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OF YOUNG INDEPENDENT RESEARCH TEAMS**

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

- 2015 -

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BRIEF REPORT

*concerning the results obtained by the project team between December 16th,
2014 – December 15th, 2015*

Objectives and activities proposed for Stage III - 2015:

Objectiv 1. *Conformational characteristics of composites/blends based on
functionalized polysulfones*

Activities: 1.1. Establishing specific interactions in multicomponent systems:
functionalized polysulfones/ cellulose derivatives /solvent;
1.2. Establishing specific interactions in multicomponent systems:
functionalized polysulfones/polyvinyl alcohol/solvent;

Objectiv 2: *Optimization of properties in solution and solid state to obtain
semipermeable composite membranes*

Activitati: 2.1. Finding optimal compositions of used blends, by optimization of the
obtained properties, in order to achieve the bioactive membranes
2.2. Development of some semipermeable membranes with controlable
pore sizes; surface study by specific tests: microscopy studies.

Objectives and activities performed.

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

1.1. Establishing specific interactions in multicomponent systems: functionalized polysulfones/cellulose derivatives/solvent

1.2. Establishing specific interactions in multicomponent systems: functionalized polysulfones/polyvinyl alcohol/solvent

The presence of the specific interaction in the complex multicomponent polymer systems namely, nanostructures, polyelectrolytes (*i.e.*, functionalized polysulfone with pendant ammonium groups, PSFQ), polymers in the presence of surfactants, complicates the structural and thermodynamic assessments. In this sense, is necessary to specify all possible interactions between the components system that can lead to the formation of multicomponent complexes according to different processes of equilibrium characterized by association/interaction constants. The specific intermolecular interactions established between the polar groups are also, important in the formation of the hydrogen bonding that must be taken into account in interpreting of the thermodynamic properties.

In this context, the multicomponent systems - functionalized polysulfone/cellulose derivatives/solvent and functionalized polysulfone/polyvinyl alcohol/solvent - were detailed investigated by viscometric and rheological studies to establish the specific interactions developed by electrostatic interactions, hydrogen bonding, and association phenomenon that occur in system (**Objective 1 - Activity 1.1 and 1.2**) and to indicate the compatibility of these polymers (**Objective 2 - Activity 2.1**) in order to determine the optimum compositions of this blends used in the design of high performance membranes with biological response.

The results outcomes from the dilute (Table 1) and concentrated solution study (Figure 1) for the polyelectrolyte/neutral polymer/solvent multicomponent systems (PSFQ/PVA/NMP and PSFQ/CAP/NMP) indicates the balance between the forces that interact in these complex polymer systems, as well as the cumulative effects of the thermodynamic and/or hydrodynamic interactions between the polymers.

Consequently, the dependence of intrinsic viscosity, $[\eta]$, on composition is complex, being influenced by the conformational changes of each type of polymer within mixing, as well as by the thermodynamic or hydrodynamic interactions among polymers. Accordingly, the intrinsic viscosity values are affected by the charge density of the alkyl radical of the PSFQ sample, composition of polymer blends, and also by the used solvent.

Table 1

Viscometer parameters evaluated for the multicomponent systems PSFQ/CAP/NMP and PSFQ/PVA/NMP at 25 °C

System	ϕ_1	$[\eta]/\text{dL g}^{-1}$	$[\eta]^\bullet/\text{dL g}^{-1}$	B
PSFQ/CAP/NMP	1	6.496	0.671	1.490
	0.75	2.473	0.204	0.655
	0.5	1.720	0.192	-1.049
	0.25	1.418	0.140	-0.138
	0	0.715	0	0.225
PSFQ/PVA/NMP	1	6.496	0.671	1.490
	0.75	1.758	0.141	0.774
	0.5	1.205	0	0.658
	0.25	0.961	0	0.611
	0	0.653	0	0.236

The hydrodynamic interaction parameter, B, also, highlights the influence of the blend polymer composition and their nature. Thus, it is observed that B parameter attains a maximum positive value for PSFQ, followed by a decrease at addition of uncharged polymers, CAP and PVA. A poor interaction between the polymer coils and the solvent appears for 50/50 and 25/75 (v/v) PSFQ/CAP mixtures, where B corresponds to negative values. This condition suggests an aggregation tendency as a result of hydrogen bonding formation.

Similarly to the dynamic viscosity, the activation energy changes, being affected by the nature of PSFQ, CAP, and PVA functional groups and also, by the composition of their blends. This behavior can be explained by the balance between the macromolecular mobility and specific interactions, reflecting the significant contribution of the electrostatic interactions and also, suggesting the manifestation of an aggregation tendency as results of the long-range interactions between polymer chains from multicomponent system. Therefore, according to these statements, based on viscometric/rheological obtained data, the PSFQ/CAP/NMP and PSFQ/PVA/NMP multicomponent systems show a high miscibility over the entire composition range, as a result of the competition between different thermodynamic interactions.

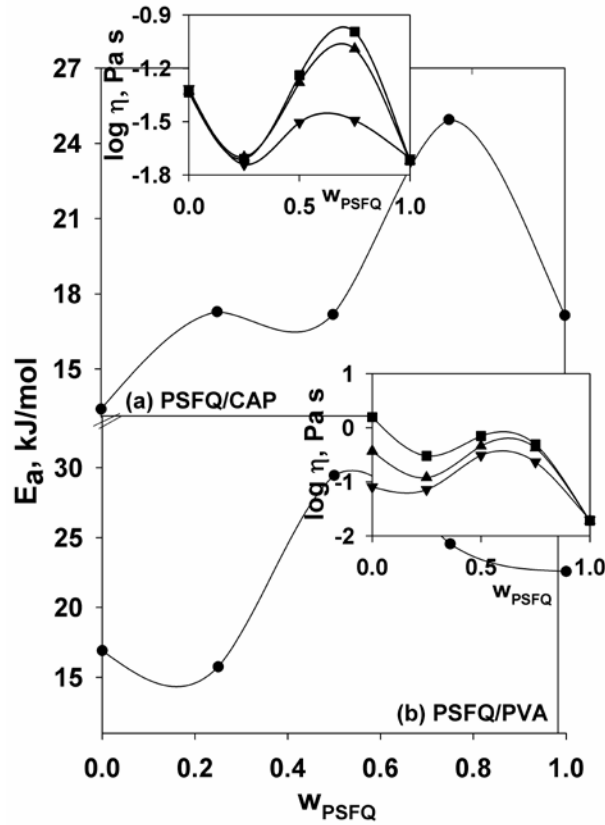
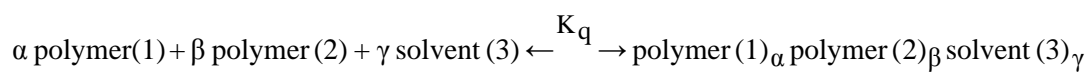


Figure 1. Flow activation energy *versus* PSFQ content for: PSFQ/CAP/NMP (a) and PSFQ/PVA/NMP (b) systems at 25°C. The small plots represent the variation of dynamic viscosity, η , experimentally determined at various shear rates, $\dot{\gamma}$, as a function of PSFQ content, at 25°C.

This study investigates the thermodynamic functions from the perspective of new theories and analyzes the optimal choice of polymer blends composition for specific applications in the biomedical field.

Specific interactions of the polyelectrolyte/neutral polymer/solvent multicomponent systems, with proton – donor and/or proton – acceptor properties, were also defined in the realised researches and evaluated through the mathematical simulations (introducing the association/interaction constants, imposed by the occurrence of the associated species). Potential specific interactions between the „P1” (PSFQ), „P2” (CAP or PVA) and „S3” (NMP) components of the polymer (1)/polymer (2)/solvent (3) ternary systems, can lead to the formation of a multicomponent complex, $\text{polymer}(1)_\alpha \text{polymer}(2)_\beta \text{solvent}(3)_\gamma$, according to the following equilibrium:



characterized by the equilibrium constant specific to the the complex formed:

$$K_q = \frac{v_q}{P_1^\alpha \cdot P_2^\beta \cdot S_3^\gamma} \quad (1)$$

where the distribution of components in this complex will be controlled by the condition of minimum Gibbs free energy.

For complete description of the possible specific interactions between all system components (such as, electrostatic interactions induced by the ionic groups of the PSFQ structure, disperse interaction, and hydrogen bonding that can generate the association phenomena – CAP or/and PVA) is necessary to know the Gibbs free energy function for a ternary system (Eq. (1) and (2) - inserting the interaction constants specific to each equilibrium (Garcia-Lopera, R. *et al.*, Eur. Polym. J. 2007; Filimon, A. *et al.*, J. Macromol. Sci. B - Phys., 2009):

$$\begin{aligned} \left(\frac{\Delta G}{RT}\right)_{\text{Ter}} &= v_1 \cdot \ln \frac{P_1}{P_1^0} + v_2 \ln \frac{P_2}{P_2^0} + v_3 \ln \frac{S_3}{S_3^0} - \sum_q v_q + \phi_1 \left(\sum_q v_q\right)_1^0 + \phi_2 \left(\sum_q v_q\right)_2^0 + \\ &\phi_3 \left(\sum_q v_q\right)_3^0 + v_1 \phi_2 g_{12}' + v_1 \phi_3 g_{13}' + v_2 r_2 \phi_3 g_{23}' \end{aligned} \quad (2)$$

g_{ij}' represent the binary interaction parameters characteristic to all types of interactions.

$$\begin{aligned} \left(\frac{\Delta G}{RT}\right)_{\text{Ter}} &= \phi_1 \ln \left(\frac{Y + X - [X^2 + 2XY]^{1/2}}{\phi_1 [2\sigma_{11} + 1 - (1 + 4\sigma_{11})^{1/2}]} \right) + s\phi_2 \ln \left(\phi_2 \frac{1 - \sigma_{12}P_1}{1 - (\sigma_{12} - \eta_{12})P_1} \right) + \\ &r\phi_3 \ln \left(\phi_3 \frac{1 - \sigma_{13}P_1}{1 - (\sigma_{13} - \eta_{13})P_1} \right)^m - \frac{P_1}{1 - \sigma_{11}P_1} + \\ &\phi_1 \left(\frac{2\sigma_{11} + 1 - (1 + 4\sigma_{11})^{1/2}}{\sigma_{11}(1 + 4\sigma_{11})^{1/2} - \sigma_{11}} \right) + \phi_1 \phi_2 g_{12}' + \phi_1 \phi_3 g_{13}' + \phi_2 \phi_3 g_{23}' \end{aligned} \quad (3)$$

The numerical values of these constants were evaluated function of system composition by mathematical simulation, and were illustrated in Figure 2. These values, mathematical obtained, correct the Gibbs free energy and implicitly, the binary interaction parameters, g_{ij}' .

The polyelectrolyte effect is due to the polyion chain expansion which leads to an progressive intensification of the ionizable groups dissociation. From this reason, the repulsive intermolecular interactions between the ionized groups *i.e.*, ammonium groups attached to the polymer chain, are

enhanced. This effect, a result of electrostatic interactions and steric hindrance leads to an increase in long-distance interactions.

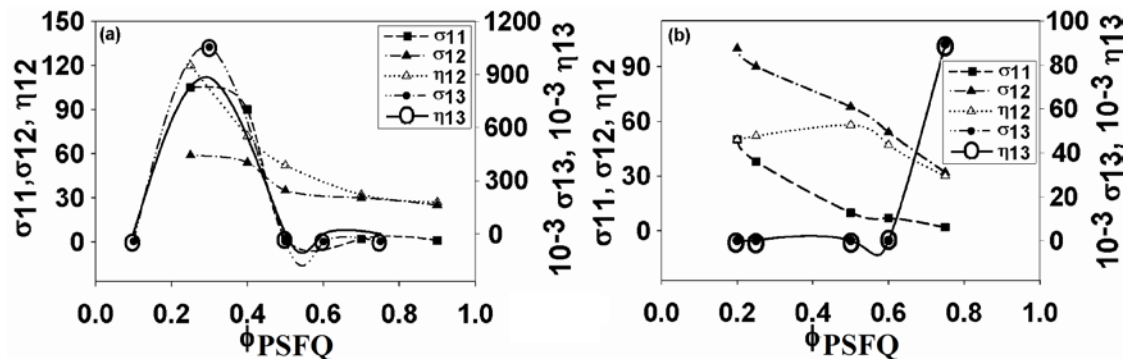


Figure 2. Interaction constants specific for each thermodynamic equilibrium, evaluated by mathematical simulations, for multicomponents systems: (a) PSFQ/CAP/NMP and (b) PSFQ/PVA/NMP

This research represent the basis for investigations concerning the PSFQ/CAP and PSFQ/PVA blends compatibilization, having as purpose the establishment of optimal composition for design the advanced biomembrane.

2.1. Finding optimal compositions of used blends, by optimization of the obtained properties, in order to achieve the bioactive membranes

High development of biomaterials based on functionalized polysulfones, which possess fundamental characteristics of biocompatibility, biofunctionality and biodurability (Filimon, A. *et al.*, Polym. Int., 2014; Filimon, A. *et al.*, Polym. Eng. Sci., 2015) was carried out as a result of their applications in membrane technology, imposing specific forms and sizes depending on the application area (microfiltration (cell separation from the suspension and cell culture); ultrafiltration (the concentration of the protein and polysaccharide solutions); reverse osmosis (separation of the inorganic salts from the water, the concentration of the antibiotics and small organic molecules)). Also, the development of this field involves the combination of various macromolecular materials with different characteristics - non porous/porous, hydrophilic/hydrophobic, etc. - which controls the membranes performance in terms of their selectivity and transport rate, as well as the improving of their biocompatibility, antimicrobial properties, etc.

The synthesized polymer (PSFQ) for the biomedical applications, shows increased reactivity, good solubility, and ability to form films. Consequently, it represents complex structures capable to perform composite/ blends that combines various specific properties favorable to proposed goal. In this context, the alternative approach to achieve composites/blends by using various "additives/ porogens" (CAP or PVA), leads to the generation of pores in the polymer matrix (PSFQ) and improving of the membrane performance.

Investigations from the solution (diluted-concentrated domain) and from solid state demonstrates that the investigated blends/composites (PSFQ/PVA and PSFQ/CAP in NMP) represent the basis of the future research concerning the obtaining of the advanced membranes with specific properties (particular morphologies, controlled porosity and hydrophilicity, biocompatibility, etc.). Thus, the flexibility, transparency, free energy of hydration, and balance between the surface hydrophilicity/hydrophobicity are properties that anticipates the existence of some characteristics which make them ideal for advanced membranes with biomedical applications. In addition, the studies in solution have offered the opportunity to determine and establish the optimal compositions that allow the formation of membranes with controlled properties (hydrophilicity and porosity).

Therefore, the knowledge of the structural parameters, as well as of physico-chemical and thermodynamic properties is essential in determining of these cationic polysulfones optimal composition in blends with neutral polymers for specific biomedical applications.

2.2. Development of some semipermeable membranes with controlable pore sizes; surface study by specific tests: microscopy studies

Polysulfone membranes with controlable degree of hydrophilicity and porosity, having optimal electrical and optical properties for biomedical applications, could be achieved in blends with other hydrophilic polymers (CAP and PVA). In this context, in order to understand the effects induced by the PVA and/or PVA presence in polysulfone matrix, a comparative analysis on the surface films aspects for pure samples of PSFQ, PVA, CAP, and their blends, is necessary. Thus, the addition of hydrophilic polymer (PVA and/or CAP) at polysulfone system improves the material properties, by reinforcing of the interactions of hydrogen bonding type, and consequently, modifies the polymer structure both molecular and morphological level (Siddaramaiah Raj, B., Somashekar, R., J. Appl. Polym. Sci., 2004).

Roughness and porous formations existence are key factors in obtaining of the advanced biomembranes used in immobilisation of active principles. Because the composite polymeric films

topography has not presented major differences, the local surface properties were investigated by atomic force microscopy (AFM) technique. The samples texture, evaluated by AFM and the results obtained based on micrographs presented in Figures 3-6, show that the nature and composition of polymer incorporated in PSFQ matrix (CAP and PVA) are main factors that influence the films morphology. In addition, the surface morphology - generated by the structural peculiarity of the polymeric chains - is influenced also, by the history of the films preparation realized from casting solutions. The morphological aspects are a consequence of the cumulative effects of the electrostatic interactions, intramolecular hydrogen bonding, and association phenomena manifested in solution.

A. Topographic reorganization of PSFQ/PVA composite films

The surface topography obtained by AFM for the pristine PSFQ, shows the existence of pores with irregular shapes disposed in some regions, in close proximity to one another. Since the occurrence of these pores on the polysulfone surface alternate with large flat areas, the surface area ratio, Sdr, defined as the increment of the total surface area relative to the sampling area in the XY plane, was relatively small, namely 0.17% (Table 2). Instead, according to Figure 3b, the pristine PVA sample presents a well-balanced surface relief. The smooth and homogeneous surface morphology was reflected also by the small value of the roughness ($S_q = 3.8$ nm) and surface area ratio ($Sdr = 0.11\%$) (Table 2).

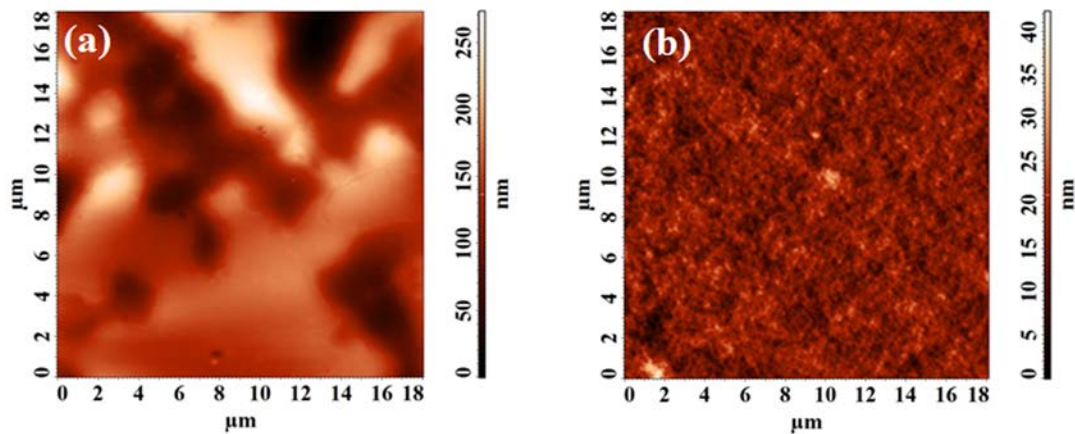


Figure 3. 2D AFM topography images of the pristine PSFQ (a) and PVA (b) samples

By creating a series of polymers blends by mixing PSFQ with PVA in different ratios, i.e., 75/25, 50/50 and 25/75 (wt./wt.), following surface features were observed:

- increasing of the PVA content leads to a decrease of the roughness, determined mainly by the increase of the pore number, and decrease of their average diameters (Figure 4, Table 2). In

this case, the surface became more complex, fact shown also by the increase of the surface area ratio value (Table 2);

- the functional volume parameters (V_{vc} , V_{vv}) undergo significant changes. The high amount of pores with small size obtained when the ratio of PSFQ was lower, induce the decreases of V_{vc} and V_{vv} parameters, indicating that the volume of air in the core and valley regions of the surface relief is also smaller.

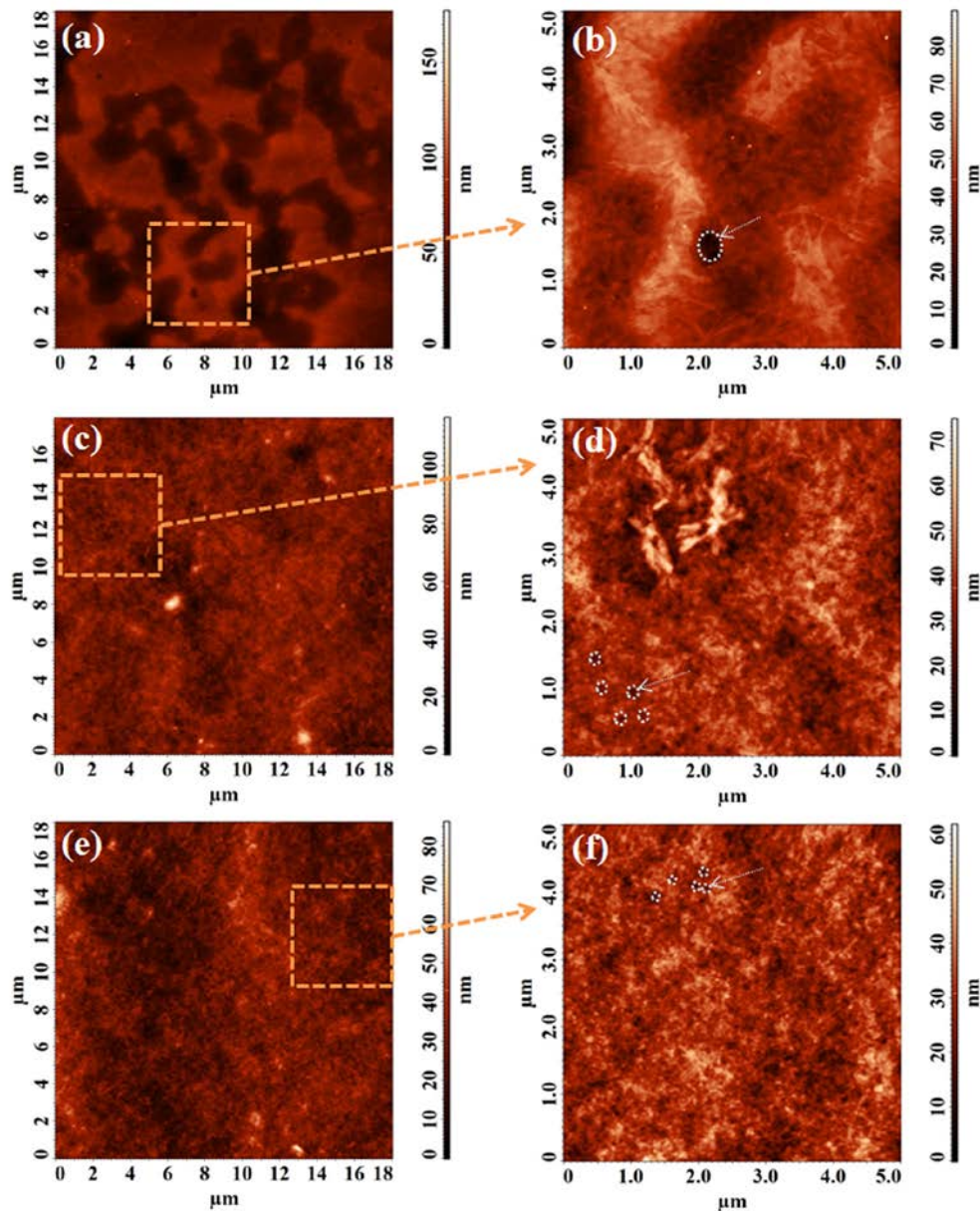


Figure 4. 2D AFM topography images of the PSFQ/PVA blend at different mixing ratios (wt./wt.) 75/25 (a, b), 50/50 (c, d), and 25/75 (e, f)

Table 2

Pores average diameter (nm) and 3D surface roughness parameters* corresponding to 2D AFM images obtained for pristine PSFQ and PVA, and their blends at different mixing ratios

Polymer/Blend	Pores average diameter		3D surface roughness parameters			
	Large pores	Small pores	Sq	Sdr	Vvc	Vvv
PSFQ	2160±280	-	45.3	0.17	54.575	5.164
75/25 PSFQ/PVA	1561±319	286±81	15.7	0.28	18.360	1.586
50/50 PSFQ/PVA	-	167±32	8.7	0.43	9.929	1.015
25/75 PSFQ/PVA	-	101±21	8.1	0.45	9.871	0.794
PVA	-	-	3.8	0.11	4.524	0.401

*3D-parameters including the root mean square roughness, Sq (nm), surface area ratio, Sdr (%), core void volume, Vvc (nm³/nm²), and valley void volume, Vvv (nm³/nm²)

B. Topographic reorganization of PSFQ/CAP composite films

Morphological analysis of the formed polymeric structures (PSFQ/CAP composites/blends) indicates the following:

- through cross section, the porous morphological formations of nanometric size, generated by the structural characteristics of CAP, were observed (Figures 5 and 6);
- morphological aspects are observable, but are not largely reflected in roughness parameters values, which are associated with a higher degree of disorder in the structure distribution, compared with PSFQ/PVA system (Table 3 compared to Table 2);
- composite systems morphology is influenced by the mixing ratio of the two components; addition of CAP generates an increases of surface roughness compared with those of PSFQ surface, instead, for a content of CAP higher than 0.75 % wt., an uniformity of the relief appears (pure CAP - Figure 5b, 75/25 PSFQ/CAP - Figure 6c).

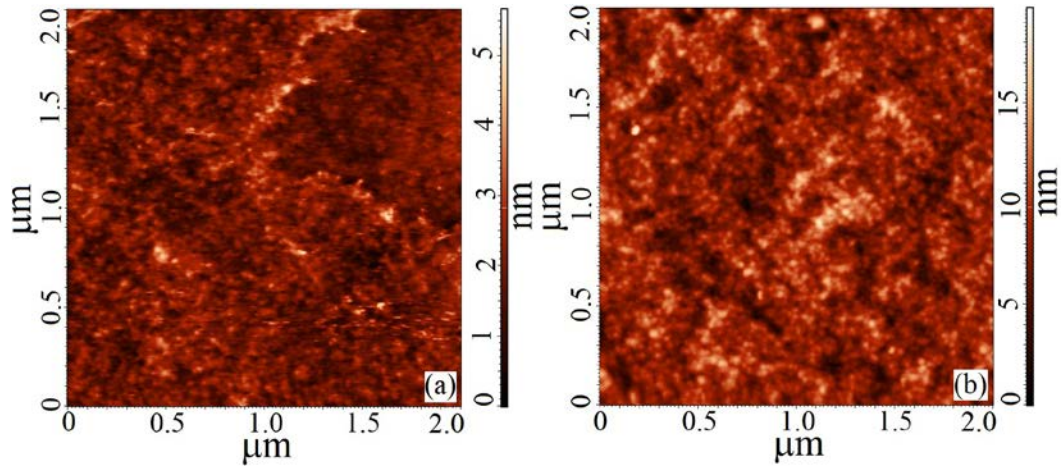


Figure 5. 2D AFM topography images of the pristine PSFQ (a) and CAP (b) samples

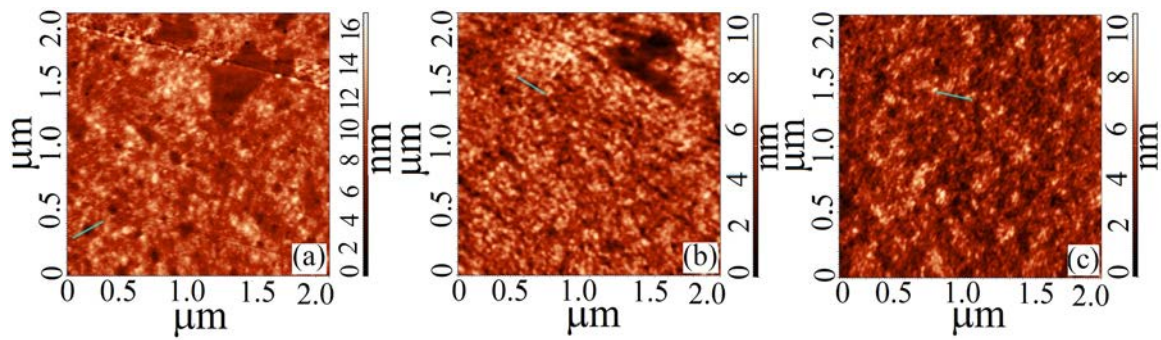


Figure 6. 2D AFM topography images of the PSFQ/PVA blend at different mixing ratios (wt./wt.): (a) 75/25, (b) 50/50, (c) 25/75

The results obtained show that both PVA and CAP can be used as "porogens" having a good control on the morphology; topographic features (generation of pores with controllable size in PSFQ matrix) is essential in the obtaining porous membranes with improved performance.

The force-distance spectroscopy has been used to measure the adhesion forces between the composite films surface and silica top of the cantilever, according to Hook's law:

$$F = -k \times \Delta x \quad (4)$$

where k is the dielectric constant of cantilever (1.97 Nm^{-1}), and Δx is the cantilever displacement.

Table 3

Pores average diameter (nm) and 3D surface roughness parameters* corresponding to 2D AFM images obtained for pristine PSFQ and CAP, and their blends at different mixing ratios

Polymer/Blend	Pores average diameter		3D surface roughness parameters				
	Large pores	Small pores	Sa	Sq	Sdr	Vvc	Vvv
PSFQ	2160±280	-	0,045	0,575	0,152	0,738	0,046
75/25 PSFQ/CAP	-	100±17	1,433	1,836	0,982	2,215	0,201
50/50 PSFQ/CAP	-	83±12	1,084	1,380	0,590	1,752	0,171
25/75 PSFQ/CAP	-	63±12	1,080	1,364	0,424	1,583	0,130
CAP	-	-	1,829	2,301	1,124	2,917	0,227

*3D-parameters including the root mean square roughness, Sq (nm), surface area ratio, Sdr (%), core void volume, Vvc (nm³/nm²), and valley void volume, Vvv (nm³/nm²)

Figures 7-10 show the approach and withdrawal representative curves realized for PSFQ, PVA, CAP, and their blends in different mixing ratio. For each experiment, the average value of the adhesion force was measured from 10 withdrawal curves. Generally, assuming that the silica surface of the cantilever, clean and dry is hydrophobic, the interactions between the hydrophobic top will be higher than those between the hydrophobic top and a hydrophilic substrate, respectively.

Analyzing the layout of these curves may be highlighting the differences between the surface properties of composite films. Therefore, the values of adhesion forces indicate the superficial wetting features, according to previous results on surface properties. Thus:

- high value of adhesion force obtained for PSFQ (Figures 7 and 8a, Table 4), relative to lower value of adhesion force recorded for PVA samples (Figure 4, Table 4) and CAP (figure 8b, Table 4) can be explained by his nature less hydrophilic ($\gamma_{sv,PSFQ}^{AB} < \gamma_{sv,PVA}^{AB}; \gamma_{sv,PSFQ}^{AB} < \gamma_{sv,CAP}^{AB}$);
- values of adhesion forces obtained for PSFQ/PVA blends increase with the increasing of the PVA content in system. This fact may be due to the hygroscopic property of PVA, which generates the change of the film superficial properties;
- values of adhesion forces obtained for PSFQ/CAP blends are similar to the wetting characteristics of the surface quantified by polar component values of the surface tension; increase the CAP content in polysulfone system, the adhesion force values decreases indicating a more hydrophilic surface;

- for mixtures, the effects due to the intensification of the repulsive interactions (reflected in the electron-acceptor/electron donor contributions) and effect of orientation and rearrangement of polar groups at the film surface interfere.

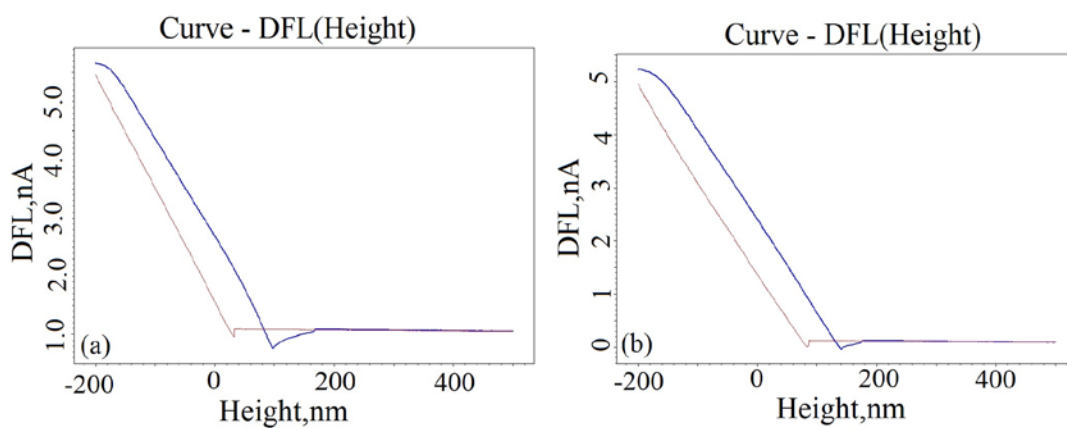


Figure 7. Adhesion curves recorded for PSFQ (a) and PVA (b) films

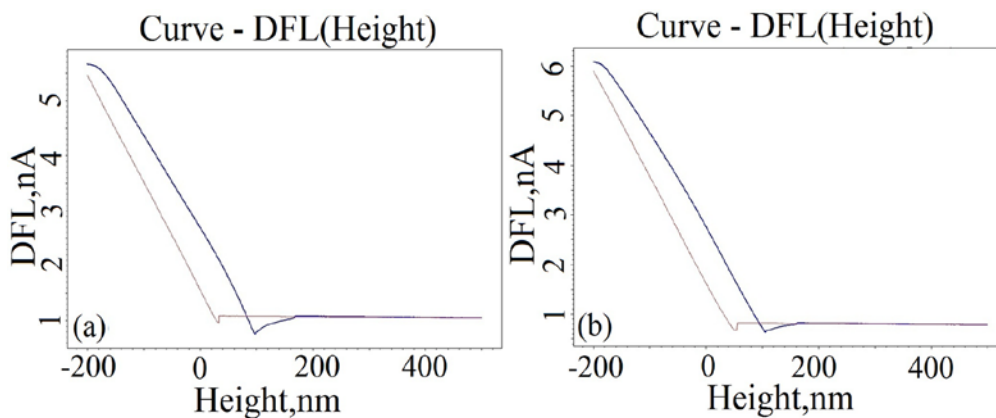


Figure 8. Adhesion curves recorded for (a) PSFQ and (b) CAP films

Table 4

Adhesion forces and polar components, γ_{SV}^{AB} , of surface tension with electron-acceptor, γ_{SV}^+ , and electron-donor, γ_{SV}^- , contributions (according to acid/base method) for PSFQ/PVA and PSFQ/CAP composite systems at different mixing ratio.

Polymer/System	F_{adez} (nN)	γ_{SV}^{AB} (mN/m)	γ_{SV}^+ (mN/m)	γ_{SV}^- (mN/m)
PSFQ	26,35±3,01	3,91	10,45	0,37
PVA	15,10±0,80	7,75	38,58	0,39
CAP	15,30±1,20	6,42	23,59	0,44
PSFQ/PVA				
75/25	17,85±2,06	3,57	14,45	0,22
50/50	20,71±1,59	6,74	3,99	2,85
25/75	29,75±0,97	9,43	13,44	1,65
PSFQ/CAP				
75/25	14,59±2,44	0,13	24,13	0,002
50/50	12,92±0,79	2,73	18,60	0,100
25/75	7,47±3,15	4,47	20,17	0,250

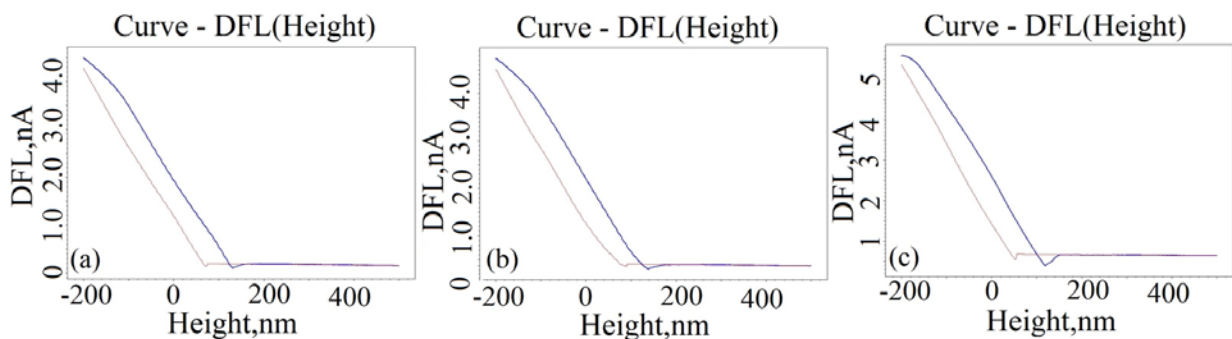


Figure 9. Adhesion curves recorded for PSFQ/PVA composite films at different mixing ratio: (a) 75/25, (b) 50/50, (c) 25/75

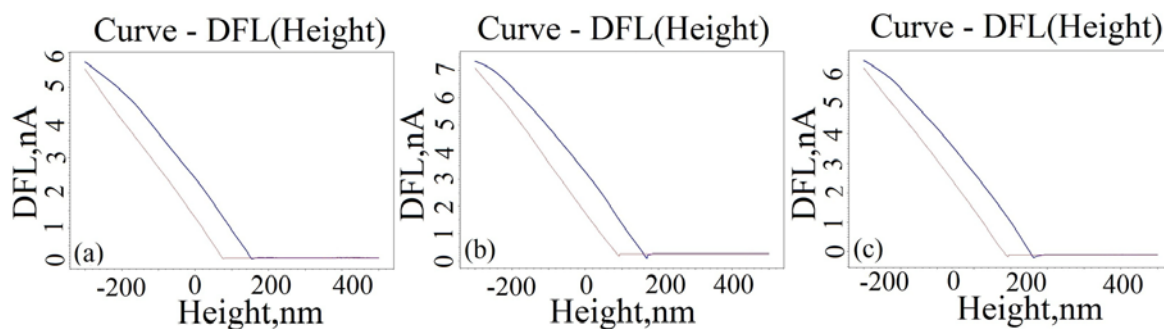


Figure 10. Adhesion curves recorded for composite films of PSFQ/CAP at different mixing ratio: (a) 75/25, (b) 50/50, (c) 25/75

In conclusion, the surface hydrophilicity can be correlated with the restructuring/reorganization degree of the surface topography by mixing; because through the mechanical mixing the polar groups from the film surface is reorienting, leading to changes of local polar moments. Tendency of composite surface modification can be associated also, with different changes of chains conformation due to the addition of CAP and/or PVA (with polar and hydrophilic groups) in the polysulfone solutions. Modification of blends composition leads to changes in the number of pores and their characteristics, suggesting that the hydrophilicity and porosity of films, which plays an important role in membrane performance, were improved.

Thus, the results presented (correlated with the surface properties, hydrophilic/hydrophobic balance control), the surface high wettability tendency and hydrophilicity implicitly, are properties necessary for biomedical applications.

All the proposed objectives for Stage 3 - 2015 were fully realized and most results were used in manuscripts published or submitted to publication.

Results dissemination:

- o 7 papers were elaborated and submitted to journals indexed by Web of Knowledge (3 published, 2 accepted, 2 in press);
- o 1 paper accepted in journal indexed in international data base (Chemical and Molecular Engineering - World Academy of Science, Engineering and Technology);
- o 1 chapter book (Ed. CRC Press Taylor and Francis Group);
- o 1 book (Ed. PIM);
- o 7 participations at scientific events (2 oral presentation and 5 posters).

Chapter book:

1. Ecaterina Avram, Anca Filimon, *Aromatic Linear Polysulfones with Pendant Functional Groups*, In: *Functionalized Polysulfones: Synthesis, Characterization and Applications*, Ed. CRC Press, Taylor & Francis Group, Chapter 2, pp. 3-35, 2015, ISBN: 13-978-1-4822-5554-6.

Book:

1. Anca Filimon, Particularitati structurale ale unor polimeri de inalta performanta cu aplicatii biomedicale, Ed. PIM, pp. 224, 2015, ISBN: 978-606-13-2643-3.

Papers:

1. Anca Filimon, Ecaterina Avram, Simona Dunca, Surface and Interface Properties of Functionalized Polysulfones: Cell-Material Interaction and Antimicrobial Activity, *Polymer Engineering and Science*, 55(9), 2184-2194, 2015, DOI 10.1002/pen.24103.
2. Mihaela Dorina Onofrei, Adina Maria Dobos, Simona Dunca, Emil Ghiocel Ioanid, Silvia Ioan, Biocidal Activity of Cellulose Materials for Medical Implants, *Journal of Applied Polymer Science*, 132, 41932(1-9), 2015, DOI: 10.1002/app.41932.
3. Adina Maria Dobos, Mihaela-Dorina Onofrei, Nita Tudorachi, Silvia Ioan, Structural Orientations of Cellulose Acetate Phthalate/Ethyl Cellulose Blends in Solution, *Journal of Macromolecular Science, Part B-Physics*, 54, 1092–1104, 2015, DOI: 10.1080/00222348.2015.1078625.

4. Anca Filimon, Ecaterina Avram, Nicolae Olaru, Florica Doroftei, Simona Dunca, Electrospun Fibers Containing Cationic Quaternary Ammonium Derivatives with Antibacterial Activity, *IEEE Xplore® ISI Proceedings (Conference Proceedings Citation Index)*, 978-1-4673-7545-0/15/\$31.00 ©2015 IEEE, 2015 (**accepted**).
5. Adina Maria Dobos, Anca Filimon, Ecaterina Avram, Ghiocel Emil Ioanid, Impact of Surface Properties of Blends Based on Quaternized Polysulfones on Modeling and Interpretation the Interactions with Blood Plasma, *IEEE Xplore® ISI Proceedings (Conference Proceedings Citation Index)*, 978-1-4673-7545-0/15/\$31.00 ©2015 IEEE, 2015 (**accepted**).
6. Anca Filimon, Raluca Marinica Albu, Ecaterina Avram, Maximizing Performance of the Membranes Based on Quaternized Polysulfones/Polyvinyl Alcohol for Biomedical Applications: Rheological Investigations, *Chemical and Molecular Engineering, World Academy of Science, Engineering and Technology* (Baza de date internationala), 2015 (**accepted**).
7. Anca Filimon, Adina Maria Dobos, Ecaterina Avram, Factors Controlling the Ionic Transport Processes in Polymer Mixture Solutions Based on Quaternized Polysulfones, *Polymer Engineering and Science*, 2015 (**in press**).
8. Luminita Ioana Buruiana, Ecaterina Avram, Valentina Elena Musteata, Anca Filimon, Optical and Electronic Properties of Quaternized Polysulfone/Polyvinyl Alcohol Blends in Relation to Structure of the Polymers, *Materials Chemistry and Physics*, 2015 (**in press**).

Oral presentations:

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