



HAL
open science

An investigation of adhesion mechanisms between plasma-treated PMMA support and aluminum thin films deposited by PVD

Mohamed Mounder Kouicem, Eric Tomasella, Angélique Bousquet, Nicolas Batisse, Guillaume Monier, Christine Robert-Goumet, Laurent Dubost

► To cite this version:

Mohamed Mounder Kouicem, Eric Tomasella, Angélique Bousquet, Nicolas Batisse, Guillaume Monier, et al. An investigation of adhesion mechanisms between plasma-treated PMMA support and aluminum thin films deposited by PVD. *Applied Surface Science*, 2021, 564, pp.150322. 10.1016/j.apsusc.2021.150322 . hal-03542530

HAL Id: hal-03542530

<https://hal.science/hal-03542530v1>

Submitted on 2 Aug 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

An investigation of adhesion mechanisms between plasma-treated PMMA support and aluminum thin films deposited by PVD

Mohamed Mounder KOUICEM^{1,3}, Eric TOMASELLA¹, Angélique BOUSQUET¹, Nicolas BATISSE¹, Guillaume MONIER², Christine ROBERT-GOUMET², Laurent DUBOST³

¹ Université Clermont Auvergne, CNRS, SIGMA Clermont, ICCF, F-63000 Clermont-Ferrand, France

² Université Clermont Auvergne, CNRS, Institut Pascal, F-63000 Clermont-Ferrand, France

³ IREIS/ HEF Groupe, Av. B. Fourneyron 42166 Andrézieux Bouthéon.

Keywords: PMMA, PVD coating, Adhesion, XPS, Plasma pre-treatment, Polymer degradation.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors

1. Introduction

Polymethylmethacrylate (PMMA) is a polymer widely used in various industrial applications [1,2]. It represents one of the most important optical materials because of its excellent transparency [3]. Furthermore, PMMA is the first choice polymer for automotive and aerospace industries because of its weather resistance, machinability, and low costs. In some decorative applications, the deposition of metallic thin film (aluminum, copper, silver ...) is needed, for which the most frequently used process is physical vapor deposition (PVD).

Unfortunately, PMMA shows poor adhesion with thin films deposited by plasma (PVD, PECVD) [4–6].

In order to improve the adhesion properties of PMMA, the industrial partner IREIS-HEF has formulated a wet deposited adhesive varnish. This solution requires many preparation steps (chemical and electrostatic cleaning, substrate transfer to the coating reactor ...) and it is a source of liquid and gaseous wastes. This is why an eco-friendly process such as cold plasma pre-treatment could be an interesting alternative to improve PMMA's adhesive properties. This technology is also easy to perform and does not affect the optical properties of PMMA before the deposition of the functional thin film. In addition, cold plasma pre-treatment is usually performed in situ (without breaking the vacuum) a few minutes before deposition of a functional coating for which allows a significant reduction in polymer treatment time and cost [7,8]. More broadly, researchers agree on the effectiveness of cold plasma treatments for modifying the surface chemistry of commercial polymers (PMMA, PC, LDPE ...) which can improve their surface properties. For instance, Peyroux et al. showed that plasma treatment of LDPE in reactive conditions (O_2/N_2) increases their surface energy which enhances their adhesion and printability properties [9]. Similar results were found by Carrino et al. and Pandiyaraj et al. who observed that air cold plasma pre-treatment increased the adhesives properties of polypropylene. As it was reported, the interaction between polymer substrates and cold plasma allows the incorporation of new polar functional groups such as C-O, C=O, O=C-O, and COOH. The interaction between these functionalities and the adhesive material leads to molecular bonds formation that contributes to improving the polymer adhesive [10,11] strength.

Moreover, up to now, previous works on the adhesion between PMMA and PVD coatings investigated mainly the inorganic oxides and not metal. For example, Ben Amor et al. [14] and Duchatelard et al. [15] studied the adhesion between PMMA and alumina coatings (Al_2O_3) for photo protection and dental applications respectively. Schultz et al. reported that Ar/ H_2O cold plasma treatment improves the adhesion between PMMA and SiO_2 thin films [8]. Schissel et al. [4] worked on the role of optically transparent inorganic interlayers (SiO_2 , Cr_2O_3 , Fe_2O_3 and MgO) deposited by PVD in improving the adhesion between PMMA and silver to manufacture organic solar reflectors that may replace glass mirrors in solar concentrators.

Hence, the improvement of the adhesion between PMMA and PVD deposited metallic films is still a challenge. The low adhesive properties of PMMA can be linked on one hand to its intrinsic properties especially its low surface energy [6], and on the other hand to the phenomenon of surface degradation of the polymer by cold plasma energetic species [16]. Hence, Schultz et al. investigated the surface modification of PMMA during oxygen plasma exposure. It was reported that reactive oxygen species such as atomic oxygen and radicals are effective in breaking chemical bonds and to initiate polymer degradation [12]. Furthermore, Melo et al. showed that high energy UV radiation (between 200 and 300 nm) can cause hemolysis in PMMA's chemical bonds. They noticed that the FT-IR spectra of UV irradiated polymers remain qualitatively unchanged but the total intensity is reduced and explained that by polymer chains scission [13].

Finally, as described in the literature, two major mechanisms seems to take place during plasma pre-treatment: Surface activation by introducing new oxygenated chemical bonds on the top surface of PMMA [17], and surface degradation caused by polymer chain scission [18,19]. Therefore, in the present, work, we will investigate these possible mechanisms during a plasma pre-treatment of PMMA and their link to the further mechanical adhesion with a PVD deposited aluminum layer.

2. Material and methods

Polymethylmethacrylate (PMMA) industrial sheets (50 x 30 x 3 mm³) from ARKEMA® were used during all experiments. We chose a transparent type of PMMA with the minimum quantity of additives: cast PMMA (ALTUGLAS®CN). No chemical cleaning was performed on PMMA before the introduction in the vacuum system. Surface pre-treatment and aluminum deposition were performed using PLASSYS MP400 PVD machine equipped with two magnetron cathodes and a rotating, heatable, and polarizable substrate holder. A base pressure of 1. 10⁻⁶ mbar is reached using a primary nXDS15i dry scroll pump and a secondary turbomolecular pump nEXT-400D from Edwards.

Argon (99.9992 % purity) and oxygen (99.995 % purity) cold plasma pre-treatments of PMMA substrates were performed in various discharge conditions (power, pressure, and time) using pulsed DC power with a constant duty cycle of 50 % and frequency of 250 kHz. To understand the effect of surface pre-treatment parameters on the quality of aluminum adhesion on PMMA, a full factorial design (3 factors, 2 levels) was carried out using a statistical software [20]. The levels of variation of plasma pre-treatment conditions are included in the following ranges: Power (20 and 300 W), Pressure (0.5 and 1.5 Pa), and duration (10 and 300 s).

After plasma pre-treatment, aluminum thin films were deposited by sputtering an aluminum target (99.9% purity, 76.2 mm diameter) in argon plasma. The target-to-substrate distance was constant at 150 mm. Films of 150 nm were obtained for a deposition time of 300 s, a DC power density of 3.3 W/cm², an argon flow rate of 19 sccm, and a working pressure of 8.10⁻³ mbar.

The adhesion between PMMA substrates and aluminum films were characterized by a tape test after cross cuts, according to the DIN EN ISO 2409 standard [22]. The adhesive tapes used for the test are 3M™2525 and 3M™202 having an adhesion strength on steel of 75 N/mm and 42 N/mm respectively. After the peeling, the processing of optical microscopic images of the samples using “image J” software allowed us to express the adhesion in terms of the percentage of aluminum remaining on the PMMA surface which eases the comparison between samples with close adhesion levels estimated visually after the tape test. It is important to mention that the use of ImageJ as image treatment software takes into account

the entire image and not just the squares inside the slices². The cuts are therefore included in the analysis. They will be counted as part of the dark area (PMMA). In addition, these cuts do not represent a true area of good or bad adhesion, but they artificially decrease the percentage of remaining Al. To ensure the accuracy of the adhesion results, we normalized the size of the microscopic images for all samples i.e. all images are taken with a magnification of 500 μm which corresponds to eight squares of grid.

To study the loss of adhesion between PMMA and aluminum film, Scanning Electron Microscopy and Energy Dispersive X-rays (SEM-EDX) analysis were carried out on the PMMA sample after the adhesion test. The SEM used is a ZEISS SUPRA 55VP, with a field emission gun. Images were taken at a voltage of 3keV with an Everhart-Thornley type secondary electron detector. To avoid surface charging, PMMA samples were coated with a very thin film of gold before the introduction in the analysis chamber.

To investigate the adhesion failure zone, ATR-FTIR analysis was performed on the tape (3MTM2525) used for the adhesion test. A NICOLET 5700 (Thermo Electron) FTIR spectrometer was used with an average of 32 measurements and a resolution of 4 cm^{-1} to collect spectrum in the 4000-400 cm^{-1} range.

The surface energy of untreated and plasma pre-treated PMMA was calculated using the conventional Owens-Wendt method [24]. Contact angle measurements of two different liquids (water and formamide) were recorded using an Attention Theta Lite Optical Tensiometer with an imaging source camera. To reduce the margin for error, five measurements were performed on five different locations on the sample surface.

The XPS spectra were obtained by the mean of an Omicron brand EA 125 spectrometer using a monochromatized $\text{MgK}\alpha$ ($E= 1253.6 \text{ eV}$) excitation radiation. Surface charging was minimized using a neutralizer gun which sprays the low energy Ar^+ ions over the sample surface. To compensate the surface charging, all the binding energies were referenced to the C1s peak at 284.5 eV [21]. XPS spectra decomposition was carried out using XPSPEAK 41 software. Plasma pre-treated samples were transferred to the XPS equipment in small vacuum chambers to avoid surface evolution after exposure to ambient air.

The atomic force microscopy (AFM) measurements were performed using Innova® Brucker AFM (France). The surface topography images of untreated and plasma pre-treated samples were captured at tapping mode with a TESP-SS tip (tip radius of curvature 2-5nm). The surface roughness has been measured on 2.5*2.5 μm^2 size.

3. Results and discussion

3.1. Adhesion failure between PMMA and aluminum films

To study the adhesion failure mode between untreated PMMA and aluminum thin film, we used scanning electron microscopy and energy dispersive X-rays (SEM-EDX) analysis. Figure 1.a represents a SEM image of a PMMA sample after peeling off a part of the aluminum film (after the adhesion test). The image shows the two zones targeted for EDX microanalysis. The corresponding EDX spectra are represented in figure 1.b and figure 1.c respectively. Before the peel test (figure 1.b), four elements were detected: carbon (C), oxygen (O), aluminum (Al), and gold (Au) coming respectively from the PMMA substrate, the aluminum film and the metallization gold film used for charge evacuation during the SEM analysis.

After the peel test (figure 1.c), no aluminum peak was detected on the EDX spectrum on which indicates that the aluminum film was completely pulled off from the PMMA surface. We can assume that the adhesion failure occurs either at the Al/PMMA interface (adhesive failure) or in the PMMA (cohesive failure on the polymer side).

Furthermore, we observed an increase in the carbon peak intensity which was attenuated by the presence of the aluminum film and a slight decrease in oxygen amount indicating that the measured oxygen had two contributions: the PMMA substrate and the oxidized aluminum film.

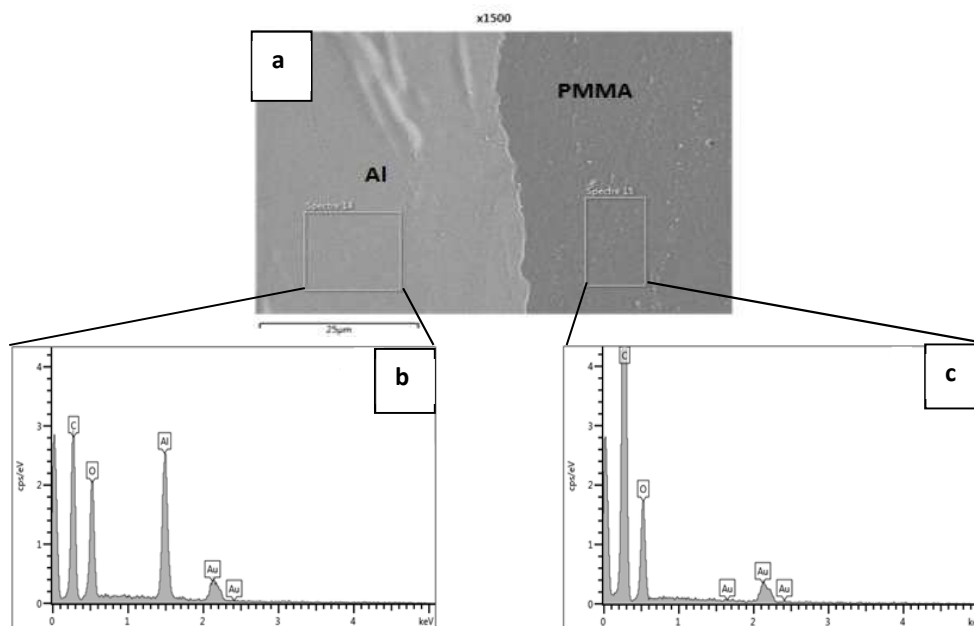


Figure 1. a) SEM analysis of PMMA after the peeling test, b) EDX analysis in aluminum film side (before the peel test), c) EDX analysis in the PMMA side (after the peel test).

To check these assumptions, ATR-FTIR analysis was performed on the 3M-2525 tape before and after the peel test and compared to the virgin PMMA spectrum (Figure 2). First, we observe a decrease in peak intensities of the tape spectrum after peeling due to the attenuation of the signal from the presence of the aluminum film. Second, PMMA characteristic peaks such as CH_3 (748.6 cm^{-1}), C-O (1147 cm^{-1}), and C=O (1730 cm^{-1}) were not observed on the tape spectrum after the peeling test. This result suggests that the adhesion failure between PMMA and aluminum film occurs at the interface between the aluminum film and the PMMA and not in the PMMA substrate.

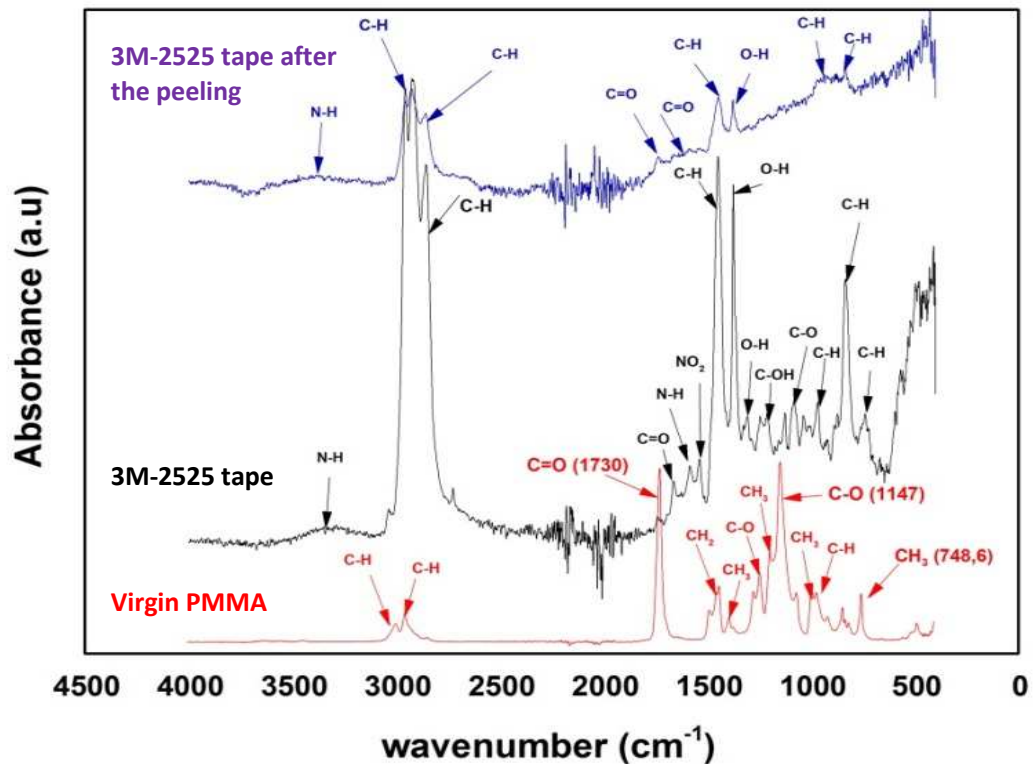


Figure 2. ATR-FTIR spectra of virgin PMMA and 3M 2525 tape before and after the peeling test

In order to improve the adhesion of aluminum thin films on PMMA substrates, cold plasma pre-treatment was performed and optimized using an experiment plan. The next section is devoted to the study of the effect of plasma parameters (gas, power, pressure, and time) on the adhesion properties.

3.2. Design of experiments

During this study, the adhesion strength between PMMA and plasma deposited aluminum is expressed in terms of aluminum percentage remaining on the PMMA surface after the peeling test. Figure 3 shows the adhesion between PMMA and aluminum film as a function of plasma pre-treatment gas mixture: Argon, oxygen-poor gas mixture, and oxygen-rich gas mixture.

First, we notice that the untreated PMMA presents a very low adhesion for the two adhesive tapes such as the remaining aluminum percentage is 6.5 % and 10.2% for the tapes 3M-2525, 3M-202 respectively. The plasma pre-treatment of PMMA by argon plasma shows a

slight improvement in adhesion. The percentage of remaining aluminum increases from 6.2 % to 10.2% for the tape 3M-2525 and from 10.8 % to 12.4 % for the 3M-202 tape. It is possible that the adhesion improvement is due to the increase of the PMMA reactive sites by chemical bonds reorganization supported by the increase of surface roughness. Indeed, and as shown by J.Frederic [18], the surface roughening increases the specific surface of the polymer substrate which increase the number of interactions between PMMA and aluminum atoms. This hypothesis will be explored in the section 3.5.

Secondly, we observe that the use of oxygen-containing plasma significantly improves the Al/PMMA adhesion strength compared to the untreated sample. For the 3M-2525 tape test for example, the surface of the adherent aluminum was increased from 6.5% to 12.4 % by the use of oxygen-poor plasma pre-treatment (50% of oxygen content). Moreover, the best adhesion strength was obtained for oxygen-rich plasma pre-treatment (70% of oxygen content). In this condition, the percentage of remaining aluminum reaches 32 % for the 3M-2525 tape and 34.6 % for the 3M-202 tape. According to Junkar et al. [19], pre-treatment using oxygen-containing cold plasma generates chemical modifications of polymer surface by the introduction of reactive functional groups such as (C=O, C-O, O-C=O). These functional groups can react with metallic atoms by the formation of covalent bonds improving the polymer/metal adhesion [22].

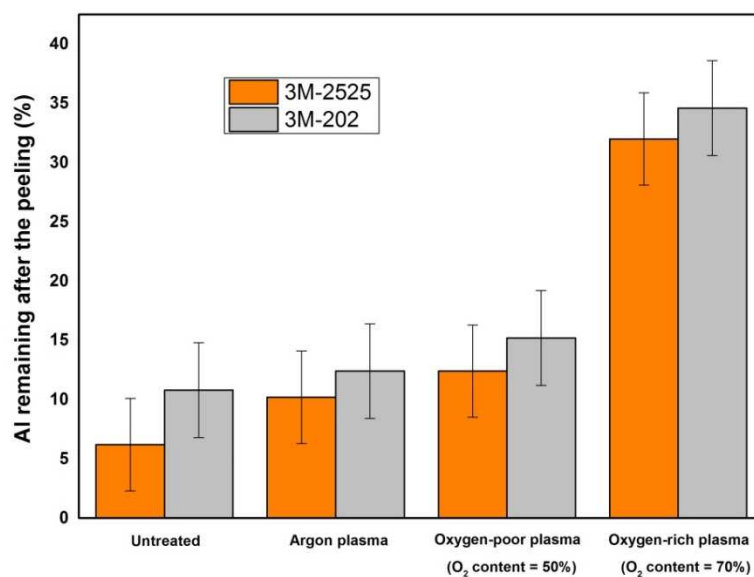


Figure 3. Evolution of the percentage of aluminum remaining on PMMA surface after the peeling test as a function of plasma pre-treatment gas mixtures

To better understand the effect of oxygen-rich plasma pre-treatment parameters (power, time, and pressure) on the adhesion of metallic aluminum films. We followed three factors and two levels full factorial design (table1). The levels of variation of each parameter were normalized by coded variables (-1 for the low level and +1 for the high level).

Table 1. Three factors and two levels experimental design and the adhesion characterization results for oxygen-rich plasma pre-treatment

Experiment	Power (W)	Time (s)	Pressure (Pa)	Adhesion results percentage of aluminum remaining on PMMA surface ($\pm 3.1\%$)
1	-1	-1	-1	52.7
2	-1	-1	1	30.0
3	-1	1	-1	37.7
4	-1	1	1	21.7
5	1	-1	-1	27.8
6	1	-1	1	23.4
7	1	1	-1	13.5
8	1	1	1	6.5

The main effects plot for adhesion (figure 4.a) shows that plasma pre-treatment power has the most significant effect on the adhesion of aluminum thin films on PMMA. The mean percentage of aluminum remaining on the surface of PMMA is 35.5% for low power plasma pre-treatment and 17.2% for high power plasma pre-treatment. Furthermore, short time and low-pressure plasma pre-treatment are suitable to increase the adhesion quality. The mean percentage of aluminum coating for short time plasma pre-treatment is 34.6%. It decreases to 19.8% for long time pre-treatment. Moreover, the quality of adhesion decreases with increasing pressure. It is 32.9% for low-pressure plasma pre-treatment and 20.4% for high-pressure plasma pre-treatment. From the results described above, the

following conclusions can be drawn: to optimize the pre-treatment process, the most important parameter to study is the plasma power. Furthermore, the best plasma pre-treatment conditions are low gas pressure, power, and time.

The interaction plot (figure 4.b) suggested that the effect of plasma pre-treatment power on adhesion is dependent on both the pre-treatment time and pressure. We observe a strong interaction between power and pressure such that the effect of plasma power is greater at low-pressure levels. We also notice a weak interaction between power and time. It seems that plasma power causes a greater degradation in adhesion for long-duration plasma pre-treatment. However, there is no interaction between plasma pre-treatment time and pressure. These two parameters are totally independent.

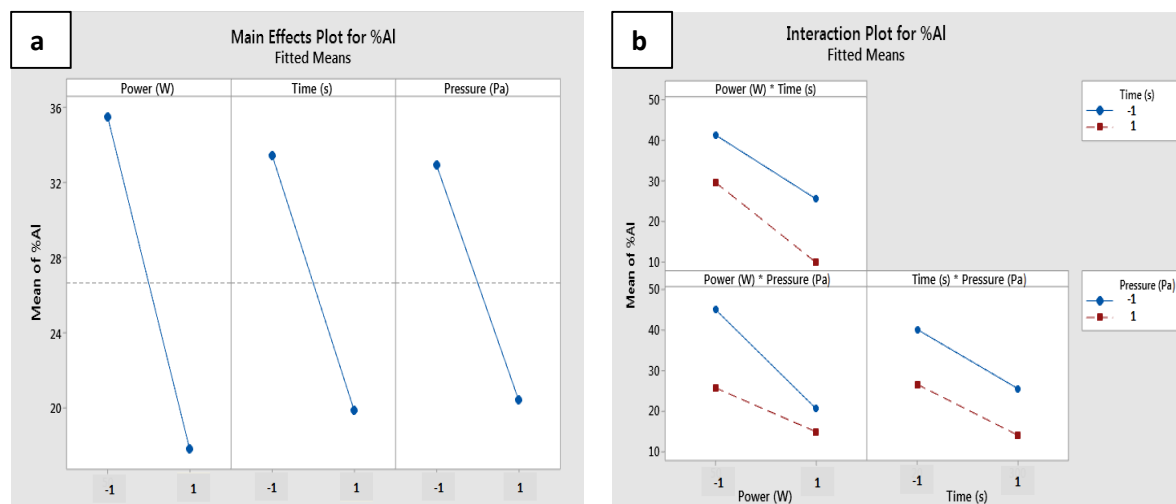


Figure 4. Effect of plasma treatment parameters on adhesion between aluminum and PMMA: a - main effects plot, b- interaction plot.

It is well known that cold plasma is composed of several species like negative and positive ions, free radical molecules, electrons, and UV photons [23,24]. According to the literature, the interaction of these plasma species with the polymer can cause many chemical and physical modifications to its extreme surface.

For a better understanding of the influence of plasma pre-treatment on the adhesive properties of PMMA, the following characterization techniques were used: contact angle

measurements for wettability, XPS analysis for chemical modifications, and AFM microscopy for morphology and roughness analysis.

3.3. Contact angle and surface energy measurements

The evolution of contact angles and surface energies of plasma pre-treated PMMA were investigated as a function of pre-treatment time. The results are reported in table 2. Compared to the untreated PMMA, short duration plasma pre-treated PMMA shows a significant decrease in contact angle with water (from $73.9 \pm 0.9^\circ$ to $52.5 \pm 0.5^\circ$) and formamide (from $52.0 \pm 1.2^\circ$ to $47.4 \pm 1.0^\circ$). The surface hydrophilicity of PMMA is significantly increased. Based on contact angle measurements, the surface energy of PMMA samples was estimated using the conventional Wendt-Owens method [25]. Untreated PMMA has a total surface energy of $36.6 \pm 0.8 \text{ mN.m}^{-1}$. A maximum value of the total surface energy is reached ($47.1 \pm 0.4 \text{ mN.m}^{-1}$) in the case of a short duration pre-treatment. The increase in pre-treatment duration does not seem to be beneficial for improving surface energy. Moreover, the surface pre-treatment mainly influences the polar component of the surface energy such that it increases significantly after plasma pre-treatment from $9.2 \pm 0.3 \text{ mN.m}^{-1}$ to $32.3 \pm 0.3 \text{ mN.m}^{-1}$. The dispersive component decreases slightly before stabilizing around 15 mN.m^{-1} .

According to the experiment plan and surface energy measurements, PMMA samples presenting the best adhesion to aluminum films are those having the highest surface energy (the polar component in particular). In the same context, Thurston et al. reported that the changes in surface energy and the increase in adhesives properties of plasma-treated polyethylene and polystyrene are primarily due to the chemical surface changes induced by exposure to the plasma [26]. In a more detailed study, Gururaj et al. stated that air plasma pre-treatment of PC and PMMA substrates allows to form polar groups such as (C–O), (C=O), and (C=O)–O [27].

The interpretation in terms of adhesion is that the likely increase of the amount of polar functional groups at the PMMA surface leads to more interactions with aluminum atoms. Therefore, new chemical bonds can be formed at the interface Al/PMMA.

Table 2. Contact angles and surface energy parameters as a function of the surface pre-treatment time by an oxygen rich plasma (Oxygen content =70%, P = 50W, Pr= 8.10⁻³ mbar)

	Samples	Contact angle		Surface energy		
		$\theta_{\text{water}} (^{\circ})$	$\theta_{\text{Formamide}} (^{\circ})$	polar component (mN. m ⁻¹)	Dispersive component (mN. m ⁻¹)	Total surface energy (mN. m ⁻¹)
	Untreated PMMA	73.9 (± 0.9)	52.0 (± 1.2)	9.7 (± 0.3)	26.9 (± 0.5)	36,6 (± 0.8)
Plasma pre-treated PMMA	20 s	52.5 (± 0.5)	47.4 (± 1.0)	32.3 (± 0.1)	14.9 (± 0.5)	47,1 (± 0.4)
	50 s	57.7 (± 0.8)	51.9 (± 0.6)	28.3 (± 0.7)	14.6 (± 0.0)	43 (± 0.6)
	180 s	58.5 (± 0.9)	52.1 (± 1.3)	27.3 (± 0.3)	15.0 (± 0.5)	42,4 (± 0.8)
	300 s	57.9 (± 0.8)	49.9 (± 1.4)	26.4 (± 0.1)	16.7 (± 0.7)	43 (± 0.7)

To go further, we have investigated the chemical modifications induced by cold plasma pre-treatment and their influence on PMMA's adhesion properties.

3.4. XPS analyses

The chemical changes of the PMMA surface after plasma pre-treatment and aluminum thin film deposition were determined by XPS. Figure 5 shows the fitted high-resolution C1s spectra of untreated PMMA, plasma pre-treated PMMA under good adhesion conditions (oxygen = 70%, Pw = 50 W, and Pr = 8.10⁻³ mbar), plasma pre-treated PMMA coated with a very thin aluminum layer (5 nm approximately) in order to analyze the Al-PMMA interface, and plasma pre-treated PMMA covered with 100 nm of aluminum. The fitting parameters are given in table 3. The deconvolution of C1s spectra of untreated PMMA revealed the contribution of three types of chemical bonding: C-C (284.5 eV), C-O (286.2 eV), and O=C-O (288.4 eV) with contribution percentages very close to the theoretical percentages calculated from the chemical formula of PMMA's monomer. Significant changes were noted after the plasma pre-treatment. The C-C and O=C-O peaks decrease in intensity and C-O peak increases. This can be explained by carbon chain scission allowing the fixation of additional oxygen [28]. We also note the appearance of a new oxygen-containing bond located at 287.4 eV, which corresponds to the carbonyl bonds (C=O). A similar result was

found by Vesel et al.[6]. They reported that oxygen plasma treatment of PMMA allows fixation of new carbonyl groups increasing the oxygen amount on the polymer surface. Aluminum/PMMA interface analysis shows a slight increase in C-C bonds contribution despite the decrease of the total area of carbon peak by a factor of two. This phenomenon was not expected. We suspect the measurement of additional carbon coming from the adsorption of carbonic impurities on the coated sample during its transfer from the PVD equipment to the XPS machine [29]. This supposition is confirmed by the presence of carbon contributions on the C1s spectrum of PMMA coated with 100 nm of aluminum (figure 5.d).

Furthermore, we observe the introduction of a new carbon bond at 283.1 eV attributed to the Al-O-C [30]. Note that Al-O-C bonds were not observed in C1s spectrum of PMMA covered with 100 nm aluminum layer (figure 5.d). Thus, we assume that these bonds were formed at the interface Al-PMMA during the aluminum film deposition.

Moreover, the comparison of the spectrum of plasma pre-treated PMMA and 5 nm aluminum-coated PMMA (figure 5.c) shows a decrease in all oxygen-containing bonds. The decrease in C-O and O=C-O bonds is almost identical (26.4% and 24.4% respectively) but carbonyls (C=O) bonds decrease is more important (33%). Based on this outcome, we assume that the decrease in C-O and O=C-O bonds is due to their attenuation by the presence of aluminum film while the decrease in C=O bonds is real. Carbonyl bonds would then be broken to form the new Al-O-C interfacial bonds. This result is in accordance with the work of Pireaux et al. [31] who reported that during aluminum film deposition onto polyimide, aluminum atoms interact with carbonyl groups in the polymer to form a C-O-metal complex.

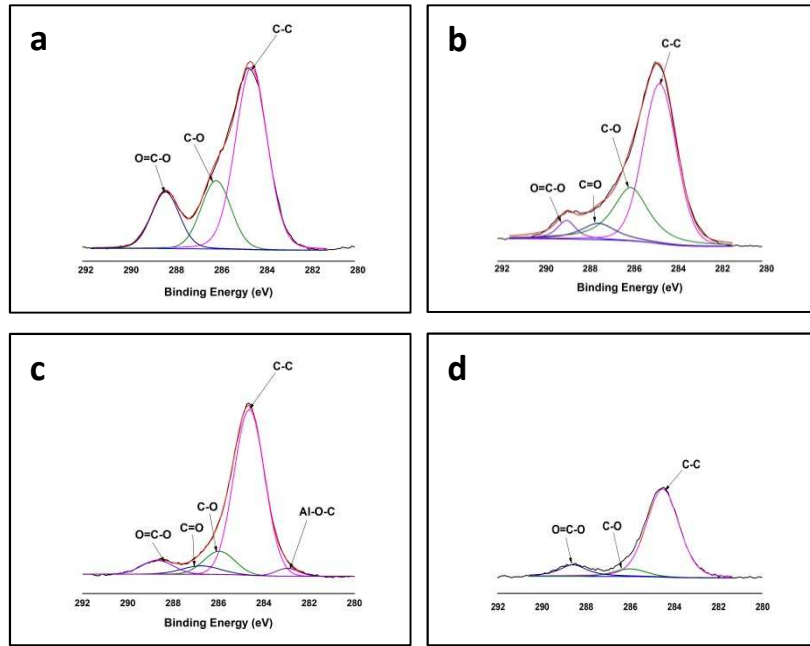


Figure 5. C1s XPS spectra of a) untreated PMMA, b) plasma pre-treated PMMA, c) plasma pre-treated PMMA covered with 5nm of aluminum, and d) PMMA covered with 100 nm of aluminum.

Table 3. Assignment of the XPS C1s spectra components

Chemical bond	Binding Energy (eV)	Theoretical percentages	Experimental percentages		
		untreated PMMA (%)	Untreated PMMA (%)	Plasma pre-treated PMMA (%)	Plasma pre-treated and 5nm Al coated PMMA (%)
C-C	284.5 [21]	60	61.5	56.3	58.7
C-O	286.0 [21,32]	20	19.5	24.6	18.1
O-C=O	288.4 [21]	20	18	11.9	9
C=O	287.5 [21,32]	-	-	7.5	5
Al-O-C	283.1 [33,34]	-	-	-	9.2

Surface energy measurements and XPS analysis of PMMA samples pre-treated under good adhesion conditions allow us to assume that the increase in their surface polarity is due to the increase in the number of oxygenated functional groups (C=O, C-O) grafted on the surface during the plasma pre-treatment. The improvement in the adhesion of aluminum films on samples pre-treated with oxygen-containing cold plasma could be affiliated to the increase of the surface reactivity of PMMA explained by the increase of its oxygen content

[34]. Being very electronegative, oxygen of carbonyl bonds is able to attract electrons from aluminum to form more Al-O-C covalent bonds at the PMMA/Aluminum interface.

Even if it is well known that plasma pre-treatment helps to improve the adhesive properties of polymers, it remains difficult to reach excellent adhesion between PMMA and plasma deposited aluminum films. Moreover, the experiment plan showed that adhesion strength increases significantly for short duration pre-treatment but decreases for long duration. Hence, it seems that excessive plasma exposure may have a negative effect on PMMA's adhesive properties. According to the literature, the adhesion loss can be due to the polymer surface degradation caused by UV radiations through the photo-chemically induced carbon chain scission [8,35], a phenomenon that we already observed in our previous XPS study (table 3).

To explore the effect of UV radiation during the plasma pre-treatment, PMMA samples were covered with glass and quartz slides. Glass and quartz slides have an absorbance edge at 350 nm and 200 nm respectively. We can, therefore, study surface modification of PMMA as a function of the plasma UV radiation energy. Figure 6 shows the UV-visible spectra of microscopic glass and quartz slides used in this study. Moreover, we may notice, that the PMMA surface is then protected against atomic and ionic bombardment, which may also have an impact on polymer surface degradation.

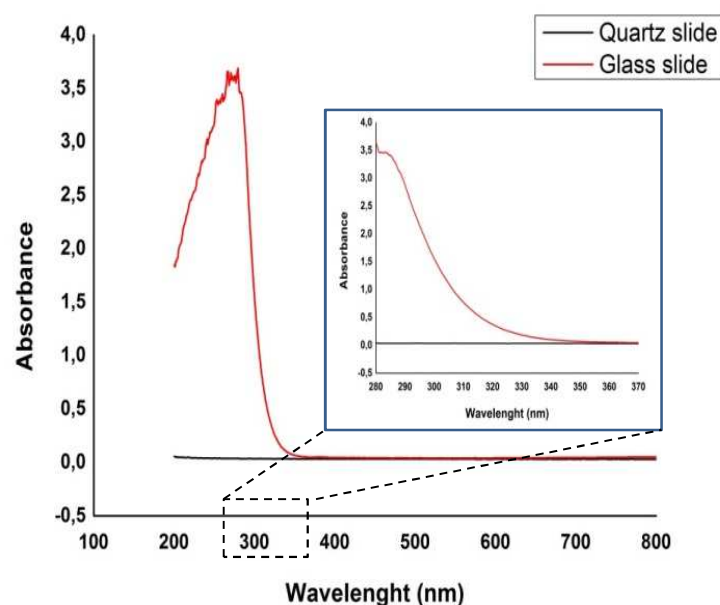


Figure 6. UV-visible spectra of microscopic glass and quartz slides

As in the previous study, PMMA surface modification was investigated by XPS. Figure 7 shows the evolution of the different chemical states of carbon atoms for untreated PMMA, and PMMA exposed to UV radiation of oxygen-rich plasma generated under good adhesion conditions.

Firstly, we might underline that the carbonyl groups do not appear which means that these bonds are not photo-created into the polymer but need oxygenated species from plasma to be formed. Secondly, we can observe a decrease in C-C bonds concentration as a function of UV radiation energy. It appears that the C-C bonds are lower for the samples exposed to 200 nm UV radiation (covered with quartz slide) than those exposed to 350 nm UV radiations (covered with glass slide). It corresponds to a carbon chain scission leading to the formation of C-O bonds. The evolution of the C-O/C-C ratio is the same whether for samples exposed to all plasma species of plasma or for samples exposed only to high energy UV radiations (table 4). This result suggests that the scission of C-C bonds to form C-O bonds is a purely photo-induced phenomenon. Moreover, we assume that the C-O bonds are formed by the oxygen present in the ambient air before the transfer of samples from the PVD machine to the XPS equipment.

At the opposite, O=C-O bonds remain stable under UV radiation exposure but decrease in normal plasma conditions. Hence, The cleavage of O=C-O bonds is due to other phenomenon involving other plasma species (oxygen atoms, ions ...) [36,37].

To link PMMA surface modification by UV radiation to its adhesion properties, the same samples were coated with aluminum and characterized using the peel test, as shown in figure 8, the PMMA substrate covered with a quartz slide had a poor adhesion to aluminum film compared to untreated PMMA and PMMA covered with a glass slide. This result could be explained by a photo-degradation phenomenon. Indeed, PMMA substrate covered with quartz slide is exposed to high energy UV radiations ($\lambda \geq 200$ nm, $E \leq 6.2$ eV). As observed in XPS spectra, these radiations lead to a break of C-C and C-H bonds having dissociations energies of 3.6 eV and 4.3 eV respectively. However, the PMMA sample covered with a glass slide is exposed to a lower UV radiation flux ($\lambda \geq 340$ nm, $E \leq 3.64$ eV). The breaking of carbon

bonds is less important in this case which justifies the slight decrease in C-C contribution of C1s XPS spectra and relatively unchanged adhesion property.

Carbon bonds scission during plasma exposure can form weakly bonded chains on the top surface of PMMA. Therefore, during the coating step, a weak interface is formed between the PMMA and the aluminum film leading to a decrease in the adhesion force.

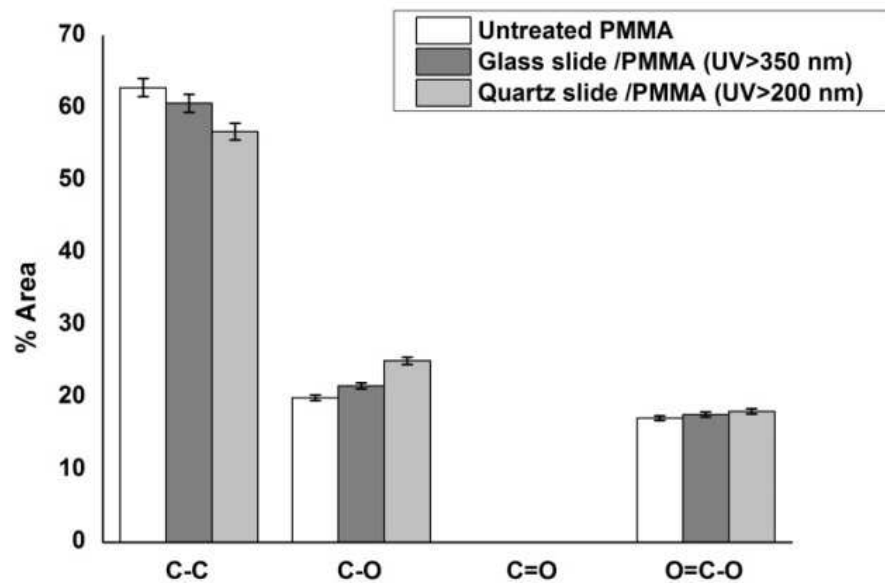


Figure 7. Evolution of the proportions of the chemical environments of carbon C1s of untreated PMMA and PMMA exposed to different wavelength UV radiation of oxygen-rich plasma

Table 4 C-O/C-C ratio (determined by XPS) of untreated PMMA, oxygen-containing plasma-treated PMMA, and PMMA exposed only to high energy UV radiations

C-O/C-C			
Theoretical ratio (PMMA)	Untreated PMMA	Plasma pre-treated PMMA (oxygen content = 70%, Pw = 50 W, and Pr = 8.10 ⁻³ mbar)	PMMA exposed to UV radiations (≥200 nm)
0.33	0.32	0.43	0.44

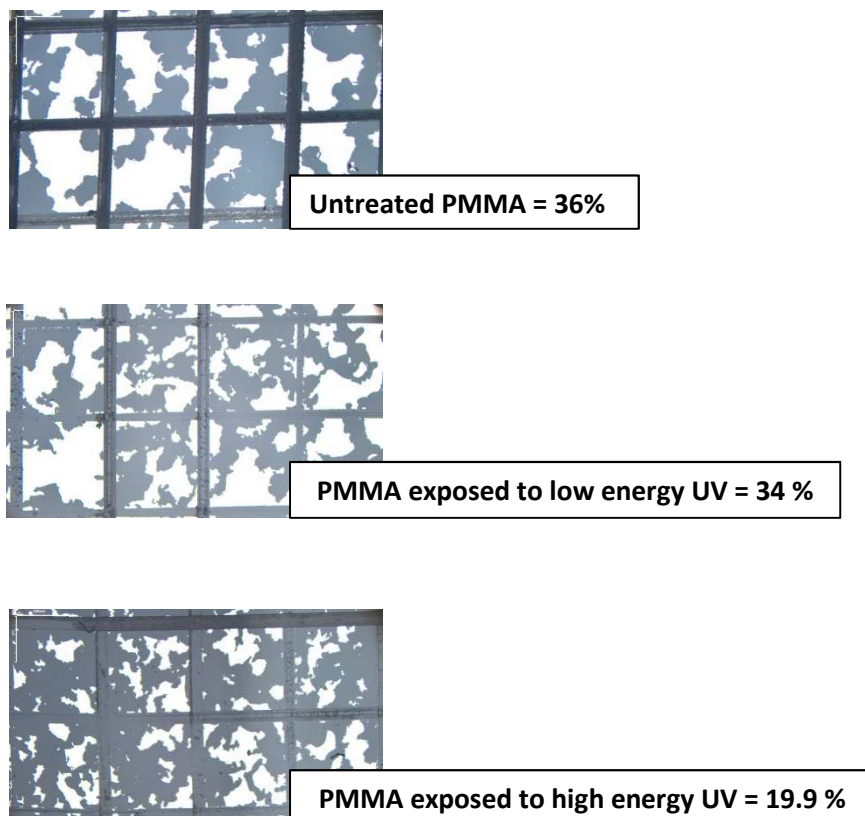


Figure 8. Adhesion test results expressed in terms of the percentage of aluminum remaining after the peeling

As an outcome, XPS study evidenced that during plasma pre-treatment, two phenomena are simultaneously present, namely the surface functionalization by the introduction of oxygenated functional groups, and photo-induced surface degradation by carbon chain scission.

Polymer surface roughening during plasma pre-treatment is a well-known phenomenon [38–40] that may play a role in extreme surface properties. The next study aims to understand the topographic modifications that undergo the PMMA during plasma pre-treatment and their effect on the adhesion to aluminum films.

3.5. Effect of surface roughening on aluminum-PMMA adhesion

The surface topography of plasma-treated samples was investigated using atomic force microscopy (AFM). Figure 9 shows the three-dimensional topography of untreated PMMA, oxygen-rich plasma pre-treated PMMA under low-power (50 W), and high-power plasma

(150 W). Root-mean-square (RMS) roughness and the corresponding Aluminum/PMMA adhesion strengths are reported in table 5.

Root-mean-squared (RMS) roughness of the untreated PMMA was 1.8 nm. The RMS roughness values of plasma pre-treated PMMA under good adhesion and bad adhesion conditions were increased to 4.87 nm and 8.81 nm respectively.

Furthermore, we observe a significant increase in adhesion for the slightly roughened sample. However, the excessive increase of surface roughness does not seem to be beneficial for adhesion improvement. To understand the cause of the lack of adhesion in this case, additional chemical analyzes were performed. C1s XPS spectra revealed that the number of reactive carbonyl groups (C=O) created on PMMA treated under bad adhesion plasma conditions is too low (C=O/C-C ratio = 0.05) compared to those created in good adhesion plasma treatment conditions (C=O/C-C ratio = 0.13). It seems that the high-power plasma is not suitable to the formation of carbonyl groups. We suspect that since carbonyl groups are created on the top surface of PMMA, they can easily be lost by etching effects either by direct scission of these bonds or by the loss of carbonyl bearing groups.

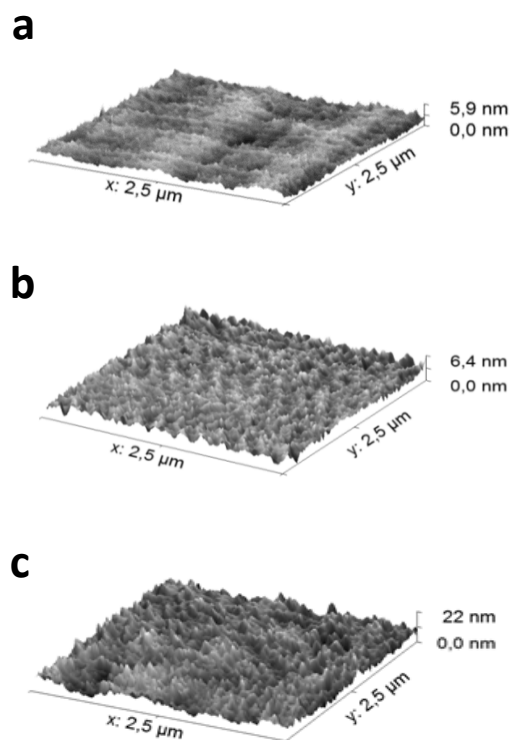


Figure 9. AFM images of a) untreated PMMA, b) PMMA treated under good adhesion conditions, and c) PMMA treated under bad adhesion conditions.

Table 5. Surface roughness of PMMA samples as a function of plasma treatment conditions

	Plasma treatment conditions	RMS roughness (nm)	Adhesion expressed in percentage of aluminum remaining on PMMA surface after peeling	C=O/C-C (Calculated from XPS)
Untreated PMMA	/	1.80 ± 0.2	6.4	0
Plasma treated PMMA	Low power plasma (50 W)	4.87 ± 1.1	52.7	0.13
	High power plasma (150 W)	8.81 ± 0.4	13.5	0.05

From the results described above, we can assume that the increase in surface roughness is not sufficient to improve the adhesion between PMMA and aluminum films. In order to confirm this hypothesis, we carried out surface pre-treatments with argon plasma which is known to modify the surface topography of polymers without altering their chemical properties. We present in Figure 10 the evolution of surface roughness of PMMA and Al/PMMA adhesion as a function of the duration of argon plasma pre-treatment (100 W, 1.10^{-2} mbar).

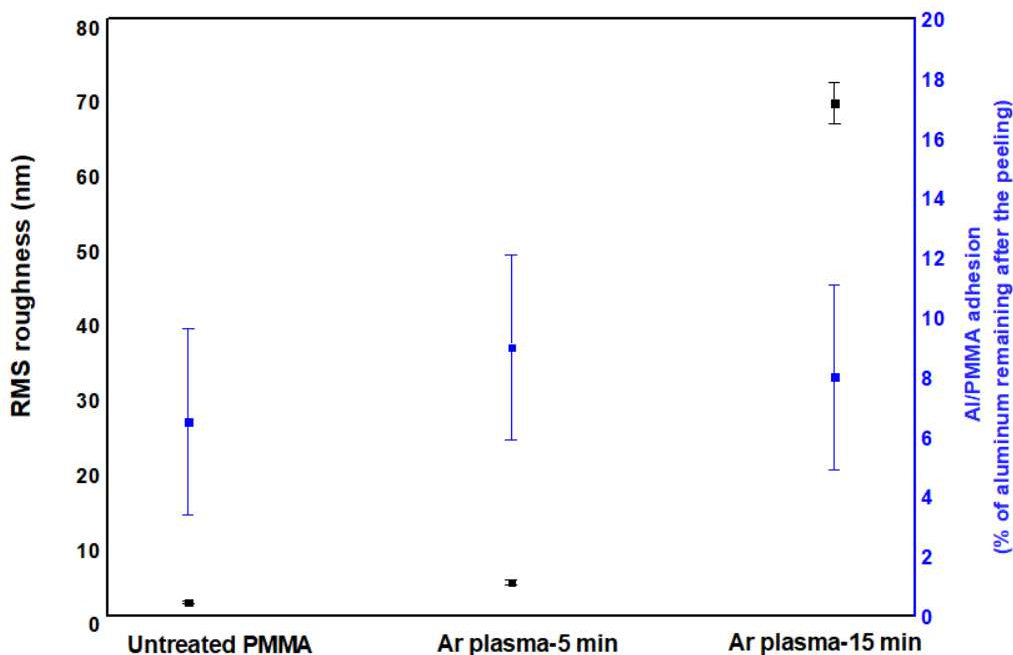


Figure 10. Evolution of surface roughness and Al/PMMA adhesion depending on the duration of the argon surface pre-treatment.

The surface roughness of PMMA increases from 1.8 nm to 4.5 nm after 5 minutes of pre-treatment with argon plasma. Increasing plasma treatment time to 15 min involved an enormous increase in the roughness value up to 68.7 nm. We also note that there is no correlation between PMMA surface roughness and adhesion such that the percentage of aluminum after peeling is almost unchanged (around an average value of $7.8 \pm 3.1\%$) despite the increase in roughness. We can therefore assume that the surface roughness does not have a direct effect on the adhesion between PMMA and aluminum.

To conclude this study, the Al/PMMA adhesion mechanisms may result from the combination of topographical and chemical modifications of the surface: the roughness increases the surface area of PMMA exposed to the plasma, which makes it possible to increase the density of the reactive chemical bonds (C=O) grafted to the extreme surface and therefore improve adhesion. However, the surface pre-treatment must be optimized to avoid surface damage by etching effects.

4. Conclusions

Metallic aluminum was successfully deposited on Polymethylmethacrylate (PMMA) substrates using magnetron sputtering. Before the deposition step, in situ pulsed DC plasma pre-treatment was performed. The plasma pre-treatment parametric study showed that oxygen-rich plasma pre-treatment improves the adhesive properties of PMMA. The correlation between contact angle measurements and XPS analysis evidenced that plasma pre-treatment increases surface wettability by the introduction of polar functional groups (C=O, C-O). During the aluminum film deposition, the reaction between carbonyl bonds and aluminum atoms allows the formation of Al-O-C covalent bonds which could explain the adhesion increase. XPS investigations revealed that the functional groups grafting is accompanied by photo-induced carbon chain scission by high energy UV photons from plasma. This phenomenon can be at the origin of the lack of adhesion. Indeed, polymer degradation by carbon chain scissions creates a weak interface between Al and PMMA during the film deposition. Finally, the correlation between XPS and AFM analysis showed that the adhesion mechanisms result from the combination of topographic and chemical modifications such as an optimized surface roughening leads to an increase in the specific surface of PMMA and consequently the amount of plasma-grafted carbonyl groups (C=O) which are essential for adhesion enhancement.

For the next studies, electron Spin Resonance (ESR) analyses are foreseen. This technique is suitable for the study of free radicals and dangling bonds and can be useful to understand more about PMMA surface degradation during plasma exposure. Furthermore, the optical emission spectroscopy (SOE) technique will be performed to explore the role of reactive plasma species (radicals, ions, atoms ...) concerning the modification of surface of PMMA and therefore on its adhesive properties.

Bibliography

- [1] U. Ali, K.J. Abd Karim, N. Buang, A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA), *Polymer Reviews*. 55 (2015) 1–28.
<https://doi.org/10.1080/15583724.2015.1031377>.
- [2] F. PARDOS, Polyméthacrylate de méthyle (PMMA) - Aspects économiques, Ref : TIP100WEB - "Plastiques et composites." (2002). <https://www.techniques-ingenieur.fr/base-documentaire/archives-th12/archives-plastiques-et-composites-tiaam/archive-1/polymethacrylate-de-methyle-pmma-am3350/> (accessed May 13, 2020).
- [3] T.O. Kääriäinen, D.C. Cameron, M. Tanttari, Adhesion of Ti and TiC Coatings on PMMA Subject to Plasma Treatment: Effect of Intermediate Layers of Al₂O₃ and TiO₂ Deposited by Atomic Layer Deposition, *Plasma Processes and Polymers*. 6 (2009) 631–641.
<https://doi.org/10.1002/ppap.200900038>.
- [4] P. Schissel, C. Kennedy, R. Goggin, Role of inorganic oxide interlayers in improving the adhesion of sputtered silver film on PMMA, *Journal of Adhesion Science and Technology*. 9 (1995) 413–424. <https://doi.org/10.1163/156856195X00356>.
- [5] R. Bandorf, S. Waschke, F. Carreri, M. Vergöhl, G. Grundmeier, G. Bräuer, Direct metallization of PMMA with aluminum films using HIPIMS, *Surface and Coatings Technology*. 290 (2016) 77–81.
- [6] A. Vesel, M. Mozetic, Surface modification and ageing of PMMA polymer by oxygen plasma treatment, *Vacuum*. 86 (2012) 634–637. <https://doi.org/10.1016/j.vacuum.2011.07.005>.
- [7] J. Peyroux, M. Dubois, Eric. Tomasella, E. Petit, D. Flahaut, Enhancement of surface properties on commercial polymer packaging films using various surface treatment processes (fluorination and plasma), *Applied Surface Science*. 315 (2014) 426–431.
<https://doi.org/10.1016/j.apsusc.2014.05.163>.
- [8] U. Schulz, P. Munzert, N. Kaiser, Surface modification of PMMA by DC glow discharge and microwave plasma treatment for the improvement of coating adhesion, *Surface and Coatings Technology*. 142 (2001) 507–511.
- [9] J. Peyroux, M. Dubois, E. Tomasella, N. Batische, L. Frezet, E. Petit, A.P. Kharitonov, D. Flahaut, Plasma and fluorination combination for stable multifunctionality of LDPE packaging films, *Plasma Process Polym.* 14 (2017) 1600066. <https://doi.org/10.1002/ppap.201600066>.
- [10] L. Carrino, G. Moroni, W. Polini, Cold plasma treatment of polypropylene surface: a study on wettability and adhesion, *Journal of Materials Processing Technology*. 121 (2002) 373–382.
[https://doi.org/10.1016/S0924-0136\(01\)01221-3](https://doi.org/10.1016/S0924-0136(01)01221-3).
- [11] K.N. Pandiyaraj, V. Selvarajan, R.R. Deshmukh, P. Yoganand, S. Balasubramanian, S. Maruthamuthu, Low pressure DC glow discharge air plasma surface treatment of polyethylene (PE) film for improvement of adhesive properties, *Plasma Science and Technology*. 15 (2013) 56.
- [12] U. Schulz, P. Munzert, N. Kaiser, Plasma Surface Modification of PMMA for Optical Applications, *Journal of Adhesion Science and Technology*. 24 (2010) 1283–1289.
<https://doi.org/10.1163/016942409X12561252292026>.
- [13] M.J. Melo, S. Bracci, M. Camaiti, O. Chiantore, F. Piacenti, Photodegradation of acrylic resins used in the conservation of stone, *Polymer Degradation and Stability*. 66 (1999) 23–30.
[https://doi.org/10.1016/S0141-3910\(99\)00048-8](https://doi.org/10.1016/S0141-3910(99)00048-8).
- [14] S. Ben Amor, G. Baud, M. Jacquet, G. Nansé, P. Fioux, M. Nardin, XPS characterisation of plasma-treated and alumina-coated PMMA, *Applied Surface Science*. 153 (2000) 172–183.
[https://doi.org/10.1016/S0169-4332\(99\)00354-2](https://doi.org/10.1016/S0169-4332(99)00354-2).
- [15] P. Duchatelard, G. Baud, J. Besse, M. Jacquet, Alumina coatings on PMMA: optimization of adherence, *Thin Solid Films*. 250 (1994) 142–150.
- [16] H. Kaczmarek, H. Chaberska, The influence of UV-irradiation and support type on surface properties of poly(methyl methacrylate) thin films, *Applied Surface Science*. 252 (2006) 8185–8192. <https://doi.org/10.1016/j.apsusc.2005.10.037>.

- [17] J. Friedrich, *Metal-Polymer Systems: Interface Design and Chemical Bonding*, John Wiley & Sons, 2017.
- [18] J. Friedrich, *The plasma chemistry of polymer surfaces: advanced techniques for surface design*, John Wiley & Sons, 2012.
- [19] I. Junkar, A. Vesel, U. Cvelbar, M. Mozetič, S. Strnad, Influence of oxygen and nitrogen plasma treatment on polyethylene terephthalate (PET) polymers, *Vacuum*. 84 (2009) 83–85. <https://doi.org/10.1016/j.vacuum.2009.04.011>.
- [20] Data Analysis, Statistical & Process Improvement Tools | Minitab, (n.d.). <https://www.minitab.com/en-us/> (accessed May 4, 2020).
- [21] P. Duchatelard, *Elaboration, caractérisation et adhésion de revêtements d'alumine sur polymère (PMMA)*, Clermont-Ferrand 1, 1996.
- [22] D.E. Packham, *Handbook of adhesion*, John Wiley & Sons, 2006.
- [23] N.N. Misra, B.K. Tiwari, K. Raghavarao, P.J. Cullen, Nonthermal plasma inactivation of food-borne pathogens, *Food Engineering Reviews*. 3 (2011) 159–170.
- [24] O. Terrier, B. Essere, M. Yver, M. Barthélémy, M. Bouscambert-Duchamp, P. Kurtz, D. VanMechelen, F. Morfin, G. Billaud, O. Ferraris, Cold oxygen plasma technology efficiency against different airborne respiratory viruses, *Journal of Clinical Virology*. 45 (2009) 119–124.
- [25] D.K. Owens, R.C. Wendt, Estimation of the surface free energy of polymers, *Journal of Applied Polymer Science*. 13 (1969) 1741–1747. <https://doi.org/10.1002/app.1969.070130815>.
- [26] R.M. Thurston, J.D. Clay, M.D. Schulte, Effect of atmospheric plasma treatment on polymer surface energy and adhesion, *Journal of Plastic Film & Sheeting*. 23 (2007) 63–78.
- [27] T. Gururaj, R. Subasri, K.R.C.S. Raju, G. Padmanabham, Effect of plasma pretreatment on adhesion and mechanical properties of UV-curable coatings on plastics, *Applied Surface Science*. 257 (2011) 4360–4364. <https://doi.org/10.1016/j.apsusc.2010.12.060>.
- [28] P. Gröning, O.M. Küttel, M. Collaud-Coen, G. Dietler, L. Schlapbach, Interaction of low-energy ions (< 10 eV) with polymethylmethacrylate during plasma treatment, *Applied Surface Science*. 89 (1995) 83–91. [https://doi.org/10.1016/0169-4332\(95\)00013-5](https://doi.org/10.1016/0169-4332(95)00013-5).
- [29] XPS Interpretation of Carbon, (n.d.). <https://xpssimplified.com/elements/carbon.php> (accessed May 23, 2020).
- [30] R. Cueff, G. Baud, M. Benmalek, J.P. Besse, J.R. Butruille, M. Jacquet, X-ray photoelectron spectroscopy studies of plasma-modified PET surface and alumina/PET interface, *Applied Surface Science*. 115 (1997) 292–298.
- [31] J.-J. Pireaux, M. Vermeersch, C. Grégoire, P.A. Thiry, R. Caudano, T.C. Clarke, The aluminum–polyimide interface: An electron-induced vibrational spectroscopy approach, *The Journal of Chemical Physics*. 88 (1988) 3353–3362.
- [32] X. Liu, S. Tang, H.-K. Choi, H.-S. Choi, Effect of plasma-treated polymer substrates on fabricating surface microsystems through LbL coating, *Macromol. Res*. 18 (2010) 413–420. <https://doi.org/10.1007/s13233-010-0506-0>.
- [33] K.L. Mittal, *Adhesion Aspects of Thin Films, volume 2: Adhesion Aspects of Thin Films*, CRC Press, 2005.
- [34] P.S. Ho, Chemistry and adhesion of metal-polymer interfaces, *Applied Surface Science*. 41 (1990) 559–566.
- [35] S. Küper, S. Modaressi, M. Stuke, Photofragmentation pathways of a PMMA model compound under UV excimer laser ablation conditions, *Journal of Physical Chemistry*. 94 (1990) 7514–7518.
- [36] F. Poncin-Epaillard, M. Aouinti, Characterization of CO₂ Plasma and Interactions with Polypropylene Film, *Plasmas and Polymers*. 7 (2002) 1–17. <https://doi.org/10.1023/A:1015277316825>.
- [37] N. Vandencastele, H. Fairbrother, F. Reniers, Selected Effect of the Ions and the Neutrals in the Plasma Treatment of PTFE Surfaces: An OES-AFM-Contact Angle and XPS Study, *Plasma Processes and Polymers*. 2 (2005) 493–500. <https://doi.org/10.1002/ppap.200500010>.
- [38] M.D. Duca, C.L. Plosceanu, T. Pop, Surface modifications of polyvinylidene fluoride (PVDF) under rf Ar plasma, *Polymer Degradation and Stability*. 61 (1998) 65–72.

- [39] O. Ozgen, E.A. Aksoy, V. Hasirci, N. Hasirci, Surface characterization and radical decay studies of oxygen plasma-treated PMMA films, *Surface and Interface Analysis*. 45 (2013) 844–853.
- [40] Y.-H. Ting, C.-C. Liu, S.-M. Park, H. Jiang, P.F. Nealey, A.E. Wendt, Surface Roughening of Polystyrene and Poly(methyl methacrylate) in Ar/O₂ Plasma Etching, *Polymers*. 2 (2010) 649–663. <https://doi.org/10.3390/polym2040649>.