



SURFACE TENSION COMPONENTS OF PLASMA TREATED POLYSULPHONE MEMBRANES

Manuela Florea-Spiroiu *, Mihaela Olteanu *, Viorica Stanescu * and G. Nechifor **

abstract: The purpose of this study is to characterize the solid surfaces of unmodified and modified by plasma treatment polysulphone asymmetric membranes by contact angle measurements. The liquids used for the contact angle measurements were water, glycerol and ethylene glycol. Equation of state of surface tension approach and van Oss-Chaudhary-Good thermodynamic approach were used to calculate Lifshitz-van der Waals (γ_s^{LW}) and Lewis acid-base (γ_s^{AB}) surface tension components of low-energy polysulphone membranes. The values of acid base components (γ_s^- and γ_s^+) of surface tension were confirmed by acid base titration.

key words: polysulphone membrane, contact angle, surface tension components

received: November 17, 2008

accepted: November 24, 2008

Introduction

Polysulfone (PSF) is one of the most frequently used polymers in the production of microfiltration and ultrafiltration membranes due to its mechanical, chemical and thermal high resistance, as well as its excellent film-forming properties [1,2]. On the other hand, polysulfone membranes themselves are often used as sublayers in composite membranes for reverse osmosis, gas separation and pervaporation [3].

Hydrophilicity of polysulfone has already been improved in several investigations through application of chemical modification methods and plasma modified film [4-6]. Filtration membranes are plasma treated for a number of reasons which include resistance of the membrane to fouling, improving the selectivity and the flux of the permeants, and increasing the surface area of the membranes. Alteration of surface characteristics is also possible by substitution of chemical groups present on the polymer chain being modified [7].

Substituting the functional groups increases the surface energy. Surface energy is estimated by contact angles by using empirical equation of state of surface tension [8, 9], Lewis acid

* University of Bucharest, Faculty of Chemistry, Physical Chemistry Department, 4-12 Regina Elisabeta blvd., 030018, Bucharest, Romania; *corresponding author e-mail:* manu.spiroiu@gmail.com

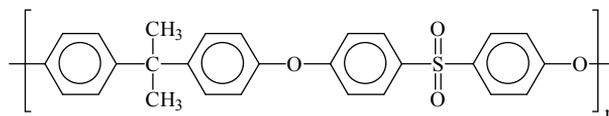
** "POLITEHNICA" University of Bucharest, Faculty of Applied Chemistry and Materials Science, Gh. Polizu 1, Bucharest, Romania

base model [10]. The surface free energy of a solid can be split into components in order to explain liquid/solid interaction.

Experimental

Materials

The polysulphone (PSF) 16% having the following structure:



was used to prepare membranes at Reserch Center for Macromolecular Materials and Membranes Bucharest. The asymmetric membranes were prepared as flat sheets starting with 16% polymer solution in dimethylformamide. A 200 μm thick solution was cast on a mettalic vat and immersed in the coagulation bath containing propanol.

The PSF membranes were air plasma treated at Institute of Physics and Technology of Radiation Devices Magurele Romania. The membranes will be lettering by PSF and the plasma treatment time in minutes will be mentioned in brackets.

Glycerol (anhydrous, $\geq 99.5\%$ purity) and ethylene glycol (anhydrous, 99.8% purity) were obtained from Sigma-Aldrich, sodium hydroxid and hydrochloric acid were purchased from Chimopar, Romania. Distilled water was used for contact angle determinations.

Contact angle measurements

The sessile drop method of contact angle determination was used through deposition of liquid drops on solid surfaces with a micrometric syringe. The volume of liquid drop varies between 3 and 5 μl . Contact angle measurements for three different liquids (distilled water, glycerol, and ethylene glycol) were carried out at room temperature by means of a horizontal microscope equipped with a video camera Philips to a computer. The contact angle was calculated from the droplet screen image. Each reported contact angle measurement represents an average value of at least four separate drops on different areas of the membranes.

Acid base titration

The solutions of hydrochloric acid and sodium hydroxide of different concentrations were used for acid base titration. Drops from these solutions were laid down on solid surfaces of polysulphone membranes and the contact angles were determined.

Results and discussion

The experimental values of contact angle of water, glycerol, and ethylene glycol on polysulphone solid surfaces are presented in Fig. 1.

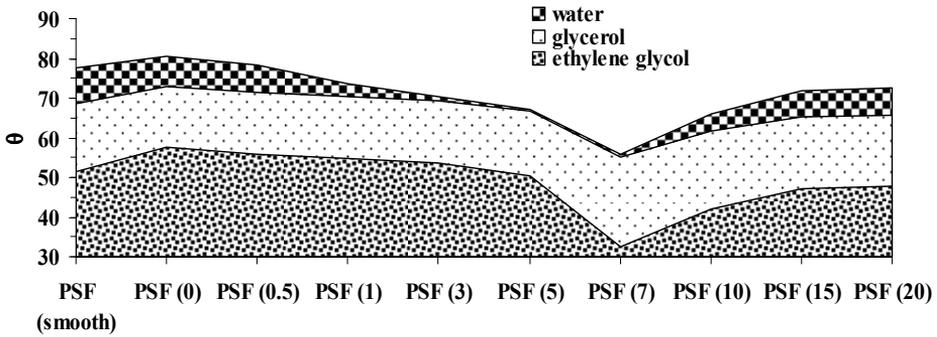


Fig. 1 Contact angles of water, glycerol, and ethylene glycol for polysulphone film and unmodified and modified by plasma treatment membranes.

The contact angle on membrane is higher than on smooth surface of polysulphone film. This result confirms the microporous structure of polysulphone membrane. The significant changes of contact angles for all liquids, after plasma treatment modification were observed. The minimum values of contact angle of all liquids were obtained for polysulphone membrane treated 7 minutes in plasma. The variation of contact angle has to be correlated with roughness modification as a result of processes which take place during plasma treatment.

The fast increase of the corrosion rate of polysulphone membrane in the first minutes can be related to a destroying attack by the excited species in plasma followed by a roughness decrease due to a substance redeposition till stabilization occurs. The steady level reached at long exposing times can be interpreted as a reflexion of building a more stable structure by plasma action.

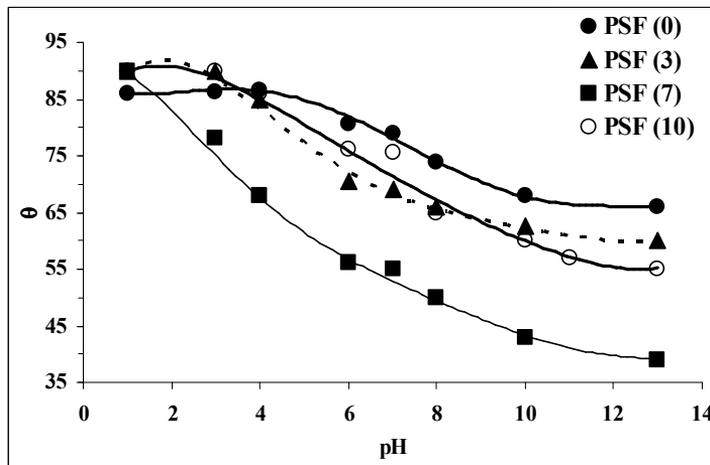


Fig. 2 Acid base titration of polysulphone membrane surfaces.

One can see from Fig. 2 that corrosion process is accompanied by a change of the solid surface polarity. While the non-treated membrane is ionized at high pH 's, the ones treated in plasma for under 7 minutes are ionized at low pH 's. After 7 minutes, it seems that plasma treatment in O_2 and N_2 atmosphere is accompanied by a redeposition of some molecules or molecular fragments from plasma and therefore some functional groups with O and N having both basic and acid characters appear at the membrane surface. The presence of these new functional groups was evidenced by means of FTIR spectrometry [11].

The plasma treatment is accompanied by a change in surface energetics. The values of Lifshitz van der Waals (γ_S^{LW}), acid (γ_S^+) and basic (γ_S^-) of the surface tension were computed with the complete equation for defining the contact angle, also known as the van Oss-Chaudhary-Good thermodynamic approach [9] :

$$\gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + 2\sqrt{\gamma_S^+ \gamma_L^-} + 2\sqrt{\gamma_S^- \gamma_L^+} \quad (1)$$

where γ_L is surface tension of liquid and γ_L^{LW} , γ_L^- , γ_L^+ are its components. Thus, by contact angle (θ) measurement with three different liquids with known values of surface tension components, three equations with three unknowns can set up, which can be solved to obtain the values of γ_S^{LW} , γ_S^+ , and γ_S^- .

Using the values of surface tension and their components for water, glycerol, and ethylene glycol (Table 1), surface free energy components of polysulphone (Table 2) were calculated with eqn (1).

Table 1 The values of surface tension and their components (mJ/m^2) for testing liquids (at $20^\circ C$).

Liquid	γ_L	γ_L^{LW}	γ_L^-	γ_L^+
Water	72.8	21.8	25.5	25.50
Glycerol	64.0	34.0	57.4	3.92
Ethylene glycol	48.0	29.0	47.0	1.92

Table 2 The values of surface free energy (mJ/m^2) components of polysulphone calculated by acid-base approach.

Solid surface	γ_S^{LW}	γ_S^-	γ_S^+	γ_S^{AB}
PSF (smooth)	30.64	8.3	0.56	4.31
PSF (0)	27.78	8.01	0.45	3.80
PSF (0.5)	30.64	9.06	0.27	3.13
PSF (1)	33.38	13.25	0.06	1.78
PSF (3)	34.67	16.41	0.01	0.81
PSF (5)	36.75	18.74	0.01	0.86
PSF (7)	38.29	24.20	0.36	5.90
PSF (10)	36.87	16.06	0.27	4.16
PSF (15)	33.03	12.25	0.43	4.59
PSF (20)	32.47	11.41	0.48	4.68

The values in Table 2 are relative ones because they are calculated from experimental data for liquid contact angle on solid surfaces with considerable roughness and porosity. Polysulphone membranes have γ_S^- values higher than γ_S^+ and thus exhibit a preponderant character of a Lewis base. The Lewis base character is explained in terms of the existence of non-participant p electrons of the etheric oxygen atoms from the polymeric structure.

Variation of γ_S^{AB} , γ_S^- and γ_S^+ with the exposure time to plasma action of the polysulphone membranes confirms the above reasoning regards of the processes which occur during the plasma treatment. The membrane changes its polarity and becomes monobasic in the first minutes and then the bipolar character becomes more pronounced.

Surface free energy was also calculated with Li-Neumann equation of state [8,9]:

$$\cos \theta = -1 + 2 \sqrt{\frac{\gamma_{SG}}{\gamma_{LG}}} e^{-\beta(\gamma_{LG} - \gamma_{SG})^2} \tag{2}$$

where β is an empirical constant ($\beta = 0,000115 \text{ (m}^2/\text{mJ)}^2$).

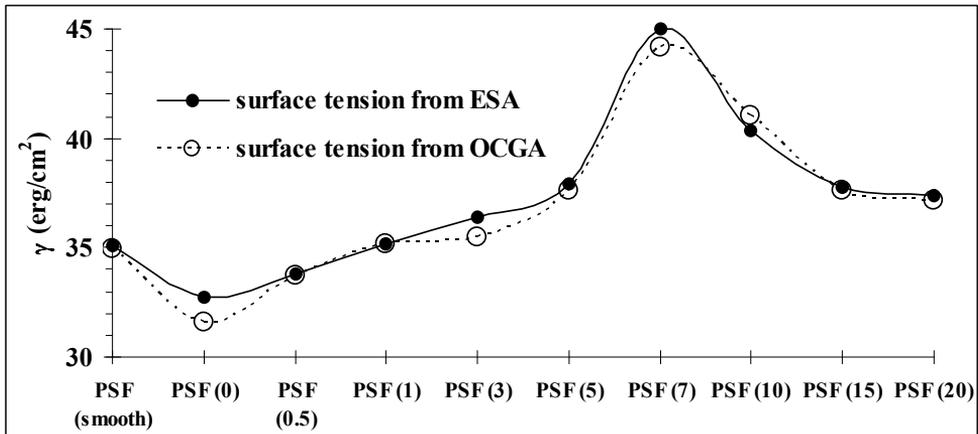


Fig. 2 Surface free energy of polysulphone membranes calculated by Equation of state approach (ESA) and by Oss-Chaudhary-Good thermodynamic approach (OCGA).

The received values of the surface free energy calculated as the sum of its Lifshitz van der Waals and acid base components, as well as its components are in a good accordance with Li-Neumann [9] equation of state approach (Fig. 3).

Conclusions

In this study, surface energies and its Lifshitz-van der Waals and acid base components were calculated for polysulphone membranes from experimental contact angle data.

Plasma treatment was used to change the hydrophobic polysulphone ultrafiltration membrane to a hydrophilic one; the maximum effect was reached in 7 minutes.

The calculated values of surface tension components of plasma treated polysulphone membranes explain the contact angle values obtained by acid base titration.

REFERENCES

1. Asfardjani, K., Segul, Y., Aurelli, Y. and Abibine, N. (2003) *J. Applied Sci.* **43**(2), 271-81.
2. Aldea, E., Dinescu, G., Mitu, B., Popescu, G., Albu, B., Rata, D. and Olteanu, M. (1999) *Proceedings of 14th International Symposium on Plasma Chemistry*, Prague, Czech Republic, August 2-6, 1803-8.
3. Mulder, M. (1991) **Basic Principles of Membrane Technology**, Kluwer Academic Publishers.
4. Gancarz, I., Pozniak, G., Bryjak, M. and Frankiewicz, A. (1999) *Acta Polym.* **50**, 317-26.
5. Won, J., Kim, M.H., Kang, Y.S., Park, H.Ch., Kim, U.Y., Choi, S.Ch. and Koh, S.K. (2000) *J. Applied Polymer Sci.* **75**, 1554-60.
6. Gancarz, I., Pozniak, G. and Bryjak, M. (1999) *European Polymer Journal* **36**, 1419-28.
7. Brijak, M., Pozniak, G., Gancarz, I. and Tylus, W. (2004) *Desalination* **163**, 231-38.
8. Neumann, A.W., Good, R.J., Hope, C.J. and Sejpal, M. (1974) *J. Colloid Interface Sci.* **49**, 291-304.
9. Li, D. and Neumann, A.W. (1990) *J. Colloid Interface Sci.* **137**, 304-7.
10. van Oss, C.J., Chaudhury, M.K. and Good, R.J. (1988) *Chem.Rev.* **88**, 927-34.
11. Aldea, E., Dinescu, G., Musa, G., Catana, G., Albu, B., Nechifor, G., Popescu, G. and Olteanu, M. (1995) *Proceedings of 12th International Symposium on Plasma Chemistry*, JV Heberlein, DW Ernie, JT Roberts eds., Minneapolis, vol. **1**, 224.