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Study of magnetic field influence upon a binary interpenetrated polymeric complex formation

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The paper is focused on the study of magnetic field (MF) influence during the preparation of an intermolecular complex (IPC) between poly(aspartic acid) – (PAS) and poly(vinyl alcohol) – (PVA). The MF influence during interpolymer complexation process between PAS and PVA was appreciated by *zeta potential values* of the prepared polymeric structure, as well as by evaluation of the *pH influence* on *zeta potential, hydrodynamic diameter* and *electrical conductivity of the prepared nanoparticles*. The MF presence during the IPC formation shows a positive effect upon colloidal stability, evidenced by the increase of the absolute value of zeta potential. Also, the dependence of zeta potential on the solution pH indicates – on the entire studied pH range – higher modulus for ζ of the IPC formed in the MF presence evidencing higher colloidal stability for these structures. The prepared IPC maintains its dimensional stability – evaluated by hydrodynamic diameter – in the pH range of 5.5 to 12, even in the MF presence. At the same time, the MF presence determines the decrease of the conductivity for either pure polymers or preformed IPC.

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1. Introduction

Specific interactions between poly(carboxylic acids) and proton-accepting nonionic polymers in solutions resulting in the formation of interpolymer complexes (IPCs) have attracted considerable attention during more than 4 decades. Bailey and co-workers [1] published one of the first experimental paper on this subject, which was devoted to the complexation between poly(carboxylic acids) and poly(ethylene oxide). They demonstrated that interaction between these polymers is governed by hydrogen bonding and the IPC stoichiometry approaches 1:1. While at low pH ($pH < 3.8$), the interaction results in phase separation, at higher pH, the polycomplex exists in solution. In the neutral pH region, they also observed some interaction between the two polymers. Since that time many studies have been done to clarify the complexation features as well as the IPC structure between poly(acrylic acid) and PEO in solutions or in the solid state [2-6]. Recently, these polymeric complexes were successfully applied for the development of pH-responsive drug delivery systems [7].

Interpolymer complexes are formed by the association of two or more complementary polymers and may arise from electrostatic forces, hydrophobic interactions, hydrogen bonding, van der Waals forces or combinations of these interactions. The complexation process is cooperative. Stable interpolymer complexes may form even if the segmental interaction energy is relatively small. The formation of complexes may strongly affect the solubility, rheology, conductivity and turbidity of polymer solutions. Similarly, the mechanical properties, permeability and electrical conductivity of the polymeric systems may be greatly affected by complexation [8, 9].

The investigations of polymer – polymer miscibility are done by the techniques, as for example turbidimetry, electronic microscopy, infrared spectroscopy, NMR, viscometry, thermal analysis and inverse gas chromatography. The more sensitive the technique is, the smaller the domain it can detect. Thus, the level of homogeneity depends on the technique used in the investigation. It is necessary to use different combined techniques for studying the polymer blends miscibility for correlation and interpretation of their results.

The present paper is focused on the magnetic field (MF) influence upon the preparation of an ntermolecular complex between poly(aspartic acid) – (PAS) – a nontoxic, biocompatible and biodegradable polymer – and poly(vinyl alcohol) – (PVA) – a synthetic polymer with film-forming capacity. The MF influence on the interpolymer complexation process between PAS and PVA was evaluated by determining the values of *zeta potential* of the prepared polymeric structures, as well as by evaluating the *pH influence* upon *zeta potential, hydrodynamic diameter* and *electrical conductivity.* Other characteristics of the prepared interpenetrated polymeric structure as for example thermal stability are also presented.

2. Experimental section

2.1 Materials and IPC preparation

Poly(vinyl alcohol) (PVA) was purchased from Oriental Chemical Ind. Korea and was used as received (PVA molecular weight was 120,000 Da).

Poly(aspartic acid) (PAS) was synthesized by thermal polycondensation of aspartic acid, at the 200°C temperature, during 6 h, using phosphoric acid as catalyst (PAS molecular weight was 15,110 and the polydispersity of 1.317).

The PAS / PVA blends were prepared by direct mixing for 120 min of the initial homopolymer solutions of the same concentrations – 1 g / dL – in different ratio (% vol), respectively PAS / PVA: 0/100; 25/75; 50/50; 75/25 and 100/0. Thus, the total polymer concentration in the mixture was maintained constant during each experiment. The solution was prepared in the absence of the magnetic field (classical way - CW) and in the presence of the magnetic field (the MF intensity was 2000 G). All the measurements were done 24 hours after the mixing, to allow for IPC realization as well as to evidence the MF effects after the exposure to the field.

2.2 IPC Characterization

FTIR spectra: The molecular structures via the bands' identification of the *FTIR spectra* has been used (on a DIGILAB, Scimitar Series, USA, spectrophotometer, the resolution recording was 4 cm^{-1}) (concentration 3 mg sample in 500 mg KCl tablet).

Thermal behavior: Thermogravimetric analysis was performed in nitrogen atmosphere from 30°C to 700°C with a TGA/SDTA 851 Mettler Toledo instrument. The heating rate used was 20°C/min. Two experiments were made for each formulation.

Zeta Potential ***ζ*** – was determined on a Zetasizer NS (Malvern Instruments, UK) and the electrophoretic mobility (μ) was calculated according to the Smoluchowski relationship:

$$\xi = \eta\mu / \varepsilon \text{, where } k\alpha >> 1$$

where: η - viscosity, ε – dielectric constant, k and α - Debye-Hűckel parameter and particle radius. pH was adjusted at 7 with HCl or NaOH, on Autotitrator MPT2 (Malvern) device.

Electric conductivity was determined on the same device in parallel with zeta potential measurement. Each measurement was made 3 times and the average values were graphically represented.

Hydrodynamic Diameter – measured on the same equipment Zetasizer NS, was determined by applying Stokes – Einstein relationship. The pH influence upon zeta potential, electrical conductivity and hydrodynamic diameter was study in the range of pH=2-12, using the Autotitrator Malvern MPT2 coupled on the Zetasizer NS.

3. Results and discussion

In order to perform spectral and thermal characterization, the interpolymer complex is dried under vacuum. The results for the samples obtained without the MF presence were complete presented before [10, 11]. In Table 1 are presented the principal characteristics of the samples prepared in and without MF presence.

The IPC spectrum is characterized by the presence of specific bands of both components confirming the complexation between PAS and PVA. The characteristic absorption bands are picked in Table 1. Some indications about structural differences registered in case of the samples prepared in the MF presence, in respect with those CW prepared are also included. Thus, some bands are amplified. The intensities of the vibration oscillation absorption corresponding to the IPC prepared in the field are higher, fact attributed to the modification of the strength constant introduced by the inductive and electromeric effects appearing supplementary in the polymeric structures obtained in the new conditions (see Table 1).

The data presented in Table 1 evidence also, the thermal stability of the blends located between the pure polymers, greater than PVA but lower than PAS. It must underline the effect of the PAS amount upon the IPC thermal stability: the increase of the PAS content in blends induces growth of the thermal stability. Differences between thermal behavior of the samples prepared in the MF presence are also registered they being concretized in higher stability of these compared with the classic ones.

In our previous papers it was presented the rheological behavior of the PAS/PVA complexes [10]. By rheological parameters correlation with the information's offered by zeta potential evaluation it was established the ratio at which the mixture between PAS and PVA forms a homogeneous interpolymer complex, thus being respectively at 70% PAS content for the blend made at 22^{o}C, and a ratio of PAS/PAV=1:1 in case of the blend prepared at 37^{o}C [10]. The study revealed a good correlation between the rheological and zeta potential measurements.

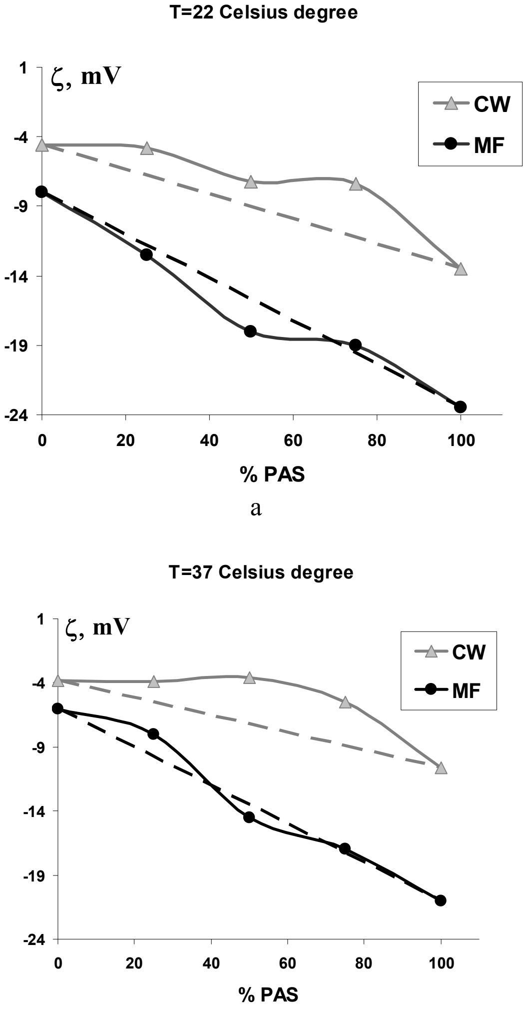
Taking into account the anterior results, the MF influence upon the interpolymer complex formation began by comparing the zeta potential data of the samples prepared with or without MF presence at two temperatures: 22^{o}C and 37^{o}C (Figure 1). The experimental zeta potential (ζ) is also compared with an "ideal value" (dashed lines in Fig. 1) which is designed to the system in the absence of specific interactions between the components. Considering a strict correlation between ζ and the intrinsic viscosity of the system we have considered any deviation from the ideal value as interactions between components [10-12].

Table 1. The main characteristics of the samples prepared in or without the MF presence.

Samples	Capacity to form films	FTIR (cm^{-1}) Band assignement	Differences observed in the spectrum of compounds obtained in the MF presence	T_i (°C)		ΔW%	
				CW	MF	CW	MF
PAS	Worse	- 1550 cm^{-1} (in succinimide) - 1710 cm^{-1} (CO from carboxylic group), - 3300 cm^{-1}, 3080 cm^{-1} (peptidic link).	- similar -higher intensity of the band in the MF presence, comparatively with CW	260	270	63	60
PAS:PVA= 3:1	Relatively good	- shifting of the characteristic bands: in the 2500 – 4500 cm^{-1} region (O-H stretching) - shifting of non-associated hydroxyl group from 3640 cm^{-1} to 3437 cm^{-1} assigned to associated -OH. - characteristic band for carbonyl shift from 1730 cm^{-1} to 1716 cm^{-1} to 1500 cm^{-1} region because of their implication in H-bonds.	Similar bands with higher intensity in the MF presence comparatively with CW.	250	255	71,6	68
PAS:PVA= 1:1	Good			240	245	76.4	72
PAS:PVA= 1:3	Very good			240	246	81	77
PVA	Excellent	- 1144 cm^{-1} (– OH groups of PVA), - 2909 cm^{-1} (symmetric stretching of $-CH_2$ groups), - 2940, 3348 cm^{-1}, (asymmetric stretching of $-CH_2$)	- higher intensity of the band in the MF presence comparatively with CW. - similar, no difference observed	180	190	94	86
T_i - onset temperature, ΔW% - loss weight.							

From Fig. 1 it is evident that the MF presence decreases the compatibility between homopolymers. The behavior was attributed to the competitive process which appears between to the capacity of the MF for ordering the functional groups with negative influence on the formation of the interpolymer complex.

However, the MF presence during the interpolymer complex formation has a positive effect on the colloidal stability (evidenced by the increase of the modulus of zeta potential). Also, the colloidal stability increases with the amount of poly(aspartic acid) in the complex. The increase of temperature at 37°C determines a light decrease of colloidal stability. The electric conductivity of the compound it is presented in Figure 2.



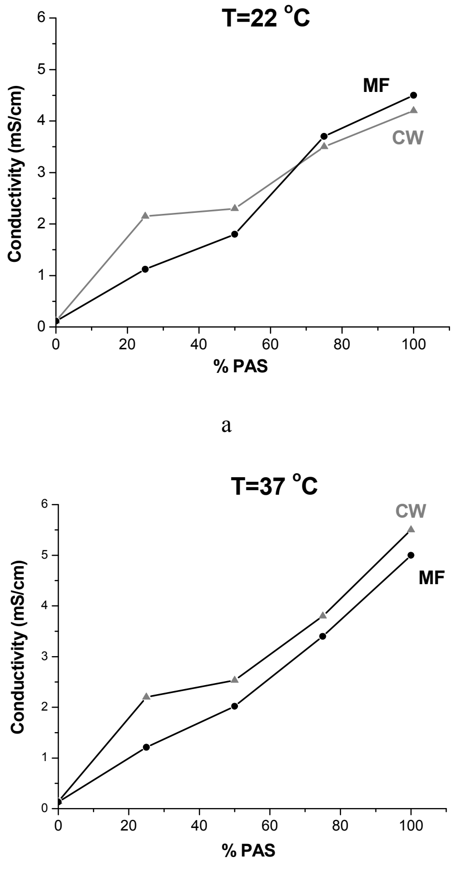
a

b

Fig. 1. The comparative behavior of zeta potential for PAS/PVA composition prepared with or without MF presence at 22 °C (a) and at 37 °C (b). The dashed lines are for the corresponding additive dependencies.

The solutions conductivity increases with the PAS content fact attributed to the increase of the functional groups (–COOH). As it was expected, the conductivity of the mixtures increases also with temperature. However the MF presence determines the decrease of the conductivity with few exceptions (at 22^{0}C the conductivity of the sample prepared in the MF presence is higher for 75-100% content of PAS in IPC).

Zeta potential measurement gives also information about the overall surface charge of the particles and how it is affected by changes in the environment (e.g. pH, presence of counter-ions, and adsorption of proteins). Also, a combination of the zeta potential measurement and size provides an insight into the mechanisms of dispersion stability. Moreover, zeta potential has proven to be extremely relevant to the practical study and control of colloidal stability and flocculation processes, because it reflects the effective charge on the particles being related to the electrostatic repulsion between them.



a

b

Fig. 2. The comparative behavior of electric conductivity for the PAS/PVA composition prepared with or without MF presence at 22 °C (a) and 37 °C (b).

For these reasons, in the next step it was studied the variation of ζ, electrical conductivity and hydrodynamic diameters as a function of pH (Figures 3, 4 and 5). The measurements were made at 37^{o}C and at ratio PAS/PVA=1/1, accordingly to our previous analyses (dynamic rheology and zeta potential measurements) [10, 11]. Data recorded for PAS and PVA as homopolymers were compared with those of IPC prepared in or without the MF presence.

From Fig. 3 it is observed the PAS solution don't achieve the isoelectric pH, regardless MF presence. The PVA solution has an isoelectric pH (pH at which $\xi = 0$ mV and colloidal stability is minimum) in strongly acid medium. In this case, the pH isoelectric value is not influenced by MF ($pH_{iz\ PVA\text{-}CW} = 2.2$ and $pH_{iz\ PVA\text{-}MF} = 2.3$). The interpolymer complex keeps the same behavior with PVA, having also isoelectric pH in acid medium. The presence of the MF during IPC formation displaces the isoelectric pH from $pH_{izPAS/PVA\text{-}CW} = 3.5$ to $pH_{iz\ PAS/PVA\text{-}MF} = 2.7$. It must underline that, on the entire pH range, the IPC formed in the MF presence has a higher modulus of ζ, which denotes a higher colloidal stability. ζ is maintained constantly in the alkaline domain. MF presence enlarges the domain of colloidal stability to pH=5.5-12 (comparative with the sample prepared without MF presence where the colloidal stability domain is in pH=7.5-12 range).

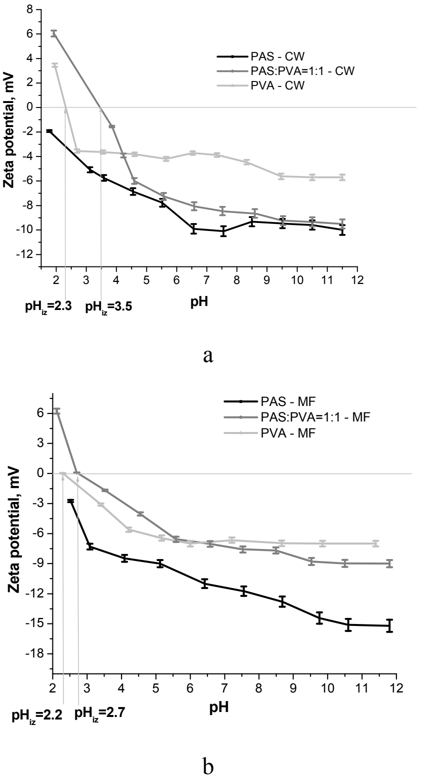


Fig. 3. ζ variation as a function of pH for PAS/PVA interpolymer complex comparative with the homopolymers solutions prepared without (a) or in the MF (b) presence.

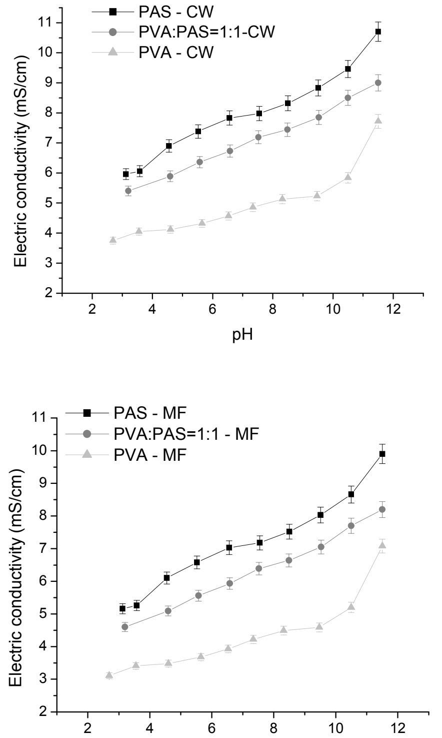


Fig. 4. Electrical conductivity variation as a function of pH for PAS/PVA interpolymer complex comparative with the homopolymers solutions prepared without (a) or in the MF (b) presence.

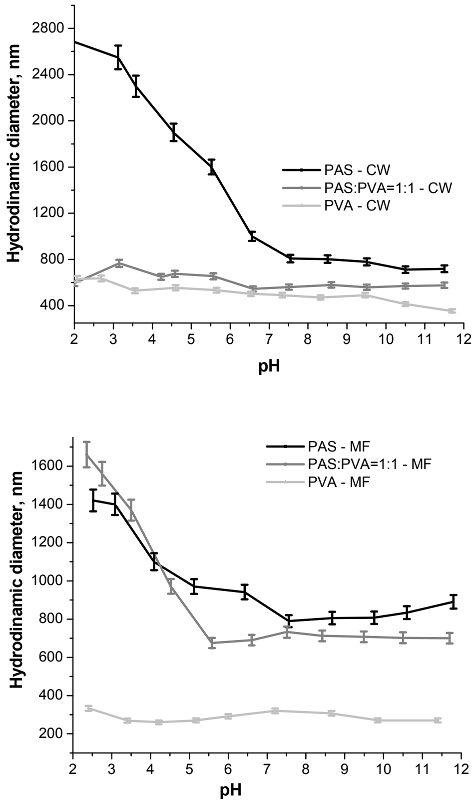


Fig. 5. Hydrodynamic diameter variation as a function of pH for PAS/PVA interpolymer complex comparative with the homopolymers solutions prepared without (a) or in the MF (b) presence

Generally, in aqueous solutions of mixtures of such complementary polymers, interpolymer association due to successive hydrogen-bonding between the carboxylic groups of the polyacid and the proton acceptor groups of the polybase leads to the formation of compact interpolymer complexes [13] soluble only within a narrow pH window. At pH values higher than 4.5-5.5 (where the ionization degree of the weak polyacid is higher than 10–15%), dissociation occurs, while at pH values lower than 3–4 they precipitate as fraction of the carboxylate anions in the polyacid chain [14-16].

In Fig. 4 are illustrated the electrical conductivities as a function of pH for PAS/PVA interpolymer complex, comparative with the homopolymers solutions prepared without (Figure 4a) or in the MF (Figure 4b) presence. The conductivity increases with the pH value due to the enhancement of the number of ionizable groups. The interpolymer complex has the value of the conductivity between those of the homopolymers, greater than PVA but lower than PAS. Anyway, in case of homopolymers or for IPC, the MF presence determines the decrease of the conductivity.

For PAS a considerable increase of hydrodynamic diameters (Figure 5) at acid pH, it is registered. Here, the stability is decreased, the repulsive forces between particles are reduced determining the aggregation of the particles (and implicit the increase of hydrodynamic diameter). PAS solution behavior evidences zwitterion character of the compound. PVA solution presents dimensional stability almost on the entire pH domain excepting the isoelectric pH, were a decrease of the stability appears, regardless MF presence. A special behavior has the PAS/PVA IPC. In the absence of MF, the dimensional stability is relatively constant, with exception of a slowly increase of hydrodynamic diameter at isoelectric pH (3.5). The presence of MF determines a considerable increase of the hydrodynamic diameter around the isoelectric pH (pH=2.7). However, the IPC maintains its colloidal stability in pH=5.5-12 range, despite MF presence.

4. Conclusions

Thermogravimetrical analyses evidence the thermal stability of the prepared interpolymer complex situated between those of the constitutive homopolymers, higher then poly(vinyl alcohol) and smaller then poly(aspartic acid). The thermal stability increases with the amount of poly(aspartic acid) and with MF presence.

The influence of the MF presence during the IPC formation emphasizes the positive effect for colloidal stability of the system, evidenced by the increase of the absolute value of zeta potential even the MF presence reduce the compatibility between homopolymers.

The zeta potential dependence on pH highlights that PAS solution doesn't achieve the isoelectric pH, even in the MF presence during solution preparation. The interpolymeric complex maintains the PVA behavior, having the isoelectric point at acid pH. The MF presence during IPC formation displaces the isoelectric point from $pH_{izPAS/PVA-CW} = 3.5$ to $pH_{iz\ PAS/PVA-MF} = 2.7$. On the entire pH range, the IPC formed in the MF presence has a higher modulus of ζ, evidencing a higher colloidal stability of the system.

The increase at acid pH of the hydrodynamic diameters in case of PAS confirms the particles aggregation. PVA solution presents dimensional stability almost on the entire pH domain, excepting at the isoelectric point were a decrease of the stability it is appeared, despite of the MF presence during solution preparation. The PAS/PVA IPC presents specific behavior. The MF presence determines the increase of the hydrodynamic diameter around of the isoelectric pH (pH=2.7). However the IPC maintains its colloidal stability in pH=5.5-12 range.

The interpolymer complex has the conductivity values between those of homopolymers, greater than PVA but lower than PAS. The MF presence during solution or IPC preparation determines the decrease of the conductivity in case of both homopolymers as well as IPC.

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