NEW APPROACHES TO DESIGN OF BLENDS BASED ON QUATERNIZED POLYSULFONES WITH OPTIMIZED CONDUCTIVE PROPERTIES

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Abstract

New blends based on quaternized polysulfones, namely quaternized polysulfone/polyvinyl alcohol and quaternized polysulfone/cellulose acetate phthalate, were investigated in terms of their electrical properties. The dielectric constants have low values for the studied blends, being dependent on the chemical characteristics of blends compounds, in relation with the charge transfer complex and free volume and, consequently, with packing of the polymer chains and of the polarizable groups per volume units. Moreover, the electrical conductivity of studied blends can be explained in terms of band conduction mechanisms, through band gap representation.

This study analyzes the possibility of using blends based on quaternized polysulfones as possible candidates in electrotechnical industry. Additionally, the outcomes highlight the importance of new polymer blends for better electrical performances.

Introduction

Conductive polymers - novel type of electroactive biomaterial - allow excellent control of the electrical stimulus, possess good electrical and optical properties, have a high conductivity/weight ratio and can be made biocompatible, biodegradable and porous [1,2]. Therefore, development of the conductive polymer blends with tailor properties for various applications, from photovoltaic devices to nerve regeneration, promises to become an important goal of the scientific community. In this context, polysulfone (PSF) a transparent engineering thermoplastic, characterized by excellent properties, such as flexibility, high mechanical strength, high glass transition temperature, and thermal stability [1,3,4], as well as good film formation property [1,5], is recommended as proper candidate for a variety of applications in medical [4,6,7], food processing equipment, electrical, and electronics components [8,9]. There are also drawbacks in using those polymers in some applications, the main disadvantage being the relative hydrophobic character of them. Thus, the latest researches are focusing on the modification of PSFs that allows a compromise between hydrophobicity and hydrophilicity, and in this way, becomes suitable for the desired applications. Chemical modification of PSF through chloromethylation [10,11] and quaternization with the ammonium groups of the chloromethylated polysulfones (CMPSF) has caused considerable interest from theoretical and practical points of view, leading to improve the properties of these materials. On the other hand, the addition of another polymer to PSF matrix, it is desirable to get a conductive polymer blends with specific properties, which can be used as multifunctional materials for different electronics applications.

Particularly, functionalized polysulfone with quaternary ammonium groups (PSFQ) was combined with cellulose acetate phthalate (CAP) and polyvinyl alcohol (PVA), yielding flexible, biocompatible, and biodegradable blends with improved conductivity compared to the PSFQ. Thus, CAP and PVA were chosen as additives, knowing that they presence in a system significantly improves besides the hydrophilicity, flexibility, biocompatibility, and tensile strength, the transparence features, as well as electrical conductivity. Therefore, the main objective of this research is to investigate the influence of effects induced by structural and compositional characteristics of polymer blends on the electrical properties. Also, the study realized on PSFQ/CAP and PSFQ/PVA blends provides a new insight into to analyze and understand the polarization and conductivity mechanisms by designing desired conditions of transparency and improved electron interactions and conductivity, for better electrical performances. It is assumed that the quaternization effect and choosing of an appropriate additive significantly improve the ionic conductivity and also, could optimize dielectric properties required by ionic exchange membrane.

Experimental

Commercial aromatic polysulfone (PSF, UDEL-3500) was used in the synthesis of chloromethylated polysulfones (CMPSF) and subsequently, of ionic polysulfones containing quaternary ammonium side groups (PSFQ) [12,13]. Detailed procedure of reactions was presented in previous study [14]. Celvol polyvinyl alcohol (PVA, Celanese Corporation) has a hydrolysis degree around 98.8% and an average weight molecular weight of 23,000 g/mol. According to manufacturer specification the cellulose acetate phthalate (CAP) has a degree of substitution for acetyl and phthaloyl groups of 1.07 and 0.77, respectively, and a number-average molecular weight of 2,534 g/mol.

The characteristics of the synthesized polysulfones are presented in Table 1. Quaternization reaction of CMPSF occurs at a transformation degree close to 98%, implicitly, can be considered that almost all chloromethylenic groups were quaternized.

Table 1. Substitution degree, DS, chlorine, ionic chlorine, and nitrogen contents, molecular weights of structural units, m_0, and number-average molecular weights, $\overline{M}_n$, of polysulfone and functionalized polysulfones

Sample/ Properties	DS	Cl (%)	Cl_i (%)	N (%)	m_0	$\overline{M}_n$ (g/mol)
PSF	-	-	-	-	443	39,000
CMPSF	1.03	7.42	-	-	492	29,000
PSFQ	-	-	5.44	2.48	582	28,000

Dielectric spectroscopy measurements were achieved using a Novocontrol Concept 40 broadband dielectric spectrometer, by sweeping the frequency between $10^0 \div 10^6$ Hz, at fixed temperatures, of 4°C intervals, when temperature varies between -120 and +120°C, and increasing temperature rate is $2°C \cdot min^{-1}$. Temperature was controlled with a 0.1°C device by the Novocontrol Quatro Cryosystem, in dry nitrogen atmosphere to avoid water absorption.

Films used for these measurements, with a thickness of around 50 μm, were prepared by solution-casting method. Homogeneous solutions of PSFQ and CAP or PVA, with known concentration of 20 g/dL, were dissolved in N-methyl-2-pyrrolidone (NMP) in a water bath with a constant temperature of 70°C under continuous stirring for 2 h. PSFQ/CAP and PSFQ/PVA blends were prepared by mixing the two solutions in different ratios and subsequently were cast on a glass plate and solidified, initially by slow drying in saturated atmosphere of the used solvents, and finally under vacuum for 2 days at 50°C. The

70/30 wt./wt. composition of PSFQ/CAP and PSFQ/PVA blends was chosen as a consequence of the structural peculiarity of polymers in the blend, as well as type of interactions, evidencing the orientation or mobility of chain segments in solution.

Results and discussion

Dielectric behavior of PSFQ, CAP, PVA, and their blends over wide frequency, 1-10^6 Hz, and temperature, -120°C ÷ +120°C was investigated according to chemical structure and compositional aspects (Figure 1).

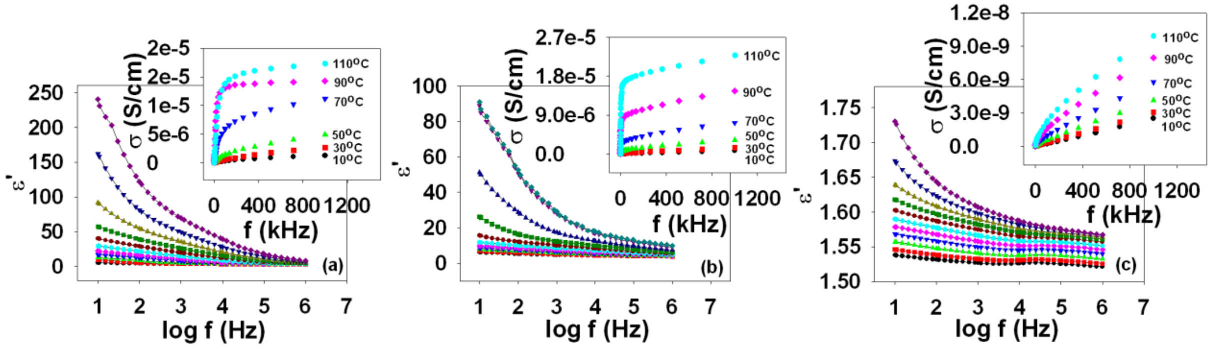

Figure 1. Variation of dielectric constant (ε') *vs.* frequency (f) at different temperatures for: (a) PSFQ, (b) PVA, and (c) CAP samples. Inserted plot represent variation of electrical conductivity *vs.* frequency at different temperatures.

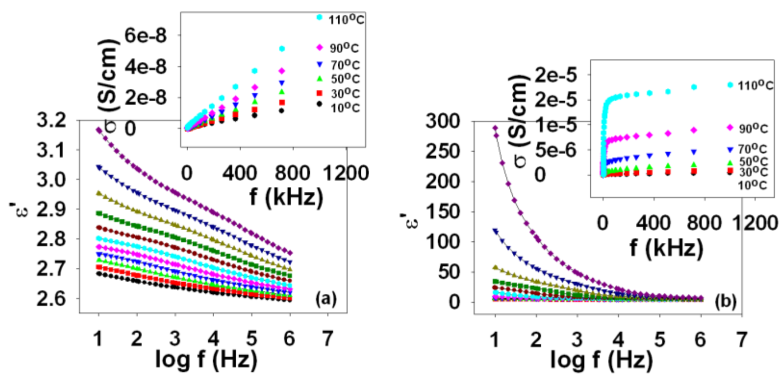

Figure 2. Variation of dielectric constant (ε') *vs.* frequency at different temperatures for: (a) PSFQ/PVA and (b) PSFQ/CAP blends. Inserted plot represent variation of electrical conductivity *vs.* frequency at different temperatures.

Increasing of the dielectric constant with temperature represents a consequence of enhanced polarization and a more intense oscillation of the molecules present in the films, while the dielectric constant decreases with increasing of frequency is due to dielectric dispersion, as a result of the molecules lagging behind the alternation of the electric field, at higher frequency [15]. Moreover, rapid decrease of ε' at higher temperatures is generated by the increase in chaotic thermal oscillations of the molecules and to the degree of dipoles orientation. According to Figure 1, the ε' value for PSFQ, is higher than for PVA and CAP. Thus, the electronic conjugations from the side chains of PSFQ contribute to the enhancement of ε' values. Instead, the decrease in ε' values for PVA and CAP may be attributed on the one hand, to the ability of macromolecules dipoles to orient themselves in the direction of the applied field in the low frequency range and, on the other hand, the inability of the dipoles to orient themselves in the direction of the applied field, in the high frequency range.

Over the 1-10^6 Hz frequency domain, the dielectric constant values of the pure components is reflected in those of the blends. Thus, ε' takes values in the 2.73-3.20 range for PSFQ/PVA blend (Figure 2a) and in 2.85-285.1 range for PSFQ/CAP blend (Figure 2b). In agreement with these remarks, influence of the composition of polymer blends and competition between the contributions the main chain and the pendant groups are reflected in the ε' values.

Also, the variation of electrical conductivity, σ, with temperature and frequency is dependent on the structural parameters of the samples. Conductivity presents a linear increase for a limited temperature domain (0.34 - 50.44°C) (see small graphs of Figures 1 and 2). This conduction takes place via localized hopping of carriers between randomly distributed trapping centers [16]. Generally, increasing temperature leads to an increase in electrical conductivity, with lower slope at high frequencies. Moreover, at higher frequencies, it is observed a deviation from linearity, which can be due to the dispersion of charge carriers produced by dipolar relaxation. On the other hand, electrical conductivity, besides electronic conduction is accompanied by an ionic conduction – generated by dimethylbutylamonium group from the PSFQ.

The results obtained from conduction studies showed that the conduction mechanism in the studied blends based on quaternized polysulfones was generated by the electronic hopping process, which can be explained in terms of band conduction mechanisms, through band gap representation.

Conclusion

The study realized on new blends of quaternized polysulfone/polyvinyl alcohol and quaternized polysulfone/cellulose acetate phthalate provides an insight into future approaches in industrial applications, due to the dielectric properties and conductivity and implicitly, electron interactions which represent fundamental features to enhance their electrical performance. The results obtained showed that the changes in the chemical structure and blends composition correlated to the dielectric behavior effect can provide information on the electronic and ionic conduction mechanisms and the molecular processes involving different relaxations. Consequently, the findings of this study demonstrate that the studied polymer blends may offer important advantages for membrane applications (*e.g.*, ionic exchange membranes).

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