

Surface Properties and Compatibility with Blood of New Quaternized Polysulfones

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ABSTRACT

The paper describes some properties of new quaternized polysulfones obtained by quaternization of chloromethylated polysulfone with different tertiary amines-N,N-dimethylethylamine and N,N-dimethyloctylamine. Hydrophilic/hydrophobic properties, morphological aspects and interface properties with red blood cells and platelets are affected by the alkyl radicals and by history of the formed films from solutions in N,N-dimethylformamide/methanol and N,N-dimethylformamide/water solvent/nonsolvent mixtures. The results obtained are useful in biomedical applications, including evaluation of bacterial adhesion to the surfaces, or utilization of modified polysulfones as semipermeable membranes.

Keywords: Quaternized Polysulfones, Surface Properties, Blood Compatibility

1.Introduction

In recent decades, considerable attention has been devoted to the investigation of new applications of polysulfones, and also, of chloromethylated and quaternized polysulfones, which was mainly due to their specific properties. Literature showed that polysulfones and their derivatives were widely used as new functional materials in biochemical, industrial and medical fields, due to their structure and physical characteristics, such as good optical properties, high thermal and chemical stability, mechanical strength, resistance to extreme pH values and low creep [1-4]. Chain rigidity is derived from the relatively inflexible and immobile phenyl and SO₂ groups, while toughness - from the connecting ether oxygen [4].

The polysulfone can be modified to improve its performance for specific applications [4,5], by chloromethylation, a reaction of considerable interest from both theoretical and practical points of view, such as obtaining of precursors for functional membranes, coatings, ion exchange resins, ion exchange fibers and selectively permeable membranes [6,7]. Also, quaternization with ammonium groups is an efficient method to obtain some properties recommended in various applications, e.g. as biomaterials and semipermeable membranes. These groups can modify hydrophilicity (of special interest for biomedical applications) [8], the antimicrobial action [9,10], solubility characteristics [11,12], allowing water

permeability and separation [13,14]. In addition, the functional groups are an intrinsic requirement for affinity, ion exchange and other specialty membranes [15]. Moreover, the bioapplication of polysulfones can be divided in two categories, namely blood contacting devices – for example, hemodialysis, hemodiafiltration and hemofiltration as membrane, and cell or tissue contacting devices for example, bioreactor made by hollow fibre membrane, nerve generation through polysulfone semipermeable hollow membrane, etc [5].

In previous publications, the synthesis [16-18] and some solution properties [11,19-23] of modified polysulfones have been presented. Studies have been carried out on the quaternization reaction of chloromethylated polysulfones, for obtaining water soluble polymers with various amounts of ionic chlorine. The conformational behavior in solution and the experimental and theoretical results on the preferential adsorption coefficients *versus* solvent composition have been discussed in correlation with the interaction parameters of quaternized polysulfones/mixed solvents [10,20,23]. Surface wettability and hydrophilicity trends, as well as the morphological characteristics of some modified polysulfones were also analyzed, for biomaterials and semipermeable membrane applications [10,12,22,24]. On the other hand, it is well-known that surface-induced blood coagulation is one of the main problems in the development of blood-contacting materials. From a clinical point of view, literature

shows that a biomaterial can be considered as hemocompatible only when its interaction with blood does not provoke damage of blood cells or change in the structure of plasma proteins [25-27]. The surface free energy of biomaterials and the corresponding values of the work of spreading can be used as characterization parameters for predicting cell spreading onto their surfaces and hence, for establishing their blood compatibility.

The objective of the present study was to investigate the morphological characteristics of quaternized polysulfones obtained from chloromethylated polysulfones with tertiary amines, N,N-dimethylethylamine and N, N-dimethyloctylamine. The corresponding films, obtained from solutions in N,N-dimethylformamide (DMF)/methanol (MeOH) and DMF/water mixtures, were analyzed by atomic force microscopy, to emphasize the influence of casting solutions on the morphological properties. The results were correlated with the hydrophilic/hydrophobic properties and red blood cells and platelets compatibility. Influence of the alkyl radical sizes from the side groups was evidenced comparatively with the modified polysulfones with N-dimethyloctylammonium chloride pendant groups [27]. In this context, such investigations were discussed in correlation with the computerized chemical structure, which provides a generalized view on the chemical conformations of the repeating units, realized by the HyperChem professional program (Demo version). This representation helps to identify aspects of molecular structure which may be relevant to the structure-property problem here under consideration, blood compatibility included.

2. Materials and Methods

2.1. Materials

UDEL-3500 polysulfone (PSF) (Union Carbide, $M_n = 39000$; $M_w/M_n = 1.625$), a commercial product, was purified by repeated reprecipitations from chloroform and dried for 24 h in vacuum, at 40°C, before being used in the synthesis of chloromethylated polysulfone. A mixture of commercial paraformaldehyde with an equimolar amount of chlorotrimethylsilane (Me_3SiCl) as a chloromethylation agent, and stannic tetrachloride (SnCl_4) as a catalyst, was used for the chloromethylation reaction of polysulfone, at 50°C. The reaction time necessary to obtain chloromethylated polysulfones with 6.58% chlorine content (CMPSF) was 72 h [7]. Finally, the samples were dried under vacuum at 40°C.

Polysulfones with different alkyl side groups, PSF-DMEA and PSF-DMOA, were synthesized by reacting chloromethylated polysulfone with different tertiary amines-N,N-dimethylethylamine (DMEA) and N, N-dimethyloctylamine (DMOA), respectively. The quaternization reaction was performed in DMF, using a CMPSF/

tertiary amine molar ratio of 1:1.5, for 24 h. The quaternary polymers were isolated from the reaction medium by precipitation in diethylether, washed three times with diethylether, and dried for 48 h under vacuum, at room temperature. The contents of ionic chlorine of 2.89 and 3.23, and total chlorine of 3.10 and 3.29 for PSF-DMEA and PSF-DMOA, respectively, were determined by Schöninger's method followed by potentiometric titration with AgNO_3 , using an automatic TitraLab Radiometer 840.

The ratios between ionic chlorine and the total chlorine contents show 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. **Scheme 1** presents the general chemical structures and conformational structures - obtained by a computerized method using the HyperChem professional program (Demo version) considering four structural units, of PSF-DMEA and PSF-DMOA.

2.2. Contact Angle

Contact angle analysis for surface tension investigations and atomic force microscopy (AFM) measurements were realized on quaternized polysulfones films. PSF-DMEA and PSF-DMOA were dissolved in DMF, DMF/MeOH (over the 75/25% - 25/75% v/v and 75/25% - 45/55% v/v composition range, respectively), and DMF/Water (over the 75/25% - 40/60% v/v and 75/25% - 50/50% v/v composition range, respectively), to reach the concentrations of approximately 7 g/dL. The solutions were cast on a glass plate and initially solidified by slow drying in saturated atmosphere with the used solvent, and finally by drying at 50°C under vacuum. Uniform drops of the 2 μL test liquid were deposited on the film surface and the contact angles were measured after 30 s, with a video-based optical contact angle measuring device, in a temperature of 25°C. The used test liquids are water, methylene iodide (CH_2I_2), and 1-brom-naphtalin (1-Bn).

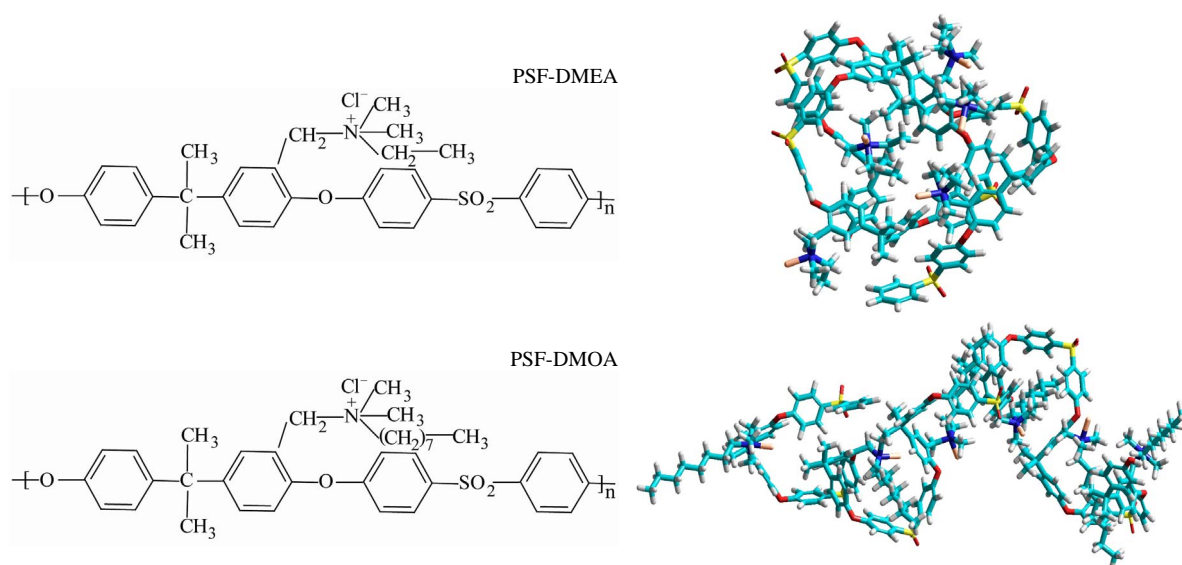
2.3. Atomic Force Microscopy

Atomic force microscopy (AFM) measurements were performed in air, at room temperature (23°C), in the tapping mode using a Scanning Probe Microscope (Solver PRO-M, NT-MDT, Russia) with commercially available NSG10 cantilevers. The manufacture's value for the probe tip radius was 10 nm and for the typical force constant was 11.5 N/m. In the tapping mode, the cantilever was oscillated at a frequency of 286 kHz, over a $20 \times 20 \mu\text{m}^2$ scan area for each sample.

3. Results and Discussion

3.1. Surface Tension Parameters

The geometric mean method (GM) (Equations (1) and (2))



Scheme 1. Chemical structures and conformational structures with minimized energies, considering four repeating units of polysulfones with quaternary groups.

[28,29] and the acid/base method (LW/AB) (equation (3) and (4) [30,31] were utilized for calculating the surface tension parameters of PSF-DMEA and PSF-DMOA, with surface properties of test liquids [32] from **Table 1**, and the contact angles measured between these solvents and quaternized polysulfone films from **Table 2**. The contact angles between these solvents and PSF-DMOA films are presented in previous paper [27].

$$\frac{1 + \cos \theta}{2} \cdot \frac{\gamma_{lv}}{\sqrt{\gamma_{lv}^d}} = \sqrt{\gamma_{sv}^p} \cdot \sqrt{\frac{\gamma_{lv}^p}{\gamma_{lv}^d}} + \sqrt{\gamma_{sv}^d} \quad (1)$$

$$\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p \quad (2)$$

where θ is the contact angle determined for test liquids, subscripts “lv” and “sv” denote the liquid-vapor and surface-vapor interfacial tension, respectively, while superscripts “p” and “d” denote the polar and disperse components, respectively, of total surface tension, γ_{sv} .

$$1 + \cos \theta = \frac{2}{\gamma_{lv}} \cdot \left(\sqrt{\gamma_{sv}^{LW} \cdot \gamma_{lv}^{LW}} + \sqrt{\gamma_{sv}^+ \cdot \gamma_{lv}^-} + \sqrt{\gamma_{sv}^- \cdot \gamma_{lv}^+} \right) \quad (3)$$

$$\gamma_{sv}^{LW/AB} = \gamma_{sv}^{LW} + \gamma_{sv}^{AB} \quad (4)$$

where $\gamma_{sv}^{AB} = 2 \cdot \sqrt{\gamma_{sv}^+ \cdot \gamma_{sv}^-}$, superscript “LW/AB” indicates the total surface tension, and also, superscript “AB” and “LW” represent the polar component obtained from the electron-donor, γ_{sv}^- , and the electron-acceptor, γ_{sv}^+ , interactions, and the disperse component, respectively.

Table 3 shows the results for the surface tension components, evaluated with both methods. The surface tension parameters are influenced by the solvent/nonsolvent composition from which the films had been prepared.

Some studies have reported that the chain shape of a polymer in solution could affect the morphology of the polymer in bulk. In this context, the conformations of both PSF-DMEA and PSF-DMOA are affected by the charged groups from different alkyl radicals of the studied quaternized samples, and also by the composition of the solvent mixtures. Thus, **Figure 1** depicts the variation of intrinsic viscosity with the volume fraction of DMF, in DMF/MeOH and DMF/water mixtures, for PSF-DMEA

Table 1. Surface tension parameters (mN/m) of the liquids used for contact angle measurements, red blood cells and platelets.

Liquid	γ_{lv}	γ_{lv}^d	γ_{lv}^p	γ_{lv}^+	γ_{lv}^-
Water [32]	72.80	21.80	51.00	25.50	25.50
Methylene iodide (CH ₂ I ₂) [32]	50.80	50.80	0	0.72	0
1-Brom-naphtalin (1-Bn) [32]	44.40	44.40	0	0	0
Red blood cell [35]	36.56	35.20	1.36	0.01	46.2
Platelet [35]	118.24	99.14	19.10	12.26	7.44

Table 2. Contact angle (°) of different liquids on films prepared from solutions of PSF-DMEA in DMF/MeOH and DMF/water (% v/v) (column 1).

Solvent mixtures	Contact angle		
	W	MI	1-Bn
100/0 DMF/MeOH	71	28	17
75/25 DMF/MeOH	70	31	22
50/50 DMF/MeOH	61	30	20
25/75 DMF/MeOH	63	31	24
75/25 DMF/water	59	35	21
50/50 DMF/water	60	33	18
40/60 DMF/water	56	33	16

Table 3. Surface tension parameters (mN/m) and contribution of the polar component to the total surface tension (%) for quaternized polysulfone films PSF-DMEA and PSF-DMOA prepared from solutions in DMF/MeOH and DMF/water (v/v %), according to the geometrical mean method and the acid/base method (equations (1) - (4)).

Solvent mixtures	Geometrical mean method				Acid/base method					
	γ_{sv}^d	γ_{sv}^p	γ_{sv}	$\gamma_{sv}^p / \gamma_{sv}$	γ_{sv}^{LW}	γ_{sv}^+	γ_{sv}^-	γ_{sv}^{AB}	$\gamma_{sv}^{LW/AB}$	$\gamma_{sv}^{AB} / \gamma_{sv}^{LW/AB}$
PSF-DMEA, DMF/MeOH										
100/0	43.7	5.9	49.7	11.9	42.5	3.6	2.6	6.2	48.7	12.6
75/25	42.5	6.6	49.2	13.5	41.3	4.3	2.8	6.9	48.1	14.3
50/50	42.9	10.7	53.7	20.0	41.8	9.9	2.5	9.9	51.7	19.2
25/75	42.1	10.0	52.1	19.1	40.6	6.5	4.1	10.4	51.0	20.4
PSF-DMEA, DMF/water										
75/25	41.8	12.2	54.0	22.7	41.5	21.4	0.1	3.18	44.68	7.1
50/50	42.6	11.4	54.0	21.1	42.3	19.0	0.2	3.83	46.08	8.3
40/60	42.8	13.4	56.3	23.9	42.7	25.4	0.2	4.15	46.85	8.9
PSF-DMOA, DMF/MeOH [27]										
100/0	40.9	5.1	46.0	11.0	42.4	0.4	1.4	1.5	43.9	3.4
75/25	39.6	3.0	42.6	6.9	42.7	0.2	0.8	0.8	43.5	1.8
50/50	43.6	1.9	45.2	4.1	43.1	1.5	2.0	1.8	44.9	3.9
45/55	39.1	3.6	42.7	8.5	41.3	1.0	0.5	1.4	42.7	3.3
PSF-DMOA, DMF/water [27]										
75/25	38.4	7.5	46.0	16.4	41.4	0.5	1.2	1.5	42.9	3.5
60/40	38.5	8.6	47.1	18.3	40.2	0.8	3.5	3.3	43.6	7.6
50/50	41.4	5.9	47.4	12.5	42.8	0.5	1.3	1.6	44.4	3.6

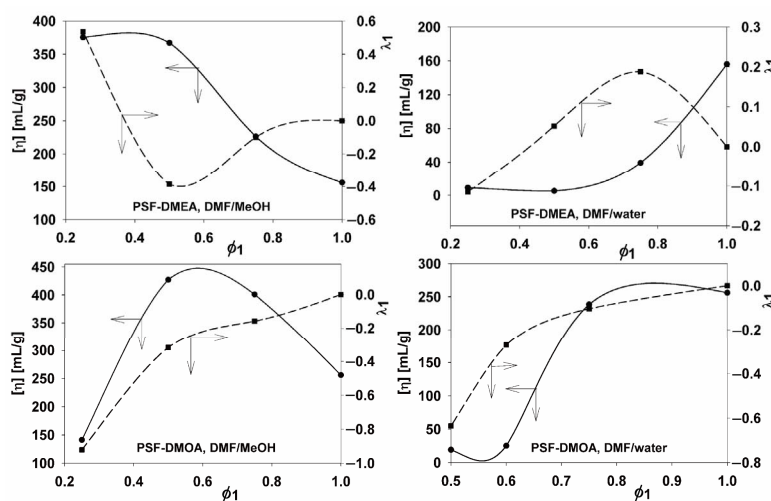


Figure 1. Influence of DMF volume fraction, ϕ_1 , on intrinsic viscosity, $[\eta]$, and on the experimental values of the preferential adsorption coefficient, λ_1 , in DMF/MeOH and DMF/water, at 25°C, for PSF-DMEA and PSF-DMOA samples.

and PSF-DMOA, respectively [23]. For the PSF-DMEA in the DMF/MeOH system, one may observe that the polymer coil dimension decreases with increasing the DMF content in the 0.25 - 1 volume fraction domain; below a 0.25 volume fraction of DMF, the polymer pre-

cipitates. For the same polymer, but in a DMF/water solvent mixture, the dimensions increase with increasing the DMF content, starting from approximately the same volume fraction of DMF. The PSF-DMOA coil dimensions possess maximum values in DMF/MeOH and DMF/

water, around 0.6 and 0.8 DMF volume fractions, respectively. For volume fractions of DMF below 0.25 in DMF/MeOH and 0.5 in DMF/water, the PSF-DMOA precipitates due to the nature of the alkyl radicals and content of nonsolvent in the system. Also, the values of intrinsic viscosity are higher for PSF-DMOA-with bulky carbon atoms in the alkyl side chain, compared with PSF-DMEA, where the alkyl side chain possesses two carbon atoms. Therefore, for a given composition of the DMF/MeOH and DMF/water solvent mixtures, one of the components is preferentially adsorbed by the quaternized polysulfone molecules in the direction of a thermodynamically most effective mixture.

These aspects influence the surface properties of the polymer. Moreover, according to previous data [27], it was found out that PSF evidences the lowest hydrophilicity, induced by the aromatic rings connected by one carbon and two methyl groups, oxygen elements, and sulfonic groups, while chloromethylation of PSF with the functional group $-\text{CH}_2\text{Cl}$ increases hydrophilicity (see the values of surface tension for PSF and CMPSF in **Table 3** from reference [27]). On the other hand, PSF-DMEA films possess low polar surface tension parameters, but slightly higher than those for PSF-DMOA. The hydrophobic character is given by the ethyl radical from the N-dimethylethylammonium chloride pendant group and by the octyl radical from the N-dimethyloctylammonium chloride pendant group, respectively, as visualized in the conformational structures from **Scheme 1**. Furthermore, the electron donor interactions, γ_{sv}^- , are smaller than the electron acceptor ones, γ_{sv}^+ , for PSF-DMEA, and electron donor interactions, γ_{sv}^- , exceed the electron acceptor interactions, γ_{sv}^+ , for PSF-DMOA, caused by the inductive phenomena from alkyl radical. The results reflect the capacity of the N-dimethylethylammonium chloride or N-dimethyloctylammonium chloride pendant groups to determine the acceptor or donor character of the polar terms, generated by these inductive phenomena.

3.2. Surface and Interfacial Free Energy

The effect of alkyl radicals of quaternized polysulfones and of the history of the films formed from solutions on surface properties was analyzed by surface free energy, ΔG_w - expressing the balance between surface hydrophobicity and hydrophilicity (equation (5)) [32], by interfacial free energy between two particles of quaternized polysulfones in water phase, ΔG_{sws}^{GM} (equations (6) and (7)), and by the work of spreading of water, W_s (equation (8)).

$$\Delta G_w = -\gamma_{lv} \cdot (1 + \cos \theta_{water}) \quad (5)$$

where γ_{lv} and θ_{water} are given in **Tables 1** and **2**, respectively.

$$\Delta G_{sws}^{GM} = -2 \cdot \gamma_{sl} \quad (6)$$

$$\gamma_{sl} = \left(\sqrt{\gamma_{lv}^p} - \sqrt{\gamma_{sv}^p} \right)^2 + \left(\sqrt{\gamma_{lv}^d} - \sqrt{\gamma_{sv}^d} \right)^2 \quad (7)$$

$$\begin{aligned} W_s &= W_a - W_c \\ &= 2 \cdot \left[\left(\gamma_{sv}^{LW} \cdot \gamma_{lv}^d \right)^{1/2} + \left(\gamma_{sv}^+ \cdot \gamma_{lv}^- \right)^{1/2} + \left(\gamma_{sv}^- \cdot \gamma_{lv}^+ \right)^{1/2} \right] - 2 \cdot \gamma_{lv} \end{aligned} \quad (8)$$

According to literature [33,34] which specifies that $\Delta G_w > -113 \text{ mJ/m}^2$ for more hydrophobic materials, ΔG_w evidences a high hydrophobicity for both samples, depending on the conditions of films preparation (**Table 4**). Moreover, the interfacial free energy, ΔG_{sws}^{GM} evaluated from solid-liquid interfacial tension, γ_{sl} , (equation (7)) has negative values (**Table 4**). Therefore, an attraction occurs between the two polymer surfaces, s , immersed in water, w , confirming the hydrophobic characteristics of both polymers, with higher hydrophobicity for PSF-DMOA films. Also, the hydrophobicity of these polymers was described by the work of spreading of water, W_s , over the surface, which represents the difference between the work of water adhesion, W_a , and the work of water cohesion, W_c . According to the negative values of the interfacial free energy of PSF-DMEA and PSF-DMOA, the work of spreading of water, $W_{s,w}$, (**Figure 2**) takes negative values, caused by the hydrophobic surfaces, where the work of water adhesion is low, comparatively with the work of cohesion; at the same time, it is observed that $W_{s,w,PSF-DMEA} > W_{s,w,PSF-DMOA}$.

3.3. Blood-Quaternized Polysulfone Interactions

Blood compatibility is dictated by the manner in which their surfaces interact with blood constituents, like red blood cells and platelets. To analyze the possibilities of using the polysulfone with N-dimethylethylammonium and N-dimethyloctylammonium chloride groups in biomedical applications, and for establishing its compatibility with blood, equation (8) was used, where $W_{s,w}$ and $W_{s,p}$ describe the work of spreading of red blood cells and platelets [35]; when blood is exposed to a biomaterial surface, adhesion of cells occurs and the extent of adhesion decides the life of the implanted biomaterials; thus, cellular adhesion to biomaterial surfaces could activate coagulation and the immunological cascades. Therefore, cellular adhesion has a direct bearing on the thrombogenicity and immunogenicity of a biomaterial, and thus dictates its blood compatibility. In this paper, we used the work of adhesion of the red blood cells as a parameter for characterizing biomaterials *versus* cell adhesion. The materials which exhibit a lower work of adhesion would lead to a lower extent of cell adhesion than those with a higher work of adhesion.

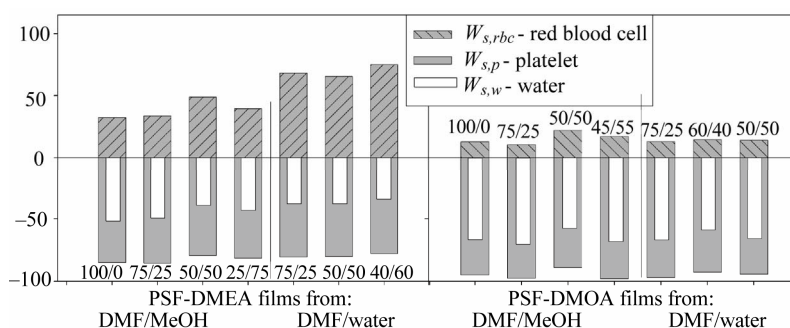


Figure 2. Work of spreading of water, of red blood cells and of platelets over the surface of PSF-DMEA and PSF-DMOA films prepared in different DMF/MeOH and DMF/water solvent mixture.

Table 4. Water interfacial tensions (γ_{sl}) and surface free energy (ΔG_w) for PSF-DMEA and PSF-DMOA films prepared in different DMF/MeOH and DMF/water (% v/v), and interfacial free energy (ΔG_{sws}^{GM}) between two particles of quaternized polysulfones in water phase.

Solvent mixtures	γ_{sl}		ΔG_w		ΔG_{sws}^{GM}	
			DMF/MeOH			
	PSF-DMEA	PSF-DMOA [27]	PSF-DMEA	PSF-DMOA [27]	PSF-DMEA	PSF-DMOA [27]
100/0	25.95	26.92	-67	-95.30	-1.90	-53.84
75/25	24.26	32.06	-68	-87.94	-48.52	-64.12
50/50	18.47	37.15	-75	-111.38	-36.94	-74.30
45/55	-	29.91	-	-89.18	-	-59.82
25/75	19.15	-	-74	-	-38.30	-
DMF/water						
75/25	16.50	21.66	-77	-102.41	-32.30	-43.32
60/40	-	20.08	-	-103.57	-	-40.16
50/50	17.60	25.30	-76	-97.70	-35.20	-50.60
40/60	15.57	-	-79	-	-31.14	-

Considering the surface energy parameters (γ_{lv} , γ_{lv}^d , γ_{lv}^+ , γ_{lv}^-) given in **Table 1** for red blood cells and platelets, the work of spreading of blood cells and platelets was estimated by equation (8), with surface free parameters for films prepared from DMF/MeOH and DMF/water solutions listed in **Table 4**.

Figure 2 shows positive values for the work of spreading of red blood cells, $W_{s,rbc}$, and negative values for the work of spreading of platelets, $W_{s,p}$, suggesting a higher work of adhesion comparatively with that of cohesion for the red blood cells, but a smaller work of adhesion comparatively with the one of cohesion for platelets. These results suggest that the exposure of platelets to PSF-DMEA and PSF-DMOA films determines an increase of platelets cohesion, which is higher for PSF-DMOA films, and that a good hydrophobicity can be correlated with a good adhesion of the red blood cells on

the surface of the polysulfone films.

In summary, both red blood cells and platelets are extremely important in deciding the blood compatibility of a material. Moreover, it is known that adhesion of the red blood cells onto a surface, *e.g.* modified polysulfones, requires knowledge of the interactions with the vascular components. Thus, endothelial glycocalyx along with the mucopolysaccharides adsorbed to the endothelial surface of the vascular endothelium reject clotting factors and platelets—which have a significant role in thrombus formation [36]. In this context, adhesion of the red blood cells and cohesion of platelets to surface films must be discussed in correlation with future specific biomedical applications. These results seem to be applicable for evaluating bacterial adhesion to the surfaces, and could be subsequently employed for studying possible implanted induced infections, or for obtaining semipermeable membranes.

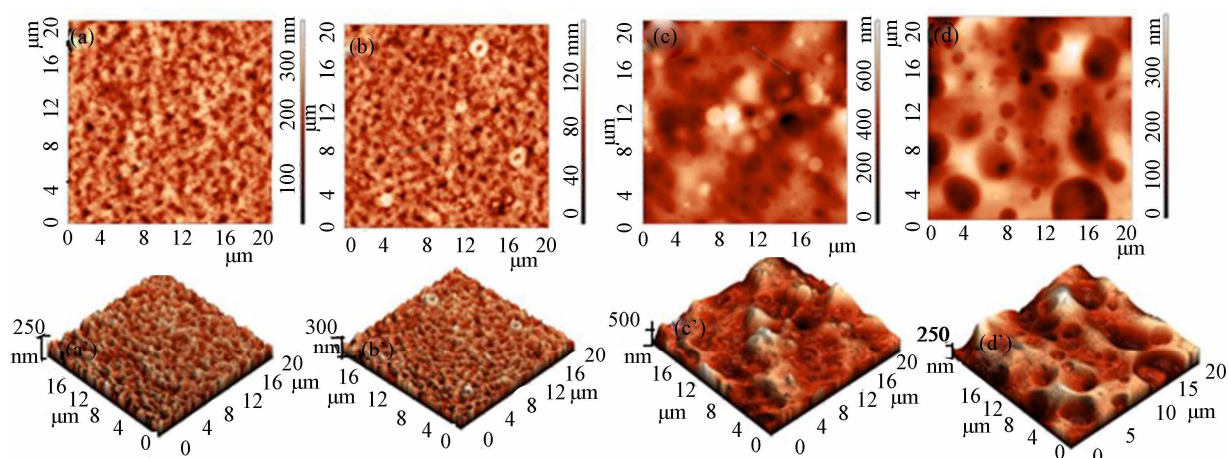


Figure 3. 2D and 3D AFM images with $20 \times 20 \mu\text{m}^2$ scanned areas of the PSF-DMEA films obtained from DMF/MeOH solutions: (a, a') - 100/0; (b, b') - 75/25 v/v; (c, c') - 50/50 v/v; (d, d') - 25/75.

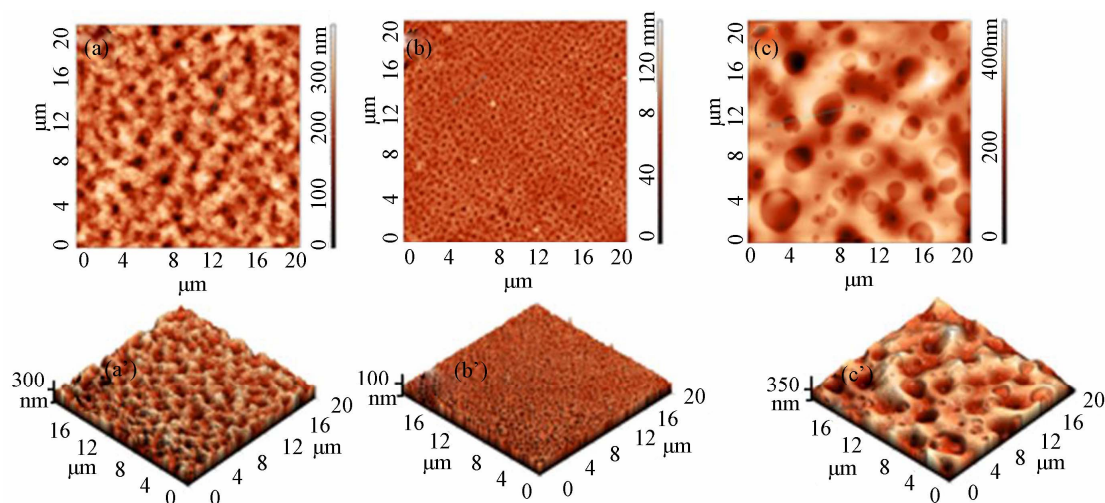


Figure 4. 2D and 3D AFM images with $20 \times 20 \mu\text{m}^2$ scanned areas of the PSF-DMEA films obtained from DMF/water solutions: (a, a') - 75/25 v/v; (b, b') - 50/50 v/v; (c, c') - 40/60.

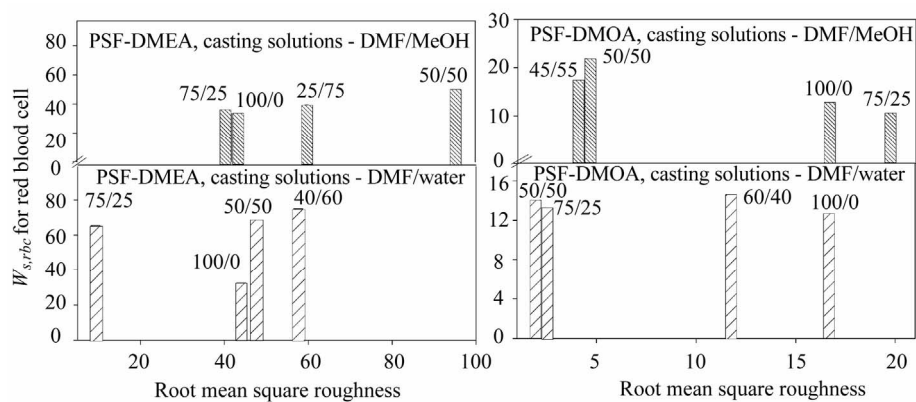


Figure 5. Effect of surface roughness on the work of spreading of red blood cells over the surface of PSF-DMEA and PSF-DMOA films prepared from solutions in different DMF/MeOH and DMF/water solvent mixtures.

Table 5. Pore characteristics, including number of pores, area (μm^2), depth (nm), diameter (μm), length (μm), and mean width (μm), and surface roughness parameters, including average roughness (S_a , nm), root mean square roughness (S_q , nm), and average height from the height histogram (H_a , nm) of PSF-DMEA and PSF-DMOA films prepared from solutions in DMF/MeOH and DMF/water (% v/v), with $20 \times 20 \mu\text{m}^2$ scanned areas, corresponding to the 2D AFM images.

Solvent mixtures	Pore characteristics						Surface roughness		
	Number of pores	Area	Depth	Diameter	Length	Mean width	S_a	S_q	H_a
PSF-DMEA, DMF/MeOH (% v/v)									
100/0	234	0.24	272.78	0.57	0.86	0.31	33.97	42.87	231.14
75/25	268	0.27	259.59	0.62	0.94	0.32	31.89	41.47	217.26
50/50	52	0.47	348.25	0.78	1.09	0.47	74.09	95.12	402.61
25/75	37	1.10	242.07	1.18	1.73	0.62	48.36	59.80	193.33
PSF-DMEA, DMF/water (% v/v)									
75/25	147	0.51	245.19	0.86	1.25	0.48	37.41	47.76	227.79
50/50	1080	0.06	89.57	0.23	0.47	0.15	6.87	9.27	77.43
40/60	42	2.19	230.10	1.64	2.43	0.86	44.98	57.61	281.80
PSF-DMOA, DMF/MeOH (% v/v) [27]									
100/0	9	10.43	25.64	3.33	6.24	1.45	14.11	16.82	58
75/25	-	-	-	-	-	-	14.43	19.90	82
50/50	34	0.70	11.37	0.89	1.56	0.42	3.09	4.41	17
45/55	44	0.80	16.02	0.98	1.53	0.49	2.77	4.24	28
PSF-DMOA, DMF/water (% v/v) [27]									
75/25	5	3.12	13.65	1.97	3.26	0.96	1.59	2.34	15
60/40	27	0.04	19.54	0.22	0.35	0.11	9.19	11.83	70
50/50	18	2.09	5.55	1.46	2.63	0.64	1.52	2.17	8

3.4. Surface Morphology

It is generally agreed that the physicochemical properties of substratum surfaces are the main factors mediating the compatibility with blood.

Figures 3 and **4** plot the bi- and three-dimensional structure evidenced by AFM investigations of PSF-DMEA films prepared with 100/0 v/v, 75/25 v/v, 50/50 v/v and 25/75 v/v, and also with 75/25 v/v, 50/50 v/v and 40/60 v/v of DMF/MeOH and DMF/water compositions solvent mixtures, respectively. According to the images, increasing the nonsolvent content in the casting solutions favored modification of surface morphology. Thus, **Figure 3** and **Table 5** show that average surface roughness attains its maximum value at 50/50 v/v DMF/MeOH, and favors the appearance of the smallest number of pores with highest depth values. Also, the area, diameter, length and mean width increase with increasing the nonsolvent content. It should be noted that the thermodynamic quality of the solvent mixtures over the studied domain increases with the addition of nonsolvent, at approximately 50/50 v/v DMF/MeOH becoming constant, while the preferential adsorption of nonsolvent takes a maximum value, according to **Figure 1**.

The presence of water as a nonsolvent in the solutions used for casting films influenced the AFM images pre-

sented in **Figure 4**; a higher water content decreases the thermodynamic quality of the DMF/water solvent mixtures (**Figure 1**) so that, at 50/50 v/v DMF/water, a minimum value of surface roughness and a maximum number of pores with minimum values of area, depth, diameter, length and mean width, were observed. It may be assumed that the specific interactions with the mixed solvents employed in the study modify the PSF-DMEA and PSF-DMOA solubility and determine modification of the solution properties [23], according to **Figure 1**.

On the other hand, previous data [27] obtained for PSF-DMOA in the same solvent mixtures evidenced that the number of pores and their average size increases, while the average surface roughness decreases with increasing the content of nonsolvent, MeOH. For films prepared from DMF/water solutions, the presence of water as a nonsolvent in the casting solution decreases the thermodynamic quality of the DMF/water solvent mixtures up to a 40 % water composition, so that, for the corresponding film, average surface roughness, the number of pores and their depths take maximum values with a minimum area.

Figure 5 plots the dependencies between root mean square roughnesses and the work of spreading of the red blood cells over the surface of PSF-DMEA and PSF-DMOA films prepared from different DMF/MeOH and

DMF/water solvent mixtures. These results show that surface morphology depends on the history of the formed films, including the characteristics of quaternized polysulfones and the thermodynamic quality of solvents. Moreover, the results suggest that surface free energy (surface hydrophobicity) and surface roughness are the key parameters controlling the compatibility with the red blood cells, known as a complicated process that depends on many factors, including surface chemistry, hydrophobicity, and surface roughness. The contribution of each of these factors is difficult to establish, however, it is clearly seen that PSF-DMOA is characterized by a lower compatibility with the red blood cells than PSF-DMEA. On the other hand, the compatibility values are higher for PSF-DMEA and lower for PSF-DMOA films prepared in DMF/water, compared with films prepared in DMF/MeOH.

4. Conclusions

New quaternized polysulfones, prepared by quaternization of chloromethylated polysulfone with N,N-dimethylethylamine and N,N-dimethyloctylamine were investigated to obtain information on their hydrophilic/hydrophobic properties and blood compatibility. The history of the formed films, prepared by a dry-cast process in DMF/MeOH and DMF/water solvent/nonsolvent mixtures, influenced the surface tension parameters, surface and interfacial free energy and the work of spreading of water, maintaining the surfaces hydrophobic characteristics of both polysulfones. On the other hand, the results reflect the capacity of N-dimethylethylammonium or N-dimethyloctylammonium chloride pendant groups to determine the acceptor or donor character of the polar terms, caused by the inductive phenomena of alkyl radicals.

The AFM images showed that surface morphology is characterized by roughness and nodules formations, depending on the composition of solvent/nonsolvent mixtures, including the characteristics of quaternized polysulfones and the thermodynamic quality of the solvents. Moreover, the results suggest that:

- surface hydrophobicity and surface roughness are the parameters controlling the compatibility with the red blood cells and platelets: a good hydrophobicity can be correlated with a good adhesion of the red blood cells and with a good cohesions of the platelets on the surface of the quaternized polysulfone films;
- high work of adhesion comparatively with work of cohesion for the red blood cells, but a smaller work of adhesion comparatively with the one of cohesion for platelets was obtained;
- the exposure of blood to both quaternized polysulfones involves higher platelets cohesion for PSF-DMOA films, comparatively with PSF-DMEA films.

- These results are useful in investigations on specific biomedical applications, including evaluation of bacterial adhesion to the surfaces, and utilization of modified polysulfones as semipermeable membranes.

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