Materials Chemistry and Physics 177 (2016) 442–454

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Optical and electronic properties of quaternized polysulfone/polyvinyl alcohol blends in relation to structure of the polymers

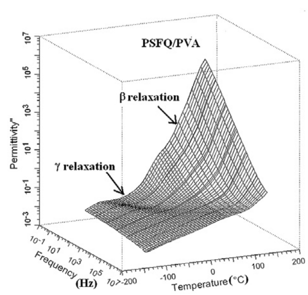
Luminita Ioana Buruiana*, Ecaterina Avram, Valentina Elena Musteata, Anca Filimon

Department of Physical Chemistry of Polymers, "Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania

HIGHLIGHTS

- New blend systems are investigated to evaluate the dielectric and optical behavior—chemical structure relationship.
- Evaluation of optical properties is reflecting transparent material characteristics.
- Correlation between optical and electrical parameters has been established.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 September 2015
Received in revised form
4 February 2016
Accepted 14 April 2016
Available online 26 April 2016

Keywords:
Polymers
Optical properties
Dielectric properties
Electrical conductivity

ABSTRACT

New blend system of quaternized polysulfone/polyvinyl alcohol was investigated, as to its optical and electronic properties. Optical properties were analyzed by refractivity and transmission spectra. In order to obtain optical parameters, an approach proposed by Tauc for amorphous semiconductors was used, because of the similarity of the absorption edges. At the same time, the frequency-dependent-dielectric properties and conductivity of these blends were studied. The dielectric constant takes low values for the studied blend, being dependent on the chemical characteristics of the blend compounds. The dielectric loss behavior exhibits two types of relaxation, γ and β, for the analyzed samples, being due to temperatures at which the two processes occur in the case of pure components. The results obtained from conduction studies showed that the conduction mechanism in the quaternized polysulfone/polyvinyl alcohol blend was based on the electronic hopping process, which can be explained in terms of band conduction mechanisms, through band gap representation. The outcomes of this work highlight the importance of new polymer blends for better electrical performances.

1. Introduction

Polysulfone (PSF), a transparent engineering thermoplastic, characterized by excellent thermal stability, good resistance to inorganic acids and bases, and good film formation property [1] is employed in a wide variety of applications from biomedicine to electronics, namely membranes for hemodialysis or gas separation, medical accessories (*i.e.*, surgical trays, nebulizers, humidifiers), and food processing equipment. Additionally, due to its excellent electrical properties is used in the electrical and electronics components, for example as a dielectric in capacitors [2–4]. Different configurations of polysulfones exhibit the transparency as an important property that, coupled with heat resistance and hydrolytic stability, makes them useful as research lab animal cages, flow

* Corresponding author.
E-mail address: luminitab25@yahoo.com (L.I. Buruiana).

http://dx.doi.org/10.1016/j.matchemphys.2016.04.051
0254-0584/

meters and sight glasses for chemical process equipments [5]. 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 polysulfones that allows a compromise between hydrophobicity and hydrophilicity, and, in this way, becomes suitable for the desired applications. Chemical modification of polysulfones – especially chloromethylation [6,7] and quaternization reactions [8] – arouses considerable scientific interest from theoretical and practical points of view, including their areas of applications. An important way to change some properties of the material (*e.g.,* solubility [9] or hydrophilicity [10]), which allows a better water permeability and separation [11,12], is represented by quaternization of the polysulfone backbone with tertiary amines. Although several studies have been done on characterization of quaternized polysulfones (PSFQ) [4,13–15], their electron conduction and stability can still be further improved. At the same time, the introduction of another polymer in the blend may lead to achieve desired properties for different electronics applications. Accordingly, polyvinyl alcohol (PVA) is a water-soluble synthetic polymer produced for its excellent chemical resistance, physical properties and complete biodegradability, which has led to broad practical applications [16]. It is a water-soluble polyhydroxy linear polymer, which contains two dimensional hydrogen-bonded network structures. Physical and chemical properties of PVA depend mostly on the method of preparation. Generally, PVA is obtained by polymerization of vinyl acetate to polyvinyl acetate, followed by hydrolysis of polyvinyl acetate to polyvinyl alcohol. Subsequently, it must be cross-linked by physical or chemical methods, in order to be suitable in the areas of medicine and pharmaceuticals sciences. The proved characteristics of binding PVA offer excellent adhesion to porous and water-absorbent surfaces. Recently, PVA employment has been evidenced in some specific medical applications, including contact lenses, catheters, wound dressings, local drug delivery systems, implantation, and synthetic cartilage in reconstructive joint surgery [17–20]. Also, other PVA uses were tested under experimental conditions like vascular grafts, artificial meniscus, and prosthetic intervertebral disk [21,22]; its application as a scaffold for biosynthetic cartilage is known in literature, as well [23,24].

Consequently, conductive polymer blends have attracted considerable attention due to their technological importance in a wide variety of applications such as materials for electrostatic charge dissipation [25], fuel cells [26] and embedded capacitors [27]. In this context by adding PVA to PSFQ matrix, it is desirable to get a conductive polymer blend with unique properties, which can be used as multifunctional materials for different applications. Although PSFQ/PVA blends were investigated recently for membrane application [28], no report is available concerning the effect of PVA on the dielectric and impedance of PSFQ/PVA blend system in the literature. In order to elucidate these aspects, modern techniques – like optic measurements and dielectric spectroscopy – are used for quaternized polysulfone/polyvinyl alcohol blend system (PSFQ/PVA).

Optical and electrical studies constitute the most convenient and sensitive methods for studying the polymer blend structure. These properties are influenced not only by the structure and nature of the polymers, but also by the concentration and preparation methods. The optical study provides important information about the absorbance and transmittance of the observed polymeric films [29]. Dielectric measurements – dielectric constant and dielectric loss – reveal significant information about the chemical and physical state of polymers. In this context, study of the dielectric relaxation provides valuable knowledge about the intermolecular interaction and, hence, the miscibility of the polymer blends [30]. Thus, it is possible to evaluate some key parameters, such as refractive index, absorption coefficient and dielectric constant on a wide frequency range. Moreover, for the determination of transparency properties and energies describing absorption edges, the method proposed by Tauc for amorphous materials can be applied, revealing the influence of polymer chain structure and structural disorder on the optical properties and probable electronic transitions. Therefore, the main objective of this study is to analyze and understand the polarization and conductivity mechanisms exhibit by PSFQ/PVA new blend systems, which display the desired conditions of transparency and improved electron interactions and conductivity, for better electrical performances. The study realized on new blend provides an insight into future approaches in industrial applications, due to the transparency, conductivity, and implicitly, electron interactions represent essential features to enhance their electrical performance. 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.

2. Experimental

2.1. Materials

Commercial polysulfone in powder form (UDEL-3500 – Union Carbide Company, Texas) ($M_n = 39{,}000$ g/mol; $M_w/M_n = 1.625$) was purified by repeated reprecipitation from chloroform (99.8% high purity, Fluka, Germany) and dried for 24 h at 40 °C, before being used in the synthesis of chloromethylated polysulfone (CMPSF) [31]. Subsequently, the ionic polysulfones containing quaternary ammonium side groups (PSFQ, $M_n = 28{,}000$ g/mol) were synthesized by reacting CMPSF (with a content in chlorine of 7.42% and $M_n = 29{,}000$ g/mol) 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 polymers were 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 ionic chlorine, ($Cl_i = 5.44\%$), and nitrogen ($N = 2.48\%$) contents, formed after the reaction of CMPSF with N,N-dimethylbutylamine, were determined analytically. Thus, the contents of ionic chlorine and total chlorine were determined by potentiometric titration (Titrator TTT1C Copenhagen), with 0.02 N $AgNO_3$ aqueous solutions. The ratio between the ionic chlorine and total chlorine contents shows 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 PVA used in this study was purchased from Celanese Corporation (Texas), having a hydrolysis degree around 98.8% and an average molecular weight of 23,000 g mol^{-1} with glass transition temperature at around 85 °C and melting point at 230 °C.

The general chemical structures of the two polymers here under study are presented in Scheme 1:

An accurate characterization of the chemical structure of quaternized polysulfones was performed by Fourier transform infrared spectroscopy (FTIR), using a Thermo-Nicolet-6700 spectrometer (Thermo Electron Corporation), and the ATR-FTIR spectra were recorded over the range 4000–500 1/cm. Additionally, to understand the formation process of the PSFQ/PVA blend and changes induced in polymer materials were analyzed and compared the features of the FTIR spectra prior and after PVA addition. Therefore, addition of PVA to quaternized polysulfone solutions, in order to