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Surface characterization of biopolyurethanes based on cellulose derivatives

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Abstract Surface tension parameters and surface morphology of biopolyurethanes based on cellulose derivatives thin films, before and after HF cold plasma treatment has been investigated. Calculations are based on the geometric mean approach of Owens and Wendt, Rabel and Kälble, on the Lifshitz-van der Waals acid/base approach of van Oss and co-workers and on the theoretical methods involving quantitative structure-property relationship. For all the investigated samples the polar component contributes significantly to the total surface tensions, as due to the large electron donor interactions. HF cold plasma treatment modifies the surface energy of biopolyurethanes by changing their surface polarity and hydrophilicity. The hydrophilic/hydrophobic balance was studied by means of the free energy of hydration between the biomaterial film and water. The protein adsorption tests of fibrinogen were effected to evaluate the applicability of these biopolyurethanes as biomedical thromboresistant devices.

1 Introduction

Segmented polyurethanes have gained considerable position as useful biomaterials for implants or biomedical devices, [1–4]. Polyurethanes have been widely used for various commercial and experimental blood contacting and tissue-contacting application, such as vascular prostheses, blood pumps end tracheal tubes, mammary prostheses, heart valves, pacemaker lead wire insulations, intra-aortic balloons, catheters and artificial hearts, because of their generally favorable surface physical properties, together with their fairly good biocompatibility and haemocompatibility characteristics [5–7]. The balance between the surface hydrophilic and hydrophobic properties is important for achieving an enhanced biocompatibility of polyurethanes. Plasma treatments or other types of stimuli may alter the surface energy of most polymers, thus changing their surface polarity, hydrophilicity and adhesiveness [8–10].

Haemocompatibility of biomaterials, in terms of thrombo-resistance is determined by surface characteristics such as: distribution of the electric charges, surface tension and hydrophobe–hydrophile balance, which confer to the material more or less thrombo-resistant qualities. It is well known that when a material is interacting with blood, first the adsorption of plasma proteins takes place. In function of the affinity of the material to certain proteins specific biological mechanisms occur, for example those of the coagulation cascade. Proteins which decide the thrombo-resistance/thrombogenesis properties are albumin and fibrinogen, the first one is conferring thrombo-resistant qualities, and the second one is conferring thrombogene qualities, this latter protein being involved directly in the clot formation. The adsorption of the fibrinogen is influenced on one hand by the chemical nature of the surface, in particular by the hydrophobe/hydrophile balance, and on the other hand can be the result of the pro-clot biological phenomena of the extrinsic pathway, such as the adhesion and platelet activation. As to the second mechanism, fibrinogen adsorption accompanied by a more accelerated prothrombin consumption, characteristic for a pro-clot

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Table 1 Compositional parameters, number-average molecular weights and polydispersity indices of the samples

Sample code	Soft segment	Hard segment	Composition macrodiol/MDI/EG/HPC, wt.%	M_n	M_w/M_n
PEA-HPC	PEA	MDI-EG;HPC	52.24/36.57/7.27/3.92	134522	1.865
PPG-HPC	PPG	MDI-EG;HPC	52.24/36.57/7.27/3.92	72951	1.669
PTHF-HPC	PTHF	MDI-EG;HPC	52.24/36.57/7.27/3.92	70291	1.590

situation with formation of the fibrin and finally the blood clot.

Our previous publications presented the synthesis and some properties of new polyurethane-cellulose [11].

The present paper studies the effects of the chemical structure of polyurethanes-cellulose on their surface properties. Investigations are based on the geometric mean approach of Owens and Wendt, Rabel and Kälble [12–14], on the Lifshitz-van der Waals acid/base approach of van Oss and co-workers [15–17] and on the theoretical methods involving quantitative structure-property relationship [18]. By scanning electron microscopy surface morphology was investigated. For estimation of the haemocompatibility properties of the obtained materials, water sorption was determined as well as the amount of fibrinogen adsorbed from solution, the amount of fibrinogen adsorbed from blood plasma, and the time of prothrombin consumption.

2 Experimental

2.1 Materials

Poly(ethylene adipate)diol (PEA, $M_n = 2{,}000$ g/mol) was purchased from Fibrex SA Savinesti, Romania; Polytetrahydrofuran (PTHF, $M_n = 2{,}000$ g/mol) and poly(propylene)glycol (PPG, $M_n = 2{,}000$ g/mol) are commercial products purchased from BASF; 4,4′-Diphenylmethane diisocyanate (MDI, Merck) was distilled, prior to utilization, under reduced pressure; Hydroxypropylcellulose LF (HPC, Klucel) and ethylene glycol (EG, Merck) was used as received.

2.2 Preparation of polyurethanes

The polyurethanes were prepared by solution polymerization using *N*,*N*-Dimethylformamide (DMF, Fluka) as solvent. First, the NCO-terminated prepolymer was prepared by dehydrating the macrodiol for 3 h at 90°C under vacuum followed by adding MDI to the vigorously stirred macrodiol. The reaction between diisocyanate and macrodiol took place for 1.5 h under nitrogen atmosphere at 90°C. The temperature was lowered to 70°C and the ethylene glycol was added. The reaction continued for 1 h, at 70°C. At the end a solution of hydroxypropylcellulose in 10 ml DMF was added and the stirring continued for another 0.5 h. The resulting polymers were precipitated in water and dried under vacuum for several days.

2.2.1 *Contact angle measurements*

Each of the polyurethanes listed in Table 1 was dissolved in DMF, to reach concentration of 1 g/dl. The solutions were cast on a glass plate and initially solidified by slow drying in DMF saturated atmosphere for 7 days and finally by drying at 50°C under vacuum (48 h). The polyurethanes films thus prepared were subjected to surface analysis. Also, the same types of samples were plasma treated. The low-pressure plasma treatment was performed using an installation, done in our laboratories [19], with the following characteristics: intensity: 100 V/cm; frequency: 1.2 MHz; pressure: 0.24 mbar; duration: 10 min. Uniform drops of the test liquids with a volume of 2 ml were deposited on the film surface and the contact angles were measured after 30 s, with a video-based optical contact angle measuring device, a modular instrument for goniometry, done in our laboratories, equipped with a Hamilton syringe in a temperature-controlled environmental chamber. In this experiment seven measurements were carried out for a single sample and the values obtained were averaged. All measurements were performed in air at a temperature of 25°C. Repeated measurements of a given contact angle were all within ± 3°. As probe liquids, double distilled water, ethylene glycol and methylene iodide were used, as purchased at maximum obtainable purity.

2.2.2 *Surface tension parameters*

For the calculation of the surface tension parameters, the geometric mean method (Eqs. 1 and 2) [12–14], the acid/base method (LW/AB) (Eqs. 3–5) [15–17], and theoretical method based on the structure-property relationship considering the group contribution techniques (Eq. 6) [18], were used.

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

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

where θ is the contact angle determine for water, ethylene glycol and CH_2I_2, subscripts 'lv' and 'sv' denote the interfacial liquid-vapour and surface-vapour tensions, respectively, while superscripts 'p' and 'd' denote the polar and disperse components, respectively, of total surface tension, γ_{sv}.

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

$$\gamma_{sv}^{AB}=2\sqrt{\gamma_{sv}^{+}.\gamma_{sv}^{-}} \quad (4)$$

$$\gamma_{sv}^{LW/AB}=\gamma_{sv}^{LW}+\gamma_{sv}^{AB} \quad (5)$$

where superscripts 'LW' and 'AB' indicate the disperse and the polar component obtained from the γ_{sv}^{-} electron donor and the γ_{sv}^{+} electron acceptor interactions, while superscript 'LW/AB' indicates the total surface tension.

$$\gamma(298\,\mathrm{K})\approx 0.75\cdot[E_{coh}/V(298\,\mathrm{K})]^{2/3} \quad (6)$$

where γ is the total surface tension, E_{coh} the cohesive energy and V the molar volume.

2.2.2.1 Scanning electron microscopy (SEM) The morphological features were also investigated by SEM with a TESLA BS 301 operating at 20 kV, with secondary electrons. The polyurethane samples were dissolved in DMF and cast from solution (1 g/dl) onto glass plates. The DMF evaporated slowly at room temperature, the films were completely dried in vacuum and then covered with thin layer of carbon–gold.

2.2.3 Water sorption

Water sorption was evaluated by weighing of the polymeric film samples (5 × 5 mm) under dry and wet state. The maximum hydration was considered at the moment of passing from floating to immersed state. Distilled water was employed. Water sorption of the films was calculated from the following relation [20]:

$$\text{Water uptake}\,(\%)=(W_w-W_d)\times 100/W_{d,}$$

where W_w and W_d represent the weights of wet and dry films, respectively. The water uptake is the average value of six samples prepared under the same conditions.

2.2.3.1 Plasma protein adsorption For adsorption experiment was used 3 mg/ml bovine serum fibrinogen (from Sigma Co, > 95% clotable) in solution 9% NaCl (similar concentration to that physiological from human blood) and human blood plasma (obtaining from human blood on 3.8% sodium citrate 9:1 v/v). A fresh solution of fibrinogen was always prepared for every adsorption experiment. Prior to adsorption experiment, the samples were brought to equilibrium with 9% NaCl solution (up to reaching of a maximum hydration, minimum 72 h). In order to perform adsorption experiments, polyurethane films with known surface area were introduced into tubes containing 0.5 ml fibrinogen solution or sanguine human plasma and kept them at 37°C for 1 h. After incubation, the films of polyurethane were removed and the amount of remaining protein in solution or plasma was determined by using Na_2SO_4 reaction and spectrophotometrical assaying with Piccos UV–VIS [21]. The adsorbed amount of fibrinogen was calculated with the following equation:

$$\text{Adsorbed protein}\,(\mathrm{mg/cm^2})=(C_o-C_e)\,V/S,$$

where C_o and C_e are the initial and equilibrium concentrations of fibrinogen solution (mg/ml), V is the volume of protein solution (ml) and S is the surface of the polyurethane sample.

3 Results and discussion

The as-prepared polyurethanes-cellulose were characterized by IR, ^{1}H-NMR(DMSO-d_6), GPC analyses in order to check the chemical structure and to evaluate the number-average molecular weights (M_n) and polydispersity indices (M_w/M_n).

Characteristic assignments have been found by IR and ^{1}H-NMR(DMSO-d_6) analyses.

IR: 3320 cm^{-1} (>NH stretching), 2870, 2960 cm^{-1} (>CH_2, –CH_3 stretching), 1720 cm^{-1} (>C=O stretching).

^{1}H-NMR (DMSO-d_6): 4.3 ppm methylene protons from ethylene glycol, 2.3 and 1.5 ppm methylene protons from adipic acid, 1.04 ppm methyl protons from HPC, 7–7.36 ppm phenyl protons, 3.78 ppm methylene protons from MDI, 8.5 and 9.6 ppm protons from urethane linkages.

3.1 Molecular weight characterization

The number-average molecular weights, M_n, and the polydispersity of the polyurethanes (polymer solutions in DMF, 1 g/dl), were determined by using a GPC PL-EMD 950 evaporative mass detector instrument. The system columns were thermostatted at 25°C. Calibration was performed with narrow polydispersity polystyrene standard (Polymmers Laboratories Ltd). The samples were eluted with DMF and the flow rate was 0.7 ml/min. Analysis of the elution data was performed by a computer program based on normalization of the chromatograms. The GPC curves of the studied samples did not evidence the presence of low-molecular-weight fractions, which might affect this study. Table 1 lists the compositional parameters, number-average molecular weight and polydispersity indices of the samples.

3.2 Contact angle

The methods used for determination of surface tension are based on contact angle measurements between the liquid meniscus and the polyurethane surface. A contact angle below 90° indicates that the test liquid readily wets the substrates, while an angle over 90° shows that the substrate will resist wetting. Table 2 lists the contact angles between double distilled water, ethylene glycol, or CH_2I_2 and polyurethane samples, before and after plasma treatment.

According to the geometric mean method, the solid surface tension components were evaluated with Eq. 1 [22], using the known surface tension components [23–25], of different liquids from Table 3 and the contact angles from Table 2. The total surface tension was calculated with Eq. 2.

Table 4 shows the surface tension parameters for both untreated and plasma treated polyurethane samples, according to the geometric mean method and to the acid/base method. In this table it was considered that γ_{sv}^{LW} is equivalent to γ_{sv}^{d} of the geometric mean method, the mean values of γ_{sv}^{-} and γ_{sv}^{+} were calculated with Eq. 3. Also, the total surface tension was calculated with Eq. 2. Following the plasma treatment the disperse component of surface tension, γ_{sv}^{d}, increases in absolute value, while the polar component surface tension γ_{sv}^{p}, decreases except PPG-HPC sample for which these dependences varies in a less extent (γ_{sv}^{p} increases from 32.2 to 38.9 mN/m, and γ_{sv}^{d} increases from 9.1 to 10.7 mN/m).

Table 5 shows the contribution of the polar component to the total surface tension obtained from the geometric mean method GM for untreated and plasma treated polyurethanes. Table 5 shows that the polar term γ_{sv}^{p} in general gives a large contribution to γ_{sv}, due to the large electron donor γ_{sv}^{-} interactions. Before and after plasma treatment all samples exhibits predominant electron donor properties. Table 5 shows that the contribution of the polar component decreases after plasma treatment, except the same PPG-HPC sample. The total, disperse and polar surface tension parameters are influenced by the matrix structure of polyurethanes possessing various soft segments. Generally, all samples possess high polar surface tension parameters, which decrease after low-pressure plasma treatment, except the PPG-HPC sample.

The studied segmented cellulose polyurethanes manifest a hydrophilic character, their contact angle being below 90°. After HF plasma treatment the hydrophile–hydrophobe balance is changed in the sense of decreasing their hydrophilicity. This can be explained through cross-linking chemical network and by the etching effect, which modifies the roughness and chemical composition of the surface. The exception is given by the PPG-HPC sample, which is less hydrophilic due to $-CH_3$ substituent in the soft macromolecular chain that is not favourable for polar interactions. It appears in our case that plasma induces competitive hydrophilic and hydrophobic effects and in the case of PPG-HPC sample these effects are equilibrated, such as the polar component is not changed after plasma treatment.

The total surface tension was estimated from the structure-property relationship, according to Eq. 6 in the following steps [18]:

1. Calculation of the zeroth-order connectivity indices ${}^{0}\chi$ and ${}^{0}\chi^{v}$ and of the first-order connectivity indices ${}^{1}\chi$ and ${}^{1}\chi^{v}$, according the values of the atomic simple

Table 2 Contact angle degrees of different liquids and polyurethane samples before and after plasma treatment

Polymer code	Untreated samples/plasma-treated samples		
	Water	Ethylene glycol	CH_2I_2
PEA-HPC	45/60	40/35	40/29
PTHF-HPC	45/52	36/29	33/29
PPG-HPC	60/50	45/30	32/27

Table 3 Surface tension parameters (mN/m) of the liquids used for contact angle measurements

Test liquids	γ_{lv}	γ_{lv}^{d}	γ_{lv}^{p}	γ_{lv}^{-}	γ_{lv}^{+}
Water	72.8	21.8	51.0	25.5	25.5
Ethylene glycol	48.0	29.0	19.0	47.0	1.92
Methylene iodide	50.8	50.8	0	0	0.72

Table 4 Surface tension parameters (mN/m) for untreated and plasma treated HPC-polyurethanes according to the geometric mean method and to the acid/base method

Polymer code	Untreated samples/plasma-treated samples				
	γ_{sv}^{p}	γ_{sv}^{d}	γ_{sv}^{-}	γ_{sv}^{+}	γ_{sv}
PEA-HPC	57.0/24.8	2.1/16.6	55.2/23.6	12.5/4.7	59.1/41.4
PTHF-HPC	53.1/34.7	4.7/12.9	50.7/33.2	10.2/6.6	57.8/47.6
PPG-HPC	32.2/38.9	9.1/10.7	30.7/37.2	6.2/7.4	41.3/49.6

Table 5 Contribution of the polar component to the total surface tension obtained from the geometric mean method for untreated and plasma treated polyurethanes

Polymer code	Untreated samples $\gamma_{sv}^{p}/\gamma_{sv} \cdot 100$ (%)	Plasma-treated samples $\gamma_{sv}^{p}/\gamma_{sv} \cdot 100$ (%)
PEA-HPC	96.5	60.0
PTHF-HPC	91.9	73.0
PPG-HPC	78.0	78.5

Table 6 Zeroth-order connectivity indices $^0\chi$ and $^0\chi^v$ and first-order connectivity indices $^1\chi$ and $^1\chi^v$

Polymer code	$^0\chi$	$^0\chi^v$	$^1\chi$	$^1\chi^v$
PEA-HPC	179.93	139.56	121.34	32.17
PTHF-HPC	175.56	149.16	123.36	90.33
PPG-HPC	180.31	140.74	119.24	84.74

connectivity indices and of the valence connectivity indices (Table 6).

2. Calculation of cohesive energy, by two methods, by applying the group contributions of Fedors [18, 26] and those of van Krevelen and Hoftyzer [18, 26], (Table 7).
3. Calculation of the molar volume at room temperature (298 K) (Table 7).

The theoretical results are closed to the experimental values, derived from the contact angle measurements.

3.3 Free energy of hydration

The hydrophobe–hydrophile balance of untreated and plasma treated polyurethanes has been evaluated by calculation of free energy of hydration, ΔG_w. The ΔG_w values were obtained from Eq. 7 [27]:

$$\Delta G_w = -\gamma_{lv}(1 + \cos\theta_{water}) \quad (7)$$

where γ_{lv} is the total surface tension of water from Table 3 and θ_{water} is contact angle of water with polyurethanes. The results are presented in Table 8.

Generally, the literature [17, 27] of the field mentions that for $\Delta G_w < -113$ mJm^{-2} the polymer can be considered more hydrophilic while when $\Delta G_w > -113$ mJm^{-2} it should be considered more hydrophobic. HF cold plasma treatment modifies ΔG_w indicating that the surface becomes more hydrophilic in the case of PPG-HPC sample and less hydrophilic in the case of PEA-HPC and PTHF-HPC samples.

Solid-liquid interfacial tension is defined with the following relation:

$$\gamma_{sl} = \left(\sqrt{\gamma_{lv}^p} - \sqrt{\gamma_{sv}^p}\right)^2 + \left(\sqrt{\gamma_{lv}^d} - \sqrt{\gamma_{sv}^d}\right)^2 \quad (8)$$

Free energy of hydration and interfacial tension are very important in that they determines the interactional force between two different media and controls the different processes: stability of the colloidal aqueous suspensions, dynamic of the molecular self-assembling, wetability of the surface, space distribution and adhesiveness. The biological and chemical processes, which take place at the level of the surface of the implant, depend on the interfacial interactions between solid and liquid (water).

Table 8 Surface free energy between polyurethane and water and interfacial tensions for untreated and plasma treated samples

Polymer code	Untreated samples/plasma-treated samples	
	ΔG_w (mJ/m^2)	γ_{sl} (mN/m)
PEA-HPC	−124.28/−109.2	10.6/5.0
PTHF-HPC	−124.28/−117.62	6.3/2.7
PPG-HPC	−109.2/−119.59	4.9/2.8

(1) When the blood-biomaterial interfacial tension is high, the blood proteins will be anchored on many points on the surface, they strongly interact with the surface and thus the solid–liquid interfacial tension decreases. Consequently, the proteins change their conformation. A new interface is formed, between the protein surface and sanguine plasma.

(2) When the blood-biomaterial tension is relatively low, the force, which determines the protein adsorption, will be smaller. Conformation of the proteins initially adsorbed is similar to that found for the proteins in solution. Therefore, the interfacial tension between the protein surface and the sanguine plasma will not be high, not being an appreciable force able to determine the adsorption of sanguine components. This corresponds to a better compatibility of the biomaterial surface with blood comparing with the case (1). The surface of the biomaterial must reduce to minimum the blood-biomaterial interfacial tension such as the modification of the initially adsorbed proteins to be little. Although, apparently an interfacial tension equal to zero would be ideal for realization of the blood compatibility, however this is not desirable in view of the mechanical stability of the blood-biomaterial interface. It is generally considered that the blood-biomaterial interfacial tension should be 1–3 mN/m for a good blood-biomaterial compatibility, as well as a good mechanical stability of the interface.

Table 7 Total surface tensions, $\gamma_{(1)}$ and $\gamma_{(2)}$, from the theoretical data calculated for cohesive energies, $E_{coh(1)}$ and $E_{coh(2)}$, and molar volume, V, for studied polyurethanes

Polymer code	$E_{coh(1)}$, (10^{-5} J/mol)	$E_{coh(2)}$, (10^{-5} J/mol)	V (298 K) (ml/mol)	$\gamma_{(1)}$ (mN/m)	$\gamma_{(2)}$ (mN/m)
PEA-HPC	13.88	15.28	2812	46.89	49.95
PTHF-HPC	12.77	16.39	2613	46.61	54.76
PPG-HPC	12.25	14.75	2560	45.98	51.87

The values for solid–liquid interfacial tensions are given in Table 8 for untreated and plasma treated samples. It can be observed that the interfacial tensions are in general low, and after plasma treatment become even lower. Moreover, 1 mN/m $< \gamma_{sl}$ for PTHF-HPC and PPG-HPC samples treated in plasma <3 mN/m which is required for a good biomaterial.

3.4 Scanning electron microscopy (SEM)

In Fig. 1 are illustrated the SEM micrographs corresponding to the treated and untreated polyurethane samples. It is obvious that plasma caused a change in the surface morphology and etching effects are observed.

3.5 Water sorption

The biocompatibility of the materials depend on their ability to swell in aqueous media. A high water level on the surface of the biomaterial provides a low interfacial tension with blood, thus reducing fibrinogen adsorption, cell adhesion and clot formation [26–29]. The results are presented in Fig. 2. It is observed that the water uptake is given by the PEA-PU sample (reference polyurethane sample without hydroxypropylcellulose, PEA/MDI/EG, $M_n = 109.613$, $M_w/M_n = 1.3$), PEA-HPC and PTHF-HPC samples (151%, 140% and 167%, respectively) and in a less extent by the PPG-HPC (92%) due to its less polar soft segment having the lateral $-CH_3$ substituents which confer

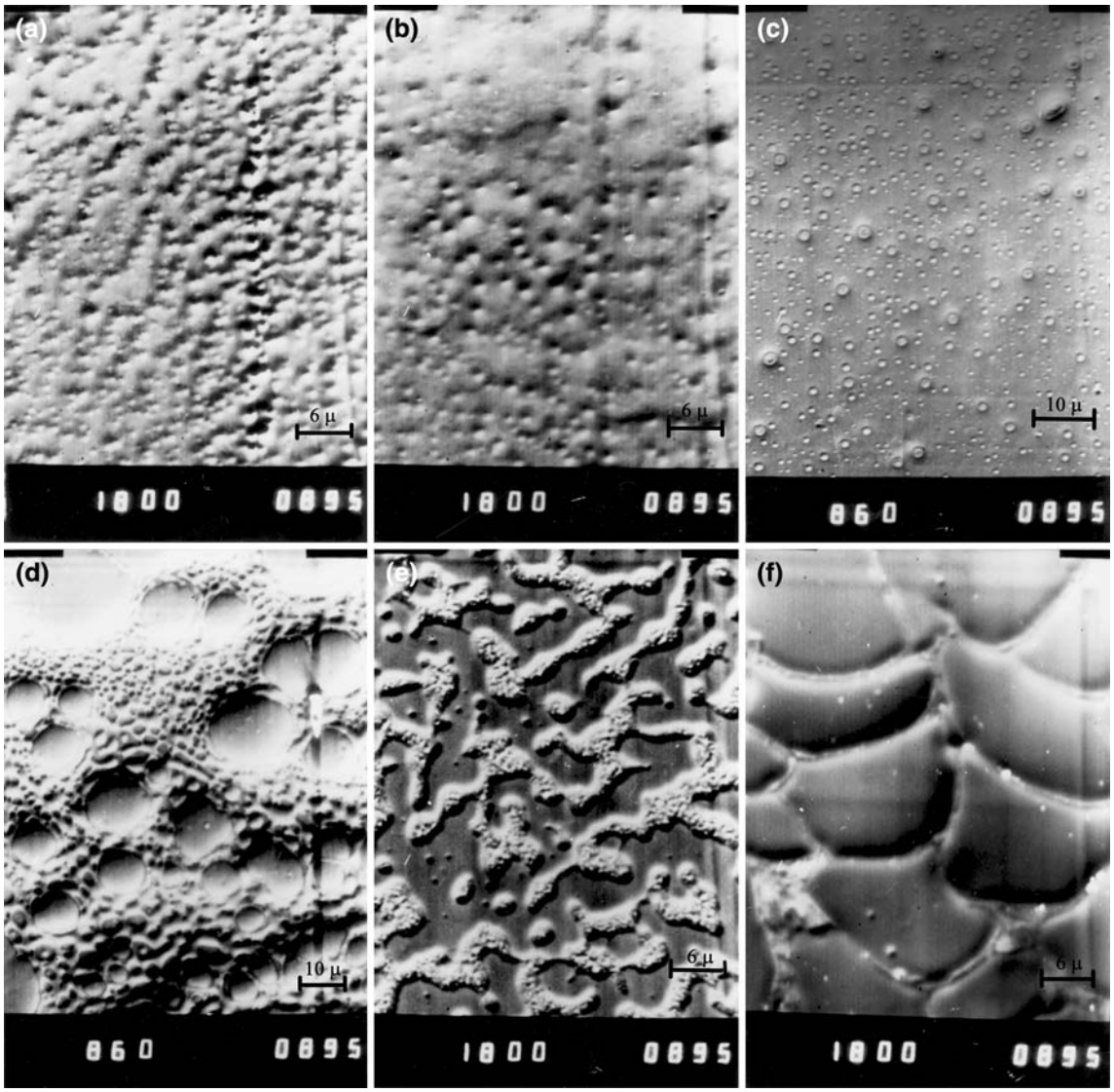

Fig. 1 SEM images of the polyurethane samples untreated and treated in HF cold plasma (PEA-HPC, **a**, **b**; PTHF-HPC, **c**, **d**; PPG-HPC, **e**, **f**)

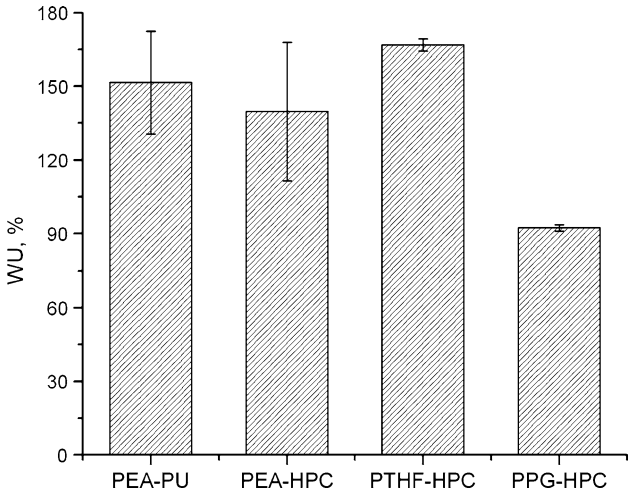

Fig. 2 Weight of polymer sample in dry and maximum hydrated state

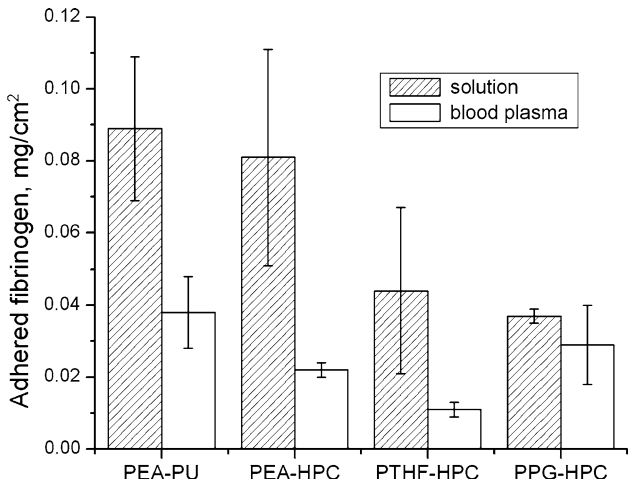

Fig. 3 Amount of adsorbed fibrinogen from physiological solution and blood plasma

a different geometry to the polyurethane internal microporous structure, unfavourable for water uptake.

3.6 Fibrinogen adsorption

The experimental data related to the amount of adsorbed fibrinogen before and after incubating of polymers with a physiological solution of fibrinogen (3.00 mg/ml) and blood plasma (2.98 mg/ml) are presented in Fig. 3.

The postincubation fibrinogen concentration for the incubated materials (1 h at 37°C), preincubation and postincubation fibrinogen concentration for reference sample in comparison with the physiological normal limits are given in Table 9. Incubation of the samples with blood plasma realized in the same conditions of the incubation in solution and leaded to the results from Fig. 3. Determination of the adhered fibrinogen from blood plasma was coupled with the determination of the prothrombin time, i.e., the time of transformation of the prothrombin in thrombin, followed by transformation of the fibrinogen in fibrin and clot formation. It is observed that the amount of fibrinogen adsorbed from blood plasma is less in comparison with that in solution, for all the materials except PPG-HPC, for which the differences are not significant. Also, it is remarked that prothrombin time stand in physiological normal limits (Table 9) so studied polyurethane samples did not affect the clot formation mechanisms.

The significant differences between adsorptions of the fibrinogen solution and blood plasma, suggest that the fibrinogen adsorption properties of the polyurethane samples, under physiological condition are affected by the concurrent affinities for other plasma proteins, which do not disturb the haemostatic mechanisms. Probably among the plasma proteins that can concur with fibrinogen is albumin, which was previously investigated [30], and it was found that the adsorption value of a sub-physiological solution of serum albumin, (3 mg/ml), to PEA-PU materials was 0.3 ± 0.06 mg/cm^2.

In the literature many research studies are dealing with polyurethanes regarding contact angle measurements, water sorption and protein adsorption. Water plays an important role in determining biocompatibility characteristics of the synthetic material. It is very well known that high water levels on the surface of the biomaterial providing a low interfacial tension with blood consequently reduce fibrinogen adsorption and cell adhesion on the surface similarly to biological tissues. In [29] for polyurethane type Biospan^{TM} evaluated water contact angle is 70°, in [31] for phospholipids-grafted segmented polyurethanes high water contact angles 99–105° and in [32] for cross-linked multiblock pellethene polyurethane water contact angle is 73°. As to our work (Table 2) water contact angles for studied polyurethanes are placed at lower values comparing with those above mentioned examples, due to the introduction of the hydrophilic cellulose derivative (HPC) which is very well known also to form hydrogels in water.

Biocompatibility may in part be due to the swelling in water capability and it was reported in [29] a water uptake value of 14% after 7 h, in [32] after 48 h a water uptake value of 37%, and in [33], water absorption after immersion in water for 24 h for polyurethane polymerized films below 600%, and for their cross-linked blends films after 48 h, up to 60% water absorption. In our work, water sorption values are determined by the film preparation procedure through precipitation in water and by the chemical composition of the polyurethane matrix including HPC.

Table 9 Prothrombin time and fibrinogen concentration after the contact blood plasma with polyurethane samples

Parameter	Physiological normal limits, mg/ml	Reference sample (blood plasma)	PEA-PU	PEA-HPC	PTHF-HPC	PPG-HPC
Prothrombin time (s)	8.3–11.3	10.43 ± 0.04	11.06 ± 0.4	10.9 ± 0.09	10.9 ± 0.09	10.9 ± 0.07
Fibrinogen concentration (mg/ml)	2.84–3.69	Preincubation 2.98 ± 0.04				
		Postincubation 2.96 ± 0.05	Postincubation 2.79 ± 0.04	Postincubation 2.87 ± 0.04	Postincubation 2.90 ± 0.01	Postincubation 2.77 ± 0.07

In contact with blood, biomaterials are limited in their usefulness primarily in thrombus formation at the blood-material interface, which is triggered by the preferential adsorption of some plasma proteins. Fibrinogen plays a central role in haemostasis participating not only in the coagulation cascade, but it also promotes adhesion of platelets and activates then when adsorbed onto certain solid surfaces. In [29] it is shown that the protein adsorption is selective relative to albumin and fibrinogen and this selectivity depend on the modified PU surfaces and in [34] the adsorbed fibrinogen on polyurethane surface depends on the migration of the amphiphilic character to the surface. In our work it is observed that the fibrinogen adsorbed from blood plasma is less in comparison with that in solution except PPG-HPC sample.

4 Conclusions

Cellulose-based polyurethanes have been studied taking into consideration that the functional groups given by cellulose chains constitute preferential sites for bioactive interactions for biocompatible devices.

HF cold plasma has been used to change the surface morphology and interfacial characteristics. SEM analyses revealed the etching effect caused by plasma treatment while the calculation of the surface tension parameters revealed that the polyurethane surfaces became less hydrophilic. Solid–liquid interfacial tension measurements effected for the polyurethane samples treated in HF plasma reveal that they become more compatible with blood and recommend this treatment to be applied for achieving biomaterial qualities.

From the present study dealing with surface properties, it can be concluded that poly(ether urethanes) are remarked in their good compatibility with blood after effecting HF plasma treatment, whereas the water sorption and fibrinogen adsorption tests emphasize that the ether-type polyurethane, PTHF-HPC is indicated for thromboresistant devices. The cellulose component, HPC, introduced in the polyurethane structure reduces the fibrinogen amount adsorbed from solution and blood plasma. These results provide that the studied polyurethanes manifest relevant haemocompatible properties under complex physiological interactions. The obtained results show that the material properties manifested in siloco should be extrapolated with studies in physiological fluids conditions, in vitro and in vivo experiments.

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