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Investigation of poly(aspartic acid) / vinylic polymer interpolymer complex

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Intermacromolecular complexation between poly(aspartic acid) known as a nontoxic, biocompatible and biodegradable polymer and a synthetic polymer with film-forming properties such as: poly(vinyl alcohol) or poly(acrylic acid) is investigated. This interpolymer complex is intended to be used as a silver-doped matrix with microbial resiliency for biomedical applications. Dynamic rheology and differential scanning calorimetry are used to evaluate interpolymer complexation.

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1. Introduction

To satisfy the growing interest of new materials with specific properties, such as engineering materials, new polymers are synthesized everyday [1-2] and chemical modifications in conventional polymers are proposed [3-4]. But the mixture of two or more polymers, forming a polymer blend, continues to be an economical method to obtain new polymeric material [5].

An interpolymer complex (IPC) is a compound formed in mixed solutions as a result of the interaction of two or more compatible polymers, by non-covalent association between groups on different polymer chains. The formation, structure, and properties of complexes based on two interacting chemically and spatially complementary flexible-chain polymers were described [6-10]. Most of interpolymer complexes reported in the literature are based on water-soluble homopolymer pairs in aqueous media due to strong interactions, e.g., van der Waals, polyelectrolyte association, hydrogen bonding, etc. For example, IPCs are formed due to hydrogen bonding between nondissociated groups of a polyacid and proton-acceptor groups of a noncharged polymer such as poly(acrylic acid) and poly(vinyl alcohol).

The final properties of a polymeric blend commonly depends on the properties of its polymeric components, composition and, mainly, on the miscibility of the polymers [11]. In some cases, by synergistic effects, such combinations may possess unique properties that are different from those of individual component.

There is a great potential in utilizing these blends in many pharmaceutical preparations especially in controlled release drug delivery systems. The presence of interactions between atoms, or group of atoms of unlike polymers is essential to obtain a miscible polymer blend [5,11]. The conformation changes in solution from hydrogen interactions are also involved in miscible blends.

For the investigations of polymer – polymer miscibility, the techniques most commonly used are turbidimetry, electronic microscopy, infrared spectroscopy, NMR, viscometry, thermal analysis and inverse gas chromatography. The more sensitive a 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 in studies of miscibilities of polymer blends.

This study is focused on the complexation of poly(aspartic acid) / poly(vinyl alcohol) and poly(aspartic acid) / poly(acrylic acid), as matrices for silver-doped compounds with biomedical applications. The interactions were examined by dynamic rheology technique (in dilute solutions) and by DSC technique (on polymer films).

2. Experimental

2.1. Materials and IPC preparation

Samples of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) are purchased from Oriental Chemical Ind. Korea and Sigma respectively, and are used as received. PVA has a M_w of 120,000 Da and PAA has a M_w of 3,000,000. Poly(aspartic acid) (PAs) was synthesized by thermal polymerization of aspartic acid, at the temperature between 160 and 260°C, time 1–4.5 h, with phosphoric acid as catalyst. It has M_w of 15,110 and a polydispersity of 1.317.

The complexes of PAs / PVA and PAs / PAA were prepared by direct mixing for 60 min of the initial polymer solutions of the same concentrations – 1 g/ dL - in different ratios (% vol). The PAs / PVA (PAA) % vol ratios of 1 g/dL solution are: 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. All the measurements were done 5 min after the mixing, to allow IPC realization and thermal equilibrium to be reached.

2.2. Rheological testing

The aqueous solutions of the components and their mixtures in different ratios were tested with a Bohlin CVO rheometer equipped with a Peltier device for temperature control.

2 ml mixture of the mentioned solutions were poured on the lower plate of rheometer, for each determination. The measurements were performed by using parallel-plate geometry. Both plates are from stainless steel, with a gap of 0.5 mm, the upper plate having the radius of 30 mm.

The experiments as a function of composition are realized at ambient temperature 22±0.1^o C and at physiological temperature 37±0.1^o C for small amplitude rheological tests, at a frequency (ω) of 0.1 rad/sec and shear stress (σ) of 1 Pa. Previous frequency sweep tests established the correctitude of the all experiments within the linear viscoelastic range of oscillatory deformation.

2.3. DSC tests

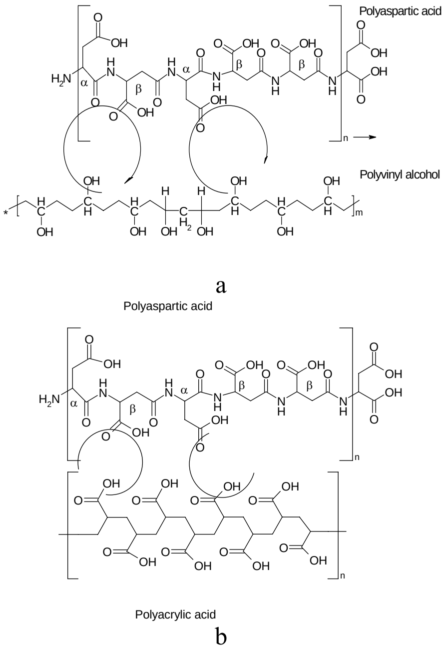
The thermal properties of all polymers and blend films were measured using a Mettler 12E type DSC (Switzerland). The instrument was calibrated using an indium standard. Sample size was kept at 10 mg and heating rate was maintained at 10 ^{o} C/min. An inert atmosphere of N_2 was maintained throughout the DSC run. The T_g value was taken as the step transition value which is obtained as the inflexion point of the slope change in the plot of heat flow vs. temperature (in ^{o}C).

3. Results and discussion

Poly(aspartic acid) PAs is an amino acid polymer that has good biodegradability, biocompatibility and dispersing activity. Biodegradation results in decomposition of PAs to environmentally benign products such as carbon dioxide and water. It can be used in many different applications, such as dispersant, antiscalant, or superabsorber, for home detergents, water treatment chemicals, oil field treatment additives, for a variety of organic and inorganic solids and scales dispersal, and in biomedical applications. Due in part to the carboxylic groups, poly(aspartic acid) has similar properties to the poly(acrylic acid), but the last one is not biodegradable.

The NMR methods have clarified the conformational characteristics and mobility of PAs which forms intermolecular hydrogen-bonds with many compounds, such as PVA or PAA [12]. It is shown that the intermolecular hydrogen-bonding is formed at the carboxylic groups of the side-chains of poly(aspartic acid) and affects no main-chain conformation, but it strongly affects the dynamics of PAs. This implies that the mobility of the side-chain carbons is obviously changed from the slow motion region to the extreme motion region over a wide range of temperatures. The formulae of PAs / PVA and PAs / PAA interpolymer complexes are given in Scheme 1 a, b.

Rheological properties of the IPC formed in aqueous solution are an important instrument for the study of interpolymer complexation. Elastic G' and viscous G'' moduli, complex viscosity η^* and loss tangent tan δ offers information on the viscoelastic state of the homopolymers as well as of their mixtures.



Scheme 1. IPC formation : a-PAs / PVA ; b-PAs /PAA.

The comparison of the experimental viscosity of a polymer mixture with an "ideal value" is proposed as a criterion for the compatibility or association of the two polymers in solution [13, 14]. The ideal value is designed to the system in the absence of specific interactions between the two components. Any deviations from the ideal value indicate interactions between components; a negative deviation points up the formation of an interpolymer association with a compact structure while a positive deviation is representative for a gel-like association [15].

The dynamic rheology results of the mixtures of PAs / PVA and PAs / PAA are presented in Figs. 1 and 2. As a general image, for all the mixtures the curves show a positive deviation of experimental data from the ideal additive; one can conclude that IPCs are formed in these mixtures. The dashed lines show the additive dependence of G', G'', η^* and tan δ of each mixture, on its composition, which corresponds to the absence of the interaction between the components.

For all the ratios of PAs / PVA, the mixtures are low-viscosity liquids (Fig. 1c) and displayed almost no elastic response; the data for elastic modulus G' presented in Fig. 1a must be reserved treated, the values being too small and attributed to the sensitivity limit of the apparatus. All the samples have no evident elasticity, they show preponderant viscous behavior. Eloquently is tan δ as ratio G''/G' (Fig. 1 d), whose great values underline the great difference between elastic and viscous behavior for PAs / PVA mixture. The G'' of the solution of polymer mixture has a maximum value comparative with additive dependence for PAs content of about 70% vol at 22°C (Fig. 1b).

At physiological temperature of 37° C, this maximum is moved at about 50% vol PAs concentration in the mixture composition.

η* (Fig. 1c) shows slight positive deviation of the experimental values from the additive dependence, reflecting the formation of IPCs. The maximum values for both 22 and 37 ° C are maintained also at the PAs concentration of 70 % vol and 50 %vol, respectively.

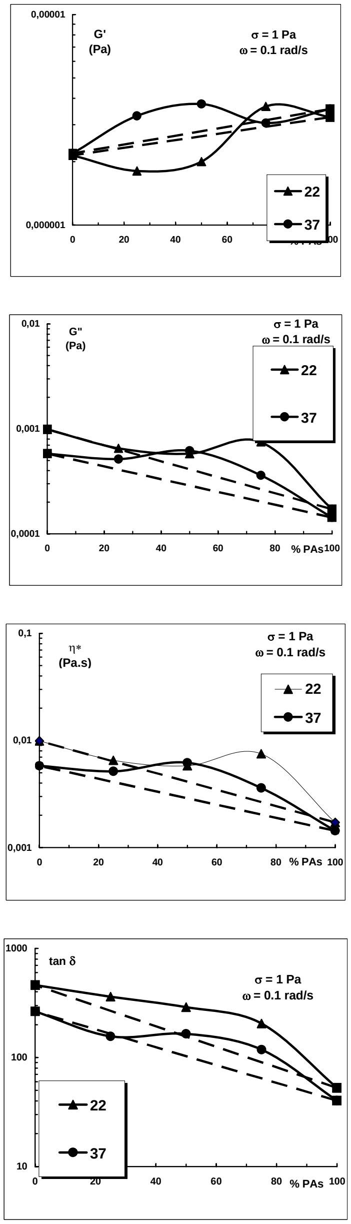


Fig. 1. PAs / PVA interpolymer complex dynamic rheological data: a - Elastic modulus G'; b - Viscous modulus G''; c- Complex viscosity η; d- Loss tangent tan δ The dashed lines are for the corresponding additive dependencies.*

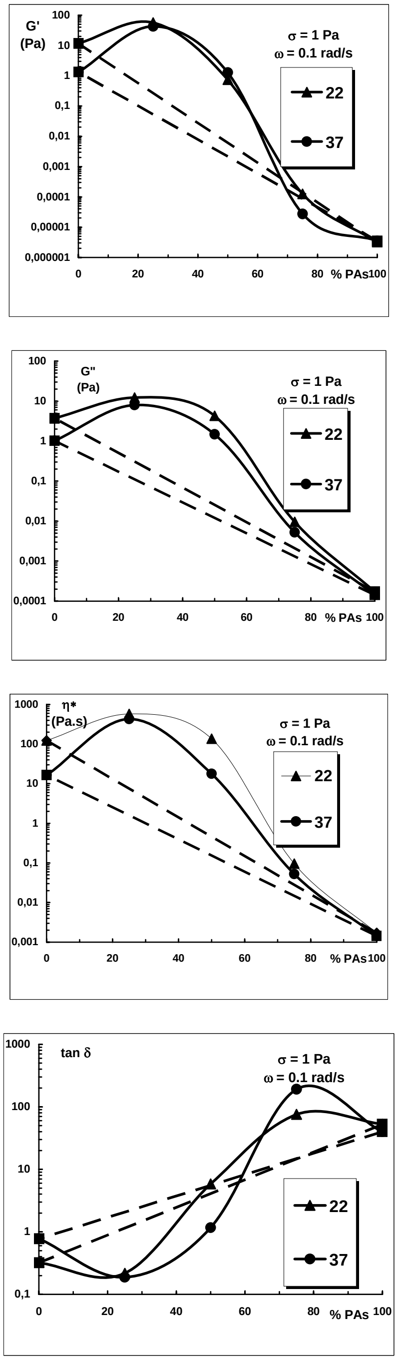


Fig. 2. PAs / PAA interpolymer complex dynamic rheological data: a - Elastic modulus G'; b - Viscous modulus G''; c- Complex viscosity η ; d - loss tangent tan δ The dashed lines are for the corresponding additive dependencies.*

Fig. 2 a, b, c, d presents the rheological behavior for the mixtures of PAs/PAA. The elastic behavior (Fig.2a) has a maximum interval for 20 – 40 % vol of PAs in the mixture, for both tested temperatures; at the same time the deviation from additive dependencies has important positive value. Taking into account the data for complex viscosity η* one can say that an IPC in these PAs / PAA mixtures is formed. The value of the deviation from ideality for η*, as the PAs / PVA mixture, gives a very good qualitative picture of the interaction among the polymers and hence the miscibility. Depending of the strength of interaction, the magnitude of deviation varies (Figs. 1c and 2c). For greater content of PAs in the mixture, the magnitude of deviation in η* plot shows almost no difference between experimental and additive viscosity, or at least, the increase of its size compared with the initial macromolecules is negligibly small.

In Figs. 3 and 4 the thermograms of the pure polymers and their mixtures of 50% vol PAs with PVA and PAA, are presented.

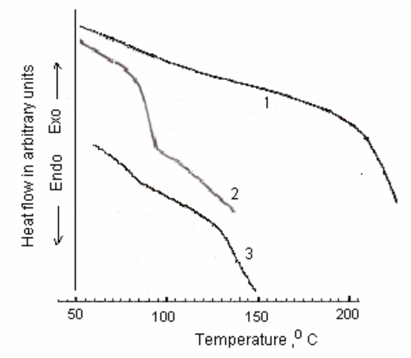


Fig. 3. DSC curves for PAs (1), PVA (2) and 50/50 % vol PAs/PVA (3).

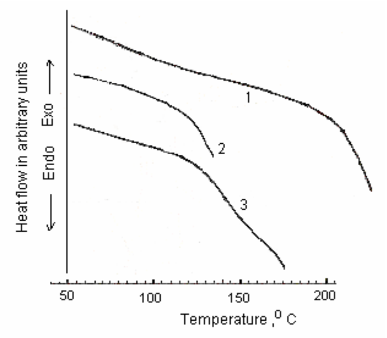


Fig. 4. DSC curves for PAs (1), PAA (2) and 50/50 % vol PAs/PAA (3).

The characteristic T_g for each polymer as indicated, is about 67 °C and 125 °C for PVA and PAA, respectively (Figs. 3 and 4, curve 2). PAs does not show glass transition temperature, but it decomposes in two steps : I – at 150 –158 °C and II – at about 200 °C, without melting (Figs. 3 and 4, curve 1). The literature specifies the T_g of the complex made by hydrogen bonding shows a significant deviation from the weight-average law or the Fox equation [10,16-17]. Often, hydrogen bonding increases the T_g because it restricts the motion of the polymer segments. Figs. 3 and 4 curves 3, show the T_g of the PAs/PVA and PAs/PAA complexes prepared by mixing the aqueous solutions. Both complexes show a single T_g at about 72 °C (PAs/PVA) and 143 °C (PAs/PAA). The appearance of a single T_g for the complex indicates that its miscibility is fairly good [18]. The fact that T_g of the complexes has higher values than of the pure polymers PVA and PAA is according to the complex structure more restricted as a result of the stronger interaction.

4. Conclusions

PAs/PVA and PAs/PAA interpolymer complexes (IPC) were prepared through the established hydrogen bonds by mixing their aqueous solutions. Dynamic rheology and differential scanning calorimetry underline the interaction between the components into the IPC and their miscibility. These complexes are investigated as structures with microbial resiliency by doping with silver, with the aim of biomedical applications. But, in view of this finality, it is necessary to include the study at higher concentrations of the polymers.

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References

[1] R. Stadler, C. Auschra, J. Beckmann, U. Krape, I. Voigt-Martin, L.Leibler, Macromolecules **28,** 3080 (1995).
[2] I. Pinnau, Polym. Adv Tech **5**, 733 (1993).
[3] K. D. Gagnon, R. W. Lenz, R. J. Farris, Polymer **35**, 4368 (1994).
[4] Y. Ykada, Biomaterials **15**, 725 (1994).
[5] L. A. Utracki. Polymer alloys and blends. Munich: hanser Publishers (1989).
[6] V. A. Kabanov, Macromol. Chem. Lect. **8** 121 (1972).
[7] N. J. Turro, K. S. Arora, Polymer ***27,*** 783 (1986).
[8] A. Bekturov, L. A. Bimendina, Adv. Polym. Sci. **41**, 99 (1981).
[9] E. Tsuchida, K. Abe, Adv. Polym. Sci. **45**, 1 (1982).
[10] M. Jiang, M. Li, M. Xiang, H. Zhou, Adv. Polym. Sci. **146**, 121 (1999).
[11] Olabisi, L. M. Robeson, M. T. Shaw. Polymer-polymer miscibility. New York: Academic Press (1973).
[12] S. M. Thombre, B. D. Sarwade, J Macromol Sci. Part A: Pure Applied Chem. **42**,1299 (2005).
[13] G. R. Williams, B. Wright, J. Polym. Sci. Part **A3**, 3, 3885 (1965).
[14] D. Staszewska, M. Bohdanecky, Eur. Polym. J. **17**, 245 (1981).
[15] G. Staikos, G. Bokias, C. Tsitsilianis, J. Appl. Polym. Sci. **48**, 215 (1993).
[16] M. K. Chun, C. S. Cho, H. K. Choi, J Controlled Release **81**,327 (2002).
[17] L. F. Wang, E. M. Pearce, T. K. Kwei, J Polym Sci Part B:Polym Phys **29**, 619 (1991).
[18] C. Lau, Y. Mi, Polymer **43**, 823 (2002).

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