Maximizing Performance of the Membranes Based on Quaternized Polysulfone/Polyvinil Alcohol for Biomedical Applications: Rheological Investigations

A. Filimon, R. M. Albu, E. Avram

Abstract—The rheological response of blends obtained from quaternized polysulfone and polyvinyl alcohol in N-methyl-2-pyrrolidone as against structural peculiarity of polymers from the blend, composition of polymer mixtures, as well as the types of interactions were investigated. Results show that the variation of polyvinyl alcohol composition in the studied system determines changes of the rheological properties, suggesting that the PVA acts as a plasticizer. Consequently, rheological behavior of complex system, described by the nonlinear flow curve, indicates the impact of polyvinil alcohol content to polysulfone solution, in order to facilitate the subsequently preparation of bioactive membranes.

Keywords—Membranes for biomedical applications, quaternized polysulfone/polyvinyl alcohol composites, rheological properties.

I. INTRODUCTION

MEMBRANE technology has been used for decades in various separation and concentration processes due to its non-destructive character in separating various species without changing their molecular structures. Recent researches have been focused to control the membrane performance in terms of the selectivity and separation accuracy [1], [2], and to improve their properties, as antifouling and antimicrobial properties [3]-[5], biocompatibility [6], and environment stimuli responsive [7], etc.

Generally, synthetic polymers are commonly used as the basic materials for membrane preparation. In this context, polysulfones (PSFs) exhibit a complex of physicochemical properties, such as thermal stability, oxidation resistance, and stability over a wide range of pH values, which determines their remarkable applicability as material for the preparation of membranes use in industry and medicine. Despite its advantages, the intrinsic hydrophobicity of those materials often causes severe problems, *i.e.,* protein adsorption and platelet adhesion, leading to decreases the performance of PSF membrane. Therefore, a simpler and more effective route to generate surface reactive groups, which plays an important role in the assuring some properties required by different applications, is chemical modification of PSF, e.g., quaternization with ammonium groups. On the other hand, an ideal approach to improve the properties of membranes, by developing advanced membrane materials for the products of our everyday life, is represented by the polymer blend concept.

Achieving of novel polysulfone systems used in modern technologies involves choice suitable of the system components able to develop advanced properties for desired applications. In this context, polymer chains containing quaternary ammonium side groups have been prepared *via* the quaternization reaction of chloromethylated polysulfone (CMPSF) with N,N-dimethylbuthylamine (PSFQ) and also, polyvinyl alcohol (PVA) was selected for its excellent physical properties, as well as for its capacity to improve the performance of polysulfone membranes [8]. 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 different properties. Thus, the work focuses on research meant at improving the properties of PSFQ by introduction of PVA for obtaining advanced membrane materials used in biomedical fields.

This study will be very helpful for understanding mechanisms through which specific interactions, developed in polymer blends, affect the rheological behavior. As a result, these data lie at the basis of future investigations on blends performance for obtaining membranes with controlled porosity used in biomedical domains.

II. EXPERIMENTAL

A. Materials

Commercial polysulfone powder form (PSF, UDEL-1700), obtained from Union Carbide Company (Texas), was purified by repeated reprecipitation from chloroform (99.8% high purity, Fluka, Germany) and dried for 24 h in vacuum at 40°C, before being used in the synthesis of chloromethylated polysulfone (CMPSF) [9]. Subsequently, the ionic polysulfone containing quaternary ammonium side groups (PSFQ) was synthesized by reacting CMPSF with a tertiary amine, N,N-dimethylbutylamine (DMBA) [10]. The quaternization reaction was performed in N,N-dimethylformamide (DMF), 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

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temperature.

The characteristics of synthesized polysulfones are listed in Table I. Also, the general chemical structure of the quaternized polysulfone (PSFQ) is illustrated in Fig. 1.

Polyvinyl alcohol (PVA, Celvol, analytically pure) was purchased from Celanese Corporation (Texas), and also have been used as such. According to product specifications, Celvol PVA has a hydrolysis degree around 98.8 % and an average weight molecular weight, $M_n = 23\,000$ g/mol.
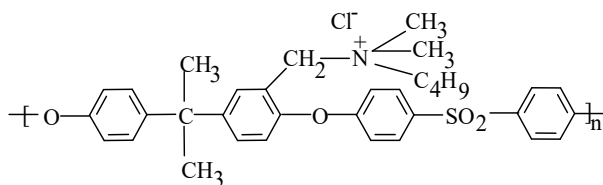
Fig. 1 Chemical structure of the monomer unit of polysulfone with quaternary groups (PSFQ)

TABLE I
CHARACTERISTICS* OF THE POLYSULFONE, CHLOROMETHYLATED, AND QUATERNIZED POLYSULFONES

Sample	DS	Cl (%)	Cl_i (%)	m_0	M_n (g/mol)
PSF	0	0	0	442.51	39 000
CMPSF	1.03	7.42	0	507.17	29 000
PSFQ	1.00	0	5.44	610.36	28 000

*Characteristics include substitution degree, DS, chlorine content, Cl, ionic chlorine content, Cl_i, molecular weights of structural units, m_0, and number-average molecular weights, M_n.

B. Methods

The rheological properties of PSFQ/PVA blends in NMP were determined on a CS50 Bohlin rheometer, manufactured by Malvern Instruments. The measuring system presents cone-plate geometry with a cone angle of 4° and a diameter of 40 mm. Shear viscosities were registered over the 0.07–3000 1/s shear rate domain, at a temperature of 25°C. In the controlled-strain test, the samples are deformed in oscillatory shearing flow until reaching a maximum strain, which is small enough to be in the linear regime. For all blends studied in the 0.5 − 10 Pa domain, the storage (G') and loss (G'') moduli are independent on shear stress. Therefore, a shear stress of 2 Pa was selected in order to perform oscillatory shear measurements in the linear viscoelastic region. During the oscillatory shear tests, frequency was varied between 0.1 and 100 Hz. Rheological tests were obtained with an accuracy of ± 5 %, for different measurements.

III. RESULTS AND DISCUSSIONS

A. Flow Behavior of PSFQ/PVA/NMP Complex System

Ionic polymers represent an important class of chemical compounds, due to their 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. Therefore, the study of solution dynamics of polyelectrolytes is necessary to gain insight into many biological and industrial processes.

It is well known that the rheological behavior of blends is influenced by the structural properties of the blend polymers (e.g., the charge density and size of polycation, hydrophilic/hydrophobic nature), their mixing rations, and the solvent used. In accord with these remarks, the flow behavior of pure components (PSFQ and PVA) and of their blends in NMP, where a complex behavior appears under specific conditions of blend composition, was observed from the dynamic viscosity - shear rate dependence (Fig. 2).
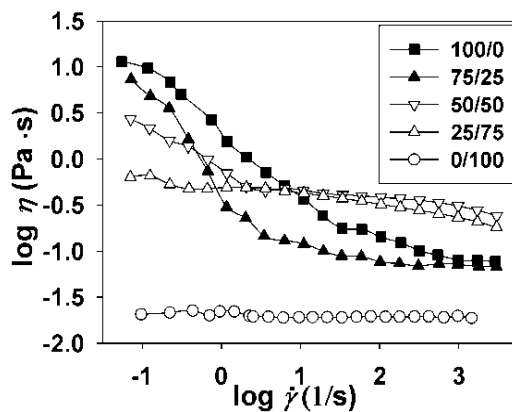
Fig. 2 Double logarithmic plot of dynamic viscosity *versus* shear rate for PSFQ/PVA blend in different mixing ratios at 25°C

Examination of flow curves (Fig. 2) reveal that, for pure PSFQ and blends with a higher amount of PVA (i.e., 50/50 and 25/75 wt./wt. PSFQ/PVA blends), a shear thinning behavior at low shear rate, while pure PVA and 75/25 wt./wt. PSFQ/PVA blend exhibit a Newtonian behavior over the entire shear rate domain. Thus, introduction of PVA over the 0.25 weight fractions, led to an increase of dynamic viscosity on the low shear rates domain, and a decrease in viscosity with increasing shear rate. At the same time, it is observed that, as shear rate increases, the slope of curves decreases, and a Newtonian plateau appears. In this context, one can conclude that these blends possess properties of pseudoplastic materials, characterized by reduced entanglement density and enhanced number of oriented segments, as a result of increasing shear rates [11]. Moreover, it is found that addition PVA in the studied system generates the specific molecular rearrangement of the system, suggesting that it acts as a plasticizer. Presence of a plasticizer in a polymeric system causes an increase in system flexibility [8], [12] and in addition, specific interactions developed by hydrogen bonding decrease chain mobility [13].

B. Inter- and Intra-molecular Interactions in PSFQ/PVA/NMP System

The flow activation energy, E_a, (Fig. 3) is influenced by the interactions between the chain segments of polymers in the presence of solvent. This parameter is evaluated from Arrhenius equation [14] (1) and derived from the dependence of dynamic viscosity on temperature.

$$\ln \eta = ln\,\eta_0 + \frac{E_a}{RT}. \tag{1}$$

where $\eta_0 \sim e^{\Delta S/R}$ represents a pre-exponential constant [15] and ΔS is the flow activation entropy, R is the universal gas constant, T, and is the absolute temperature.

Similar to dynamic viscosity, the nature of the functional groups from PSFQ and PVA, and also by the PVA content and solvent, affect the activation energy. Thus, the value of E_a for PSFQ in NMP is lower than for PVA in NMP, due to the flexibility slightly lower of the PVA chains, comparatively with the PSFQ chain. Instead, for 25/75, 50/50 and 75/25 wt./wt. mixing ratios of PSFQ/PVA blend, the values of E_a are influenced by the rigidity or flexibility of the polymeric chains, and also by the competition between intra- and intermolecular interactions. Thus, addition of PVA (polymer (2)) to the PSFQ solution (polymer (1) in NMP) favors intermolecular interactions (polymer (1) – polymer (2) interactions), while the PVA chains dissolved in NMP exhibits association phenomena as a result of hydrogen bonding. On the other hand, the hydrophilic or hydrophobic characteristics of polymers influence the compatibility in NMP, generating molecular restructurations in solution, under the influence of hydrogen bonding and association phenomena. The effect of the different thermodynamic interactions from the system, such as hydrogen bonding, association phenomena, ion-ion pairing, and electron-donor and electron-acceptor interactions, which generate miscibility between components, modified the rheological behavior in solution. Thus, it is relevant that the rheological properties are influenced by polymers characteristics, which permit limitation of compatibility and a well-established compatibility domain. Analysis of the dynamic viscosity dependence on composition (the small graphs of Fig. 3) shows different miscibility domains with minimum and maximum values, resulting from the competition among different thermodynamic interactions. Consequently, the results allow us to conclude that these blends are optimum and possess specific properties that make them suitable for future investigations on obtaining of membranes used in biomedical applications.

C. Viscoelastic Behavior of PSFQ/PVA/NMP Complex System

Viscoelastic measurements can significantly contribute to the knowledge and differentiation of polymer systems, completing the rheological studies developed in shear regime. Monitoring the visco-elastic transition was performed by following the viscoelastic parameters (storage modulus, G', and loss modulus, G'' – Fig. 4) during the physical entanglements and/or chemical crosslinks of quaternized polysulfone and polyvinyl alcohol chains in NMP.
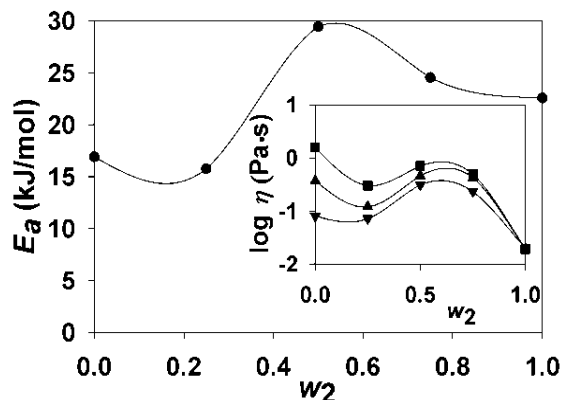

Fig. 3 Activation energy as a function of the PVA weight fraction for PSFQ/PVA blend at 25°C. The small graphic represent the variation of dynamic viscosity as a function of the PVA weight fraction at 25°C and different shear rates (1/s): (■) $\log \dot{\gamma} = -0.155$, (▲) $\log \dot{\gamma} = 1.037$, (▼) $\log \dot{\gamma} = 2.988$
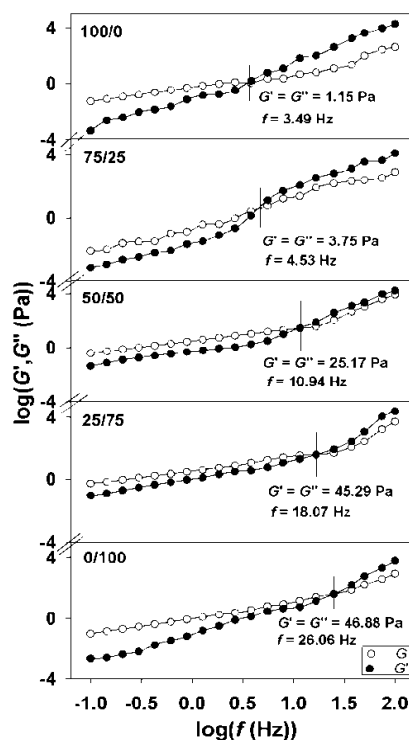

Fig. 4 Double-logarithmic plots of storage G' and loss G'' moduli versus oscillatory frequency (f) for PSFQ/PVA blend at various mixing ratios at 25 °C

Fig. 4 shows the rheological response over the studied frequency regime by the gradual addition of PVA; over the low oscillation frequency range, all investigated blends behave as viscous liquids (the loss modulus being always higher than the storage one, $G'' > G'$), as a result of unrecoverable viscous loss. At high frequencies, the storage (G') modulus becomes higher than the loss (G'') modulus; the solid-like character becomes predominant and determines reversibility of the

energy stored in the sample, as a result of the number and strength of interactions from the system [16]. Generally, over this range, the storage and loss moduli exhibit a power-law dependence on frequency, where $G' \sim f^2$ and $G'' \sim f^1$, respectively, being characteristic to viscoelastic fluids [17]. This dependence was observed for PSFQ/PVA blend compositions where G' and G'' are proportional to $f^{1.59 \div 2.08}$ and $f^{0.90 \div 1.02}$, respectively. These exponents decrease as PVA composition in the systems increases, as a result of specific interactions, hydrogen-bonding and association phenomena, according to the above-mentioned assertions concerning dynamic viscosity and activation energy.

Moreover, the influence of the structural characteristics of PSFQ and PVA and of the used solvent is also reflected in the crossover frequency values (f_c) for which $G'=G''$. One can remark that the crossover frequencies exhibit lower values for PSFQ in NMP, which become higher when the PVA content in the polymer blends increases; consequently, appearing as strongly related to the chemical structure of polymers, reflecting the influence of flexibility. These results are due to the specific interactions and to some association and structural phenomena.

IV. Conclusion

Influence of the structural characteristics of polyelectrolyte (PSFQ) and neutral polymer (PVA), composition of mixed polymers, used solvent, and also of specific interactions between components mixtures are reflected on the rheological properties, by means of the dynamic viscosity, thermodynamic and viscoelastic parameters. Specific interactions and association phenomena present in the complex system were discussed in correlation with rheological data, induced by the effects of shear flow. The results can be summarized as follows:

- the Newtonian and thinning behavior is reflected from the flow curves;
- PVA acts as a plasticizer in the studied system, determining the specific molecular rearrangement of the system;
- the values of flow activation energy are generated by the rigidity or flexibility of the polymeric chains, and also by the competition between intra- and intermolecular interactions;
- the shear moduli exhibit a power law dependence on frequency, where exponents are characteristic to viscoelastic fluids, and the frequency corresponding to shear moduli overlapping increases with increasing the PVA content.

Study has demonstrated that the investigated blends may provide some important advantages in specific applications. Consequently, these results lie at the basis of future investigations on blends performance for obtain of membranes with controlled porosity used in biomedical domains.

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