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Wettability and Other Surface Properties of Modified Polymers

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Abstract

Surface wettability is one of the crucial characteristics for determining of a material's use in specific application. Determination of wettability is based on the measurement of the material surface contact angle. Contact angle is the main parameter that characterizes the drop shape on the solid surface and is also one of the directly measurable properties of the phase interface. In this chapter, the wettability and its related properties of pristine and modified polymer foils will be described. The wettability depends on surface roughness and chemical composition. Changes of these parameters can adjust the values of contact angle and, therefore, wettability. In the case of pristine polymer materials, their wettability is unsuitable for a wide range of applications (such as tissue engineering, printing, and coating). Polymer surfaces can easily be modified by, e.g., plasma discharge, whereas the bulk properties remain unchanged. This modification leads to oxidation of the treated layer and creation of new chemical groups that mainly contain oxygen. Immediately after plasma treatment, the values of the contact angles of the modified polymer significantly decrease. In the case of a specific polymer, the strongly hydrophilic surface is created and leads to total spreading of the water drop. Wettability is strongly dependent on time from modification.

Wettability plays a key role, e.g., in the development of biomaterials in tissue engineering and regenerative medicine. Biocompatibility tests of the cell adhesion, proliferation and viability are performed in an aqueous medium, and it is necessary to control the surface wettability. Various cell types have different requirements on surface properties, but while maintaining suitable parameters, the optimal value of

water contact angle for cell adhesion is in the interval of 50-70°. In the case of polymers, which have usually higher values of contact angles, the decrease in water contact angle and adjustment of the surface may be accomplished by introducing selected chemical groups (by plasma treatment), chemical compounds (by grafting, i.e., chemical bath deposition), or nanoparticles. In the case of grafting of polyethylene glycol (PEG) on the plasma activated high-density polyethylene was under “properly” selected conditions of modification (molecular weight of PEG, concentration of PEG in solution) prepared layers that positively influenced the cell adhesion. In addition, low concentration of gold nanoparticles increased the number of adhered cells without decreasing cell viability.

Whether the surface of the polymeric substrate is attractive for the adhesion and proliferation of cells is determined not only by wettability but also by a range of other surface properties of the substrate. Some of these properties, e.g., morphology, chemical composition, and electrokinetic potential (zeta potential), will be discussed in this chapter. These properties will also be discussed in relation to the cytocompatibility of surface.

Keywords: wettability, polymer, surface modification, plasma, morphology

1. Introduction

Polymeric materials can be used in many applications due to their mechanical (e.g., elastic) characteristics, chemical stability, and light weight, as well as their several design possibilities. Polymers are very well applied in tissue engineering, in particular, due to a wide range of physical, mechanical, and chemical properties, cytocompatibility, microstructure, and biodegradability [1, 2]. These properties can precisely be controlled by the composition and processing of polymers. Many of these polymers were originally developed as plastics, elastomers, or fibers for medical and industrial applications, but the latter have been adopted for biomedical use [3–5]. Polymeric materials differ in their molecular weight, polydispersity, crystallinity, thermal transitions, and decomposition rate, which can significantly affect the properties of the polymer matrix [6]. The chemical composition, structure, and morphology of polymers influence the surface-free energy and thus have a great influence on wettability [7, 8]. Wettability is a fundamental property of solid-state surfaces that plays important roles in the industry [9]. The wettability of a material surface is generally characterized in terms of the contact angle (CA) between solid and liquid interfaces [10]. Wettability can be described as a property governed by intermolecular interactions that characterizes the degree of wetting of a solid surface by a liquid droplet. One common way of characterizing wettability is through the measurement of the static CA θ_{eq} that results from the equilibrium between the interfacial tensions between solid, liquid, and vapor phases [11]. A surface is typically defined as water wetting for (approximately) $\theta_{int} < 60^\circ$ to 75° (measured through the aqueous phase), NAPL (non-aqueous phase liquid) wetting for $\theta_{int} > 105^\circ$ to 120° , and intermediate wetting for

$75^\circ < \theta_{\text{int}} < 105^\circ$ [12]. The exact boundaries between each class are quite inexact, particularly regarding the limits that separate hydrophilicity/hydrophobicity and hydrophobicity/superhydrophobicity. Wettability is a very important parameter of materials that specifies and limits the next material's application [13, 14]. Assessment of the wettability, namely, measurement of the CA, can also be used to determine the surface stabilization of the modified polymer [15].

Summarized results of our scientific group in the field of research

Ing. Nikola Slepíková Kasálková, Ph.D., born 1981; assistant professor; plasma modification of polymers; surface structure characterization; study of polymer surface cytocompatibility (cell adhesion and proliferation) and goniometry; according to Web of Science - publications 36, H index 8, citations 188.

References: [15, 57, 78, 79, 80, 92, 106, 107, 109, 110, 112]

Doc. Ing. Petr Slepíčka, Ph.D., born 1980; associate professor of Materials Science and Engineering; plasma and laser beam modification of polymers; modification of surface structure; coatings patterning; microscopy (AFM, confocal and FIB SEM) characterization; according to Web of Science - publications 94, H index 17, citations 874).

References: [15, 16, 18, 19, 38, 40, 42, 43, 57, 78, 79, 92, 106, 107, 109, 110, 112, 114]

Doc. Ing. Zdeňka Kolská, Ph.D., born 1969; associate professor of Physical Chemistry; modification of surface structure of materials; physicochemical characterization of material surfaces (electrokinetic and surface area analyses, goniometry); according to Web of Science - publications 76, H index 14, citations 543.

References: [15, 16, 18, 38, 40, 41, 78, 92, 111, 112]

Prof. Ing. Václav Švorčík, DrSc., born 1957; professor of Materials Science and Engineering; ion, plasma and laser beam modification of polymers; modification of surface structure; surface, chemical, physical properties and cytocompatibility of polymers, metal nanostructures, preparation and characterization; according to Web of Science - publications 324, H index 28, citations 3051.

References: [15, 16, 18, 19, 38, 40, 41, 42, 43, 57, 78, 79, 80, 81, 92, 95, 102, 106, 107, 109, 110, 111, 112, 114, 116]

2. Laser-treated surfaces

Surface modification can be applied with respect to the applicability of polymer surface and interface in the construction of surface-enhanced substrates, which, for instance, provide biocompatibility or anti-microbial properties, may be used in sensor applications or for support of metal layers deposition [16-20]. Surface properties, such as wettability, morphology, and surface chemistry, play a crucial role in polymer/material application. A compilation of surface and interface analysis techniques will be described in this chapter, since besides the surface laser treatment itself, it is of great importance to understand the surface changes induced by a particular laser type (semiconductor, excimer, etc.) or by set up of input irradiation parameters. The determination of the CA and surface-free energy is one the most widely used surface characterization techniques. It provides very valuable information on the wetting properties of the surface and is determined by the upper molecular layer at the surface. The interpretation of measured values is complex and also involves discussion of measured values

for different liquids, surface roughness influence, and other factors that involve surface chemistry changes, which can significantly be modified by the laser beam treatment [16–24].

The surface and interfacial properties of polymers play a key role in many technological processes, such as polymer processing, metallization, or their cytocompatibility. All these processes are controlled by wetting and adhesion phenomena. Based on the conclusions of wettability measurement, we can estimate the surface chemistry with regard to polar or nonpolar functional groups as well as acidic or basic sites available at the modified surface region. In addition, the interaction of the solid surface with consequently applied (e.g., grafted and sputtered) surface-active substances can be influenced, or the biocompatibility is enhanced [16, 17, 20]. The importance of wettability in adhesion lies in the quality of adhesive bonding and coatings, which strongly depend on the spreading of these materials on the adherent or solid substrate. The laser surface treatment also significantly influences the surface energy (SE), and CA measurements are believed to be one of the simplest and most straightforward approaches to obtain surface-free energies of pristine or modified solids. The solid surfaces may very often be chemically heterogeneous, roughness can significantly be altered, or the reorientation of functional surface groups may occur during aging processes.

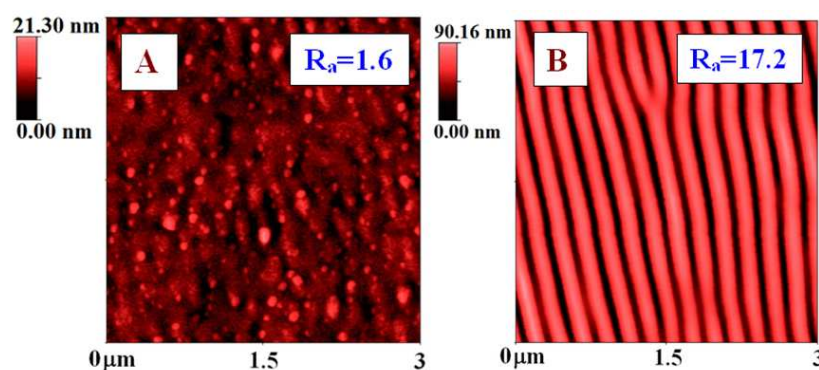


Figure 1. Detail of surface morphology (2D, $3 \times 3 \mu\text{m}^2$) of PEN treated with 10 mJ cm^{-2} and the number of laser pulses (A) 1000 and (B) 6000. R_a represents the average surface roughness in nanometers [18].

Several types of polymers may be changed by the laser treatment of the polymer surface. A broad spectrum of wavelengths, laser types, and pulse durations can be used. One of the most important types of polymer surface treatment is excimer irradiation. The excimer laser treatment of polymers can deliver periodic dimensional features in arrays across the surface of a substrate with lateral dimension close to 100 nm. Excimer laser can induce periodic nanopatterns on the surface of different polymers, which can absorb appropriate wavelengths [16, 17]. Besides polymers such as polyethylene naphthalate (PEN) [18], polyethyleneterephthalate (PET) [19], polystyrene (PS) [20], and polyethersulfone (PES) [21], surface changes (e.g., morphology and chemistry) can also be induced (Fig. 1) by excimer laser treatment on biopolymers or biocompatible polymer blends.

Laser surface modification of polyether-ether-ketone (PEEK) as a polymer with great mechanical and chemical properties was performed with the aim of wettability changes. A systematic approach of the laser irradiation wavelength influences the modification of surface layers of

PEEK under laser wavelengths ($\lambda = 1064, 532$, and 355 nm), with the focus on the determination of the optimal experiment parameters to increase the roughness and wettability, was executed [22]. It was found that a statistically significant factor during the processing using the 1064 nm laser radiation is the combination of pulse frequency, scanning speed, spot diameter, and pulse overlapping. In order to minimize the CA and improve wettability, the utilization of high-pulse-frequency, low-scanning-speed, low-overlapping, and small spot diameter was determined. On the other hand, the most influencing factors, using the 532 nm laser radiation, were the scanning speed and spot diameter [22]. Ultraviolet (UV) irradiation (172 nm) was used for the exposure of chosen polymer foils, i.e., polyethylene (PE), polyimide (PI), and polytetrafluoroethylene (PTFE), in air atmosphere [23]. The wettability (characterized by CAs and water drops) of the PE and PI films significantly increased after the exposure of excimer laser in air atmosphere. The subsequent X-ray photoelectron spectroscopy (XPS) study of the irradiated layers determined that the decrease of CAs was ascribed to the increase in the oxygen concentration at the modified surface. The surface characteristics of the PTFE film, however, was not considerably changed by the UV exposure. The aged UV exposed PE and PI films exhibited a significant decrease in wettability [23]. The influence of surface morphology on wettability was reported in [24], wherein a novel approach to creating hierarchically patterned PEEK surfaces composed of nanostructures and microstructures was introduced. The method was reported to be fast, easy, and applicable to large areas without using complicated lithography and mask-based techniques. Surfaces with a wide spectrum of wetting parameters ranging from a super-hydrophilic to a hydrophobic nature were reported [24]. The biological response on the performed surface materials modification is strongly dependent on the changes in surface properties (e.g., surface morphology, roughness, and composition). The modification of the surface of carbon-coated high-molecular-weight polyethylene (HMWPE) by different laser wavelengths ($\lambda = 1064, 532$, and 355 nm) was conducted [25]. The influence of experimental conditions (pulse frequency, scanning speed, and spot overlapping) on the changes in the surface properties of material was studied. It was found that the laser treatment of these carbon-coated samples always improved the wettability of the samples. The effect of the laser power on wettability was similar under the three laser treatments. The results suggested that the increment in the scanning speed reduces the CA during the surface treatment at 1064 nm. On the contrary, this parameter increments the CA during the surface treatment at 355 nm [25]. KrF laser was successfully applied for both laser-induced patterning and whole-area irradiative processing to modulate the wettability characteristics and osteoblast cell response following 24-h and 4-day incubation [26]. For the patterned samples, the CA was increased by up to 25° , which was attributed to a mixed-state wetting regime. For all samples, CA was a decreasing function of the SE [26]. The effects of using CO_2 and F_2 lasers to modify the wettability of a nylon,6-6 by producing $50\text{ }\mu\text{m}$ spaced (with depths between 1 and $10\text{ }\mu\text{m}$) trench-like patterns using various laser parameters such as laser power for the CO_2 laser and the number of pulses for the excimer laser was studied in [27]. The CO_2 laser couples into the material through resonant coupling, which gives rise to bond vibrations, allowing the temperature to rise and melt the material. Upon cooling, the molten material resolidifies, and a protrusion away from the surface becomes evident on the surface. The CO_2 laser was proved to be capable of producing CAs that are slightly larger compared with the as-received sample.

In contrast, for the F₂ excimer laser-patterned samples, the apparent polar component and surface O₂ content decreased by up to 11.69 mJ.m⁻² and 1.6 at %, respectively. It has been proposed that the increase in CA that results from the laser modifications is due to the patterned topographies [27].

The type of atmosphere during the modification process was reported to have a great influence on the wettability of a polymer [28]. The surface of poly(ϵ -caprolactone) (PCL) fiber scaffolds was significantly altered by femtosecond laser irradiation. Variations in input parameters (e.g., laser fluence and scanning area) led to a change in the surface CA. Scaffolds that were treated in ambient air or oxygen exhibited increased atomic oxygen concentration and also ablation of material. The concentrations of oxygen were generally larger, and sessile drop CAs smaller for surfaces for which the ablation was more pronounced. This effect was independent of the fact that the ablation was caused by higher laser power, decreased scanning space, or smaller defocusing distance [28]. The influence of roughness changes induced by femtosecond laser on the polypropylene (PP) surface was investigated in [29], wherein the influence of multi-scale roughness on CA measurements was described. An experimental investigation of the static CA measured on PP textured surfaces by a femtosecond laser with multi-scale roughness shown the dependence of the 3D roughness parameters. The proposed physical approach showed that the drop is not in such a case as in the state described by Wenzel or Cassie–Baxter, even with the roughness parameters calculated at the relevant scales [29]. The use of CO₂ laser-induced surface patterns to modify the wettability of poly(methyl methacrylate)(PMMA) with respect to the surface roughness of patterns was reported [30].

Different types of polymers were treated with excimer lasers, with the aim of modifying the surface wettability of treated samples. Polystyrene (PS) substrates were modified with excimer laser (ArF excimer pulsed laser, $\lambda=193$ nm) argon, and oxygen plasmas (radio frequency (RF) glow discharge). The substrates were processed at different experimental conditions (number of pulses or treatment times) [31]. Contact angle determination showed higher wettability for the modified PS with both argon and oxygen plasmas and lower wettability for the laser-treated samples. It was also observed that, in the case of laser irradiation, wettability and surface morphology affect cell attachment and spreading [31]. Laser modifications of PS using suitable exposure doses and an appropriate choice of the processing gas (helium or oxygen) enabled a highly localized control of wetting. The hydrophilic and hydrophobic behavior was caused by chemical and topographical surface changes [32]. The wettability of PI surfaces that were microstructured using KrF laser radiation at fluences above the material ablation threshold was studied by static CA measurements. The morphology of laser-treated surfaces consisted of conical features whose dimensions and areal density depended on the fluence [33]. The effect of the cone geometry on the surface CA depended on the wetting regime. When wetting occurred in the homogeneous regime, the CA of the treated surfaces increased with the radiation fluence because the cone dimensions increased. In contrast, for the heterogeneous regime, an increase in CA was observed due to an increase in the average distance between cones [33].

Surface wettability changes may also influence the growth and adhesion of consequently deposited metal layers. The effect of an excimer laser treatment at low laser fluences on a PET

surface was investigated, as well as its efficiency in improving the metal/polymer adhesion when the treated polymer is coated with aluminum [34]. For all treatments, an important increase in hydrophilicity was detected at low pulse numbers. When increasing the pulse number (>200), the evolution of the hydrophilicity depended on the laser process parameters. At 248 nm, the wettability either remained constant or even decreased at a high number of pulses due to the surface decarboxylation. At 193 nm, increasing the pulse number improved the hydrophilicity, and very low water contact angles (WCAs) were obtained [34].

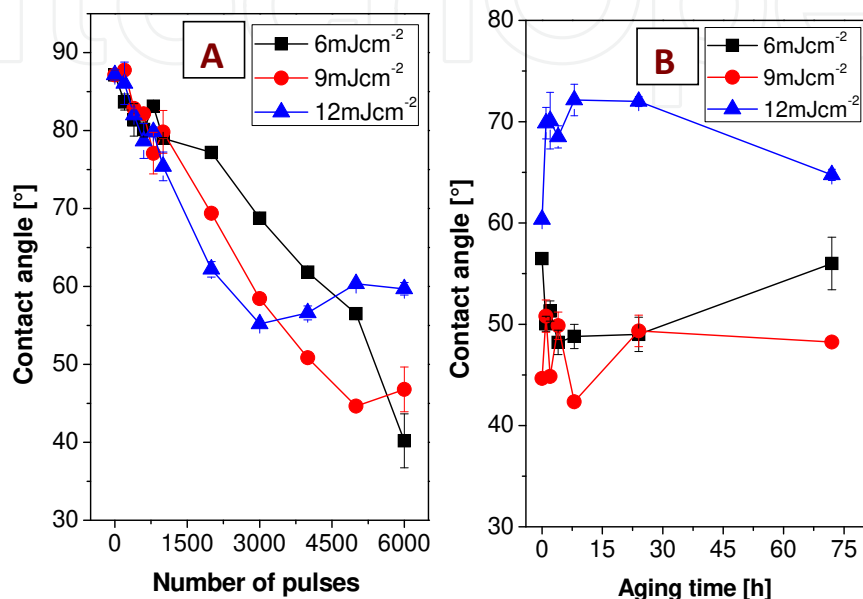


Figure 2. A) Dependence of the CA of laser-treated PS on several laser pulses treated with fluences of 6–12 mJ cm⁻². (B) Dependence of the CA on time from the laser treatment (aging time) for samples exposed with 6 000 pulses and laser fluence of 6, 9 and 12 mJ cm⁻² [38].

Excimer laser and femtosecond laser were also used for the surface modification of PCL membranes for tissue engineering applications [35]. In the case of femtosecond laser, the results gathered from the wettability test revealed that the PCL membranes with holes perforated at lower pulse numbers had higher SEs. At lower pulse numbers, the degree of surface roughness was higher because there were more surface asperities due to a greater “splattering” effect [35]. If compared, the results from the KrF treatment suggested that increasing the pulse number (corresponding to a longer laser irradiation time) at both energies increased the surface hydrophilicity of the PCL. The improvement in surface hydrophilicity after laser irradiation was proposed to be due to the sufficient energy of the excimer laser provided to overcome the bond strength of the PCL chemical structure at these irradiated regions [35]. Advanced functional surface patterns with high lateral resolution can be obtained by an appropriate combination of laser microstructuring or nanostructuring and laser surface modification. A flexible and rapid surface functionalization of amorphous carbon films showed a great potential for various applications such as biological surfaces and tribological systems [36]. The formation of carboxyl groups at the surface was detected, which corresponds to an improved wettability of water. The SE has shown a linear dependence on the laser energy dose and laser pulse number, respectively. For laser fluences near the ablation threshold, a selective ablation

of hydrogen-enriched domains seems to be responsible for the formation of micro-sized cones [36]. Recently, a modification of a method for CA measurement, an axisymmetric drop shape method, has also been used for wettability analysis [37]. Contact angle hysteresis phenomena on polymer surfaces have been studied through CA measurements using sessile liquid droplets and captive air bubbles in conjunction with a drop shape. This method was reported to be promising also for characterization of wettability of laser treated surfaces with controlled roughness and chemical composition [37].

Excimer laser is able to create regular or semi-regular patterns on the surface of polymer, which comply with specific parameters (e.g., ability to absorb the wavelength). A study of KrF laser treatment on a PS foil surface was performed. The influence of several laser pulses and laser fluence on surface properties (morphology, wettability, and chemistry) of PS was investigated [38]. The optimal input parameters for ripple nano-patterning with high regularity were determined. It was observed that increasing the number of laser pulses at all laser fluences applied led to a decrease in CA (Fig. 2A), which confirms the increase in wettability after laser exposure and is also with an excellent agreement with the work in [20]. Hydrophilicity is increased due to the formation of surface radicals after polymer bonds breakage caused by the impact and absorption of laser beam and consequent creation of new oxygen (polar) groups. Consequently, samples treated with 6–12 mJ cm⁻² and 6 000 pulses remained at ambient atmosphere, so they can undergo aging procedures for an interval of 1–72 h (Fig. 2B).

When a laser fluence of 6 mJ cm⁻² was applied, a mild decrease in CA was observed, down to 50°. The treatment with a fluence of 9 mJ cm⁻² at the first stages of aging primarily resulted in the fluctuation of CA. After 24 h of consequent aging, the mild constant decrease was determined. A different situation was observed when a fluence of 12 mJ cm⁻² was applied. At this laser fluence, a sharp increase of up to 70° was first observed, and after achieving its maximum, a slow decrease was detected. After 72 h, the polymer surfaces can be signed as “aged,” i.e., with no further significant changes. The modification induced in PS by the ArF excimer laser radiation has also been investigated [39]. The disperse component of the SE approximately raised linearly with the R_a value, whereas the polar component remained approximately constant. Surprisingly, laser-induced oxidation of the PS surface layer had no appreciable impact on the SE polar component. Laser-induced surface roughness was reported to be the main factor that influences the SE.

The wettability of laser-induced nano-ripples on PEN foils was studied in [40]. Polyethylene naphthalate (PEN) is chemically “similar” to PET, which is a widely industrially used polymer. Due to the presence of condensed benzene rings PEN has “higher” properties (mechanical, chemical, and thermal) compared with PET. The consequent measurements of PEN foils treated with several laser pulses (1000–6000) and laser fluence of 6–12 mJ cm⁻² were conducted from the point of wettability changes. A sharp decrease in surface CA was observed for all three studied laser fluences with an increasing number of laser pulses. The selected samples were chosen for the consequent aging studies. The CA of the laser-modified surface was evaluated for 1, 2, 4, 8, 24, and 72 h from the treatment. The lowest laser fluence first exhibited a small decrease during the process. After 8 h, no significant fluctuation could be observed. Rather, a different situation occurred for samples treated with higher laser fluences (9 and 12 mJ cm⁻²). A sharp increase during the initial stage of the aging process was observed. After

approximately 8 h, a mild decrease was determined, and the surface CA was almost constant after 72 h. For longer aging periods, no more fluctuations have been observed [40].

Polymer films (PE, PP, PTFE, PS, and PET) were modified by a F_2 laser (157 nm) [41]. The modification led to a degradation of the polymer surface layer and ablation. Wettability, characterized by the measurement of the CA, was determined as a function of the number of laser pulses. The laser irradiation led to a decrease in contact in all cases, except for PP substrates. The values of the CAs are affected not only on surface morphology but also on chemical composition. After an initial fast increase in wettability, a saturation of the CA was achieved. For more than 2000 laser pulses the CA remained unchanged [41]. An initial fast increase in wettability was detected on PE and PET, and a much slower increase for PTFE and PS.

Biopolymer surfaces can also be significantly altered by the use of laser treatment. Excimer laser irradiation can induce significant morphology (Fig. 3) and wettability changes [42, 43], or even a regular nanopattern can be constructed [44]. Different types of laser treatment also lead to the significant degradation of biopolymers. Degradation of poly(L-lactide) under a CO_2 laser treatment above the ablation threshold was reported in [45], but ablation of the poly(L-lactide) by CO_2 laser did not affect the wettability of the surface of the material, which confirmed the lack of formation of polar functional groups. A different situation can be observed if excimer laser is used.

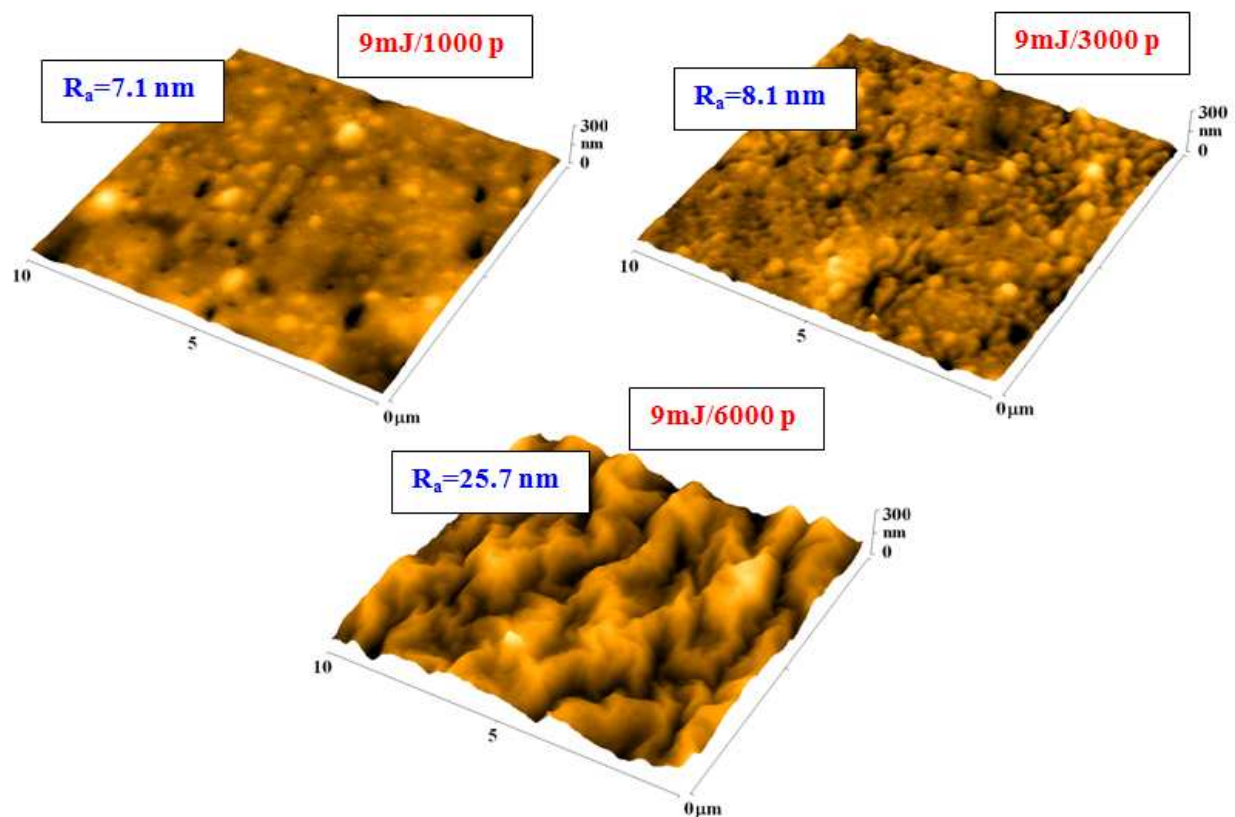


Figure 3. Surface morphology of plasma pretreated PLLA, consequently exposed with a laser beam of 9 mJ cm^{-2} and different numbers of pulses (1000, 3000, and 6000). R_a represents the arithmetic mean roughness in nanometers [43].

Surface ablation of poly(L-lactide acid) (PLLA) induced by excimer laser was studied in [42]. It was found that irradiation by KrF laser results in an increase in wettability of PLLA. This increase significantly depended on processing parameters (e.g., the number of pulses and laser fluence). The substrates treated with 500 pulses exhibited the smallest difference in wettability compared with the pristine PLLA. With an increasing count of laser pulses, the wettability increased (see Fig. 4). However, for laser fluences above 30 mJ cm⁻², the increase in wettability was neutralized, and a “constant” behavior was detected. This phenomenon is probably connected with both a significant change in surface morphology, roughness, and changes in structure and with the ablation of the biopolymer (Fig. 5).

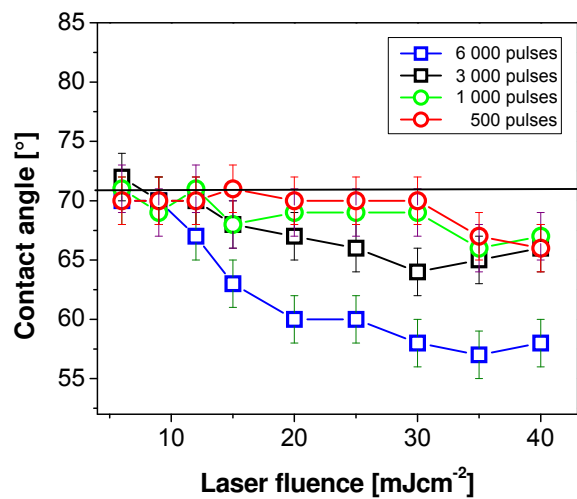


Figure 4. Dependence of the PLLA CA on the KrF laser fluence by different numbers of pulses (500–6 000) [42].

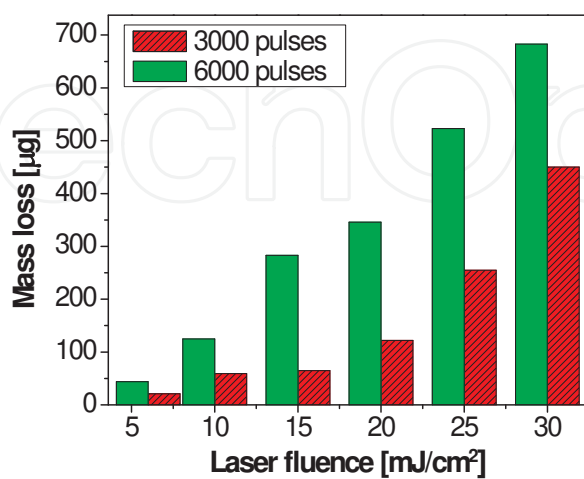


Figure 5. Dependence of the mass loss of PLLA on the applied KrF laser fluence. The treatment was accomplished at 3 000 and 6 000 pulses [42].

Plasma pretreatment strongly influences the CA of consecutively treated biopolymer [37]. The samples that were pretreated with plasma and aged for more than 72 h (which means that the input values of the PLLA CA before laser exposure were those of 90° (surface is stabilized)) were consecutively treated with KrF laser. The samples treated with 500 pulses exhibited the highest values of CA compared with the samples exposed to a higher number of pulses. With increasing laser fluence, the surface morphology was strongly influenced, and surface chemistry was significantly altered. The macromolecular chains' rearrangement ability and the chemical structure of the modified surface were influenced by the laser fluence. Slight fluctuations of CA appeared, probably due to the ablation of the polymer surface. The most pronounced decrease in CA was observed for samples treated for 6 000 pulses. However, a slight increase with higher laser fluence (40 mJ cm⁻²) was observed, probably due to more pronounced ablation [43].

3. Plasma-treated polymer

Many polymers have good bulk properties, which are used in a wide range of applications. In many application areas, surface properties besides bulk characterization are equally important for their successful use. However, their surface properties, especially adhesion, wettability, and cytocompatibility, are unsuitable for many applications. The effective method leading to the modification of the surface and changes of the chosen parameters is modification by plasma discharge [46, 47].

The polymer generally has a low surface reactivity. Using physical modification requires the use of high-energy particles, by which an inert polymer surface is bombarded. Most of the modifications are performed using low-temperature or "cold" plasma [48]. When we speak of plasma, we mean the highly ionized gas consisting of neutral and charged particles (ions, radicals, excited molecules, and electrons), wherein the total charge remains neutral [49]. Plasma can provide modification of the upper layer of polymer surface without using solvent or generating chemical waste and with less degradation and roughening of the material compared with many wet chemical treatments [50]. This procedure enables the modification of heat-sensitive materials, e.g., polymers [48, 51]. This type of plasma can be generated in many ways, e.g., by corona discharge treatment, UV radiation, X-ray beam, and gamma irradiation.

The plasma modification of polymers is very often used in surface cleaning or etching [52], changes in surface wettability and adhesion [53], reducing friction [54], or regulation of the cell adhesion in cytocompatibility studies [55]. The creation of the polar groups on the modified surface reaction by the reaction of activated polymer surface with gas atmosphere leads to the augmentation of adhesion, increasing hydrophilicity, or modifying the surface morphology (Fig. 6). It is known that modification by plasma treatment leads to changes in the surface layers (approximately 10 nm or less), whereas the bulk properties are not affected. The choice of the gas used to modification may affect the chemical composition of the "newly created" functional groups introduced to the polymer surface [56,57].

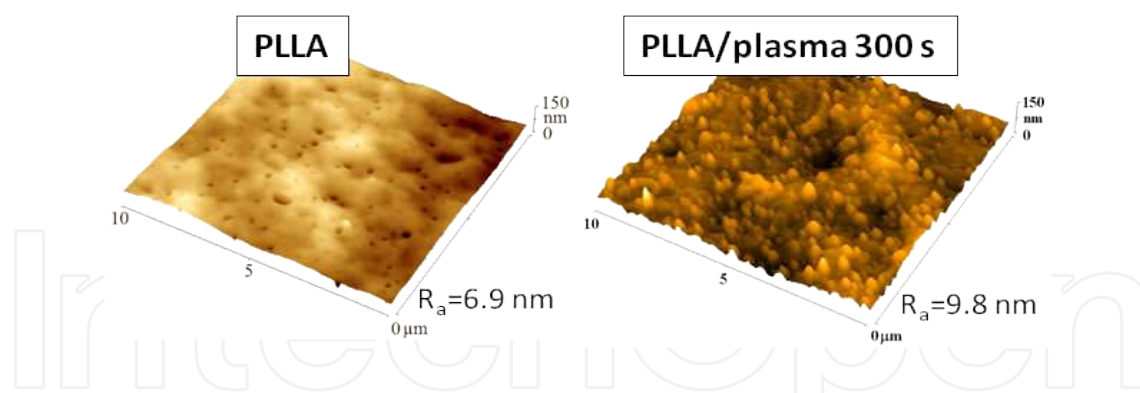


Figure 6. Surface morphology of pristine PLLA and PLLA treated in Ar plasma discharge (discharge power: 3 W; time of modification: 300 s). R_a represents the arithmetic mean roughness in nanometers.

The plasma treatment is a complex process, and a variety of chemical and physical reactions can occur. Plasma processing is generally used for film deposition or etching and may also be used for resist development and removal [58]. The type of functionalization can be varied by a selection of plasma gas (Ar, N₂, O₂, CO₂, and NH₃) and processing parameters (power, time, pressure, and gas flow rate). Plasma treatment with oxygen or nitrogen plasma provides polar functional groups on the surface, which alters the SE of polymers [59–61] and enhances the attachment of consequently applied chemical substances or particles. It is known that oxygen plasma can react with a wide range of polymers to produce a variety of oxygen functional groups. Oxygen plasma provides different functional groups on the polymer surface, e.g., the C–O, C=O, and O=C–O groups [61–63]. The wettability of surface as well as its biocompatibility can significantly be altered by plasmas containing nitrogen [64]. Cell affinity was enhanced using ammonia plasma treatment on PS [65]. Nitrogen- or ammonia-based plasmas were applied to create amino-binding sites [66] or to increase the peel strength between polymers [67]. The plasma is able to increase adhesive strengths on the polymer surface [68].

3.1. Oxygen in plasma gas and the surface wettability of modified polymer

Although PLLA and polyhydroxybutyrate with 8 % polyhydroxyvalerate (PHBV) can be found in biomedical applications, both are hydrophobic, making their interaction with cells difficult. Thus, the surface modification of these polymers is important for all applications involving their contact with physiological components [69, 70]. The influence of the oxygen and nitrogen plasmas on the hydrophilicity of the PLLA and PHBV was studied. The oxygen plasma treatments on both PLLA and PHBV samples, in general, caused a reduction in the CA and an increase in the SE. This increase in the SE reflects an increase in surface hydrophilicity. Changes in the surface morphology were observed, as well as a decrease in CA, and an increase in SE and polar components was detected. These modifications were associated with the plasma parameters (pressure, power, and time) and made both polymers more hydrophilic [49]. In a study aimed at the evaluation of plasma treatment effects on the surface properties of PLLA, film air plasma was used at a pressure of 10–20 Pa, and a discharge current of 50 mA for 60 s was applied. The CA of wettability measurements of the films showed that plasma modification led to an increase in hydrophilicity and SE [71]. The use of oxygen plasma

treatment on fibril tip surfaces in polymer elastomeric polyurethane (PU) and polydimethylsiloxane (PDMS) fibrillar adhesives improved their wettability and adhesion capacity. Surface modifications of fibril tips involved UV/ozone and oxygen plasma treatments to make the fibril tips more hydrophilic. Treatment of fibril tip surfaces renders them more hydrophilic, and the adhesion capacity of treated fibrillar arrays is sensitive to the relative humidity of the environment [72]. Surface effects induced by oxygen plasma exposition (time of treatment: 60 s; constant pressure: 15 Pa; and at different process powers, ranging from 20 W to 200 W) on PET wettability were investigated by WCA measurements. Plasma treatment produced surface modifications with the incorporation of hydrophilic functional groups such as carbonyl (C=O) and carboxylic (–COOH) groups. At a low power level (20 W), the plasma was mainly rich of radical species that react with methylene (C–O) and ester groups (O–C=O) present in the polymeric chains, producing a slight etching of the material and new hydrophilic species as carbonyl groups are introduced. At a high power level (200 W), a more efficient incorporation of hydrophilic species into the PET surface was observed. Contact angle measurements confirmed the enhancement of the surface wettability as a function of plasma power [73]. The degree of hydrophilicity of the treated HMWPE surface was determined by measuring the CA of a water droplet on the surface. The plasma was generated using compressed air as the ionization gas. It was found that plasma power and scan speed affect the grafting process. The lower power and lower scan speed generally resulted in a greater change in CA from the HMWPE [74]. Experiments on plasma treatment of PP and PET foils were carried out with the use of atmospheric pressure plasma sources operating with ambient air as plasma forming gases. The atmospheric pressure plasma source was ambient airflow as a plasma-forming gas. Airflow was perpendicularly directed to the electric current. The velocity of airflow was about 20 m s^{-1} . The average power of this dc plasma source was 35 W. The results of measurements made within about 1 min after plasma processing indicated that the air plasma processing of PP and PET resulted in a decrease in CA till a processing time value of 1 s, followed by a phase of a nearly constant value of 36° for PP and 30° for PET. The effect was noticeably stronger for the PP surface. This was explained by different chemical compositions of these polymers [75]. The effect of low-pressure O_2 plasma treatments on the surface-free energy and morphology of PP films was studied in [76]. The treatment was performed at a pressure of 0.35 bar. Each PP sample was treated at 10, 30, and 50 W for 10, 20, 30, 60, 120, 180, and 300 s, respectively. Based on the surface-free energy calculation and Fourier transform infrared spectroscopy-attenuated total reflection (FTIR–ATR) spectroscopy, it was evident that the changes in the SE PP film significantly increased already after a very short treatment time (20 s). The surface modifications with O_2 plasma proceeded only with hydrophilic modification. The SE reached the maximum value for a short treatment time and then leveled off [76]. For improving wettability, RF plasma treatment in the air atmosphere was reported to be a very effective tool. The high-density polyethylene (HDPE) was modified by air and oxygen plasmas (operating pressure from 0.1 to 1 Torr, power ranging between 5 W and 10 W). The CA measurement, ATR FTIR, and XPS analysis showed that plasma treatment leads to a dramatic increase of the hydrophilic character of the HDPE surfaces. A hydrophilic surface was created mainly due to the generation of the carboxylic, carbonyl, and peroxide groups at the surface interface [77].

In all the above-mentioned cases, the oxygen-containing plasma treatment leads to a decrease in WCA and increase in hydrophilicity of the polymer surface.

3.2. Inert plasma treatment and wettability of modified polymers

The influence of Ar plasma on the surface polarity and wettability on the PLLA and poly-4-methyl-1-pentene was studied by measuring the CA. The samples were modified in diode plasma discharge for 0–240 s, using DC Ar plasma (gas purity: 99.997%; power: 3 W and 8 W). Exposed samples exhibited a sharp decrease in CA immediately after modification. It was found that the values of CA depend on both exposure time and discharge power. As a reset of the plasma treatment, the polarity of the polymer surface increased, the CA decreased, and the SE increased. With an increasing aging time, the surface polarity was spontaneously reduced. The increase in CA of the polymer surface and decrease in wettability may be caused by the reorientation of polar groups into the polymer bulk [78]. The dependence of the WCA and surface-free energy on exposure time at different discharge powers was determined on plasma-modified PHBV. The samples were modified in diode plasma discharge on Balzers SCD 050 device for 0–240 s, using dc Ar plasma (gas purity: 99.997%; power: 3 W, 5 W, and 8 W). Based on the CA measurement using a goniometry technique, it was concluded that the treatment of PHBV in Ar plasma leads to a decrease in the measured WCA (increase in wettability). Exposure to the lowest plasma discharge power of 3 W led to fast decrease in CA after 10 s of treatment. For a 40-s exposure, WCA achieved a minimum value of about 30°. For exposure times above 40 s, WCA slowly increased with increasing exposure times. It was proposed that this turnout in WCA dependence may be due to the surface ablation and change in surface roughness. A similar trend was observed at a higher discharge power of 5 W, where the lowest WCA (36.6°) was observed for an exposure time of 10 s. At 8 W, the discharge power was monotonous, but a slow WCA decrease with an increasing exposure time was shown. Differences in WCA and SE during the aging of the plasma-modified PHBV were observed; however, after some time, a saturated, constant value was achieved. Both effects strongly depended on the plasma discharge power [79]. The work focused on the modification of PHBV and PLLA foil with Ar plasma and presented the influence of different conditions of plasma treatment on the wettability of the two biopolymers. Both biopolymers were treated with Ar plasma discharge (discharge power: 3 W; time of modification: 25–400 s). For both polymers, it was determined that immediately (5 min) after irradiation, all samples exhibit a sharp decrease in CA to a minimum value. With an increasing aging time, the CA increases. The stabilization of the polymer surface was observed after 10 days (for PLLA) and 13 days (for PHBV) from the treatment (Fig. 7). Finally, the CA was strongly dependent on the exposure time. Substrates modified for a shorter times (5–75 s) had a significantly lower CA than substrates modified for longer times (300–400 s) [57].

The changes in wettability of 2-hydroxy-ethyl-methacrylate (HEMA) and 2-ethyl-oxy-ethylmethacrylate (EOEMA) induced by Ar plasma treatment were measured using goniometry. The experiment was performed on a Balzers SCD 050 device, and the processing parameters were as follows: the time of modification was 0–400 s, and the discharge power was 1.7 W [80]. Based on the analyses, the creation of the “new” groups containing oxygen on HEMA and EOEMA chains leads to changes in wettability. The CAs were immediately evaluated (in 6 min) and 386 h after the plasma irradiation. It was found that the plasma modification leads to the rapid decrease in CA in the first few minutes after modification. The

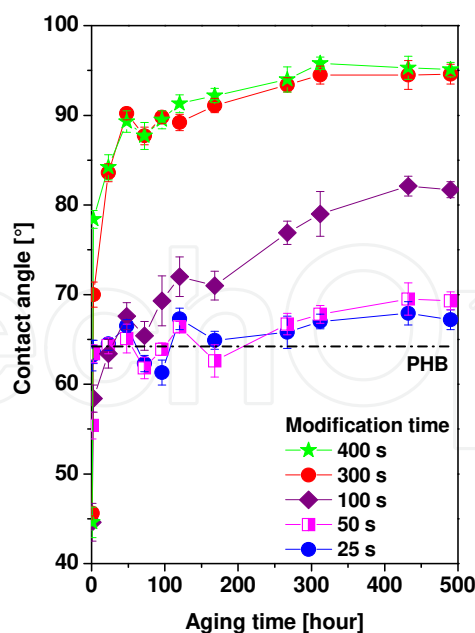


Figure 7. Dependence of the CA of PHB plasma treated by 3 W on the aging time (after modification). Plasma exposure times were 25, 50, 100, 300, and 400 s. The CA value for the pristine PHB is shown as a dotted line [57].

decrease was higher for longer modification times. Comparable dependence was observed for both polymers. Then, 386 h after plasma modification, the CA increased compared with the CA measured immediately after the plasma treatment. The experiment in [81] proved that the concentration of oxygen groups created by Ar plasma irradiation does not change with time from modification. This result [81] and the finding from goniometry analyses [80] can be explained by the reorganization of surface layers and rotation of degraded macromolecules and newly created structures to the “free volume of polymer” [80, 82]. The studies of plasma treatments processed by Ar on the drug release from the poly(ethylene-co-vinyl acetate) (EVA) polymer films demonstrated the effects of plasma modification on the wettability of a typical biocompatible polymer. Plasma treatment was carried out using RF plasma-enhanced chemical vapor deposition: power was 200 W, and the total pressure was kept at 13.3 Pa. The plasma processing time was changed from 0 s (untreated) to 45 s in order to evaluate the plasma processing time effects on the drug eluting characteristics. After stabilizing the sample in air for 1 day, the CA measurements of the samples were performed. The plasma treatment by Ar resulted in a significant reduction in WCA, even by a short plasma treatment time of only 5 s. By longer than 5 s of the plasma treatment, the WCA became relatively low and stayed almost constant thereafter, regardless of the plasma processing time. This behavior led to a reduction of the drug release amount from EVA by only a short plasma processing time [83]. The aging behavior of the plasma-irradiated PP and PET polymer foils was studied by goniometry. Measurement was performed by the determination of the WCA. Plasma modification causes the creation of oxidized structures on the polymer surface. The exposure of the irradiated samples to the air atmosphere occurs at the reorientation of the oxygen groups from the surface into the bulk of the material. The influence of aging time on the CA showed the change of the values of CAs of the plasma-modified polymer foils (PP and PET) as a function of storage time.

Based on the results, it is evident that the aging is characterized by a fast decrease in wettability during the first few hours of storage. At longer storage times, the wettability decreases more slowly, and the CA finally reaches a plateau value [84].

4. Grafting of plasma-treated polymers

The plasma treatment of polymers leads to a modification of polymer surface due to the production of reactive sites or changes in cross-linking or molecular weight. The bombardment of polymer surfaces by energetic particles breaks the covalent bonds, and this process results in the formation of surface radicals. The typical gas used for activating the polymer surface by forming radicals is Ar or He. These active sites (radicals) can later react with other chemical substances. The polymer surface can also be functionalized by “plasma-induced grafting,” which is the combination of plasma activation and conventional chemistry [46]. Grafting is a method in which new compounds are bounded from the gas or liquid phase on the activated polymer surface [85]. Grafting may be realized to the polymer surface with the use of one or more substances. In the first case, modification is performed in one step, and in the latter case, it may occur for networking several substances simultaneously or in consecutive steps. Not only radicals but also the functional groups created due to plasma treatment, such as carboxyl, hydroxyl, or amine groups, can be used for subsequent modification of the polymer surface.

For many applications, it is necessary to bind suitable substances on the polymer surface. In tissue engineering, development of biosensors and other biodiagnostic devices is of great importance, and immobilizing of proteins onto a surface is a key step in many biotechnological processes and applications. Various immobilization techniques such as physical adsorption, covalent immobilization, and bioaffinity immobilization have widely been practiced [86]. For polymers, a technique for covalently binding of proteins, i.e., pretreating the polymer surface in plasma discharge combined with the bath deposition, may be used. On plasma-activated surfaces, proteins can be immobilized through a reaction with the amine and carboxyl groups [87].

In the development of, e.g., biomarkers and biosensors or in molecular design, nanoparticles are very often applied [88-90]. These may be prepared from organic materials (e.g., polymers) and inorganic materials (e.g., metal nanoparticles). In addition, one can design nanoparticles with controlled hydrophilic/hydrophobic characteristics, with positive or negative charge, with response to external pH or thermal stimuli, and, finally, with high resistivity or conductivity. It is therefore clear that combining nanoparticles with different nature, shape, chemistry, and physical properties together with polymer substrates permits the design of an infinity of systems for a plethora of applications [91]. Metal nanoparticles can be prepared through physical (mechanical separation of metal aggregates) or chemical (nucleation and growth nucleus) methods. Colloidal solutions of metal nanoparticles and nanoparticle composites with ceramic or various organic materials are currently prepared in particular. The most widely used metals include gold, silver, and platinum, as well as iron and their compounds. Hence, a key aim of materials science is to understand roles that substances or particles bonded

on material surface play at the interface of materials. It is clear that the grafting a new material on the surface leads to changes in chemical structures and composition, surface morphology (Fig. 8), roughness, and other parameters, and they affect surface wettability.

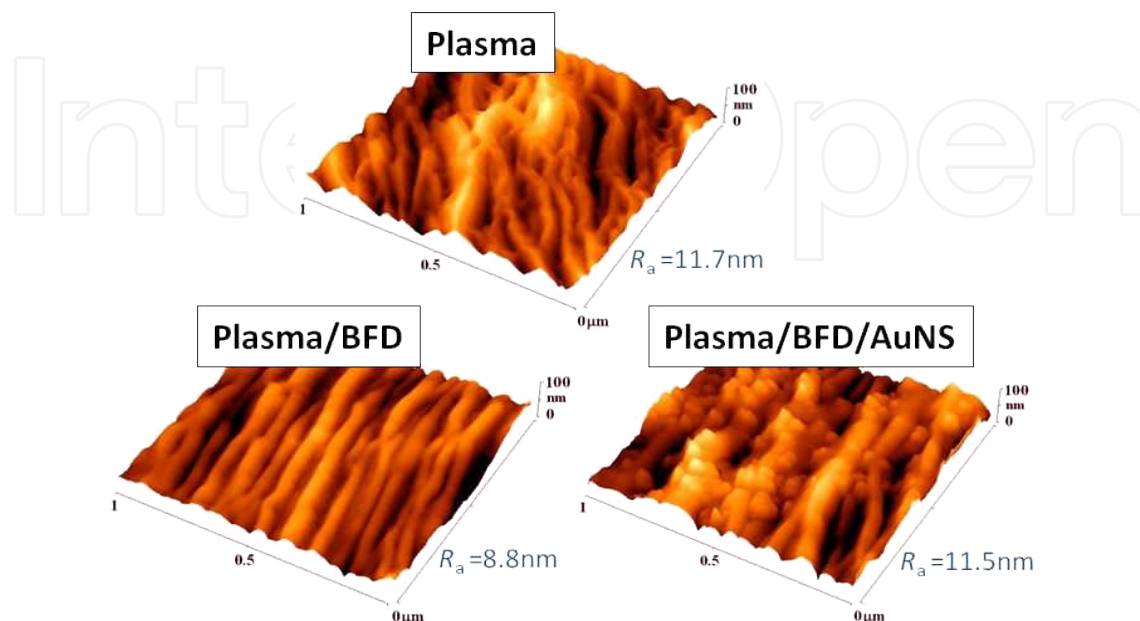


Figure 8. Surface morphology of the PE treated with plasma for 100 s (Plasma), PE treated with plasma and subsequently grafted with biphenyl-1,4-dithiol (Plasma/BFD), and PE grafted with biphenyl-1,4-dithiol and Au nanoparticles (Plasma/BFD/AuNS). R_a represents the arithmetic mean roughness in nanometers [92].

4.1. Wettability of grafted polymer surface and cytocompatibility

One of the most studied nanomaterials for biomedical applications are carbon materials (nanotubes as a carrier for biosensors, fullerenes), polymer nanofibers with high porosity (dressings, tissue engineering, and targeted drug delivery), hydrogels (dressings for open wounds and materials release medicines), or dendrimers (cancer treatment) and inorganic materials (silica and metal nanoparticles) [93, 94]. Fullerenes, spherical molecules composed solely of carbon atoms (e.g., C60), exhibit a broad spectrum of biological activity. Their unique shape and ability to “capture” some substances or compounds within their structure make fullerenes significant, especially in their potential use for targeted drug delivery or gene therapy [95, 96]. After irradiation with ultraviolet or visible light, fullerenes may convert molecular oxygen to become highly reactive and cause photodynamic disintegration of biological systems. This effect can be used in the therapy against cancerous growths, viruses, and bacteria that are resistive to broad-spectrum drugs. In their original unmodified state, fullerenes are highly hydrophobic and insoluble in water. On the other hand, they are relatively reactive, allowing modification of their structure. The modification leads to the increase in their hydrophilicity and wettability. They will also become soluble in aqueous solutions, which improves their interaction with biological systems [97, 98]. Deposition and grafting of gold–silver particles on polymer grafts has been the subject of a large number of studies for their

potential application in electronic and optical detection systems, therapeutics, catalysis, and the environment [99-101]. Metallic nanoparticles such as iron oxide, gold, and silver have been developed and adopted for use in targeted drug delivery and diagnostic imaging. Super paramagnetic nanoparticles composed of nanoparticles of oxides, such as magnetite (Fe_3O_4) and hematite (Fe_2O_3), allow sensitive detection with high-resolution MRI. Elemental silver and silver salts are well known due to their relative non-toxicity in human cells and their antibacterial effects. Silver nanoparticles have been developed for antibacterial applications, because they more easily penetrate the cell wall of microbes and, thus, are more effective [102].

In the case of modification of the material that is in contact with cells, the nanoparticles or the other compounds grafted on the polymer surface change the surface wettability (Fig. 9) and thus significantly affect the adhesion and proliferation of living cells.

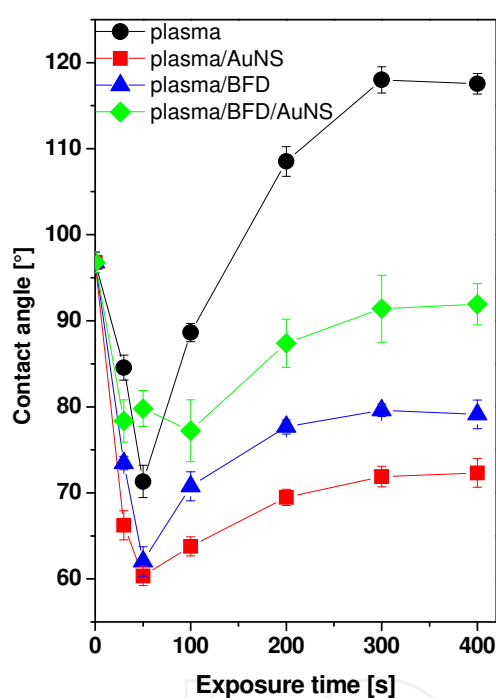


Figure 9. Dependence of the CA on the plasma exposure time for plasma-treated PE (plasma), plasma-treated and Au nanoparticle grafted PE (plasma/AuNS), plasma-treated and biphenyl-1,4-dithiol grafted PE (plasma/BFD), and plasma-treated and biphenyl-1,4-dithiol and Au nanoparticle grafted PE (plasma/BFD/AuNS) [92].

It was found that the unique properties of nanomaterials may not only affect the cell adhesion and interconnectivity across the cell structure on the surface of the sample but also represent an important factor for the structural and organizational stability of the cells [103]. The properties of the substrate significantly affect the subsequent establishment and organization of various cell types. Cells are “attached” to the substrate surface through the adhesive points that constitute the communication channels between the substrate’s surface and the cellular cytoskeleton. Formation of this interface is influenced not only by the surface chemistry of the substrate but also by the surface charge, wettability, and modulus of elasticity [104, 105]. One widely accepted advanced “trend” in tissue engineering is the creation of surfaces that promote

cell colonization. For this application, it is necessarily suitable to adjust not only chemical composition but also surface wettability. The decrease in surface wettability influenced by the grafting of adhesive molecules was studied in [106]. In this work, the changes in surface properties and biocompatibility of PE substrates after the plasma activation and subsequent grafting with chosen molecules glycine (Gly), tripeptide arginine–glycine–aspartate (RGD), fibronectine (FN), vitronectin (VN), and collagen (CG) were determined. It was found that plasma activation and grafting with molecules led to significant changes in the surface properties (polarity, chemical composition, morphology, and roughness) of the substrates.

Grafting of PE with molecules led to a strong decrease in CA. The biocompatibility of the substrates and cell–material interactions were studied by *in vitro* experiments. It was found that the surface activation of PE samples by Ar plasma discharge had a favorable effect on the adhesion, spreading, homogeneity of distribution, and, moderately, proliferation activity of mouse embryonic fibroblasts (NIH 3T3 cells). This effect was even more apparent on the samples coated with biomolecules. In the experiment, it was demonstrated that the treatment of PE by Ar plasma discharge and subsequent grafting with molecules dramatically increased the attractiveness of the presented polymer foils for cytocompatibility of NIH 3T3 cells [106]. The decrease in CA on polyolefins (e.g., PE) may also occur due to the interaction of their surfaces with Gly [80]. The grafting of this molecule on the PE surface leads to the increase in oxygen concentration on the modified surface and decrease in WCA. Combination with other surface properties (morphology and roughness) leads grafting with Gly to an increase in the attractiveness of PE for vascular smooth muscle cell (VSMC) colonization [107].

Grafting of poly(ethylene)glycol (PEG) on polymer surface grafts has been the subject of a large number of recent studies because of their properties applicable for creating polymer brushes. Polymer brushes are used as model systems in polymer science, in colloids and surfactant sciences, colloidal stabilization, lubrication polymers, and compatibilization between organic and inorganic materials. In particular, PEG brushes can be used to repress protein adsorption, which is responsible for several unwanted effects, such as fouling of contact lenses, clotting on blood-containing devices, and triggering of inflammation around artificial organs [108]. Several studies were focused on the grafting of PEG in order to improve the cytocompatibility of substrate and creating the cell's attractive scaffolds [60]. Three PEGs with different molecular weights (molecular weight was 300, 6 000, and 20 000 g mol⁻¹) were grafted on the plasma-activated polymer surface [109]. Dependences of the CA on the aging time for plasma-modified PE and plasma-modified PE and subsequently grafted with PEG showed a pronounced decrease in CA after PEG grafting due to the binding of oxygen-rich compounds onto the activated polymer surface. Based on the biological experiments performed *in vitro* with the VSMCs, it was found that the cell's adhesion, proliferation, and viability is strongly dependent on PEG concentration on the polymer surface and on the length of its chain (Fig. 10).

Cells very well proliferated and were grown on the substrates grafted with PEG with very low or very high molecular weight. In addition, the viability of cells cultivated on these samples was very high. The best results (the higher number of the cells) was achieved on the samples treated in plasma for 50 s and subsequently grafted with 20 000 g mol⁻¹ PEG. On the other hand, the samples grafted with 6 000 g mol⁻¹ PEG showed a significant anti-adhesion character and were for the cell's undesirable cultivation (Fig. 11) [109].

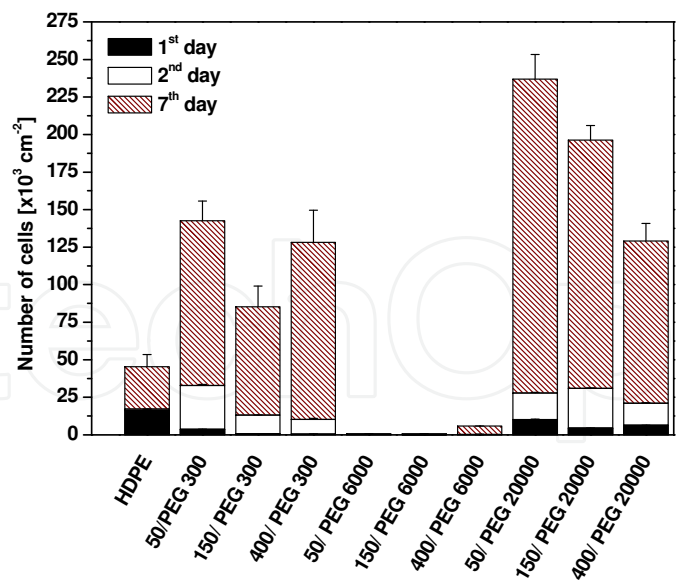


Figure 10. Number of adhered (first day) and proliferated (second and seventh days) VSMCs on pristine HDPE and HDPE treated in plasma discharge for 50, 150, or 400 s and subsequently grafted with PEG with a molecular weight of 300, 6 000, or 20 000 g mol⁻¹.

The influence of the presence of the gold nanoparticles on the surface wettability and biocompatibility of substrates was investigated in [110]. Golden, spherically shaped nanoparticles (AuNPs) with an average diameter of 12 nm were bound on the plasma pretreated polymer surface, which is concretely polyolefin, HDPE. The AuNPs were “grafted” from the citrate colloid solution. Surface wettability was measured by goniometry, i.e., the static (sessile) water drop CA method. The samples exhibited an increase in wettability after modification by plasma discharge and AuNPs. This increase was more pronounced for samples pretreated in plasma for a lower time. The cell–material interaction was studied using two different types of cells (VSMCs) and mouse embryonic fibroblasts (NIH 3T3)). Based on the test results, it was evident that the plasma treatment of the polymer and the presence of AuNPs had a positive influence on the spreading, proliferation activity, and homogeneity of the distribution of VSMCs and NIH 3T3 on the material surface [110].

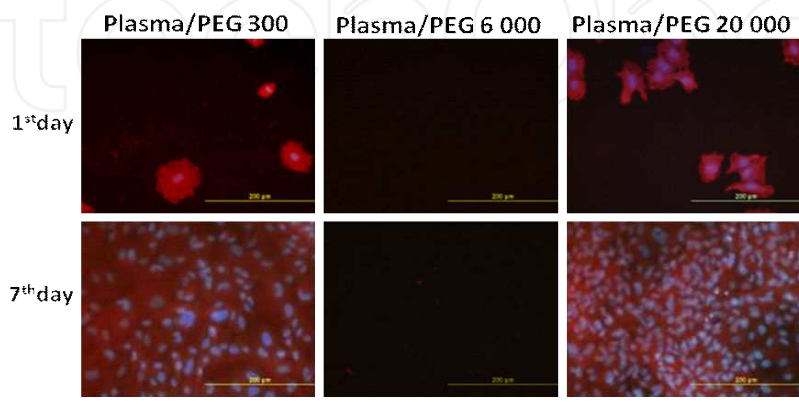


Figure 11. Photographs of the adhered (first day) and proliferated (seventh day) VSMCs on PE treated on plasma discharge and subsequent grafted by PEG with a molecular weight of 300, 6 000, or 20 000 g mol⁻¹.

Several vicinal compounds grafted on plasma-treated polymer foils were studied in [111] and [112]. First, surfaces of PET and PTFE were modified by plasma discharge and subsequently grafted with three different thiols: (i) 2-mercaptoethanol; (ii) 4,4'-biphenyldithiol; and (iii) cysteamine. The thiols are expected to be fixed through one of $-OH$, $-SH$, or $-NH_2$ groups to reactive places on the polymer surface created by the plasma treatment. "Free" $-SH$ groups are allowed to interact (graft) with gold nanoparticles and nanorods [111]. During this research, we have found an interesting behavior of cysteamine molecule, which bonds to the surface through either the $-SH$ group with the "free" $-NH_2$ group or reversely depending on the polarity of substrate surface.

Cysteamine was grafted on several polymer foils of different polarity (PLLA, PS, low-density polyethylenes (LDPE), HDPE, PET, PTFE, polyvinylfluoride (PVF) and polyvinylidene fluoride (PVDF)) previously activated in plasma discharge [112]. Surface properties including surface wettability of the sample before and after plasma treatment and cysteamine grafting were studied using various methods. Surface chemistry was studied with X-ray photoelectron spectroscopy, chemistry, and polarity by electrokinetic analysis and by goniometry, and roughness and morphology by atomic force microscopy. Representatives of unmodified and modified polymers were used for an *in vitro* study of the adhesion and proliferation of VSMCs [112].

Wettability was determined by measurement of WCA on all samples, pristine, plasma treated for different times, plasma treated, and subsequently cysteamine grafted. It was found that plasma treatment leads to a dramatic decrease in CA, indicating an increase in surface wettability of all polymers. For some polymers, this CA decrease strongly depended on the plasma exposure time (e.g., PTFE), but for others, the plasma exposure time is not of such importance (e.g., HDPE and LDPE) [112]. The most dramatic dependence of CA is observed on PTFE. The cysteamine grafting caused a dramatic increase in CA (i.e., decrease in surface wettability) on all polymers, and the increase was the highest on PTFE. These results are mainly a combination of the so-called aging process on polymer surface after plasma treatment, which has been earlier studied for different polymers [92, 112–114] and subsequent grafting of cysteamine. Aging of the plasma-treated surface leads to an increase in CA and hydrophobicity due to the rearrangement of polar groups created on the surface during plasma treatment [92, 112–114], whereas subsequent grafting of hydrophilic functional groups on the surface increased surface hydrophilicity [112]. Due to a small concentration of cysteamine bonded on the surface, the hydrophilicity only slightly increased in this case, and the combination of these steps resulted in hydrophobicity increase compared with the freshly plasma-treated surface.

Electrokinetic analysis and XPS measurement work provided information on surface chemistry and surface charge. Both of these are important for cell adhesion. Fig. 12 shows the results of electrokinetic analysis (zeta potential values) for pristine polymers, plasma-treated polymers, and plasma-treated polymers subsequently grafted with cysteamine. The zeta potential is known to depend on surface chemistry, polarity, charge, and surface morphology and roughness [115]. It is evident in Fig. 12 that the zeta potential depends on the polymer surface properties and it changes after plasma treatment and also after cysteamine grafting. Plasma treatment leads to changes in the surface charge, chemistry, and polarity and to a change in the zeta potential too. A significant increase in the zeta potential was observed on PTFE, HDPE,

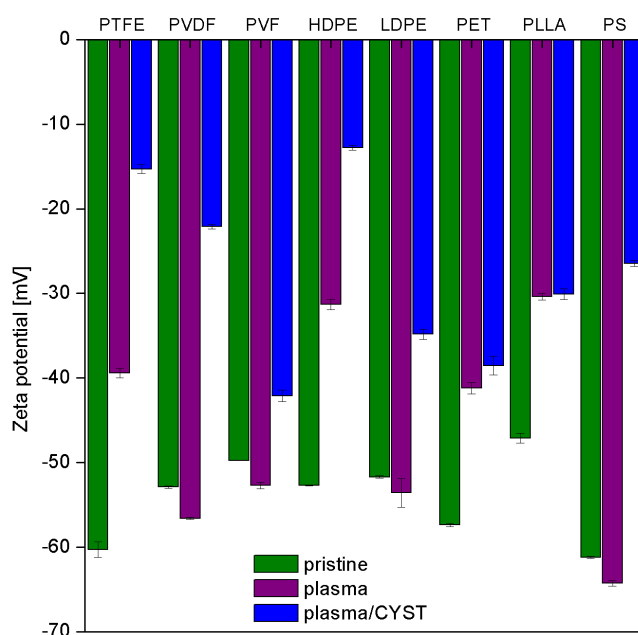


Figure 12. Zeta potentials of polymers: pristine (pristine), plasma treated for 120 s (plasma), and plasma treated and cysteamine grafted (plasma/CYST) determined by streaming the current method and calculated by the Helmholtz–Smoluchowski equation [112].

PET, and PLLA. Plasma treatment resulted in a cleavage of original bonds (e.g., C–H, C–C, and C–O) and the creation of new reactive places on the polymer surface (“free” radicals, double bonds, and new chemical groups, e.g., carbonyl, carboxyl, and ester groups) [116]. The plasma treatment led to the creation of excessive oxygen containing groups and subsequently to an increase in surface polarity on these four polymers mentioned above [112]. On PVF, PVDF, LDPE, and PS, the plasma treatment caused only a mild decrease in the zeta potential, indicating a decrease in surface polarity. The effect may also be due to an increase in surface roughness [112]. More pronounced results are obtained after cysteamine grafting. The most dramatic increase in the zeta potential was obtained on nonpolar polymers (PTFE and HDPE), whereas on more polar polymers (PET and PLLA), the zeta potential remained almost unchanged. The different behavior of these two groups of polymers may be due to (i) different amounts of grafted cysteamine and also (ii) different characters of the preferential bond of cysteamine (via the –SH or –NH₂ group) to the surface. Cysteamine grafting resulted in the creation of the new chemical functional groups on the polymer surface.

The results of ARXPS measurement of C, O, N, S, and F atomic concentrations on pristine polymers, plasma-treated polymers, and plasma-treated polymers subsequently grafted with cysteamine confirmed changes in the surface chemistry of all polymers after (i) the plasma treatment and (ii) subsequent cysteamine grafting [112]. After subsequent cysteamine grafting, the sulphur (S) and the nitrogen (N) containing groups appeared on the surface of all polymers, but their concentrations were different for individual polymers [112]. The highest concentration of N and S was detected at PTFE, PS, PVF, and PVDF, quite less at HDPE and LDPE, and minimal at PET and PLLA. This correlates well with the results of electrokinetic analysis (see Fig. 12), according to which the highest amount of cysteamine was grafted (the highest increase

of zeta potential) at PTFE, PS, PVF, and PVDF, quite less at HDPE and LDPE, and almost none at PET and PLLA. Comparison of the XPS results obtained on grafted samples showed a higher amount of concentration of N on PTFE, PS, PVF, and PVDF compared with S [112]. This indicates that cysteamine is preferentially bonded at these surfaces through the $-SH$ group to the surface and with the $-NH_2$ group remaining “free”. On the other hand, the concentrations of N and S at PET and PLLA are almost the same, so no preferential bonding of cysteamine at these polymers was observed [112]. Cysteamine is bonded to these polar polymers without preference through the $-SH$ and $-NH_2$ groups. Both electrokinetic analysis and XPS measurement confirmed the successful grafting of cysteamine. The schematic diagram of cysteamine grafting on different polymers is presented in Fig. 13. On PTFE, PS, PVF, and PVDF, cysteamine is bonded with a higher amount and even preferentially through the $-SH$ group with the “free” $-NH_2$ group, which creates a positive charge on the surface in the presence of a KCl water solution. As a result, the zeta potential increases to more positive values. On the other hand, on polar polymers (PET and PLLA), cysteamine is grafted much less (the concentration of N and S is significantly lower), and none of the possible bonding mechanisms is preferred [112]. Probably, on these polymers, the binding of cysteamine is accomplished by both mechanisms, i.e., via (i) the $-SH$ group with the “free” $-NH_2$ group, which creates a positive charge on surface in presence of a KCl water solution and also (ii) the $-NH_2$ group with the “free” $-SH$ group, which creates a negative surface charge in the presence of a KCl water solution connected with a more negative zeta potential [112].

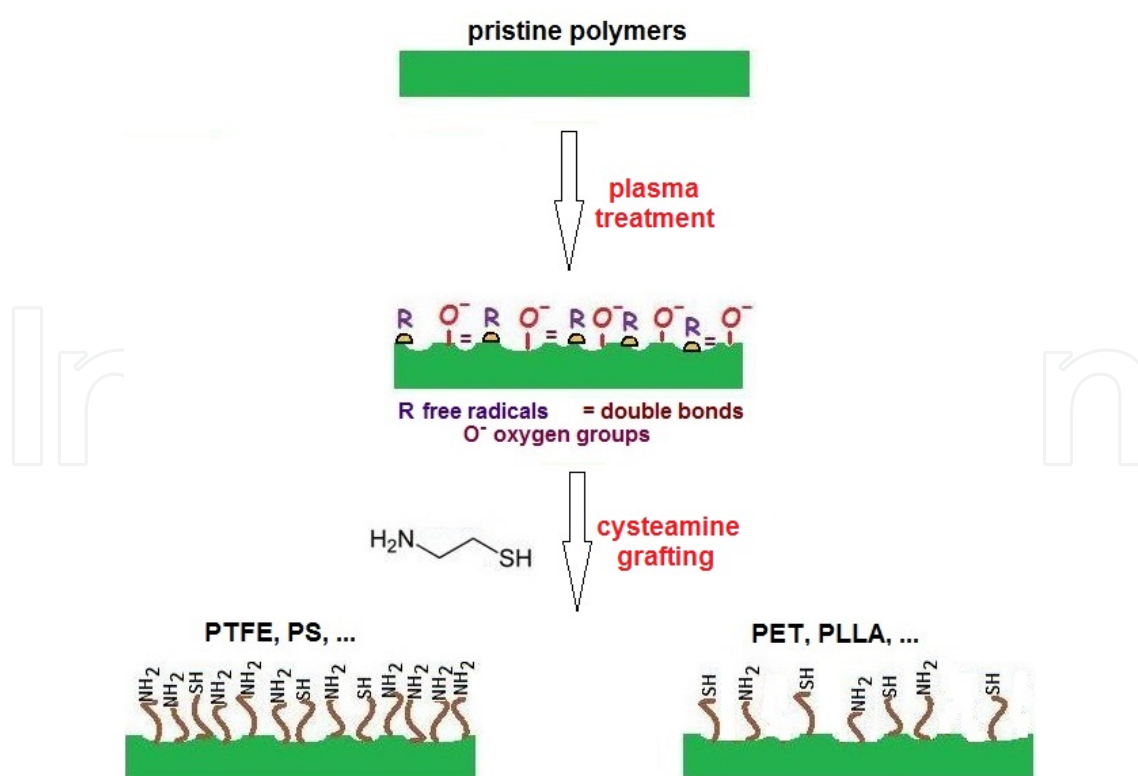


Figure 13. Schematic diagram of the grafting of cysteamine on plasma-treated polymers [112].

5. Conclusions

Surface properties of polymer substrates may be significantly enhanced by different treatment methods. Laser and plasma treatment or grafting processes can be applied to alter surface wettability, which can be also influenced by several other factors, including surface chemistry (introducing new functional groups on the solid substrate surface) or morphology (specific pattern and roughness change). The surface and interface properties of polymers play a key role in many technological processes, such as polymer processing, metallization, or their biocompatibility. All these processes can be controlled by wetting and adhesion phenomena. Based on the conclusions of the wettability measurement, we can estimate the surface chemistry with regard to polar or nonpolar functional groups as well as acidic or basic sites available at the modified surface region. The wettability changes in the laser-treated surface with respect to the type of laser treatment (excimer laser, fs/ns laser, etc.) and the dependence of the CA on the processing parameters of laser treatment (number of pulses and laser fluence) were described. The changes in wettability of polymers and biopolymers due to the treatment and during aging were described. Related properties (morphology and chemistry changes, and ablation) were discussed with respect to the CA and surface-free energy of the surface. The polymer generally has a low surface reactivity. Different types of plasma treatment were described in detail with respect to the change of the surface properties of exposed substrates. A broad range of functional groups can be introduced at the surface by variation of the gas that is used or by consequential grafting processes. The influence of grafting of either metal nanoparticles (e.g., Au) or chemical substances (e.g., PEG) on the wettability of modified polymers was described in detail. The properties of plasma treatment and grafting procedures that have a positive influence on the spreading, proliferation activity, and homogeneity of the distribution of several cell types were introduced.

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