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Optimization of surface wettability of polytetrafluoroethylene (PTFE) by precise dosing of oxygen atoms

Dane Lojen [a,b], Rok Zaplotnik [a], Gregor Primc [a], Miran Mozetič [a], Alenka Vesel [a,*]

[a] Jožef Stefan Institute, Department of Surface Engineering, Slovenia
[b] Jozef Stefan International Postgraduate School, Slovenia

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ABSTRACT

Fluorinated polymers such as PTFE cannot be functionalized with polar, oxygen-containing functional groups by a one-step treatment with oxygen plasma because the treatment would preferentially lead to surface etching rather than substitution of fluorine with oxygen. A novel method for the functionalization of PTFE is presented. PTFE was initially treated in low-pressure non-equilibrium inductively coupled RF hydrogen plasma in the H-mode to obtain an appropriate surface finish for functionalization with oxygen atoms. The hydrogen-plasma treatment ensured the formation of a polyolefine-like surface film, which was functionalized with polar groups by subsequent exposure to a fluence of O atoms in the range between approximately 1×10^{22} m^{-2} and 1×10^{26} m^{-2}. The evolutions of the surface wettability and composition were studied systematically in this range of O-atom fluences. A deep and rather broad minimum of the water contact angle (WCA) was observed. The minimum of the WCA was correlated to the concentrations of elements in the surface as analysed by X-ray photoelectron spectroscopy. A complete hydrophobic recovery was observed at the largest O-atom fluence, which coincided with the restoration of the surface composition. The surface kinetics upon exposure to O atoms or a weakly ionized oxygen plasma was studied and explained.

1. Introduction

Polytetrafluoroethylene (PTFE) is a non-biodegradable polymer with high chemical and biological resistance and inertness [1]. Because of its physical and chemical properties, PTFE can be used in various applications, from kitchenware to polymeric body implants. Due to its composition, the polymer exhibits low surface energy, large water contact angle (WCA), and thus low wettability, which in turn causes inadequate adhesion of many materials. The consequences include poor printability [2] and glueability [3], as well as the inability for covalent bonding of biomolecules to fluorine-containing materials [4]. These effects were recognized decades ago as limiting factors in the widespread application of such polymers [5,6].

Extensive research has been performed on surface functionalization and improvement of adhesion properties of PTFE. Conventional chemical methods involve etching with sodium-containing corrosive solutions such as Na-naphthalene followed by BH_3 and H_2O_2/NaOH treatments [7,8], immersion in a solution of sodium in anhydrous liquid ammonia [9], solutions of sodium naphtalenide in tetrahydrofuran, direct electrochemical reduction, treatment with an alkali metal amalgam, reduction with benzoin di-anion, deposition of aluminum by evaporation [10]. The latter technique, however, only increases the wettability but not the adhesion since a metal film evaporated on the PTFE surface exhibits a very poor adhesion. The disadvantages of chemical etching include toxicity to humans, ecological hazard, malodor, and PTFE surface coloration [7,11,12]. Other methods for modification of PTFE surface properties are ion irradiation [3], corona treatment [13], and plasma treatment [14].

An environmentally friendlier and safer alternative for the improvement of adhesion and wettability of polymers is treatment with various gaseous plasmas. Gaseous plasma is a medium containing electrons and ions, neutral atoms in the ground and excited states, as well as radiation. Particularly important for surface modification of polymers are photons of energy above the threshold for breaking bonds in polymer materials, i.e. in the UV-C and vacuum ultraviolet (VUV) ranges [15–17]. The VUV radiation is particularly intensive in plasmas sustained by discharges of large power density [18] and often causes significant modifications in surface properties of polymer materials [19]. The surface kinetics upon plasma functionalization also depends on the kinetic energy of positively charged ions and the oxidation potential of

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* Corresponding author.
E-mail address: alenka.vesel@guest.arnes.si (A. Vesel).

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neutral reactive species [20].

Through decades, authors used different plasmas for the functionalization of PTFE: argon [21,22], hydrogen [23–26], oxygen [22,27], nitrogen [21], ammonia [23], water [28] and methane [29]. However, wettability improvements, as measured by WCA, were inadequate compared to the chemical treatments. The best results obtained with plasmas of single molecular gases were WCAs in the range between 50 and 45° and PTFE surface oxygen contents between 10 and 30 at. % [20]. Carefully designed experiments, however, may provide plasma conditions where a superhydrophilic surface finish of PTFE is obtained. For example, [30] reported very low WCA of about 4° after prolonged treatment with argon plasma at the pressure of 10 Pa. The treatment for almost 10 min at the discharge power of 8 W enabled both nanostructuring and surface oxidation.

The authors reported different types of plasmas used for surface modification of PTFE. The first type is treatment with plasmas rich in oxygen. Reactive oxygen species, however, do not have sufficient potential energy for breaking C − F bonds in PTFE. The consequence is a low level of functionalization when treating PTFE by oxygen plasma. The etching process prevails instead of substituting fluorine with oxygen in the surface film [20]. Treatment with oxygen plasma results in the formation of volatile $C_xF_yO_z$ fragments that are desorbed from the surface [31]. The effect was further elaborated by [27], who found that no oxygen was bound to the PTFE surface upon RF self-biasing during the plasma treatment, and the surface roughness increased by the appearance of alveolar structures.

Some authors used oxygen-free plasmas (for example, hydrogen plasma) for the treatment of PTFE. They reported defluorination of the surface film, which was explained by the formation of dangling bonds due to bond-scission by VUV radiation [19,20,32]. Low-pressure RF hydrogen plasma emits up to 20% of power as VUV radiation [15]. Oxygen from the residual atmosphere (particularly water vapour) in the discharge tube or/and after the treatment, when the sample is exposed to air, is bound to the dangling bonds [20].

In our previous research [19], we exposed PTFE to low-pressure RF inductively coupled (ICP) H_2 plasma. We managed to separate the VUV radiation, the flux of charged particles, and the flux of neutral atoms to selectively treat the samples. The samples exposed to H_2 plasma for 1 s exhibited the F/C ratio 0.4, as analysed by XPS. The same ratio was observed for samples exposed to VUV/UV radiation and H atoms. The exposure to VUV only resulted in an F/C of 0.6. Exposure to H atoms only did not cause considerable defluorination. It was hypothesized that the mechanism of defluorination of PTFE in H_2 plasma is based on synergistic effects of VUV radiation (breaking C − F bonds) and H-atoms binding to the dangling bonds [19]. It was reported by several authors including [33–35] that the treatment of polymers with VUV radiation only (for example from exciplex sources) causes significant modification of surface properties. Some polymers treated by VUV radiation at prolonged treatment times assume the superhydrophilic surface finish. However, the effect may be due to the extensive dissociation of oxygen in the gas phase by VUV radiation. For example, it was clearly demonstrated that the oxygen concentration in the ambient atmosphere upon treatment of polymers contributes significantly to the observed polymer wettability [36].

In another research [37], we exposed PTFE to low-pressure RF ICP H_2 plasma running in different discharge modes. We found that PTFE exposed to H_2 plasma in the H-mode for 1 s resulted in a decrease of F/C ratio to 0.2, but the static WCA remained rather large at 83°. If experiments were repeated in the E-mode, longer times were needed to obtain the minimum – i.e. minimal F/C ratio of 0.6 was obtained after several seconds of plasma treatment. The difference between E- and H-modes was assigned to the lack of VUV radiation in the E-mode. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) confirmed the presence of $C_xH_y^+$ and the absence $C_xF_y^+$ ions on the surface film, indicating the formation of a polyolefin-like surface layer. Additionally, the measured WCA value of 80° is typical for polyolefins [37]. This is in accordance with the findings of Yamada et al., who treated PTFE in the afterglow of low-pressure RF ICP H_2 plasma and found the immeasurably low F/C ratio within the surface layer with a thickness of 1 nm using AR-XPS [26].

2. Materials and methods

PTFE foil was purchased from Goodfellow Ltd. (Huntington UK). The foil with a thickness of 0.5 mm was cut to rectangular pieces of 25 × 9 mm. Prior to treatments, the samples were cleaned with ethanol.

The plasma system is schematically shown in Fig. 1. The experimental system consisted of a borosilicate glass discharge tube, a water-cooled copper coil with 6 loops with an additional forced-air cooling and a stainless steel electromagnetic field shielding mounted directly onto the Dressler Hochfrequenz-Technik GmbH impedance matching network, a CESAR Dressler RF generator from Advanced Energy (13.56 MHz), an Aera FC7700 flow controller from Advanced Energy, a MKS baratron and an Edwards E2M80 two-stage vacuum pump.

The PTFE samples were first pretreated in the H_2 plasma. The inductively coupled plasma was sustained in the H-mode. The samples were placed inside the RF coil, as shown in Fig. 1. The treatment time in the H_2 plasma was 1 s. This treatment time enabled defluorination of the surface film [19,37]. The forward power of the RF generator was 385 W, whereas the reflected power was 30 W. The H_2 pressure was set to 25 Pa, and the H_2 flow rate was 140 standard cm^3/min (sccm).

After the hydrogen plasma pretreatment, the samples were treated in the flowing afterglow of oxygen plasma. Oxygen plasma was also sustained in the H-mode. Prior the O_2 plasma treatment, the samples were moved away from the RF coil to the positions marked in Fig. 1. We have chosen the afterglow because the direct exposure of the pretreated samples to a dense plasma in the center of the RF coil would cause immediate etching and thus the loss of the fluorine-depleted surface film. The forward power of the RF generator was set to 465 W, and the reflected power was 100 W. The O_2 flow rate was 105 sccm, whereas the O_2 pressure was 30 Pa. A photo of the O_2 plasma in the discharge tube is shown in Fig. 2. The dense plasma in the H-mode is concentrated in the volume inside the coil, while weak radiation is also observed in the flowing afterglow region, in the direction from the coil towards the pump duct. The samples were treated in the flowing afterglow at various positions, i.e. 150, 300, and 500 mm away from the coil. These positions of the samples are marked in Figs. 1 and 2. Fig. 2 reveals very weak emissivity of the plasma in the flowing afterglow, so a skilled person may conclude that the density of charged particles and/or electron temperature in the afterglow is much smaller than in the plasma within the RF coil. The treatment times of samples exposed to the oxygen plasma afterglow were varied between 0.03 and 100 s.

Neutral oxygen atom densities were measured using a cobalt catalytic probe at the selected coil-to-sample distances. A probe is presented to details elsewhere [38,39]. The O-atom densities at the selected positions are shown in Table 1.

From Table 1, it can be seen that the differences in the O-atom densities and fluxes between all the three coil-to-sample distances are quite small. This means that the recombination of the neutral O atoms along the discharge tube is relatively ineffective. The reasons have been explained elsewhere [16,40].

The samples treated by the flowing afterglow of oxygen plasma were analysed by X-ray photoelectron spectroscopy (XPS) and WCA. WCAs on treated PTFE surface were measured with Krüss DSA-100 drop shape analyzer in conjunction with Krüss Advance 1.10 software (Krüss, Hamburg, Germany). A static water contact angle was measured. A volume of water droplet was 1.5 μL.

The chemical composition of treated PTFE samples was determined by XPS instrument TFA–XPS from Physical Electronics (Munich, Germany) equipped with the hemispherical analyzer and monochromatic X-ray source. The samples were excited with monochromatic Al $K\alpha_{1,2}$ radiation at 1486.6 eV over an area of 400 μm^2. The photoelectron take-off

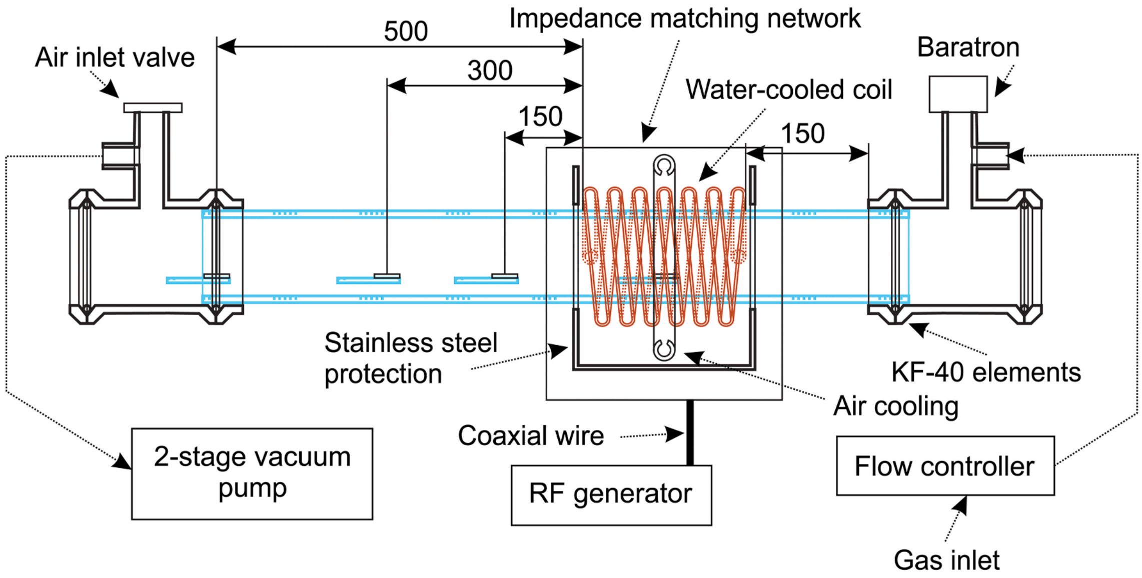

Fig. 1. System configuration for the coil-to-sample distances of 150, 300 and 500 mm.

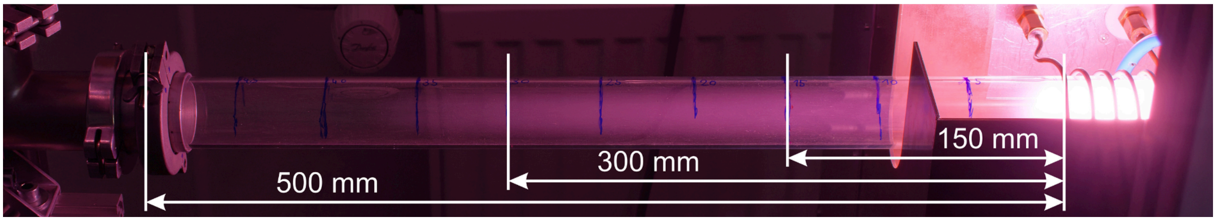

Fig. 2. Oxygen plasma in the discharge tube (positions of samples are marked).

Table 1
Neutral O atom densities and the corresponding fluxes measured with the cobalt catalytic probe at chosen coil-to-sample distances.

Experimental series	Neutral O-atom density [m^{-3}]	Neutral O-atom flux [m^{-2} s^{-1}]
150 mm coil-to-sample distance	3.4×10^{21}	5.3×10^{23}
300 mm coil-to-sample distance	3.2×10^{21}	5.1×10^{23}
500 mm coil-to-sample distance	2.4×10^{21}	3.7×10^{23}

angle was 45°. During XPS measurements, an electron gun was used for the surface charge neutralization. The measured spectra were referenced to the C–C/C–H peak of the C 1 s at 284.8 eV. The software MultiPak v8.1c (Physical Electronics, Munich, Germany) was used for the evaluation of the measured spectra.

3. Results and discussion

The wettability of the samples was evaluated immediately after treatments. The WCA of original samples was 111 ± 4°. The treatment of PTFE samples in a dense H_2 plasma in the H-mode caused a small increase of the wettability because the WCA dropped to 94 ± 3°. The decrease of the WCA after H_2 plasma treatment is explained by defluorination of the surface film and thus the formation of a very thin film of polyolefin-like structures. The composition of the surface of H_2 plasma-treated samples as deduced from the XPS survey spectra was 75.4 at.% of carbon, 20.8 at.% of fluorine, and 3.8 at.% of oxygen. Here we should note that the composition of the untreated PTFE was 32 at.% of carbon and 68 at.% of fluorine.

Systematic measurements of the surface wettability after the treatment with oxygen atoms were performed for all positions marked in Fig. 2. The evolution of the surface wettability of samples pretreated by H_2 plasma and then treated in the afterglow of O_2 plasma is shown in Fig. 3. The measured value at the treatment time of 0 s corresponds to the sample treated with H_2 plasma only. The evolution of surface wettability, presented in Fig. 3, shows interesting results that are worth discussing. One can observe deep, almost overlapping minima in all curves. As mentioned above, the WCA of the H_2 plasma-treated sample is large at about 94°. Even a very short treatment time in O_2-plasma afterglow causes a dramatic drop in the WCA. The very low WCA is explained by surface activation, i.e. formation of oxygen-functional groups on the surface of H_2 plasma-pretreated samples. After the

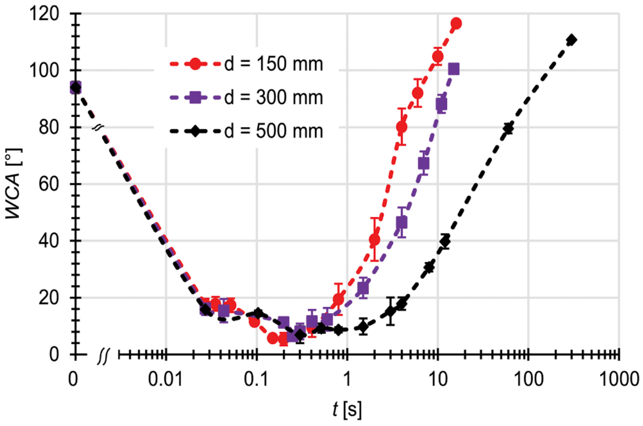

Fig. 3. Dependence of WCA on treatment time for all series of experiments.

shortest treatment time of 0.03 s, the WCA drops to approximately 15° to 18°. Fig. 3 indicates that this initial drop does not depend on the position of the sample in the afterglow. Further treatment in the afterglow of the O_2 plasma causes an additional decrease of the WCA for about 10°. The prolonged treatment, however, causes an increase of the WCA until a complete hydrophobic recovery is observed. The hydrophobic recovery is faster for samples treated closer to the RF coil. The x-axis scale in Fig. 3 has to be logarithmic because the duration of the hydrophobic recovery depends significantly on the position of the sample in the oxygen plasma afterglow upon treatment.

Detailed examination of the Fig. 3. indicates that the WCA minima at coil-to-sample distances of 150, 300, and 500 mm are between 5° and 7°. The minima are achieved at the treatment times between 0.2 and 0.3 s. It is evident from Fig. 3 that functionalization occurs quickly, especially at the closest coil-to-sample distance.

It is generally accepted that the main reactants in O_2 plasma afterglows are atoms in the ground state. The O-atom density in the afterglow is several orders of magnitude higher than the density of other reactants, particularly ionized atoms or molecules [17,41]. Fig. 4 shows the WCA versus the fluence of neutral O-atoms for the samples treated at all three positions in the O_2 afterglow. The distance between the curves is somehow smaller but the effect is not significant. The minima appear at the O-atom fluences of 1×10^{23} m^{-2}, 1.3×10^{23} m^{-2}, and 3×10^{23} m^{-2} for the afterglow distances of 150, 300, and 500 mm, respectively.

The minima on the curves, shown in Figs. 3 and 4 can be explained by two competitive surface reactions: functionalization and etching. The pretreatment of PTFE samples with H_2 plasma results in the depletion of fluorine in the surface layer. The reactive oxygen species readily interact with − CH groups and carbon dangling bonds on the surface layer of the PTFE, which is almost free of fluorine. The O atoms in the afterglow have a kinetic energy of only about 1/25 eV. However, the chemical bonding of the O atoms to the surface is a highly exothermic process and thus likely to occur [42]. Experimental results on the evolution of the functional groups on the surface of a polyolefine confirmed a very high probability for the formation of hydroxyl groups on the surface of pristine polyolefine [43,44]. At optimal, O atoms are chemically bound to the sample surface, thus forming polar functional groups resulting in the WCA decrease. Simultaneously to binding of O atoms to hydrocarbons, etching occurs as well, resulting in thinning of the fluorine-depleted surface layer. The etching rate is very low, but the fluorine-depleted film's thickness is very small, too. At large O-atom fluences, the entire fluorine-depleted film is etched away, and the polymer wettability regains the original value, typical for the untreated PTFE.

Because the WCA minima of the samples treated at various afterglow positions are achieved at very similar O-atom fluences, and the absolute WCA values are very similar, it is reasonable to hypothesize that the initial stage of functionalization depends on the fluence of received O atoms. However, after receiving the O-atom fluences above 3×10^{23} m^{-2}, the WCA of samples treated closer to the coil starts to rise faster than the WCA of samples treated further away from the coil. The differences in the wettability among samples treated at different positions in the oxygen plasma afterglow at the same received O-atom fluence could be explained by different etching rates at the different coil-to-sample distances. Higher etching rates at closer coil-to-sample distances could be a consequence of other reactive oxygen species. Fig. 2 qualitatively shows that the density of charged particles decreases with increasing distance from the RF coil. The presence of higher amounts of ions may well explain the faster etching of samples closer to the coil. The absolute density of ions is, of course, orders of magnitude lower than the density of O atoms, but the etching rate may also be orders of magnitude higher than at the presence of only O atoms. However, the presence of oxygen ions should not influence the initial functionalization because the initial interaction probability is high [42].

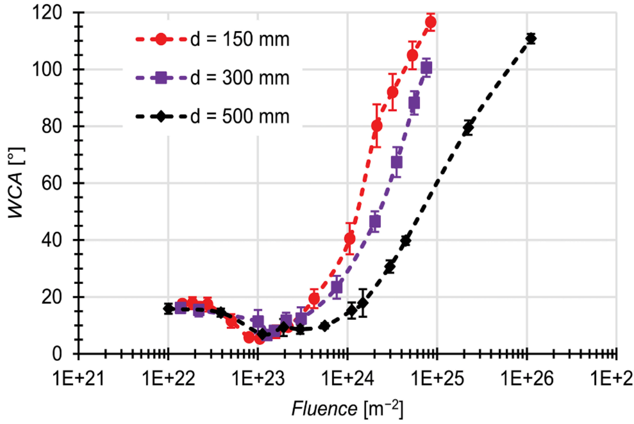

Fig. 4. WCA versus the fluence of neutral-O atoms - parameter is the distance of the sample from the RF coil.

The upper discussion proposes surface kinetics, particularly functionalization and etching upon the treatment of the H_2-plasma pretreated PTFE in the flowing afterglow of O_2 plasma. Both processes shall influence the surface composition. Functionalization shall cause an increase in the oxygen concentration, while etching shall cause the reappearance of the fluorocarbon layer at the surface. We performed a systematic XPS analysis of treated samples to further elaborate on both effects. Fig. 5 and Fig. 6 show the dependences of elemental compositions of the PTFE surfaces on treatment times in O_2 afterglow for the experiments performed at the coil-to-sample distances of 150 and 500 mm, respectively.

Both Figs. 5 and 6 reveal the results that are sound with the upper discussion regarding the evolution of the surface wettability. The oxygen and fluorine concentrations of the sample treated with H_2 plasma only are low (this case is shown at treatment time 0 s in Figs. 5 and 6). The oxygen concentration increases to approximately 20 at.% even at the shortest treatment time in the O_2 plasma afterglows. The pronounced increase in the oxygen concentration, as measured by XPS, corresponds to the significant increase of the surface wettability (decrease in the WCA). The oxygen concentrations remain fairly constant in ranges of treatment times from 0.03 s to about 1 s (at the coil-to-sample distance of 150 mm) or 10 s (at the coil-to-sample distance of 500 mm). This behavior clearly confirms the statement about the saturation of the sample surface with polar oxygen-containing functional groups. The fluorine contents remain relatively intact in these ranges of treatment times and are essentially the same as of the sample treated only with H_2 plasma. After prolonged treatment, however, the F concentration starts increasing and eventually reaches the value typical for the pristine PTFE. The XPS results are, therefore, in agreement with the WCA measurements.

Comparison of Figs. 5 and 6 show that the curves representing the WCA and the elemental compositions are similar at both coil-to-sample distances. A difference appears after prolonged treatment in oxygen plasma afterglow. This difference could be attributed to somewhat higher O-atom density at the coil-to-sample distance of 150 mm (Table 1), but the more feasible explanation is the lack of other reactive species capable of etching polymers at the coil-to-sample distance of 500 mm.

Additionally, Fig. 5 shows the evolutions of elemental composition and WCA on the sample surface versus the fluence of neutral O atoms of the experiments performed at the coil-to-sample distance of 150 mm (see the secondary x-axis at the top of the diagram). Within the fluence range from 1.5×10^{22} to 6×10^{23} m^{-2}, the amount of oxygen in the treated surface layer is approximately 20 at. %. The amount of oxygen at the sample's surface remains constant, while the WCA starts to decrease with increasing O-atom fluence and reaches its minimum of 5° at the O-atom fluence of 1×10^{23} m^{-2}. Interestingly enough, the oxygen content in the surface layer remains constant (at about 20 at. %) up to the fluence of 5×10^{23} m^{-2}, at which WCA reaches the value of 20° again. Within the O-atom fluence range of 1.5×10^{22} to 1×10^{23} m^{-2}, the F

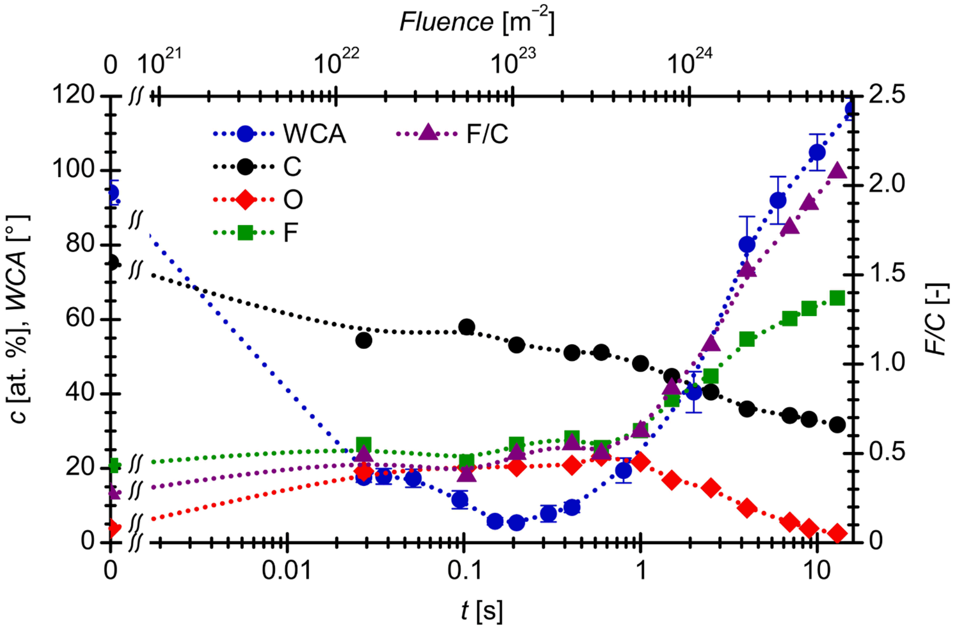

Fig. 5. Dependences of elemental composition and WCA versus: the treatment time and the fluence of neutral O-atoms of samples treated at coil-to-sample distance of 150 mm.

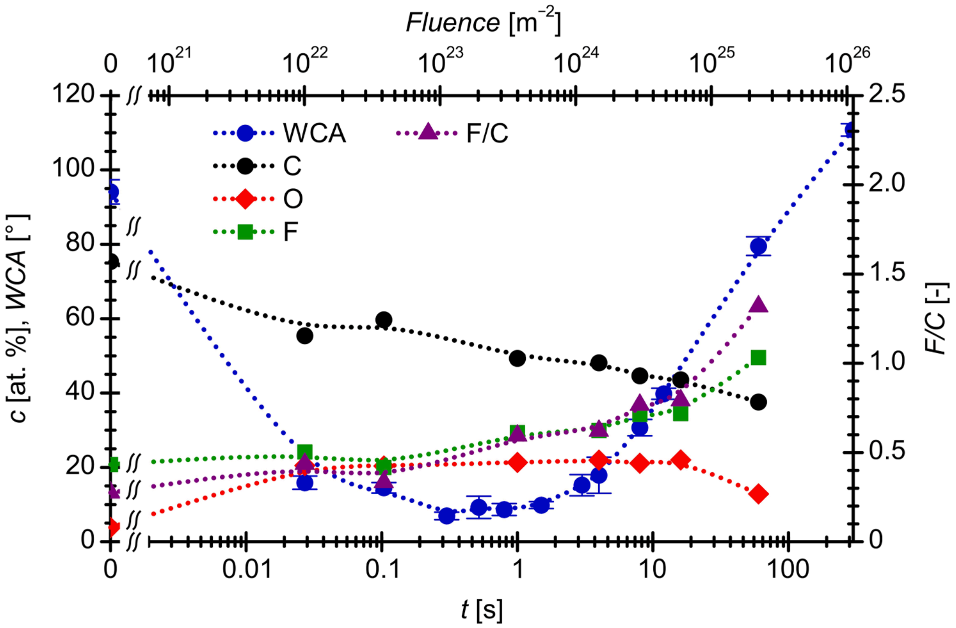

Fig. 6. Dependences of elemental composition and WCA versus: the treatment time and the fluence of neutral O-atoms of samples treated at coil-to-sample distance of 500 mm.

content and the F/C ratio in the surface layer are approximately constant in ranges of 20 to 25° at. % and 0.3 to 0.5, respectively. Above the O-atom fluence of 1×10^{23} m^{-2}, where WCA reaches its minimum, both F content and F/C ratio start to rise moderately. Constant O and F contents and F/C ratio in the surface layer at the O-atom fluences between 1.5×10^{22} and 1×10^{23} m^{-2}, where WCA decreases from 18 to 5°, could be explained by the fact that the WCA of treated PTFE surface does not depend only on its elemental composition, but it also depends on surface roughness, that is known to increase with the increasing O-atom fluence causing continuous etching [27,45]. The discrepancy between the behaviors of WCA and surface composition might also be explained by the etching of initially formed hydroxyl groups and the formation of less hydrophilic groups [46,47].

The diagram of Fig. 6 also shows the dependences of the elemental composition and the WCA of the treated PTFE surface versus the fluence of neutral O atoms (secondary x-axis) at the coil-to-sample distance of 500 mm. The results are similar to those presented in Fig. 5, but there are some differences. At the position of 500 mm, the WCA is rising slower with the increasing O-atom fluence in the range between 1×10^{23} m^{-2} and 6×10^{23} m^{-2} than at position 150 mm. Above the O-atom fluence of 1.5×10^{24} m^{-2}, both WCA and F/C start to rise rapidly.

The slight shift of WCA minimum to somewhat higher O-atom fluence and the extended range of O-atom fluences before WCA starts to rise rapidly, at a coil-to-sample distance of 500 mm, could be explained by slower etching of the surface layer at this position, where the density of other reactive species (charged molecules) is marginal as compared to the density of neutral O-atoms. Consequently, a somewhat higher O atom fluence is needed to achieve optimal surface roughness at a longer distance from the RF coil.

Plasma-treated polymers usually do not exhibit stable wettability over prolonged ageing. All experiments reported in this manuscript were performed immediately after the plasma treatment (WCA in particular) or in a reasonable time, say about 10 min after the plasma treatment (XPS). The ageing of plasma-activated polymers (or hydrophobic recovery) is explained by different effects including the reorientation of polar groups into the surface layer of polymer or the ablation of molecular fragments from the polymer surfaces [48]. The ageing was not only observed when a polymer was treated with oxygen plasma but also with a plasma sustained in argon at the pressure of 10 Pa and discharge power as low as several W [49]. Interestingly enough, the WCA did not increase monotonously with ageing time for the case a plasma-treated polymer was mixed with graphene nanomaterials [50]. The grafting of hydrophilic polymers on plasma-activated polymer substrates suppresses the hydrophobic recovery, but the ageing phenomenon persists even in such cases [51].

4. Conclusion

A new method was presented for the hydrophilization of fluorine-containing polymers in a highly controllable manner. The method comprises two steps. First, the PTFE samples are exposed to dense H_2 plasma sustained by an inductively coupled RF discharge in the H-mode. Then, the samples are exposed to O_2 plasma afterglow. The treatment with H_2 plasma causes the depletion of fluorine and the binding of hydrogen within the surface film. Reactive oxygen species in the afterglow cause functionalization with polar functional groups. The range of O-atom fluences useful for the optimization of the surface wettability was determined. The fluences of the order of 10^{22} m^{-2} caused significant functionalization, while fluences above approximately 10^{24} m^{-2} caused the loss of hydrophilicity, which was due to the etching of the fluorine-depleted surface film. Excellent wettability of PTFE with the water static contact angle as low as 5° was achieved in a limited range of O-atom fluences peaking at about 1×10^{23} m^{-2}.

The first treatment was performed in a dense H_2 plasma, and the treatment time was 1 s. Such a short treatment caused a drop in the fluorine concentration within the surface film as probed by XPS from 66 as found for the uuntreated PTFE to approximately 20 at.%. Knowing the penetration depth of the photoelectrons, one can conclude that the surface is almost free from fluorine after the hydrogen plasma treatment. The rapid removal of F atoms was explained by the $C - F$ bond scission due to irradiation of the sample surface with VUV radiation arising from resonant states of both H atoms (Lyman series) and H_2 molecules (Lyman and Werner bands). The dangling carbon bonds were most probably occupied with hydrogen atoms, thus forming a very thin surface film resembling polyolefins.

Polyolefins are known to chemically interact with oxygen atoms, even at room temperature, forming polar oxygen-containing functional groups. These functional groups, in turn, cause a significant increase in wettability. The oxidation kinetics was studied systematically versus the fluence of oxygen atoms. Well-defined minima in the WCA, corresponding to the maxima in the oxygen concentrations as measured by XPS, were observed at various experimental conditions. The minima appear after receiving the fluences of approximately 1×10^{23} O-atoms / m^{-2}. Increasing O-atom fluence causes slow etching of the modified surface film. Large fluencies of the order of 10^{25} m^{-2} cause almost complete removal of the surface film depleted of fluorine, and thus the loss of hydrophilicity and the re-establishment of the original surface composition typical for the untreated PTFE materials. An excellent agreement between wettability, as determined by WCA, and surface composition as measured by XPS was observed.

Experiments on the surface functionalization with polar functional groups were performed in flowing O_2 plasma afterglow. The samples were positioned at a few distances from the dense plasma within the RF coil, to study details, in particular the influence of other reactive oxygen plasma species on the surface kinetics. Neutral oxygen atoms in the ground state are by far the most important reactants governing the functionalization kinetics, but the experiments showed rather clearly that other species (probably positively charged ions) also influence the etching rate. Namely, the full restoration of the original surface composition was observed at the O-atom fluence of 1×10^{25} m^{-2}, in the case in which samples were placed 150 mm away from the RF coil, while an order of magnitude higher O-atom fluence was necessary at the distance of 500 mm. The O-atom densities at both afterglow locations were measured with a catalytic probe, and they were approximately 3.4×10^{21} m^{-3} at 150 mm, and 2.4×10^{21} m^{-3} at 500 mm. The difference was, therefore, marginal as compared to the fluences required for complete restoration of the original structure, thus suggesting more complex surface etching kinetics than only interaction with O atoms.

The results reported in this paper can give directions for any upscaling of the treatment procedure. The results clearly show that the decisive parameter is the fluence of O atoms. If such a fluence is feasible to assure in a large system, the technique is useful for ecologically benign surface activation of PTFE or similar materials.

CRediT authorship contribution statement

Dane Lojen: Visualization, Investigation, Formal analysis, Writing – original draft. **Rok Zaplotnik:** Conceptualization, Methodology, Supervision. **Gregor Primc:** Validation, Data curation. **Miran Mozetič:** Writing – original draft, Funding acquisition. **Alenka Vesel:** Supervision, Formal analysis, Project administration, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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