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Novel PEEK-WC membranes with low plasma protein affinity related to surface free energy parameters

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There has been growing interest in innovative materials with specific physico-chemical properties that provide an improved blood/cell compatibility.

In this paper we evaluated the performance of new membranes prepared from a modified polyetheretherketone (PEEK-WC) contacting human plasma proteins. These membranes were prepared by using the phase inversion technique. Membrane wettability and affinity to proteins were evaluated by means of contact angle experiments, roughness measurements, and quantitative UV analysis. The energy parameters of membrane surfaces were determined according to Good, van Oss and Chaudhury's theory.

The extent of human albumin, fibrinogen and immunoglobulin G adsorption was related to quantitative expressions of the membrane surface hydrophilicity: the base parameter of surface free energy and the free energy of interfacial interaction. The performance of PEEK-WC membranes was compared to that of commercial membranes, which conventionally are used in biomedical applications. The experimental results showed a reduction of protein adsorption on PEEK-WC membranes with respect to other commercial membranes.

The low protein affinity of PEEK-WC membranes is due to the intrinsic physico-chemical characteristics of the polymeric material which makes these membranes interesting for potential use in biomedical applications.

Introduction

Medical devices in contact with blood must completely avoid clot formation and immunoreactions [1, 2]. Several studies have shown that the biocompatibility of a material is linked to protein–surface interactions which constitute the first phase of blood/tissue interactions [3, 4]. Surface properties such as chemistry, topography and thermodynamics affect protein adhesion to polymeric materials (i.e. membranes, sheets, etc.) [5]. Depending on the size, shape, overall charge, hydrophobicity and internal stability of the molecule, proteins could adsorb on hydrophobic or hydrophilic substrata [6]. As a result, the interfacial properties of the polymer material are modified by the physical adsorption of protein molecules with consequent changes in the extent of cell adhesion. Several studies have related the wettability properties of a material surface to protein adsorption and cell adhesion [7, 8]. With this in mind, different methods were used to characterize interfacial reactions. The contact angle is one of the most common methods used to provide information about the physico-chemical characteristics of material surface and proteins [9, 10]. Currently, the contact angle is often used as a physical parameter indicative only of surface wettability, but it allows more quantitative information concerning the energy parameters of a material surface to be obtained [11]. In this work, the contact angle is applied to characterize surface free energy parameters, the free energy of interfacial interactions of new modified polyetheretherketone (PEEK-WC) membranes related to protein adsorption. Membranes were prepared from PEEK-WC, which exhibits chemical stability and excellent thermal and mechanical resistance similar to traditional PEEKs, which are used in medical implants. As opposed to PEEKs, PEEK-WC is soluble in various solvents owing to lack of crystallinity. This characteristic allows it to be used for preparing membranes by phase inversion, which proved to be a cheap and flexible method [12]. Previous studies have shown that this novel membrane is very promising for various applications [13]. The developed PEEK-WC membranes combine the advantageous properties of the polymer with those of permeability, selectivity and stability of the membranes.

In this study the physico-chemical properties of

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PEEK-WC membrane surface were investigated compared to commercial membranes and polyurethane (PU) membranes prepared by using the same phase inversion technique. In particular, interfacial interactions between membranes and human plasma proteins such as albumin, fibrinogen, immunoglobulin G were characterized. Since the morphological properties of the membrane surface are important in interfacial behaviour, the roughness of the membrane surface was also assessed, which presents a topographical heterogeneity as real material.

In order to evaluate the plasma protein affinity to membranes, the extent of protein adsorption to physical and chemical parameters of membrane surfaces was related.

Materials and methods

Membranes

Two novel modified polyetheretherketone membranes (PEEK-WC20 and PEEK-WC60), made in our laboratory by phase inversion technique using the direct immersion–precipitation method, were investigated. PEEK-WC solutions in N,N-dimethylformamide (DMF) were mixed to Polyvinylpirrolidone (PVP) at 80/20 (PEEK-WC20) and 40/60 wt % (PEEK-WC60), respectively. In a similar way PU membranes were prepared from solid medical grade Pellethane® 2363-80AE (Dow Chemical Company, The Netherlands); a detailed description of the preparation procedure was reported elsewhere [14].

As commercial membranes, five flat sheet microporous membranes with different physico-chemical properties were used: cellulose acetate (CA) (Dow Liquid Separations, Cheshire, England); polycarbonate (PC) (Cyclopore-Whatman, MA, USA), polypropylene (PP) (Membrana GmbH, Wuppertal, Germany), Polyethersulfone (PES) (Membrana GmbH, Wuppertal, Germany) and modified Polyethersulfone (Ultrabind protein binding US450) (Gelman Science, Pall, USA).

Membrane characterization

Roughness measurements and correction of sessile contact angle values

Average surface roughness (Ra) as well as roughness parameters (δ_H, δ_V) of the investigated membranes were evaluated by using Atomic Force Microscopy, Nanoscope III (Digital Instruments, VEECO Metrology Group). Tapping Mode™ AFM operated by scanning a tip attached to the end of an oscillating cantilever across 1 μm^2 of sample surface for 512 points at a rate of 2.54 Hz [15]. The surface roughness length scales (mean horizontal, δ_H, and vertical, δ_V) were obtained from 350 measurements of the width (mean horizontal peak to peak) and the depth (mean vertical distance of top of peak to bottom of trough) for each membrane, according to the ''zigzag'' model proposed by Taniguchi *et al*. [16]. This approach consists in considering a non-ideal surface having a zigzag profile. In order to test the effect of surface roughness and chemistry on contact angle measurements, all contact angle values were corrected by the surface slope calculated according to the following equation:

$$\alpha = \tan^{-1}\left(\frac{\delta_V}{\delta_H}\right)$$

When approaching the membrane zigzag surface the liquid drop moves from a negative slope to a positive slope until it reaches an equilibrium position corresponding to a negative slope according to the zigzag model [16]. For this reason the sessile contact angle, θ_S, for an ideal surface was calculated from the measured contact angle, θ:

$$\theta = \theta_s - \alpha$$

Physico-chemical parameters

The physico-chemical properties of all the membranes were characterized by using the Good–van Oss approach. This approach gives the possibility of estimating an acid–base contribution to the solid surface tensions and allows the determination of attractive and repulsive interactions [17]. The contact angle of various test liquid droplets on the membrane surfaces were measured by the sessile drop method at room temperature by using a CAM 200 contact angle meter (KSV Instruments Ltd., Helsinki, Finland). The sessile drop was formed by depositing the used test liquid from above, using an automatic microsyringe on the membrane surfaces. Among the different solvents considered for testing the physico-chemical properties of the membrane surface, three reference liquids (ultrapure water, diiodomethane and glycerol) were used to determine the apolar γ^{LW}, the acid–base γ^{AB}, acid (electron acceptor) γ^+, base (electron donor) γ^-, components of surface free energy (γ) by means of Good, van Oss and Chaudhury's method. Owing to the high solubility of some polymers in common organic solvents, these probe liquids were chosen, they being suitable for all of the investigated polymeric membranes. Thus, a comparison between all the membrane surface was possible. The surface tension of the three reference liquids was measured by using the pendant drop method. The Lifshitz–van der Waals component γ^{LW} of the membrane surface tension reflecting the dipole interactions was calculated from the measured diiodomethane contact angles under the assumption that diiodomethane is an apolar test liquid:

$$\gamma_s^{LW} = \frac{\gamma_l^{LW}(1+\cos\theta)^2}{4}$$

After the γ^{LW} of membrane surface had been measured, it was possible to calculate the other components (γ^{AB}, γ^- and γ^+) by using two polar liquids: glycerol and water:

$$\gamma_l(1+\cos\theta) = 2\left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_s^-\gamma_l^+}\right)$$

and

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^-\gamma_s^+}$$

The surface tension of each liquid, measured by pendant drop method, was in agreement with literature data [11, 14, 17], which were used for the calculation of membrane surface free energy parameters. The free energy of interfacial interaction (ΔG_{iwi}) was calculated

between the membrane and the water according to the following equation:

$$\Delta G_{iwi} = -2\left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_w^{LW}}\right)^2 - 4\left(\sqrt{\gamma_i^+\gamma_i^-} + \sqrt{\gamma_w^+\gamma_w^-} - \sqrt{\gamma_i^+\gamma_w^-} - \sqrt{\gamma_i^-\gamma_w^+}\right)$$

where the subscripts i, w refer to the membrane and the water.

The results are the mean of sixty measurements of the different regions of the sample surface. To avoid cross-contamination of liquids a dedicated microsyringe was used for each liquid.

Protein adsorption

In this study we used human plasma albumin, fibrinogen and immunoglobulin G (IgG), supplied by Sigma. The proteins were dissolved in phosphate buffered saline at pH 7.4 at plasmatic (40 mg/ml for albumin, 3 mg/ml for fibrinogen and 7 mg/ml for IgG) and at lower concentrations (3 mg/ml for albumin, 0.3 mg/ml for fibrinogen and 3 mg/ml for IgG).

The physico-chemical properties of the three proteins used were characterized by using the method described by van Oss *et al*. [18], which consists in contact angle measurements taken on the hydrated protein layer in three different liquids: water, glycerol and diiodomethane. A thick layer of proteins was collected upon an ultrafiltration support with pores too small to avoid passage of the protein molecules. Protein filtration was continued until no further solvent passed through the support. Thereafter, the protein layer was permitted to dry at room temperature until a constant contact angle with drops of H_2O was obtained. The surface free energy parameters of the hydrated proteins were determined [18].

The investigated membranes were incubated in a protein solution for 1 h at 37 °C. Each incubation was performed using quadruplicate samples to monitor the extent of protein and plasma adsorption onto any single membrane sample. Thereafter, the samples were incubated in a buffer constituted of Tris 10 mM and EDTA 1 mM and were mixed for 6 h at 3–4 °C. In this way the plasma adsorbed on the surface was removed from the sample and was determined by protein assay using bicinchoninic acid solution (Sigma, St Louis, MO, USA) by spectrophotometer analysis. This procedure permits the removal of all proteins [8].

The statistical significance of the experimental results was established according to the Unpaired Statistical Student's *t*-test ($p < 0.05$).

Results

AFM analysis of the membrane surface evidenced differences in roughness of the membranes. For all membranes the average roughness (Ra) and roughness parameters such as the mean horizontal (δ_H), vertical (δ_V) length scales and the surface slope (α) values are reported in Table I. The membrane surfaces differ in the morphological parameters. The less rough membranes proved to be PEEK-WC and CA membranes. As is shown in Fig. 1, the effect of surface roughness on the wettability of the membranes was negligible except for US450 and PES membranes. The mean difference between measured and corrected contact angle values for most of the membranes was about 5%.

The contact angle measurements of various test liquids on investigated membranes are summarized in Table II. The energy parameters: acid, base, acid–base and Lifshitz–van der Waals parameters of the membrane surface free energy demonstrated the actual surface physico-chemical characteristics of the membranes.

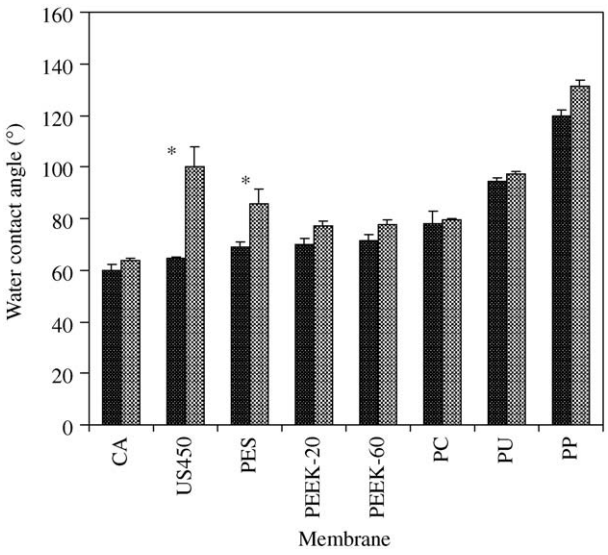

Figure 1 Measured (■) and corrected (□) sessile contact angle of membranes according to zigzag model [17]. *Statistically significant $p < 0.05$.

TABLE I Surface roughness parameters of membranes analyzed by AFM

Membrane	Ra (nm)	δ_V (nm)	δ_H (nm)	α (°)
PP	12.903 ± 0.87	19.93 ± 4.19	100.61 ± 24.67	11.26 ± 2.37
PC	5.40 ± 0.37	10.51 ± 3.00	389.94 ± 55.20	1.55 ± 0.51
US450	40.84 ± 2.88	101.88 ± 16.97	143.33 ± 35.59	35.31 ± 7.87
PES	14.82 ± 0.85	25.62 ± 13.08	85.95 ± 21.41	16.60 ± 5.90
CA	3.23 ± 0.15	5.34 ± 1.76	80.86 ± 26.42	3.79 ± 0.99
PU	5.92 ± 0.42	6.33 ± 2.31	139.39 ± 75.80	2.72 ± 1.07
PEEK-WC-60	2.92 ± 0.05	7.13 ± 1.72	61.38 ± 10.63	6.60 ± 1.51
PEEK-WC-20	3.78 ± 0.02	7.90 ± 2.06	62.60 ± 9.99	7.30 ± 1.96

Ra: average roughness; δ_H: mean horizontal; δ_V: vertical of length scales; (α) surface slope. Values are means of 350 measurements ± standard deviation.

TABLE II Measured contact angles in water (W), glycerol (Gl) diiodomethane (DIM) and calculated parameters, γ^{LW}, γ^{+}, γ^{-}, γ^{AB}, of surface tension γ for different polymeric membranes

Membrane	θ DIM (°)	θ W (°)	θ Gl (°)	γ^{LW} (mJ/m^2)	γ^{-} (mJ/m^2)	γ^{+}(mJ/m^2)	γ^{AB}(mJ/m^2)	γ(mJ/m^2)
PP	58 ± 2.8	120 ± 2.2	130 ± 5.9	29.5	2.9	9.7	10.6	40.0
PC	53 ± 1.5	78 ± 5.0	73 ± 3.5	32.3	10.2	0.07	1.7	33.9
US450	25 ± 2.8	64.7 ± 0.4	61.8 ± 1.3	46.1	16.8	0.006	0.65	46.8
PES	34.4 ± 2	69 ± 1.9	71.6 ± 0.4	42.3	19.4	0.35	5.2	47.5
CA	57 ± 1.4	60 ± 2.5	69 ± 2	30.0	33.4	0.0003	0.2	30.3
PU	35 ± 3.6	94.4 ± 1.4	100.9 ± 1.6	42.0	9.0	5.52	14.1	56.1
PEEK-WC-60	26.2 ± 2.5	71.2 ± 2.8	68.4 ± 0.9	45.7	13.7	0.15	2.9	48.6
PEEK-WC-20	24.6 ± 2.4	69.9 ± 2.2	69.5 ± 1.0	46.3	15.7	0.32	4.5	50.8

The surface tension and its parameters were calculated according to Good and van Oss [11, 17] by average values of measured contact angles. Values are means of 60 measurements ± standard deviation.

Most of the membranes have a high energy surface with $\gamma > 40\,\text{mJ/m}^2$ and are mainly electron-donors. For PEEK-WC-20 and PEEK-WC-60 membranes as well as for other commercial membranes such as PC, CA, PES and US450 membranes, the base parameter (γ^-) is much greater compared to the low acid parameter (γ^+). In contrast, PP membranes show a small base parameter and an acid parameter value of $9.7\,\text{mJ/m}^2$. Few membranes appear to be both electron-donors and electron-acceptors like the PU membrane.

Fig. 2 shows the relationship between the water contact angle measured on the membrane and the base parameter of the membrane surface free energy. The water contact angle decreased strongly when increasing the base parameter of the membrane surface free energy, owing to chemical heterogeneity of the different membranes.

Fig. 3 shows albumin adsorption on the investigated membranes at plasmatic (40 mg/ml) and low (3 mg/ml) concentrations. Albumin adsorption at both concentrations followed the same trend: the adsorption increased when increasing the base parameter of the membrane surface free energy with maximum adsorption on the membranes with $\gamma^- = 33.4\,\text{mJ/m}^2$ corresponding to CA. On PEEK-WC-20 and PEEK-WC-60 membranes, albumin adsorption at physiological concentration decreased by 60% with respect to that measured on the CA membrane. The amount of adsorbed albumin reduced significantly on PP membranes. A protein concentration-dependent effect was also observed, at a concentration of 3 mg/ml the amount of protein adsorbed was significantly lower compared to that at physiological concentration.

Despite the different nature of the proteins, fibrinogen followed the same trend as the albumin: the lower the base parameter of the membrane surface free energy, the lower the amount of adsorbed protein (Fig. 4). Also in this case a reduced amount of adsorbed protein on PEEK-WC-20 and PEEK-WC-60 and PU membranes was measured: about 50% of the proteins being adsorbed on these membranes compared to CA. Decreasing the fibrinogen concentration, the protein adsorption decreased on all tested membranes. The extent of adsorption followed the sequence CA > US450 > PES > PC > PEEK-WC-60 > PEEK-WC-20 > PU > PP.

Polymeric surfaces with a low base parameter of surface free energy exhibited low IgG adsorption, as illustrated in Fig. 5. At a concentration of 3 mg/ml, the amount of IgG adsorbed on PEEK-WC-20 and PEEK-WC-60 membranes was reduced to 45 and 47% of the CA value, respectively.

Table III shows the results of the measured contact

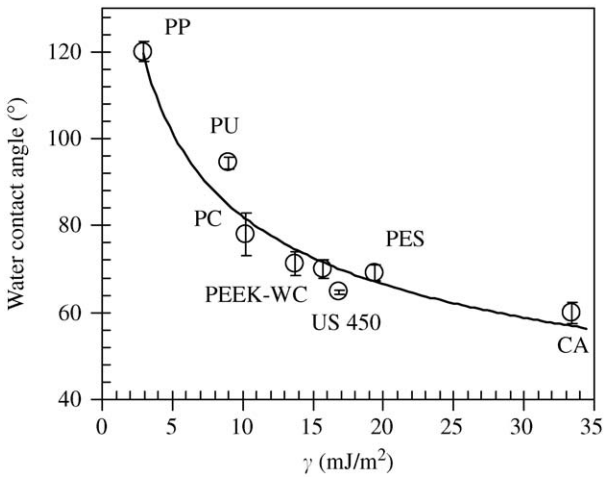

Figure 2 Relationship between water contact angle and surface free energy base parameter (γ^-) of investigated membranes calculated according to Good and van Oss [11, 17]. Values are means of 60 measurements ± standard deviation.

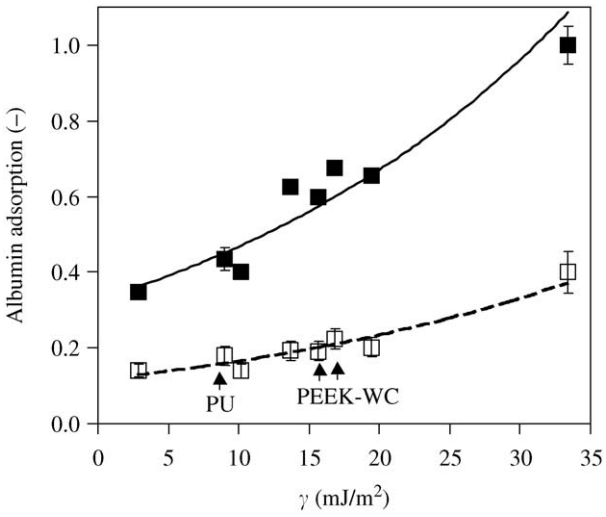

Figure 3 Extent of human plasma albumin adsorption on membranes with different base parameter of surface free energy at bulk protein concentration of (■) 40 mg/ml and (□) 3 mg/ml. Interpolation of experimental data is reported as line. Data were normalized with respect to the value of CA membrane at plasmatic concentration. The experimental values are the mean of eight experiments ± standard deviation.

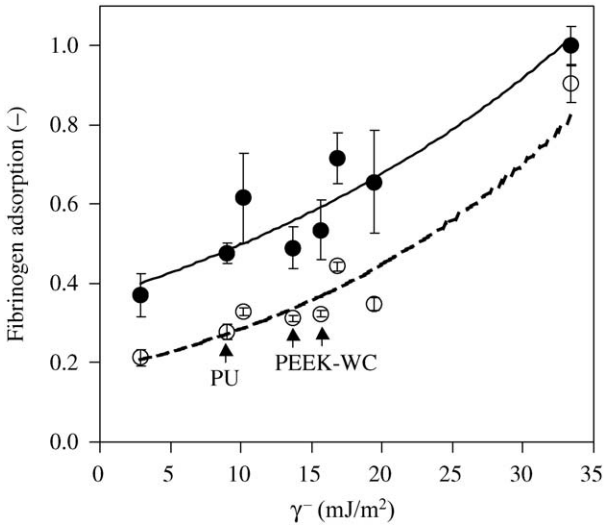

Figure 4 Extent of human plasma fibrinogen adsorption on membranes with different base parameter of surface free energy at bulk protein concentration of (●) 3 mg/ml and (○) 0.3 mg/ml. Interpolation of experimental data is reported as line. Data were normalized with respect to the value of CA membrane at plasmatic concentration. The experimental values are the mean of eight experiments: ± standard deviation.

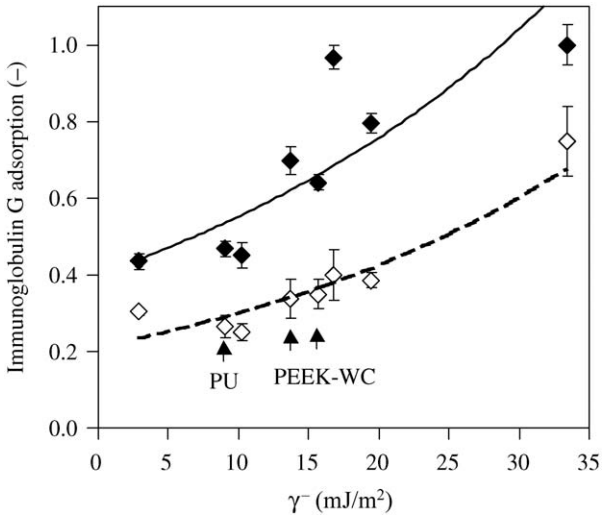

Figure 5 Extent of human plasma IgG adsorption on membranes with different base parameter of surface free energy at bulk protein concentration of (◆) 7 mg/ml and (◇) 3 mg/ml. Interpolation of experimental data is reported as line. Data were normalized with respect to the value of CA membrane at plasmatic concentration. The experimental values are the mean of eight experiments: ± standard deviation.

angle in different liquids used to calculate the surface free energy and its parameters of albumin, fibrinogen and IgG solution at a concentration of 3 mg/ml. Albumin has the highest values of the total surface free energy γ and of the acid–base parameter γ^{AB}, which correspond, respectively, to 57.1 mJ/m^2 and 21.0 mJ/m^2. These values decreased slightly in the case of fibrinogen and some more in the case of IgG, which exhibited the lowest total surface free energy and the acid–base parameter.

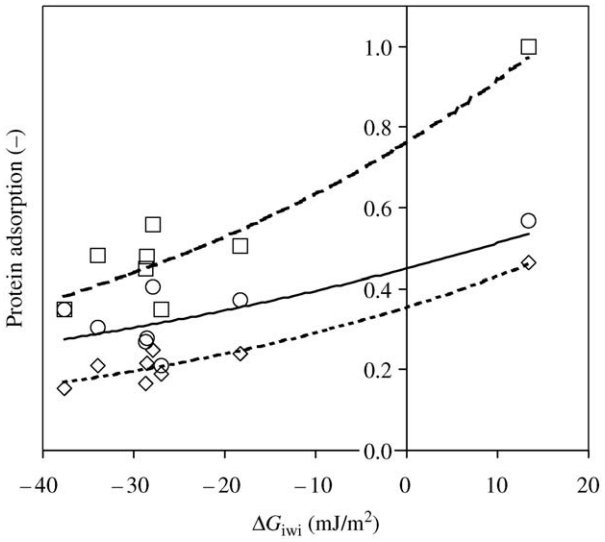

Figure 6 Correlation between protein adsorption at the concentration of 3 mg/ml and free energy of interfacial interaction (ΔG_{iwi}). (□) Albumin; (○) fibrinogen; (◇) IgG. Interpolation of experimental data is reported as line. Data were normalized with respect to the value of albumin adsorbed on CA membrane.

The adsorption of plasmatic albumin, fibrinogen and IgG was also related to the membrane free energy of the interfacial interaction ΔG_{iwi} and the acid–base parameter of the protein surface free energy (γ^{AB}) (Figs. 6 and 7). For all three proteins, the free energy of the interfacial interaction was positive only for the CA membranes, as opposed to most of the membranes, the ΔG_{iwi} values were negative. However, hydrophobic membranes exhibited more negative values. Protein adsorption increased when increasing the value of the interfacial interaction free energy. The lower the free energy of the interfacial interaction, the lower the amount of adsorbed protein. Protein were adsorbed on membranes in the following sequence: Albumin > Fibrinogen > IgG. As confirmed in Fig. 7, the adsorption of albumin, fibrinogen and IgG on investigated membranes was dependent on the polar component of their own surface free energy.

Discussion

The contact angles, surface free energy and its parameters calculated on the basis of Good–van Oss model evidence the different physico-chemical properties of the investigated polymeric membranes (Table II). PEEK-WC and PU membranes as well as most of the

TABLE III Measured contact angles in water (W), glycerol (Gl), diiodomethane (DIM) and calculated parameters, γ^{LW}, γ^{+}, γ^{-}, γ^{AB}, of surface tension γ for different human plasma proteins

Proteins	θ DIM (°)	θ W (°)	θ Gl (°)	γ^{LW} (mJ/m^2)	γ^{-} (mJ/m^2)	γ^{+}(mJ/m^2)	γ^{AB}(mJ/m^2)	γ(mJ/m^2)
Albumin	46.7 ± 1.5	16.9 ± 2.3	27.8 ± 4.2	36.1	49.9	2.2	21.0	57.1
Fibrinogen	31.7 ± 3.3	86.5 ± 3.7	91.2 ± 6.0	43.5	11.4	3.3	12.3	55.8
IgG	43.5 ± 1.9	45.0 ± 3.9	51.8 ± 2.6	37.8	37.4	0.2	6.2	44.0

The surface tension and its parameters were calculated according to Good and van Oss [11, 17] by average values of measured contact angles. Values are means of 60 measurements ± standard deviation.

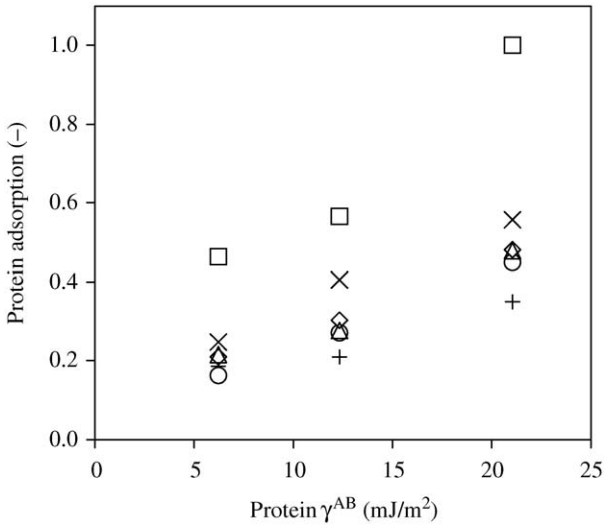

Figure 7 Changes of protein adsorption as function of acid–base parameter of surface free energy of proteins. Data were normalized with respect to the value of albumin adsorbed on CA membrane. (△) PEEK-WC20; (◇) PEEK-WC60; (○) PU; (+) PP; (□) CA; (×) US450 membrane.

commercial membranes have a much greater base parameter of surface free energy than small acid parameter. The oxygen atoms contained in the polymer as ether and carbonylic functionalities constitute effective Lewis base sites [9]. An increase in the concentration of such groups in the polymeric membranes is responsible for the high Lewis base character of the surface, and hence its hydrophilicity, with little influence on the Lewis acid character. The presence of hydroxyl groups in the membranes gives rise to an increase in both Lewis acid and Lewis base character [19]. A comparison of the base parameter of PEEK-WC membranes with those of the other membranes evidenced the moderate hydrophilic character of this membrane with respect to the CA (highest base surface character) and the PP (lowest base surface character) surfaces. The moderate hydrophilicity of PEEK-WC surfaces was directly evaluated by wettability experiments. Although the membranes exhibited different surface roughness, the effect of this physical parameter on membrane wettability was remarkable only for US450 and PES membranes. The low influence of the surface roughness on wettability for most of the investigated membranes allowed the measured water contact angle to be related to one quantitative expression of hydrophilicity such as γ^- (Fig. 2).

On the basis of protein adsorption experiments, the base parameter of the material surface free energy plays an important role in interfacial interactions with proteins. PEEK-WC20, PEEK-WC60 and PU membranes proved to be surfaces with minor protein affinity with respect to other commercial membranes such as CA, PES and US450 (Figs. 3–5). In particular, the amount of fibrinogen on the PEEK-WC20, PEEK-WC60 and PU membrane was significantly reduced with a value closer to the minimum of adsorption measured on the PP membrane (Fig. 4). Similar behaviour was observed with IgG solutions contacting PEEK-WC and PU membranes, as can be seen from Fig. 5. A relationship between the base parameter of the surface free energy and protein adsorption at both plasmatic and lower concentrations was found. Protein adsorption on the membrane increased when increasing the base parameter of the surface free energy (Figs. 3–5). This result is not completely unexpected because other authors observed an increase in plasma protein adsorption when increasing the surface wettability of the modified polymer [20, 21] and clean glass [11]. The reduction of protein adsorption on PEEK-WC and on other less hydrophilic surfaces could be explained on the basis of the model proposed by Lu *et al*. [22]. This theory is based on the key role played by bound water in the adsorption of proteins: protein adsorption occurs owing to an exchange of bound water between proteins and the polymeric surface. Therefore, a hydrophobic surface that cannot construct hydrogen bonds with water cannot adsorb proteins. A further confirmation of the importance of water in protein adsorption on the material surface was provided by another indicator of hydrophilicity: the free energy of interfacial interaction. This parameter measures the affinity of the surface to water: positive values of ΔG_{iwi} indicate a high level of hydrophilicity. The amount of protein adsorbed on surfaces as a function of this parameter evidences how the amount of bound water greatly affects the interactions between a surface such as PEEK-WC and proteins. In agreement with the base parameter of surface free energy, a great amount of adsorbed protein was obtained on surfaces with the highest ΔG_{iwi} values, corresponding to CA membrane, where ΔG_{iwi} assumes a positive value (Fig. 6).

Among the three plasmatic proteins the albumin adsorb to a larger extent than the other proteins with the following sequence: albumin > fibrinogen > IgG. The adsorption of proteins is also affected by their own physico-chemical properties: in fact, the proteins have different values of interfacial tension and of their respective components (Table III). Protein adsorption depends on the acid–base parameter of the protein surface free energy (Fig. 7). Albumin is the protein with the highest value of total surface free energy γ and of acid–base parameter γ^{AB} with respect to fibrinogen and IgG, therefore it adsorbs to the greatest extent. All three proteins exhibited a minor affinity to PEEK-WC, PU and PP membranes. The reduction of protein adsorption that was observed on PEEK-WC membranes makes the use of these materials interesting for biomedical applications.

Conclusions

PEEK-WC membranes proved to be surfaces with a low human plasma protein adsorption compared to the other investigated commercial membranes. Human plasma protein adsorption was dependent on the physico-chemical properties of the membranes and of the proteins. A relationship between one expression of hydrophilicity such as the base parameter of the membrane surface free energy and protein adsorption was found.

The moderate wettability of PEEK-WC surfaces was responsible for the reduction in interfacial phenomena between the membrane and proteins. The low extent of protein adsorption measured on PEEK-WC surfaces was

comparable to that detected on the PP membrane having the lowest value of surface free energy base parameter. In the interfacial interactions between membrane surfaces and protein solutions an important role was also played by the hydrophilic character of the proteins.

Owing to PEEK-WC membranes easy manufacture, their intrinsic polymeric physico-chemical characteristics and their interesting surface properties, they seem to be promising biomaterials. The results obtained from protein adsorption experiments encourage further investigation in order to evaluate the full potential of these membranes for use in biomedical devices.

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