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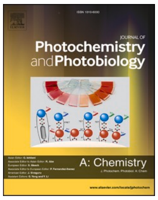

Advanced method for efficient functionalization of polymers by intermediate free-radical formation with vacuum-ultraviolet radiation and producing superhydrophilic surfaces

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A B S T R A C T

An efficient approach for tailoring surface properties of polymers is presented, which enables rapid modification leading to superhydrophilic properties. The approach is based on vacuum-ultraviolet radiation (VUV) pretreatment of the surface to create reactive dangling bonds. This step is followed by a second treatment using neutral oxygen atoms that react with the dangling bonds and form functional groups. The beneficial effect of VUV pretreatment for enhanced functionalization was clearly demonstrated by comparing VUV pretreatment in plasmas created in different gases, i.e., hydrogen, nitrogen, and oxygen, which differ in the intensity of VUV/UV radiation. The emission intensity of VUV radiation for all gases was measured by vacuum ultraviolet spectroscopy. It was shown that VUV has a strong influence on the treatment time and final surface wettability. A superhydrophilic surface was obtained only if using VUV pretreatment. Furthermore, the treatment time was significantly reduced to only a second of treatment. These findings show that such an approach may be used to enhance the surface reaction efficiency for further grafting of chemical groups.

1. Introduction

Plasmas are nowadays often used for improving the surface wettability of materials, especially polymers [1]. The obtained hydrophilicity depends on the treatment conditions and also on the type of polymer material [2]. The surface of some polymers is rather easily changed to hydrophilic or even superhydrophilic by plasma treatment, however, some other polymers still maintain moderate hydrophobicity. Especially aromatic polymers are prone to modification of their surface to very hydrophilic because of the possibility of the destruction of the aromatic ring and the formation of highly oxidized functional groups [2]. However, unlike aromatic polymers, aliphatic do not show such a pronounced change in hydrophilicity, especially if they belong to the group of halogen polymers [3].

Non-equilibrium gaseous plasma can be sustained by various discharges in a broad range of pressures. Of particular interest is a low-pressure radio-frequency (RF) plasma. The absorption of power supplied by an RF generator involves complex mechanisms, which are explained in [4]. The RF discharge can be sustained in various modes, such as capacitively and inductively coupled [5]. The Inductively coupled plasma can be sustained either in the E or H mode. The E-mode ("electrostatic mode") stands for the predominant capacitive character of the discharge impedance, while the H-mode stands for the inductive character [6]. The transition between the modes occurs abruptly as a critical power is supplied by the RF generator and is observed with the naked eye because the plasma luminosity is several orders of magnitude larger in the H-mode than in the E-mode [7]. The density of neutral radicals, however, is not so sensitive to the transitions because a rather low discharge power is needed to obtain a large dissociation fraction of simple molecular gases like oxygen [8]. Therefore, the inductively coupled RF plasma in the H-mode is an intense source of radiation, while the predominant reactants in the E-mode are neutral reactive plasma species, which are useful for polymer functionalization [9].

Plasma treatment is a complex process because of the presence of various reactive plasma species as well as radiation that are involved in plasma-polymer interaction processes [10]. However, also the densities and fluxes of reactive species to the polymer surface may vary significantly depending on plasma geometry, excitation, power, pressure etc. [10–12]. Furthermore, the type of reactive species and radiation depends on the type of gas used for plasma excitation. For polymer surface activation and improving wettability, often oxygen-containing plasmas are used to introduce polar oxygen functional groups to the surface [1].

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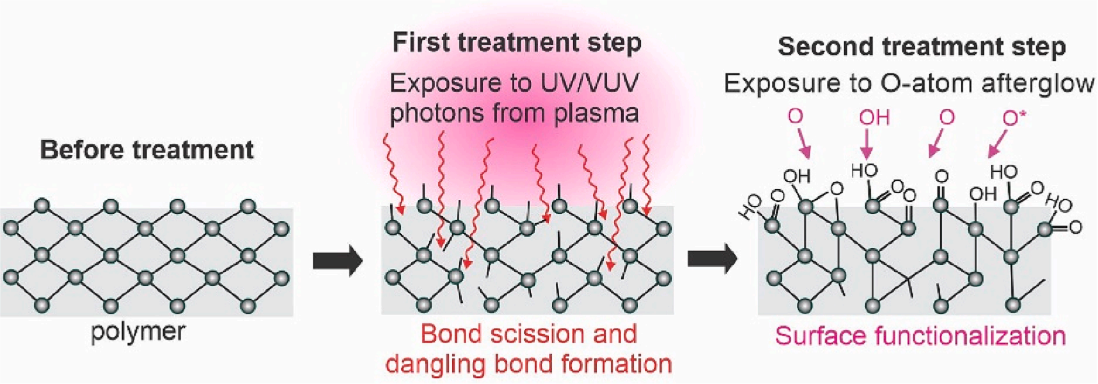


Fig. 1. Schematic of the treatment process.

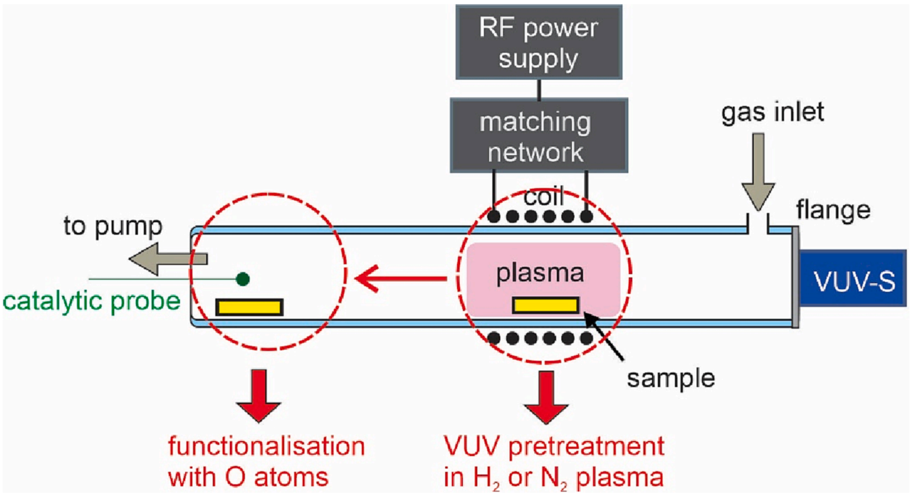


Fig. 2. Schematic setup of plasma system for modification of PVC with VUV pretreatment and O-atom post-treatment.

Oxygen plasmas are a source of neutral oxygen atoms in the ground state, metastables of oxygen molecules and ions [10]. Among these species, oxygen atoms are the most important for the surface modification of polymer materials [13]. Consequently, instead of using oxygen glows, treatments are often performed in afterglows which lack other particles and thus allow controlled oxidation of materials at room temperature [14]. Therefore, afterglows can be successfully used for the hydrophilization of especially aromatic polymers, but if other types of polymers are needed to be functionalized, a different approach must be used to increase hydrophilicity.

Plasmas are also a source of radiation with different wavelengths ranging from visible to ultraviolet (UV) range (200 – 400 nm) and further down to vacuum (VUV) ultraviolet range (10 – 200 nm) [15–17]. High-energy photons of UV and VUV radiation can cause polymer bond scission, formation of dangling bonds, and initiation of photochemical reactions [18–20], thus triggering the propagation of free-radical reactions [21]. Therefore, the energetic fluxes of VUV photons may be important for the processing of materials [21,22]. Especially hydrogen and also nitrogen plasmas are good sources of UV/VUV radiation [17]. However, oxygen plasmas that are usually used for functionalization with polar functional groups are not rich in UV/VUV radiation. This obstacle can be overcome by exposing the polymer to VUV radiation originating from H_2 or N_2 plasma to create dangling bonds before further treatment with oxygen atoms. We have recently shown for the case of polytetrafluoroethylene (PTFE) that using a two-step approach, involving exposure of PTFE to VUV radiation first, followed by O-atom treatment can produce highly wettable surfaces [23].

In this paper, we present the influence of VUV pretreatment on functionalization of polymer PVC with plasma. The surface effect of such a two-step treatment was compared to treatment using oxygen atoms only. For this investigation, polyvinyl chloride polymer was chosen for two reasons: (*i*) it is used for urinary medical catheters which need to be plasma-activated to improve the adhesion of antibacterial coatings, and (*ii*) there are only a few reports on modification of surface properties of this polymer by plasma treatment in comparison to numerous publications dealing with polymers used in more widespread applications.

2. Experimental

2.1. Polymer treatment conditions

Unplasticized polyvinyl chloride (PVC) polymer foil with a thickness of 0.2 mm was purchased from Goodfellow Ltd. The polymer was functionalized in oxygen afterglow created by inductively coupled radio-frequency plasma (ICP-RF). However, before performing oxygen functionalization, pretreatment of PVC was first carried out using plasma rich in VUV radiation such as hydrogen and nitrogen. A schematic of the treatment process is shown in Fig. 1.

Experiments were performed in the plasma system shown in Fig. 2. The plasma system consisted of an 80 cm long borosilicate glass discharge tube pumped with a two-stage rotary pump with a nominal pumping speed of 80 m^3/h. The diameter of the tube was 4 cm. For sustaining the plasma, a coil with 6 turns was used, which was connected to the RF generator (13.56 MHz) via a matching network. The

Table 1
Overview of plasma treatment conditions.

	1st step – VUV pretreatment					2nd step – Functionalization				
	Gas	Power (W)	Pressure & Flow	Treat-ment time	Sample posit-ion	Gas	Power (W)	Pressure & Flow	Treat-ment time	Sample posit-ion
1.	H_2	400	25 Pa 100 sccm	1 s	glow	O_2	500	30 Pa 75 sccm	1 – 300 s	after-glow
2.	N_2	400	33 Pa 100 sccm	1 s	glow	O_2	500	30 Pa 75 sccm	1 – 300 s	after-glow
3.	O_2	400	33 Pa 100 sccm	1 s	glow	O_2	500	30 Pa 75 sccm	1 – 300 s	after-glow
4.	No pretreatment					O_2	500	30 Pa 75 sccm	1 – 300 s	after-glow

power was adjusted to run the plasma in the H–mode, where the glowing plasma was concentrated in the center of the coil. Because the transition from the E- to H-mode appears at high powers, which also depends on the gas type and pressure, we had to choose different treatment conditions for each gas. To avoid thermal damage to the sample, we chose the lowest power where the plasma was still operating in the H-mode (400 W). When performing pretreatment in H_2, O_2 or N_2 gas, the sample was placed inside the coil, where the intensity of VUV radiation was maximal. The treatment time was 1 s to avoid thermal degradation. After pretreatment, the sample was moved to the afterglow region without opening the vacuum system and further treated with oxygen atoms for different treatment times. The list of experiments and corresponding treatment conditions are shown in Table 1.

2.2. *Plasma characterization*

The difference in UV/VUV radiation from H_2, N_2 and O_2 plasma was characterized by vacuum-ultraviolet spectroscopy. The spectroscopic

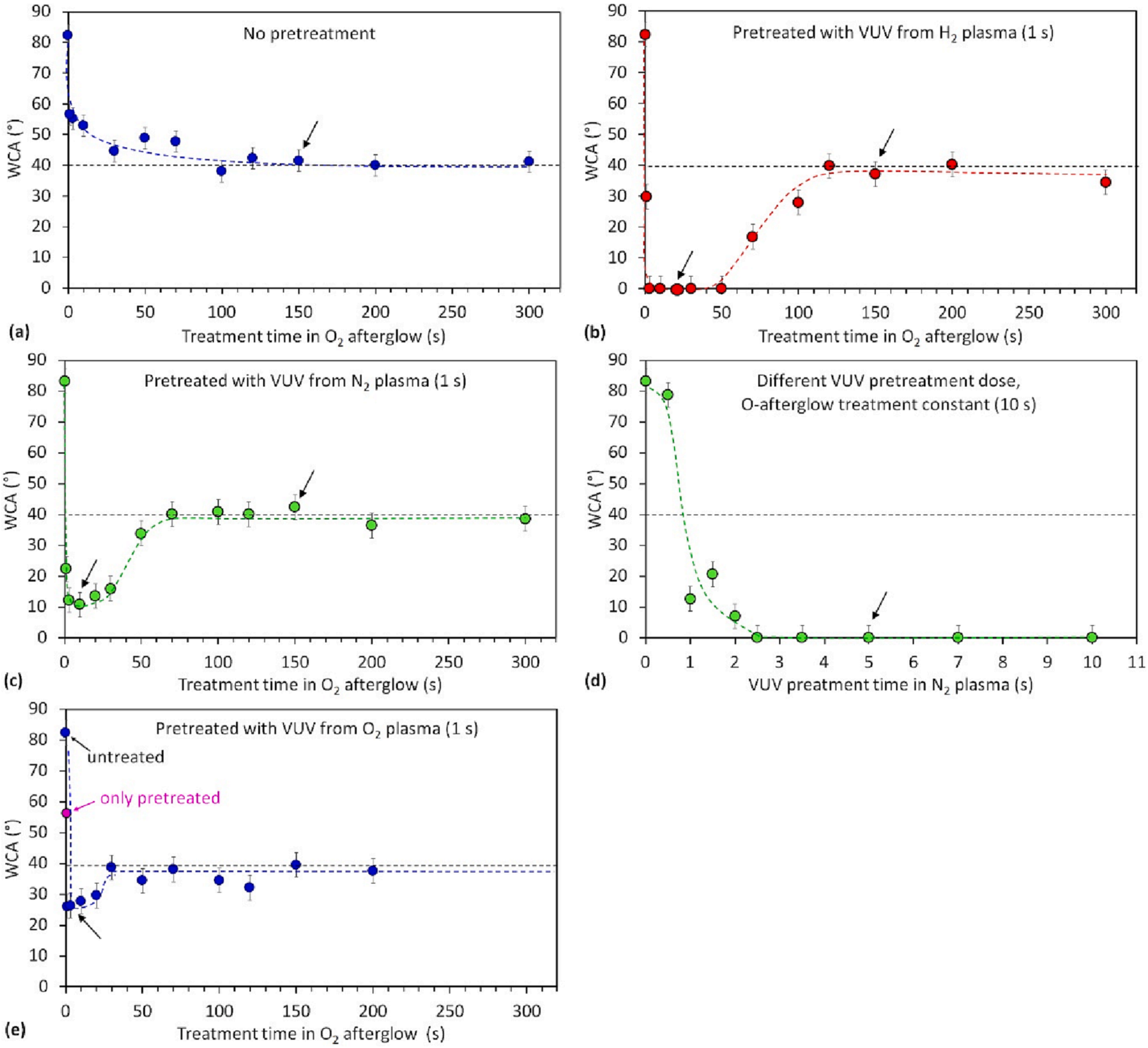


Fig. 3. Wettability of PVC exposed to: (a) O atoms without pretreatment, (b) VUV radiation from H_2 plasma followed by O-atom treatment, (c) VUV radiation from N_2 plasma followed by O-atom treatment, (d) VUV radiation from N_2 plasma (different times) followed by O-atom treatment for 10 s, and (e) VUV radiation from O_2 plasma followed by O-atom treatment. The points marked with arrows were also analysed by XPS (see Table 2).

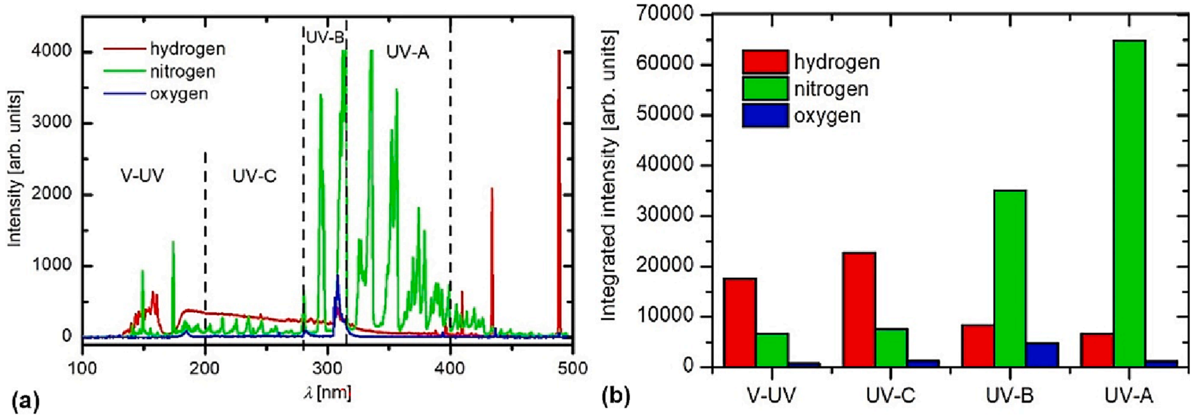


Fig. 4. (a) Vacuum ultraviolet spectra of H_2, N_2 and O_2 plasmas (400 W, 100 sccm) that were used for VUV pretreatment and (b) integrated values for different UV ranges.

system for VUV measurements consisted of a VS7550-VUV spectrometer with a krypton wavelength calibration lamp (VS-CLS-6LP) from Resonance Ltd. Spectrometer has a laminar flow purge system, which allows operation down to the window short-wavelength cut-off. MgF_2 window with 112 nm wavelength cut-off was used. Nitrogen was used as a purging gas. The integration time was 6 ms, and 10 averages were made. The grating angle was set to $-4°$, and the slit to 25 μm so that the resolution was around 0.2 nm. The aperture was set to F8.4.

The density and flux of oxygen atoms were determined with a cobalt catalytic probe which is described in [24]. The O-atom density was 4.1×10^{21} m^{-3}, whereas the O-atom flux was 6.4×10^{23} $m^{-2}s^{-1}$.

2.3. Polymer characterization

The effect of surface treatment conditions was monitored with water contact angle measurements (WCA) using Drop Shape Analyser DSA 100 (Krüss GmbH). A static contact angle was measured using a sessile drop method. The volume of a drop was set to 2 μL. MiliQ water was used for the determination of wettability. Five measurements were made for each sample.

A standard method for the evaluation of the surface kinetics upon treatment of polymer materials with gaseous plasma is X-ray photoelectron spectroscopy (XPS). A sample is mounted into an ultra-high vacuum chamber and illuminated with X-rays. The X-rays cause the emission of photoelectrons in a broad range of electron energies coming from the surface film with a thickness of a few nm. The relative intensity of photoelectrons' current arising from elements will reveal the concentration of these elements, while the shape of specific peaks will indicate the functional groups. Determination of functional groups requires the acquisition of specific peaks in a narrow energy region with a higher resolution which can be altered by changing the pass energy to allow only electrons of a given energy, i.e. pass energy, to be focused at a detector slit. Lower pass energy results in a better energy resolution. Selected samples were characterized by XPS using an instrument model TFA XPS (Physical Electronics). The samples were irradiated with monochromatic Al $K\alpha_{1,2}$ radiation with a photon energy of 1486.6 eV. Spectra were measured at an electron take-off angle of 45°. Survey spectra were acquired at a pass energy of 187 eV using an energy step of 0.4 eV. High-resolution C1s spectra were measured at a pass energy of 29.35 eV using an energy step of 0.125 eV. An additional electron gun was used for compensation for the accumulation of surface charge. The main C1s peak was set a value of 285 eV. Measured spectra were analyzed using MultiPak v8.1c software, which was supplied with the spectrometer. A Shirley-type background subtraction was used.

3. Results and discussion

3.1. Influence of VUV pretreatment on the surface wettability

In the first experiment, the afterglow of O_2 plasma was used for the treatment of PVC polymer as usually performed by researchers. The wettability was measured to monitor the effect of this treatment. Fig. 3a shows the water contact angle (WCA) of PVC exposed to O atoms for various treatment times. The curve shows a typical trend that is usually observed for plasma-treated polymers – i.e., a very fast drop of the WCA at initial treatment times followed by a steady state where the polymer surface is saturated with functional groups. The minimum WCA was approximately 40°, and it was obtained after approximately 100 s of treatment.

In the second experiment, PVC was first pretreated in H_2 plasma for very short time 1 s, moved to the afterglow without exposing it to the air, and then treated with O atoms. Such a treatment procedure caused a completely different trend in surface wettability as shown in Fig. 3b. Opposite to Fig. 3a, the WCA in Fig. 3b dropped from the initial value of 82° to almost zero (immeasurably low) already in the first second of treatment. This treatment, therefore, caused not just obtaining a superhydrophilic surface but also the time needed to modify the surface was reduced from 100 to just 1 s. Moreover, another difference can be observed in Fig. 3b with respect to Fig. 3a. If treatment with O atoms was too long, the WCA increased and reached the same plateau of approximately 40° as in Fig. 3a. The explanation for this effect is the surface etching, as proved by XPS and explained further below.

In the next step, the experiment shown in Fig. 3b was repeated. However, instead of using H_2 plasma for pretreatment, the polymer was rather pretreated with N_2 plasma (again for just 1 s) and then exposed to O atoms. The wettability of this surface is shown in Fig. 3c. The curve is similar to the one in Fig. 3b: i.e. (*i*) the minimum wettability was obtained already after 1 s of treatment with O atoms, and (*ii*) at longer treatment times, the WCA increased and stabilized at 40°. The minimum WCA in Fig. 3c was 10° so not as low as in Fig. 3b, which is a consequence of different doses of VUV radiation received in 1 s of pretreatment with H_2 or N_2 plasma, respectively. This was proved with a further experiment shown in Fig. 3d. Here, we changed the pretreatment time in N_2 plasma from 1 to 10 s to expose the surface to a higher dose of VUV radiation, whereas treatment with O atoms was kept constant at 10 s (this time corresponds to the minimum WCA in Fig. 3c). Fig. 3d shows that also N_2 plasma pretreatment can help to obtain a superhydrophilic surface as in the case of H_2 pretreatment, however, the N_2 treatment time must be longer (more than 2.5 s). From this result, we can conclude that both pretreatment procedures can lead to the same final result if the received dose of radiation is high enough. Because VUV radiation in N_2 plasma is less intense than in H_2 plasma, also the optimal time needed to

Table 2
XPS surface composition of the samples.

Sample	C	N	O	Si	Cl	O/C	Cl/C
untreated	79.0		9.8	0.9	10.3	0.12	0.13
Pretreated in H_2 (1 s)	92.0		6.0	0.9	1.2	0.06	0.01
Pretreated in N_2 (1 s)	79.1	4.1	12.6	2.0	2.2	0.16	0.03
Pretreated in N_2 (5 s)	69.7	12.9	13.8	1.5	2.1	0.20	0.03
Pretreated in O_2 (1 s)	68.4		21.7	0.4	9.7	0.32	0.14
Only O_2 treated (plateau)	61.6		24.0	1.1	12.0	0.39	0.19
H_2 pretreated + O_2 treated (minimum)	66.6		29.7	1.0	2.7	0.45	0.04
H_2 pretreated + O_2 treated (plateau)	63.9		22.6	0.2	13.3	0.35	0.21
N_2 pretreated (1 s) + O_2 treated (minimum)	63.2	3.9	29.8	0.0	3.1	0.47	0.05
N_2 pretreated (1 s) + O_2 treated (plateau)	64.3	1.6	22.2	0.5	11.3	0.35	0.18
N_2 pretreated (5 s) + O_2 treated (minimum)	70.6	2.4	24.5	0.8	1.7	0.35	0.02
O_2 pretreated (1 s) + O_2 treated (minimum)	63.5		26.2	0.0	10.3	0.41	0.16

receive the required dose is higher.

It should also be mentioned that in the pretreatment procedure, which was performed in the glowing plasma, the samples were not only exposed to VUV radiation but also to ions and other species, which may also have an influence on the pretreatment step. Therefore, in yet another experiment, the pretreatment was performed in O_2 glow which is poor in UV/VUV radiation, to prove the importance of UV/VUV radiation. These results are shown in Fig. 3e. Because of poor UV/VUV radiation of O_2 glow, the pretreatment with glowing O_2 plasma caused only a minor improvement of the surface wettability. The results in Fig. 3 thus clearly support the importance of UV/VUV pretreatment for bond scission and the creation of free radicals that can then further react with oxygen atoms and form new functional groups.

3.2. VUV emission intensity of H_2, N_2, and O_2 plasmas

For the estimation of the UV/VUV irradiation dose received by the samples, we measured VUV-UV emission from H_2, N_2, and O_2 plasma. A comparison of the VUV spectra of all three plasmas is shown in Fig. 4. The VUV spectrum of H_2 plasma is dominated by the intense radiation of molecular hydrogen in the Lyman band (resonant B-X transitions, 130 – 170 nm) and Werner band (resonant C-X transitions, below 130 nm) [17]. In the VUV spectrum of N_2 plasma, Lyman-Birge-Hopfield system is dominant. Fantz et al. have shown that the radiant power of N_2 plasma is only half of the radiant power emitted by H_2 plasma which also explains the lower effectivity of N_2 pretreatment in comparison with H_2 unless if the pretreatment times were prolonged. Compared to H_2 and N_2, O_2 plasma is a poor emitter in the VUV range. In the spectrum of O_2 plasma in Fig. 4a only one small peak at around 130 nm, which corresponds to $^3S°$ to ^3P transition, is observed. However, these spectra were not calibrated for spectral response, so this emission line is probably much higher because, according to NIST simulated spectra presented in [25], it is the most intensive line of O_2 plasma. There is also one band with a bandhead around 184 nm, which could be an emission from O_2 Schumann-Runge system.

To compare the emission of H_2, N_2, and O_2 plasmas, spectra were integrated in four different UV ranges: the VUV range from 100 to 200 nm, the UV-C range from 200 to 280 nm, the UV-B range from 280 to 315 nm, and the UV-A range from 315 to 400 nm. The results are presented in Fig. 4b. In the VUV region, H_2 plasma emits 2.6 times and 25 times more than N_2 and O_2, respectively. These ratios are quite similar in the UV-C region, whereas in the UV-B and UV-A region, the N_2 plasma is the most intense emitter. The ratio in the VUV region correlates perfectly with the results in Fig. 3. In N_2 plasma, the superhydrophilic surface was achieved with about 2.5 times longer treatment time than in H_2 plasma. This means that the dose of VUV light was the same for the samples treated for 1 s in H_2 plasma and samples treated for 2.5 s in N_2 plasma.

3.3. Influence of VUV pretreatment on the chemical composition

The surface chemical composition of the untreated and VUV-pretreated samples was also investigated by XPS to gain a further understanding of the role of the pretreatment procedure. Selected samples (marked with the arrows in Fig. 3) were analyzed. The measured surface composition is shown in Table 2 and summarized in Fig. 5. A remarkable drop in Cl concentration can be observed for the samples pretreated in H_2 and N_2 plasma but not for the one pretreated in O_2 glow. The Cl concentration dropped from the original 10 at.% to just 2 at.% or even less in H_2 plasma. The pretreatment step in H_2 or N_2 plasma with strong UV/VUV radiation has therefore an important effect on the dehydrochlorination of the surface (elimination of HCl).

Functionalization of H_2– or N_2–plasma pretreated PVC with O atoms caused a noticeable increase of the concentration of oxygen on the PVC surface. The maximum O concentration (approximately 29 at.%) was found for the samples exhibiting minimum WCA in Fig. 3b, c. Also, the surface concentration of Cl for these samples is still very low. The

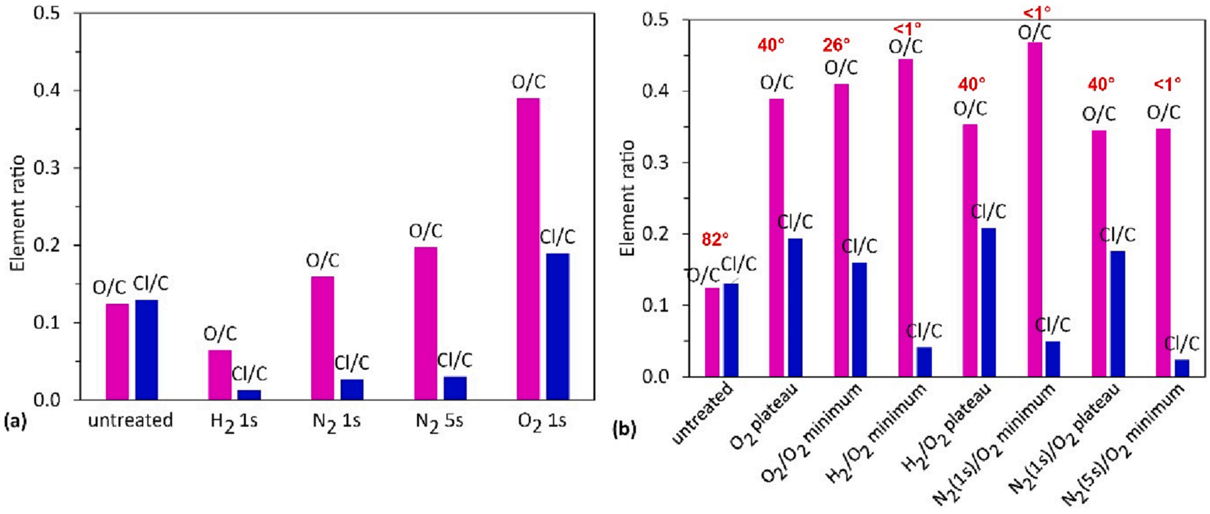


Fig. 5. O/C and Cl/C ratio for (a) pretreated samples and (b) selected samples functionalized with O-atoms which are marked with the arrows in Fig. 3. The wettability of these samples is shown in red.

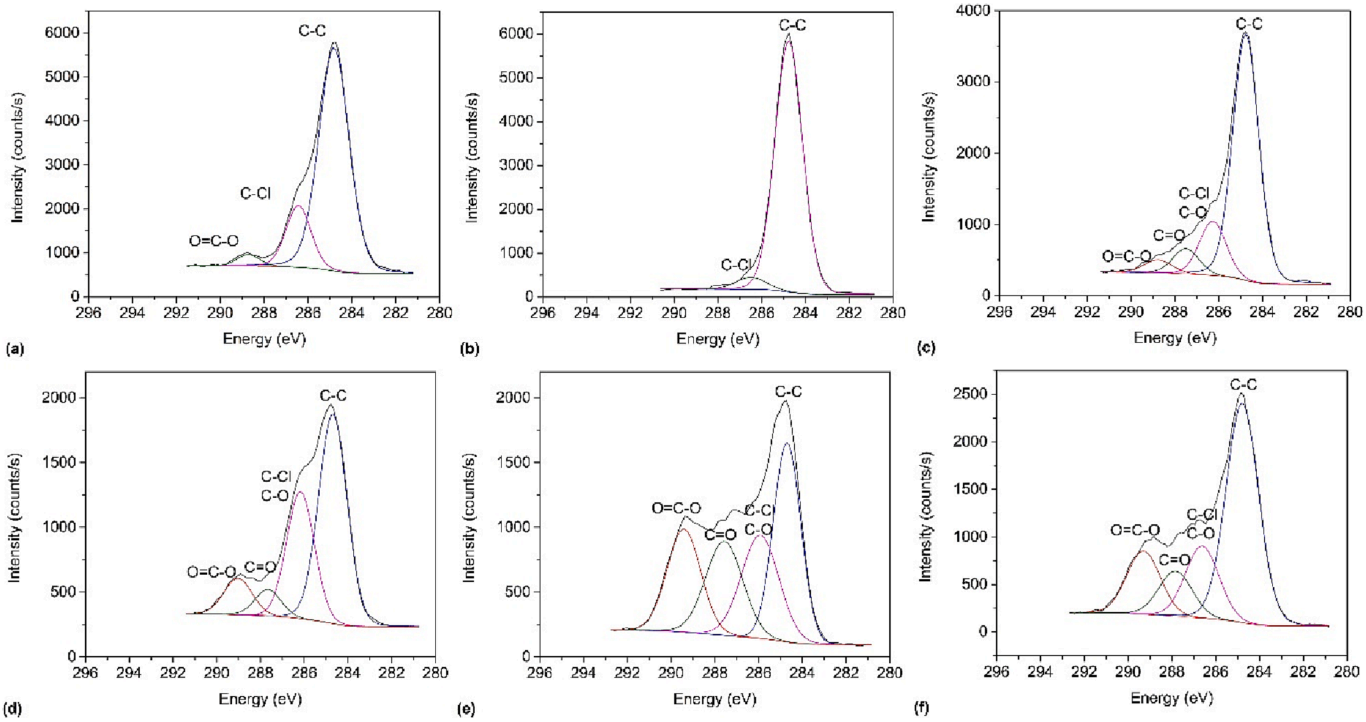


Fig. 6. HRES XPS spectra of the (a) untreated PVC, (b) H_2-plasma pretreated, (c) N_2-plasma pretreated, (d) O_2-plasma pretreated, (e) H_2 pretreated and functionalized with O atoms, (f) functionalized with O atoms without pretreatment.

minimum WCA is thus not only related to a high O content but also to a low Cl content. For example, the sample pretreated in O_2 plasma has a high O concentration but also a high Cl concentration, therefore, its wettability is not the best.

Opposite to the surface composition of the samples exhibiting low WCA, we can observe that for all samples with WCA of approximately 40° (the plateau), the O concentration was lower (22–24 at.%), regardless of using pretreatment or not. An important observation is that the concentration of Cl for these samples increased back to values similar to the untreated PVC. This again proves that surface concentrations O and Cl have a synergistic role in the wettability of the samples. This is further shown in Fig. 5, where the ratio of O/C and Cl/C is plotted. Here we can see that all pretreated samples (Fig. 5a) as well as the samples with the minimum wettability (Fig. 5b) have the lowest Cl/C ratio.

Variations in the elemental composition (i.e. dehydrochlorination and oxygen functionalization) are also reflected in the shape of carbon high-resolution (HRES) spectra, which are shown in Fig. 6 for different treatments. For the untreated PVC (Fig. 6a), three peaks are observed. The major two peaks correspond to C-C and C-Cl, whereas the third minor peak can be associated to carbon–oxygen contamination. The sample exposed to VUV radiation from H_2 plasma clearly shows signs of dehydrochlorination (Fig. 6b). The peak C–Cl almost disappeared; therefore, this sample is characterized by a distinct C–C peak. Opposite to H_2 plasma, VUV radiation from N_2 plasma (Fig. 6c) gives the impression that no dehydrochlorination is present. But this observation is misleading, as several new peaks are observed that appear at a similar binding energy as C–Cl. These peaks are a consequence of slight sample oxidation during N_2-plasma treatment because of the presence of water vapor, which is dissociated in plasma to OH radicals that may react with the dangling bonds. If PVC is treated with VUV from O_2 glow (Fig. 6d) also some surface oxidation occurs, however, the intensity of oxygen-related peaks is not high. Opposite to that, the sample pretreated by H_2 and then exposed to O-atoms (Fig. 6e) shows pronounced peaks related to different oxygen functional groups. As a comparison, we also show the spectrum of PVC treated only with O atoms without pretreatment, where the efficiency of incorporation of oxygen atoms is much lower because of missing dangling bonds (Fig. 6f). Fig. 6 thus correlates well with the previous results showing the best functionalisation of the sample treated by H_2 (VUV) and O_2 plasma.

3.4. Discussion on the reaction mechanism of VUV photons for surface modification

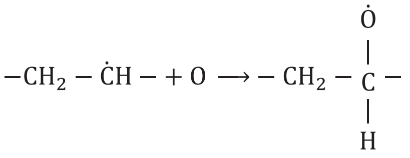
We can therefore conclude that pretreatment has a significant effect on the elimination of Cl atoms from PVC and the formation of dangling bonds, as already shown schematically in Fig. 1. PVC is a polymer known to be sensitive to UV solar radiation causing its degradation. It was reported that the main photodegradation of PVC is dehydrochlorination (Reaction (2)), followed by crosslinking and chain scission [26]. Dehydrochlorination can also lead to the formation of polyene (–CH_2 = CH_2–)$_n$ sequence chains (see Reaction (3)) [27]. Therefore, for UV/VUV plasma-treated PVC by, the following reaction mechanisms leading to dehydrochlorination and formation of free radicals can describe PVC modification:

$$- \mathrm{CH_2} - \mathrm{CHCl} - \xrightarrow{h\nu} - \mathrm{CH_2} - \dot{\mathrm{C}}\mathrm{H} - + \dot{\mathrm{C}}\mathrm{l} \tag{1}$$

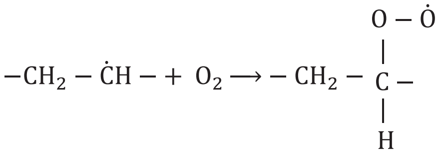
$$-CH_2 - CHCl - +\dot{C}l \rightarrow - \dot{C}H - CHCl - + HCl \tag{2}$$

$$-CH_2 - CHCl - \xrightarrow{h\nu} -CH = CH - + HCl \tag{3}$$

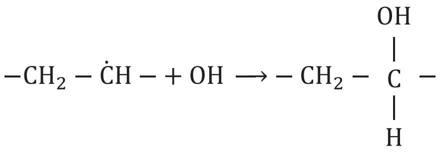
This is in agreement with our results which clearly prove that the dehydrochlorination process leads to the formation of the chlorine-depleted layer, which is more susceptible to further interaction with oxygen atoms than the untreated PVC polymer. Upon exposure to oxygen plasma species, the following reactions may appear:



$$-CH_2-\dot{C}H-+O\longrightarrow -CH_2-\overset{\overset{\dot{O}}{|}}{\underset{\underset{H}{|}}{C}}- \qquad (4)$$



$$-CH_2-\dot{C}H-+O_2\longrightarrow -CH_2-\overset{\overset{O-\dot{O}}{|}}{\underset{\underset{H}{|}}{C}}- \qquad (5)$$



$$-CH_2-\dot{C}H-+OH\longrightarrow -CH_2-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}- \qquad (6)$$

The reactions (4–6) may follow different propagation paths until their termination, as described in [13].

These reactions enabled polymer functionalization with oxygen groups and thus the formation of a superhydrophilic surface, which was the case at short treatment times. Opposite to short treatment times, long treatment times caused recovery of the Cl concentration, indicating the removal of the Cl-depleted layer because of the etching effect of O atoms, producing a surface similar to the sample without pretreatment. This also explains obtaining the same value of WCA (40°) at long treatment times independent if pretreatment was used or not. Also Wertheimer et al. [21] proposed the reaction scheme of a polymer with free radicals generated by VUV photons if exposed to oxygen-containing plasmas. The reaction scheme led to the formation of a wide variety of oxidation products which was shown in the case of polyethylene (PE). Wertheimer also reported that the absorption coefficient for various polymers differs, being the simplest for polymers containing - CH_2 - backbone such as polyethylene (PE) and similarly also polypropylene (PP), however, polymers with multiple bonds and aromatic polymers have much stronger absorption. Because of the different absorption coefficients for various polymers, also the penetration depth of VUV differs, being of the order of 60 nm for PE, and over 100 nm for O-containing functional groups, whereas for UV photons, the penetration depth can exceed 1 μm [21].

The absorption of photons for various polymers was investigated by Onari et al. [28], who found a strong absorption dependence on their wavelength. For PVC, there was an enormous increase in the absorption of UV at wavelengths below 160 nm [28]. Also for other types of polymers, it was found that a threshold value for huge absorption of photons was at wavelengths lower than either 160 or 180 nm [28]. Absorption lower than 160 nm was typical for simple alkanes, whereas for functionalized polymers like polyethylene glycol and polymethylmethacrylate, the threshold was approximately 180 nm. Moreover, some polymers exhibited additional absorption features at higher wavelengths. E.g. various styrene types of polymers and alkenes, such as polybutadiene, showed another maximum of absorption at approximately 200 nm [28]. Therefore, we can conclude, that the influence of photons on polymer modification to initiate reactions, which is presented here for the case of PVC, also applies to other polymers.

Furthermore, as reported by Holländer at al., molecular oxygen absorbs photons with wavelengths between 135 and 170 nm [29]. Such absorption leads to the dissociation of the O_2 molecule into the ground-state oxygen atom (O^3P) and an excited atom (O^1D). This means that in the presence of O_2 molecules in plasma, only radiation with wavelengths below 135 nm and above 170 nm can reach the polymer surface and cause its modification. The experiment performed by Holländer also proves that the surface reactions are substantially accelerated by simultaneous VUV irradiation. For polyethylene (PE) treated with H_2, H_2/He, and H_2/O_2 plasma, the rate of oxidation and the maximum oxygen concentration was the highest when treating the polymer with H_2 plasma emission, followed by H_2/He plasma emission and the smallest for H_2/O_2 plasma. If additional O_2 was added, the rate of oxidation decreased. Based on the order of the oxidation rates in these three experiments, the authors concluded that the radiative excitation of PE was more important for the oxidation reaction than the attack of the inactivated polymer by atomic oxygen, which is in agreement with the results presented above.

Table 3
Literature review of PVC wettability obtained by other authors.

REF	Treatment conditions*	Gas	WCA initial → final	XPS ratio O/C and Cl/C initial → final
[42]	Atmospheric DBD	air	86°→ 65°	O/C = 0.149 → 0.265 Cl/C = 0.03 → 0.03
[30]	Capacitive RF, 50–125 W, 1 h	Ar ion treatment	~90° →~15° after 1 day	O/C = 0.087 → 0.5 Cl /C = 0.63 → 0.083 after 1 day
[31]	RF ICP, 30–120 W, 10 Pa, 60 s	N_2	~85° →~25° at the highest power	Cl /C = 0.144 → 0.014 O/C = 0.116 → 0.301
[43]	RF ICP, 30–180 W, 20 cm^3/min, 0.5–3.5 min	remote AE direct AR	107°→ 22° (29°direct) if t > 3 min and 60–180 W	remote O/C = 0.06 → 018 Cl /C = 0.14 → 0.01 direct O/C = 0.06 → 0.15 Cl /C = 0.14 → 0.03
[32]	Plasmotron 2860 MHz, air, 0.04 mbar, 140 mA, 10 s, or UV Mercury lamp 254 nm, 1 h	air or UV irradiation	88.5°→ 17°: air and 88.5°→ 54°: UV	/
[33]	Ion implantation up to 1500 W, up to 1 h, 35 sccm, 5 × 10^{-5} Torr, 30 Hz, bias 4 kV	O_2 or H_2O ion treatment	97.2°→ 21.7° for O_2, 1000 W, 30 min 97.2°→ 29.9° for H_2O, 600 W, 30 min	O/C = 0.068 → 0.334 O2 O/C = 0.068 → 0.563 H2O
[44]	RF 13.56 MHz, 60 cm remote, 100 W, 60 cm^3/min, 60 s	O_2 remote	/	O/C = 0.152 → 0.228 Cl /C = 0.14 → 0.03
[45]	Atmospheric DBD, 20 W, 30–37 kHz	air	107°→ 57°	O/C = 0.12 → 0.21 Cl /C = 0.01 → 0.05
[46]	Atmospheric SBD, 200 W, 1.1 A, 15 s	air	85.9°→ 64.9°	O/C = 0.15 → 0.26 Cl /C = 0.03 → 0.03

*Abbreviations: DBD – dielectric barrier discharge, SBD – surface barrier discharge, RF – radiofrequency, ICP – inductively coupled.

The results above thus clearly show that the pretreatment step can significantly improve the final surface activation of polymers. However, one should be aware that if using N_2 plasma as a source of VUV for surface pretreatment, it can also cause incorporation of nitrogen atoms from plasma [31,32]. This has happened also in our case as shown in Table 2. Incorporation of nitrogen is, of course, absent in the case of H_2

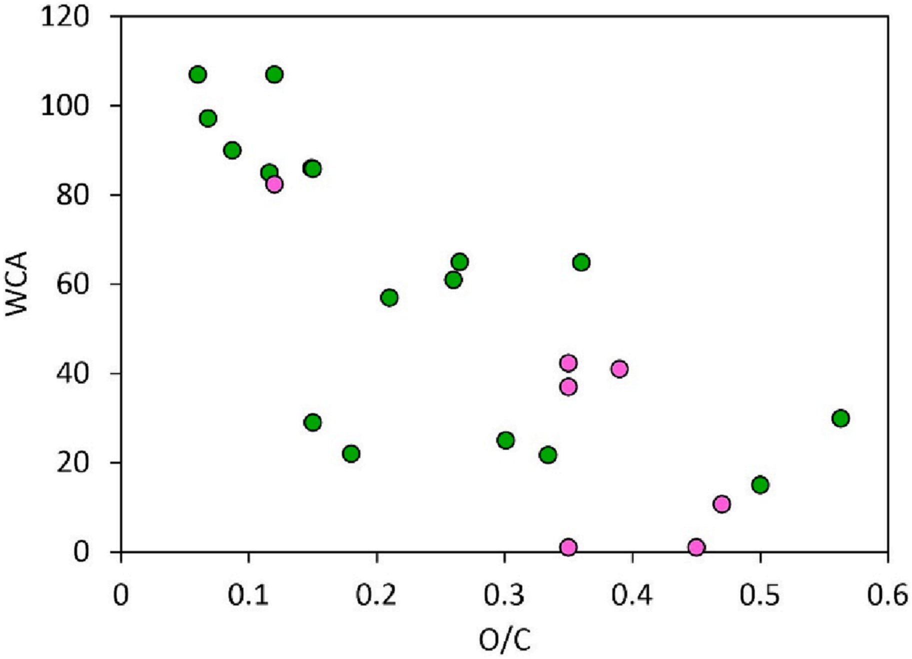


Fig. 7. Wettability of PVC versus the O/C ratio as obtained by other authors (green symbols) and our results (pink symbols).

plasma treatment. It may happen that traces of nitrogen may be undesirable for some applications, so in that case, it is better to use H_2 pretreatment. However, in industrial applications, where H_2 is not the preferred gas because of security reasons, H_2 may be replaced with N_2 if nitrogen traces do not pose a problem for the particular application.

At the end, it is also worth mentioning the results regarding the surface wettability and composition of PVC obtained by other authors, which are summarized in Table 3 and Fig. 7. It can be summarized that most of the treatments were performed either in atmospheric DBD plasma or low-pressure RF plasma. Rangel et al. [30] and Xiao-Jing et al. [31], who used RF plasma created in argon or nitrogen, respectively, found that WCA decreased with increasing power up to 125 W. Xiao-Jing has also found that chlorine concentration decreased with increasing power, whereas oxygen was increasing. He was using nitrogen plasma which is a source of UV/VUV radiation, therefore, a decrease in WCA can be related to increased radiant power. Kaczmarek et al. [32] compared air plasma treatment with UV radiation from a Mercury lamp (254 nm). He found better wettability of PVC after air-plasma treatment than after UV-lamp treatment, indicating that a radiation dose from a Mercury lamp was not as efficient as radiation from air plasma, including synergistic effects of ions. Some authors have also performed the treatment with ions (ion implantation), which, like irradiation, led to the formation of a surface with good hydrophilicity [30,33]. However, for plasma ion implantation, treatment times were much longer of the order of an hour, whereas, for regular plasma treatments, it was minutes or a few tens of seconds. There is no report on obtaining a superhydrophilic surface in a few seconds of treatment, as in our case.

Finally, it is worth mentioning that the creation of free radicals as a consequence of irradiation and their decay has been already investigated by some authors using electron spin resonance (ESR) [31,34–38]. The dangling bonds are usually just temporally stable, so they do not last long, because several radical recombination mechanisms can occur: (1) random diffusion of radicals in polymer until combined together by molecular radical termination reaction, and (2) recombination of radicals near the surface with gas species [34]. Most often it was reported that radicals can be stable for minutes or several hours, which also depends on the storage condition and temperature [34,36,39–41].

4. Conclusions

The influence of VUV and UV radiation on the degree of polymer surface modification was investigated. The source of radiation was H_2, N_2, and O_2 plasma. These plasmas were chosen because of a large difference in the intensity of radiation in VUV and different UV regions. As shown by VUV spectroscopy measurements, the most intensive radiation was found for hydrogen and nitrogen. Hydrogen radiation dominated in VUV and UV-C regions, whereas nitrogen dominated in UV–A and UV-B regions. Oxygen radiation was very poor and mostly in the UV-B region. The effect of VUV/UV radiation on the dangling bond formation and on the enhancement of the efficiency of further surface modification was investigated in the case of PVC polymer. PVC polymer was first pretreated with VUV radiation to make dangling bonds before further functionalization with neutral oxygen atoms. It was found that pretreatment of polymer in plasma rich with radiation in the VUV range can significantly improve treatment efficiency in terms of obtaining better hydrophilicity in very short treatment times. For example, 1 s of pretreatment in hydrogen plasma followed by 3 s of treatment with neutral oxygen atoms was already enough to obtain a superhydrophilic surface.

CRediT authorship contribution statement

Alenka Vesel: Writing - original draft, Writing - review & editing, Supervision, Data curation, Validation, Project administration, Funding acquisition. **Rok Zaplotnik:** Conceptualization, Methodology, Investigation, Formal analysis, Validation. **Miran Mozetic:** Supervision, Writing - review & editing. **Nina Recek:** Visualization, Investigation, Formal analysis.

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.

Data availability

Data will be made available on request.

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