

Surface analysis of some amphiphile polyurethanes

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Amphiphile polymers find widespread applications because of their unique ability to self-assemble and modify interfacial properties. Smart polymers have very promising applications in the biomedical field as delivery systems of therapeutic agents, tissue engineering scaffolds, cell culture supports, bioseparation devices, and sensor or actuators systems. Polyurethanes and polyurethane-ureas based on Pluronic macrodiols have been prepared. The morphological and self-assembly characteristics were tuned in function of the structural parameters related to the soft matrix and H-bonding. HF plasma was employed to change the interfacial characteristics. The plasma action was evaluated by contact angle measurements. SEM and AFM analyses evidenced the microheterogeneous morphology and the self-assembling behaviour.

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1. Introduction

The biocompatibility of polymer surfaces in contact with either living organisms or liquid samples of biological origin is a crucial issue of modern surface chemistry. The physics of block copolymers solutions is rich because of the solvent selectivity towards the blocks causes self-assembly into various structures. The exact structure formed can be "tuned" by the relative molecular weight of the blocks, the temperature and polymer concentration, and the solvent composition. Such variety and tunability have led to many applications and an extensive literature. A class of widely used in many biomedical applications [1-6] and studied [7-12] triblock copolymers because of their excellent biocompatibility is represented by poly(ethylene oxide) - poly(propylene oxide) - poly(ethylene oxide) (PEO-PPO-PEO) type known as Pluronics (or Poloxamers). They are amphiphiles due to the water solubility against PEO block and water insolubility against PPO block. The amphiphile molecules are remarkable in their self-assembly and modifying the interfacial characteristics. PEO-PPO block copolymers can form the whole spectrum of self-assembled structures, from micellar solutions in water to lyotropic liquid crystals in both aqueous and non-aqueous solutions [13-16]. Lately, modifications of PEO-PPO-PEO block copolymers are being explored for various applications [17-21]. This increases the need for detailed knowledge of the interactions in the systems.

Here we report the surface study of some polyurethanes and polyurethane-ureas comprising the hydrophilic and hydrophobic molecular segments. Polyurethanes have been popular candidate materials in several blood-contacting applications and their good blood compatibility has been attributed to their multidomain structure [22-24]. The multiphase structure is responsible

for surface restructuring at a large scale to minimize interfacial energy and affects the ability of the polymer to reorient in response to environmental changes. Adding into the formulation of polyurethanes of active hydrophilic, hydrophobic, or amphiphilic components was found to change the structure and molecular reorganization of their surfaces [25-27]. Surface properties of biomedical polymers, especially surface morphology and surface energy are key factors determining antithrombogenicity of the materials. Whereas highly hydrophilic surface as well as highly hydrophobic surface does not have good antithrombogenicity, the balanced surface having amphiphilic character has good antithrombogenicity [23]. The pattern of hydrophilic and hydrophobic microdomains at the surface may also be of importance for protein adsorption and blood-material interaction. This type of surfaces including self-assembled films is one of the perspectives way for creation of medical devices.

These types of "smart" or "self-monitoring" materials possess ability for fast reorientation of its surface structure during contact with blood. Development of self-monitoring coatings is one of perspective way to improve biological properties of medical devices using the minimization of protein sorption processes onto blood-material interface. The contact angle gives information about the macroscopic surface wettability. Plasma treatments as external stimuli alter the surface energy of the polymers and affect the wettability. Surface chemistry of polyurethanes modified by means of high frequency cold plasma was characterized by calculation of the surface tension parameters [28,29].

It is our goal to characterize polyurethane surface structures, to evaluate their dependence upon their local environment, and to determine the significant material properties controlling blood compatibility.

Contact angle has been shown to be sensitive to surface composition, microheterogeneity, reorientation, topography or roughness. Contact angle measurements will be used to establish correlations of surface chemistry and interfacial response. Microscopic techniques (SEM, AFM) are employed to complete the study of the surface properties and morphology of these polyurethanes and polyurethane-ureas.

2. Experimental

2.1 Materials

Poly(ethylene glycol) – block –poly(propylene glycol)-block-poly(ethylene glycol) (P₁₂₃) (PEO was purchased from Sigma-Aldrich, M_n = 5800 g/mol ; Poly(ethylene glycol) (PEG600) was purchased from Sigma-Aldrich, M_n = 600 g/mol; 1,6- Hexamethylene diisocyanate (1,6-HDI) was purchased from Fluka and used as received; 1,6- Hexane diol (HD) and 1,6- Hexamethylene diamine (HDA) (Fluka), were used without further purification. Four different polyurethanes and polyurethane-ureas were prepared by the two-step solution polyaddition using dry N,N-Dimethylformamide (DMF, Fluka) as solvent. First, the NCO-terminated prepolymer was prepared by dehydrating the macrodiol (P₁₂₃) or the mixture of P₁₂₃:PEG600 (1:1) for 3 h at 90 °C under vacuum followed by adding 1,6-HDI to the vigorously stirred macrodiol. The amounts of diisocyanate and macrodiol were kept at a molar ratio 2:1. The reaction between diisocyanate and macrodiol took place for 2.5 h under nitrogen atmosphere at 90 °C in the presence of dibutyltin dilaurate (95 %, Aldrich) as catalyst. The temperature was lowered to 70 °C and the chain extender (1,6-Hexane diol or 1,6- Hexamethylene diamine) was added. The reaction continued further for 1.5 h. The resulting polymers were precipitated in water and dried under vacuum for 7 days. Characteristic assignments have been found by IR and ¹H-NMR (DMSO-d₆) analyses. The general chemical structure of the synthesized amphiphilic multiblock polyurethanes and polyurethane-ureas is presented in Scheme 1.

PU-1:

...-O-R₁-O-CO-NH-R₂-NH-CO-O-R₃-O-CO-NH-R₂-NH-CO-...

PU-2:

...-O-R₁-O-CO-(NH-R₂-NH-CO-O-R₃-O-CO-NH-R₂-NH-CO)_q-(O-R₄-O-CO-NH-R₂-NH-CO)_r-...

PU-3:

...NH-R₁-NH-CO-NH-R₂-NH-CO-O-R₃-O-CO-NH-R₂-NH-CO-...

PU-4:

...-NH-R₁-NH-CO-(NH-R₂-NH-CO-O-R₃-O-CO-NH-R₂-NH-CO)_q-(O-R₄-O-CO-NH-R₂-NH-CO)_r-...

where:

R₁ and R₂ = -(CH₂)₆- ; R₃ = -(CH₂CH₂O)_n-
(CH₂CH(CH₃)O)_m-(CH₂CH₂O)_n-;

R₄ = -(CH₂CH₂O)_s-.

Scheme 1. Chemical structure of the synthesized poly (urethanes) and poly (urethane-ureas)

IR: 3300-3500 cm⁻¹ (>NH stretching), 2870-2970 cm⁻¹ (>CH₂, -CH₃ stretching), 1718-1620 cm⁻¹ (>C=O stretching), 1100-1150 cm⁻¹ (C-O-C stretching).

¹H-NMR (DMSO-d₆): 1.14 ppm -CH₃ (PPO) ; 3-3.7 ppm -CH₂-CH₂-O- (PEO), >CH-CH₂-O- (PPO); 2.5 ppm -CH₂-CO-; 4.2 ppm -CH₂-O-CO-; -NH- urethane groups 7.2 ppm, -NH- urea groups 5.7 ppm.

2.2 Measurements

The molecular weights of the polyurethanes (polymer solutions in 1 % DMF), were determined by using a GPC PL-EMD 950 evaporative mass detector instrument. Infrared Spectroscopy (FT-IR) was done using a VERTEX 7 Instruments spectrum range 600-4000 cm⁻¹; thin films onto KBr pellets, resolution 2 cm⁻¹.

2.3 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 polyurethane 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 with the following characteristics: intensity: 3000 V/cm; frequency: 1.3 MHz; pressure: 58 Pa; duration: 10 min. 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, with a video-based optical contact angle measuring device equipped with a Hamilton syringe in a temperature-controlled environmental chamber.

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 diiodine methane were used, as purchased at maximum obtainable purity.

2.4 Scanning electron microscopy

The morphological features were also investigated by scanning electron microscopy (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.

2.5 Atomic force microscopy

AFM measurements are performed in air at room temperature, in the tapping mode using a Scanning Probe Microscope (Solver PRO-M, NT-MDT, Russia) with commercially available NSG10/Au Silicon cantilevers. The manufacturer's values for the probe tip radius are 10 nm, and the typical force constants are 11.5 N/m. In the tapping mode, the cantilever is oscillated at a frequency of

183,228 kHz. For AFM investigations thin films resulted after casting the polyurethane DMF solutions (1 g/dL) onto glass slides, followed by drying under vacuum, were employed.

3. Results and discussions

In Table 1 compositional parameters, molecular weights (M_n : number-average molecular weights; M_w/M_n : polydispersity indices estimated from GPC) of the synthesized polyurethanes/polyurethane-ureas are presented.

Table 1. Compositional parameters, molecular weights values and polydispersity indices

Code	SS	HS	% SSC _a	M_n g/mol	M_w/M_n
PU-1	P ₁₂₃	HDI-HD	91	15600	1.05
PU-2	P ₁₂₃ / PEG600, 1:1	HDI-HD	87	41900	1.42
PU-3	P ₁₂₃	HDI-HDA	91	30500	1.18
PU-4	P ₁₂₃ / PEG600, 1:1	HDI-HDA	87	88200	2.05

^aSoft-segment concentration (SSC) is defined as : $SSC = (m_{pol} - m_{OH}) \times 100 / m_{total}$, where m_{pol} is mass of polyol, m_{OH} mass of hydroxyl groups and m_{total} is total mass of polymer; hard-segment concentration (HSC) is $HSC = 100 - SSC$.

3.1 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 CH₂I₂ and polyurethane samples, before and after plasma treatment. A decrease in contact angle after plasma treatment indicates a higher oxygenation of the surface, leading to an increase in hydrophilicity.

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

Polymer code	Untreated samples/Plasma treated samples		
	Water	Ethylene glycol	CH ₂ I ₂
PU-1	58/36	35/20	19/25
PU-2	43/31	45/29	26/25
PU-3	42/20	19/11	-/15
PU-4	53/42	52/17	29/23

3.2 Calculation of the surface tension parameters

For the calculation of the surface tension parameters, the geometric mean method (Eqns. (1) and (2)) [30-32], the acid/base method (LW/AB) (Eqns. (3)-(5)) [33-35], and theoretical method based on the structure-property relationship considering the group contribution techniques (Eqn. (6)) [36] were used.

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

$$\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p \quad (2)$$

where θ is the contact angle determined for water, ethylene glycol and CH₂I₂, 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} .

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

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

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

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.

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

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

According to the geometric mean method, the solid surface tension components were evaluated with Eqn. (1) [37], using the known surface tension components [38-40] of different liquids from table and the contact angles from Table 2. The total surface tension was calculated with Eqn. (2).

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 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 Eqn (3). Also, the total surface tension was calculated with Eqn. (5).

Table 4. Surface tension parameters (mN/m) for untreated and plasma treated 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}
PU-1	28.14/ 57.46	14.54/ 6.29	26.83/ 54.92	5.38/ 10.96	42.68/ 63.75
PU-2	66.90/ 72.29	0.975/ 3.12	63.82/ 68.09	12.83/ 12.25	67.88/ 75.41
PU-3	24.20/ 76.31	21.98/ 1.21	40.97/ 74.65	3.35/ 18.66	46.18/ 77.52
PU-4	53.92/ 45.76	1.58/ 10.52	51.41/ 43.69	10.33/ 8.76	55.50/ 56.28

The data presented in Table 4 show that following the plasma treatment the polar component, γ_{sv}^p , corresponding to less hydrophilic surfaces (PU-1 and PU-3) increases, while the disperse component, γ_{sv}^d , decreases. As to more heterogeneous and hydrophilic surfaces having incorporated hydrophilic PEG molecular segments (PU-2 and PU-4), it is evident that after effecting plasma treatment the disperse component is more affected: γ_{sv}^d increases, whereas for γ_{sv}^p no important changes (for PU-2 γ_{sv}^p slightly increases, and for PU-4 γ_{sv}^p slightly decreases) are remarked. In other words for polar surfaces, the plasma treatment induces changes for the disperse component rather than for the polar component.

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 exhibit predominant electron donor properties. Table 5 shows that the contribution of the polar component increases after plasma treatment in the case of PU-1 and PU-3 samples whereas in the case of PU-2 and PU-4 samples the contribution of the polar component decreases and this corresponds to the introduction of hydrophilic PEG600 as co-soft segment in the polyurethane/polyurethane-urea matrix. The total, disperse and polar surface tension parameters evaluated before and after plasma treatment are strongly influenced by the matrix structure of polyurethanes.

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/Plasma treated samples
	$\gamma_{sv}^p / \gamma_{sv} \cdot 100$ (%) GM
PU-1	65.93/90.13
PU-2	98.55/95.86
PU-3	52.40/98.44
PU-4	97.15/81.30

The total surface tension was estimated from the structure-property relationship, according to Eqn. (6) in the following steps [36]:

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

Table 6. Zeroth-order connectivity indices ${}^0\chi$ and ${}^0\chi^v$ and of the first-order connectivity indices ${}^1\chi$ and ${}^1\chi^v$.

Polymer code	${}^0\chi$	${}^0\chi^v$	${}^1\chi$	${}^1\chi^v$
PU-1	276.53	279.97	209.14	161.14
PU-2*	52.90	44.11	36.42	26.54
PU-3	276.53	280.50	209.14	160.92
PU-4*	52.90	44.29	36.42	26.77

PU-1 and PU-3 are equivalent to group contributions corresponding to PEO₂₀PPO₇₀PEO₂₀ soft segments in the polyurethane and polyurethane-urea matrix structure with $M_n=5800$ g/mol; PU-2* and PU-4* are equivalent to group contributions corresponding to PEG600 soft segments in the polyurethane and polyurethane-urea matrix structure with $M_n=600$ g/mol.

2. Calculation of cohesive energy, by two methods, by applying the group contributions of Fedors [36, 41] and those of van Krevelen and Hoftyzer [36, 41] (Table 7).

3. Calculation of the molar volume at room temperature (298 K) (Table 7).

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 polyurethanes

Polymer code	$E_{coh(1)}$, (10^5 J/mol)	$E_{coh(2)}$, (10^5 J/mol)	V (298K), mL/mol	$\gamma_{(1)}$, mN/m	$\gamma_{(2)}$, mN/m
PU-1	19.1263	25.6899	5782.62	35.87	43.67
PU-2*/ PU-2	3.7924	5.2665	928.73	41.29/ 38.58	51.39/ 47.53
PU-3	19.1980	25.7659	5461.01	37.36	45.45
PU-4*/ PU-4	3.8641	5.2658	934.31	41.63/ 39.50	51.17/ 48.31

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

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 Eqn.(7) [42] :

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

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.

Table 8. Surface free energy, ΔG_w , between polyurethane and water for untreated and plasma treated samples, and solid-liquid interfacial tension, γ_{sl}

Polymer code	ΔG_w (mJ/m ²), Untreated samples/Plasma treated samples	γ_{sl} (mN/m), Untreated samples/Plasma treated samples
PU-1	-111.38/-131.70	4.13/4.86
PU-2	-126.04/-135.20	14.62/10.26
PU-3	-114.56/-141.21	4.93/15.30
PU-4	-116.61/-126.20	11.67/2.18

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

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

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, wettability 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).

The calculated surface free energy, ΔG_w values for the studied polyurethanes and polyurethane-ureas thin film samples reveal that they are generally hydrophilic, those with incorporated PEG segments are more hydrophilic affecting the hydrophilic-hydrophobic balance; the plasma treatment increased the hydrophilicity of the samples, especially for the less hydrophilic ones. The more polar urea groups in the polyurethane structure confer hydrophilicity, too. The low percentage of the urea hard segments may not produce large differences in the calculated values. The resulted phase segregated morphology may also be important in the hydrophilic-hydrophobic balance, due to the segregation in hydrophilic and hydrophobic microdomains. 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.

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 higher for the samples with incorporated PEG segments and decrease after plasma treatment and γ_{sl} evaluated for PU-4 sample after plasma treatment, fall within 1-3 mN/m interval required for a good biomaterial.

According to the common definition, amphiphilic molecules have affinities for two different environments. The incompatible blocks may interact differently with their environment due to their chemical nature and behave distinctively in solution (selective solvent). These differences can induce microphase separation of amphiphilic block copolymers, not only in aqueous media but also in organic solvents. The phase behaviour is related to the microphase separation which takes place when the interblock segregation and micellar interfacial association are sufficiently high and results in nano- and microscale various geometrical types of assemblies depending on the relative block length.

Morphology of a multiphase system plays an important role in determining the properties of the polymer. The morphology of the polyurethanes is very complicated not only because their two phase structure (soft/hard) but also because of other physical phenomena, such as crystallization and hydrogen bonding in both segments and amphiphilic structuring. From thermodynamical point of view, the incompatibility between the polar hard segment and less polar soft segment in polyurethanes causes the heat of mixing to be positive and drives the segments to phase separate. The degree of phase segregation between the hard and soft segments depends on molecular surface. Phase segregation degree between hard and soft segments depends on molecular weight (P₁₂₃ with M_n=5800 g/mol; PEG600 with M_n=600 g/mol) and the interaction of hard segments with each other and with the soft segment. The hard, rigid segment segregates into a glassy or semicrystalline domain and the soft segments form amorphous or rubbery matrices in which the hard segments are dispersed at varying content levels. The degree of phase separation or domain formation depends on the weight ratio of the hard to the soft segment, type of chain extender, the type and molecular weight of the soft segment, the hydrogen bond formation between the urethane linkages. The morphology at different levels of structuring of segmented polyurethanes can be studied by microscopy techniques by which the size, shape, connectivity domains, and interfacial thickness as a function of segment content and sample history, are evidenced.

In Figs. 1a, b, c, d, e, f the SEM micrographs revealing the morphology developed by the synthesized polyurethanes and polyurethane-ureas are presented.

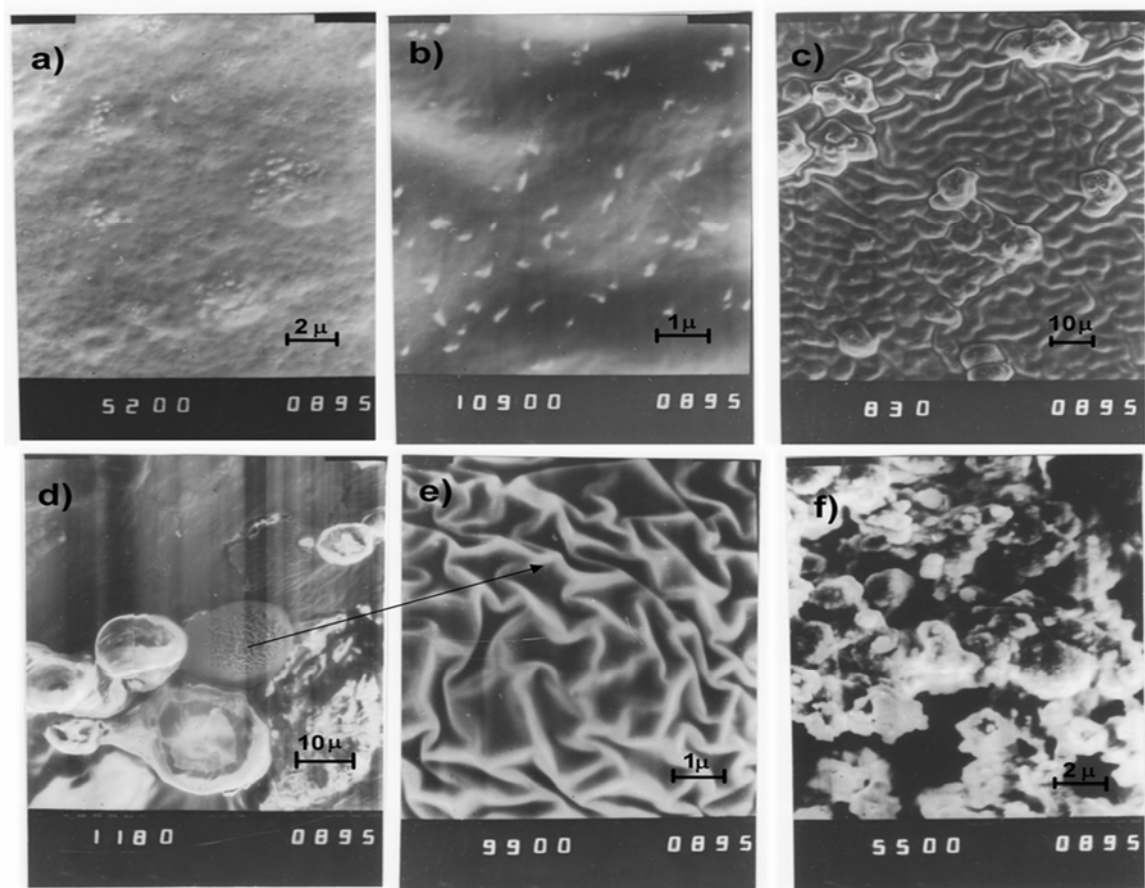


Fig.1. SEM micrographs of the polyurethane/polyurethane-ureas samples (a–PU-1; b, c–PU-2; d, e (detail)–PU-3; f–PU-4).

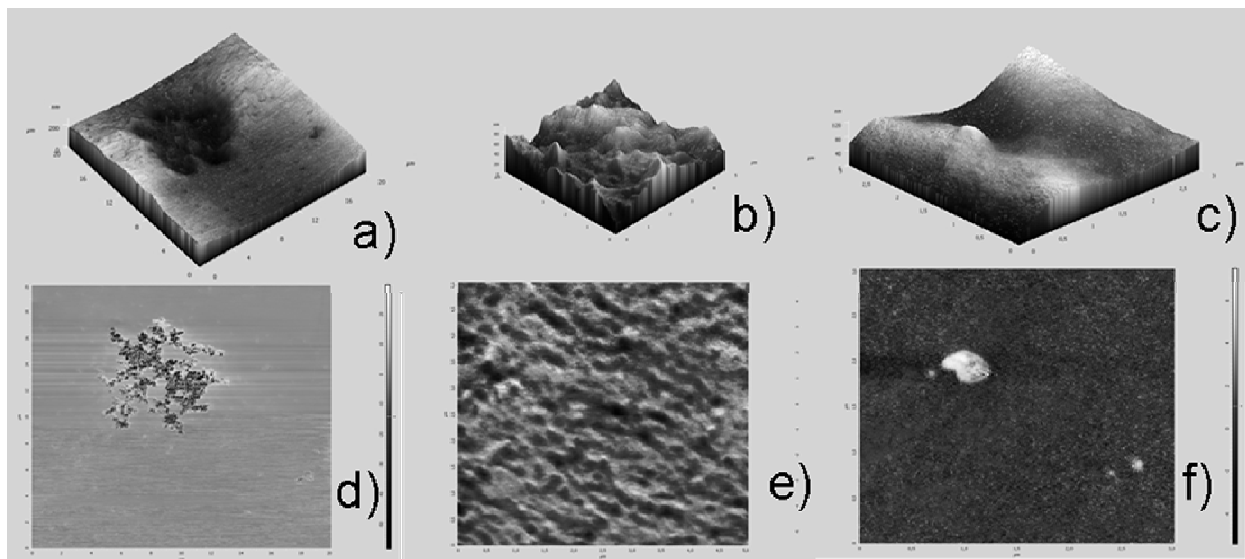


Fig. 2. AFM images of the studied samples. a, d) PU-1 sample : a) 3 D topography image, 20x20 μm ; d) phase image; b, e) PU-2 sample : b) 3 D topography image, 5x5 μm , e) phase image; c, f) PU-4 sample : c) 3 D topography image, 3x3 μm , f) phase image.

One can remark the phase segregated and microheterogeneity of the surfaces of the thin film samples. In Fig. 1a (PU-1 sample) morphological features related with microdomain aggregation are observed. In Fig. 1b (PU-2 sample) at a larger magnification self-assembled within nanostructures developed at the surface are remarked, whereas in Fig. 1c at a lower magnification, a phase segregated convoluted morphology is evidenced. In Figs. 1d, and 1f for PU-3 and PU-4 samples, the formation through micellar chain growth of globular particle assemblies is evidenced. The particle size seems to be different when comparing the two samples, for PU-4 sample (Fig. 1f) the particles are smaller than those of PU-3 sample (Fig. 1d), explainable by amphiphilic phase segregation and conformational chain flexibility. One can remark for these particles, different surface features like undulated (see detail, Fig. 1e) or “jelly-fish” like appearance microcapsules as revealed in Fig. 1d.

In Fig. 2 the AFM images (3 D topography and phase) of polyurethane samples are presented.

Phase segregation and microheterogeneity of the thin films is revealed also by AFM pictures. Polyurethane samples contain a few amount of hard segment (10 %) and for this reason the hard segment phase is dispersed in the soft matrix. An interconnected phase segregated morphology is revealed by the PU-2 sample and the surface shows roughness, too. The other two samples reveal smooth surfaces, due to predominant soft phase, and some features caused by microdomain aggregates.

4. Conclusions

Polyurethanes and polyurethane-ureas have been prepared by varying the structural components in order to achieve different bulk and surface characteristics. In addition, plasma treatment technique was applied to modify the surface properties. Contact angle measurements proved the sensitivity related to the interfacial tension parameters of the studied thin films. Matrix composition is determinant for surface microheterogeneity which dictates the contact angle.

Following the plasma treatment the obtained results show their dependence on the surface composition. SEM and AFM observations reveal the typical phase segregated morphology of these materials and moreover the self-assembled structures obtained due to the amphiphilic blocks.

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