Full Length Article

Grafting of carboxyl groups using $CO_2/C_2H_4/Ar$ pulsed plasma: Theoretical modeling and XPS derivatization

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ABSTRACT

The grafting of carboxyl groups enhances cell adhesion and can be used for immobilization of different biomolecules onto plasma-treated materials. The process, however, was not well optimized due to lack of clear understanding of the mechanisms of carboxylic group incorporation into plasma and their grafting to polymer surface. In this work the deposition of COOH plasma polymers from $CO_2/C_2H_4/Ar$ pulsed discharge has been studied depending on the gas mixture and duty cycle. We have demonstrated that the $CO_2/C_2H_4/Ar$ plasma with adjustable thickness of COOH functionalized layer and high stability of the grafted functions in water is a better solution for the COOH surface functionalization compared to the thoroughly analyzed CO_2 plasma. The concentration of different carbon environments and the density of COOH groups have been measured by using chemical derivatization combined with X-ray photoelectron spectroscopy. It has been found that the $CO_2/C_2H_4/Ar$ plasma mainly contains ester groups (COOC), the COOH/COOC ratio being between 0.03 and 0.08. The water stability of the COOH groups was significantly higher compared to ester environment, so immersing in water for 24 h allowed to increase the COOH/COOC ratio by a factor of 3. The mechanisms of the CO_2 molecule attachment to hydrocarbon chains on the polymer surface and those located inside the plasma were modeled using *ab initio* calculations.

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1. Introduction

The CO_2 and CO_2/H_2O plasma treatment as well as the plasma deposition of thin films in a gaseous mixtures of CO_2 with different hydrocarbon gases (CH_4, C_2H_4, *etc.*) have been used for decades to modify the surface chemistry of polymers by introducing the COOH and other polar groups to improve their hydrophilicity [1–4]. The introduction of COOH groups allows to improve cell adhesion [5] and to immobilize different vital biomolecules [6]. However, the mechanisms hidden behind incorporation of COOH groups and other carbon/oxygen functionalities are not well understood.

The density and stability of COOH groups are important characteristics of plasma modified biomaterials because the grafting of carboxyl groups enhances cell adhesion and promotes immobilization of different biomolecules onto plasma treated materials [7,8]. Simple CO_2 plasma treatment, which was of great interest in the past, is not currently used because this method leads to rapid surface degradation. In addition, the amount of the COOH(COOR) groups introduced by this method was too low [9–12]. Medard et al. unsuccessfully tried to increase the COOH density by adding water vapors into the gas mixture [9]. On the contrary, the introduction of the H_2O led to the depletion of the COOH concentration due to quenching of the CO_2^* reactive plasma species that they expected to be the initiators for the COOH grafting [13]. Hegeman et al. improved the stability of the COOH functionalization by adding ethylene in the CO_2/Ar plasma [14]. The deposition of stable thin films containing COOH groups (**C**(O)O contribution estimated by

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Table 1
Plasma conditions, film thickness, and content of $C(O)O$ and COOH groups on the surface of CO_2/C_2H_4 plasma polymers.

R	Q_{CO2} (sccm)	Q_{C2H4} (sccm)	Q_{H2} (sccm)	Q_{Ar} (sccm)	DC (%)	Pressure (Pa)	[$C(O)O$] (at.%)	[COOH] (at.%)	Thickness (nm)
0.135	2.5	16.0	0	50	5	3.5	1.7	0.13	186
0.350	8.6	16.0	0	50	5	4.0	8.0	0.25	107
0.391	10.3	16.0	0	50	5	4.0	9.7	0.33	75
0.723	16.2	6.2	0	50	5	3.8	11.3	0.57	37
0.839	16.2	3.1	0	50	5	3.6	12.6	0.77	41
0.391	10.3	16.0	0	50	15	4.1	9.4	0.30	105
0.391	10.3	16.0	0	50	33	4.3	4.3	0.10	177
0.391	10.3	16.0	10	50	15	4.1	8.6	0.27	53

XPS C1s curve fitting varied from 5 to 15%) improved cell adhesion to the polycaprolactone nanofibers and enabled the immobilization of the vascular epidermal growth factor on the plasma coated surface [7,15,16]. The high level of crosslinking was achieved by introducing of the ethylene, which changed plasma characteristics and improved mechanical stability of the COOH functional coating. The durability of CO_2/C_2H_4 plasma coatings was reported to be several times higher compared with plasma polymerized acrylic acid films [17]. Although Hegemann et al. showed that the composition of plasma coating can be adjusted by tuning the CO_2/C_2H_4 ratio a deeper understanding of the CO_2/C_2H_4 plasma polymerization is needed. The high chemical stability of the CO_2/C_2H_4 plasma coatings (*i.e.* low thickness loss) has been only achieved for very low CO_2/C_2H_4 ratios, which correspond to low $C(O)O$ percentages. Note that authors did not perform the derivatization of the COOH groups and analyzed different carbon environments concentrations ($C(O)O$, $C—O$, CH_x, *etc.*) measured by XPS. Since the $C(O)O$ component positioned at ~289 eV included both the carboxylic acid (most reactive group) and ester groups, the COOH grafting was not clearly evidenced.

Terlingen et al. suggested that reactive atomic oxygen is responsible for the grafting of functional groups onto the surface of polymeric substrates (*e.g.* polyethylene). [18]. Authors discussed a simplified grafting mechanism using a very rough approximation, but no clear explanation or experimental evidence which could shed light on the mechanism were proposed. Medard et al. improved the Terlingen's model by employing numerous optical emission spectroscopy and mass spectrometry to obtain valuable information about the active species in CO_2 plasma [4,9,13] and found several important excited species (CO, O) and reactive CO^+ and CO_2^+ ions. By analyzing the dependence of these species on plasma and gas parameters, authors were able to define the different regimes of CO_2 plasma, namely CO_2^- and CO^+ and O controlled. At low discharge power, the main active species presented in plasma were CO_2^+ and CO_2^*. With raising power or increasing the polymer (polyethylene and polypropylene) treatment time, the decrease of the CO_2^+ and CO_2^* intensities was observed [1,13]. The same effect for CO_2 plasma-processed polystyrene was confirmed by Wang et al. [11,19].

The available literature data demonstrated that, depending on the CO_2 plasma power and composition of the gas, different active species played significant role in the surface functionalization. Moreover, the presence of polymeric substrate in the reactor decreases the intensity of important active species emission lines by 20% due to the change in the plasma chemistry (mainly due to the introduction of hydrogen and water) [1,9]. Authors thoroughly described the kinetics of processes occurring in plasma and concluded the importance of ions and excited species such as CO_2^* in the surface functionalization. They proposed very interesting mechanism initiating the grafting of COOH groups *via* eliminating of hydrogen followed by recombination of $^*O—C=O$ radical from gas phase with $^•CH$ radical in the polymer chain [13]. Then the uptake of hydrogen would lead to the formation of COOH moiety. Interestingly, authors proposed that the CO_2^* species will attach to the polymer chain *via* a carbon atom allowing the possible formation of the COOH groups and not *via* an oxygen atom leading to the formation of ester function [13]. The possibility of the COOH grafting *via* the recombination of $COOH^+$ ions formed in the gas phase was also considered, but the mass spectroscopy study of CO_2 and CO_2/H_2O plasmas did not revealed $COOH^+$ ions in the discharge [9]. Thus, it has been concluded that the main mechanism for the incorporation of COOC and COOH functions is the interaction of excited CO_2^* molecules with the free radicals on the polymer surface. It is worth noting that the plasma chemistry of the $CO_2/C_2H_4/Ar$ plasma is more complicated compared with the CO_2 plasma, so it is expected that the mechanism for the formation of COOH and $C(O)O$ environments will be even more complicated.

In the present study the chemical structure, stability, and density of carboxylic groups in the CO_2/C_2H_4 plasma coatings were analyzed. The concentration of the carboxylic groups was evaluated by chemical derivatization combined with X-ray photoelectron spectroscopy (XPS). The influence of the plasma parameters on the properties of the deposited layers was investigated. The mechanism of the incorporation of carboxylic groups was also discussed based on modeling using density functional theory (DFT).

2. Materials and methods

2.1. Deposition of plasma polymers

The deposition of plasma polymers was carried out using a vacuum system UVN-2M equipped with the rotary and oil diffusion pumps providing the residual pressure in a vacuum chamber below 10^{-3} Pa. The capacitively coupled radio-frequency (RF) plasma was driven by a Cito 1310-ACNA-N37A-FF (Comet) RF power supply connected to a RFPG-128 disk generator (Beams & Plasmas), 135 mm in diameter, installed into the vacuum chamber. The RF power was set to 500 W, whereas the duty cycle (DC) was varied from 5 to 33%. The deposition time was 15 min.

Ar (99.998%), CO_2 (99.995%), and C_2H_4 (99.95%) gases were used as precursors. Gas flow control was carried out using a Multi Gas Contoller 647C (MKS). Working and residual gas pressures were measured by a VMB-14 unit (Tokamak Company) and D395-90-000 BOC Edwards controllers. The distance between RF-electrode and the substrate was set to 8 cm. The IR-transparent Si (111) plates, 1×1 cm^2 in size, were used as a substrate material and placed on ground electrode. The substrates were cleaned in isopropyl alcohol for 5 min using a UZDN-2T ultrasonic bath.

The influence of gas flow ratio R ($R = Q_{CO2}/(Q_{CO2} + Q_{C2H4})$, where Q_{CO2} and Q_{C2H4} are the CO_2 and C_2H_4 flow rates) on the properties of plasma polymers was studied at fixed DC of 5% and power of 500. In addition, the effect of H_2 addition into the gas mixture on the layer chemistry was studied. H_2 (99.99%) gas was generated by distilled water decomposition using a CAM1-30 electrolyser (Regnatiss Company) with power of 350 W. The plasma conditions are summarized in Table 1.

2.2. Chemical derivatization

In order to quantify the carboxyl groups concentration [COOH], the CO_2/C_2H_4 plasma polymers were reacted with trifluoroethanol using the method proposed by Chilkoti et al. [20]. The samples were placed on the glass slide inside the 100 mL flask. The 0.9 ml of TFE (99%), 0.4 ml of pyridine (99.8%), and 0.3 ml of N,N′-Di-tert-butylcarbodiimide (99%, all from Sigma Aldrich) were subsequently dripped to the bottom of the flask with an interval of 15 min. The reaction proceeded in the closed flask at room temperature (~25 °C) for 1.5 h. By measuring XPS after the derivatization, the atomic concentration of carboxyl groups [COOH] was estimated using Eq. (1), where [C] and [F] are atomic concentrations of carbon and fluorine, respectively [21].

$$[COOH] = \frac{[F]}{3\,[C] - 2\,[F]}[C] \qquad (1)$$

2.3. XPS analysis

The chemical composition of the sample surfaces was characterized by XPS using an Axis Supra (Kratos Analytical) spectrometer. The maximum lateral dimension of the analyzed area was 0.7 mm. To avoid differential charging of samples, spectra were acquired with charge neutralization in overcompensated mode. The spectra were subsequently normalized by shifting hydrocarbon component CH_x to 285.0 eV. The spectra were acquired at pass energy of 20 eV. The fitting of XPS C1s and O1s peaks was done using the CasaXPS software (version 2.3.17) after subtraction of the Shirley-type background employing Gaussian–Lorentzian (G—L) peaks with the fixed G—L percentage of 30%. The values of binding energies (BEs) of C and O environments were taken from the literature [22–24].

2.4. Optical characterization

The transmittance in the spectral range from 370 to 7500 cm^{-1} was measured using a Fourier transform infrared (FTIR) spectrophotometer (Bruker Vertex 80 v) with a parallel beam transmittance accessory. The data were collected at a pressure of 250 Pa with the resolution of 4 cm^{-1} and 100 scans. The transmittance of the films deposited onto Si substrate was divided by the transmittance of bare Si substrate in order to calculate a relative transmittance.

The thickness of plasma polymers was determined by ellipsometry using a phase modulated ellipsometer (JobinYvon UVISEL) in the spectral region of 1.5–6.5 eV at an incidence angle of 65°. The data were fitted using PJDOS dispersion model for SiO_2-like materials and the structural model of wedge-shaped non-uniform thin film [25].

2.5. SEM

The microstructures of as-deposited plasma polymers and those after immersion in water were studied by scanning electron microscopy (SEM) using a JSM F7600 (Jeol Ltd.) device. The SEM micrographs were obtained at accelerating voltage of 5 kV and the scan time of 1 min. In order to compensate the surface charging, the samples were coated with a ~5 nm thick Pt layer by using magnetron sputtering.

2.6. Theoretical modeling

The possible mechanisms of CO_2 molecule attachment to hydrocarbon chains both on the substrate surface and inside the plasma were modeled within the framework of DFT with B3LYP exchange-
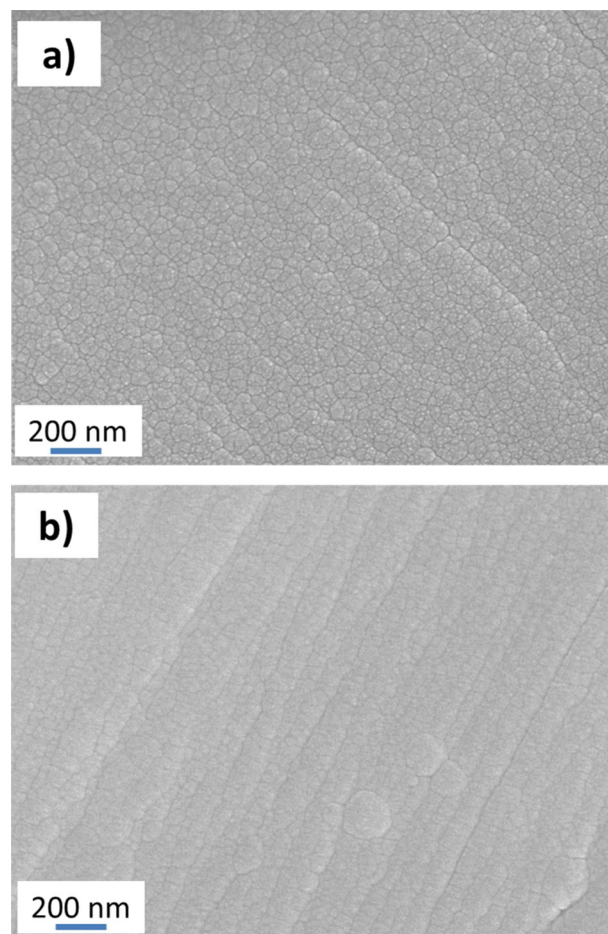

Fig. 1. SEM micrographs of CO_2/C_2H_4 plasma polymer as-deposited at R = 0.391 (a) and after immersion in water for 24 h (b).

correlation functional [26,27] and using 6-311 + +G(d,p) basis set as implemented in GAMESS code [28].

3. Results and discussion

3.1. Stability and homogeneity of plasma polymers

The pulsed plasma deposition from the $Ar/CO_2/C_2H_4$ mixture led to the formation of homogenous and well adherent layers at all deposition parameters used. The SEM micrographs revealed no pinholes, cracks, or other damages in the as-deposited layers (Fig. 1a). The immersion of the plasma polymers in water at room temperature for 24 h led to no changes in the layer morphology, regardless of the deposition conditions (Fig. 1b).

According to the FTIR results, the CO_2/C_2H_4 plasma polymers exhibited the features of hydrocarbon (which is confirmed by the presence of C-H_3, C-H_2 and C-H peaks at 2978, 2937 and 2884 cm^{-1}, respectively), carboxyl/ester groups (C=O stretching at 1730 cm^{-1}), and OH band at ~3300 cm^{-1} (Fig. 2). The analysis of FTIR spectra of as deposited layers and air storage plasma polymers within 1 month revealed no changes in the layer chemistry. The immersion of the CO_2/C_2H_4 plasma polymers in water for 3 h did not lead to any layer degradation that was also confirmed by both FTIR and XPS analyses. In contrast, the immersion of the layers for 24 h resulted in the formation of a new peak at 1590 cm^{-1} that can be attributed to the carboxylates. However, this peak may also overlap with amide, as XPS revealed the presence of nitrogen peak ([N] ~ 1 at.%) in the spectrum. The formation of carboxylates can be caused
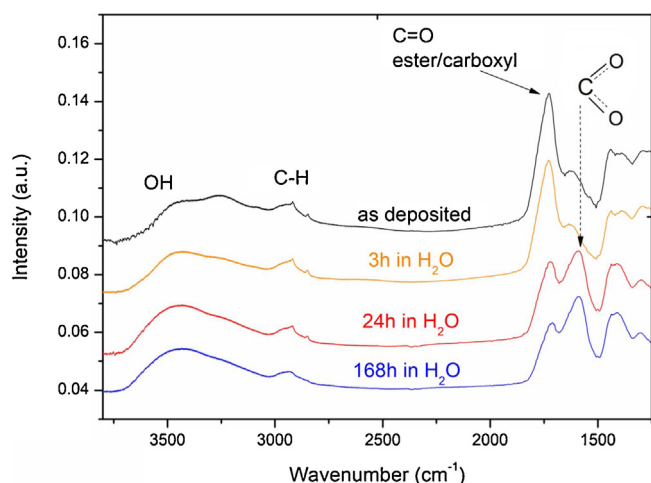
Fig. 2. FTIR spectra of sample as-deposited at R = 0.839 and those after immersion in water for 3, 24, and 168 h.

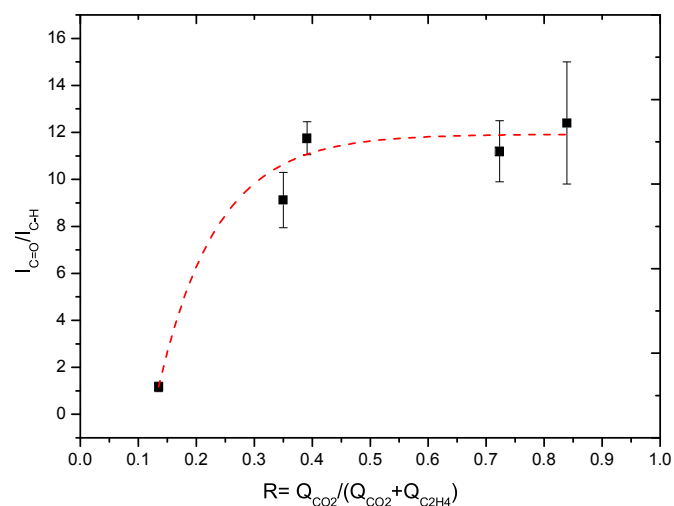**Fig. 3.** $I_{C=O}/I_{CH}$ ratio as a function of gas ratio R. The $I_{C=O}/I_{CH}$ ratio was calculated as the total area under the C=O peaks divided by the total area occupied by the CH peaks.

by deprotonation of the carboxylic acid functions during soaking in the de-ionized water. The immersion for 7 days did not lead to any significant changes in the FTIR spectra compared with those obtained from the samples after immersion for 1 day only (Fig. 2).

According to the ellipsometry results, the thickness of plasma polymers decreased after immersion in water for 24 h. The highest thickness loss (approximately 39%) was observed for the layer deposited at highest concentration of CO_2 (R = 0.839). Interestingly, the chemical derivatization of COOH groups revealed that the concentration of carboxyl groups [COOH] decreased by only 0.12 at.%, whereas the concentration of ester groups decreased by ∼8 at.%. It is reasonably to conclude that the dissolution of the CO_2/C_2H_4 plasma polymers is related to the hydrolysis of the ester bonds, whereas the COOH groups are mostly preserved even at highest R. Therefore, the concentration of the carboxyl groups can be increased by simply soaking the plasma polymers in water. Note, that the preferential hydrolysis of ester groups can be employed for some biomedical applications. For example, the water-degradable layers can be used for the adjustable release of drugs from the nanoparticles or nanofibers.

3.2. Influence of R on the layer chemistry

The changes in the layer chemistry were first studied by FTIR. The $I_{C=O}/I_{CH}$ ratio (total area under the C=O peaks located at 1800 to 1620 cm^{-1} divided by the total area of peaks positioned at 3050 to 2800 cm^{-1} dependence on gas ratio is shown in Fig. 3. It can be seen that in the range of R values from 0.135 to. 0.391, the $I_{C=O}/I_{CH}$ ratio increased and then reached the steady state value around 12. Hence, the concentration of chemical groups containing carbonyl function (C=O) increased with increasing the CO_2 concentration only within a narrow range of R. In order to better understand dependence of each chemical group (ester, carboxylic groups, *etc.*) on gas ratio R, the same layers were further analyzed by XPS and chemical derivatization.

The XPS analysis has revealed that all CO_2/C_2H_4 plasma polymers only consist of carbon and oxygen. The increase in R leads to the increase of oxygen concentration at the expense of carbon. As shown in Fig. 4, the O/C ratio *versus* R exhibits very similar behavior as the $I_{C=O}/I_{CH}$ ratio. In order to investigate the chemical composition of plasma polymers in more detail, the XPS C1s spectrum (Fig. 5a) was fitted with a sum of four components: hydrocarbons **C**H$_x$ (BE = 285.0 eV, used for BE scale calibration), carbon singly bonded to oxygen **C**—O (BE = 286.55 ± 0.05 eV), carbon doubly bonded to oxygen **C**=O (BE = 287.8 ± 0.05 eV), and
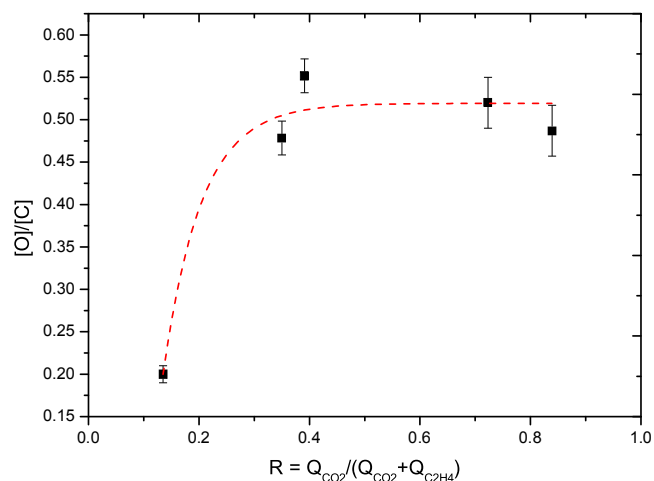
Fig. 4. The O/C ratio as a function of gas ratio R.

carbon of ester or carboxylic group **C**(O)O (BE = 289.0 ± 0.03 eV). The full width at a half maximum (FWHM) for all peaks was set to ∼1.5 eV. Note that the direct XPS C1s fitting can not provide the reliable information regarding the density of carboxylic groups [COOH] because they overlapped with the ester functions COOC. Thus, we have used the well-known chemical derivatization with trifluoroethanol (TFE) [20,29] to determine the [COOH]. The reaction between COOH groups of the CO_2/C_2H_4 plasma polymer and OH groups of the TFE leads to the incorporation of fluorine into the plasma layer and the concentration of fluorine [F] in the as-deposited layer depends on the [COOH] according to Eq. (1). In addition, the reaction between the plasma polymer and TFE leads to the incorporation of a new type of carbon, namely a carbon with three bonds to fluorine **C**F$_3$. The corresponding carbon peak positioned at 292.8 eV, as shown in the XPS C1s spectrum of the derivatized CO_2/C_2H_4 (Fig. 5b). Note, that apart from the CF$_3$ appereance the gas phase derivatization with TFE did not alter the carbon envirionment and, therefore, the derivatization results can be assumed to be reasonable. The dependence of different carbon environments as a function of R is exhibited in Fig. 6.

As shown in Fig. 6, the **C**—O and **C**=O contributions exhibited the same dependence on gas ratio as the O/C ratio *versus* R, *i.e.* the concentration of these carbon environments increased with increasing

Fig. 6. The evolution of carbon environments as a function of gas ratio.

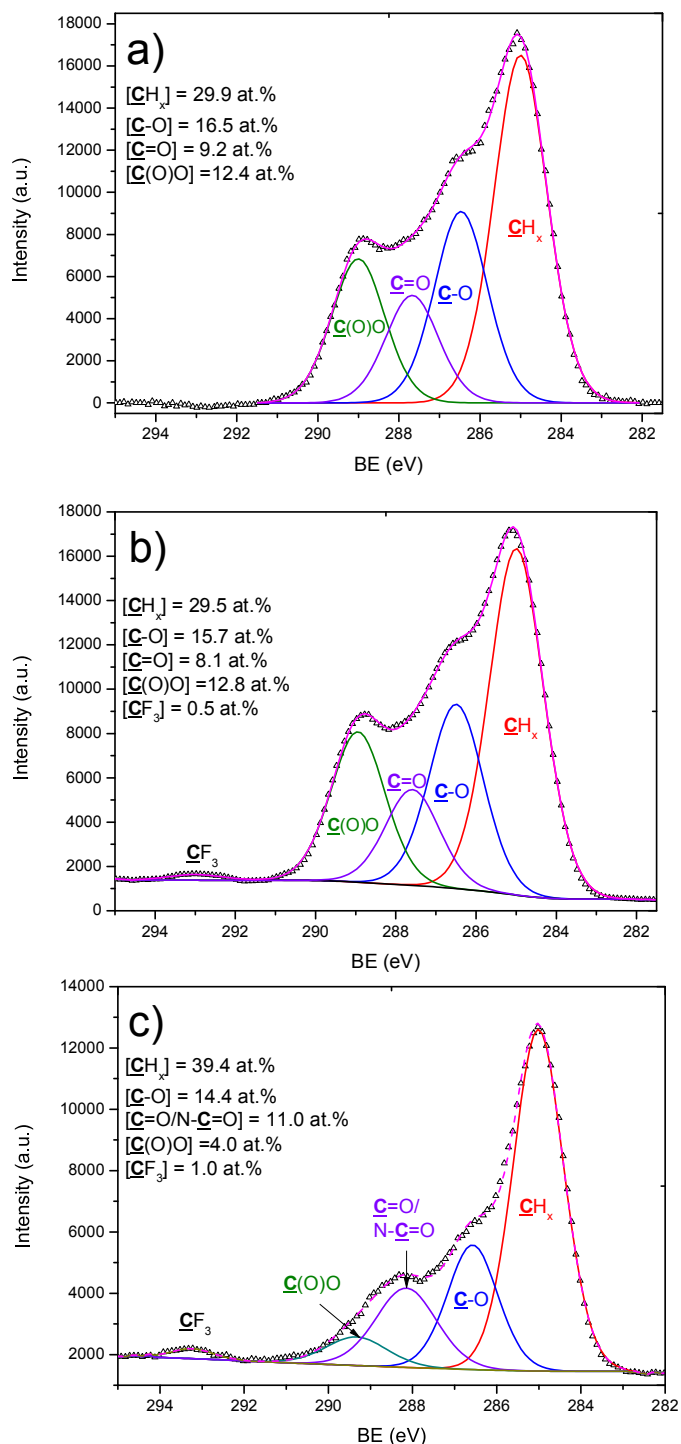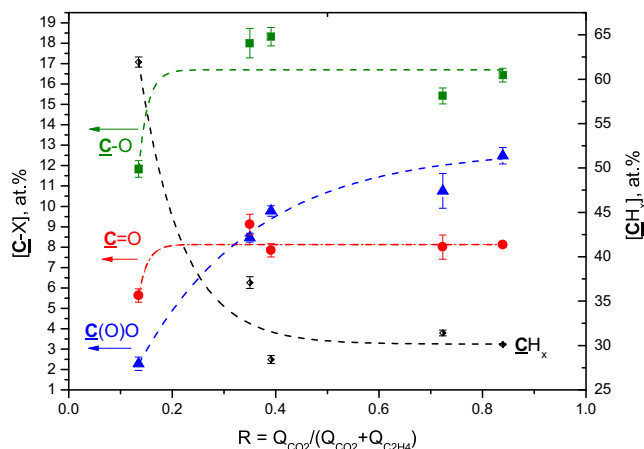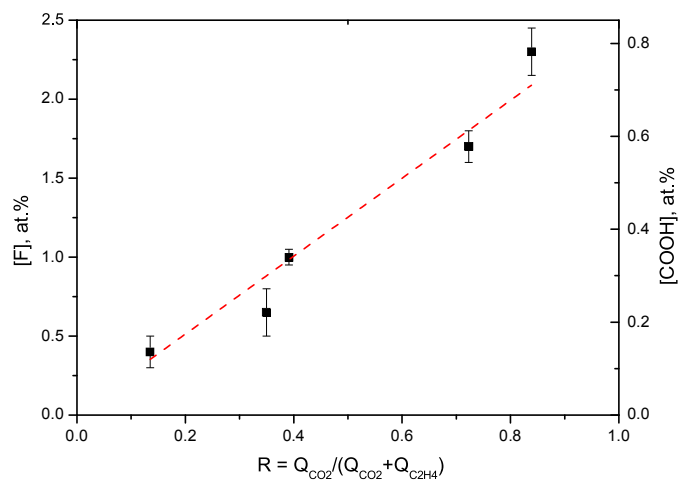**Fig. 7.** Fluorine [F] and [COOH] concentrations as a function of gas ratio R.

Fig. 5. XPS C1s spectra of (a) as-deposited plasma polymer (R = 0.839), (b) derivatized plasma polymer and (c) the same sample after immersion in water for 24 h followed by derivazitation.

R while decreasing $\mathbf{C}H_x$ until R = 0.350 and then the curve went to the plateau at R > 0.2. The $\mathbf{C}(O)O$ component reached maximum values at R > 0.8. The increase in the incorporation of oxygenated carbon environments with increasing R can be explained by the higher concentration of oxygen radicals and other oxygenated species in the plasma. Indeed, it was suggested that the grafting of COOH groups from CO_2, CO_2/H_2O, and CO_2/C_2H_4 plasmas occurred due to the interaction of CO_2 plasma species (CO_2^+, CO_2^*) [9,13] or atomic oxygen [18] with a hydrocarbon polymeric network. Hence,

the increase in the CO_2 concentration in the gaseous mixture should enhance the formation of CO_2 active species and, consequently, the density of $\mathbf{C}(O)O$ environment in the plasma polymer network.

Since the main focus of our work was to study the grafting of COOH groups, particular attention was paid to the derivatization of carboxylic groups and further comparison of the measured [F] and calculated [COOH] from Eq. (1) values with the [$\mathbf{C}(O)O$] obtained from XPS C1s fitting. The corresponding dependences of [F] and [COOH] *versus* R are shown in Fig. 7. It can be clearly seen that the atomic concentration of fluorine (maximum value equal to 2.2 at.% observed for R = 0.839) is significantly lower as compared to the concentration of $\mathbf{C}(O)O$ contribution and the [COOH]/[$\mathbf{C}(O)O$] value falls between 0.03 and 0.08. Additionally, the evolution of [COOH] as a function of R is very different from those observed for the $\mathbf{C}(O)O$, O/C, and $I_{C=O}/I_{CH}$ parameters. The [F] and [COOH] values were observed to linearly increase with R in the entire range of gas ratio R. This means that an increase in CO_2 concentration leads to higher incorporation of carboxyl groups, although the O/C ratio and $\mathbf{C}(O)O$ value reach the plateau at approximately R = 0.350–0.500. Thus, an increase in the CO_2 concentration in the gaseous mixture leads to an increase in the [COOH]/[C(O)O] ratio.

It should be remarked that both the O/C = 0.45 and [$\mathbf{C}(O)O$] = 9.7 at.% obtained in our study at R = 0.391 and DC = 5% are higher compared with the best values reported by Korner et al. obtained for plasma deposited COOH coatings from the same CO_2/C_2H_4 gaseous mixture using low pressure RF discharge [14]. Note, however, that the [COOH] obtained in present work was lower compared with the

acrylic acid [30,31] and the maleic anhydride [29,32] polymerization.

3.3. Influence of duty cycle

The FTIR and XPS data showed that the $I_{C=O}/I_{CH}$, [$\underline{C}$(O)O], and concentration of COOH groups decreased with increasing DC (Table 1). A decrease in functional group density is generally observed for different plasma-deposited polymers including COOH and NH_2 coatings and can be ascribed to either the degradation of the precursor molecules in the gas phase, or the ion bombardment of deposited layers. In the present study the lowest used value of DC = 5% was optimal, because the coatings exhibited highest concentration of COOH. It is also worth noting that the COOH groups were stable in water, which follows from the results of chemical derivatization (Fig. 5). Thus an increase in DC did not lead to the improvement of stability or homogeneity of the as-deposited plasma polymers, but only suppressed the COOH concentration.

3.4. Influence of hydrogen admixture

According to the available literature data, the incorporation of COOH groups into the CO_2 plasma occurs *via* attachment of $\dot{C}$OO radical to the hydrocarbon chain and subsequent recombination of $-C(O)\dot{O}$ with hydrogen atom [13,33]. If the density of hydrogen atoms in the plasma is not sufficient, the addition of hydrogen into the gaseous mixture should increase the density of hydrogen radicals and, consequently, improve the conversion efficacy of the $C(O)\dot{O}$ species into COOH groups. To test this hypothesis further, for one selected condition (R = 0.391, DC = 5%) we added 10 sccm of hydrogen into the plasma. Our results indicated that the concentration of $\mathbf{C}$(O)O decreased from 9.7 to 8.6 at.% after addition of H_2. The derivatization of COOH groups revealed that the [COOH] was 0.27 and 0.33 at.% for the layers deposited with and without addition of hydrogen, respectively. Since the addition of hydrogen did not improve the efficacy of COOH group incorporation, it is reasonably to assume that the recombination of $-C(O)\dot{O}$ species with hydrogen radicals is not a limiting factor affecting the COOH grafting. However, it should be noted that the addition of hydrogen to the plasma also changes the plasma chemistry and increases the VUV emission. As a result it may lead to the splitting of the carboxylic acid groups by VUV photons. Therefore, the influence of the H_2 addition can be more complex. The possible mechanisms of the COOH group incorporation in the $CO_2/C_2H_4/Ar$ plasma are discussed in the next section.

3.5. Modeling of COOH group deposition

The chemistry of $CO_2/C_2H_4/Ar$ plasma is more complex than the CO_2 plasma. It can be assumed that the main difference between these two discharges is that in the CO_2 plasma treatment all processes leading to the COOH grafting are expected to proceed at the surface of the polymer, whereas in the $CO_2/C_2H_4/Ar$ plasma the chemical interaction of [$-\dot{C}H-CH_{2-}$], CO_2^*, and CO_2^+ species can also occur in the plasma gas phase. According to both the literature and our own results, the percentage of $\mathbf{C}$(O)O environment in the CO_2/C_2H_4 plasma deposited layers is 3–4 times higher compared with that in the CO_2 plasma-treated polyethylene, polystyrene, and polypropylene [9,10,18]. Therefore, ethylene molecules positively enhance the process of the $\mathbf{C}$(O)O incorporation. It is reasonable to assume that the plasma-deposited layer formed from the $CO_2/C_2H_4/Ar$ mixture with many open bonds and trapped radicals is a better precursor for the incorporation of carboxyl and ester groups, because the same density of free radicals (active sites) is formed in the $CO_2/C_2H_4/Ar$ plasma at lower power compared with the CO_2 plasma treatment. Thus it is possible to decrease the etch-
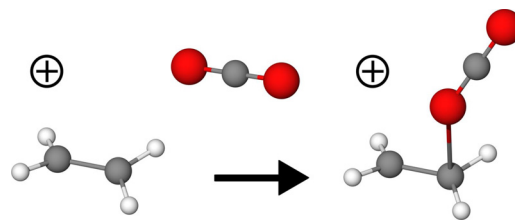

Fig. 8. Schematics of the possible CO_2 attachment process to C_2H_4. The carbon, oxygen, and hydrogen atoms are colored in gray, red and white, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ing effect of the CO_2 plasma by adding hydrocarbon molecules into discharge. Wang et al. and Medard et al. showed that an increase in plasma power over some threshold leads to the degradation of the carboxyl groups accompanied by the decrease of the CO_2^+ and CO_2^* species concentration in the plasma gas phase [4,9,11,19]. Another clear advantage of the $CO_2/C_2H_4/Ar$ plasma is a higher thickness of COOH functionalized layer and a better stability of the grafted functions in water. This statement is also confirmed by our own results. We observed the degradation of $\mathbf{C}$(O)O and COOH environments with raising DC, indicating an increase in the average energy transferred to monomer molecule. Moreover, our plasma conditions allowed to initiate the deposition of $\mathbf{C}$(O)O environment at significantly lower energies compared with CO_2 treatment.

From our point of view, the COOH groups can be grafted similarly in both the CO_2 and CO_2/C_2H_4 processes. Note, although usually the formation of the esters (COOC) is neglected [13], the COOC groups can be formed along with the grafting of COOH functions, and the COOH/COOC ratio has not been investigated before. Indeed, although the titration of the COOH groups using the spectrophotometry and fluorescent microscopy revealed the concentration of the COOH groups at the level of 2–3 nm^{-2}, these values cannot be correctly compared with the $\mathbf{C}$(O)O component measured by XPS. The determination of [COOH] concentration by chemical derivatization and [$\mathbf{C}$(O)O] amount using XPS C1s curve fitting appears to be more accurate method because the densities of COOH and COOC groups are measured at the same depth and within the same volume. Our results revealed that the ester groups are incorporated more efficiently compared with the carboxyl functions. The highest [COOH]/[$\mathbf{C}$(O)O] ratio was determined to be 0.08. It can be assumed that the grafting of ester COOC functions is much more efficient compared to the incorporation of COOH groups. However, it is also possible that COOH groups can be etched away at a faster rate compared to the ester groups, but this process was not studied in present work. To shed some light on the possible ways of the CO_2 molecule attachment to hydrocarbon chains on the polymer surface and those located inside the plasma *ab initio* calculations were carried out.

In our calculations we did not consider the break-up of CO_2 molecule because the dissociation of CO_2 molecule (*e.g.* to CO + O [1]) will lead to very low probability of the COOH group formation. When the O=C=O groups attach to a hydrocarbon chain *via* a carbon atom, a carboxyl group can be formed by direct linkage of hydrogen atom or some radical to the only dangling bond of an oxygen atom. In case when O=C=O groups attach to a hydrocarbon chain *via* one of the oxygen atoms, an ester R—O—$\dot{C}$=O group is expected to be formed, which cannot be converted to a carboxyl group directly.

The possible reaction between the CO_2 and C_2H_4 in plasma was considered first (Fig. 8). Since the bonding, either through the carbon or oxygen atoms, is not stable, the two molecules go apart in both singlet and triplet configuration. If the system is singly charged, however, the attachment become possible for $^+CH_2-CH_2-O-\dot{C}=O$ configuration with the binding energy of 0.32 eV. According to the literature data, the density of CO_2^+ ions
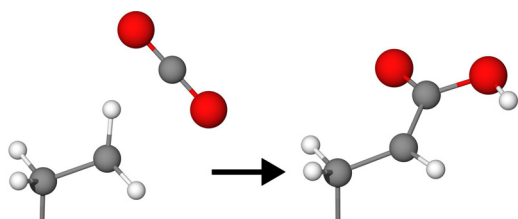
Fig. 9. Schematics of the possible formation of COOH group in the process of CO_2 attachment to hydrocarbon surface. The carbon, oxygen, and hydrogen atoms are colored in grey, red and white, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

can be very high in the carbon dioxide plasma [1,17,34] and, therefore, this process leading to the formation of ester groups has very high probability. The binding energy was calculated using Eq. (2):

$$E_{bind} = E(^+CO_2) + E(C_2H_4) - E(^+CH_2-CH_2-O-\dot{C}=O) \qquad (2)$$

where $E(CO_2)$ and $E(C_2H_4)$ are the energies of freestanding molecules or corresponding ions.

In the next stage, the attachment of CO_2 to a radical was modeled as the following reaction: $H_3C-\dot{C}H_2 + O=C=O$. The $H_3C-\dot{C}H_2$ radical can be formed by attachment of a hydrogen radical to the C_2H_4 molecule (Fig. 9). Once again note that in the uncharged system the connection *via* carbon or oxygen atoms is unstable and the two molecules go apart in both singlet and triplet configuration. When the system has a charge of $+1e$, the CO_2 molecule can be attached *via* an oxygen atom with the binding energy of 2.00 eV. It is important to note that the charge resides mainly on a radical. Although it is unlikely that this could occur at ambient conditions, but it may well happen in the plasma. As highlighted above, the CO_2 attachment through oxygen will lead to the formation of ester COOC groups.

Another possible pathway of CO_2 attachment includes the transfer of a H atom from the hydrocarbon chain to the dangling bonds of the attached group. In contrast to the previous cases, the only stable configuration was the attachment *via* a C atom with the formation of the COOH group in uncharged system. The binging energy in this case is 0.16 eV.

Note, however, that in order for the reaction to proceed in this way, the system has to overcome some barriers. According to our estimates, the most significant barrier is Pauli repulsion of the CO_2 molecule when it approaches the radical. The map of potential energy depending on mutual disposition of frozen molecules is depicted in Fig. 10-a with the smallest distance between the C_2H_5 radical and CO_2 molecule being 1.32 Å. The changes in charge density distribution due to thermal vibrations in the CO_2 molecules coming from the hot plasma areas were estimated by calculating the similar map of potential energy with the bended CO_2 (Fig. 10b). While the barriers for the bended molecule are lower, their absolute values (>3 eV) are still too high for the reaction pathway to be plausible in normal conditions, but the process can be expected in the energetic plasma. Indeed, during interaction of precursor molecules with energetic electron and ions, a large portion of energy can be absorbed by precursor molecules. Particularly for CO_2 plasma, the detachment of oxygen atoms from CO_2 with the formation of CO and O radicals has been observed before, although this process also exhibits very significant energy barriers [1,4,9]. Nevertheless, to understand the mechanism of the COOH group formation in the CO_2/C_2H_4 plasma, further investigation and ab initio calculations for other possible pathways leading to the formation of stable structures containing carboxyl groups are needed.

4. Conclusions

In this study we have demonstrated that the $CO_2/C_2H_4/Ar$ plasma can be successfully used for the deposition of stable organic
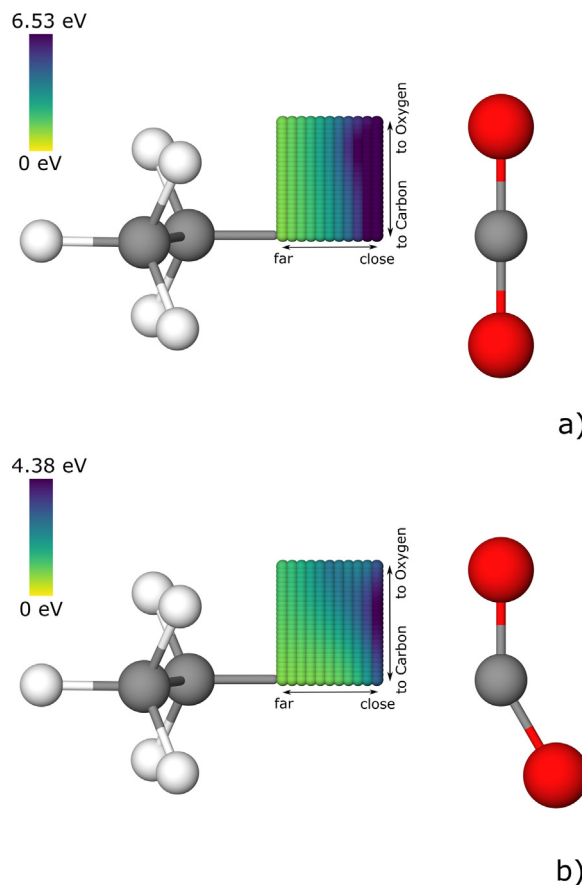

Fig. 10. The map of potential energy depending on mutual disposition of frozen molecules: a) original CO_2; b) bended CO_2. The carbon, oxygen, and hydrogen atoms are colored in grey, red and white, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

coatings containing different oxygenated carbon environments. The chemical derivatization revealed the ratio between carboxylic and ester groups in the deposited plasma polymers varied from 0.03 to 0.08, *i.e.* only 3-8% of the C(O)O component belonged to the COOH groups. The layers deposited at highest gas ratio $Q_{CO2}/(Q_{CO2} + Q_{C2H4})$ exhibited a significant thickness loss (up to 39%), but high stability of COOH groups. The ester groups were hydrolyzed in water and led to the partial layer dissolution. The hydrolysis of ester groups can be employed for controlled drug release and other biomedical applications.

It can be assumed that the grafting of ester COOC functions is much more efficient compared to the incorporation of COOH groups. However, it is also possible that COOH groups can be etched away at a faster rate compared to the ester groups. Modeling has indicated that there are different ways of attachment of CO_2 active species (including CO_2^+ ions) *via* an oxygen atom. These processes would end up with the grafting of ester functions. Modeling has also demonstrated that the grafting of COOH groups must proceed through the attachment of CO_2 active species *via* a carbon atom. Number of such opportunities is very limited and their probability is lower due to high energy barriers.

We have demonstrated that the $CO_2/C_2H_4/Ar$ plasma with adjustable thickness of the COOH functionalized layer and good stability of the grafted functions in water is a better solution for the COOH surface functionalization compared with the CO_2 plasma. Nevertheless, the density of COOH groups in the CO_2/C_2H_4 plasma polymers is lower compared with the maleic anhydride and acrylic acid plasma polymers.

Acknowledgements

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