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**RESEARCH PROJECTS FOR ENCOURAGING ESTABLISHMENT
OF YOUNG INDEPENDENT RESEARCH TEAMS**

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**HIGH PERFORMANCE POLYMERIC BIOMATERIALS BASED ON
FUNCTIONALIZED POLYSULFONES
WITH MEDICAL APPLICATIONS**

- 2014 -

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BRIEF REPORT

***concerning the results obtained by the project team between December 16th, 2013 –
December 15th, 2014***

Objectives and activities proposed for Stage II - 2014:

Objectiv 4. *Characterization of composites/blends based on functionalized polysulfones films*

Activities: 4.1. Establishing the hydrophobic/hydrophilic balance by studying surface tension and free energies of hydration;

4.2. Determinations of absorption limits, the dielectric properties and conductivity in a wide range of frequencies and temperatures.

Objectiv 5. *Optimization of properties in solution and solid state to obtain semipermeable composite membranes*

Activity: 5.1. Establishing of some additives for the hydrophilicity control and increasing performance of the semipermeable membranes

Objectives and activities performed.

All activities proposed for this stage were performed and are briefly presented in this report.

The research theme of the project for stage II (2014), aims obtaining and characterization of composite films with the controlled porosity and hydrophilicity for biomedical applications, considering the transparency and film-forming properties of the studied polymers (Objective 4 and 5 - partially).

4.1. Establishing the hydrophobic/hydrophilic balance by studying surface tension and free energies of hydration

The phenomena that occur at the interfaces present technological importance and constitute a fundamental theoretical problem. Study of the interfacial properties, such as the excess interfacial free energy and excess entropy of the surface provide information on the molecular interactions. In this context, the development of new complex polymeric systems for applications in modern technology involves the suitable selection of the system components, capable to develop complex properties for desired applications.

Hydrophobicity/hydrophilicity of the surface can be correlated with the flexibility degree of the polymer. It is known that, the flexible polymers are more able to form membranes used in biomedicine, than the rigid ones, because it possess a better biocompatibility. Good compatibility is dictated by the surface hydrophilicity. From this reason, the evaluation of the hydrophobic/hydrophilic balance is indispensable in the study of the compounds used as biomaterials with medical application.

In the context of the above-mentioned, changes in the polarity that occur on the surface polymeric films - formed from pure polymers (quaternized polysulfone - PSFQ, cellulose acetate phthalate - CAP and polyvinyl alcohol - PVA) and their mixtures in different compositions, respectively - were evaluated knowing the contact angle values measured at the polymeric surface - different liquid test interface (Table 1)¹, and the surface tension parameters of liquids test used (Table 2)^{2,3}. Evaluation of the surface energy allows the analysis of the surface tension according to the surface tension components generated by the synergistic effects of the polar forces, disperse (van der Waals) and hydrogen bonds, according to the Equations (1) - (3) (Table 3).

$$1 + \cos \theta = \frac{2}{\gamma_{lv}} \left(\sqrt{\gamma_{sv}^{LW} \gamma_{lv}^d} + \sqrt{\gamma_{sv}^+ \gamma_{lv}^-} + \sqrt{\gamma_{sv}^- \gamma_{lv}^+} \right) \quad (1)$$

$$\gamma_{sv}^{AB} = 2\sqrt{\gamma_{sv}^+ \gamma_{sv}^-} \quad (2)$$

$$\gamma_{sv}^{LW/AB} = \gamma_{sv}^{LW} + \gamma_{sv}^{AB} \quad (3)$$

where: θ is the contact angle determined for the liquids test used, the subscript "lv" and "sv" indicates the interfacial tension at the liquid-vapor and polymer-vapor surfaces, the superscript "LW" or "d" and "AB"

indicates disperse and polar components obtained from the electron-donor γ_{sv}^- and electron-acceptor γ_{sv}^+ interactions and $\gamma_{sv}^{LW/AB}$ represent the total surface tension.

Table 1. Contact angle measured at the surface polymer-vapor interface (°) for functionalized polysulfone/cellulose acetate phthalate and functionalized polysulfones/ polyvinyl alcohol composite systems

Polymer/ System	Contact angl		
	Water	Diiodomethane	Bromonaphthalene
PSFQ	79	35	12
CAP	55	33	16
PVA	40	30	10
PSFQ/CAP			
75/25	60	34	17
50/50	60	42	16
25/75	55	33	10
PSFQ/PVA			
75/25	74	37	18
50/50	71	29	17
25/75	60	30	16

Table 2. Disperse and polar components of the surface tension (mN/m) of the liquid test used in contact angle evaluation

Liquid test	γ_{lv}	γ_{lv}^d	γ_{lv}^p	γ_{lv}^-	γ_{lv}^+
Water	72.80	21.80	51.00	25.50	25.50
Diiodomethane	48.00	29.00	19.00	47.00	1.92
Bromonaphthalene	44.40	44.40	0	0	0

For analyzed systems, the contact angle values are influenced by the polyion charge density, structural particularities of the polymers and polymer blends composition, as shown in Table 1, which presents the results for relatively hydrophobic surfaces (with high contact angles) transformed in hydrophilic surfaces (with low contact angles) by changing the composition of the studied mixtures.

Table 3. Surface tension parameters (mN/m): disperse, γ_{sv}^{LW} , and polar γ_{sv}^{AB} , components of the total surface tension, $\gamma_{sv}^{LW/AB}$, and electron-donor γ_{sv}^- and electron-acceptor γ_{sv}^+ parameters, according to acid-base method (LW/AB) for studied composite films

Polyme/ System	LW/AB method				
	γ_{sv}^{LW}	γ_{sv}^{AB}	γ_{sv}^+	γ_{sv}^-	$\gamma_{sv}^{LW/AB}$
PSFQ	43.77	3.91	10.45	0.370	47.68
CAP	42.73	6.42	23.59	0.440	49.15
PVA	44.57	7.75	38.58	0.390	51.81
PSFQ/CAP					
75/25	43.78	0.13	24.13	0.002	43.91
50/50	42.73	2.73	18.60	0.100	45.46
25/75	42.51	4.47	20.17	0.250	46.98
PSFQ/PVA					
75/25	42.58	3.57	14.45	0.220	46.14
50/50	42.81	6.74	3.99	2.850	46.80
25/75	43.03	9.43	13.44	1.650	52.46

Modification of the surface wettability characteristics can be explained by:

- intensification of the repulsive intramolecular interactions between the ammonium groups (electrostatic interactions generated by quaternary ammonium group of PSFQ). From the obtained results, it can be assumed that the predominant electrostatic interactions are those repulsive, who reject the polar groups from the surface;
- the chemical structure of the CAP or PVA neutral polymer (higher polarity of PVA compared to that of CAP) responsible for the formation of the intramolecular hydrogen bonds;
- the conformational change of the polymers from blend, as well as the cumulative effects of the electrostatic interactions, intramolecular hydrogen bonds and of association phenomena manifested at different mixing ratios;
- the effect of chain orientation and the rearrangement of the polar groups from the film surface after the mixing process, because the mechanical mixing forces the polar groups from the film surface to shift, leading to modifications of the local polar moments;

- increasing of the dispersive character of the surfaces due to intensification of the *London* dispersion forces (generated by fluctuations of the electron density in non-polar molecules and attractions between the instant dipoles created) and *Debye* dispersion forces (dipole forces between the permanent dipoles and induced dipoles).

Knowledge of the balance between the hydrophilic and hydrophobic properties of the surfaces via contact angles is essential in the applications of the composite systems based on the functionalized polysulfones. Therefore, the capacity of wettability and the hydrophobic/hydrophilic balance of the studied composite films represent the measure of the free energy of hydration, ΔG_w , parameter calculated according to the Equation (4), using the surface tension of water, γ_{lv} , and the contact angle values, evaluated at the surface polymer – water interface, from Table 1. The results thus obtained, are shown in Figure 1, and support the previous conclusions in which it stated that the chemically modified polysulfone with N, N-dimetilbutilamine groups (PSFQ) is less hydrophilic than the CAP and PVA, respectively, and after the mixing, the hydrophilicity degree increases as the amount of the CAP and PVA from the mixture increases (the effect of chain orientation and the rearrangement of the polar groups from the film surface).

$$\Delta G_w = -\gamma_{lv}(1 + \cos \theta_{apa}) \quad (4)$$

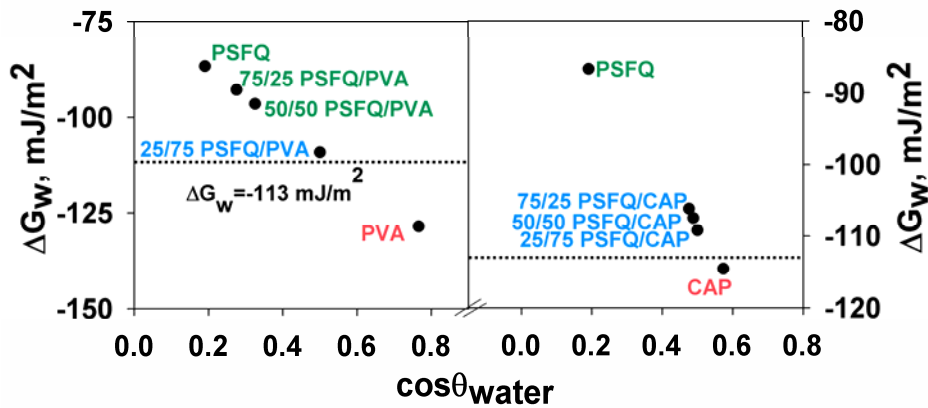


Figure 1. Surface free energy *versus* contact angle of water for studied composite films

Generally, the literature^{4,5} mentions that the surface polymer can be considered more hydrophilic for $\Delta G_w < -113 \text{ mJ/m}^2$, whereas, when $\Delta G_w > -113 \text{ mJ/m}^2$, it should be considered more hydrophobic. Thus, the negative values of the surface free energy generally reveals an increasing trend of wettability, and implicitly a high hydrophilicity, property necessary for biomedical applications.

In conclusion, the surface properties, as well as the establishing of the hydrophobic/hydrophilic balance are very important in the mentioned domains, existing the possibility to adjust them by chemical modifications or mixing process to match to proposed goal.

4.2. Determination of absorption edges, dielectric and conduction properties, on a wide range of frequency and temperature

Influence of polymer structures on the transmission spectra and optical energies

Materials transparency represents a key feature for obtaining optical performances used in specific applications. Typical transmission spectra of pure polymer films, PSFQ, PVA, CAP, and, also of the 60/40 (v/v) composition of PSFQ/PVA and PSFQ/CAP blend films, prepared from NMP solution, over the 200-1100 nm range wavelengths, are shown in Figure 2.

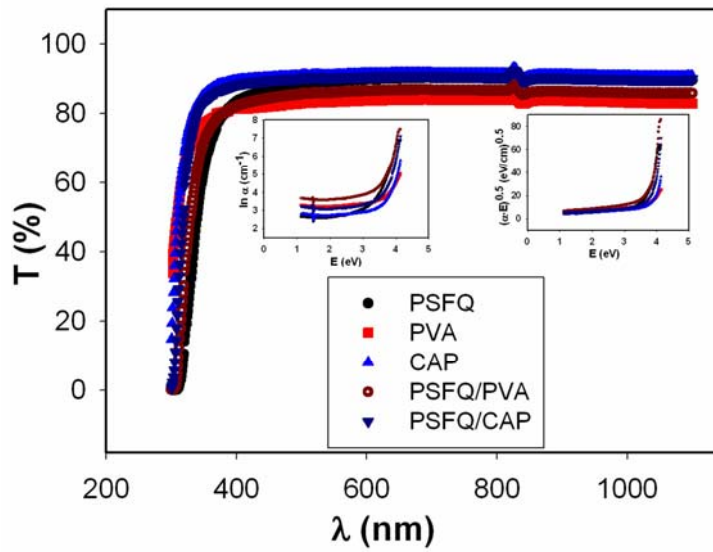


Figure 2. Typical overall transmission spectra of polymer films obtained from NMP solutions. Small plots represent the absorption coefficient and Tauc dependence, respectively, *versus* photon energy for the same films⁶

One can observe that for all studied samples, the transmission spectra, initiated in the ultraviolet domain - towards higher wavelengths, present a high transparency value of about 85%.

Equation (5) is used for obtaining the absorption coefficient, α (Figura 2) from transmittance data, for all studied polymers:

$$\alpha = (1/d) \ln(1/T) \quad (5)$$

where d is film thickness.

Generally, for a typical amorphous semiconductor, three domains are distinguished in the variation of the absorption coefficient *versus* photon energy⁷, as follows:

- the first region is characteristic to the optical gap energy, E_G , in amorphous semiconductors, being described by the absorption coefficient, due to interband transition near the bandgap;
- the second region is characterized by the Urbach edge energy, E_U - defined as absorption at photon energy below the optical gap - that depends exponentially on photon energy. In semiconductors, the exponential edges are due to the electric fields produced by charged impurities;
- the third region is characterized by E_T energy, the so-called Urbach tail, which describes the optical absorption generated by the defects that appear at an energy lower than the optical gap. This energy, referring to the weak absorption tail, describes the state defects, being rather sensitive to the structural properties of the materials. This absorption tail lies below the exponential part of the absorption edge, its strength and shape being dependent on the preparation, purity and thermal history of the material, varying only slightly with its thickness.

The shape of Urbach curves is similar to the behavior proposed by Tauc for a typical amorphous semiconductors^{8,9}, although the absorption level is lower than for amorphous, inorganic thin films. These results agrees with other literature data, which assume that a lower absorption in polymer materials is due to a lower degree of bonding delocalization^{10,11}.

Urbach energies for polymer films with higher transparency were obtained in 240-317 meV range, while for PSFQ films that are less transparent, value of Urbach energy being smaller (218 meV). At the same time, E_T energy values of CAP and PVA samples are higher than for PSFQ; for their blends this parameter values are 637 meV for PSFQ/PVA and 599 meV for PSFQ/CAP, respectively.

Table 4. Optical parameters of the quaternized polysulfone, polyvinyl alcohol, cellulose acetophthalate and 60/40 content of their blends

Sample	d (mm)	E_T (meV)	E_U (meV)	E_G (eV)
PSFQ	0.078	657	218	3.78
PVA	0.070	667	317	3.54
CAP	0.060	741	231	3.44
PSFQ/PVA	0.040	637	289	3.68
PSFQ/CAP	0.043	599	240	3.72

These two parameters are related to the localized state induced by the polymeric atomic structures. Possible structural defects, such as breaks, configurational imperfections or torsions of the polymer chains are responsible for the energy described by the Urbach tail energy. Moreover, larger structural disorders may cause an increase of the Urbach energy and E_T parameter. In this context, the presented data point out that

E_U and E_T take lower values for PSFQ films in comparison with the other two polymers. This results can be attributed to the different structure of the studied polymers.

Variation of dielectric constant with frequency and temperature

Dielectric properties for PSFQ, PVA, CAP samples and their blends, were emphasized by dielectric measurements in the 1 Hz-10⁶ Hz frequency range and the -120⁰C and +120⁰C temperature range⁶. Figure 3 presents dielectric constant (permittivity, ϵ') versus frequency at different frequencies, for PSFQ, PVA and CAP, while in Figure 4 is represented dielectric constant for PSFQ/PVA and PSFQ/CAP blends.

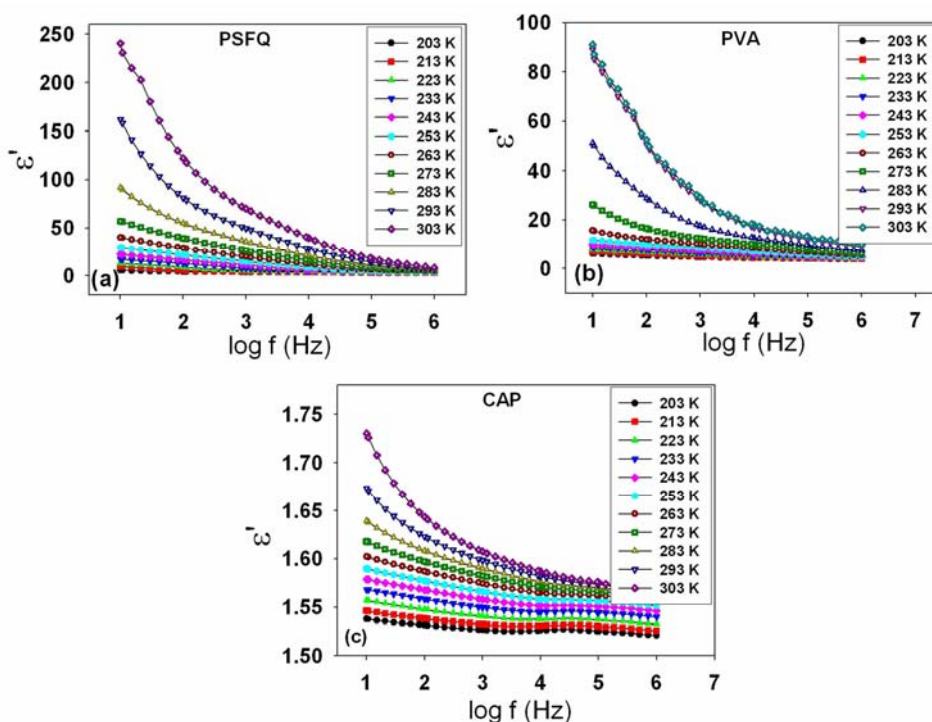


Figure 3. Frequency dependent dielectric constant, at different temperatures for: (a) PSFQ, (b) PVA and (c) CAP

Dielectric constant increases with increasing temperature, due to the enhancement of total polarization, arising from dipoles orientation and trapped charge carriers, and, at the same time, decreases with increasing frequency due to dielectric dispersion, as a result of molecules lagging behind the alternation of the electric field, at higher frequencies¹².

For PSFQ samples, the dielectric constants value is higher than for other polymers; that depends on the main chain and the pendant groups, a competition between these two contributions being observed. Thereby, the electronic conjugations from the side chains contribute to the enhancement of the dielectric constant values¹³. These higher values of dielectric constant caused by quaternized polysulfone are more obvious in the case of PSFQ/CAP (Figure 4).

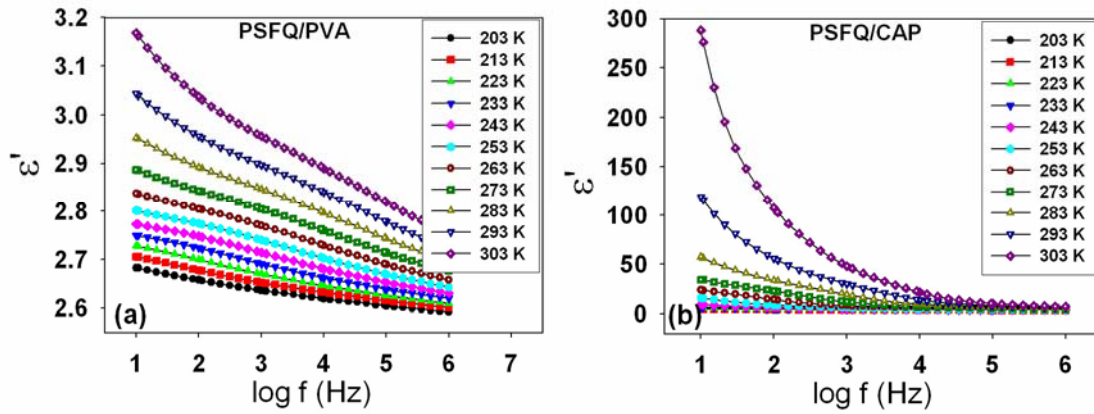


Figure 4. Frequency dependent dielectric constant, at different temperatures for: (a) 60/40 PSFQ/PVA and (b) 60/40 PSFQ/CAP blends

Variation of dielectric loss with frequency and temperature

Figures 5 and 6 show tridimensional variation of dielectric loss, ϵ'' , with frequency and temperature for PSFQ, PVA, CAP samples and their blends. One can observe that the main contribution to dielectric relaxation appears in the frequency range used only for the side groups motion, no contribution from the backbone of the main chain being noticed⁶. In the dielectric relaxation spectrum, two types of relaxation (γ and β) in the $-120\text{ }^{\circ}\text{C}$ și $120\text{ }^{\circ}\text{C}$ temperature range, are observed. These processes are named secondary or local relaxations.

Generally, polymer films are characterized by the following relaxation processes¹⁴:

- α relaxation (or glass transition) arise at high positive temperatures, being caused by the rotatory diffusional motion of the molecules from one quasi-stabile position to another around the skeletal bond; it involves large-scale conformational rearrangement of the main chain. The α relaxation does not appear in the studied range of temperature for the analyzed polymers;

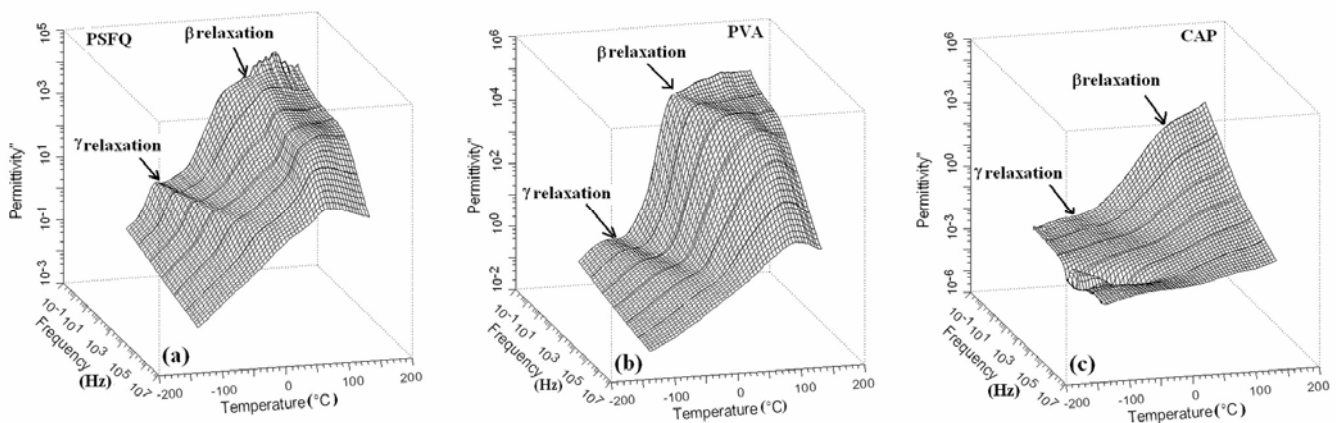


Figure 5. Dependence of dielectric loss of frequency and temperature for: (a) PSFQ, (b) PVA and (c) CAP

- β relaxation (secondary relaxation) appears at higher temperatures than α relaxation, being caused by the micro-Brownian motion of the main chain segments, due to the flexibility of their molecules; this process imply localized and intermolecular motions;
- γ relaxation (secondary or local relaxation) appears at negative temperatures, being attributed to molecular units motions lower than those for β relaxation.

In this context, according to Figure 5 (a), γ relaxation for PSFQ is noticed at low temperatures (i.e., $-115 \div -90$ °C) for different frequencies, while β relaxation appears at 90 °C and high frequencies. One can say that polysulfone side chain produces on the one hand a decrease in the interchain attraction manifested in the starting chloromethylated polysulfone and, on the other, imparts skeleton rigidity. Generally, the behavior of β process corresponds to a localized and cooperative molecular origin, as intra/intermolecular contribution effect.

Figure 5 (b) illustrates γ relaxation for PVA at low temperatures ($-105 \div -80$ °C), and β relaxation at 70 °C temperature. The local-mode γ relaxation of the main chain involves a localized and noncooperative spectrum of motions. For CAP, γ relaxation arises at $-100 \div -80$ °C temperature range, while β relaxation appears very weak at 70 °C and high frequencies, and becomes almost indistinguishable at lower frequencies (Figure 5 (c)).

Figure 6 (a) and (b) evidences two types of relaxations that appear for blend samples, such as: PSFQ/PVA blend present γ relaxation at approximately -100 °C, and β relaxation appears very weak at 80 °C, while for PSFQ/CAP blend sample γ local relaxation appears at -90 °C, and β relaxation at 80 °C. As a conclusion, relaxations temperatures that occur in the case of blend samples are due to the temperatures at which the two processes occur in the case of pure components.

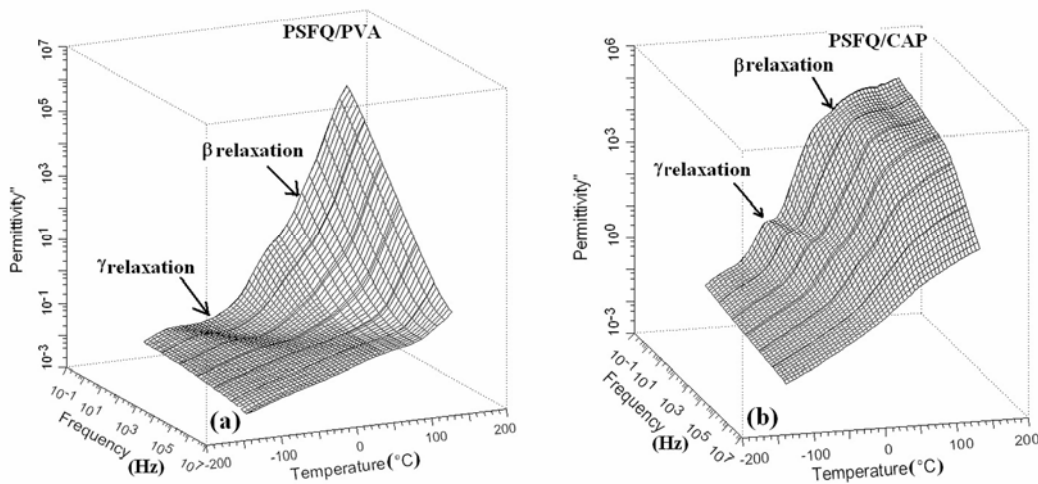


Figure 6. Dependence of dielectric loss of frequency and temperature for: (a) 60/40 PSFQ/PVA and (b) 60/40 PSFQ/CAP

Electrical conductivity properties

Polarization mechanism due to migration of electric charges represents the basis of conductivity. The conductivity process studied by dielectric spectroscopy takes into account both contribution from *extrinsic* migrating charges (ionic impurities) and *intrinsic* migrating charges (proton transfers along hydrogen bonds). Extrinsic conductivity is assumed to be inversely proportional to viscosity according to the viscous model for charge transfer (Stokes law), implying that materials with high viscosity should exhibit zero conductivity. This means that the origin of conductivity in highly cross-linked polymer networks could be attributed, at least partially, to the intrinsic migrating charges¹⁵.

Variation of conductivity, σ , with frequency at different temperatures is depicted in Figure 7 for PSFQ, PVA, CAP samples, and, in Figure 8 for PSFQ/PVA and PSFQ/CAP blend films⁶. It is known that the conductivity of many substances is governed by the $\sigma \propto f^n$ dependence. The n exponent decreases with increasing temperature for all studied samples, generally occurring within the $0.5 < n < 1$ limits, for a limited domain of temperature. The n values lower than the unity characterize electronic conduction *via* a hopping process, being in accordance to results obtained for amorphous materials^{16,17}. Deviation from linearity at higher frequencies is generated by the dispersion of charge carriers, being produced by dipolar relaxation.

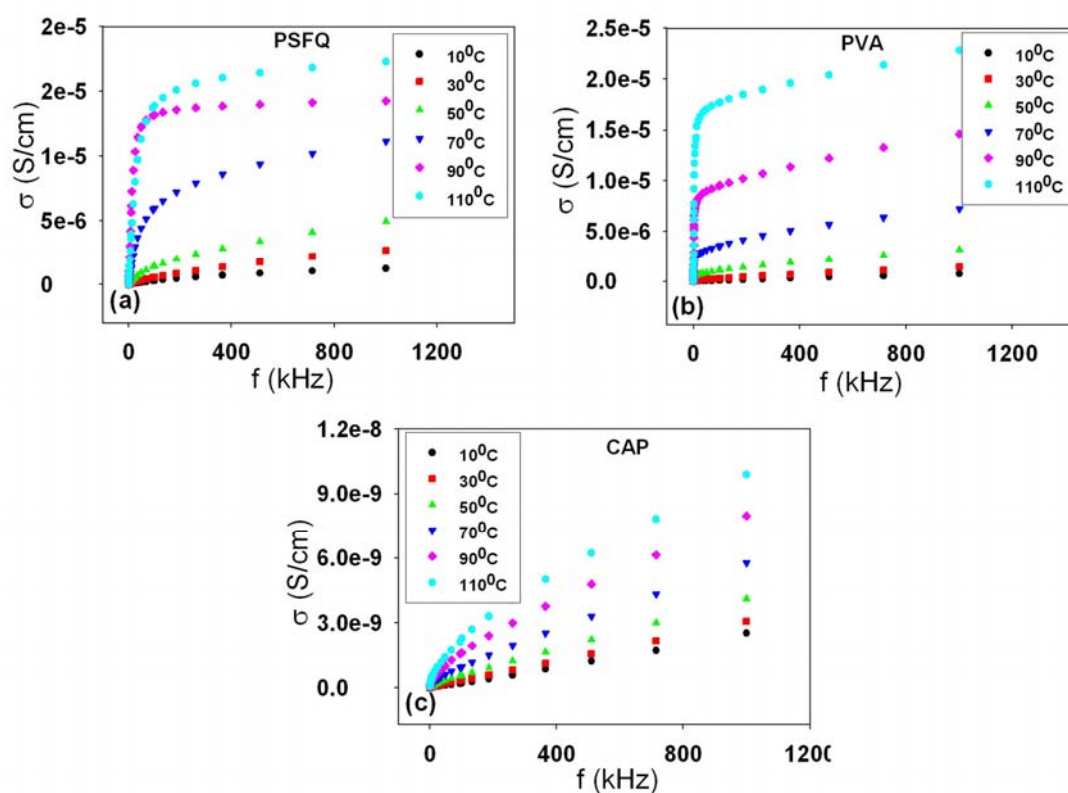


Figure 7. Frequency dependence of electrical conductivity at different temperatures for (a) PSFQ, (b) PVA, (c) CAP

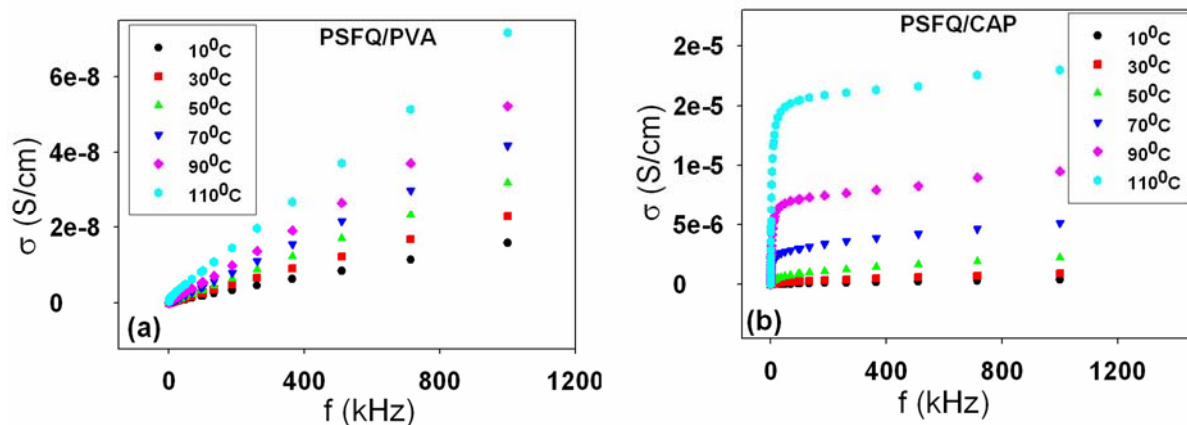


Figure 8. Frequency dependent conductivity at different temperatures for: (a) 60/40 PSFQ/PVA and (b) 60/40 PSFQ/CAP blend films

Generally, temperature increasing leads to an increase in electrical conductivity, with lower slope at high frequencies, for all studied samples. In this context, the electrical conductivity of the studied samples can be explained in terms of band conduction mechanisms, through bandgap representation.

For quaternized polysulfone, electronic conduction is accompanied by ionic conduction – due to quaternized groups from the side chain. According to literature data¹⁸, the higher slopes correspond to intrinsic electrical conduction, while the decreasing slopes at lower temperatures denote a reduction in the impurity concentration of the samples.

As a conclusion, the findings of these studies can constitute the origin for obtaining performant, semipermeable membranes used in biomedicine, taking into consideration their adhesion, hydrophilicity, compatibility, flexibility and transparency properties.

Objectiv 5. Optimization of properties in solution and solid state to obtain semipermeable composite membranes

5.1. Establishing of some additives for the hydrophilicity control and increasing performance of the semipermeable membranes

The membranes technology has been developed as a consequence of applications which imposed the specific shapes and sizes. The development of the synthetic membranes is very important, because it allows the selective transport by biological membranes, using certain macromolecules and supramolecular assemblies. It is well known that, due to optical, mechanical and chemical properties, and also, of the film-forming properties, *polysulfones* are included in the category of *membrane materials*, and, by their

functional properties, represent some of the best materials used in many areas of everyday life¹⁹⁻²⁵. The chemical modification of polysulfones (for example, functionalization with tertiary amines leads to quaternary ammonium side groups) plays an important role in establishing some properties required by the different applications. Quaternary ammonium groups modify hydrophilicity (which is of special interest for biomedical applications)²⁶, the antimicrobial action²⁷ and solubility characteristics^{28,29}, thus allowing higher water permeability and better separation.

Due to the complexity of the aspects connected with chemistry, kinetics and thermodynamics of the implied physico-chemical processes involved in the study polysulfones, despite the previous research efforts presented in the literature, there are question marks, or new fields insufficiently explored, especially when structure-properties-new utilization field correlation must be established. The products designed for biomedical purposes can be improved by creation of new structures in synthetic processes, as well as preparation of macromolecular composites/blends which combines various properties, in accord with the proposed objective. In this context, the project aims to investigate new aspects of polysulfones compounds with applications in medicine, other than those reported in the literature. Therefore, we propose an alternative approach to achieve composites/blends through the use of different "additives" to generate pores within the polymer matrix and improve membranes performance.

The expected results for obtained composites/blends, functionalized polysulfones/synthetic additive, concerning the flexibility, transparency, free energy of hydration and balance between hydrophilicity and hydrophobicity surfaces, prefigures the existence of some specific characteristics that recommend them for manufacturing membranes with biomedical applications. Thus, studies in solution will offer the opportunity to determine the blends optimal compositions, which allow obtaining of membranes with controlled pore size. Consequently, the choosing of pore-forming "additives" or "porogen" is an important tool proposed by us to control the morphological and porous properties needed to obtain membranes with biomedical applications.

Bibliografie

1. A. Filimon, E. Avram, E. G. Ioanid, *Coll. Surf. B, Biointerfaces*, under review 2014.
2. R. J. Good and C.J. van Oss, *Wettability*, Plenum Press, New York, 1992.
3. C. J. van Oss, *J. Mol. Recognit.*, 16, 177, 2003.
4. W. Wu, R. F. Jr. Giese, C. J. van Oss, *Langmuir*, 11, 379, 1955.
5. R. S. Faibish, W. Yoshida, Y. Cohen, *J. Colloid Interface Sci.* 256, 341, 2002.
6. L. I. Buruiana, A. Filimon, E. Avram, S. Ioan, *Polymer*, under review 2014.
7. L. I. Buruiana, E. Avram, A. Popa, V. E. Musteata, S. Ioan, *Polym. Bull.* 68, 1641, 2012.
8. J. Tauc, A. Menth, D. L. Wood, *Phys. Rev. Lett.* 25, 749, 1970.
9. J. Tauc, A. Menth, *J. Non-Cryst. Solids*, 8-10, 569, 1972.
10. B. Jarzabek, J. Wieszka, A. Burian, G. Poczrowski, *Thin Solid Films*, 279, 204, 1996.
11. B. Jarzabek, E. Schab-Balcerzak, T. Chamenko, D. Sek, J. Cisowski, A. Volozhin, *J. Non-Cryst. Solids* 299, 1057, 2002.
12. A. M. A. Nada., M. Dawy, A. H. Salama, *Mater. Chem. Phys.* 84, 205, 2004.
13. S. Ioan, L. I. Buruiana, E. Avram, O. Petreus, V. E. Musteata, *J. Macromol. Sci. B*, 50, 1571, 2011.
14. P. Saxena, M. S. Gaur, P. Shukla, P. K. Khare, *J. Electrostat.*, 66, 584, 2008.
15. F. M. Gray, *Solid Polymer Electrolytes*, VCH Publication, New York, 1991.
16. P. J. Clarke, A. K. Ray, J. Tsibouklis, A. R. Werninck, *J. Mater. Sci.: Mater. Electronics* 2, 18, 1991.
17. S. Muruganad, S. K. Narayandass, D. Mangalara, T. M. Vijayan, *Polym. Int.* 50, 1089, 2001.
18. R. Smith, *Semiconductors*, Cambridge University Press, London, 1980.
19. D. Guiver, G. P. Robertson, M. Yoshikawa, C. M. Tam, Functionalized polysulfones: methods for chemical modification and membrane applications, In *Membrane Formation and Modification*, Eds. I. Pinnau, B. D. Freeman, American Chemical Society, 10, 137, 2000.
20. M. Barikani, S. Mehdipour-Ataei, *J. Polym. Sci., Part A: Polym. Chem.*, 38, 1487, 2000.
21. S. Nie, J. Xue, Y. Lu, Y. Liu, D. Wang, S. Sun, F. Ran, C. Zhao, *Coll. Surf. B, Biointerfaces*, 100, 116, 2012.
22. A. Higuchi, K. Shirano, M. Harashima, B. O. Yoon, M. Hara, M. Hattori, K. Imamura, *Biomaterials*, 23, 2659, 2002.
23. J. Barzin, S. S. Madaeni, H. Mirzadeh, M. Mehrabzadeh, *J. Appl. Polym. Sci.*, 92, 3804, 2004.
24. H. D. Sluma, J. Passlack, B. Buttner, M. Scherf, U.S. Patent 5, 582, 1993.
25. C. M. Bell, M. Pirner, R. Buck, H. J. Gohl, U.S. Patent 5, 465, 1996.
26. S. Ioan, A. Filimon, E. Avram, G. Ioanid, *e-Polymers*, 031, 1, 2007.
27. A. Filimon, E. Avram, S. Dunca, I. Stoica, S. Ioan, *J. Appl. Polym. Sci.*, 112, 1808, 2009.
28. A. Filimon, E. Avram, S. Ioan, *J. Macromol. Sci. Part B – Phys.*, 46, 503, 2007.
29. A. Filimon, R. M. Albu, E. Avram, S. Ioan, *J. Macromol. Sci. Part B – Phys.*, 49, 207, 2010.

Dissemination of the results:

All objectives were fully realized and some results were used in manuscripts submitted to publication.

Book chapters:

1. Adina Maria Dobos, Mihaela Dorina Onofrei, Silvia Ioan, Liquid Crystals and Cellulose Derivatives Composites, In: Green biorenewable biocomposites from knowledge to industrial applications, V. K. Thakur, M. Kessler (Eds.), CRC Press/Taylor and Francis, USA/Canada, (2014) ISBN 9781771880329.
2. Anca Filimon, Mathematical Models and Numeric Simulations of Specific Interactions in Solutions of Modified Polysulfones, In: Functionalized polysulfones: Synthesis, characterization, and applications, S. Ioan (Ed.), Taylor & Francis Group, CRC Press (2014) (in press) ISBN 9781482255546
3. Anca Filimon, Raluca Marinica Albu, Silvia Ioan, Structure-Properties Relationships of Functionalized Polysulfones, In: Functionalized polysulfones: Synthesis, characterization, and applications, S. Ioan (Ed.), Taylor & Francis Group, CRC Press (2014) (in press) ISBN 9781482255546
4. Anca Filimon, Silvia Ioan, Antimicrobial Activity of Polysulfone Structures, In: Functionalized polysulfones: Synthesis, characterization, and applications, S. Ioan (Ed.), Taylor & Francis Group, CRC Press (2014) (in press) ISBN 9781482255546

Book:

1. Anca Filimon, Particularitati structurale ale unor polimeri de inalta performanta cu aplicatii biomedicale, Ed PIM, (2014) (in press)

Scientific papers:

1. Mihaela Dorina Onofrei, Adina Maria Dobos, Iuliana Stoica, Nicolae Olaru, Liliana Olaru, Silvia Ioan, Lyotropic Liquid Crystal Phases in Cellulose Acetate Phthalate/Hydroxypropyl Cellulose Blends, *Journal of Polymer and the Environment*, 22, 99-111, 2014, DOI 10.1007/s10924-013-0618-7.
2. Raluca Marinica Albu, Ecaterina Avram, Valentina Elena Musteata, Silvia Ioan, Dielectric Relaxation and AC-conductivity of Modified Polysulfones with Chelating Groups, *Journal of Solid State Electrochemistry*, 18, 785-794, 2014, DOI: 10.1007/s10008-013-2323-9.
3. Anca Filimon, Ecaterina Avram, Iuliana Stoica, Rheological and Morphological Characteristics of Some Polysulfones Induced by the Presence of Polyvinyl Alcohol, *Polymer International*, 63,1856-1868, 2014, DOI 10.1002/pi.4716.
4. Raluca Marinica Albu, Iuliana Stoica, Ecaterina Avram, Emil Ghiocel Ioanid, Silvia Ioan, Gold Layers on Untreated and Plasma-Treated Substrates of Quaternized Polysulfones, *Journal of Solid State Electrochemistry*, 18, 2803-2813, 2014, DOI: 10.1007/s10008-014-2540-x.
5. Anca Filimon, Adina Maria Dobos, Ecaterina Avram, Silvia Ioan, Ionic polymers based on quaternized polysulfones: hydrodynamic properties of polymer mixtures in solution, *Pure Applied Chemistry*, 86, 1871-1882, 2014, DOI: 10.1515/pac-2014-0603.
6. Anca Filimon, Ecaterina Avram, Simona Dunca, Surface and interface properties of quaternized polysulfones: Cell-material interaction and antimicrobial activity, *Colloids and Surfaces B: Biointerfaces*, (Under review 2014)
7. Adina Maria Dobos, Mihaela-Dorina Onofrei, Nita Tudorache, Silvia Ioan Structural Orientations of Cellulose Acetate Phthalate/Ethyl Cellulose System in Solution, *Journal of Macromolecular Science Part B* (Accepted 2014)
8. M.-D. Onofrei, A. M. Dobos, S. Dunca, E. G. Ioanid, S. Ioan Antimicrobial Cellulose Materials for Medical Implants, *Journal of Applied Polymer Science*, (Under review 2014)

Communications:

1. Anca Filimon, Adina Maria Dobos, Ecaterina Avram, Silvia Ioan, Ionic Polymers Based on Quaternized Polysulfones: Hydrodynamic Properties of Polymer Mixtures in Solution, 15th International Conference Polymers and Organic Chemistry, IUPAC 2014, Timisoara, Romania, June 10-13, 2014.
2. Luminita-Ioana Buruiana, Anca Filimon, Ecaterina Avram, Silvia Ioan, Interpretation of optical absorption edges in quaternized polysulfones/polyvinyl alcohol blend films, A XXXIII-a Conferinta Nationala de Chimie, Calimanesti, Caciulata, 1-3 Octombrie 2014.
3. Mihaela-Dorina Onofrei, Anca Filimon, Ecaterina Avram, Silvia Ioan, Effect of cellulose acetate phthalate on surface characteristics of quaternized polysulfone films, A XXXIII-a Conferinta Nationala de Chimie, Calimanesti, Caciulata, 1-3 Octombrie 2014.

Posters:

1. Mihaela Dorina Onofrei, Adina Maria Dobos, Simona Dunca, Silvia Ioan, Antibacterial Activity of Cellulose Derivatives Blends, 15th International Conference Polymers and Organic Chemistry, IUPAC 2014, Timisoara, Romania, June 10-13, 2014.
2. Mihaela Dorina Onofrei, Adina Maria Dobos, Silvia Ioan, Induced processes in cellulose derivative systems, Zilele Universitatii "Alexandru Ioan Cuza", Conferinta Facultatii de Chimie, Editia 2014, Iasi, 31 October – 1 November, 2014.
3. Anca Filimon, Raluca Marinica Albu, Ecaterina Avram, Silvia Ioan, Testing of rheological properties of quaternized polysulfones/polyvinyl alcohol blends for upgrading biomembranes. 2nd International Conference on Chemical Engineering Innovative Materials and Processes - ICCE 2014, Iasi, Romania, November 5-8, 2014.
4. Adina Maria Dobos, Mihaela Dorina Onofrei, Emil Ghiocel Ioanid, Silvia Ioan, Blood components adhesion to cellulose acetate phthalate/hydroxypropyl cellulose substrate, 2nd International Conference on Chemical Engineering Innovative Materials and Processes - ICCE 2014, Iasi, Romania, November 5-8, 2014.
5. Luminita-Ioana Buruiana, Ecaterina Avram, Adriana Popa, Silvia Ioan, Phosphorus-functionalized polysulfones with antithrombogenic activity for potential biomedical application, 2nd International Conference on Chemical Engineering Innovative Materials and Processes - ICCE 2014, Iasi, Romania, November 5-8, 2014.
6. Adina Maria Dobos, Anca Filimon, Ecaterina Avram, Silvia Ioan, Transport phenomena of polymer mixtures solution based on quaternized polysulfones, 2nd International Conference on Chemical Engineering Innovative Materials and Processes - ICCE 2014, Iasi, Romania, November 5-8, 2014.

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