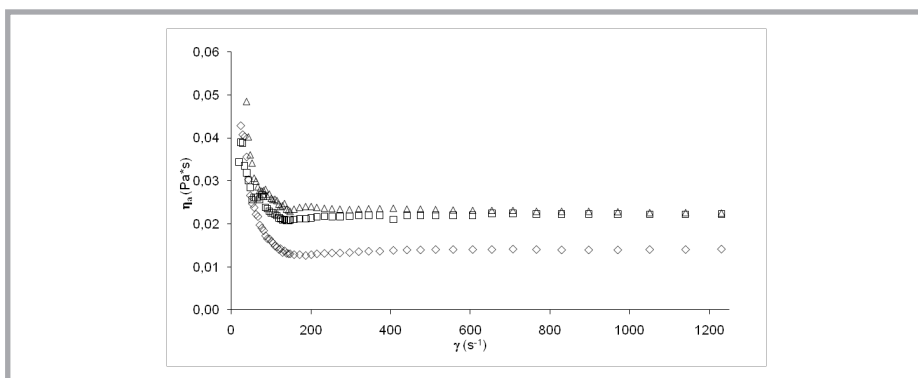


Figure 1. Apparent shear viscosity versus shear rate of 1% chitosan solution, $T = 298\text{K}$, solvent: \square - 0.1 M CH_3COOH , \diamond - 0.1 M $\text{CH}_3\text{COOH}/0.2 \text{ NaCl}$, Δ - 0.1 M $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$.

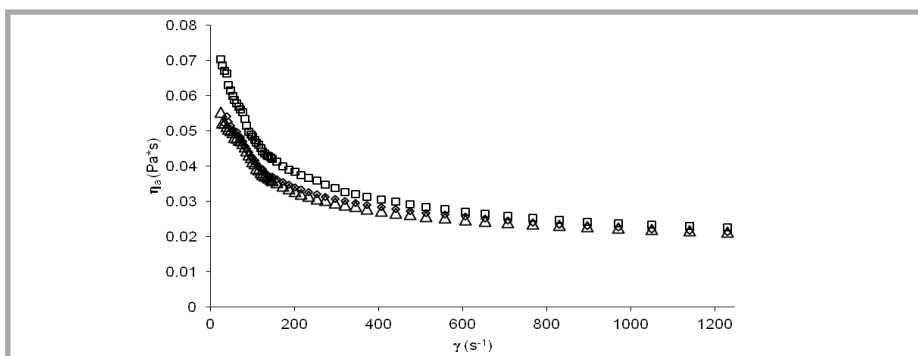


Figure 2. Apparent shear viscosity versus shear rate of 1% HPAM solution, $T = 298 \text{ K}$, solvent: \square - water, \diamond - 0.1 M $\text{CH}_3\text{COOH}/0.2 \text{ NaCl}$, Δ - 0.1 M CH_3COOH .

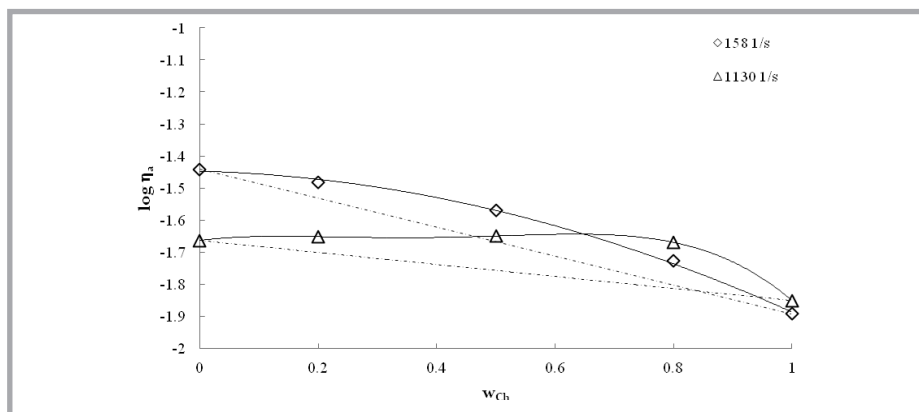


Figure 3. Logarithm of apparent shear viscosity of Ch and HPAM and their blends versus weight fraction of Ch in the blend; $T = 298\text{ K}$, solvent: $0.1\text{M CH}_3\text{COOH}/0.2\text{NaCl}$, dotted line - the values calculated according to the additivity rule.

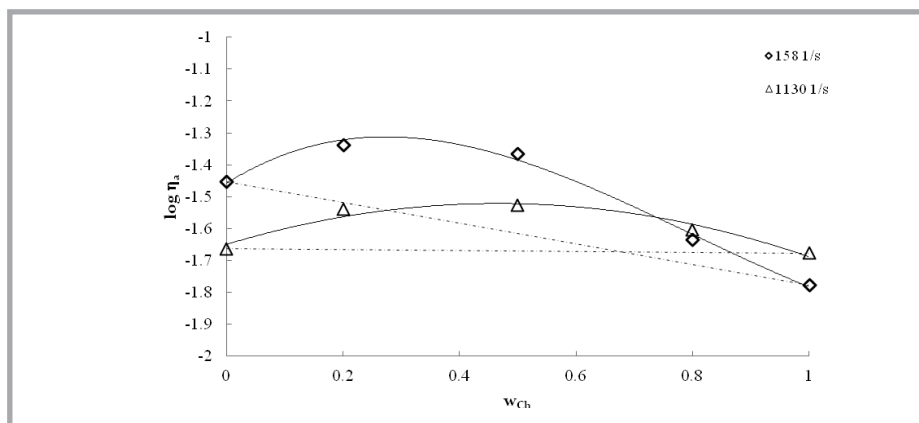


Figure 4. Logarithm of apparent shear viscosity of Ch and HPAM and their blends versus weight fraction of Ch in the blend; $T = 298\text{ K}$, solvent: $0.1\text{ M CH}_3\text{COOH}$, dotted line - the values calculated according to the additivity rule.

Figures 3 and 4 shows the logarithm of apparent shear viscosity ($\log \eta_a$) investigated blends versus weight fraction of Ch (w_{Ch}) in different solvents. The positive deviations from the additivity rule have been observed in all cases. The deviations of $\log \eta_a$ decrease with the increase of the temperature. In **Figure 4**, it is observed that the mixtures in $0.1\text{M CH}_3\text{COOH}$ presented larger relative viscosities than would be expected by the contribution of each homopolymer. This synergy could be explained by the electrostatic interactions between the cationic chitosan and the partially anionic polyacrylamide molecules.

The shear dependence of the viscosity was analyzed by using either the well-known power law relationship (**Equation 1**) [1, 4]. The obtained values of rheological parameters

Table 1. Values of rheological parameters of Ch, HPAM and their blends at 298 K.

Solvent	w _{Ch}	n	k	R ²
0.1 MCH ₃ COOH/0.2 NaCl	0.0	0.72	0.15	0.999
	0.2	0.76	0.12	0.999
	0.5	0.86	5.62×10 ⁻²	0.998
	0.8	0.94	2.87×10 ⁻²	0.992
	1.0	0.92	2.26×10 ⁻²	0.980
0.1 M CH ₃ COOH	0.0	0.73	0.14	0.998
	0.2	0.74	0.17	0.998
	0.5	0.71	0.21	0.990
	0.8	1.04	1.99×10 ⁻²	0.993
	1.0	1.14	8.07×10 ⁻³	0.993

Table 2. Activation energy of viscous flow of Ch, HPAM and their blends at $\dot{\gamma} = 1130 \text{ s}^{-1}$.

Solvent	w _{Ch}	E _a , kJ/mol	R ²
0.1 M CH ₃ COOH/0.2 M NaCl	0.0	10.80	0.997
	0.2	12.01	1.000
	0.5	14.56	0.999
	0.8	11.90	0.992
	1.0	9.08	0.880
0.1 M CH ₃ COOH	0.0	11.49	0.998
	0.2	11.89	0.992
	0.5	16.00	1.000
	0.8	21.59	1.000
	1.0	23.33	1.000

are listed in **Table 1**. As shown, the n values are less than 1 indicating the shear-thinning behavior. In the case of Ch solution in aqueous acetic acid, the n value is higher than 1, which indicates shear-thickening behaviour.

Table 2 presents the change of the activation energy of viscous flow of Ch/HPAM blends of various weight fractions of chitosan. The values of E_a , were calculated using **Equation 2**. The solution of chitosan in 0.1 M CH₃COOH is characterized by higher value of E_a than the solution of HPAM. The highest E_a value is obtained for 80/20 Ch/HPAM blend. Moreover, for the blend in 0.1 M CH₃COOH/0.2 NaCl, the activation energy is higher than that individual polymers at a given shear rate.

4. Conclusions

1. The solutions of chitosan and HPAM samples as well as their solution blends behave as non-Newtonian fluids (**Figures 1 & 2**).
2. Apparent shear viscosity of chitosan chains depends on their conformation (**Figure 1**). In aqueous acid solvent (this is the limit of low ionic strength), the electrostatic interactions are weakly screened and the polyelectrolyte effect of chitosan is observed.

3. The n values are less than 1, indicating the pseudoplastic behavior of HPAM, Ch and their blends (**Table 1**). In the case of Ch solution in aqueous acetic acid, the n value is higher than 1, which indicates shear-thickening behaviour.
4. The highest E_a value is obtained for chitosan solution in aqueous acetic acid. E_a of the solution blends is higher than that of the individual component solutions in aqueous 0.1 M $\text{CH}_3\text{COOH}/0.2$ M NaCl (**Table 2**). This indicates on some interactions between the polymer components in the solution blends.

5. References

1. Lewandowska K.; (2007) Comparative studies of rheological properties of polyacrylamide and partially hydrolyzed polyacrylamide solutions. *J App Polym Sci*, 103, pp. 2235-2241.
2. Lewandowska K., Staszewska D.U., Trzciński S.; (1998) Blends of hydrophilic high molecular weight compounds. Part I: Rheological properties of chitosan-poly(N-vinylpyrrolidone) solutions blends. *Progress on Chemistry and Application of Chitin and Its Derivatives*, Monograph, Polish Chitin Society, Vol. IV, In: Struszczyk H. (ed), Łódź, pp. 17-36.
3. Skellard A.H.P.; (1967) *Non-Newtonian Flow and Heat Transfer*. Wiley, New York.
4. Mucha M.; (1998) Rheological properties of chitosan blends with poly(ethylene oxide) and poly(vinyl alcohol) in solutions. *Reactive & Functional Polymers*, 39, pp. 19-25.
5. Lewandowska K.; (2009) Rheological properties of chitosan acetate blends with vinyl polymers. *Progress on Chemistry and Application of Chitin and Its Derivatives*, Monograph, Polish Chitin Society, Vol. XIV, In: Jaworska M.M. (ed), Łódź, pp. 41-48.
6. Zhang L.M.; (1999) Synergistic blends from aqueous solutions of two cellulose derivatives. *Colloid Polym Sci*, 277, pp. 886-890.