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Surface Functionalization of Organic Materials by Weakly Ionized Highly Dissociated Oxygen Plasma

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Abstract. A review on surface modification of different polymers by treatment in oxygen plasma is presented. Plasma is created in a high frequency inductively coupled gaseous discharge at the power of about 200 W. In such discharge created in pure oxygen, plasma with the following parameters is obtained: the electron temperature of about 50.000 K, the charged particle density around $1 \times 10^{16} \text{ m}^{-3}$, and the neutral oxygen atom density of the order of 10^{21} m^{-3} . A huge flux of neutral oxygen atoms on the surface of samples exposed to plasma assures for rapid interaction with polymer materials. The modification of surface properties of the following polymers was studied: polyethyleneterephthalate (PET), polyethersulphone (PES), polyphenylenesulfide (PPS), Nylon 6 polyamide (PA6), polytetrafluoroethylene (PTFE), polystyrene (PS), polypropylene (PP) and cellulose (ink-jet paper and textile). The polymer samples were treated for 3 s in oxygen plasma at a pressure of 75 Pa where the O-atom density was the largest at $4 \times 10^{21} \text{ m}^{-3}$. The appearance of the functional groups on the surface of the samples was monitored by high resolution X-ray photoelectron spectroscopy (XPS). The results show that oxygen plasma treatment is an effective tool for surface modification. On all polymer surfaces increased concentration of oxygen is detected. The high resolution C1s peaks indicate formation of several new oxygen-containing functional groups. On all polymers groups like C-O, C=O and O=C-O are observed. The concentration of these groups depends on the type of polymer. The highest uptake of oxygen by the polymer was found for cellulose and the lowest for polypropylene. The only exception was polymer PTFE where practically no chemical changes were observed after plasma treatment.

1. Introduction

1.1. Surface energy and adhesion

Surface properties of materials depend on the properties of bulk materials as well as surface contaminants. The surface energy is largest for metals, followed by ceramics and glasses, and is lowest for non-polar polymers. Even carefully cleaned materials are often covered with very thin films of different impurities such as native oxide films and traces of hydrocarbons that definitely modify the original surface energy of pure materials. The surface energy often determines the adhesion of different coatings on the substrates. Apart from the roughness, the surface energy is usually the key parameter that affects the quality of coatings on polymers and polymer matrix composites. Modern industry requires components that are made from materials with desired mechanical, chemical, optical and electrical properties, and are coated with different films often incompatible with the substrates. In such cases, the surface properties should be modified without modification of the bulk properties.

Several techniques have appeared to reach this goal: they include a variety of wet chemical treatments, modification by energetic particle beams and application of gaseous plasma. Although atmospheric plasmas are increasingly popular, low pressure plasmas have some advantages. The main advantage of low pressure plasma is spreading over a large volume that assures for rather uniform treatment of three dimensional objects with a complex shape.

1.2. Plasma treatment of selected polymers – state of the art

Many materials including most polymers and polymer matrix composites have poor adhesion properties and wettability. This is especially the case of hydrophobic polymers (such as polypropylene, polystyrene and polytetrafluoroethylene). The surface energy should be increased in order to assure a rather good adhesion of various coatings. The process that allows for increasing the surface energy is called surface activation. The surface of organic materials should be activated before printing, painting, coating, for improving biocompatibility etc. One of the best methods for modifying the surface properties of polymer materials is plasma treatment. Plasma treatment is an ecologically benign method and is gradually replacing traditional wet chemical techniques, which usually involve application of ecologically unfriendly chemicals. A broad range of surface energy can be achieved by using appropriate plasma for polymer treatment, from extreme hydrophilicity to significant hydrophobicity. Increased hydrophobicity is usually achieved by application of plasma rich with fluorine, while hydrophilicity is often achieved using oxygen plasma. In some applications, especially to increase the biological compatibility of organic materials, nitrogen or ammonia plasma gives better results [1]. It should be noted that plasma treatment usually does not produce only one type of a functional group on a polymer surface. Typically, several different functional groups appear on the surface of polymer during plasma treatment. It is therefore necessary to apply such plasma that facilitates formation of the functional groups that are most important for a given application and to attempt to shift the distribution in favour of a specific functionality by changing plasma parameters [2]. Oxygen plasma treatment usually causes formation of different functional groups such as C-O, C=O, O=C-O. Sometimes, more exotic groups can be produced on the surface of some polymers [2,3].

Literature reports different treatment times used for surface modification of polymers ranging from milliseconds [4,5] to several minutes [6]. A millisecond treatment often causes oxidation and removal of surface contaminants which is often sufficient to improve surface wettability. A further treatment usually causes chemical bonding of oxygen atoms at active sites on the polymer surface, leading to formation of various functional groups that modify the surface wettability. With prolonged treatment time excessive chain scission may appear leading to a layer of low-molecular-weight fragments on the surface [3]. Also, prolonged treatment often causes chemical etching of polymer materials, increased sample temperature and eventual irreversible damage of the bulk properties. In many cases, the longer exposure of the surface, not only of polymers, leads to creation of various nanostructures [7-12].

An important drawback of plasma treatment for activation of polymers is ageing. Functional groups formed on the plasma treated surface are not stable with time, as the surface is in non-equilibrium condition and tends to approach more energetically favorable state, often recovering to its untreated state. Thus, the surface keeps losing its hydrophilic character spontaneously. The ageing effect is obviously more pronounced at higher substrate temperature. Two different processes have been reported to be responsible for surface ageing: the first one is the reorientation of the polar groups into the bulk polymer, and the second one is mobility of small polymer chain segments into the matrix, both leading to different free surface energy. It was also reported that the chain mobility mainly occurs in the amorphous phase of polymers while the mobility in the crystalline phase is fairly limited due to orderly packed structure. Therefore more crystalline polymers are ageing slower. Since plasma treatment can increase the surface crystallinity due to preferential etching of the amorphous phase, the polymers treated for longer times are usually ageing slower [3-5,13]. This is not always true, however – too long treatment times may again lead to faster ageing due to formation of small fragments loosely bound on the surface. Such surface has a greater tendency to ageing because of migration of small

fragments to the bulk. Also, as mentioned above, prolonged treatment often causes chemical etching and thus increasing temperature, that definitely affects the characteristics of plasma treated materials.

Plasma treatment usually affects the surface layers of polymer, often only first few nanometers of material. The bulk properties remain fairly intact [14]. The quickest method to check the effect of plasma treatment on the surface properties is a wettability test by measuring the contact angle of a suitable liquid drop with a well known surface energy – often distilled water. This method is extremely easy to apply although the results are sometimes dubious. As it is a macroscopic method, it does not say anything about the local distribution of surface functional groups, let alone the type of the groups. A suitable method for determination of the type of functional groups on a polymer surface is X-ray Photoelectron Spectroscopy (XPS), often called Electron Spectroscopy for Chemical Analysis (ESCA) [14-16]. Unfortunately, commercial XPS instruments have poor lateral resolution so a microbeam ESCA at an appropriate synchrotron is required for determination of the distribution of functional groups on micro scale. The interpretation of XPS spectra may be quite difficult, too. A fundamental problem in polymer analysis is surface charging due to a loss of surface electrons by X-ray irradiation. This effect is often more pronounced when using a monochromatic source of X-rays, which improves the energy resolution otherwise. To avoid charging effects, neutralization with a low energy electron flux is used. A common practice is manual shifting of unfunctionalized C1s peak (C-C) to 284.8 eV. In some cases, however, almost all carbon atoms in the surface layer of polymer are chemically shifted – an example is cellulose, where all carbon atoms are bound to at least one oxygen atom. For analyses of these materials, a peak which is assigned to hydrocarbon contamination can be used as a reference (if such contaminants are presented). Obviously, it is not possible for polymers treated with oxygen plasma since reactive particles often remove such contaminants even at short treatment time as mentioned above.

Polymers are usually quite stable during typical analysis times. Prolonged exposure to X-rays, however, may cause radiation damage of the sample. In such cases, the photoelectron spectrum slowly changes. A visual evidence of this effect is sample discolouration [17]. For example, this can be very easily observed on paper substrates. Halogen containing polymers can be also quite sensitive to X-ray induced sample degradation. The result is a depletion of halogen atoms with the exposure time [18].

1.3. Oxygen plasma

Plasma is usually created in a gaseous discharge. Electrons are accelerated in an electric field and quickly thermalize at elastic collisions. Their energy distribution function is therefore roughly Maxwellian with the temperature of several eV. Electrons in the high-energy tail of the distribution function have enough energy for direct ionization of gaseous molecules, while those in the low energy part of the distribution function are only capable to excite rotational and vibrational excited states of molecules. In the case of oxygen molecules, the excitation energy for metastable molecules $O_2^1\Delta$ and $O_2^1\Sigma$ is about 1 and 2 eV, respectively, the dissociation energy is 5.2 eV, while the ionization energy is 12 eV. Electrons with the average energy of few eV are therefore likely to excite molecules into metastable states and ro-vibrational states, while dissociation and ionization is less probable.

Excited particles tend to de-excite. There are many channels for de-excitation of oxygen molecules, some of them occur in the gas phase, while the others take place on the surface of the discharge chamber. In any case, the conservation of energy and momentum as well as rules of quantum mechanics should be obeyed. Vibrationally excited states are de-excited in the gas phase primarily by vibration interchanges (V-V transitions) and super-elastic collisions with atoms (V-T transitions) [19]. Neutral oxygen atoms in the ground state can recombine to molecules only at three-body collisions that are unlikely to occur at low pressure (say below few mbar) so they are rather stable in the gas phase.

Surface de-excitations often play a dominant role in low-pressure plasmas. The probability for ion recombination is close to 1 [20], while the recombination of neutral oxygen atoms depends largely on the type of material facing plasma as well as its temperature and morphology. The probability for heterogeneous surface recombination ($O + O \rightarrow O_2$) for many glasses and some ceramics is often low

(the typical order of magnitude in 10^{-4}), while for many metals and some porous ceramics it is of the order of 10^{-1} [21-22].

The density of different excited species in plasma depends on excitation and de-excitation probabilities. The excitation probabilities depend mostly on electron density and temperature, while the de-excitation probabilities depend on gas pressure and surface properties. By choosing smooth materials with low recombination coefficients for recombination of O atoms it is often possible to achieve plasma with a low density of ions but a very high density of neutral atoms. It is often possible to obtain oxygen plasma with the ion density below 10^{16} m^{-3} and the neutral atom density above 10^{21} m^{-3} [23-26].

Reactive particles created in oxygen plasma react with organic materials at certain rates. The rates depend on the type of polymer and particle as well as the sample temperature and particles kinetic temperature. High oxidation selectivity for different types of organic materials can only be obtained with cold plasmas. Cold plasma is a state of gas with a low kinetic energy of heavy particles, i.e. all particles except electrons. The low kinetic energy of heavy particles is assured if their heating is minimized. There are some channels for heating heavy particles in plasmas. Elastic collisions between fast electrons and heavy particles do not lead to substantial kinetic energy exchange due to a small mass of the electrons. The major channel for heating heavy particles at collisions with energetic electrons is a dissociation event. At direct electron impact dissociation, the excessive kinetic energy of the electron can be observed as the kinetic energy of newly formed atoms, which can move apart with a substantial kinetic energy. Such energetic atoms get effectively thermallized at elastic collisions with other heavy particles. A good way to avoid this sort of plasma heating is application of plasma with a rather low electron temperature.

Another mechanism of heating heavy particles is super-elastic collisions between vibrationally excited molecules and oxygen atoms. The reaction cross-section is large [20]. The only way to avoid such collisions is application of fully dissociated plasma where such collisions are unlikely to occur.

An important channel for heating heavy particles may be acceleration of ions in an electric field. The ions are accelerated in electric field as are the electrons. As long as the electric field frequency is low, the ions can follow any change of the local electric field. The energy an oxygen ion can pick from the electric field is

$$W = (e^2 E^2) / (2m\omega^2). \quad (1)$$

Here, e is the ion charge, E peak electric field, m ion mass and ω electric field frequency. The kinetic energy an oxygen ion in a high vacuum can gain in the electric field therefore depends on the frequency. As long as the frequency is low (say below 100 kHz), the ions are well accelerated in the field. But as the frequency is increased, the ions are not able to follow the field. At the frequency of about few MHz, the kinetic energy an ion can pick from the field is less than the average thermal energy of an ion at room temperature. This means that ions in the electric field with a frequency above 10 MHz cannot pick energy worth mentioning. As long as the electric field frequency is higher than 10 MHz, the ions thus cannot be accelerated in the field and cannot contribute to neutral gas heating.

Upper considerations lead to the conclusion that best oxygen plasma for selective oxidation of different materials is created in a radio-frequency discharge. A high degree of dissociation of oxygen molecules is obtained in a discharge chamber made from glass, which has a smooth surface and a low coefficient for recombination of oxygen atoms. There are two extreme modes for RF generator coupling: i) capacitive, and ii) inductive. In practice, the coupling is often a mixture of both extremes. Inductive coupling is often obtained using a coil wounded around a glass tube. In this case, electrons are accelerated in induced electric field sustained due to alternating magnetic field in the coil. The electric field at the axis is rather low, and is increasing towards the edge of the glass tube.

Another extreme is capacitive coupling. In this case, the charged particles are accelerated in the alternating electric field between two parallel electrodes. A sheath with a substantial potential is established next to the powered electrode (which often has a smaller area than the grounded chamber). As long as the sheath is almost collisionless (i.e. the mean free path is larger than the sheath thickness)

the ions entering the sheath from the gas phase are accelerated towards the electrode and do not transfer kinetic energy to other particles. They bombard the electrode and some are reflected as neutral fast atoms or molecules. These fast particles do heat the neutral gas. The heat exchange between positive ions and other heavy particles is increased in the case the sheath is not collisionless. In such cases there are more channels for kinetic energy exchange in the gas phase. This often occurs at elevated pressure, say above 0.1 mbar.

As the electric field frequency increases towards the microwave range, the ions can gain practically no energy from the field, and also electrons cannot pick as much energy as in the case of radio-frequency discharges. As a general rule, the electron temperature in simple microwave discharges is always lower than in radio-frequency discharges with comparable power. More energy is transferred to neutral gas heating so the microwave plasma is never as cold as the RF plasmas.

Parameters of low pressure plasma created by inductively coupled RF discharge in a glass tube depend on discharge power and pressure. Typical values are as follows: neutral gas kinetic temperature is often equal to ion kinetic temperature and is a bit more than room temperature - values between 300 and 500 K are common. The electron temperature is often about 50.000 K or more. At the pressure of few 10 Pa, the density of electrons and ions is often between 10^{15} and 10^{16} m^{-3} , while the density of neutral oxygen atoms is of the order of 10^{21} m^{-3} . The plasma potential is often of the order of 10 V and the Debye length about 10^{-4} m . The density of neutral oxygen atoms is certainly the most important parameter.

Several methods have appeared to measure the O density in highly dissociated oxygen. The methods include optical spectroscopy [27-36], mass spectrometry [37,38], gas titration [25,39] and catalytic probes [40-55]. The latter was found to have some advantages over other techniques, as catalytic probes enable real/time measurements and do not disturb the original concentration of O atoms. The disadvantages include a poor understanding of surface recombination phenomena and sensitivity to high-frequency interferences. From the latter point of view, fiber optics catalytic probes (FOCP) have a definite advantage: as any connection is made optical, they are completely immune to stray effects caused by a high frequency electromagnetic field [51-55]. On the other hand, the FOCPs cannot measure low densities of O atoms.

The interaction of inductively coupled oxygen plasma with solid materials is almost entirely potential. As shown in upper text, the ion density is usually below 10^{16} m^{-3} and their kinetic energy at the sample surface about 10 eV. On the other hand, we have neutral atoms with the density often exceeding 10^{21} m^{-3} . The dissociation degree therefore exceeds the ionization fraction by 5 orders of magnitude if not more so. A large flux of O atoms onto a sample surface assures rich surface chemistry if the samples are organic materials. The first effect of interaction is removal of surface organic impurities, followed by surface functionalization with oxygen-rich functional groups. Next effect is slow etching of the organic material. [56-58] Since the interaction is almost purely potential, the etching largely depends on the nature and structure of organic materials.

2. Experimental

2.1. Experimental setup

Experiments were performed with different polymers including PP, PS, PET, PES; PPS; PA6, PTFE and cellulose materials like ink-jet paper and textile. The samples of these materials were treated in the experimental system shown in figure 1. The system is pumped with a two-stage oil rotary pump with a pumping speed of $16 \text{ m}^3/\text{h}$. The discharge chamber is a borosilicate glass (Schott 8250) cylinder with a length of 200 mm and an inner diameter of 36 mm. A narrow glass tube with an inner diameter of 5 mm and a length of 6 cm leads to the afterglow chamber, which is also a borosilicate glass cylinder, with a length of 400 mm and an inner diameter of 36 mm. Plasma is created inside the discharge chamber with an inductively coupled RF generator [59-62], operating at a frequency of 27.12 MHz and an output power of about 200 W. The plasma parameters are measured with a double Langmuir probe and a catalytic probe. The Langmuir probe is placed into the discharge chamber, while the

catalytic probe is mounted in the afterglow chamber. Commercially available oxygen is leaked into the discharge chamber, as shown in figure 2. The pressure is measured with an absolute vacuum gauge. The pressure is adjusted during continuous pumping using a precise leak valve.

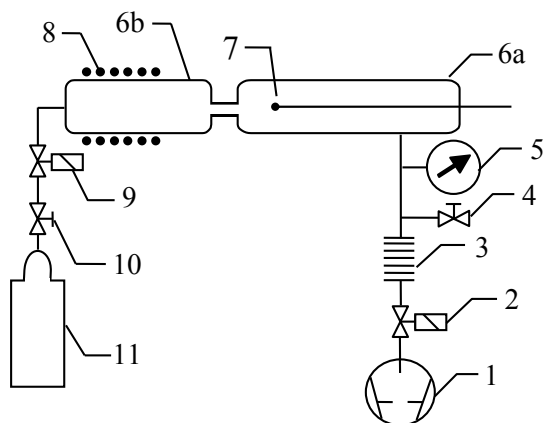


Figure 1. Schematic of the experimental setup: 1 – rotary pump, 2 – gate valve, 3 – Hopkins trap, 4 – air inlet valve, 5 – vacuum gauge, 6a – discharge chamber, 6b – post-discharge chamber, 7 – catalytic probe, 8 – RF coil, 9 – leak valve, 10 – high-pressure valve, 11 – oxygen.

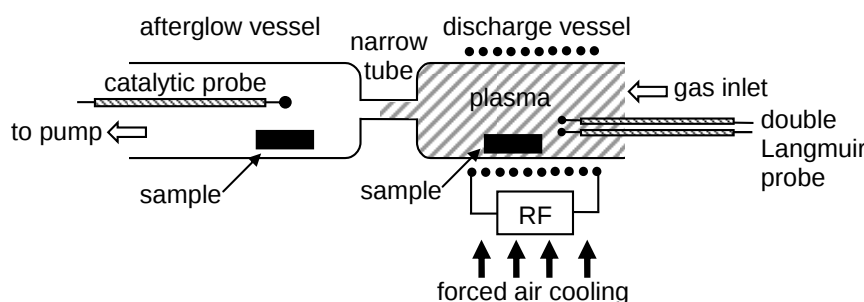


Figure 2. The discharge chamber.

2.2. XPS characterization

The samples were exposed to air for a few minutes after the plasma treatment and then mounted in an XPS instrument (TFA XPS Physical Electronics). The base pressure in the XPS analysis chamber was about 6×10^{-10} mbar. The samples were excited with X-rays over a 400- μ m spot area with monochromatic Al $K_{\alpha 1,2}$ radiation at 1486.6 eV. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. The energy resolution was about 0.6 eV. Survey-scan spectra were made at a pass energy of 187.85 eV, while C 1s, S 2p, N 1s, F 1s and O 1s individual high-resolution spectra were taken at a pass energy of 23.5 eV and a 0.1-eV step. Since the samples are insulators, we used an additional electron gun to allow for surface neutralization during the measurements. The spectra were fitted using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer. The curves were fitted with symmetrical Gauss-Lorentz functions. The peak width (FWHM) was fixed during the fitting process.

3. Results and discussion

3.1. Plasma characterization

Figure 3 represents the density of electrons in the discharge tube as measured with a double electrical probe. The density reaches its highest value at the pressure of about 20 Pa. At lower pressure it decreases rapidly with decreasing pressure (below about 1 Pa plasma cannot be ignited any more) while at higher pressure it decreases slowly with increasing pressure. This phenomenon is explained

by more frequent collisions of electrons at higher pressure. Namely, as mentioned above, the electrons gain maximal energy from the induced electric field when the mean free path is equal to the oscillation amplitude. As pressure becomes large, this is not the case any more: electrons suffer collisions before they can reach the maximal oscillating energy in the electric field. As the result of such collisions the electron temperature is lowered and so is the ionization probability. At pressure above 200 Pa plasma cannot be ignited any more.

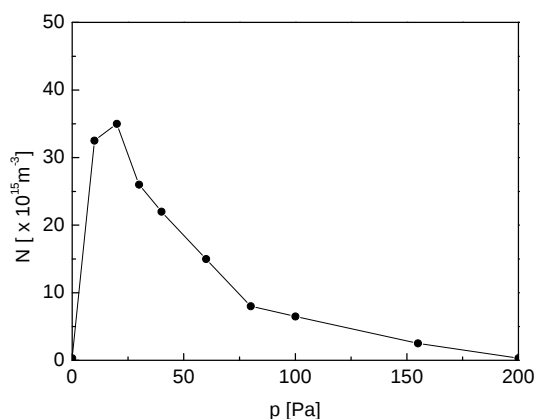


Figure 3. The plasma density versus pressure.

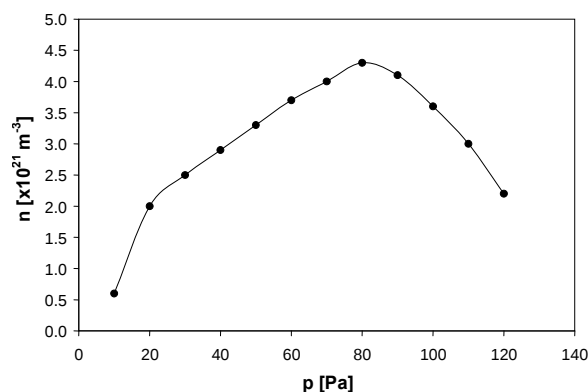


Figure 4. The density of neutral oxygen atoms versus pressure.

Figure 4 represents the density of neutral oxygen atoms in the early afterglow (at the catalytic probe position). In the plasma itself, the O-atom density is somewhat larger. At low pressure the O-atom density is rather low and slowly increases with increasing pressure. As the pressure is increased, the O-atom density increases monotonously until it reaches a broad maximum. At high pressure, the O-atom density decreases with increasing power. The appearance of maximum on the curve presented in figure 4 is explained by different mechanisms of oxygen atom production and loss. At low pressure, the O-atom density is limited by surface effects rather than the discharge power. At high pressure the limiting factor is the poor density of electrons as well as their temperature. At even higher pressure the gas-phase atom loss by three-body would become important if the power were increased. The optimal conditions for a large O-atom density are met at pressure between about 50 and 100 Pa. In this range, the O-atom density depends largely on the discharge power: a higher power would cause a higher density. The pressure at which the maximum appears depends on power, too: at higher power the maximum is shifted to a higher pressure. In any case, the theoretical limit of the O-atom density is full dissociation.

Since the neutral oxygen atom density exceeds the oxygen ion density by orders of magnitude, the experiments with polymer treatment were performed at the maximum of the O density, i.e. the pressure of 75 Pa.

3.2. Surface activation of polymers

Different polymers were exposed to oxygen plasma. They include:

- only carbon and hydrogen containing polymers: aliphatic polypropylene PP (figure 5a) and aromatic polystyrene PS (figure 5b)
- polymers containing oxygen: polyethyleneterephthalate PET (figure 5c) and cellulose CELL (figure 5d) like textile and ink-jet paper
- polymers containing sulphur: polyphenylenesulfide PPS (figure 5e) and polyethersulphone PES (figure 5f)
- a polymer containing nitrogen: Nylon 6 polyamide PA6 (figure 5g)
- a polymer containing fluorine: polytetrafluoroethylene PTFE (figure 5h)

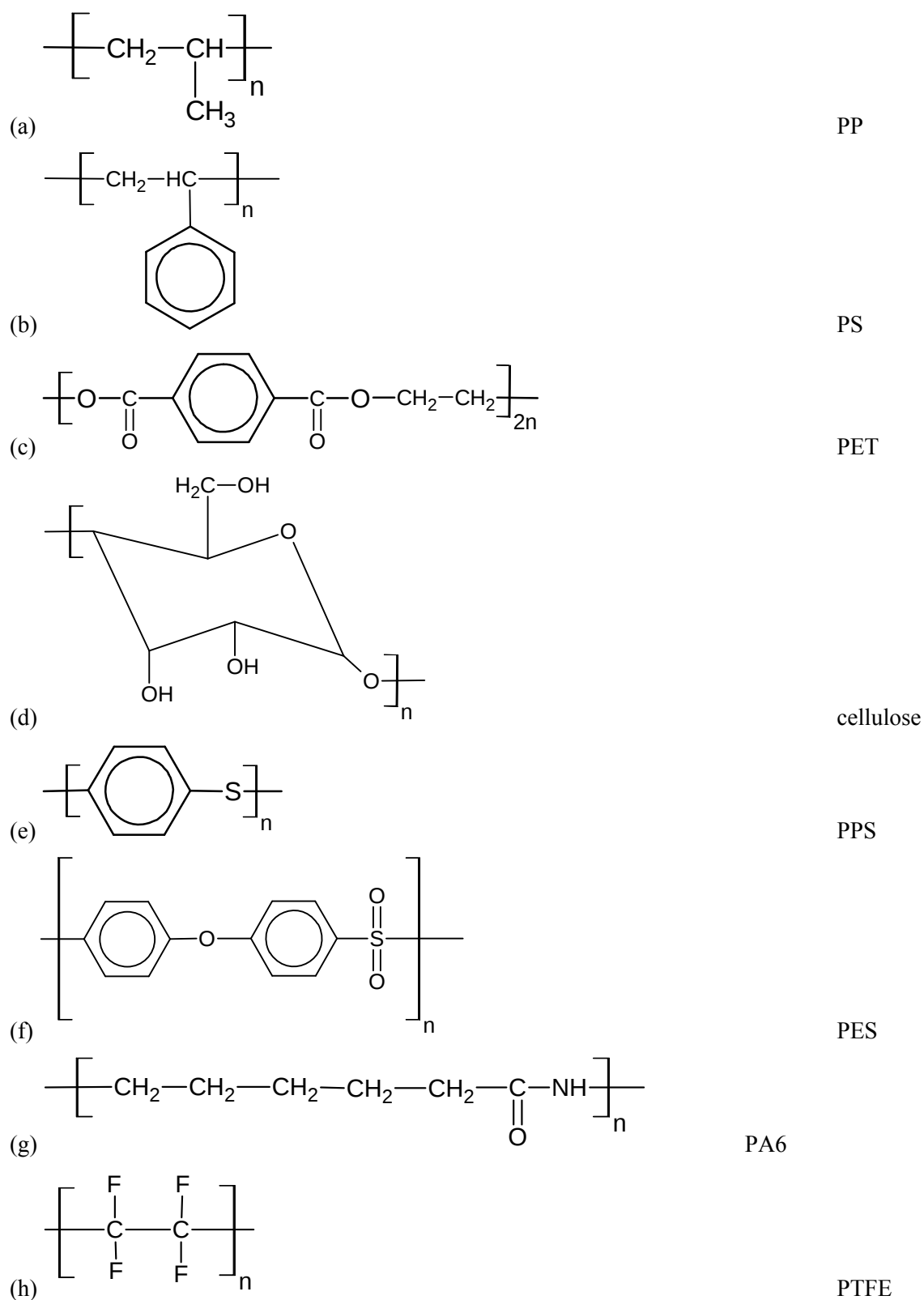


Figure 5. Structure of polymers used for plasma activation: (a) PP, (b) PS, (c) PET, (d) cellulose, (e) PPS, (f) PES, (g) PA and (h) PTFE.

3.2.1. Carbon containing polymers. Carbon containing polymers consist of carbon and hydrogen only. Therefore their high resolution XPS C1s peak (thereafter: carbon peak) is rather uniform and positioned at a binding energy of 285 eV which corresponds to C-C and C-H bonds. Since there is no oxygen in the original polymers, they are very good candidates for studying the effect of oxygen plasma treatment, because it is easy to observe new peaks due to oxygen incorporation into the surface after plasma treatment. One of such candidates is PP which consists of aliphatic chain containing carbon atoms (figure 5a). Figure 6a represents the carbon peak for the untreated PP and PP treated in oxygen plasma for 3 s. As already mentioned the C1s peak of untreated sample is uniform, while the peak after the treatment clearly reveals an appearance of new peaks resulting from plasma oxidation. A more detailed picture of these new functional groups is obtained using a curve fitting procedure (figure 6b). Besides the main peak that corresponds to C-C bonds and is assigned C1 in figure 6b, there is another peak C2 which corresponds to C-O bonds, a peak C3 which corresponds to C=O bonds and a peak C4 which corresponds to O-C=O bonds.

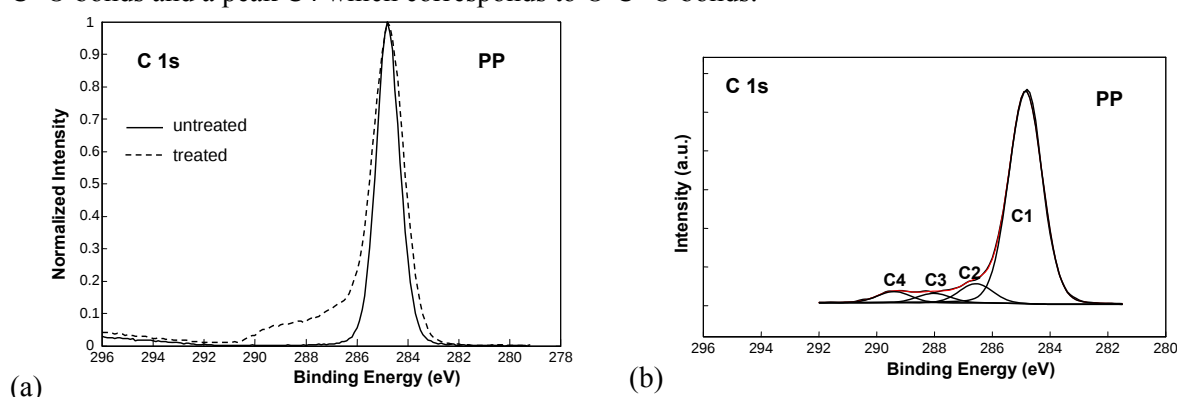


Figure 6. High-resolution C 1s peak of untreated (a) and treated (b) PP surface.

Similar effect is observed for plasma treated PS (figure 7a) which is another example of a structurally simple polymer. Here, plasma induced modifications are more pronounced indicating a higher concentration of new functional groups at the surface. In this case, not only peaks C2, C3 and C4 are observed, but an additional peak C5 appears at a binding energy of 290 eV (figure 7b) which may correspond to -C(=O)-O-C(=O)- or to -O-C(=O)-O- functional groups on the surface [18].

Another important characteristic of untreated PS in comparison with untreated PP is a small peak at a binding energy of about 291.5 eV (figure 7a), which is not observed in the case of PP. This peak is due to the $\pi\text{-}\pi^*$ shake-up transition and it is characteristic for the aromatic phenyl ring. Therefore, this peak is observed only at polymers having phenyl rings [2,18]. Changes in the intensity of this peak can provide information regarding the extent of ring-opening induced by plasma treatment. In our case, after the plasma treatment, the intensity of this peak decreased significantly indicating that plasma caused a destruction of the phenyl ring in PS.

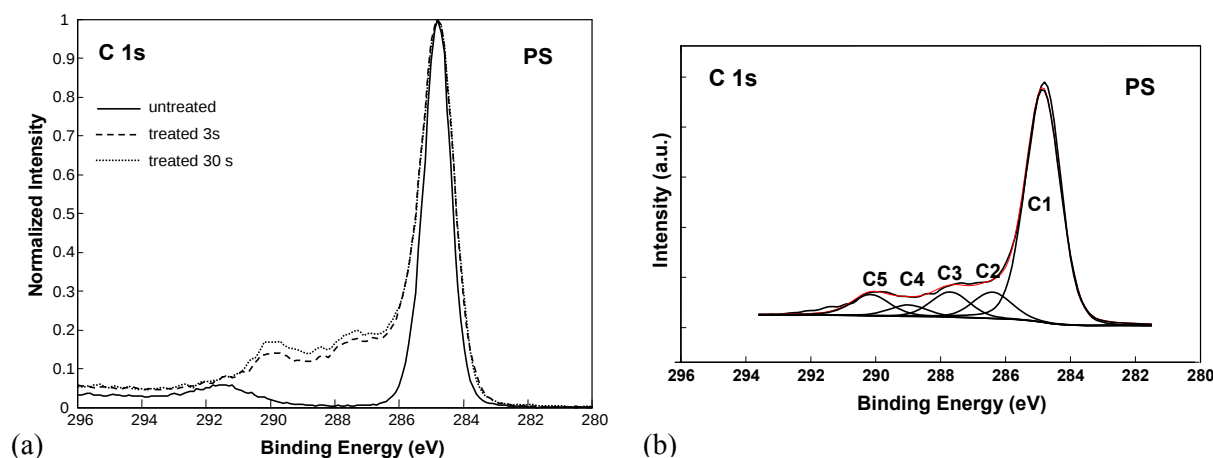


Figure 7. High-resolution C 1s peak of untreated (a) and treated (b) PS surface.

3.2.2. Oxygen containing polymers. The carbon C1s peak of oxygen containing polymers does not have such a simple shape like that of pure hydrocarbons. The interpretation of XPS spectra after oxygen plasma treatment of these polymers can be quite difficult due to problems in distinguishing between original and newly formed oxygen functional groups on the surface. A polymer which has been extensively studied is PET (polyethyleneterephthalate) [4,5,12,63-66]. Figure 8a shows the carbon peak for an untreated PET. We can observe three peaks: C1 corresponds to C-C bonds in phenyl ring, C2 corresponds to C-O bond (ether) and C3 corresponds to O=C-O bond (ester group) (figure 5c). After the plasma treatment the intensity of the peaks C2 and C3 increases remarkably (figure 8b) and a new peak C4 is observed. This peak has been attributed to C=O functional group [63-67]. The modifications of the functional groups on PET polymer are clearly visible indicating extremely strong surface activation.

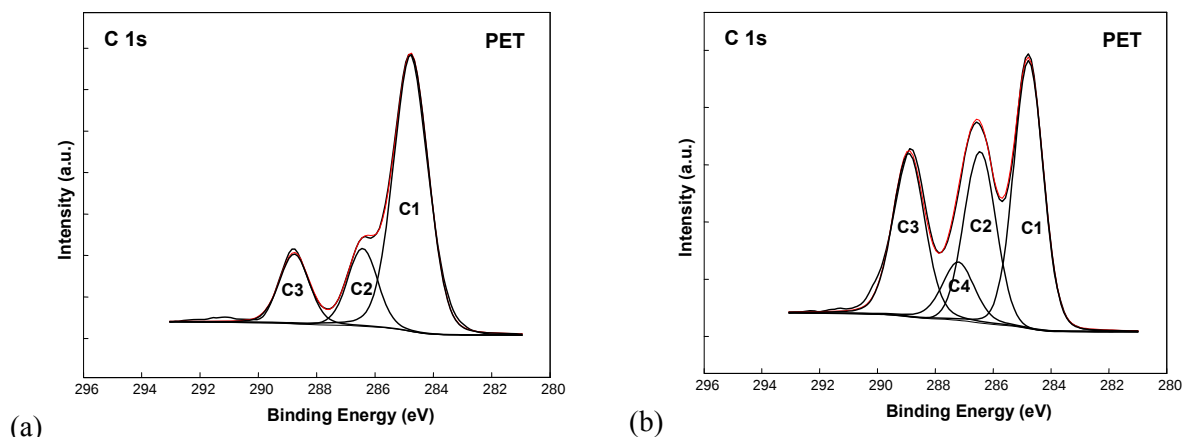


Figure 8. High-resolution C 1s peak of (a) untreated and (b) treated PET surface.

Interesting enough, such increase in the surface activation is not observed for cellulose [68]. In this material, all carbon atoms are bound to at least one oxygen atom (figure 5d): each cellulose unit contains five carbon atoms with a single bond to oxygen C-O (hydroxyl groups) and one carbon atom with two bonds to oxygen O-C-O. Thus, for pure cellulose one would expect just two peaks C2 and C3. In our case we study 2 different products made from cellulose: textile and paper. For the case of textile (figure 9a), C1 peak is clearly observed as well. This peak is probably due to the presence of surface contaminants that appeared on the surface during or after production. After the plasma

treatment of textile (figure 6b), the contribution of C3 peak is increased, while the contribution of C2 and C1 peaks decreased. Furthermore, a new peak C4 with a binding energy of 289.2 eV appeared. An increase of the C3 peak is associated with either an increase of the surface concentration of O-C-O group, or a formation of a new functional group C=O, or both. The new peak C4 is attributed to a formation of the O=C-O group. Here, it is worth mentioning that, since carbon atoms in the cellulose are already bonded to at least one oxygen atom, the incorporation of more oxygen atoms from plasma causes strong degradation of the molecule. This can be a reason for the decrease of the relative intensity of the C2 peak.

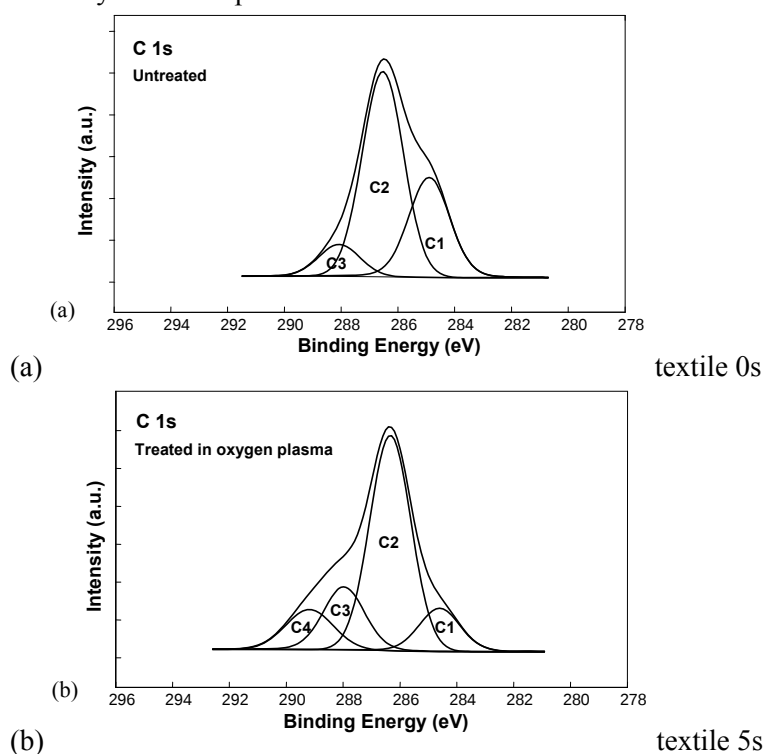


Figure 9. High-resolution C 1s peak of untreated (a) and treated (b) textile surface.

oxidized and partially removed (“burnt”), while inorganic particles (calcium carbonate) remained. In the carbon peak of the ash we can observe peaks C1, C2, C3 and C4 like in the case of textile, and a new peak C5, which is associated to carbon atoms in CaCO_3 . Such prolonged plasma treatment is known as plasma ashing and it allows for detection of inorganic material which is present in organic samples in so small quantities that cannot be detected with standard methods, since the concentration is below the detection limit of many techniques for surface characterization.

Interesting results are obtained at plasma activation of another cellulose-made product, ink-jet paper. Commercially available paper was used for current experiments. Apart from cellulose, it contains about 10 weight % of alkyl ketene dimer (AKD) and few weight % of CaCO_3 . In the untreated sample (figure 10a) we can see a carbon peak typical for cellulose. We can not observe any carbon peak associated with carbon in CaCO_3 , although this material is present in the bulk. The situation after 3 s of treatment (figure 10b) is quite the same as for untreated sample – it is difficult to see any changes (apart from largely increased C4 peak), while after 200 s of treatment the situation is much different (figure 10c). After 200 s of plasma treatment the organic part (cellulose) was probably heavily

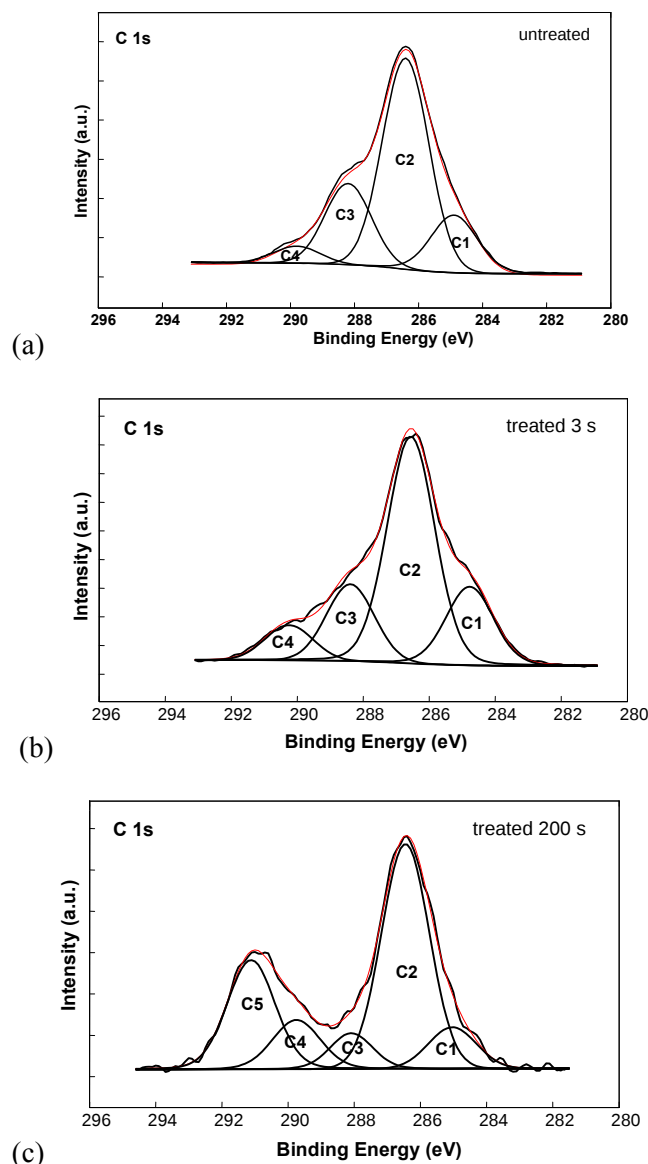


Figure 10. High-resolution C 1s peak of untreated (a) and treated (b) surface of ink-jet paper.

3.2.3. Sulphur containing polymers. In XPS characterization of sulphur containing polymers there is a well known problem with overlapping of the peaks due to C-C bond at a BE of 285 eV and C-S bond at a BE of 285.3 eV [69,70]. The carbon peak of an untreated PES consists of 2 peaks only (figure 11a): the larger one C1 at 285 eV and the smaller one C2 at 286.5 eV. The larger peak corresponds to C-C bonds, while the smaller peak corresponds to C-O bonds. As already mentioned, it is difficult to see the C-S peak since it is overlapping with the peak C1. Figure 11b shows the carbon C1s peak of the plasma treated sample. The carbon peak of the plasma-treated sample is different from the peak of untreated sample. Now, four separate peaks can be observed; a peak C3 that corresponds to C=O, and a peak C4 that corresponds to O=C-O. The peak C2 is somehow enlarged in comparison to the untreated sample [70]. Obviously, carbon atoms in PES polymer get well oxidized during plasma activation.

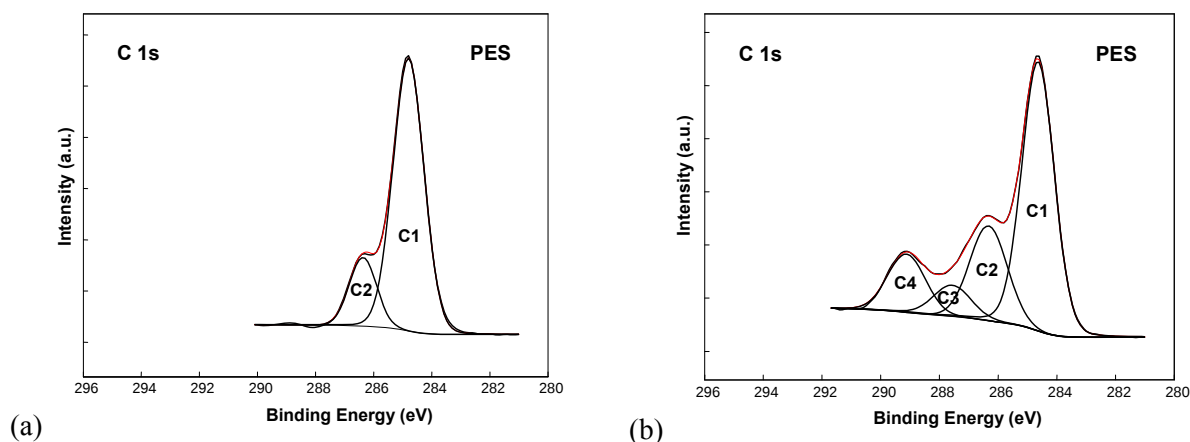


Figure 11. High-resolution C 1s peak of untreated (a) and treated (b) PES surface.

Interesting results are obtained for plasma activation of PPS polymer. As shown in figure 5, sulphur is not bonded to oxygen atoms as in the case of PES, but only to carbon atoms. Figure 12a represents the shape of the carbon peak before and after plasma treatment. Surprisingly enough, the carbon peak of oxygen plasma treated sample is not much different from the untreated sample. One can therefore conclude that the oxygen–carbon bonds are presented in rather small concentrations. Nevertheless, oxidation of carbon (figure 12c) results in formation of C-O, C=O and O-C=O functional groups on the surface like in the case of PES, but at lower concentration. The right mechanism for PPS activation by oxygen plasma can be deduced from figure 12b, however. This figure represents the high resolution S2p peak before and after plasma treatment. We can see that in this case not only carbon is oxidized but also sulphur [45]. Before plasma treatment, sulphur S2p peak (duplet) is positioned at a BE of 163.7 eV corresponding to oxidation state S^{2-} (C-S-C bond). After the oxidation, a new broad peak appears at a BE of about 169 eV. According to the literature, this peak corresponds to either of the double peaks S^{4+} or S^{6+} . Namely, the S^{4+} oxidation state is found at 168.2 and 169.4 eV, and S^{6+} at 169.1 and 170.2 eV, respectively. The oxidation state of sulphur therefore changes dramatically during the treatment with oxygen plasma.

From the XPS results of plasma activation of PPS we can conclude that sulphur is more easily oxidized in this material than carbon. We can not observe this in the case of polymer PES because sulphur atoms in virgin PES (figure 5f) are already bonded to oxygen and further oxidation is not possible. Prolonged oxygen plasma treatment of PES can cause formation of SO_3^{2-} (leading to polymer degradation) which is desorbed from the surface as shown by other authors [69].

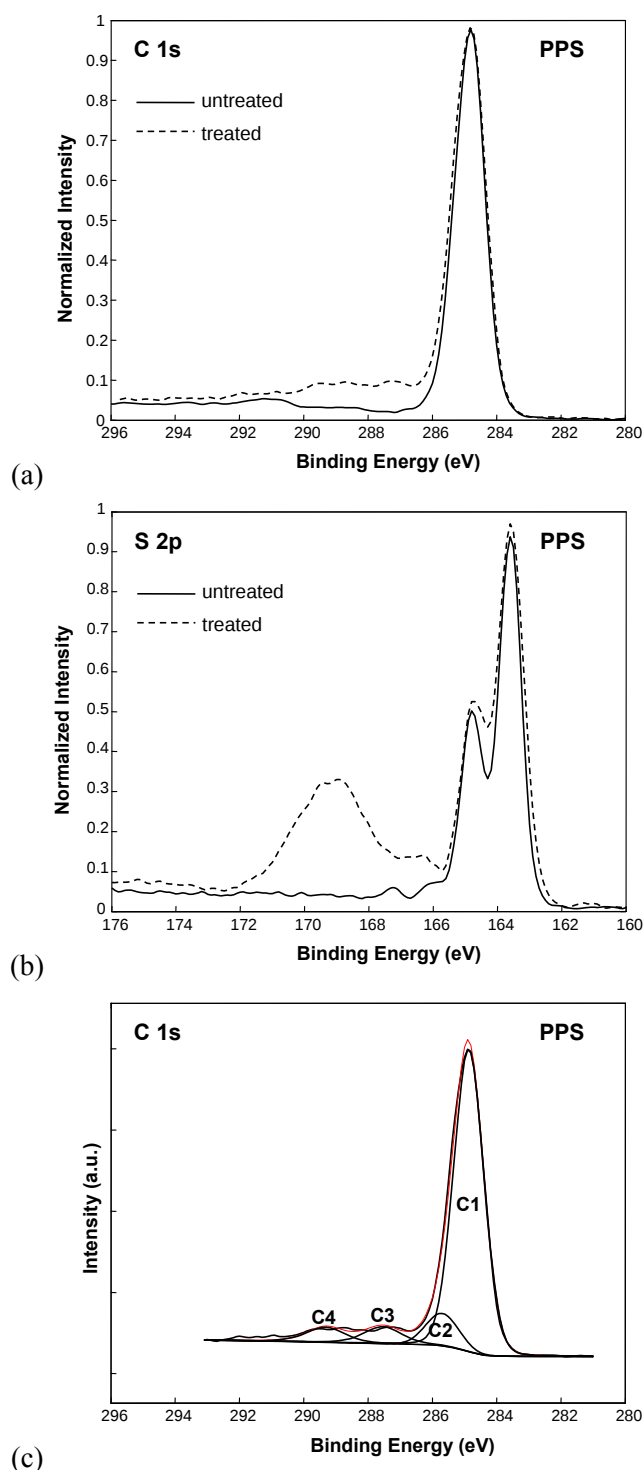


Figure 12. High-resolution C 1s peak of untreated (a) and treated (b) PPS surface.

3.2.4. Nitrogen containing polymers. At plasma treatment of nitrogen-containing polymers we have never observed oxidation of nitrogen atoms (what one might have expected from the results with PPS). Only carbon atoms get oxidized during treatment with oxygen plasma.

One problem associated with XPS characterization of nitrogen containing polymers is a difficult determination of the exact type and concentration of nitrogen functional groups, since there is a

problem with strong overlapping of oxygen- and nitrogen-containing functionalities. They appear at very similar binding energies (figure 13) [18]. Moreover, relevant literature reports different data for binding energies of different nitrogen peaks which are positioned quite close together: C-N (285.5 eV – 286.3 eV), C=N (285.5 eV – 286.6 eV), C≡N (286.7 eV – 287.0 eV) [72-77] and this makes the interpretation of XPS high resolution C1s peak extremely difficult.

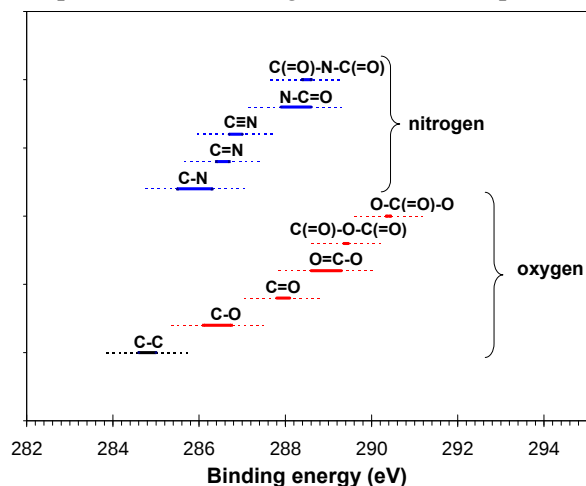


Figure 13. Expected positions of oxygen and nitrogen functional groups: full line – position of the peak maximum, dotted line – peak width (FWHM).

Also, the N1s peak can not give a decisive answer about the nitrogen containing functionalities [78]. The N1s peak is always composed of a single relatively broad symmetric peak that could correspond to different nitrogen states. According to the literature we can find several carbon-nitrogen species (like amines, amides, imides, nitriles, etc.) in the range between 399.1 eV and 400.2 eV [18,78]. As reported by Morent et al., it is very difficult to incorporate nitrogen into polymer surfaces [78]. Therefore, he assumed that during plasma treatment only C-N groups are usually formed on the surface. Amide groups (N-C=O) can be also present on the surface, while the presence of the groups where nitrogen is bounded to oxygen (nitro, oxime and nitrate groups) can be definitively excluded, since they should appear at energies 406-408 eV [18,78] and this is never observed for nitrogen containing polymers treated with oxygen plasma.

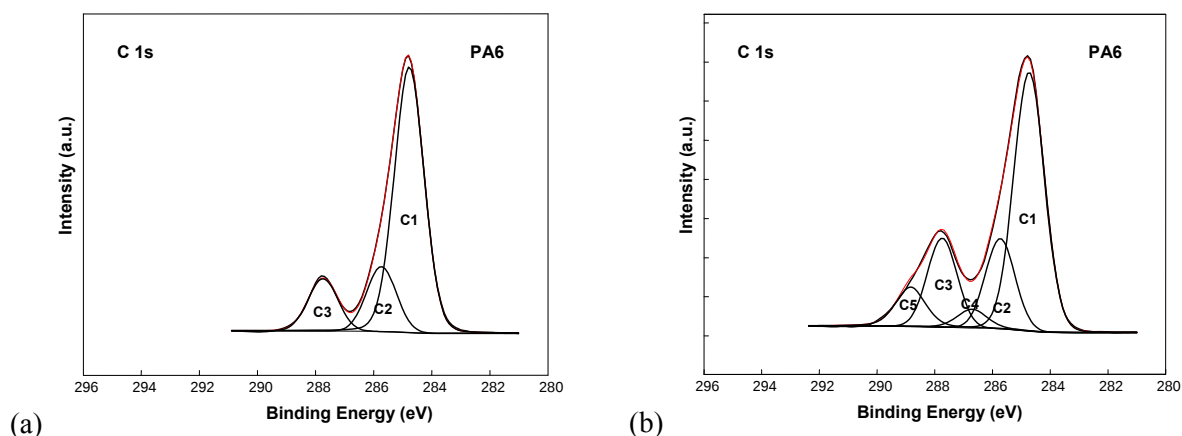


Figure 14. High-resolution C 1s peak of untreated (a) and treated (b) PA6 surface.

As an example of nitrogen-containing polymer we used a commercial polyamide PA6. Figure 14a shows the carbon peak of the untreated PA6 sample. The carbon peak is composed of three peaks: C1 corresponding to C-C bond, C2 at a BE of 286.1 eV corresponding to C-N bond and C3 at a BE of 287.9 eV corresponding to O=C-N bond (amide group). The carbon peak of a PA6 sample treated in

oxygen plasma (figure 14b) shows that the peaks C2 and C3 are increased, and another peak C4 appears as well,. This peak corresponds to the O=C-O functional group. The increase of the C2 component can be explained by formation of C-O groups, that appear at a similar binding energy as C-N group, while the increase of the C3 peak can be explained by the formation of the C=O functional group.

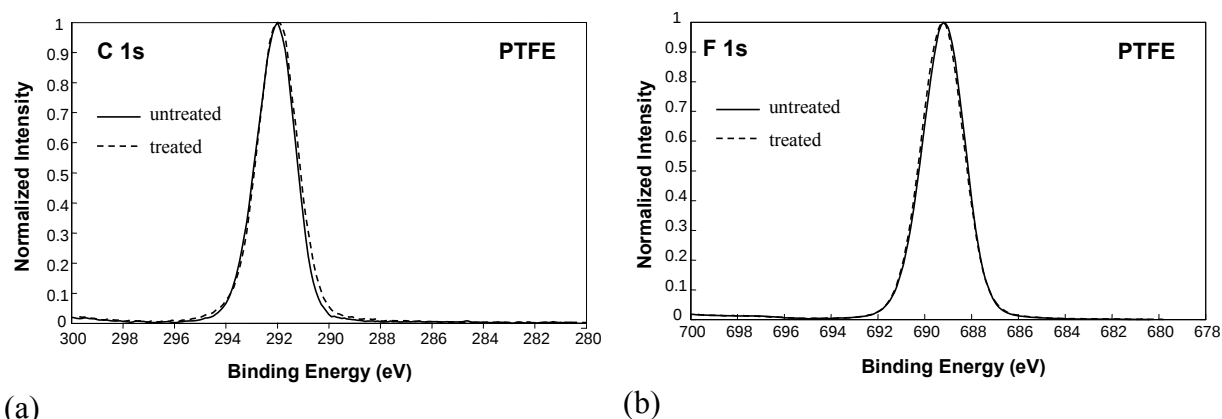


Figure 15. High-resolution C 1s peak of untreated (a) and treated (b) PTFE surface.

Table 1. Surface composition of the polymer samples before and after plasma treatment.

Sample	C	O	N	S	F	Ca	Na	K	O/C
Untreated PA6	76.2	13.1	10.7						0.17
Treated PA6	63.0	25.3	11.7						0.40
Untreated PET	73.4	26.6							0.36
Treated PET	60.0	40.0							0.67
Untreated PES	74.6	20.4		5.0					0.27
Treated PES	57.3	37.8		5.0					0.66
Untreated PTFE	33.3	0.6			66.1				0.02
Treated PTFE	31.7	0.5			67.8				0.02
Untreated textile	64.2	35.8							0.56
Treated textile	49.6	50.4							1.02
Untreated paper	75.3	23.0	1.4			0.4			0.31
Treated paper	48.9	45.2	2.3			2.4	1.2		0.92
Treated paper-ash	29.8	47.6				8.5	2.9	11.2	1.60

3.2.5. Halogen containing polymers. PTFE is a chemically inert polymer. It is very difficult to activate its surface by plasma treatment. Figure 15a shows a comparison of the carbon peak for untreated and plasma-treated PTFE surface. There is practically no difference in the shape of the

carbon peak [79]. Furthermore, the comparison of the fluorine peaks (figure 15b) does not show any difference, either. The survey-scan measurements showed no changes in oxygen concentration at the surface (table 1). For the case of PTFE we performed prolonged treatment in oxygen plasma but no modifications were observed. Even after 10 min of treatment the XPS peaks remained quite the same. So oxygen plasma treatment seems to be ineffective for the case of this polymer. Here it is also worth mentioning that halogen-containing polymers are known to be sensitive to X-ray irradiation, resulting in a decrease in the halogen peak intensity and an increase in the C1s peak intensity [17,18,80]. In our case we did not observe this effect even after several hours of exposure to X-rays.

Table 2. Comparison of concentration of different functional groups for different polymers.

	C-C ³ C-S	C-O ⁴ C-N	C=O ⁴ O=C-N	O=C-O	¹ -C(=O)-O-C(=O)- ² CO ₃ ²⁻
PP untreated	100%	/	/	/	/
PP treated 3s	78.2%	12.1%	5.3%	4.5%	/
PS untreated	100%	/	/	/	/
PS treated 3s	70.7%	8.9%	8.6%	4.1%	7.8% ¹
PET untreated	75.8%	13.0%	/	11.2%	/
PET treated 3s	34.0%	30.4%	3.9%	31.7%	/
Paper untreated	16.3%	57.0%	22.0%	4.7%	/
Paper treated 3s	19.0%	54.9%	18.0%	8.2%	/
Paper treated 200s	8.9%	48.3%	7.1%	11.1%	24.6% ²
Textile untreated	30.7%	60.0%	9.3%	/	/
Textile treated 3s	12.2%	57.7%	17.7%	12.4%	/
PES ³ untreated	82.1%	17.9%	/	/	/
PES ³ treated 3s	52.4%	22.3%	9.8%	15.6%	/
PPS ³ untreated	100%	/	/	/	/
PPS ³ treated 3s	78.9%	9.0%	6.4%	5.7%	/
PA ⁴ untreated	70.2%	16.5%	13.3%	/	/
PA ⁴ treated 3s	55.8%	17.7%	19.0%	7.5%	/

4. Conclusions

Oxygen plasma was found as an effective method for surface modification of different polymers. The only exception was PTFE, which is known as chemically very inert material and it was not possible to functionalize it by exposure to our plasma. On all other samples, a higher oxygen concentration was detected on the surface after the plasma treatment (Table 1). Plasma treatment did not produce only one unique functionality on a polymer surface but different functional groups was created. On all polymers except PTFE new groups like C-O, C=O and O=C-O were observed; only their concentration was different depending on polymer type (Table 2). For example, the rate of incorporation of new species after oxygen plasma treatment at identical conditions was found to be greater for PS than for PP, although both polymers contain carbon and hydrogen only. The surface incorporation of new species depends on the number of available carbon atoms that can bond with the reactive species in the plasma. The primary available carbon atoms are those that are only bonded to

other carbon atoms or hydrogen. Secondary sites would be carbon atoms with only a single bond to oxygen or nitrogen [2,77]. Plasma treatment of sulphur containing polymers resulted in oxidation of sulphur atoms (unless they are already oxidized in the original material), while this is not the case for oxidation of nitrogen containing polymers, where no groups with nitrogen bounded to oxygen were found. The surface chemistry of plasma-treated polymers containing carbon–oxygen or carbon–nitrogen functionalities is more complex and is significantly different from polymers containing only carbon–carbon bonds. Characterization of plasma-induced changes on oxygen- or nitrogen-containing polymers is more difficult due to the more complex chemical structure of the polymer and the number of possible chemical species that can be produced.

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