Applications of highly non-equilibrium low-pressure oxygen plasma for treatment of polymers and polymer composites on an industrial scale

A Vesel, G Primc, R Zaplotnik and M Mozetič

Department of Surface Engineering, Jozef Stefan Institute, Jamova cesta 39, Ljubljana, Slovenia

E-mail: miran.mozetic@guest.arnes.si

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Abstract

Scientific aspects of technologies based on application of non-equilibrium oxygen plasma are presented. Oxygen plasma is sustained by an electrodeless discharge to facilitate a high concentration of neutral reactive species, in particular O atoms. The species interact with solid materials causing surface functionalization, removal or organic impurities, nanostructuring of polymers, selective etching of polymer composites or synthesis of metal-oxide nanoparticles. The flux of O atoms onto the surface-facing plasma is often between $10^{20}$ and $10^{23}$ m$^{-2}$ s$^{-1}$.

While the physical interaction with solid materials (i.e. heterogeneous surface recombination) does not depend much on the sample temperature, the chemical interactions (functionalization, etching, oxidation) increase significantly with increasing temperature. The key treatment parameters are therefore the fluence of O atoms onto the sample surface and its temperature. The recommended ranges of parameters for various technologies are shown in the graphical abstract.

Keywords: polymer modification, surface engineering, functionalization, etching, O-atom fluence

(Some figures may appear in colour only in the online journal)

1. Introduction

Non-equilibrium oxygen plasma is usually sustained with gaseous discharges. A variety of discharges have been used on an experimental scale, operating at different voltages, powers, frequencies, pressure ranges, gas flows etc. The samples are treated with plasma for various periods, often of the order of seconds or minutes. Most discharge parameters are known, so a typical scientific paper reports the effect of plasma treatment versus selected discharge parameters. Because there are numerous parameters that should be considered, any systematic treatment of samples is usually beyond the aim of a scientific paper. Instead of a systematic approach, most authors try to fix almost all treatment parameters and vary only one or two parameters. One of these is usually the treatment time—it is the easiest to vary. The second is often the discharge power or the gas pressure (or flow rate) if the discharge operates at a fixed nominal power. Such an approach is not very useful for treatment of materials on an industrial scale because the surface finish does not depend directly on the discharge parameters but rather on the plasma parameters. To be more specific, the surface finish usually depends on the fluxes or fluences of plasma species onto the surfaces of treated materials. A flux of atoms to the surface is proportional to the atom density in the vicinity of the surface and the average random velocity of atoms, whereas a fluence (or dose) is a product of a flux and exposure time. There is a correlation between the discharge and plasma parameters, but any direct transformation is questionable.
because the plasma parameters depend on many factors, often even on the history of the discharge chamber, let alone the properties of treated materials. A useful representation of interaction between oxygen plasma and solid materials should therefore involve at least the most crucial plasma parameter, if not more than one.

Oxygen in thermal equilibrium at room temperature consists practically of only neutral two-atom molecules in the ground electronic state. The opto-chemical assignment of this state is $X^3\Sigma_g^−$. A variety of excited states are formed upon non-equilibrium conditions, predominantly by inelastic collisions with plasma electrons. Some excited states relax by electrical dipole radiation. The lifetime of such states is usually so short that their flux onto materials facing plasma is marginal. Such states, however, represent an intensive source of radiation. Figure 1 represents simulated spectra of oxygen plasma with electron temperatures of 3 and 5 eV and electron density $1 \times 10^{16}$ m$^{-3}$. The data presented in figure 1 were obtained using Saha-LTE spectrum simulation on the NIST web page [1]. They reveal intensive radiation in the hard UV range peaking at 130.2 nm and 115.2 nm. This radiation arises from the transition of excited O atoms from the $2s^22p^4(^4S^o)3S_1^0$ to $2s^22p^4^3P_2$ state and from the $2s^22p^4(^4D^o)3S_1^0$ to $2s^22p^4^1D_2$ state, respectively. The radiation in the soft UV range from oxygen plasma at reasonable electron temperature is poor and so it is in the visible range of the spectrum, apart from a very intense line at 777 nm, which has the typical red color of oxygen plasma with a high dissociation fraction of molecules. The line at 777 nm and another in the IR range at 845 nm correspond to transitions of neutral oxygen atoms from higher to lower excited states. In practice, spectra as in figure 1 are difficult to measure (especially in the hard UV range) but even measured spectra often differ significantly to those presented in figure 1. While the radiation in the red part of the spectra has little influence on the material properties, the hard UV radiation definitely breaks bonds in polymer materials, thus causing its degradation, as reported recently by Hori’s group [2]. This effect should be considered when designing an oxygen plasma reactor for tailoring surface properties of polymers.

The metastable stable states do not represent significant sources of radiation because they are either quenched or pumped away from the system before the relaxation by radiation occurs. They represent interesting (although often neglected in scientific literature) intermediate states for excitation to highly excited states. Among the oxygen neutral excited molecular states there are two electronic states with long lifetimes, whereas the neutral atoms have several metastable states but with much shorter lifetimes.

$a^1\Delta_g$ is the first excited electronic state of neutral oxygen molecules at an excitation energy of 0.978 eV. It is often called the ‘oxygen molecule singlet state’ or simply ‘oxygen molecule “a” state’. The radiative lifetime of these molecules is almost an hour. Many authors reported large concentrations of these molecules in their oxygen plasma reactors [3–5]. While the gas phase reactions of these molecules were elaborated decades ago, their interaction with surfaces of different materials is yet to be explored. In fact, very little literature is available on the quenching mechanisms or chemical reactions of these molecules on dielectrics or organic materials. Ryskin et al measured the coefficients for numerous materials by calorimetry and found the lowest value of approximately $5 \times 10^{-3}$ for glass and the highest value of $1 \times 10^{-2}$ for silver [6]. Sharpless et al used the same technique and found coefficients an order or two larger [7]. Some authors just took into account zero relaxation probability on the walls facing plasma [8]. This assumption is reasonable taking into account the results of Ryskin et al [6].

Energy-wise, the next species found in oxygen plasma in large quantities are neutral atoms in the ground state $2s^22p^4^1S_0$. The typical discharge time needed for establishment of a constant O-atom density in a simple plasma reactor is of the order of ms [10]. Their lifetime in the gas phase depends on the pressure. At atmospheric pressure it is as low as roughly a microsecond, whereas at pressures below 1 mbar it is so long that losses by gas-phase reactions are negligible. This is the reason that large densities of O atoms are reported by numerous authors. Booth et al used a dc discharge in a Pyrex tube and found the O-atom density to be as high as $10^{22}$ m$^{-3}$, peaking at a few mbar [11]. This is almost two orders of magnitude higher than the density observed by Dedrick et al in an rf plasma at atmospheric pressure [12]. Tsuchimori et al measured the O-atom density in plasma sustained with an inductively coupled rf discharge and found it to be of an order of magnitude $10^{20}$ m$^{-3}$ at an rf voltage of 200 V and pressure close to 1 mbar [13]. Double the voltage and a lower pressure resulted in an increase in the O-atom density.
density close to $10^{21} \text{m}^{-3}$. A value close to $5 \times 10^{21} \text{m}^{-3}$ was also found by Baeva et al using pulsed microwave discharge at a pressure of 10 mbar [14]. Keckhar et al measured the O-atom density in the metallic chamber where rf plasma was sustained in the capacitive mode, and found an O-atom density of about $10^{20} \text{m}^{-3}$ at a discharge power of 100 W and pressure of 13 Pa [15]. One of the highest O-atom densities was reported by Kutasi et al for the case of microwave discharge in the surfatron mode [16]. The O-atom density was approximately $2 \times 10^{22} \text{m}^{-3}$ in a range of pressures peaking at about 10 mbar.

Low-pressure plasma will therefore abound in atomic oxygen. The loss on surfaces is by heterogeneous surface recombination. The probability for such surface effects varies from about $10^{-5}$ for inert materials such as glass [17] to almost 1 for catalytic materials of rich surface morphology such as carbon nanowalls [18]. Polymers often exhibit low recombination coefficients, typically between $10^{-3}$ and $10^{-2}$ [19–21]. The chemical reactivity is rather poor at room temperature—the probability that an O atom could cause etching of organic material is often below $10^{-3}$. Nevertheless, because the atoms abound in oxygen plasma they are often used for chemical modification of solid materials.

$2^2S_2^2p^34D_2$ is the first metastable state of oxygen atoms at the excitation energy of 1.967 eV. The radiative lifetime is approximately 150 s. The concentration of these atoms is often about 0.1% [4]. They are supposed to be much more reactive than the O atoms in the ground state but little experimental evidence is available [22].

$X^2\Pi_g$ is the assignment of a positively charged molecular ion. The ions are usually thermal in plasma (their kinetic temperature is very close to the neutral gas kinetic temperature, which in turn is close to the temperature of walls facing plasma) but they are accelerated in the sheath next to the surface of a material-facing plasma. The interaction with solid material is both kinetic and potential. The kinetic component is adjustable by adjusting the voltage drop between the plasma and the surface of a solid material. It is believed that the chemical reactivity of positively charged ions is large. However, little experimental evidence is available because the ions are rarely the major reagents. The reason is that the loss probability (neutalization) on a surface-facing plasma is almost 1 for all known materials, therefore the density of ions in moderately ionized oxygen plasma is orders of magnitude lower that the density of neutral atoms [17].

There are numerous other species in oxygen plasma but their concentration in reactors suitable for processing materials on an industrial scale is marginal.

2. Initial interaction and surface functionalization

Probably the most widely used technology that employs non-equilibrium oxygen plasma is modification of a material surface by chemical bonding of oxygen atoms. A recent review of functionalization of polymer materials with oxygen plasma was published in [23]. The materials are exposed to either oxygen plasma or its afterglow. Atomic oxygen interacts chemically with a polymer surface, forming a bond with a surface carbon atom. The first effect of a polymer’s exposure to oxygen atoms is formation of a hydroxyl group. The probability of such a reaction on the surface of an untreated polymer seems to be high. In one experiment, a surface monolayer of hydroxyl groups was established on the surface of polystyrene even after receiving an O-atom fluence as low as $3 \times 10^{21} \text{m}^{-2}$ [24]. The fluence (often called ‘dose’) is defined as the product of the flux of reactive particles onto the surface and the exposure time. If we assume a surface atom density of the order of $10^{19} \text{m}^{-2}$, the initial reaction probability could be several percent. Unfortunately, no scientific data is available for extremely small fluences of O atoms onto a polymer surface. Other functionalities like carbonyls, carboxyls, esters and even carbonate bonds appear at fluences above $10^{22} \text{m}^{-2}$ [24].

The surface of a polymer becomes saturated with functional groups after receiving a certain fluence of O atoms, often of the order of $10^{23} \text{m}^{-2}$ [24]. This fluence is achieved at a treatment time that could be as low as a millisecond. Figure 2 represents the fluence versus O-atom density for treatment times 1 and 100 s at O-atom kinetic temperatures of 300 and 1000 K, which are supposed to be the common values in non-equilibrium oxygen plasma at low pressure and low-to-moderate power density. Very few scientific papers, however, report treatment times of the order of milliseconds for functionalization of polymer materials with oxygen-rich functional groups. Papers more commonly report much longer treatment times, typically of several seconds or even minutes. Other effects become significant for such prolonged treatment times, including destruction of the subsurface film of a polymer by absorption of UV and/or VUV (vacuum ultraviolet) radiation, chemical etching by O atoms (and perhaps metastables, both molecular and atomic), physical effects due to heterogeneous surface recombination of O atoms, any relaxation of metastables, and bombardment with positively charged oxygen molecules. All these effects are exothermic, and thus the surface of a polymer material is subject to heating. The power dissipated on the polymer
surface is a sum of all these contributions:

\[ P = j_{ph} \cdot W_{ph} + j_a \left( W_{a-ch} + \gamma W_D \right) + j_{net} \cdot \eta \cdot W_{net} + j_{ion} (W_i + W_e). \] (1)

Here, \( j_{ph} \) is the flux of the photons on the polymer surface and \( W_{ph} \) is the energy of the photons. According to figure 1, oxygen plasma is a source of numerous photons of various energies so the first term in equation (1) is actually a sum of different contributions to polymer heating by plasma radiation. Because the VUV protons prevail (see figure 1), the majority of available power is dissipated in the surface film, the thickness of which corresponds to the absorption depth of VUV radiation, which is typically of the order of several tens of nm.

The quantity \( j_a \) in equation (1) is the flux of O atoms onto the polymer surface. The flux is

\[ j_a = 1/4n_a \cdot \langle v_a \rangle, \] (2)

where \( n_a \) is the atom density in the vicinity of the surface and \( \langle v_a \rangle \) is the average random velocity of O-atoms. The atom density can be measured in oxygen plasma by different techniques including two-photon absorption laser-induced fluorescence (TALIF) [25] or catalytic probes (CP) [26], whereas \( \langle v_a \rangle \) is often assumed to be

\[ \langle v_a \rangle = \sqrt{8k_B T_g \pi m_a}, \] (3)

where \( k_B \) is the Boltzmann constant, \( T_g \) is the neutral gas kinetic temperature and \( m_a \) is the O-atom mass, i.e. \( m_a = 16 \text{Da} \). The assumption may not always be correct because the O atoms are produced by an electron impact dissociation of \( \text{O}_2 \) molecules, which leads to super-thermal O atoms because a fraction of the available electron energy could be spent as kinetic energy of newly formed O atoms. The atoms quickly thermize with the surrounding gaseous atoms and molecules by elastic collisions, so the exact value of the velocity in equation (3) is not known.

The quantity \( W_{a-ch} \) in equation (1) is the absolute value of the difference in binding energy of carbon or hydrogen in the polymer and in the molecules formed as a result of polymer oxidation with O atoms, i.e. CO, CO\(_2\) OH, \( \text{H}_2\text{O} \) and products of incomplete oxidation. The energy is of the order of eV and obviously depends on the type of the polymer and the reaction product. It is dissipated on the very surface of the polymer and is often neglected at short treatment times because the intensity of chemical reactions at room temperature is weak.

The term \( \gamma W_D / 2 \) in equation (1) represents the energy dissipated on the surface of the polymer upon exposure to oxygen atoms. \( W_D \) is the dissociation energy of the molecule, and the factor \( 1/2 \) comes from the fact that an oxygen molecule consists of two atoms. The quantity \( \gamma \) is the recombination coefficient, i.e. the probability that an O atom touching the polymer surface associates to an \( \text{O}_2 \) molecule. The coefficient depends on the type of the polymer, surface morphology and surface temperature. Various authors reported different results on the value of \( \gamma \) but almost all authors agree that the value should be between \( 10^{-5} \) and \( 10^{-2} \) at room temperature [19–21, 27, 28]. Some authors reported increasing \( \gamma \) with increasing surface temperature; however, the scientific literature is scarce [29–31]. Furthermore, some authors suggested that the recombination coefficient in the afterglow (where charged particles and radiation are absent) is different from the coefficient in the glowing plasma, indicating the possibility of synergistic effects [11]. Knowledge on the recombination coefficient versus ion and/or photon fluxes is insufficient. Some authors reported unexpectedly large recombination even for fluorinated polymers upon exposure to highly dissociated, weakly ionized oxygen plasma [32]—much larger than in the case where the same material was exposed to O atoms only [20].

The term \( j_{net} \cdot \eta \cdot W_{net} \) in equation (1) indicates the heating of the polymer surface by surface relaxation of metastable atoms and molecules. \( j_{net} \) is the flux of metastables on the surface and \( W_{net} \) is the excitation energy. The quantity \( \eta \) represents the probability for surface relaxation. Very little work has been done even on measuring the fluxes of metastables, let alone the surface relaxation probabilities [33]. As mentioned earlier in this paper, the densities of metastables in oxygen plasma are estimated by modeling rather than measured [34]. The heating of a polymer material by relaxation of metastables is therefore unknown. Once the appropriate data are available, one will be able to evaluate this heating method by considering the flux calculated from equations (2) and (3), using appropriate densities and assuming the metastables are well thermalized with surrounding atoms and molecules so that the neutral gas kinetic temperature could be taken as in equation (3).

Finally, the term \( j_{ion} (W_i + W_e) \) in equation (1) represents heating by positively charged ions. The ion flux is calculated using equation (2) with an appropriate density and omitting the factor \( 1/4 \) because the ions are directed towards the surface. The velocity of ions approaching the surface cannot be calculated as in equation (3) because the ions gain kinetic energy already in the pre-sheath so the velocity at the sheath boundary is the Bohm velocity:

\[ v_{Bohm} = \sqrt{\frac{k_B T_e}{M}}. \] (4)

Here, \( T_e \) is the electron temperature and \( M \) is the ion mass. There are not many positively charged O atoms in a weakly ionized plasma suitable for surface modification of polymer materials, so the molecular mass should be taken into account in equation (4), i.e. \( M = 32 \text{Da} \). \( W_i \) is the ionization energy of \( \text{O}_2 \) molecules (13.6 eV) and \( W_e \) is the kinetic energy gained in the sheath next to the surface. If there are not many collisions of ions within the sheath (often referred as ‘collision-less sheath approximation’) the ions gain energy corresponding to the difference in plasma and surface potentials. In the case where the surface is not biased deliberately (the material is at a floating potential, typical for electrically non-conductive materials like polymers), the difference is calculated as

\[ \Delta V = 1/2 \left( \frac{k_B T_e}{e} \right) \cdot \ln \left( \frac{M}{2\pi m_e} \right). \] (5)
Here, $m_e$ is the electron mass, i.e. $m_e = 9 \times 10^{-31}$ kg. If the electron temperature is 3 eV, the voltage across the sheath as in equation (5) will be close to 10 V and the ion kinetic energy 10 eV.

Whatever the heating mechanism is, a polymer material exposed to oxygen plasma or its afterglow is always subjected to heating. While the heating in the afterglow is often neglected so the authors take into account the room temperature of any polymer sample, the heating in glowing plasma should be taken into account in any decent study on plasma–surface interaction. The temperature of a material-facing plasma depends on numerous parameters and could remain close to room temperature, providing the material is massive enough and the treatment time is not too long. Thin foils, however, are quickly heated to elevated temperatures because of the exothermic reactions summarized above. Foils may eventually melt upon exposure to oxygen plasma even at short treatment times.

The high surface temperature is usually detrimental for surface functional groups. The large concentration of polar groups on a polymer surface is thermodynamically not stable so the groups decay spontaneously. Several mechanisms have been proposed but the consequence is always the loss of surface polarity what in turn causes spontaneous decrease of the surface wettability. The phenomenon is sometimes referred as ‘hydrophobic recovery’ or simply ‘ageing’. The effect of thermal de-functionalization of an oxygen-plasma-treated polyethersulfone was elaborated in [35] by heating of the polymer sample in situ in an XPS instrument upon ultrahigh vacuum conditions to reveal the kinetics of the hydrophobic recovery.

The surface temperature has a negative effect on durability of polar functional groups. Overtreatment causes excessive heating and consequently loss of the surface functional groups and loss of wettability. On the other hand, the insufficient treatment time at a given flux of reactive oxygen species (predominantly atoms) does not enable saturation of the surface with functional groups because the required fluence of the O atoms should be of the order of $10^{23}$ m$^{-2}$. In between, there are optimal treatment conditions as long as the functionalization of a polymer with oxygen-rich functional groups is the merit. The two effects are shown qualitatively in figure 3. Little work on quantification of the curve in figure 3 has been published in scientific literature. Some examples based on the work of Semenic [36] are shown in figure 4. The functionalization of both high- and low-density polyethylene as well as polyvinyl chloride versus treatment time was studied in a glass plasma reactor powered by an inductively coupled RF discharge at a pressure of 30 Pa and forward power of about 150 W. Oxygen plasma of an ion density close to $10^{16}$ m$^{-3}$ and O-atom density of approximately $3 \times 10^{21}$ m$^{-3}$ was sustained at these discharge parameters. The plasma parameters were measured with a double electrical probe and a catalytic probe. The thicknesses of the polymer foils were 1 and 0.5 mm for polyethylene (PE) and polyvinyl chloride (PVC), respectively. The curves presented in figure 4 show minima, which depend on the type of polymer. The minimal water contact angle for PVC occurs at a treatment time of about 5 s, whereas for PE it occurs at approximately 30 s. The rapid loss of hydrophilicity for the case of PVC was explained by extensive chemical reactions on the PVC material upon treatment with oxygen plasma [37]. The optimal fluence of O atoms onto the polymer surfaces was thus of the order of $10^{24}$ m$^{-2}$, so an order of magnitude larger than what was found in [24]. The discrepancy is explained by the fact that the water contact angle does not depend only on surface functionalities but also on the roughness on the nanoscale, as explained by details in monograph [38].

3. Etching and nanostructuring of polymers

As explained above, the polymer surface is soon saturated with polar functional groups upon treatment with oxygen plasma of high O-atom density. Further treatment causes etching. The etching by neutral O atoms in the late plasma of high O-atom density. Further treatment causes etching. The etching by neutral O atoms in the ground state has been elaborated in [39]. The authors deposited thin polyethylene terephthalate (PET) films on quartz substrates and measured the thickness of the film by quartz crystal microbalance (QCM) versus the fluence of O atoms in the late afterglow of oxygen plasma. Samples were kept at room temperature at all times. The etching rate was independent

![Figure 3. Two competitive effects in wettability of polymers versus plasma treatment time.](image)

![Figure 4. Time evolution of water contact angles on low- and high-density polyethylene and polyvinyl chloride foils upon treatment in oxygen plasma of O-atom density of $3 \times 10^{21}$ m$^{-3}$.](image)
from time and was as low as approximately \(10 \text{ pm s}^{-1}\). The known flux of O atoms onto the sample surface allowed for determination of the probability that an O atom touching the polymer surface will remove a carbon atom, which was as low as \(10^{-6}\) [39]. The etching of such polymers in the afterglow is therefore negligible.

The same group used the same materials and methods to determine the etching rate in glowing plasma of an ion density close to \(10^{16} \text{ m}^{-3}\) and comparable atom density [40]. The samples were kept at a floating potential so the ions’ kinetic energy was approximately \(10 \text{ eV}\). In this case, the etching rate was close to \(10 \text{ nm s}^{-1}\), and thus 1000 times larger than in the afterglow. The results were explained by synergistic effects of atoms, ions and perhaps VUV radiation and metastables. In both cases (etching in the afterglow or glowing plasma) the polymer developed rich morphology upon treatment. A typical atomic force microscopy (AFM) image of an originally smooth polymer material after treatment with oxygen plasma or afterglow for a prolonged time is shown in figure 5.

The reasons for development of such a rich morphology of polymers upon treatment with oxygen plasma are not known. There are several hypotheses that consider different mechanisms. The trivial one takes into account local modifications of binding forces. Bruce et al [41] explained the evolution of the surface roughness by buckling instability. He proposed the existence of a surface film with a structure that differs significantly enough from the structure of a bulk polymer to cause a large mismatch in the stiffness, and thus spontaneous wrinkle formation to minimize the elastic energy. This hypothesis was confirmed by Phaneuf et al [42] for selected conditions. The explanation is feasible for the case in which a polymer is treated in glowing plasma where the samples are subjected to VUV radiation (figure 1) of a penetration depth of the same order as the height of the wrinkles (figure 5). For the case in which the polymers are treated in the afterglow, however, such a surface film may not be formed because the VUV radiation and ions are absent.

Other authors took into account etching by metastable singlet oxygen molecules of functionalized polymer surfaces to explain the rich surface morphology [43, 44]. In one study, blood proteins were exposed to early and late afterglows of oxygen plasma and the resultant etching rates did not depend linearly with the O-atom flux, but fitted well with the product of atom flux and metastable molecule flux [45].

The formation of rich surface morphology on the PET surface upon exposure to VUV radiation was reported recently by Hori’s group [2]. They used oxygen plasma and measured the flux of VUV photons on the polymer surface. The sample was either exposed directly to plasma or covered with a VUV-transparent window to separate the effect of radiation. Interestingly, the etching rate was significant even upon exposure to VUV radiation only. In fact, the authors measured reduction of the polymer thickness by \(10 \text{ nm}\) after receiving VUV fluence of about \(10^{20} \text{ m}^{-2}\). Prolonged radiation did not cause significant etching, so the etching mechanism by VUV radiation may be dehydration of the surface polymer film. No significant nanostructuring was observed in these experiments, indicating the crucial role of reactive oxygen species (atoms, ions, metastables) in nanostructuring of polymer materials.

Whatever the mechanism, the etching of a polymer material upon exposure to oxygen plasma for a prolonged time is important and should be considered in any application of plasma technology for modification of polymer surface properties. The typical etching rate in a weakly ionized oxygen plasma is roughly of the order of \(10^{-3}\) so rich surface morphology is achievable after a few seconds of plasma treatment. This time is prohibitively long for many industrial applications, so other solutions should be adopted in cases where rich surface morphology is desired. A feasible method for fast nanostructuring of a polymer surface is application of a moderately ionized oxygen plasma. As explained above, there are numerous heating mechanisms for polymers upon exposure to oxygen plasma. A large flux of ions will cause significant heating of a polymer at a power as in equation (1).

In one experiment, a polymer rod made from PET was exposed to a powerful oxygen plasma created by an inductively coupled rf discharge in the H-mode [46]. The oxygen pressure was \(30 \text{ Pa}\) and the discharge power was about 500 W. A dense plasma in the H-mode expanded in the volume of about 21 so the power density was over \(10^{3} \text{ W m}^{-3}\). The plasma density was close to \(10^{19} \text{ m}^{-3}\) and
the dissociation fraction of oxygen molecules was close to 100%. In a fraction of a second, the polymer assumed surface morphology similar to that shown in figure 5. Such a rich morphology achieved in a very short time can be attributed to thermal effects: the surface layer of the polymer becomes soft enough that reorganization occurs in the form of wrinkles. From this point of view, the hypothesis launched by Bruce et al [41] is highly appealing.

The short treatment of polymers with powerful oxygen plasma definitely helps to create a rich morphology, but is detrimental to surface functionalization. As explained in detail above, the high temperature causes a quick hydrophobic recovery so the wettability of the material treated this way is poor. A feasible solution useful for industrial application is subsequent treatment with both a powerful and a mild plasma. The polymer first enters the powerful plasma, where it assumes the surface morphology shown in figure 5. After cooling down to room temperature, the foil enters the mild plasma or its afterglow, where it is functionalized with polar oxygen-rich functional groups. Such a surface finish enables (super)hydrophilic properties of many polymers.

Etching of organic materials by oxygen plasma is also useful for degreasing of various materials. As explained above, all organic materials are etched upon treatment with oxygen plasma or its afterglow. From this point of view, organic impurities including adsorbed/chemisorbed organic molecules and thin films of oily compounds behave similar to polymers: they interact chemically with reactive oxygen species (predominantly atoms with possible synergy with other reactants), forming simple molecules that desorb from the surface, especially under low-pressure conditions. The removal of organic impurities using this technique is often called discharge cleaning or degreasing, and is widely used in industry for ensuring surfaces are free from organic contaminants. Figure 6 represents the experimental confirmation of complete removal of a thin layer of oil from the surface of a silicon wafer. The wafer was exposed to afterglow of O-atom density of $1.1 \times 10^{17}$ m$^{-3}$ for 10 min. The fluence of O atoms was thus $1.0 \times 10^{22}$ m$^{-2}$. The samples were characterized by x-ray photoelectron spectroscopy (XPS) before and after the treatment. The carbon peak for a treated sample is below the detection limit of this technique (~1 atomic %), so the surface is practically free from organic impurities and thus suitable for further treatment.

4. Selective etching of polymer composites

As previously explained, the etching of polymer materials always occurs upon treatment with oxygen plasma and the etching rate depends on the fluxes of various species onto the polymer surface. Modern plastics are rarely made from pure polymers but contain substantial amounts of fillers. A schematic of a plastic is shown in figure 7 (left). The fillers are often inorganic compounds that may or may not be etched upon exposure to oxygen plasma. In any case, the etching rate for a polymer matrix is different from the etching rate of the fillers. This effect was found useful in tailoring surface properties of polymer composites. The plastics are usually produced by extrusion or injection moulding. The surfaces of the plastics are covered with polymer and the fillers are dispersed in the polymer matrix. The surface properties of the plastics are therefore governed by the properties of the polymer, not the fillers. The surface properties will change if the polymer is selectively removed, leaving the fillers stretching from the surface. In that case, the surface properties of plastics are governed by the properties of the fillers, not the polymer. A suitable technique for selective removal of a polymer from the surface of the polymer composite is treatment with oxygen plasma. Reactive oxygen species interact with the polymer material, causing etching, as explained in the previous section of this paper. If the fillers are inorganic (typically glass or ceramic particles including fibers) they will not interact with the oxygen plasma as long as the material is kept at a floating potential (to prevent significant kinetic energy of ions and thus sputtering), and the material temperature is reasonably low (to prevent thermal degradation including melting). The result of oxygen plasma treatment of a polymer composite is presented schematically in figure 7 (right).

The typical size of fillers in modern plastics is often of the order of a micrometer, so the required fluxes of reactive oxygen species onto the surface to obtain the finish presented in figure 7 should be rather large. As explained above, the typical etching rates for polymers upon treatment with oxygen plasma of a low ion density at room temperature is of the order of nm/s. Removal of a $\mu$m-thick polymer film would therefore take minutes, which is usually too long for industrial applications. The problem could be solved by heating the plastic materials during the oxygen-plasma treatment or even before exposing the composite material to oxygen plasma. The latter technique has the advantage of uniform heating, which is not always easy to achieve in plasma reactors of an industrial size due to gradients in plasma parameters and thus poor heating uniformity across the reactor using the mechanisms of equation (1). As the etching rate increases with the polymer temperature, the treatment time could be shortened significantly by this type of pre-heating. This technique is suitable for treatment of various plastics, and one
of the first attempts was published as [47]. The required fluence of oxygen atoms onto a graphite–polymer composite to achieve super-hydrophilic character of this originally hydrophobic material was found to be of the order of $10^{25} \text{m}^{-2}$ [48]. The subsequent cooling to room temperature after accomplishing the etching step and treatment with mild plasma (for surface functionalization) was reported as essential for this surface finish in [48].

The technology for selective etching of polymer composites also represents a unique technique for recognition of distribution and even orientation of fillers in the surface film of such products. As early as 2000 it was used to determine any agglomeration of carbon nanoparticles in a polymer matrix of wood paints [47]. The quality of such paints depends enormously on the dispersion of fillers in the polymer matrix. Brief treatment with oxygen plasma enabled removal of the epoxy resin from the surface, thus revealing the distribution of any fillers in the matrix. The epoxy resin exhibits higher etching rate than many other polymers, so the required fluence of O atoms as used in [47] was just $2 \times 10^{24} \text{m}^{-2}$. Obviously, the method is suitable for reverse engineering in any industry producing plastics.

5. Conclusion

In spite of the fact that oxygen plasma is widely used in industry in the technological processes of surface functionalization, discharge cleaning, nanostructuring and selective etching, the exact mechanisms involved upon interaction of gaseous plasma with solid materials are not always known. One reason is the lack of scientific literature on the fluxes and fluences of various reactants onto the surfaces of treated materials. Polymers are affected by both reactive oxygen species and VUV radiation; the latter causes not only etching but also modification of the surface film of a thickness of several tens of nm. Any polymer exposed to oxygen plasma will be etched and the obtained surface finish is usually rich morphology on the nanoscale. The combination of such morphology and functionalization with oxygen functional groups leads to a superhydrophilic surface finish, which is beneficial in cases where the polymer should be coated with different materials and a good adhesion of the coating is the goal, for instance in painting, printing, gluing and metallization. Polymer composites are etched extremely selectively because of enormous differences in the chemical affinity of different materials to reactive oxygen species. Most technological processes employ oxygen atoms in the ground state and synergistic effects with ions and/or VUV radiation is often beneficial, but sometimes detrimental, in particular where the subsurface film should remain intact. The best surface finish of polymers and composites is often achieved at low temperature of the treated material; however, elevated temperatures may be useful in selective plasma etching, whereas high temperatures are beneficial for formation of metal-oxide nanowires. The recommended fluences of O atoms and temperatures of treated materials upon exposure to oxygen plasma depend on the type of material and required surface finish. The most useful parameters are presented in the graphical abstract. The range of O-atom fluences is between $10^{17}$ and $10^{27} \text{m}^{-2}$. Lower fluences have negligible effect, whereas higher fluences are impractical for industrial applications.

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ORCID iDs

G Primc @ https://orcid.org/0000-0002-3959-776X
R Zaplotnik @ https://orcid.org/0000-0002-1366-9147
M Mozetič @ https://orcid.org/0000-0003-3782-6001

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