EFFECT OF POLYMER STRUCTURE AND MORPHOLOGY ON INTERFACIAL INTERACTION TO SOME MICROORGANISMS

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Abstract: *The role of synthetic polymers in the biomedical field is exponentially growing as reflected in the variety of applications, ranging from implants to medical equipment (syringes, tubes, filters, pipettes, wound dressing materials, etc.). This work aims to study the influence of the chemical structure of two synthetic polymers on the resulted morphology. Atomic force microscopy (AFM) investigations are used for mapping the surface morphology of the prepared films. Also, AFM data are used to characterize the surface features of each polymer by monitoring specific roughness parameters. Based on surface energy properties, the interfacial interactions of samples with several microorganisms are evaluated to check the suitability of the studied materials in production of medical equipment. The resistance to the action of undesired biological media (like enterococci, staphylococci, lactobacilli, etc.), which are causing harmful effects to human health upon entering in the organism, is discussed.*

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Keywords: *synthetic polymer, morphology, interface*

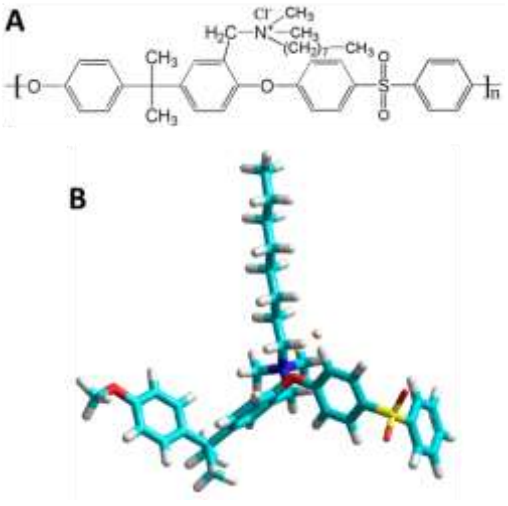
1. Introduction

Polymers are more and more integrated in medicine as biomaterials for a variety of uses, starting from implants, pacemakers, hemocompatible membranes, artificial organs, bio-diagnosis and medical equipments [Kalia, 2011]. Among the biopolymers, a particular attention was ascribed to polysulfones (PSF), which are known for their elevated toughness and resistance at high temperatures, combined with great stability to oxidation and hydrolysis [Chukov,2019]. In order to accomplish new materials with particular properties adapted to bio-applications, many studies were devoted to chemical modification of the PSFs [Boer, 2017; Mamah,2020; Serbanescu, 2020]. These reports revealed that by different chemical mechanisms, it is possible to introduce certain reactive groups into PSF structure. As a result, novel quaternized PSF can be prepared through the quaternization reaction of the chloromethylated polysulfone (PSFC) with triphenylphosphine or N,N-dimethyloctylamine, which have an important potential in biomedicine [Filimon,2010; Albu; 2011; Buruiana,2013]. Such applications require close examination of the surface wettability and morphology. The surface polarity of the polymer could improve the interfacial interaction with biological molecules (e.g. proteins). However, in other cases, like blood contact, high cohesion is preferable since platelets adhesion could trigger clotting [Wang, 2016]. Also, the surface morphology parameters are also involved in the interaction of the PSF with the biological materials, like blood, microorganisms, etc.

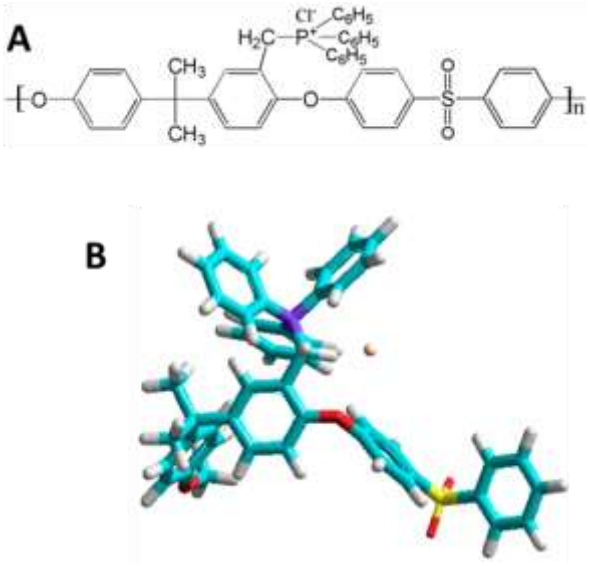
Having all these aspects in consideration, this work is focused on the characterization of the surface properties of two PSFs having different chemical structures. Molecular modeling was undertaken to investigate the conformational properties of these biopolymers. Atomic force microscopy (AFM) and interfacial adhesion analyses were done to check the sample suitability for use in manufacturing of biomedical equipments.

2. Materials and methods

Two modified PSFs with different bulky side groups were synthesized through the reaction of chloromethylated PSF with N-dimethyloctylamine (PSF-N) or triphenylphosphine (PSF-P), the quaternization reaction being performed in N,N-dimethylformamide (DMF). The details regarding the synthesis of these quaternized polysulfones are presented in literature [Avram,1997; Ioan,2011; Buruiana,2013]. To evaluate the chain flexibility, the chemical structure and molecular modeling, used as a tool of projecting the conformations at lowest energy (using HyperChem demo version) for PSF-N and PSF-P are presented in Schemes 1 and 2, respectively. The colors used to represent the atoms are: C-cyan, H-gray, O-red, S-yellow, Cl-orange, N-blue, P-violet.



Scheme 1: *Chemical (A) and conformational structure (B) of PSF-N*



Scheme 2: *Chemical (A) and conformational structure (B) of PSF-P*

The atomic force microscopy (AFM) measurements were performed (using Nova v1.1.1.19891 software from NT-DMT) in atmospheric conditions, at room temperature on a Solver Pro-M Scanning Probe Microscope (NT-MDT, Zelenograd, Moscow, Russia), with a NSG10 cantilever, with the resonance frequency of 177 kHz, using semicontact topography mode. The scan physical size was 30x30 μm^2. The origin of the scan was horizontal left bottom. The scanning velocity was 36 μm/s, the set point 7 V and the feedback gain 0.1. The morphological characteristics and surface texture parameters were calculated using Image Analysis 3.5.0.19892 software from NT-DMT.

Surface tension investigations of the synthetic polysulfones were obtained from static contact angle analysis with a device made in the laboratory. This is performed using an approach, which is largely detailed in our previous reports [Ioan,2011; Buruiana,2013]. Based on these surface energy measurements, it was possible to estimate the adhesion and cohesion forces acting at the film sample interface with some materials of biological interest, namely enterococci, staphylococci, and lactobacilli.

3. Results and discussion

3.1 Surface morphology

To highlight the influence of the chemical structure of the samples on the resulted morphology, atomic force microscopy investigations were conducted on the prepared films. The 2D and 3D representations of AFM topography images obtained for PSF-N sample are presented in Figure 1 and for PSF-P sample in Figure 2. Analyzing these images, it can be observed the ability of both samples to form porous membranes, the predominant morphological formation being that of pores. There are two categories of pores for both samples. On the large scanning surface (of 30x30 μm^2), the pores of considerable size can be identified, even of the order of micrometers, while on the small scanning surface (of 3x3 μm^2) pores of nanometric dimensions can be highlighted. Over each AFM image, Pore Analysis was used to evaluate the pores average length, mean width and mean depth. The results are displayed in Table 1. For PSF-N sample, oval-shaped micropores can be seen individually, but especially joined two, three or even four, creating appreciable ones. Instead, the nanopores are very well defined (see the inset from Figure 1A), evenly distributed over the entire surface between the micropores, which is apparently smooth when the investigation takes place on a large scale (Figure 1A).

When quaternized polysulfone with triphenylphosphonium pendant groups (PSF-P) sample was investigated, the same trend is observed, namely distinct micropores with a merge tendency. This time, according to Table 1, these micropores have smaller dimensions than those obtained in the case of quaternized polysulfone with N-dimethyloctylammonium groups, mostly due to the film obtaining method and the solvent evaporation during the drying process. Conversely, the dimensions of the individual well highlighted nanopores (inset from Figure 2A were significantly higher (Table 1), due to the lower chain flexibility and steric hindrances induced by the bulky triphenylphosphonium pendant groups, as observed from the molecular modeling in Scheme 2 B.

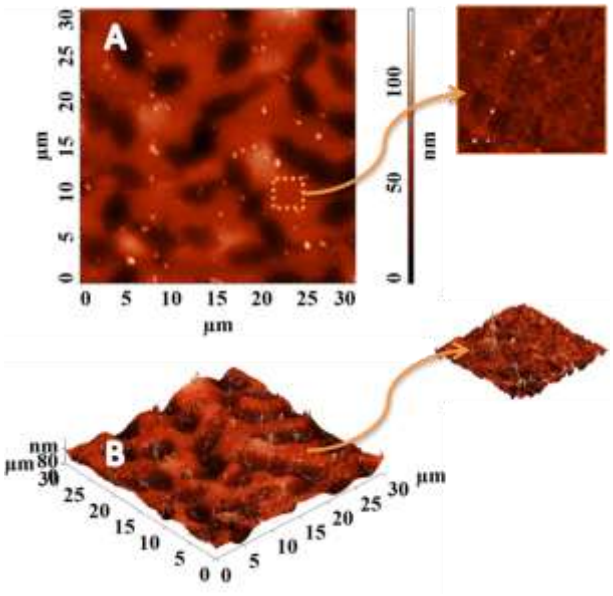


Figure 1: *2D (A)and 3D representation (B) of AFM topography images obtained for PSF-N sample over 30x30 μm^2 and 3x3 μm^2 (in detail)*

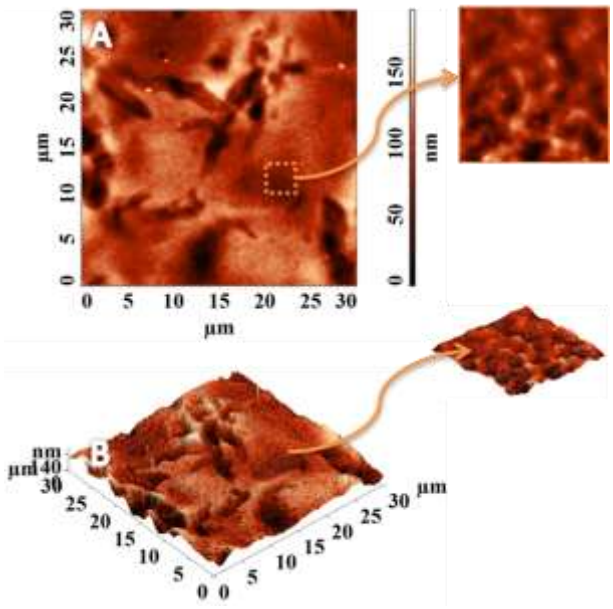


Figure 2: *2D (A)and 3D representation (B) of AFM topography images obtained for PSF-P sample over 30x30 μm^2 and 3x3 μm^2 (in detail)*

Table 1. *Morphological characteristics of the investigated PSFs.*

Sample	Micropores characteristics on 30x30 μm²		
	L (μm)	W (μm)	D (nm)
PSF-N	4.6±0.4	3.1±0.3	62±8
PSF-P	2.5±0.3	0.8±0.1	144±17
	Nanopores characteristics on 3x3 μm²		
	L (nm)	W (nm)	D (nm)
PSF-N	129±39	44±18	5±1
PSF-P	417±59	114±11	12±1

L: pores average length; W: pores mean width; D: pores mean depth

Although the PSF-N sample showed pores of considerable size, the surface of the PSF-P sample had a higher root mean square roughness (Table 2) and complexity of morphology, due to their much greater depth and the existence of a multitude of larger nanopores.

Table 2. *Surface texture parameters calculated for the investigated PSFs.*

Sample	Surface texture parameters on 30x30 μm²				
	Sq (nm)	Stdi	Sbi	Sci	Svi
PSF-N	16	0.739	0.262	1.330	0.113
PSF-P	28	0.700	0.504	1.354	0.135

Sq: root mean square roughness of the surface (nm); Stdi: surface texture direction index; Sbi: surface bearing index; Sci: core fluid retention index; Svi: valley fluid retention index.

Both investigated surfaces presented high isotropy, suggested by the values over 0.700 of the surface texture direction index (Table 2), indicating the existence of the same morphological properties in all directions. Regarding the functional parameters, the quaternized polysulfone with triphenylphosphonium pendant groups presented improved surface bearing properties (Sbi) and better fluid retention in the core (Sci) and valley regions (Sci) (Table 2).

3.2 Interfacial adhesion

The surface properties of the PSFs, here under study, are previously published [Albu,2011; Buruiana,2015]. These data are further used for the assessment of the adhesion/cohesion with some microorganisms, such as enterococci, staphylococci, lactobacilli. This can be quantified by means of the work of spreading (Ws), defined below:

$$W_s = 2\left(\sqrt{\gamma_s^d \gamma_b^d} + \sqrt{\gamma_s^p \gamma_b^p}\right) - 2\gamma_b^t \qquad (1)$$

where γ is the surface tension, the letter d, p and t mean the disperse, polar and total surface tension, whereas the letters s and b refer to the sample and biological materials.

The obtained data for Ws at the interface of PSFs with *Enterococci faecalis, Lactobacillus gassei, Streptococcus sanguinis, and Streptococcus mitis*, are displayed in the Figure 3. The considered microbial strains are found in either the gastrointestinal tracts of humans, digestive and urinary tracts, oral cavity and bloodstream, or in throat, nasopharynx and mouth, respectively. Analysis of the results shows that E. faecalis presents adhesion interaction with the samples, while for the other microbial organisms the adhesion is either very low or is prevailed by cohesion. The PSF-P sample shows higher potential for bio-applications, given its smallest interaction with these microbial strains.

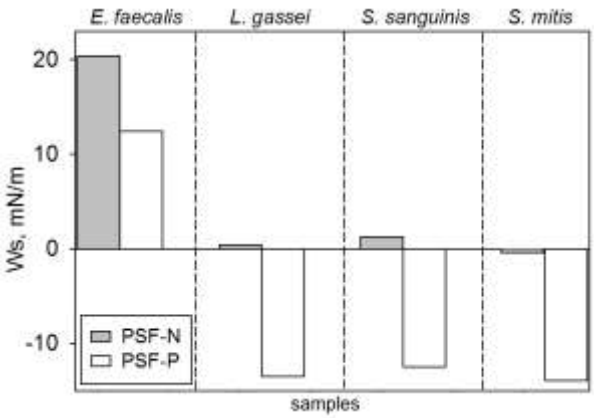


Figure 3: *The spreading work values at the sample interface with some microbial strains.*

This is consistent with other works that prove the antimicrobial potential of the PSF-based blends and composites [Sabri,2019; Xu,2016;Harun,2016]. In this study the advantage is that the PSF itself has antimicrobial activity owing to its modified chemical structure by quaternization procedure. These results are very useful for future design of biopolymers with antimicrobial activity that can be employed in the fabrication of biomedical equipments, such as tubes, syringes, membranes or wound dressing.

4. Conclusions

The presented study concerns two synthetic polymers, namely two quaternized polysulfones one with triphenylphosphonium pendant groups and the other one with N-dimethyloctylammonium groups. The chemical structure and the conformational arrangement of these samples favored the appearance of a porous surface morphology. Both investigated surfaces presented high isotropy. The polysulfone enriched with triphenylphosphonium groups presented higher roughness and complexity of the morphology, improved surface bearing properties and better fluid retention in the core and valley zones, due to its lower chain flexibility and steric hindrances induced by the bulky pendant groups. Among the studied samples, PSF-P presents low adhesion or mainly cohesion with the considered enterococci, staphylococci, and lactobacilli.

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