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Investigations on the interactions between xanthan gum and poly(vinyl alcohol) in solid state and aqueous solutions



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ABSTRACT

In the present study, the polymer mixtures based on an anionic polysaccharide, namely xanthan gum (XG), and a neutral polymer, poly(vinyl alcohol) (PVA), were investigated by FTIR spectroscopy, viscometry and zeta potential measurements. The hydrogen bond intermolecular interactions between functional groups of xanthan gum and those of PVA were evidenced by FTIR spectroscopy. The experimental viscometric data of polymer mixtures in aqueous solutions were interpreted by using the Wolf approach. This model allows the determination of the intrinsic viscosity and other hydrodynamic parameters irrespective of structural characteristics of macromolecular chains, polymer mixture composition and polymer concentration. The chain conformation and polyelectrolyte feature of xanthan gum have a high contribution on the behavior of XG/PVA mixtures; high values of the hydrodynamic parameters were obtained for XG rich polymer mixtures. The viscometric results and FTIR analysis revealed the formation of intermolecular associations between XG and PVA due to the hydrogen bonds interactions. The absolute value of the zeta potential for XG/PVA mixtures decreases as the poly(vinyl alcohol) content in the polymer mixtures increases.

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1. Introduction

The design of new materials with improved or tailored properties without altering the individual structure of polymers or development new synthesis represents a goal of the chemists. On the other hand, the increasing concern for environment made that the researchers attention to be focused on environmentally friendly technologies and materials. The natural polymers are biocompatible, biodegradable, bioadhesive, abundant in nature and cheap, but exceedingly poor cohesive strength of them makes inappropriate their use in certain applications. At the opposite pole are the synthetic polymers which, due to excellent combination between physical and mechanical properties, are widely used in the formulations of various systems, increasing their strength. However, they may contain some unreacted monomers which are usually toxic. Therefore, physical mixing of natural and synthetic polymers represents an attractive way to obtain polymeric materials with desired features, improved mechanical characteristics and biological performances. These materials have found applications in wastewaters treatment, food industry, medicine, etc. [1].

Xanthan gum (XG) is an anionic polysaccharide composed of (1,4)-β-p-glucose residues as main chain at which a trisaccharide side chain is linked at C3 position to every other glucose residues. The side chain consists of (1,4)-β-p-glucuronate unit between (1,2)-α-p-mannose and β-p-mannose units [2] (Scheme 1a).

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Scheme 1. Chemical structure for (a) xanthan gum and (b) PVA.

XG is used as thickening, suspending and emulsifying agent for various kinds of water-based systems from food, pharmaceutical, cosmetic, agricultural, textile, ceramic and petroleum industries and in conjunction with other biocompatible polymers it can form stable gel systems [3,4] or it is involved in matrix formulations for oral controlled-release drugs [5–8].

Poly(vinyl alcohol) (PVA) (Scheme 1b) is a water soluble polymer synthesized by hydrolysis of poly(vinyl acetate) and commercially available with different molecular weights and hydrolysis degrees; the content of the residual acetyl groups strongly influences the reactivity of hydroxyl groups of PVA and its biodegradability [8,9]. Chain flexibility, biocompatibility, air permeability, excellent film-forming and water absorption properties, ability to form physical aggregates in aqueous solution by hydrogen bonds, etc., are some features required in different applications (such as, in formulation of biomedical and pharmaceutical devices [10–13], paper coating, packaging manufacturing or other materials [14]). XG/PVA system was used as basis in preparation of controlled drug delivery formulations [6–8], pH and electrolyte sensors [3] and some plastic materials [14] for which different cross-linking agents (i.e., epichlorohydrin, glutaraldehyde, poly(acrylic acid) or low dose electron beam) and synthesis conditions (temperature and time of reaction, emulsion or basic medium, a given ratio of XG/PVA) were used. As far as we know, there are no reported data regarding the behavior of XG/PVA physical mixtures in dilute aqueous solutions.

In this context, the current study aims to investigate XG/PVA mixtures and to discuss the interactions between XG and PVA by using FTIR spectroscopy, viscometry and zeta potential measurements.

2. Experimental

2.1. Materials

Commercial samples of XG and PVA were used as received without further purification. XG in a powder form was provided by Sigma-Aldrich. Previous papers reported the viscometric molecular weight of xanthan gum used in the present study as being 1.165×10^6 g/mol [15] and the type of metallic ion from xanthan sample is potassium (K⁺) [16]. PVA with the degree of hydrolysis of 80% and molecular weight of 6.5×10^4 g/mol was purchased from Loba Feinchemie AG (Austria Chemical Companies).

2.2. Samples preparation

Pure polymer stock solutions were prepared in Millipore water (obtained from a Milli-Q PF apparatus). Xanthan gum was dissolved at room temperature under gentle stirring. In order to prevent the degradation of polysaccharide chains, the stock solution was kept at temperature of 5 °C. PVA dissolution was carried out at 80–90 °C under magnetic stirring. After preparation, PVA solution was allowed to equilibrate overnight at room temperature.

XG/PVA mixture solutions were obtained by combining the stock solutions in different ratios. The composition of polymer mixtures was expressed as weight fractions of PVA (w_{PVA}). All investigated solutions were prepared with one day before measurements.

2.3. Measurements

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The infrared measurements were carried out on a Bruker Vertex 70 spectrometer (Bruker Optics, Germany). The spectra in solid state were recorded in transmission mode in the range of $4000-400\,\mathrm{cm}^{-1}$ at a resolution of $2\,\mathrm{cm}^{-1}$ by using the

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