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Effects of chemical structure and plasma treatment on the surface properties of polysulfones

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Abstract: The correlation between surface tension parameters and the chemical composition of polysulfone, chloromethylated polysulfone and quaternized polysulfone membranes, before and after plasma treatment, was investigated. Calculations are based on the geometric mean approach of Owens, Wendt, Rabel and Kälble, as well as on the theoretical methods involving quantitative structure-property relationships on the basis of the group contribution techniques. The chemical modifications of polysulfone membranes and the low pressure plasma treatment affect the contact angle corresponding to different liquids. Consequently, the total surface tension and the polar component increase with the substitution degree of chloromethylated polysulfone and with the quaternization degree of the ammonium groups, in quaternized polysulfone samples. The plasma treatment modifies the surface energy of the samples, increasing their surface polarity and wettability. Surface wettability trends were also studied by means of the free energy of hydration between compounds and water.

Key words: modified polysulfones, surface properties, plasma treatment

Introduction

Polysulfones (PSF) represent a class of polymers containing sulfone groups and aromatic nuclei, characterized by good optical properties, thermal and chemical stability, mechanical strength and resistance to extreme pH values and low creep [1-3]. Chain rigidity is derived from the relatively inflexible and immobile phenyl and SO_2 groups, while toughness - from the connecting ether oxygen [4].

While these materials have excellent overall properties, their intrinsic hydrophobic nature precludes their use in membrane applications that require a hydrophilic character. Therefore, such polymers may need some modification to improve their performance for specific applications [5, 6]. The chemical modification of poly sulfones, especially the chloromethylation reaction, is a subject of considerable interest from both theoretical and practical points of view, including obtaining of the precursors for functional membranes, coatings, ion exchange resins, ion exchange fibers and selectively permeable membranes [2, 7, 8]. Functionalized polymers, chloromethylated polysulfones and quaternized polysulfones have evidenced many interesting properties that permitted a wide spectrum of industrial and environmental applications [9-11]. Quaternization of the ammonium groups is an efficient method for increasing hydrophilicity. Accordingly, these polymers can be utilized for multiple applications, e.g. as biomaterials and semipermeable membranes. Also, the different components of a block or graft copolymer may segregate in bulk, yielding nanometer-sized patterns or mesophasic structures. Also, numerous applications involve nanodomained solids [12]. By matching the periodicity of the patterns with the wavelength of visible light, literature studies have demonstrated that block copolymers, including polysulfones, act as photonic crystals. Segregated block copolymers, polysulfones included, have been also used as precursors for the preparation of various nanostructures, including nanospheres, nanofibers, annotates and thin membranes containing nanochannels. Thin membranes containing nanochannels have been used as membranes, pH sensors or templates to prepare metallic nanorods.

In the above mentioned applications, information regarding the balance between the hydrophilic and hydrophobic properties of the surface is also essential for enhancing biocompatibility.

The information obtained from contact angle measurements, for a wide range of solid substrates, has proved vital to the formulation of adhesives, polymer fibers and biocompatible materials, and also for assuring fundamental understanding of the solid-solid and solid-liquid intermolecular interactions [13]. Plasma treatments (application of discharge in the presence of gases or monomers) or other types of stimuli, such as the ones induced by heat or electrical potentials, may alter the surface energy of most polymers, changing their surface polarity, wettability, and adhesiveness [14,15]. In recent years, an increasing number of papers have been devoted to separation membranes as an objective of plasma treatment of polysulfone [16-18]. A careful choice of plasma medium and process parameters allows for tailoring of a combination of pore size, bulk and surface properties in the individual separation process.

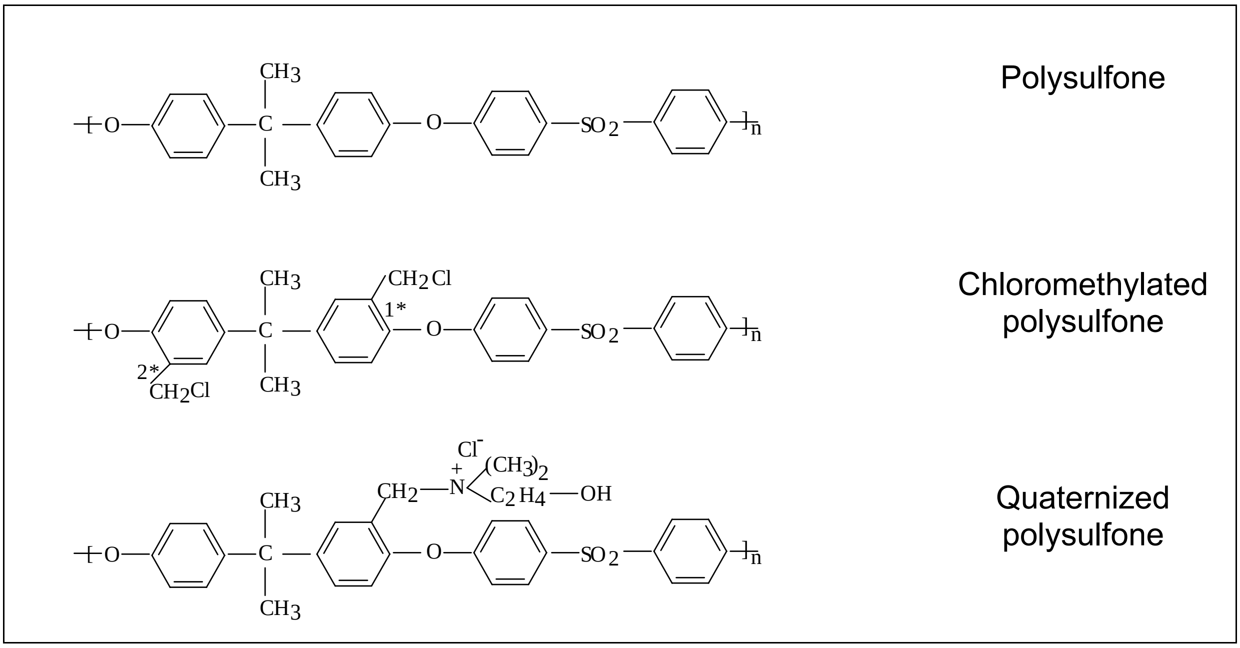
Previous publications have presented the syntheses [19, 20] and some solution properties [21-24] for a series of polysulfones. Studies have been carried out on the chloromethylation reaction for obtaining soluble chloromethylated polymers with different degrees of substitution. The influence of concentration and temperature on the coil densities and dimensions, as well as the influence of the chlorine content on unperturbed dimension parameters, were analyzed. Also, information on the conformational behaviour in different mixed solvents of quaternized polysulfones with different content of ionic chlorine, obtained from chloromethylation processes, was analyzed.

The objective of the present study is to determine the surface tension components and to investigate the relation between the chemical structure of the polymeric membranes and the surface tension parameters before and after low pressure plasma treatment. Surface wettability trends for polysulfones were also investigated by means of the free energy of hydration between the compounds and water.

Results and discussion

Contact angles and surface tension parameters

The general chemical structures of the studied polysulfone (PSF), chloromethylated polysulfone (CMPSF) and quaternized polysulfone (PSFQ) are presented in Scheme 1. The chloromethylation reaction of polysulfone may occur in position 1* for CMPSF1, when $DS \leq 1$ (where DS is the substitution degree from Tab. 1). For samples CMPSF2 and CMPSF3, when $DS > 1$, the chloromethylation reaction occurs in positions 1* and 2*. Thus, the difference between these two samples lies in the different values of the chlorine content, according to Tab. 1.



Scheme 1. General structure of the studied polysulfones

Tab. 1 lists the chlorine content, the degree of substitution, the molecular weights of the structural units, m_0, the number-average molecular weights, M_n, of the chloromethylated polysulfones, determined from the polymerization degree of the polysulfone (DP = 90), and the molecular weights of the structural units of chloromethylated polysulfones, along with the intrinsic viscosity determined in N,N-dimethylformamide (DMF) at 25 °C [23].

The characteristics of the quaternized polysulfones (PSFQ) are presented in Tab. 2

Tab. 1. Chlorine content, substitution degree, DS, molecular weights of the structural units, m_0, number-average molecular weights, M_n, and intrinsic viscosities in DMF at 25 °C, $[\eta]$, of polysulfone and chloromethylated polysulfones.

Sample	Cl in %	DS	m_0	M_n	$[\eta]$ in dL/g
PSF	0	0	442.51	39000	0.3627
CMPSF1	3.34	0.437	463.68	40866	0.3929
CMPSF2	10.53	1.541	517.17	45580	0.4703
CMPSF3	12.13	1.828	530.83	46785	0.6970

Tab. 2. Ionic chlorine content, Cl_i, molecular weights of the structural units, m_0, and number-average molecular weights, M_n, of quaternized polysulfones.

Sample	Obtained from:	Cl_i in %	m_0	M_n
PSFQ1	CMPSF1	2.15	479.47	42300
PSFQ2	CMPSF2	5.71	647.31	57000

The methods used for the determination of surface tension begin from the contact angle measurements between the liquid meniscus and the polymer surface. Contact angle is the measure of material surface wettability. A contact angle below 90° indicates that the substrate is readily wetted by the test liquid, while an angle over 90° shows that the substrate will resist wetting.

The surface tension data of the doubly-distilled water (W), ethylene glycol (EG), glycerol (G) and formamide (FA) used in the calculations of the surface tension parameters of the studied polysulfones are presented in Tab. 3.

Tab. 3. Surface tension parameters (mN/m) of the liquids used for contact angle measurements: total surface tension, γ_{lv}, disperse component of surface tension, γ_{lv}^{d}, polar component of surface tension, γ_{lv}^{p}, electron-donor contribution on polar component, γ_{lv}^{-}, and electron-acceptor contribution on polar component, γ_{lv}^{+}.

Test liquid	γ_{lv}	γ_{lv}^{d}	γ_{lv}^{p}	γ_{lv}^{-}	γ_{lv}^{+}
Water [25]	72.8	21.8	51.0	25.50	25.50
Ethylene glycol [26]	48.0	29.0	19.0	47.00	1.92
Glycerol [27]	64.0	34.0	30.0	57.40	3.92
Formamide [27]	58.0	39.0	19.0	39.60	2.28

Tab. 4 shows the contact angle values between water, ethylene glycol, glycerol or formamide and PSF, CMPSF and PSFQ membranes both before and after plasma treatment.

Tab. 4. Contact angle of different probe liquids (in °), before and after plasma-treatment.

Sample	Untreated samples				Plasma treated samples			
Solvent	W	G	FA	EG	W	G	FA	EG
PSF	79	70	65	60	35	33	10	15
CMPSF1	78	72	66	57	32	31	13	13
CMPSF2	73	69	65	54	30	27	13	13
CMPSF3	71	68	64	52	30	26	15	11
PSFQ1	64	63	64	51	29	26	12	13
PSFQ2	64	56	69	48	28	25	12	11

For the calculation of the surface tension parameters, the geometric mean method (Eqs. (1) and (2)) [28-30] was used.

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

$$\gamma_{sv}=\gamma_{sv}^{d}+\gamma_{sv}^{p} \tag{2}$$

where θ is the contact angle determined for water, ethylene glycol, glycerol and formamide, subscripts "*lv*" and "*sv*" denote the interfacial tensions between liquid-vapor and surface-vapor, respectively, while superscripts "*p*" and "*d*" denote the polar and disperse components, respectively, of total surface tension, γ_{sv}.

The solid surface tension components γ_{sv}^d and γ_{sv}^p were determined from the intercept and the slope of the linear dependence described by Eq. (1), using the known surface tension components [25-27] of different liquids from Tab. 3 and the contact angles from Tab. 4. Thus, Fig. 1 exemplifies the contact angle data plotted according to Eq. (1) for the PSF, CMPSF1, PSFQ1 samples. Total surface tension γ_{sv} was calculated with Eq. (2). In this study was used only the polar solvents. In this context, literature shows that the contact angles of apolar liquids do not fit into Eq. (1) derived from the polar liquids, i.e., the contact angles calculated for apolar liquids by this equation are higher or lower than those obtained from experimental data [31].

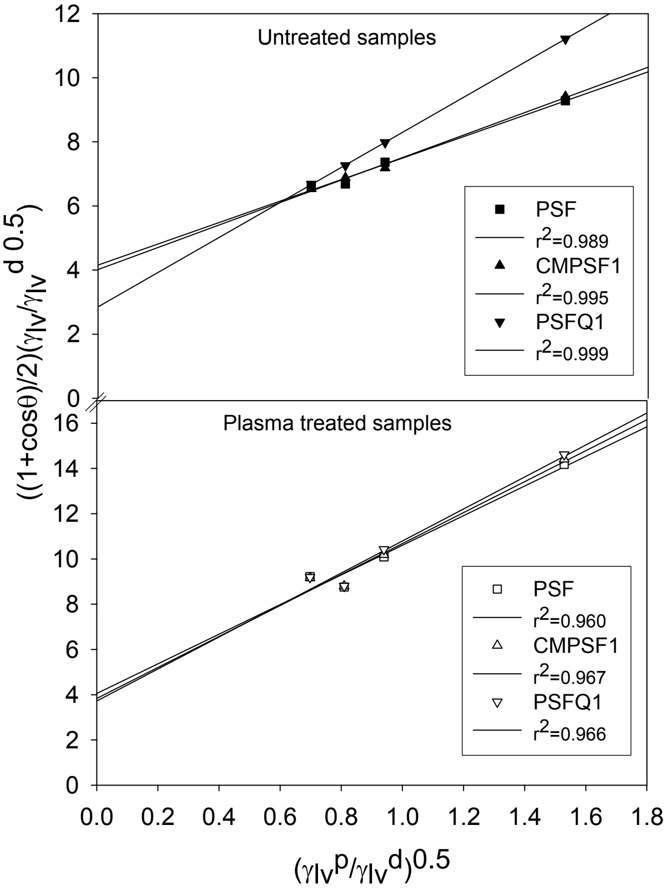


Fig. 1. $\frac{1+\cos\theta}{2}\cdot\frac{\gamma_{lv}}{\sqrt{\gamma_{lv}^{d}}}$ *vs.* $\sqrt{\frac{\gamma_{lv}^{p}}{\gamma_{lv}^{d}}}$ for untreated and plasma treated PSF, chloromethylated polysulfone – CMPSF1 and quaternized polysulfone – PSFQ1, according to Eq. (1).

Tab. 5 lists the surface tension parameters γ_{sv}^{d}, γ_{sv}^{p} and γ_{sv} obtained for studied samples.

Tab. 5. Surface tension parameters (mN/m) and contribution of the polar component to the total surface tension (%) for untreated and plasma treated polysulfone, chloromethylated polysulfones and quaternized polysulfones, according to the geometric mean method (Eqs. (1), (2)).

Sample	Untreated sample				Plasma treated sample			
	γ_{sv}^{d}	γ_{sv}^{p}	γ_{sv}	$\gamma_{sv}^{p}/\gamma_{sv}$	γ_{sv}^{d}	γ_{sv}^{p}	γ_{sv}	$\gamma_{sv}^{p}/\gamma_{sv}$
PSF	17.28	11.21	28.49	39.35	16.42	42.90	59.32	72.32
CMPSF1	16.13	12.32	28.45	43.30	14.72	46.87	61.59	76.10
CMPSF2	13.23	17.56	30.79	57.03	14.13	49.07	63.20	77.64
CMPSF3	12.66	19.43	32.09	60.55	14.14	49.18	63.32	77.67
PSFQ1	8.12	29.88	38.00	78.63	13.86	50.04	63.90	78.31
PSFQ2	8.04	31.11	39.15	79.46	13.64	50.95	64.60	78.88

It is generally known that the PSF formed from the aromatic rings connected by one carbon and two methyl groups, oxygen elements, and sulfonic groups, possesses the lowest hydrophilicity. Chloromethylation of PSF with the functional group $-CH_2Cl$ increases hydrophilicity. Moreover, the results indicate that the PSFQ membranes are the most hydrophilic ones from the studied samples (lowest water contact angle), due to the N,N-dimethylethanolamine hydrophilic side groups. Hence, it is observed that total surface tension, γ_{sv}, and the polar component, γ_{sv}^{p}, increase with the degree of substitution of CMPSF and with the quaternization degree of the ammonium groups for PSFQ samples. Therefore, the relative ratio of the polar component to the total surface tension ranges from approx. 39% for PSF and 43% for CMPSF1, with the substitution degree DS<1, to 57-61% for CMPSF, with the substitution degree DS>1, and to 79% for PSFQ. The apolar component, γ_{sv}^{d}, decreases from PSF to CMPSF and PSFQ. The total surface tensions of PSF and CMPSF1, where the substitution degree DS<1, are dominated by the apolar component, while the total surface tension of CMPSF2, CMPSF3, (DS>1) and PSFQ are dominated by the polar term. Thus, the functional groups $-CH_2Cl$ attached by chloromethylation process increase the polarity for chloromethylated polysulfones with a substitution degree DS>1; also, the N, N-dimethylethanolamine side groups introduced by the quaternization process increase the polarity. The change is moderate for chloromethylated polysulfone with DS>1, with different chloride content.

Della Volpe *et al.* [32] show that an improper utilization of three liquids without dispersive liquids, or with liquids prevalently basic or prevalently acidic, strongly increases the ill-conditioning of the system. Literature postulates that contact angles should be measured with a liquid whose surface tension is higher than the anticipated solid surface tension [33].

In order to anticipate the solid surface tension parameters the theoretical study based on the structure-property relationships considering the group contribution techniques (Eq. (3)), can be used, by the following steps [34]:

$$\gamma(298K) \approx 0.75 \cdot [E_{coh} / V(298K)]^{2/3} \tag{3}$$

where γ - total surface tension, E_{coh} - cohesive energy, V - molar volume

-Calculation of the zeroth - order connectivity indices $^{0}\chi$ and $^{0}\chi^{v}$ and of the first-order connectivity indices $^{1}\chi$ and $^{1}\chi^{v}$ described in Appendix A. The values of the atomic simple connectivity indices δ and of the valence connectivity indices δ^{v} used in the calculations are listed in Tab. 6. Tab. 7 gives the values obtained for $^{0}\chi$, $^{0}\chi^{v}$, $^{1}\chi$ and $^{1}\chi^{v}$.

Tab. 6. δ and δ^{v} values used for the calculation of zero- and first-order connectivity indices [34].

Atom	Hyb	N_H	δ	δ^{v}	Atom	Hyb	N_H	δ	δ^{v}
C	sp^3	3	1	1	N	sp^3	0	3	5
		2	2	2	O	sp^3	1	1	5
		0	4	4			0	2	6
	sp^2	1	2	3	S	sp^3 [a)]	0	4	8/3
		0	3	4	Cl	-	0	1	7/9

[a)] These numbers refer to sulfur in its highest oxidation state, as typically encountered in the bonding configuration $R\text{-}SO_2\text{-}R'$

Tab. 7. Zero- order connectivity indices, $^{0}\chi$ and $^{0}\chi^{v}$, and first-order connectivity indices, $^{1}\chi$ and $^{1}\chi^{v}$ for polysulfone, chloromethylated polysulfones and quaternized polysulfones.

Sample	$^{0}\chi$	$^{0}\chi^{v}$	$^{1}\chi$	$^{1}\chi^{v}$
PSF	22.35	17.98	15.32	10.71
CMPSF1	23.04	18.75	15.73	11.18
CMPSF2	24.78	20.70	16.78	12.37
CMPSF3	25.23	21.21	18.38	13.93
PSFQ1	25.16	20.58	17.03	12.05
PSFQ2	32.17	27.06	21.30	15.38

- Calculation of cohesive energy by two methods (Appendix B), applying the group contributions of Fedors (Eqs. (B1)-(B3)) and the group contributions of van Krevelen and Hoftyzer (Eqs. (B4) and (B5));

- Calculation of the molar volume V at room temperature (298 K), according to Appendix C.

Total surface tension parameters calculated with the cohesive energy, $E_{coh}(1)$ or $E_{coh}(2)$ and molar volume, V, are presented in Tab. 8. The differences observed between these results and the geometric mean method reflects the influence of the chemical composition without supplementary interactions observed and included in the experimental data. Thus, for the PSF and CMPSF neutral polymers, an increase of the total surface tension with increase in the substitution degree, according to the values obtained from contact angles, has been observed. Also, the total surface tension obtained for the PSFQ polar samples by contact angles measurements of different solvents increases with increasing charge density. Nevertheless, the theoretical results indicate decrease of the total surface tension with increasing charged density, because the supplementary interactions of electrostatic nature are not considered in the calculation of cohesive energies.

Tab. 8. Total surface tension parameters, $\gamma_{(1)}$ (Eqs. (B1), (C1), (6)) or $\gamma_{(2)}$ (Eqs. (B4), (C1), (6)) from the theoretical data calculated with cohesive energy, $E_{coh}(1)$ (Eq. (B1) or $E_{coh}(2)$ (Eq. (B4)) and molar volume, V, (Eq. (C1)) for the studied polysulfones.

Sample	$E_{coh}(1)\cdot 10^{-4}$ in J/mole	$E_{coh}(2)\cdot 10^{-4}$ in J/mole	V (298 K) in cc/mole	$\gamma_{(1)}$ in mN/m	$\gamma_{(2)}$ in mN/m
PSF	17.36	17.13	360.15	46.11	45.70
CMPSF1	18.06	17.72	373.82	46.17	45.60
CMPSF2	19.80	19.22	408.43	46.29	45.37
CMPSF3	21.57	20.87	433.30	47.11	46.09
PSFQ1	20.05	22.33	407.29	46.76	50.25
PSFQ2	24.95	26.92	524.81	45.69	48.07

Modification of surface properties by low pressure plasma treatment

Low pressure plasma treatment causes significant changes of polymer surface tension. Generally, application of a plasma treatment to polysulfone membranes induces modifications of surface properties, because the highly energetic particles interact with the polymer surface. They may generate several kinds of reactions, such as breaking of the covalent bonds along the chain, crosslinking, grafting, interaction of surface free radicals, alteration of the existing functional groups and/or incorporation of the chemical groups in the plasma, but the mechanism of these reactions has not been recognized yet. However, polymer etching (involving a whole bunch of destructive reactions that remove the surface material and may enlarge pore diameter), modification of surface chemistry (altering of surface chemistry by change of functionalities) and deposition of plasma polymer (including those processes that allow material to be deposited on the surface in the form of a thin layer), are the three main groups of processes which can be considered [17, 35].

Tab. 5 lists, the surface tension parameters γ_{SV}^{d} , γ_{SV}^{p} and γ_{SV} for plasma treated samples, calculated with Eqs. (1) and (2). The polar component of surface tension significantly increases after plasma treatment for all studied neutral (PSF and CMPSF) and polar (PSFQ) polymers. This may be also seen from Tab. 4, where the relatively hydrophobic surface (higher contact angle for water) is converted into a more hydrophilic surface (lower contact angle for water), by a plasma treatment applied to all studied samples. Also, Tab. 5 shows that the values of the $\gamma_{SV}^{p} / \gamma_{SV}$ ratio increase for neutral polymers after plasma treatment. For polar polymers, the values of the $\gamma_{sv}^{p} / \gamma_{sv}$ ratio are close, both before and after plasma treatment, due to a considerable increase of disperse components after plasma treatment, an aspect still to be cleared by further studies.

Free energy of hydration

The hydrophilic or hydrophobic nature of untreated and plasma-treated samples was evaluated *via* knowledge of the free energy of hydration, i.e., the interaction free energy between polymer and water, ΔG_W. The ΔG_W values were obtained from Eq. (4) [36] with the total surface tension of water, γ_{lv} (Tab. 3) and from the contact angle of water, θ_{water} (Tab. 4).

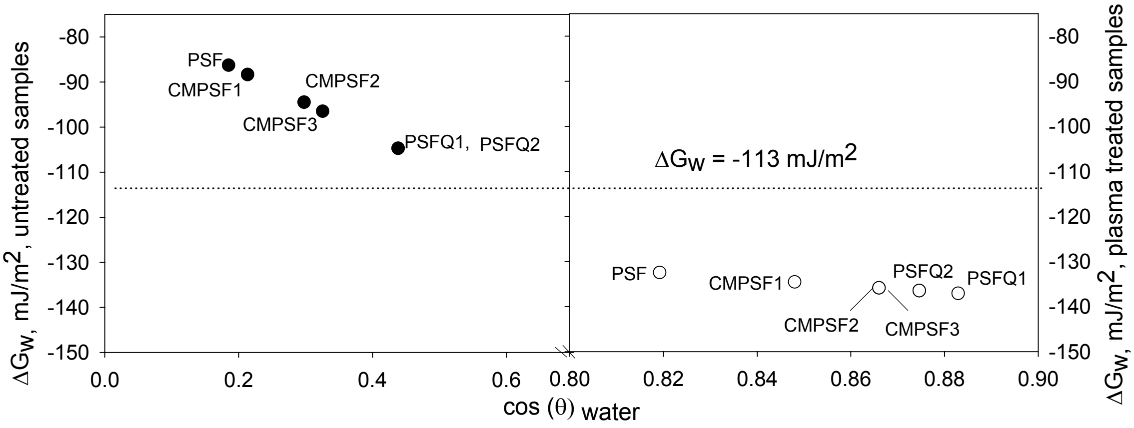


Fig. 2. Surface free energy between untreated (●, left y axis) and plasma treated (○, right y axis) samples and water *vs*. water contact angles. The dotted line delimitates the hydrophilic domain (for $\Delta G_W < -113$ mJ/m^2) from the hydrophobic domain (for $\Delta G_W > -113$ mJ/m^2).

$$\Delta G_W = -\gamma_{lv} \cdot \left(1 + \cos\theta_{water}\right) \tag{4}$$

The results are plotted graphically in Fig. 2.

Generally, the literature [36, 37] mention that for $\Delta G_W < -113$ mJ/m^2, the polymer can be considered more hydrophilic while, when $\Delta G_W > -113$ mJ/m^2, it should be considered more hydrophobic. It is observed from Fig. 2 that the surface free energy for PSF and CMPSF samples possesses lower wettability comparatively with the quaternized samples; the plasma treatment “cleans” by chemical and physical processes the surface of the samples and increases the wettability, having satisfactory values for different applications, e.g. as biomaterials and semipermeable membranes.

Experimental part

Materials

UDEL-1700 polysulfone (Union Carbide; Texas City, Texas) (M_n=39000; M_w/M_n=1.625) is a commercial product. Mixture of commercial paraformaldehyde with an equimolar amount of chlorotrimethylsilane (Me_3SiCl), as a chloromethylation agent, and stannic tetrachloride ($SnCl_4$), as a catalyst, were used for the chloromethylation reaction of polysulfone at 50 °C. The reaction time was varied from 24 to 140 h, to obtain different substitution degrees of the chloromethylated polysulfones [19, 20]. Finally, the samples were dried under vacuum at 40 °C.

The CMPSF was dissolved in N,N-dimethylformamide vacuum distilled over P_2O_5, and then the N,N-dimethylethanolamine quaternized derivative was poured into the reactor. The reaction time was of 48 h, at 60 °C [38]. The content in chloride, Cl_i and in total chlorine, were determined by potentiometric titration (Titrator TTT1C Copenhagen) with 0.02 N $AgNO_3$ aqueous solutions. The ratios between the chloride and the total chlorine contents show that the quaternization reaction of chloromethylated polysulfones occurs with a transformation degree close to 96 % - 98 %. Thus, one may consider that almost all chloromethylenic groups were quaternized.

Contact angle measurements

The samples presented in Tabs. 1 and 2 were dissolved in chloroform (PSF, CMPSF1-CMPSF3, PSFQ1 samples) and methanol (PSFQ2 and PSFQ3 samples), to reach a concentration of 1g/dL. The solutions were cast on a glass plate and solidified initially by slow drying in saturated atmosphere to the used solvent, and finally by drying at 50 °C under vacuum.

The PSF, CMPSF and PSFQ membranes thus prepared were subjected to surface analysis.

Uniform drops of the test liquids with a volume of 2 μL were deposited on the film surface, and the contact angles were measured after 30 s using a video-based optical contact angle measuring device equipped with a Hamilton syringe at a temperature-controlled environmental chamber. All measurements were performed in the atmosphere, at a temperature of 25 °C. Repeated measurements of a given contact angle were all within $\pm 3^\circ$.

Low pressure plasma treatment

The low pressure plasma treatment of the studied samples consists of exposing the polymer films to a low temperature and low pressure glow discharge. Cold air plasma was produced using a high frequency system - 1.3 MHz, with 3000 V/cm intensity, 0.58 mbar pressure and 100 W power, equipped with inner aluminum electrodes. The duration of plasma treatment was of 10 minutes, the contact angles measurements having been performed immediately after.

Appendix A

Calculation of the zeroth-order connectivity indices and of the first-order connectivity indices

$$^{0}\chi \equiv \sum\left(1/\sqrt{\delta}\right) \tag{A1}$$

$$^{0}\chi^{V} \equiv \sum\left(1/\sqrt{\delta^{V}}\right) \tag{A2}$$

$$\beta_{ij} \equiv \delta_i \cdot \delta_j \tag{A3}$$

$$\beta_{ij}^{v} = \delta_i^{v} \cdot \delta_j^{v} \tag{A4}$$

$$^{1}\chi \equiv \sum\left(1/\sqrt{\beta}\right) \tag{A5}$$

$$^{1}\chi^{v} \equiv \sum\left(1/\sqrt{\beta^{v}}\right) \tag{A6}$$

Appendix B

Calculation of cohesive energy

$$E_{coh}(1) \approx 9882.5 \cdot {}^{1}\chi + 358.7 \cdot (6 \cdot \mathrm{N}_{atomic} + 5 \cdot N_{group}) \tag{B1}$$

$$N_{atomic} \equiv 4 \cdot N_{(-S-)} + 12 \cdot N_{sulfone} - N_F + 3 \cdot N_{Cl} + 5 \cdot N_{Br} + 7 \cdot N_{cyanide} \tag{B2}$$

$$\begin{aligned} N_{group} \equiv {} & 4 \cdot N_{hydroxyl} + 12 \cdot N_{amide} + 2 \cdot N_{(nonamide-(NH)-unit)} + \\ & + 4 \cdot \mathrm{N}_{\text{(nonamide-(C=O)-next to nitrogen)}} + \\ & + 7 \cdot \mathrm{N}_{\text{(-(C=O)-in carboxylic acid,ketone or aldehyde)}} + 2 \cdot N_{(other-(C=O)-)} - \\ & - \mathrm{N}_{\text{(alkyl ether-O-)}} - N_{C=C} + 4 \cdot N_{(\mathit{nitrogen}\text{ atoms in six-membered aromatic rings})} \end{aligned} \tag{B3}$$

$$E_{coh}(2) \approx 10570.9 \cdot ({}^{0}\chi^{v} - {}^{0}\chi) + 9072.8 \cdot (2 \cdot {}^{1}\chi - {}^{1}\chi^{v}) + 1018.2 \cdot N_{VKH} \tag{B4}$$

$$\begin{aligned} N_{VKH} \equiv {} & N_{Si} + 3 \cdot N_{(-S-)} + 36 \cdot N_{sulfone} + 4 \cdot N_{Cl} + 2 \cdot N_{Br} + 12 \cdot N_{cyanide} + \\ & + 16 \cdot N_{(nonamide-(C=O)-next\ to\ nitrogen)} + \\ & + 7 \cdot N_{(\mathit{nitrogen}\text{ atoms in six-membered aromatic rings})} + 12 \cdot N_{cyanide} + \\ & + 2 \cdot N_{(\mathit{nitrogen}\text{ with }\delta=2\text{, but not adjacent to C=O, and not in a six-membered aromatic rings})} \\ & + 20 \cdot N_{(carboxylic\ acid)} + 33 \cdot N_{HB} - 4 \cdot N_{cyc} + 19 \cdot N_{anhydride} + \\ & + \sum\left(4 - N_{row}\right)_{(\mathit{substituents}\text{ with }\delta=1\text{ attached to aromatic rings in the backbone})} \end{aligned} \tag{B5}$$

where:

in Eq. (B2): $N_{(-S-)}$ - numbers of sulfur atoms in the lowest (divalent) oxidation state; $N_{sulfone}$ - numbers of sulfur atoms in the highest oxidation state (commonly in –SO_2); N_F - numbers of fluorine atoms; N_{Cl} - numbers of chlorine atoms; N_{Br} - numbers of bromine atoms; $N_{cyanide}$ - number of -C≡N groups; in Eq. (B3): $N_{hydroxyl}$ - number of –OH; N_{amide} - number of amide groups; $N_{(nonamide-(NH)-unit)}$ -number of NH units from the nonamide structure; $N_{(nonamide-(C=O)-next\ to\ nitrogen)}$ - number of C=O units from the nonamide structure next to nitrogen; $N_{(-(C=O)-in\ carboxylic\ acid,\ ketone\ or\ aldehyde)}$ - number of C=O groups in carboxylic acid, ketone or aldehyde structures, $N_{(other-(C=O)-)}$ - number of other C=O groups; $N_{(alkyl\ ether-O-)}$ - number of alkyl ether-O- groups, $N_{C=C}$ - number of carbon-carbon double bonds, excluding any such bonds found along the edges of the rings; $N_{(\mathit{nitrogen}\text{ atoms in six-membered aromatic rings})}$ - number of nitrogen atoms in six-membered aromatic rings; in Eq. (B5): N_{Si} - number of silicon atoms; $N_{(carboxylic\ acid)}$ - number of carboxylic acid; N_{HB} - total number of strongly hydrogen-bonding structural units such as alcohol-type or phenol-type hydroxyl (-OH) groups and amide groups – the –OH groups in carboxylic acid and sulfonic acid moieties are not counted in N_{HB}; N_{cyc} - number of nonaromatic rings (*i.e.*, “cyclic” structures) with no double bonds along any of the ring edges. When more than one such rings share the edges, N_{cyc} is determined by using simple counting rules, which avoid double counting of any of the shared edges, and may result in a noninteger value of N_{cyc}; $N_{anhydride}$ - number of anhydride groups, N_{row} - row of an atom in the periodic table. Methyl (-CH$_3$) groups and halogen atoms are substituents with $\delta = 1$, *i.e.*, bonded to only one nonhydrogen atom, commonly encountered in polymers;

$N_{(nitrogen\ \text{with}\ \delta=2,\ \text{but not adjacent to}\ C=O,\ \text{and not in a six-membered aromatic rings})}$ - number of nitrogen atoms with specification from subscript.

Appendix C

Calculation of the molar volume

$$V(298K) \approx 3.642770 \cdot {}^{0}\chi + 9.798697 \cdot {}^{0}\chi^{v} - 8.542819 \cdot {}^{1}\chi + 21.693912 \cdot {}^{1}\chi^{v} + 0.978655 \cdot N_{MV} \qquad \text{(C1)}$$

$$N_{MV} \equiv 24 \cdot N_{Si} - 18 \cdot N_{(-S-)} - 5 \cdot N_{sulfone} - 7 \cdot N_{Cl} - 16 \cdot N_{Br} + 2 \cdot N_{(backbone\ \text{ester})} + 3 \cdot N_{ether} + 5 \cdot N_{carbonate} + 5 \cdot N_{C=C} - 11 \cdot N_{cyc} - 7 \cdot (N_{fused} - 1) \qquad \text{(C2)}$$

(last term only to be used if $N_{fused} \geq 2$)

where: $N_{(backbone\ ester)}$ - number of ester (-COO-) groups in the backbone of the repeating units; N_{ether} - total number of ether (-O-) linkages in the polymeric repeating unit. Note that only the (-O-) linkages between two carbon atoms will be counted as ether linkages in N_{ether}; $N_{carbonate}$ - number of carbonate (-OCOO-) groups; N_{fused} - number of rings in fused ring structures. A “fused” ring structure is defined in the present context as any ring structure containing at least one aromatic ring that shares at least one edge with another ring and with all the other rings with which it shares an edge.

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