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Blends based on ionic polysulfones with improved conformational and microstructural characteristics: Perspectives for biomedical applications

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ABSTRACT

Ionic polysulfones have received widespread attention for their promising roles as ionic exchange membranes, antibacterial coatings, and dialysis membranes. Therefore, the blends of the quaternized polysulfone with a tunable content of polyvinyl alcohol were obtained to create new materials that can modulate the membrane properties. The rheological response of quaternized polysulfone/polyvinyl alcohol in *N*-methyl-2-pyrrolidone blends to the structural peculiarity of polymers from the blend, composition of polymer mixtures, as well as the types of interactions was investigated. Rheological behavior of the complex system, described by the non-linear flow curve, indicates the plasticizer effect of polyvinyl alcohol to quaternized polysulfone solutions, in order to facilitate the subsequently preparation of the bioactive membranes. Additionally, the specific microarchitecture of the blends, determined using atomic force microscopy, represents an excellent porous membrane scaffold with expected future developments in the biomedical fields.

1. Introduction

Membrane technology has been developed for widely applications in waste water treatment, biotechnology, food technology, biomedicine and pharmaceutical industries [1,2], due to its efficiency, ease implementation, and cost effectiveness. Recently, researchers have been focused on controlling the membrane performance in terms of the selectivity and separation accuracy [3,4], and improving their properties, such as antifouling and antimicrobial properties [5–8], biocompatibility [9] and environment stimuli responsive [10], etc. In this direction, considerable efforts have been put towards the obtaining of novel membrane materials. Polysulfones (PSF) or PSF based composites have been developed and used as membrane materials due to their outstanding oxidative, excellent thermal and hydrolytic stability. The key feature of the polysulfone membranes, apart from their good transport properties, is their excellent biocompatibility. These membranes exhibit only slight complement activation [11], minimal decrease of leukocytes, and low release of leukocyte elastase [12]. Therefore, PSF is the most applied membrane material in biomedicine for hemodialysis. Despite its advantages, the intrinsic hydrophobicity of these materials often causes severe problems, i.e. protein adsorption and platelet adhesion, leading to a decreased performance of the PSF membrane. The foremost drawbacks of the PFS membrane materials are mechanical strength and fouling, characteristics directly related to a short membrane lifetime and an unpredictable separation performance [13]. Furthermore, PSF membrane acts only as a barrier in the separation process.

An appropriate approach to design a practical membrane material is blending with a modifying agent – additive – or the chemical modification [14,15]. Therefore, a simplest and more effective route to generate surface reactive groups, which plays an important role in the assuring of some properties required by different applications, is chemical modification of PSF. Thus, in order to improve its performance [7], the polysulfone can be modified through chloromethylation, a reaction of considerable interest from theoretical and practical points of view, to obtain precursors for functional membranes, coatings, ion exchange resins, ion exchange fibers and selectively permeable membranes [16,17], and quaternization with the ammonium groups of the chloromethylated polysulfones (CMPSF) to improve the hydrophilicity and hemocompatibility of these materials [7,18]. Moreover, ionic polymers represent an important class of chemical compounds, due to their

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special physical and chemical properties, being used as multifunctional materials for a wide variety of applications, as a result of their particular behavior in solution.

On the other hand, an ideal approach to improve the properties of membranes by developing advanced materials, which contributes significantly at the quality and efficiency of the systems that address to human health, is represented by the polymers blend concept. The interest in this direction is justified both by theoretical approaches – fundamental research (i.e. study of the interaction between polymer raw materials, or interactions between the polymer matrix and low molecular weight compounds immobilized or filtered through porous material, performing chemical modifications of macromolecular compounds which will allow changes in the membrane transfer properties or the reaction with biologically active compounds), and especially by practical systematic approach and development. Therefore, the research in physical chemistry and technology of polysulfones blending with polymeric additives, usually hydrophilic polymers, were recently focused mainly on the preparation of new performant porous materials with application in the various forms, namely films, membranes, tubes, micro- and nanoparticles, gels, etc. These can be used to immobilize the active principles (drugs, enzymes, food additives, cosmetics, microorganisms, cells), to obtain prostheses, as media for tissue regeneration, dialysis membranes, filter media, ion exchange, etc. [15,19–22].

In this context, the polyvinyl alcohol (PVA) is notable not only for its physical and chemical properties [23–27], high hydrophilicity, flexibility, tensile strength, chemical-resistant properties, and good performances in film forming, but also represent an excellent barrier and an inexpensive polymer. Thus, due to its features, PVA has been widely used, being applied in the fields of enzyme immobilization, fiber coating, adhesives, gas separation, and fuel cells [28–32]. Therefore, it is of interest to find out whether polysulfones can be designed for specific applications in blends with PVA and to establish their impact on the different properties.

However, in literature a low attention has been paid on the direct blending of ionic polymers (e.g. quaternized polysulfones (PSFQ)) with PVA. For this reason, the main challenge of the present paper is to achieve new blends by choosing PVA as hydrophilic modifier and pore-forming agent, capable to improve the performance of the quaternized polysulfone membranes for biomedical applications. Consequently, the present approach concerning embedding PVA in PSFQ matrix is complementary to the previous studies which have been focused mainly on the solution properties [33–38] of a series of functionalized polysulfones [39,40]. Also, surface wettability trends, as well as the morphological characteristics of these functionalized polysulfones were also analyzed for biomaterials and semipermeable membrane applications [7,8,15,18,41]. Thus, unlike the mentioned study, the present paper is based on extended research designed to improve the quaternized polysulfones (PSFQ) properties by use of PVA, for obtaining performant membranes.

Particularly, the rheological behavior of the obtained blends was examined, delivering data on the interactions occurring in ternary system at different PVA compositions. In addition, the cumulative effects of the structural characteristics and specific interactions were reflected on the morphological changes induced by PVA incorporation; these aspects were investigated for a better understanding and control of membranes preparation with desirable properties for future applications in biomedicine, namely membranes used to immobilize active principles. Thus, the choosing PVA as performant hydrophilic additive represents an important tool proposed by us to control the porosity and hydrophilic properties of membranes. Therefore, the results of this work will provide insight on the development of high-performance membranes for subsequent researches by testing biocompatibility and antimicrobial activity for their employment in biomedicine field.

2. Experimental

2.1. Materials

UDEL-1700 polysulfone (PSF) was purchased from Union Carbide Company (Texas) and was purified by repeated reprecipitation from chloroform (99.8% high purity, Fluka, Germany) and dried for 24 h in vacuum at 40 °C. For the synthesis of chloromethylated polysulfone (CMPSF) a mixture of commercial paraformaldehyde with an equimolar amount of chlorotrimethylsilane (Me_3SiCl) (99%, Merck, Germany) as a chloromethylation agent, and stannic tetrachloride ($SnCl_4$) (Fluka, Germany) as a catalyst, were used. In order to obtain chloromethylated polysulfone with a certain substitution degree (Table 1) [39], the reaction was performed at 50 °C for 140 h. Subsequently, the cationic polysulfone containing quaternary ammonium side groups (PSFQ) was synthesized by reacting CMPSF with a tertiary amine, *N*,*N*-dimethylbutylamine (DMBA). The quaternization reaction was performed in *N*,*N*-dimethylformamide (DMF) as solvent, at a CMPSF/tertiary amine molar ratio of 1:1.2, for 24 h at 80 °C. The quaternary polymer was isolated from the reaction medium by precipitation in diethylether, washed 3 times with diethylether, and dried for 48 h under vacuum, at room temperature.

The general chemical structures of the synthetized polysulfones are illustrated in Scheme 1.

The characteristics of the synthesized polysulfones are presented in Table 1. The total chlorine content was determined by Schöninger modified method [42] and ionic chlorine content was determined by potentiometric titration (Titrator TTT1C Copenhagen) with $AgNO_3$ aqueous solutions 0.02 N. The ratios between the ionic chlorine and total chlorine contents show that the quaternization reaction of CMPSF occurs at a transformation degree close to 98%. Thus, one may consider that almost all chloromethylenic groups were quaternized.

Biodegradable polyvinyl alcohol (PVA), used in this study as additive, was purchased from Celanese Corporation (Texas), having a hydrolysis degree around 98.8% and an average molecular weight of 23 000 g/mol.

2.2. Preparation of the PSFQ/PVA blends

PSFQ homogeneous solution of 11 g/dL was prepared by dissolution in NMP and kept for 24 h at room temperature. In the same time, a solution of PVA, having the same concentration (11 g/dL), was obtained by dissolution in NMP heated at 85 °C, in a water bath with a constant temperature of 80 °C by continuous stirring for 7 h, followed by degassing. After complete dissolving, the PVA solution was blended with the PSFQ solution to obtain different mixing ratios, i.e. 100/0, 75/25, 50/50, 25/75, and 0/100 wt./wt.

Table 1
Characteristics of the synthetized polysulfones including the chlorine content, Cl (%), ionic chlorine content, Cl_i (%), substitution degree, DS, molecular weights of structural units, m_0, and number-average molecular weights, $\overline{M}_n$.

Properties	Sample	
	CMPSF	PSFQ
Cl (%)	7.42	–
Cl_i (%)	–	5.44
DS	1.03	–
m_0	492	582
$\overline{M}_n$	29 000	28 000