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Electrokinetic Potential and Other Surface Properties of Polymer Foils and Their Modifications

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1. Introduction

In most of heterogeneous systems consisting of solid material in liquid medium the phase interface exhibits an electrical charge. This charge can play an important role in stability of these systems and in their behaviour in liquid surrounding. The knowledge of this behaviour is necessary for next usage of these materials. The electrical charge at solid-liquid interface is a key parameter for surface science and engineering. When the surface is charged, then it can attract ions of opposite charge (counter-ions) from the liquid. In this way the electrical double layer is created, consisting of two oppositely charged layers. Between the surface and volume liquid phase is a potential gradient and the potential of volume liquid phase is equal to zero. When the liquid flows along the solid surface, the electrical double layer divides. Inner layer (the solid phase) does not move, and adsorbed or bonded counter ions, while the outer layer flows along. The potential created between solid surface and this mobile interface is known as an electrokinetic potential or zeta potential (ζ -potential) [1]. The electrical charge at the interface can be caused by several mechanisms: (i) ionization or dissociation of surface groups of surface layers, e.g. either dissociation of a proton from a carboxylic group, which leaves the surface with a negative charge; (ii) preferential solution of some ions of crystal lattice in contact with liquid; (iii) preferential adsorption of some ions from the solution on initially uncharged surface, e.g. adsorption of either hydroxide or hydronium ions created by the enhanced autolysis of water at the surface; (iv) isomorphic substitution of ions of a higher valence by ions of lower valence in the case of clay minerals (e.g. Si^{4+} for Al^{3+}); (v) accumulation of electrons in the case of metal-solution interface, etc. [1-3].

Dissociation of the surface groups is a common charging mechanism in the case of latex particles, which are frequently used in biomedical applications [1]. The adsorption of hydroxide ions created by enhanced autolysis of water at hydrophobic surfaces may be the reason for the hitherto unexplained charge of hydrophobic micro-fluidic substrates [2-4]. The behavior at hydrophobic and hydrophilic polymer surfaces is quite different. While on hydrophobic surface the surfactants displace water from the solid surface, it cannot displace water from the hydrophilic surface. In that case adsorption occurs mainly by electrostatic interactions between the surfactant "head" group and the surface groups [5]. Pristine polymers exhibit the first (polymers without any functional groups on surface) or the third (when surface presents any functional groups able to dissociate in liquid) type of mechanisms depending on their surface chemistry. When polymers are deposited by metal nanostructures, the accumulation of electrons begins to play a role.

Zeta potential is a characteristic parameter for description of solid surface chemistry. It is an important physico-chemical property of cellulose [6], glass, metals, textile fabrics [7,8], wafers, ceramics [9], etc., giving information about chemistry, polarity, swelling, porosity and other surface characteristics. Zeta potential is used for characterization of natural and synthetic fibres and in investigation of their hydrophilicity, which is important for their interactions with dyes and surfactants [5,6,8]. It is also important for research of membranes, filters [10,11], pristine polymers [12-15] or polymers modified by plasma [12,15-18], by laser or by chemical coatings, e.g. by chitosan [16], biphenyldithiol [17], polyethyleneglycol [18] or by gold coatings [14,17]. It can also be used in research of textiles, where ζ -potential plays an important role in the electrical characterization in wet processing [7], hairs [19], biomaterials [20] and glass [21,22] and as a parameter of colloid stability (paints, printing inks, drilling muds etc.). Zeta potential of human enamel is of physiological importance since it affects interactions between enamel surfaces and the surrounding aqueous medium of saliva [23]. It is also of importance for sewage treatment, especially for industrial and domestic wastewater treatment [24]. Zeta potential can further be used for examination of micro-environment effects on bioactivity of compounds at the solid-liquid interface. Zeta potential, combined with pH of liquid phase, determines electrostatic interactions between the polymer surface and the immobilized bioactive compound. These interactions affect the kinetics between the bioactive compound and its target (metabolite, antigen/antibody, enzyme substrate, etc.) in the liquid [25]. Also properties of different thin layers deposited on solid substrates (glass, polymers, silica, etc.) can be characterized by ζ -potential, e.g. thin carbon layers deposited on silica [26,27] or Ag doped hydroxyapatite layers on silica [28]. Also gold nanoparticles stabilized in solution by citrate were characterized by ζ -potential [29]. Research effort has been devoted to the suppression of ζ -potential by different techniques including coatings with organosilanes, and deposition of polymer films [30]. There are fundamental differences between silica and polymer surfaces. Silica surfaces usually have high charge density (pronounced hydrophilicity) and polymers with lower charge density, are mostly hydrophobic and their surfaces can be affected by fabrication procedure [13,31].

Our team provides the study of different polymer foils and especially their variable modification for consequent usage in optics, electronics, tissue engineering, etc. For description and characterization of surface properties and their changes we apply a wide variety of analyses, such as X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), goniometry, infrared spectroscopy (IR), sheet resistance, *in vitro* living cell growth and proliferation study and many other methods. During last years we have also applied the electrokinetic analysis as a first, easy and fast identification and characterization of changes of surface properties before and after modifications. In this chapter we present the collection of results for zeta potential determination of pristine polymer foils and modified ones by different techniques and their comparison with other analyses. In comparison with these methods, the electrokinetic analysis is the fast, the easy and it can give us the first information if the surface was successfully modified.

Zeta potential was determined for many polymer foils at constant pH value and also in the pH range for an isoelectric point study (zeta potential equals to zero). Polymer foils were than exposed to plasma, laser, gold sputtering and different chemical grafting. Changes of zeta potential values help us quickly recognize the chemical changes on modified surfaces due to different behaviour of surfaces in liquid surrounding. Polymer foils were modified in variable ways: by (i) plasma treatment, (ii) laser exposure, (iii) gold sputtering and consequent annealing, (iv) polyethylene glycol grafting, (v) dithiols grafting, (vi) cysteamine grafting, (vii) subsequent Au nanoparticles grafting, etc. All zeta potential results indicating different changes were subsequently confronted with other surfaces analyses.

2. Zeta potential determination

The zeta potential of planar samples represents the surface behaviour which occurs in the presence of an aqueous solution. It gives information about the nature and dissociation of reactive (functional) groups, about polarity, hydrophilicity or hydrophobicity of the solid surface, indirectly the chemical nature of studied sample and about ion or water sorption too [7,32]. This information is important for other polymer foils usage. Zeta potential can be determined using electrokinetic measurements, inclusive electrophoresis, sedimentation potential, electroosmosis, streaming current or streaming potential [7,24,30-35]. Measurements using multiple techniques are invaluable, since the errors with different techniques are often of opposite sign [30]. The more detailed research and comparison of different techniques was presented previously [36]. Most suitable for the planar samples is the streaming current or streaming potential approach [8,24,30,32,36,37]. Streaming current or streaming potential is generated by pressure-driven flow through a conduit [30]. It is accomplished by applying a pressure, and the potential is induced as a result [24,35]. The zeta potential derived from the streaming potential or the streaming current is considered as ζ -potential at the hydrodynamic phase boundary against the bulk liquid.

Streaming potential, streaming current and Helmholtz-Smoluchowski equation approach is correct and valid when electrolyte solution is forced through a narrow slit formed by two similar measured surfaces. This ensures that the thickness of the electrochemical double

layer of the studied surface is smaller than the slit width and an overlapping of the double layers can be excluded [8,35].

While the determination of ζ -potential on colloidal samples is quite frequent there are not much studies accomplished on flat samples. The data on ζ -potential of polymer foils are important for physics and chemistry of surfaces, for electronics, material science, for packaging of food, even for biology and medicine [38]. Survey of ζ -potentials for some polymers are given in [31]. There are summarized data obtained by many authors measured and by several techniques for PDMS, PC, PET, PMMA, PE, PS, PVC and PTFE along with the data for colloidal samples and for polymer foils.

Zeta potential depends on many solution and substrate parameters, such as pH, counter-ions concentration, valence and size, temperature, substrate material and its surface properties, etc. [30,31]. Strong effect on the ζ -potential has the valence and concentrations of applied electrolytes [30]. Therefore some of authors tested various electrolytes and different electrolyte concentrations [39]. The effects of counter-ion valence and size do not play role in the case of potassium and sodium ions, differences being small for silica and also polymer substrates and are only important in cases where larger ions dominate the counter-ion concentration [30,31]. The bivalent cations exhibit specific adsorption which can be ignored for monovalent cations, such as Li^+ , Na^+ and K^+ [30]. It can be concluded that monovalent cations are more suitable and there are no significant differences between e.g. KCl and NaCl. Therefore we used KCl and KNO_3 for our studies.

The study of pH effect has been accomplished by some investigators. Some of them find a linear variation with pH, while others reported a plateau at some pH values [30]. Therefore we studied zeta potential of polymers at constant pH, only for isoelectric point determination we provided pH dependence. Also the effect of temperature should not be neglected, e.g. the ζ -potential of silica increases approximately 1.75% per 1°C [30]. It is therefore important to preserve the constant temperature during zeta potential determination.

Zeta potential of polymer foils is also strongly affected by their surface roughness and other surface properties [13,32]. The roughness leads to geometry-induced changes, which can affect an electroosmotic flow and ζ -potential. Surface roughness affects the position of the charged surface and bulk solution, which is not homogenous. It can lead to higher surface conductivity [30,35].

2.1. Principle

Our ζ -potential determination of planar samples is based on the measurement of the streaming potential dU and/or the streaming current dI as a function of continuously increasing pressure dp of electrolyte circulated through the measuring cell containing the solid sample. The relationships between ζ -potential and the streaming potential dU or the streaming current dI are linear, with the slope dU/dp , resp. dI/dp [9,24,30,32,34,36,37]. Streaming potential dU or alternatively the streaming current dI are detected by electrodes

placed at both sides of the sample. The electrolyte conductivity, temperature and pH values are measured simultaneously [34,37].

The measured values of Δp and ΔU or ΔI serve to calculate ζ -potential by the following Helmholtz-Smoluchowski (HS) and Fairbrother-Mastins (FM) equations [8,34,37] (eqs. 1, resp. 2):

$$\zeta = \frac{dI}{dp} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L}{A} \quad (1)$$

$$\zeta_{\text{apparent}} = \frac{dU}{dp} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \kappa_B \quad (2)$$

where dU/dp , resp. dI/dp are slopes of streaming potential, resp. streaming current versus pressure p , η is an electrolyte viscosity, ε is a dielectric constant of electrolyte, ε_0 is a vacuum permittivity, L is a length of the streaming channel, A is a cross-section of the streaming channel (the rectangular gap between the planar samples), κ_B is an electrolyte conductivity.

Comparison of ζ (eq. 1) and ζ_{apparent} (eq. 2) potentials reveals additional information about excessive conductivity that is present in the measuring cell representing solid surface properties. Properties that influence the conductivity inside the streaming channel involve sample porosity, surface swelling, surface roughness and morphology and bulk material conductivity. The ratio L/A in eq. 1 is given by equation: $L/A = \kappa_B \cdot R$, where R is a cell resistance inclusive the electrolyte and sample properties [34]. The width of measuring space between samples should be much higher than the thickness of shear plane (the space at surface when the double layer is created due to arrangement of ions) [30]. More detailed description of the ζ -potential determination, applied equations and their limitations, was given in [30].

Because of strong dependence of the measured values on experimental conditions discussed above, it is strongly recommended that all data on ζ -potential should be supplemented with detailed information on particular measuring conditions (pH, ionic strength, counter-ion type and concentration, temperature, etc).

We study zeta potential of several densities of polymer foils. Therefore zeta potential depends on counter-ion type and valence, but these effects do not play a role in the case of potassium and sodium counter-ion and observed differences are small for all polymer substrates [30], we finally used only potassium ions. The standard electrolyte was 0.001 mol/dm³ solution of KCl. The low electrolyte concentration ensures high sensitivity of the method [30,31,34]. To investigate the influence of electrolyte type and concentrations on ζ -potential determination, two monovalent (symmetric) electrolytes KCl and KNO₃ of concentration 0.001 mol/dm³ and KCl also of 0.005 mol/dm³ we used [40].

2.2. Materials

The following polymers in form of foils were used in this study (supplied by Goodfellow Ltd., UK): low density polyethylene (LDPE, density 0.92 g/cm³ in the form of 30 μ m thick

foils), biaxially oriented polyethyleneterephthalate (PET, density 1.3 g/cm³, 50 μm), polytetrafluoroethylene (PTFE, density 2.2 g/cm³, of three thicknesses 100, 50 and 25 μm), biaxially oriented polystyrene (PS, density 1.05 g/cm³, 30 μm), polypropylene (PP, density 0.9 g/cm³, 50 μm), polyamides (PA6 and PA66, both of them 40 μm), poly L-lactic acid (PLLA, density 1.25 g/cm³, 50 μm), polymethylpentene (PMP, density 0.84 g/cm³, 50 μm), polyimides (Upilex R, Upilex S and Kapton, all of them 50 μm), polyaramide (PAr, 10 μm), polybutyleneterephthalate (PBT, 25 μm), poly(ethylene-2,6-naphthalene) (PEN, 7 μm), polymethylmetacrylate (PMMA, 7 μm), polycarbonate (PC, 2 mm). Oriented high density polyethylene (HDPE, density 0.952 g/cm³, 40 μm, supplied by Granitol Ltd., Czech Republic); polytetrafluoroethylene with perfluorovinyl pendant side chains ended by sulfonic acid groups (Nafion, total acid capacity: 0.95 to 1.01 meq/g, density 1.97 g/cm³, 173 μm, manufacturer DuPont, USA).

2.3. Modifications

Polymer foils were studied in pristine form and also after modifications in the following variable ways: (i) plasma treatment, (ii) laser exposure, (iii) gold sputtering and consequent annealing, (iv) polyethylene glycol grafting, (v) dithiols grafting, (vi) methanol, dithiol and cysteamine grafting, (vii) steps (iv)-(vi) were supplemented by the subsequent Au nanoparticles/nanorods grafting.

2.3.1. Plasma treatment

Plasma treatment was performed on Balzers SCD 050 device under the following conditions: gas purity was 99.997%, flow rate 0.3 l/s, pressure 10 Pa, electrode distance 50 mm and its area 48 cm², chamber volume approx. 1000 cm³, plasma volume 240 cm³. Exposure times differ for individual tested polymer foils and individual consequent modifications from 15 to 500 s, discharge power was 3.8 or 8.3 W and the treatment was accomplished at room temperature [12].

2.3.2. Laser irradiation

For laser irradiation of samples we employed the F₂ laser (Lambda Physik LPF 202, wavelength of 157 nm, pulse duration of 15 ns). For the irradiation with the F₂ laser, the light was polarized linearly with a MgF₂ prism. For homogeneous illumination of the samples, we used only the central part of the beam profile by means of an aperture (10 mm - 3.5 mm). We performed the irradiation at fluences well below the ablation threshold of PET at 157 nm (29.6 mJ/cm²). The samples were mounted onto a translation stage and scanned at a speed of 14 mm/s. At a repetition rate of the laser of 11 Hz. We carried out the experiments in a flow box purged with nitrogen at a pressure of 110 kPa [41].

2.3.3. Gold sputtering and subsequent annealing

We deposited the gold nanostructures or nanolayers from a gold target (99.999%) by diode sputtering (BAL-TEC SCD 050 equipment) onto pristine polymers. The deposition was

performed at room deposition temperature with a different deposition time and a current of 20 mA.

Post-deposition annealing of Au-covered PTFE was carried out in air at 300°C ($\pm 3^\circ\text{C}$) for 1 h using a thermostat Binder oven. The heating rate was 5°C/min and the annealed samples were left to cool in air to room temperature (RT) [42].

2.3.4. Polyethylene glycol grafting

Polymers (PE and PS) were used for modification in Ar⁺ plasma discharge on a Balzers SCD 050 device. Immediately after the plasma treatment, plasma activated polymers were grafted by immersion into an aqueous solution (24 hours, room temperature, 2 wt.%) of polyethylene glycol (PEG, molecular weights (M_{PEG}) 300, 6000 and 20 000 g/mol). The non-bounded PEG was removed by rinsing the samples in distilled water for 24 hours [18].

2.3.5. Dithiols grafting and subsequent gold nanoparticles grafting

The plasma activated surface of PTFE was firstly grafted from methanol solution of biphenyl-4,4'-dithiol (BFD), 24 hours, room temperature, concentration $4 \cdot 10^{-3}$ mol/dm³). Same samples was put in the colloidal solution of Au nanoparticles (24 hours, concentration $2.75 \cdot 10^{-9}$ mol/dm³, size of nanoparticles was ca 15 nm [43]. This solution was prepared by citrate reduction of K[AuCl₄] [44]. The non-bound chemicals were removed by immersion of the samples into distilled water for 24 hours [45].

2.3.6. Different thiols grafting and subsequent gold nanoobjects grafting

The samples were modified in direct (glow, diode) Ar⁺ plasma on Balzers SCD 050 device under the conditions presented in 2.3.1. Immediately after the plasma treatment the samples were inserted into water solution (2 wt. %) of 2-mercaptoethanol (ME), methanol solution ($5 \cdot 10^{-3}$ mol/dm³) of biphenyl-4,4'-dithiol (BPD) or into water solution (2 wt.%) of cysteamine (CYST) for 24 hours. To coat the polymers with the gold nanoobjects the plasma treated polymers with grafted thiols were immersed for 24 hours into freshly prepared colloidal citrate stabilized solution of Au nanoparticles (AuNPs), [44,46] or Au nanorods (AuNR), 0.1 mol/dm³ water solution of cetyltrimethylammonium bromide).

2.4. Diagnostic methods

The ζ -potential measurement is advantageously used as one of methods for characterization of various materials [12-15,17,18]. The ζ -potential measurements often supplement other analyses characterized surface properties, as X-ray photoelectron spectroscopy (XPS) [12,17], goniometry (contact angle) [12-18,26,28], atomic force microscopy (AFM) [12,14,17,27,28] or other measurements [14,17,28].

2.4.1. Electrokinetic analysis

Zeta potential of all samples was determined by SurPASS Instrument (Anton Paar, Graz Austria). The SurPASS instrument is an electrokinetic analyzer for the investigation of the ζ -potential of macroscopic solids based on the streaming potential and/or the streaming current method. Samples were studied inside the adjustable gap cell in contact with the electrolyte 0.001 mol/dm³ KCl. Only for investigation of electrolyte and its concentration we have also tested the 0.005 mol/dm³ KCl or 0.001 mol/dm³ KNO₃ [40]. All measurements were accomplished in temperature range of 22–24 °C. Due to strong dependence of ζ -potential on pH, we studied all polymers at pH=6.0-6.2 with the relative error of $\pm 10\%$. Only for study of isoelectric points of polymer foils we used pH dependence of zeta potential in range of 7.0 to 2.5. For each measurement a pair of polymer foils with the same top layer was fixed on two sample holders (with a cross section of 20x10 mm² and gap between 100 μ m) [14,40].

The samples to be studied by streaming potential/current measurements have to be mechanically and chemically stable in the aqueous solutions used for the experiment. First, the geometry of the plug must be consolidated in the measuring cell. This can be checked by rinsing with the equilibrium liquid through repeatedly applying Δp in both directions until finding a constant signal [35]. Capacitance at the electrodes can lead to a long time constant for the system to reach equilibrium. Measurements must be conducted by ramping the pressure up and down to confirm that no hysteresis is observed [30]. Other serious problem of ζ -potential determination are bubbles, not only at suspensions but also at flat samples measured in a very small channels [35]. When bubbles are present, whole sample surface is not covered by electrolyte and results for both directions vary, and the values obtained are not stable. Due to these it is necessary to rinse the samples before experiment and repeat the measurement to exclude all adverse effects. Therefore all samples were rinsed several times before measurement and every experiment comprises 4 ramps. If ζ -potential values are constant during this multiple measurement, the surface is stable and values obtained are correct.

Because the ζ -potential of polymer foils is strongly affected by their surface roughness and other surface properties of measured samples [13,32,40], two approaches to determine ζ -potential were used, streaming current and streaming potential. For calculation of ζ -potential we used eqs. (1) and (2) presented above, to investigate and to disclose possible effects of the surface roughness or other surface properties.

2.4.2. Contact angle

Contact angles of distilled water were measured at room temperature at two samples and at seven positions using a Surface Energy Evolution System (SEES, Masaryk University, Czech Republic). The „static“ contact angle was measured for all samples immediately after the plasma treatment (<10 min delay). Drops of $8.0 \pm 0.2 \mu$ l volume were deposited using automatic pipette (Transferpette Electronic Brand, Germany) and their images were taken with 5 s delay. Then the contact angles were evaluated using SEES code [12,13].

2.4.3. Surface roughness and morphology

The surface morphology and surface roughness R_a were examined by AFM microscopy. The AFM images were taken under ambient condition of a Digital Instruments VEECO CP II set-up. "Tapping mode" was chosen in preference to "Contact mode" to minimize damage to the samples surfaces. Si probe RTESPA-CP with the spring constant 20-80 N/m was used. By repeated measurements of the same region ($2 \times 2 \mu\text{m}^2$) we proved that the surface morphology does not change after three consecutive scans. The mean roughness value (R_a) represents the arithmetic average of the deviations from the centre plane of the sample [12,13].

2.4.4. X-ray photoelectron spectroscopy

Concentrations of individual elements (O, C, F, N, Au and S) in the pristine and modified surface layer was measured by X-ray photoelectron spectroscopy (XPS). Omicron Nanotechnology ESCAProbeP spectrometer was used to measure photoelectron spectra (error of 10%). Exposed and analyzed area had dimension $2 \times 3 \text{ mm}^2$. X-ray source was monochromated at 1486.7 eV with step size 0.05 event. The spectra evaluation was carried out by CasaXPS programme [46].

2.4.5. Sheet resistance

Electrical sheet resistance (R_s) is a suitable method for characterization of conductive surfaces. R_s of the gold nanostructures and nanolayers was determined by a standard two-point technique using KEITHLEY 487 pico-ampermeter. For this measurement additional Au contacts, about 50 nm thick, were created by sputtering. The electrical measurements were performed at a pressure of about 10 Pa to minimise the influence of atmospheric humidity. The typical error of the sheet resistance measurement did not exceed $\pm 5\%$ [47].

2.4.6. Infrared spectroscopy

In some cases the changes of chemical structure were examined by Fourier Transform Infrared Spectroscopy (FTIR) on Bruker ISF 66/V spectrometer equipped with a Hyperion microscope with ATR (Ge) objective.

3. Results

The ζ -potential measurement is advantageously used as one of fast and easy methods for characterization of various material surfaces. We used this for characterization of polymer surface and their variable modifications mentioned above. ζ -potential measurements is always in our papers supplemented with other analyses characterized surface properties, as X-ray photoelectron spectroscopy (XPS) [12,17], goniometry (contact angle) [12-18,26,28], with atomic force microscopy (AFM) determination [12,14,17,27,28] or with other measurements [14,17,28]. In this chapter we presented selected and interesting results for pristine polymers and their surface modified by variable ways.

3.1. Pristine polymers

ζ -potential of 21 polymer foils was determined for investigation of electrolyte type and concentration effect [40]. Fig. 1 presents ζ -potential of polymer foils in 0.001 mol/dm³ KCl (left) and 0.005 mol/dm³ KCl (right) electrolytes determined by streaming current and streaming potential approaches and calculated by both of equations, eq. 1 (HS, black columns) and eq. 2 (FM, red columns). Obtained results correspond with others presented previously [30,43].

Firstly, it is evident ζ -potential is a suitable characteristic for characterization and distinction of different polymer foils, generally variable solid substrates. Results for both electrolytes, even for both of concentrations, have the same trend, but the absolute values differ for particular electrolytes and individual concentrations [40]. It is in agreement with previously presented studies for silica, glass and some polymers [30,31], ζ -potential is an increasing function of electrolyte concentration, which corresponds to results presented previously for other systems [2,21,22,30,31,39,48]. It is necessary all zeta potential results supplement with information about type and concentration of applied electrolyte.

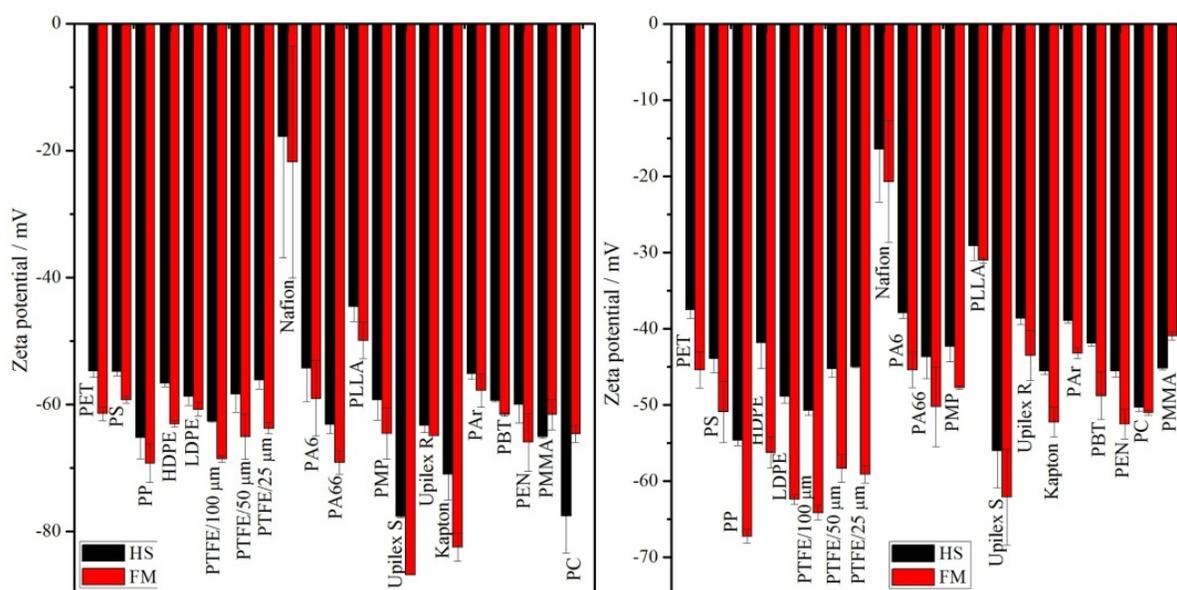


Figure 1. Zeta potential of 21 polymer foils under our study measured in 0.001 mol·dm⁻³ (left) and in 0.005 mol·dm⁻³ (right) KCl electrolyte and calculated by eq. 1 (HS, black columns) and by eq. 2 (FM, red columns) [40]

Fig. 1 shows that most of studied polymers are thought to be chemically inert, without reactive surface groups and displaying negative ζ -potential at neutral pH. The ζ -potential of these polymer foils, except Nafion, is generated only by the preferential adsorption OH⁻ or H₃O⁺ ions on the surface. Zeta potential value and the differences between individual polymers are given only by the distinct adsorption range depending on polarity or non-polarity of individual polymers [49]. Interfacial charge at the non-polar polymer is caused by the preferential adsorption of OH⁻ ions and less strongly adsorbed H₃O⁺ ions in KCl solution. K⁺ and Cl⁻ ions behave indifferently at these non-polar polymer surfaces in

comparison with polar ones. This effect is apparent from Fig. 1. The non-polar polymers have the lower ζ -potential values. In some cases ζ -potentials as polar and non-polar polymers (e.g. PTFE, PP, PE) seem to be the same, e.g. for polar PET and non-polar PE (HDPE or LDPE), but as it is clear from Fig. 1, at these polymers are different difference between zeta potential determined and calculated by both of methods and equations. Possible explanation could be found in our previous study [50] and it can be connected with oxygen containing molecular segments oriented toward the polymer bulk and also with surface roughness.

The higher ζ -potentials are found on polar polymers without any functional surface groups (e.g. PLLA). Polymers of similar surface chemistry exhibit similar ζ -potentials, e.g. three samples of PTFE foils differing only in the thickness, or HDPE and LDPE. Only one of used polymers, Nafion, contains sulfonic acid groups on the surface disposed to dissociation in contact with electrolyte. This dissociation is a key action to zeta potential generation at thie polymer. Due to this dissociation zeta potential of Nafion is the lowest. In some cases it can be even positive due to this [40].

Zeta potential of polymer foils is strongly affected by their surface roughness R_a and other surface properties as well [12,32]. Surface roughness R_a of selected polymers determined by AFM is summarized in Table 1. For confirmation of surface roughness effect we used two approaches to determine ζ -potential (streaming current and streaming potential) and two equations (eqs. 1 and 2) for calculation. For polymers, with higher surface roughness R_a , larger differences between both calculated values of ζ -potential (ζ and ζ_{apparent} , see eqs. (1) and (2)) are observed (e.g. on PTFE foils known to have the highest surface roughness). Also HDPE with higher roughness (see Table 1) exhibits more significant differences in ζ -potentials in comparison with LDPE of lower surface roughness [40].

Polymer	R_a (nm)	Polymer	R_a (nm)	Polymer	R_a (nm)
PET	0.5	PTFE/25 μm	17.2	Kapton	0.7
PS	1.3	Nafion	1.9	PAr	0.8
PP	2.1	PA6	7.4	PBT	1.6
HDPE	11.1	PA66	4.1	PEN	4.8
LDPE	2.5	PLLA	1.2	PMMA	0.4
PTFE/100 μm	12.3	Upilex S	4.1	PC	1.7
PTFE/50 μm	13.9	Upilex R	4.4	PMP	5.0

Table 1. Surface roughness (R_a) in nm of polymers under our study determined by atomic force microscopy [40]

We compare our results with those presented previously by other authors. As we mentioned above, many results cannot be compared in principle since the measurements were done using different techniques and quoted errors are often of opposite sign [30] or at different experimental conditions. Data on ζ -potential for polydimethylsiloxane (PDMS), PC, PET, PMMA, PE, PS, polyvinylchloride PVC, PTFE obtained by many authors and by different techniques were summarized in [31]. Values of ζ -potential for PC and PMMA, -70.0 mV and

-45.0 mV respectively, obtained with 0.001 mol/dm³ KCl solution (for PMMA the higher concentration of electrolyte was used), pH=6 and at room temperature and reported in [31] are in reasonable agreement with ours, -77.6 and -65.0 mV respectively, with a knowledge about concentration effect for PMMA. Also ζ -potential for some type of PTFE -58 mV in 0.01 mol/dm³ KCl reported in [49] is in good agreement with our presented values varying from -56.1 to -62.6 mV depending on the foil thickness.

Other comparison is difficult due to the authors examined the samples, combining polymer membrane foils, polymer fibres and colloidal dispersions for which the ζ -potential values vary strongly in dependence on their surface properties. Another chance is to compare results for PET [37], but the previous results were obtained for pH=5 and the ζ -potential = -33.6 mV is lower than presented here (see Fig. 1) due to the pH dependence mentioned above. Zeta potential for PET was determined [50] to be about -40 mV (only approximate estimation from figure [50]) using the same instrument as we used (the same cell, electrolyte, concentration, pH=6), this value agrees well with the present one of -54.7 mV, obtained for pH=6.2. Some polymers inclusive PC and PS have also been measured in 0.001 mol/dm³ KCl, but in different analyser [51] and the data are not comparable with present ones. In addition PS was not in form of foil and other polymers were used without purification and the results can be affected by contaminants (stabilizers) in the polymers.

Zeta potential values are often correlated with contact angle measurements and/or surface roughness determination. As we discussed previously, that is not correct in all cases [40]. Most of polymers used in this study have no "reactive" surface groups in water solution and the surface charge only arises due to preferential adsorption of hydroxide ions in water solutions. The adsorption on the polymer surface is a drive force for ζ -potential initiation. Because both of contact angle and ζ -potential are connected to surface chemistry, some authors correlated only these two characteristics. At polymers with "active" functional groups the most important is "surface chemistry" and the correlation of the ζ -potential with contact angle measurement is better. For polymers, for which the adsorption of hydroxide ions is predominant, the surface roughness plays the more important role in ζ -potential due to a rough surface and not homogenous electrical double layer. Therefore, for correlation of zeta potential must be taken both contact angle and also surface roughness. We supplemented this study of polymers with contact angle values and also with surface roughness. Fig. 2 shows contact angle values for all polymers studied in this work measured in distilled water. Surface roughness R_a of samples examined is presented in Table 1. A general trend is that the "more" polar polymers have lower contact angle (e.g. PMMA, PLLA, PA), that means the higher hydrophilicity and wettability, the non-polar polymers the higher contact angle (PTFE, HDPE, LDPE, PMP) corresponding to their higher hydrophobicity. Polymers of the same surface chemistry embody the similar contact angle, as e.g. HDPE and LDPE or all PTFE samples (PTFE/25 μ m, PTFE/50 μ m, PTFE/100 μ m), slight differences between them is caused by distinct surface roughness. From the comparison of the results of surface roughness presented in Table 1 and of contact angle presented in Fig. 2 follows that the polymers with lower R_a (e.g. PET, PS and PP) exhibit higher wettability and vice versa. The same conclusion has been done for zeta potential determination.

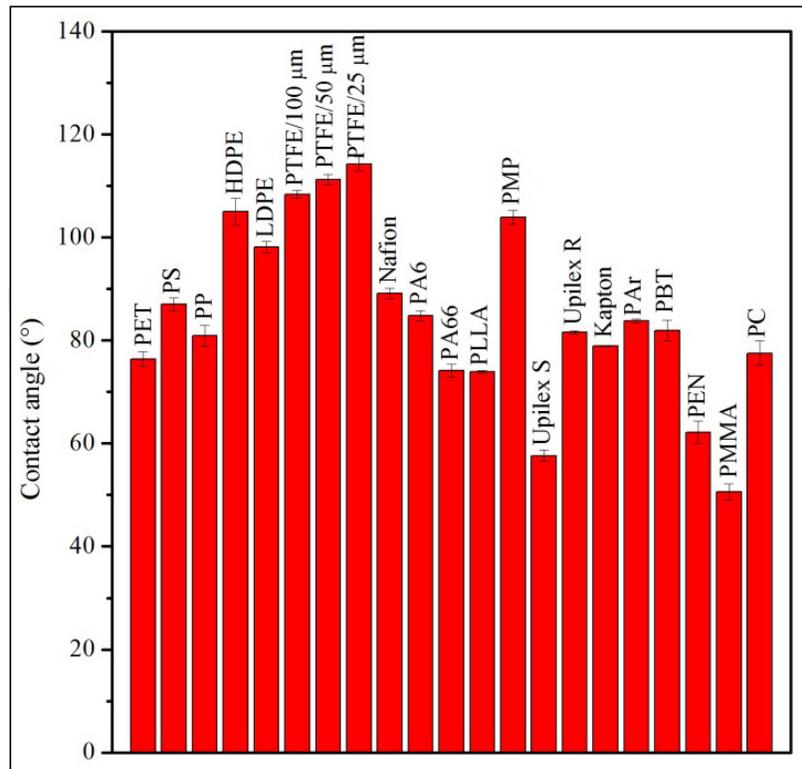


Figure 2. Contact angle for 21 polymer foils under study determined by goniometry [40]

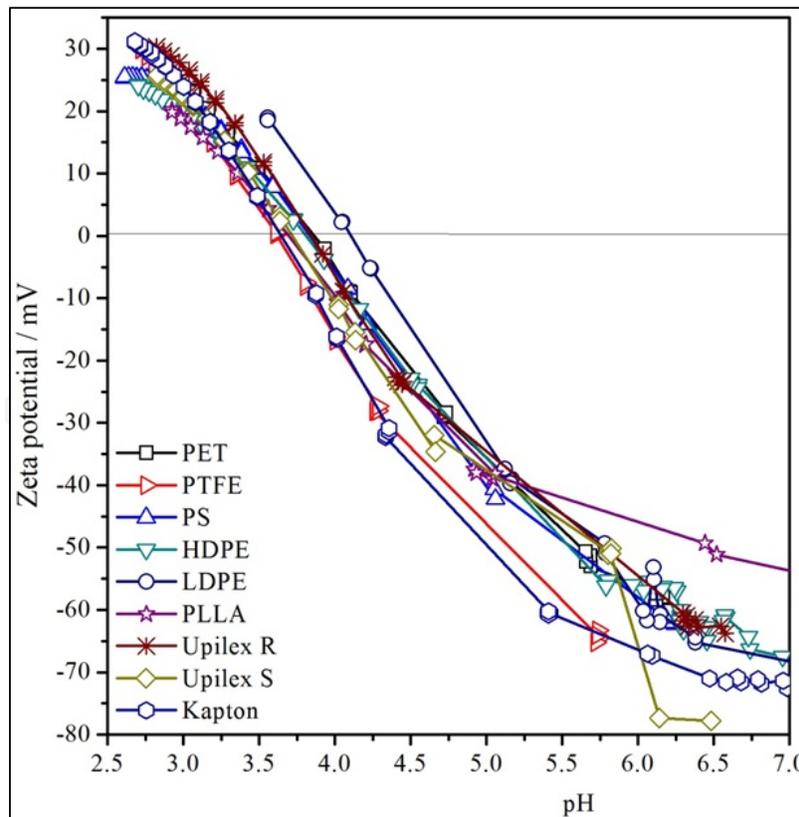


Figure 3. pH dependence of zeta potential of selected polymer foils. Isoelectric point is the point of zero value of zeta potential [52]

Zeta potential also serves for determination of isoelectric point (IEP), which is defined as the point at which the electrokinetic potential equals zero. It is also important characteristic for wrappers, for material for study of living cell adhesion, etc. Fig. 3 present zeta potential of several polymer foils as pH dependent. As it is clear, IEP of all polymer samples are obtained at pH ca 4. For this determination we have titrated samples by 0.1 mol/dm³ HCl in pH range from 7.0 to 2.5 [52].

3.2. Plasma and laser treatment of polymers

As it is known, plasma treatment affects the polymer surface to the depths from several hundred to several thousand angstroms but the bulk properties of polymers remain unchanged [12]. Therefore only surface properties are changed dramatically by this treatment. Generally, during the plasma treatment the macromolecular chains are degraded, cleaved and oxidized. Due to this, plasma treatment results in a dramatic increase of polymer wettability. The wettability increase is caused by creation of polar groups, exhibiting enhanced hydrophilicity, at the polymer surface [12]. The similar effect on surface properties has also the laser irradiation [53]. Fig. 4 shows the effect of plasma treatment (left) and laser irradiation (right) on zeta potential of selected polymer foils. For more transparent presentation only results obtained by streaming current method (eq. 1) are shown.

As it is clear from Fig. 4, plasma treatment results in a dramatic increase of the zeta-potential due to that the plasma modification of polymer surfaces leads to dramatic change of surface chemistry (e.g. chains and bonds scission, ablation, oxidation and cross-linking) and creation of polar groups [12]. The effect of laser irradiation is not too strong due to that this treatment way influences surface chemistry and surface properties more weak [12,53]. Even in some causes zeta potential decreases after laser irradiation. It can be explained by the fact the cleavage of original bonds is most significant than surface oxidation after laser exposure in comparison with the plasma one. These effects strongly depend on plasma power or number of laser pulses.

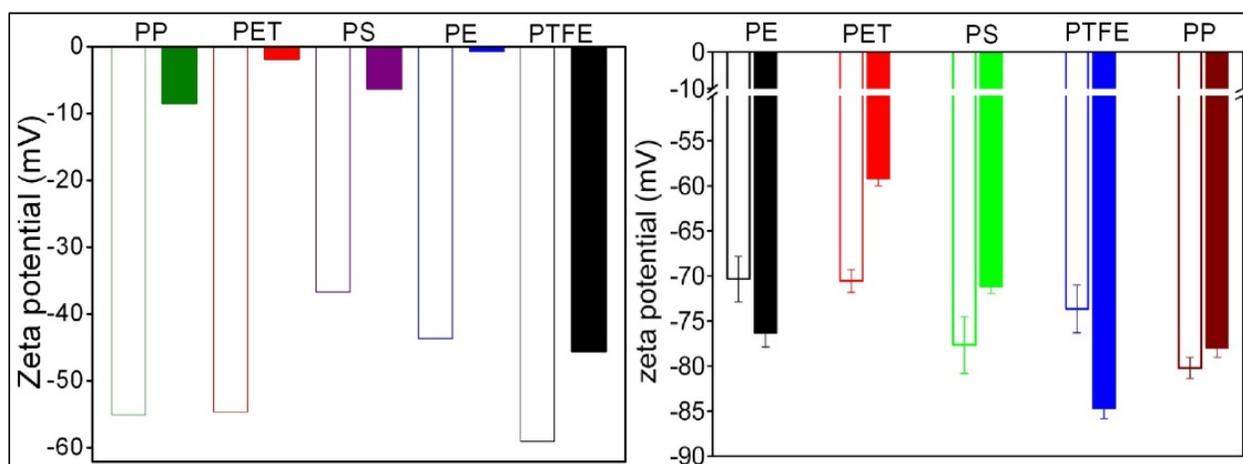


Figure 4. Zeta potential of selected polymer foils and effect of plasma (left, [12]) or laser (right, [53]) treatment determined by electrokinetic analysis. Empty columns presents pristine polymers, full columns treated ones

For explanation of zeta potential behaviour on pristine and treated polymer surfaces we analysed surface chemistry by other techniques. Oxygen concentration in the surface layer of the laser modified polymers was determined from XPS spectra, the surface wettability and polarity were characterized by the measurement of contact angle of distilled water. These results are presented in Figs. 5 and 6. As it is clear from Fig. 5, after plasma or laser treatment increase the presence of oxygen groups on polymer surface. This increase in the oxygen content is much lower (Fig. 5, left) in comparison with that observed on the same polymers treated in plasma discharge (Fig. 5, right) [12,53].

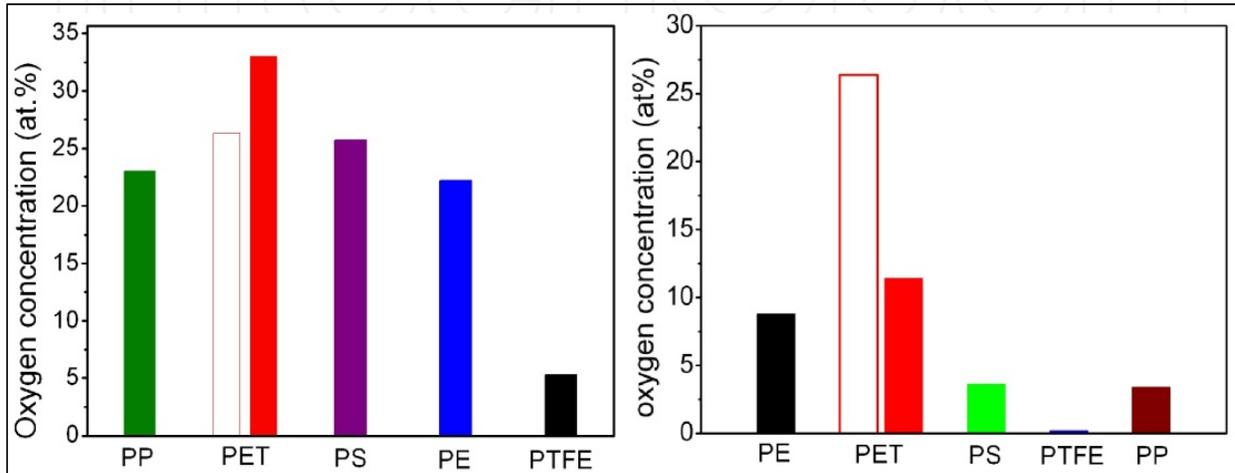


Figure 5. Concentration of oxygen groups on surface of selected polymer foils after plasma (left, [12]) or laser (right, [53]) treatment determined by XPS. Empty columns are pristine polymers (only at PET), full columns treated ones

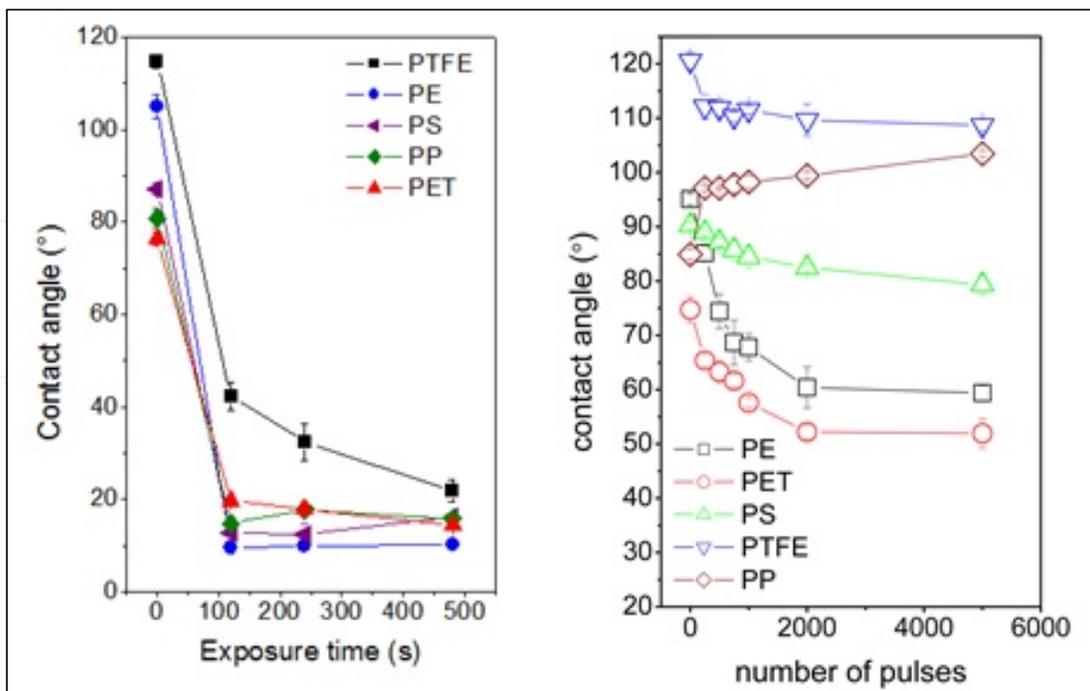


Figure 6. Contact angle on surface of selected polymer foils after plasma (left, [12]) or laser (right, [53]) treatment determined by goniometry

Plasma treatment or laser irradiation result in a dramatic decline of the contact angle and corresponding increase of polymer wettability as it shown in Fig. 6. As is presented above, also contact angle analyses compare the result that laser irradiation effects surface chemistry and surface properties much less (Fig. 6, left) in comparison with plasma treatment (Fig. 6, right).

3.3. Gold sputtering and consequent annealing

In this part of work we have studied the changes of surface morphology and some other physico-chemical properties of sputtered gold nanostructures and nanolayers on polymer surface (PTFE) induced by post-deposition annealing [42]. Fig. 7 presents zeta potential (left) and sheet resistance (right) of pristine PTFE (Fig. 7, thickness = 0) and Au coated PTFE in Au thicknesses dependences for room temperature (RT) and the same samples after annealing by different temperatures (100°C red line, 200°C green line, 300°C, blue line). Zeta potential was determined only for samples deposited by gold at RT and at 300°C.

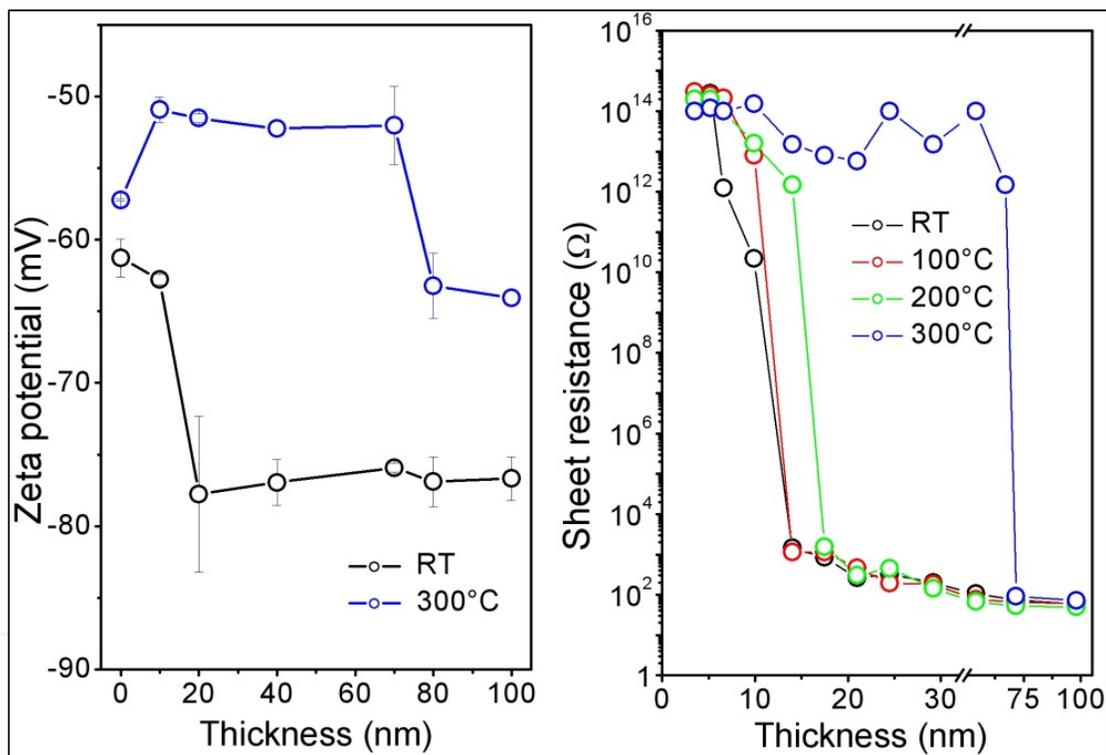


Figure 7. Zeta potential (left) and sheet resistance (right) of gold nanostructures and annealed ones [42]

We can see, that after deposition of metal layer zeta potential dramatically decrease due to increasing presence of surface coverage by metal and accompanying surface conductivity. For as-sputtered samples and very thin gold nanolayers, the zeta potential is close to that of pristine PTFE due to the discontinuous gold coverage since the PTFE surface plays dominant role in zeta potential value. Then, for thicker layers, where the gold coverage prevails over the original substrate surface, the zeta potential decreases rapidly and for the thicknesses above 20 nm remains nearly unchanged, indicating total coverage of original substrate by gold. For annealed samples, the dependence on the layer thickness is quite different. It is seen that the annealing leads to a significant increase of the zeta potential for

thin nanolayers. This increase may be due to thermal degradation of the PTFE accompanied by production of excessive polar groups on the polymer surface, which plays the important role when the gold coverage is discontinuous [42].

These results on zeta potential are in good agreement with sheet resistance measurement and other surface analyses [42]. As its obvious from Fig. 7 (right), for the as-sputtered samples the sheet resistance decreases rapidly in the narrow thickness from 10 to 15 nm when an electrical continuous gold coverage is formed. After annealing at 300°C a dramatic change in the resistance curve is observed. The annealed layers are electrically discontinuous up to the Au effective thickness of 70 nm above which the continuous coverage is created and a percolation limit is overcome. These results confirmed zeta potential analysis well as it is presented in Fig. 7, blue lines of both diagrams.

3.4. Polyethylene glycol grafting

As a representative of polymers grafted by polyethylene glycol we present PS grafted by polyethylene glycol (PEG) of different molecular weight 300 (PEG 300), 6000 (PEG 6000) and 20000 (PEG 20000) g/mol in Fig. 8. Modification of polymer surface by PEG plays important role in research of living cell adhesion and proliferation. Due to improving grafting process of PEG on PS it is better to treated polymer surface by plasma. We exposed PS surface by plasma for 50, 100 and 300 s and subsequently we grafted these surfaces by PEGs of mentioned molecular weights. These results have usage in tissue engineering due to positive effect to living cell adhesion and proliferation discussed below in Fig. 9.

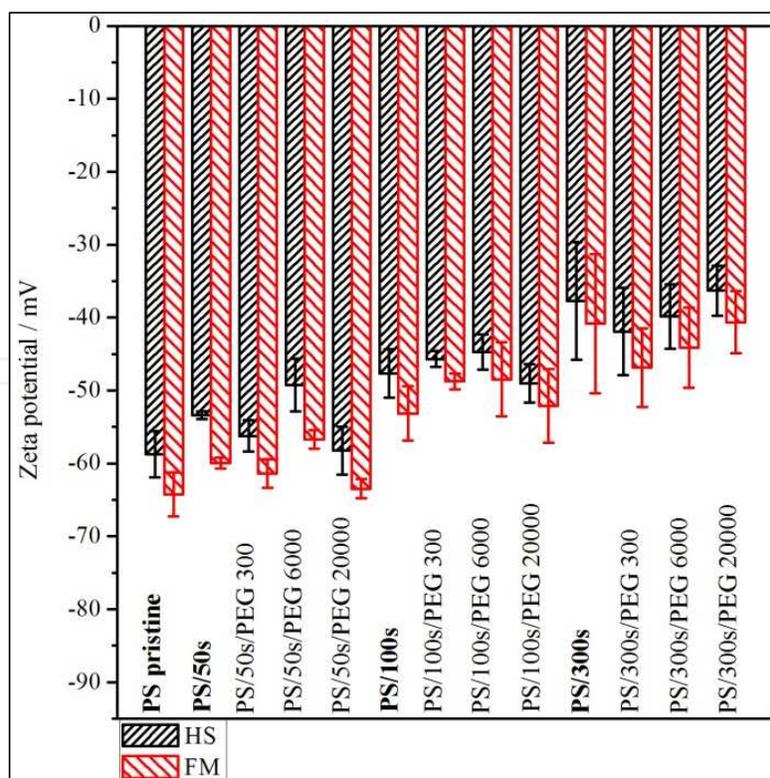


Figure 8. Zeta potential of PS treated by plasma for 50, 100 or 300 s and subsequently grafted with PEG of different molecular weight 300 (PEG 300), 6000 (PEG 6000) and 20000 (PEG 20000) g/mol

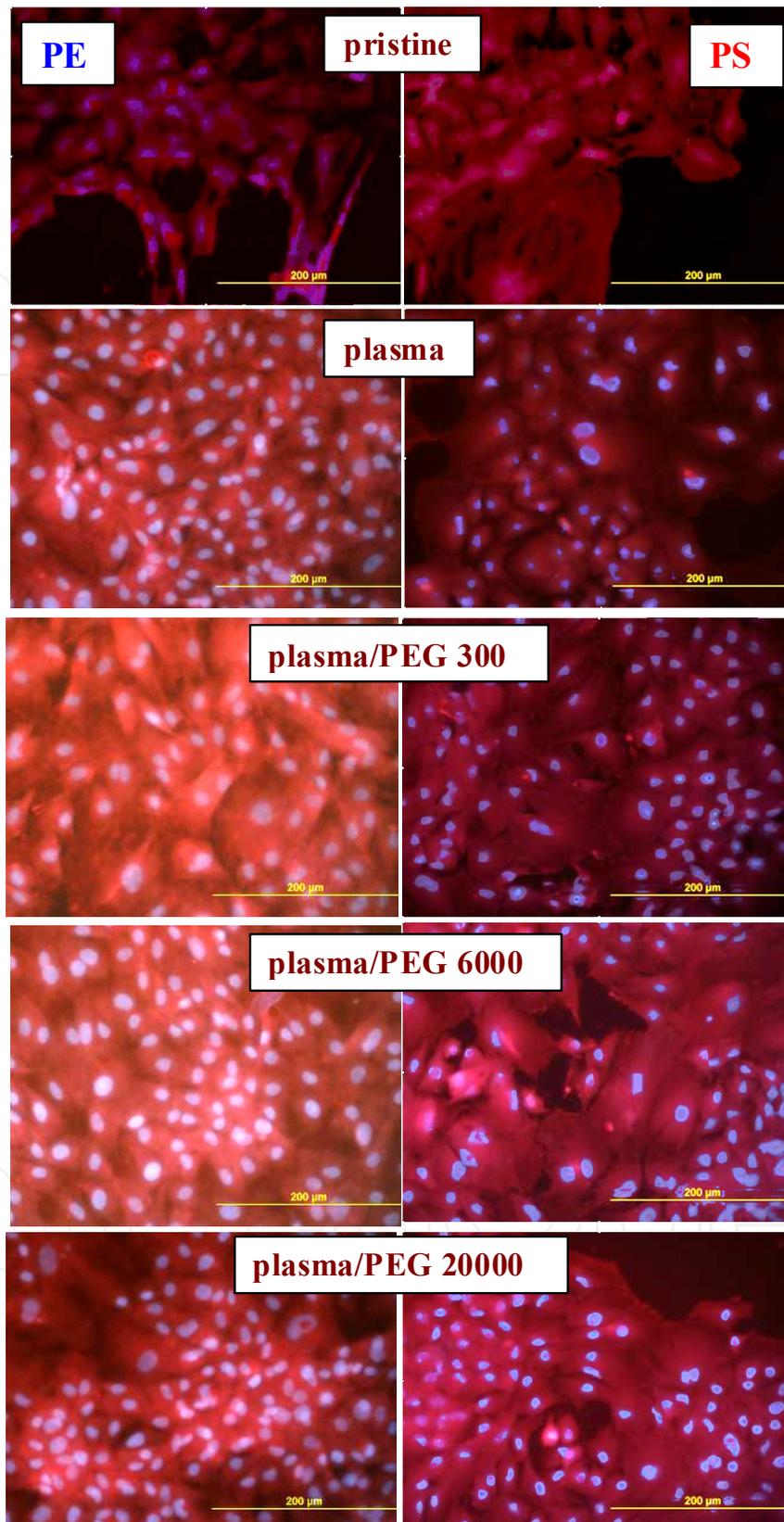


Figure 9. Photographs of cells (VSMC) proliferated (7th day) on pristine PE and PS, polymers treated with plasma (plasma) and plasma modified and subsequently grafted with PEG (plasma/PEG ...). The molecular weights of PEG were $M_{\text{PEG}} = 300, 6000$ and 20000 [18]

As it is clear from Fig. 8, plasma treatment leads to increase of zeta potential due to creation of more polar groups on surface and this effect depends on exposure time positively. Subsequent grafting of PEG influences surface chemistry dependently on its molecular weight. While PEG 300 and PEG 20000 in most cases causes a slight decrease of zeta potential, PEG 6000 for shorter exposure time causes increase of zeta potential. It indicates quite different surface chemistry and nevertheless these changes are quiet slight, they play important role in process of adhesion and proliferation of living cells (see Fig. 9).

Adhesion and proliferation of rat vascular smooth muscle cells (VSMC) were studied on the pristine, plasma modified and subsequently PEG grafted PE and PS samples. It is supposed that the PEG bonds to several positions on the same macromolecular chain, limits chain mobility and in this way facilitates adsorption and colonization of the cells. Moreover, the oxygen-containing groups present in the PEG molecules might also enhance the colonization of the material by VSMCs as indicated by the highest final cell numbers on the PEG grafted PE observed on the 7th day after cell seeding [18].

Attractiveness of a substrate for cells is manifested not only by the number of growing VSMC cells but also by the homogeneity of their spreading over substrate surface. In Fig. 9 images of the cell cultures cultivated on PE and PS substrates subjected to different modification steps are shown. On pristine polymers the coverage with proliferating cells is not homogenous. It could be explained by the tendency of cells to compensate the insufficient cell-material adhesion by cell-to-cell adhesion, which leads to formation of cell clusters (aggregates) on the material surface. Plasma modification and especially the PEG grafting improves the coverage homogeneity substantially on both polymers.

3.5. Biphenyldithiol grafting and subsequent Au nanoparticles grafting

We tested several polymers (PE, PS, PET) for influence of surface properties affected by grafting of dithiols (methanol solution of biphenyl-4, 4'-dithiol (BFD) or 1, 2-ethanedithiol (ED)) and subsequent grafting by gold nanoparticles [42,54]. Before this grafting has also been polymer surface exposed to plasma discharge. As it is clear from Fig. 10 (left) for PET and BFD grafting, the zeta potential dramatically increases after plasma treatment due to creation of polar oxygen groups, which has been discussed above several times. The grafting of BFD leads to other zeta potential changes caused by thiol groups SH⁻ bonded at polymer surface, which results in dissociation of this group in liquid surrounding during zeta potential measurement. This process leads to creation of negative charge on polymer surface and more presence of positive charge in electrolyte following by decrease of zeta potential. Subsequent Au nanoparticles grafting results to other decrease of zeta potential due to presence of metal gold nanostructures on polymer surface. From data obtained by both of methods and eqs. (1) and (2) (Fig. 10, left, HS, FM data resp.) it is clear the higher difference between HS and FM data for surface with Au nanoparticles which is caused by presence of some gold nanostructures and due to this increasing conductivity and also surface roughness.

In this case, the results on zeta potential were compared with infrared spectroscopy (Fig. 10, right), where the blue curve indicates the sulphur presence and the red curve indicates the gold presence in sample, confirming both of successful chemical graftings. FTIR spectroscopy was used for the characterization of chemical composition of modified PET samples. In the Fig. 10 (right) the differential FTIR spectra of the PET samples plasma treated and grafted in biphenyldithiol (BFD) and with Au nanoparticles are shown. The band at 790 cm^{-1} corresponds to absorption of the S-C group and the band at 761 cm^{-1} is assigned to the S-Au group. That is confirmation that both of graftings were successful as has been established by zeta potential analysis.

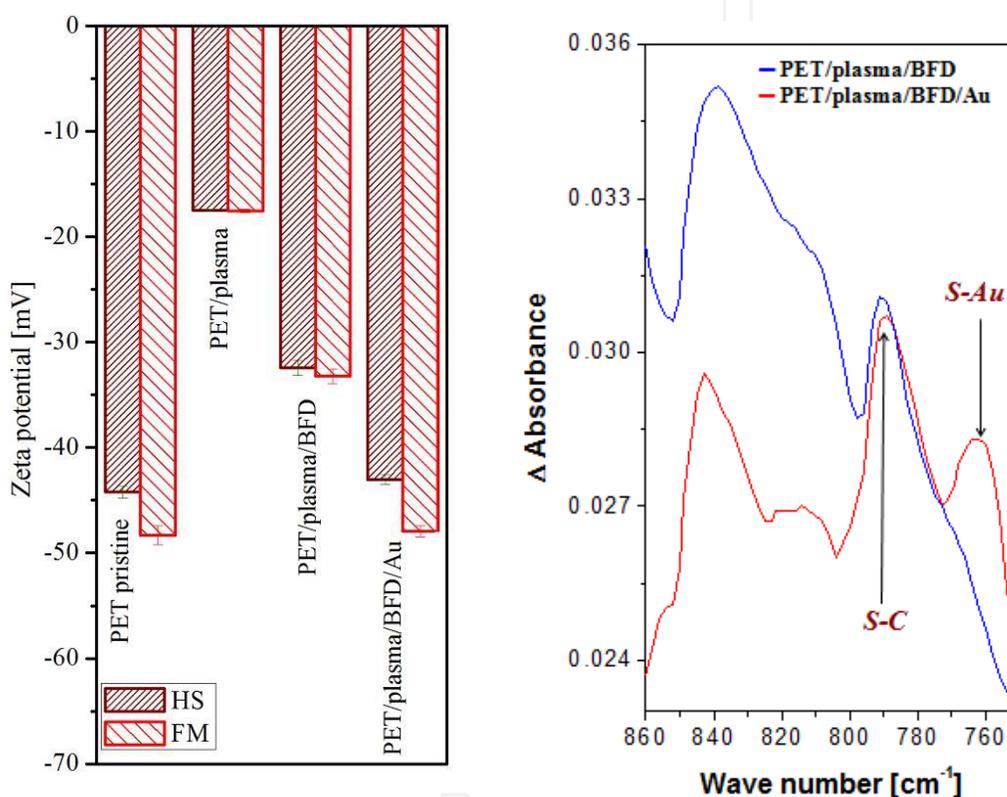


Figure 10. Zeta potential (left) and infrared spectroscopy (right) results for pristine PET, PET treated by plasma and consequently grafted by BFD and subsequent grafting by Au nanoparticles [54]

On the other hand, grafting of ED on PET was not successful. After the grafting of plasma treated PET with ED and Au nanoparticles the peak at 761 cm^{-1} (S-Au) in FTIR spectra was not detected. This finding supports the conclusion that no Au nanoparticles are bonded to the PET treated in ED [54].

3.6. Different thiols grafting and subsequent Au nanoobjects grafting

Other attempt to modify polymer surfaces was treatment of PET and PTFE by plasma discharge and subsequent grafting with different thiols (mercaptoethanol, ME, biphenyldithiol, BFD and cysteamine, CYST). Thiols are expected to be fixed via one of their

functional groups $-OH$, $-SH$ or $-NH_2$ to reactive places created by the preceding plasma treatment. The remaining „free“ $-SH$ group is then allowed to interact with gold nanoparticles or gold nanorods. The main goal of this study is to examine the effect of the plasma treatment and the thiol grafting on the binding of gold nanoobjects on the polymer surface. Chemical structure of the modified polymer films is expected to influence substantially their electrokinetic potential in comparison with pristine polymers. Zeta potential results for PET (left) and PTFE (right) modified by mentioned ways are presented in Fig. 11. Zeta potential of pristine PET, resp. PTFE, plasma treated PET, resp. PTFE, subsequently grafted with thiols and then with gold nanoobjects (nanoparticles, AuNP or nanorods, AuNR) are presented in Fig. 11. Zeta potential is affected by several factors, such as surface morphology, chemical composition (e.g. polarity, wettability) and electrical conductivity of surface. As it is clear from Fig. 11, zeta potential increases after plasma treatment. Due to higher ablation PTFE this increase is more significant at PET. After grafting of thiols in most cases zeta potential decreases due to presence of dissociative groups on surface. The Au nanoobjects grafting results in decrease of zeta potential values due to presence of gold nanostructures on surfaces.

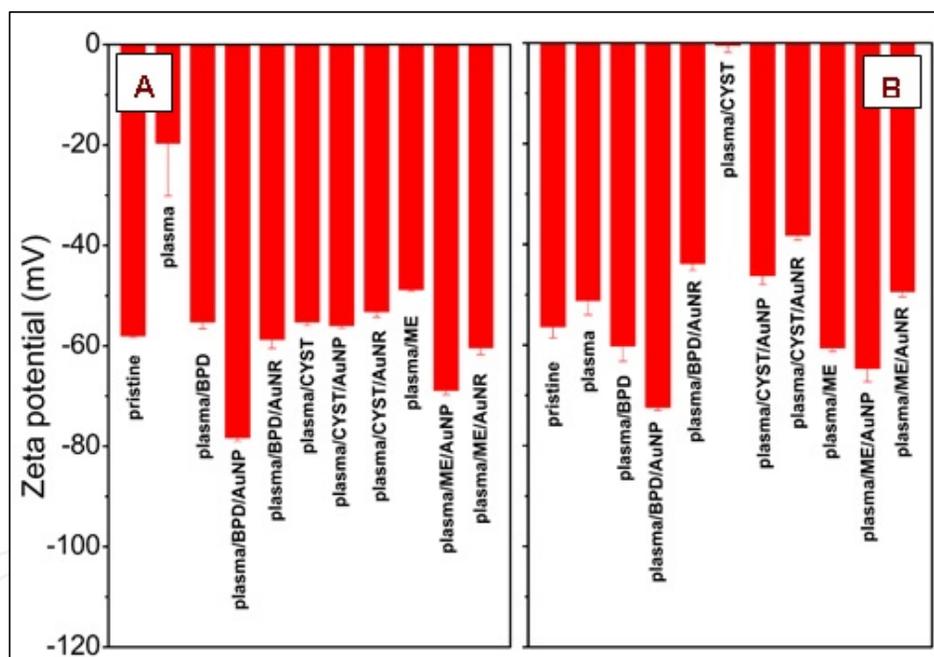


Figure 11. Zeta potential determined by SurPASS of pristine (pristine) and modified (A) PET and (B) PTFE. The polymer foils were plasma treated (plasma), plasma treated and grafted with (i) thiols (biphenyldithiol-BPD, cysteamine-CYST and mercaptoethanol-ME) and then (ii) grafted with Au nanoobjects (nanoparticles-AuNP and nanorods-AuNR).

Very interesting results we obtained after CYST exposition on PTFE, which results in dramatic increase of zeta potential. It can be explained by presence of „free“ NH_2 - groups on surface caused probably by not preferential binding of cysteamine to plasma treated PTFE. This compound can be bonded probably not only via NH_2 - group on activated surface but also via SH - group. This result was obtained only at PTFE, not at PET. At both of polymers

the highest decrease of zeta potential after gold nanoobjects was found out after BPD grafting and subsequent grafting of Au nanoparticles.

Also in previous cases, zeta potential sensitively indicates all changes in surface chemistry and surface properties after any modification. These chemical changes were studied by XPS analysis. Elements (C(1s), O(1s), F (1s), S(2p), N (1s) and Au (4f)) concentrations (in at.%) determined by XPS measurements for PET and PTFE pristine and plasma treated (for 120 s) and grafted with (i) thiols (biphenyldithiol-BPD, cysteamine-CYST and mercaptoethanol-ME) and then (ii) grafted with Au nanoobjects (nanoparticles-AuNP and nanorods-AuNR) are presented in Table 2. The interesting results is for cysteamine on plasma treated PTFE, where nitrogen contents is not significantly different from the same sample of PET, but contents of bonded gold nanoparticles embody significantly lower value. It can confirm the zeta potential results discussed above. At both polymers obtained results clearly indicate the gold nanoparticles grafted at these substrates more easily than gold nanorods.

PET	C(1s)	O(1s)	F(1s)	S(2p)	N(1s)	Au(4f)
Pristine	73.7	26.3	-	-	-	-
plasma treated	67.0	33.0	-	-	-	-
plasma/BPD	73.8	18.5	-	7.7	-	-
plasma/BPD/AuNP	81.1	12.7	-	6.1	-	0.1
plasma/BPD/AuNR	82.2	12.1	-	5.0	-	0.7
plasma/CYST	71.6	20.9	-	3.1	4.4	-
plasma/CYST/AuNP	70.1	21.4	-	2.3	2.9	3.3
plasma/CYST/AuNR	75.5	19.9	-	1.8	2.7	0.1
plasma/ME	72.0	26.8	-	1.2	-	-
plasma/ME/AuNP	77.4	21.7	-	0.6	-	0.3
plasma/ME/AuNR	80.5	16.4	-	1.0	-	2.1
PTFE	C(1s)	O(1s)	F(1s)	S(2p)	N(1s)	Au(4f)
pristine	33.4	-	66.6	-	-	-
plasma treated	39.8	5.2	55.0	-	-	-
plasma/BPD	78.0	6.2	4.7	11.1	-	-
plasma/BPD/AuNP	60.5	4.9	29.7	4.4	-	0.5
plasma/BPD/AuNR	58.8	4.5	33.0	3.0	-	0.6
plasma/CYST	48.9	5.4	39.2	3.4	3.1	-
plasma/CYST/AuNP	44.3	5.1	45.4	2.7	2.3	0.2
plasma/CYST/AuNR	57.4	5.9	31.2	2.4	3.0	0.1
plasma/ME	41.2	8.0	49.0	1.8	-	-
plasma/ME/AuNP	52.8	6.7	35.1	0.3	-	5.1
plasma/ME/AuNR	50.1	5.6	40.6	1.0	-	2.6

Table 2. Elements (C(1s), O(1s), F (1s), S(2p), N (1s) and Au (4f)) concentrations (in at.%) determined by XPS measurements in pristine PET and PTFE and plasma treated (for 120 s) and grafted with (i) thiols (biphenyldithiol-BPD, cysteamine-CYST and mercaptoethanol-ME) and then (ii) grafted with Au nanoobjects (nanoparticles-AuNP and nanorods-AuNR).

4. Conclusion

The ζ -potential of many polymer foils was determined and the effect of different modification approaches was studied to confirm that this analysis is sensitive to indicate all changes in surface chemistry. Zeta potential can distinguish individual pristine polymer foils due to their different polarity, which causes that ζ -potential is generated by the preferential adsorption OH^- or H_3O^+ ions on the surface. Zeta potential of planar samples of polymer foils depends on many surface properties of samples (surface chemistry, wettability, polarity, surface roughness and morphology), as well as on electrolyte solution properties (counter-ion type and concentration and pH). As was confirmed, the best electrolyte for study of planar polymer foils was 0.001 mol/dm^3 KCl. Zeta potential is also strongly dependent on measurement conditions, temperature, pH, etc. All zeta potential must be supplemented by this experimental information.

In our research all zeta potential values are always complemented with contact angle measurement by goniometry and determination of surface roughness and surface morphology by AFM, by spectroscopy analyses or other techniques.

Pristine polymer foils can be distinguished by electrokinetic analysis, as same as all modifications of polymer surface were indicated by changes in zeta potential. Due to this electrokinetic potential can serve as a fast and easy characteristic for study of changes in surface chemistry. Elektrokinetic analysis is the fast, the easy and very sensitive method for characterization solid substrates.

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