




Article

# Environmentally Friendly Plasma Activation of Acrylonitrile–Butadiene–Styrene and Polydimethylsiloxane Surfaces to Improve Paint Adhesion

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**Abstract:** Generally, polymeric materials present an issue related to their low surface energy: low painting ability. The main aim of this work is to improve the adhesion between polymeric surfaces (polydimethylsiloxane (PDMS), and acrylonitrile-butadiene-styrene (ABS)) and paints (epoxy (EP), and polyurethane (PU)-based). In order to increase adhesion, hydrophilic modification of surfaces by atmospheric pressure plasma torch treatment (APPT) was proposed. Furthermore, it can permit dissimilar joints, i.e., ABS with a metal joined by a silicone (based PDMS), to be painted. The surface modifications were characterized by measurements of surface energy and roughness. In addition, the effectiveness of the pre-treatment on improving paint adhesion was confirmed by scratch, cross-cut, and adhesion tests. Results showed the possibility of coating both ABS and PDMS with a PU-based paint when treated with plasma. As a novel result, polymer and metal panels joined by silicone were able to be painted with the PU paint.

**Keywords:** polydimethylsiloxane; acrylonitrile-butadiene-styrene; atmospheric pressure plasma torch; epoxy paint; polyurethane paint; adhesion tests

## 1. Introduction

Acrylonitrile-butadiene-styrene (ABS) and polydimethylsiloxane (PDMS) polymers are widely used, as they offer excellent intrinsic properties such as lightweight, high strength or chemical resistance, among others. PDMS was first used in biomedical and organic applications [1], and it protects against corrosion as a coating for metal substrates [2] and it is extensively used on the manufacturing of lab-on-a-chip devices [3]. Besides, the hydrophobic and insulating character of PDMS makes it possible to expand its applications, such as electrowetting-on-dielectric systems [4]. However, PDMS is mainly used as an adhesive, because its inorganic backbone provides unique properties. It can work under higher temperatures than other organic adhesives and presents good electrical insulation and excellent chemical properties combined with high visco-elastic properties [5].

On the other hand, ABS is usually used to manufacture automotive components, where they can be produced by injection moulding [6] in order to obtain samples in large quantities and qualities with high reproducibility. However, the use of PDMS and ABS in other products or applications is often limited, as they cannot be strongly bonded to other materials, due to their low surface energy, especially for PDMS.

Chemical surface treatments on polymers usually apply highly oxidizing reagents in order to enhance surface wettability and adhesion capability through the formation of polar groups, and to generate a certain surface roughness [7]. Some industrial products are used by the chemistry of

highly reactive carbene [8,9], which are processed as wet formulations and require a curing step to form a chemically cross-linked network that provides the bonding of the coating to the substrate. These industrial products can also be used as a discrete layer, applied prior to the coating, or mixed inside the coating formulation. However, the generation of toxic waste during these procedures is an environmental and health issue to overcome.

An attractive environmentally friendly and effective route for polymer surface pre-treatment is the use of plasma sources. Plasma's main effects are to clean, etch, and activate the surface. Etching is produced by plasma flux impact, and activation is driven through the introduction of new surface polar functionalities [10,11], due to the rupture of bonds in the most external layer of the polymers and reaction with existing reactive species in plasma.

Depending on the working pressure, two different plasma treatments can be found: low-pressure plasma and atmospheric-pressure plasma. The effect of low pressure-plasma on ABS surfaces was studied in terms of roughness and wettability [12]. It was found that plasma increases both nanoroughness and wettability, as expected. The effect of these kinds of plasma was also observed in polydimethylsiloxane (PDMS–PDMS) bondings [13]. Parameters were optimized to obtain the maximum fracture energy and toughness. The etching effect of plasma was applied for the formation of polymer nanostructures in poly(methylmethacrylate), polystyrene, or polydimethylsiloxane, as an alternative for lithography methods [14].

Atmospheric-pressure plasma (APPT) operates without increasing the sample temperature. APPT has been widely used in adhesives, sealants, and coatings fields [15]. It usually creates polar oxygen-containing groups ( $-\text{COOH}$ ,  $-\text{OH}$ ), thus increasing the surface energy and wettability, and enhancing the adhesion capabilities of polymers [16]. Previous works have reported improvements of adhesion between PDMS and acrylic adhesive tape [17], and between two PDMS surfaces [18] by using atmospheric-pressure plasma.

However, polymers show a tendency towards hydrophobic recovery [19–21], due to the high mobility of the siloxane backbone, and the migration of untreated polymer chains and additives from the bulk to the surface. It is mandatory for an industrial process to define the active life of a polymer after plasma treatment (aging behavior).

In previous works, APPT was optimized on the ABS [22] and PDMS [19] polymers; the treatment effects were sensitive to the speed and to the time after the treatment. In both cases, more hydrophilic surfaces were obtained and characterized by XPS, the creation of polar groups was checked ( $\text{C}-\text{O}$ ,  $\text{C}/\text{OH}$  and  $\text{R}/\text{COO}-$ ). Onto PDMS,  $\text{Si}-\text{OH}$  groups were introduced onto the polymeric surface, while hydrophobic methyl groups were removed. In addition, scanning electronic microscopy (SEM) analyses showed changes in the surface roughness, due to the etching effect of plasma.

Based on previous research, this work is focused on studying the APPT effect on the adhesion of epoxy (EP) and polyurethane (PU) paints on ABS and PDMS. This improved paint ability could extend the use of these polymers in the habitat industry. Both, epoxy and polyurethane-based paints were selected with attention to their high performance features, including chemical resistance, gap filling capability, vibration damping, or short curing time properties, as well as their wide use in the industry, where the use of these polymer types are becoming more frequent. One of the main applications in this field includes dissimilar joints between ABS and metals. In this work, PDMS is proposed for use as an adhesive for these kinds of unions, and then painted with epoxy- or polyurethane-based paints.

## 2. Experimental

### 2.1. Materials

Commercial polymers (ABS and PDMS) were provided by Ketersa (Pinto, Madrid, Spain). The specimens were cleaned and degreased with methyl-ethyl-ketone (MEK).

The paints are in the branch Rocha, provided by Pinturas Landecolor S.L. (Madrid, Spain). One of them was bi-component epoxy resin (EP) and the other was aliphatic bi-component polyurethane (PU). Both of them were red, and they are usually used to paint galvanic steel traffic signs.

## 2.2. Treatment

The APPT device from Plasma Treat GmbH (Steinhagen, Germany), described in previous paper [18], was used to treat the polymers. The setup operated at a frequency of 17 kHz and a high-tension discharge of 20 kV, and it was provided with a rotating torch ending in a nozzle (1900 rpm), through which plasma was expelled. The system contained an electronically speed-controlled platform where the samples were placed. The air plasma was generated at a working pressure of 2 bars inside the rotating nozzle by a non-equilibrium discharge, and expelled through a circular orifice onto the samples. The previously optimized parameters were  $1 \text{ m}\cdot\text{min}^{-1}$  and 6 mm between the sample and the nozzle [19,22,23].

Contact angle measurements (following UNE-EN828:2013 [24]) were used to determine the wetting properties, and to calculate the surface energy using the mathematical Owens–Wendt–Rabel–Kaelble (OWRK) method, which take into account various components that are related to the forces found in the solid-liquid-vapour system that is formed when the drop is on the solid surface [19]. Sessile drop method measurements were performed with an OCA 15 plus goniometer from DataPhysics (Neurtek Instruments, Eibar, Guipúzcoa, Spain). Static drops of 3  $\mu\text{L}$  of deionized water, glycerol, diiodomethane, and 1,5-pentanediol were deposited onto smooth and uniform PDMS and ABS samples, and measured after stabilization of the drop. Surface energy was evaluated before and after APPT treatment.

According to the OWRK method [25], the total surface energy of a solid is the sum of a dispersion parameter ( $\gamma_s^D$ , due to London-type forces) and a polar parameter ( $\gamma_s^P$ , which arises by the action of hydrogen bonding and dipole–dipole interactions in the system). Both components are calculated with Equations (1) and (2), knowing the polar and dispersive components of the liquids ( $\gamma_l^P$  and  $\gamma_l^D$ , respectively), and  $\theta$  is the drop angle on the substrate.

$$\gamma_T = \gamma_D + \gamma_P \quad (1)$$

$$\frac{(1 + \cos \theta) \cdot \gamma_l}{\sqrt{\gamma_l^D}} = \sqrt{\gamma_s^P} \cdot \sqrt{\frac{\gamma_l^P}{\gamma_l^D}} + \sqrt{\gamma_s^D} \quad (2)$$

The polar component of liquids used (deionized water, 1,5-pentanediol, glycerol, diiodomethane) to measure the contact angle are 50, 37, 30 and 2  $\text{mJ}\cdot\text{m}^{-2}$ , respectively. This method is selected to understand the mechanism of the hydrophobic recovery of a surface.

Besides, the surfaces were characterized by atomic force microscopy (AFM), which allows for the study of surfaces at the nanometric scale, giving information on surface roughness. The AFM studies were made with a MultiMode Nanoscope<sup>®</sup> IV (Digital Instruments/Veeco Metrology Group, Santa Barbara, CA, USA). The measurement conditions were room temperature, tapping mode, silicon tips with a force constant of  $40 \text{ N}\cdot\text{m}^{-1}$ , and a resonance frequency of 300 kHz, simultaneously recording height and phase images.

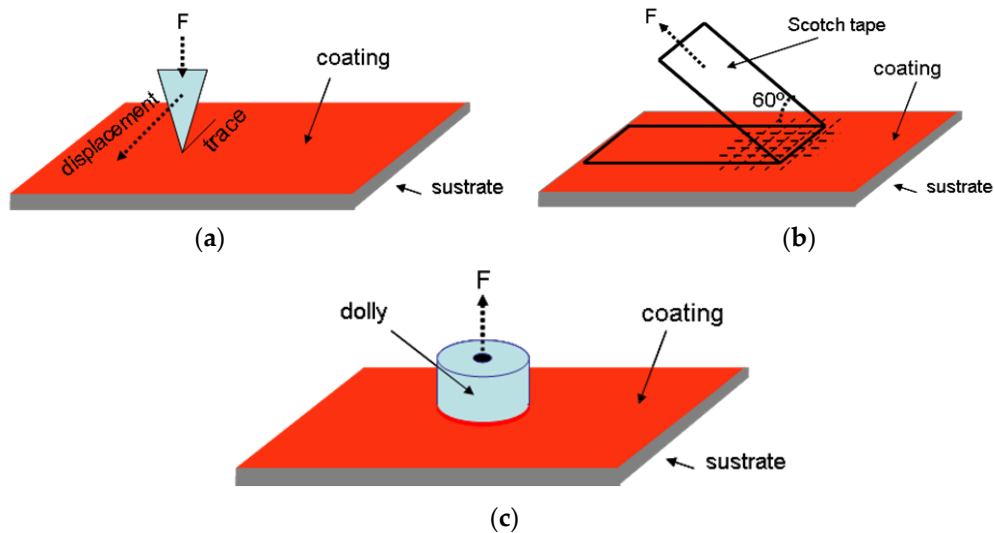
## 2.3. Characterization of the Paints' Adhesion to Polymeric Surfaces

To study the adhesion, three different tests were carried out: scratch test, cross-cut test, and adhesion pull-off test, all of them typical for paints.

### 2.3.1. Scratch Test

According to standard ISO 1518:2011 [26] this test uses a fixed load on a hemispheric needle to scratch the surface. This test was carried out with a Clemen Scratch tester by Neurtek Instruments

(Eibar, Guipúzcoa, Spain). The resulting trace is analyzed in order to determinate the delamination or the adhesion of the paint layer on the substrate (Figure 1a). Tests were conducted on a “go/no go” basis using a single specified load (from 2 to 4 kg), higher than the minimum load at which the coating was penetrated. Depending on the substrate and the coating, different loads were used.



**Figure 1.** Schemes of (a) scratch test, (b) cross-cut test, (c) adhesion pull-off test.

### 2.3.2. Cross-Cut Test

Following standard ISO 2409:2013 [27], a cutting tool with the adequate pressure to indent the substrate was used (Figure 1b). Then, scotch tape was applied and removed, forming an angle of 60 degrees. The remaining surface percentage without paint was studied according to standard EN 2409, to classify the samples. The equipment used in this test was Cross Cut tester NK2000 (Neurtek Instruments, Eibar, Guipúzcoa, Spain)

### 2.3.3. Adhesion Pull-Off Test

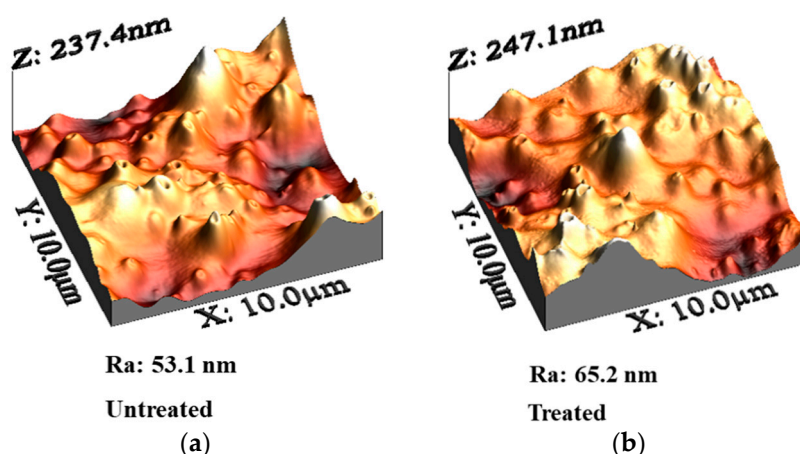
Adhesive bonds have low tensile strengths, so this failure mode represents the most aggressive condition on adhesive joints. Thus, if the joint has a good tensile strength is very likely it will resist other effort types. According to Figure 1c and following ISO 4624:2016 [28], in this study, a Universal Testing machine EM1/200FR (Microtest, Madrid, Spain) with a load cell of 1 kN was used, at a load speed of  $1 \text{ mm} \cdot \text{min}^{-1}$ , using aluminium dollies of 20 mm diameter.

In order to determine the mechanism of failure, the surfaces were observed after testing with a DSX500 opto-digital microscope (OM) supplied by Olympus Corporation (Tokyo, Japan), as well as by SEM (PhilipsXL-30 FEI EUROPE microscope, Eindhoven, the Netherlands).

## 3. Results and Discussion

### 3.1. Roughness Modification

The samples were characterized by AFM to study plasma effect on the surface roughness. Figure 2 shows the changes produced by treatment on ABS, where an increase of arithmetic average of the absolute values of the profile height deviations from the mean line ( $R_a$ ) from 53.1 to 65.2 nm was observed. This 18% increase is expected to favor the mechanical anchoring of the coating on ABS as a higher surface area is available.



**Figure 2.** AFM micrographs of untreated (a) and atmospheric pressure plasma torch (APPT)-treated (b) acrylonitrile-butadiene-styrene (ABS).

On the contrary, according to previous studies, PDMS becomes smoother at the microscale level [19,29]. This is assumed to be a consequence of wear effects, due to the etching of the plasma flux. However when the surface is studied at the nanoscale, PDMS presents an increment in nanoroughness from 34 to 58 nm, due to the plasma treatment. This effect had already been observed before on composite (polyethylene/boron) [30]. Then, it can be concluded that the etching effect of the plasma is different, depending on the scale: at the microscale surface, it becomes smoother, but at the nanoscale, the roughness is increased.

### 3.2. Effect of Aging on the Surface Energy after Atmospheric Pressure Plasma Torch Treatment (APPT)

Industrial polymer samples are usually stored before being painted. Therefore, it is necessary to establish their activation life, to assure a good performance. In this work, aging time is based on the evolution of surface energy, and on its polar and dispersive components.

ABS behavior after APPT over 336 h of aging at  $25 \pm 2$  °C and 40% relative humidity (RH) is shown in Table 1. Immediate enhancement of surface energy after treatment was mainly due to the creation of oxygen-containing polar moieties, which change the polar component [15]. The hydrophobic recovery over storage time was not significant, and it was allocated in the range of 10% to 17% for the total and polar fractions of surface energy, respectively [8]. Therefore, a maintenance on the improved wetting and adhesive behavior of the ABS surfaces after APPT modification is expected after long aging times (ca. 14 days) as a function of surface energy.

**Table 1.** Effect of atmospheric pressure plasma torch (APPT) treatment on acrylonitrile-butadiene-styrene (ABS) surface energy components ( $\text{mJ}\cdot\text{m}^{-2}$ ) with aging.

Surface Energy	Untreated	3 min	1 h	48 h	168 h	336 h
Total	$30 \pm 2$	$59 \pm 2$	$59 \pm 2$	$62 \pm 2$	$62 \pm 2$	$53 \pm 2$
Dispersive	$16 \pm 2$	$18 \pm 2$	$19 \pm 2$	$16 \pm 2$	$14 \pm 2$	$19 \pm 2$
Polar	$14 \pm 2$	$41 \pm 2$	$39 \pm 2$	$45 \pm 2$	$47 \pm 2$	$34 \pm 2$

In relation to the PDMS, high chain mobility and additive migration allowed for a faster hydrophobic recovery compared to ABS (Table 2). As previously reported, the polar component of surface energy of these surfaces recovered its pristine value after approximately 30 min of storage [10,19]. Thus, these samples must be painted in the first five minutes after the treatment in order to obtain proper adhesion.

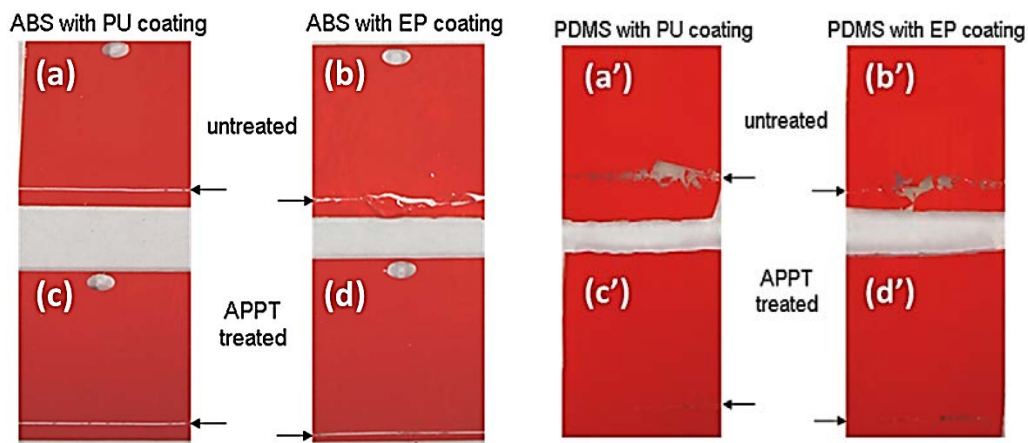


**Table 2.** Effect of APPT treatment on polydimethylsiloxane (PDMS) surface energy components ( $\text{mJ}\cdot\text{m}^{-2}$ ) with aging.

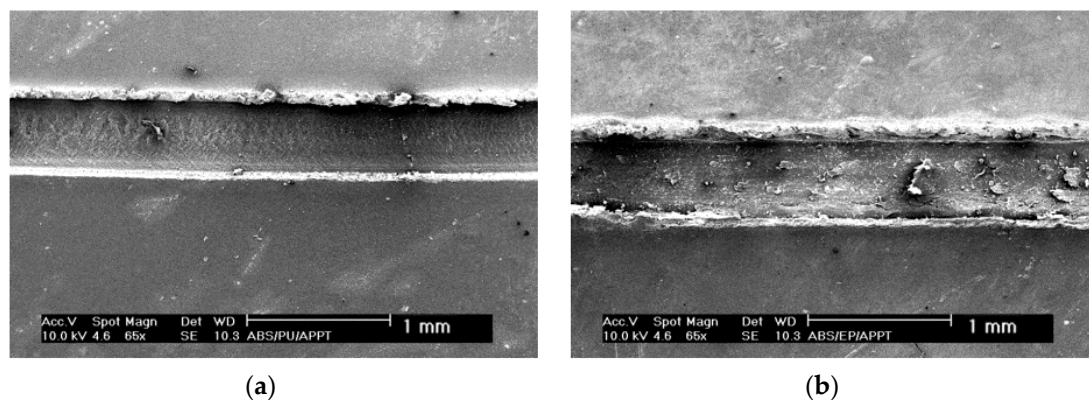
Surface Energy	Untreated	3 min	5 min	15 min	30 min	1 h
Total	$27 \pm 2$	$43 \pm 2$	$41 \pm 2$	$37 \pm 2$	$35 \pm 2$	$30 \pm 2$
Dispersive	$24 \pm 2$	$32 \pm 2$	$30 \pm 2$	$31 \pm 2$	$32 \pm 2$	$27 \pm 2$
Polar	$2 \pm 1$	$11 \pm 2$	$11 \pm 2$	$6 \pm 1$	$3 \pm 1$	$3 \pm 1$

### 3.3. Scratch Test

This simple test allows for a first qualitative evaluation of the substrate-paint bond strength. If the paint comes unstuck at the edge of the scratch, the test fails. In the case of ABS without APPT treatment there was good resistance after the test on PU paint (Figure 3a), but EP paint (Figure 3b) tore and detached from the substrate. After APPT treatment, both paints presented proper adhesion on the ABS surface (Figure 3c,d). SEM micrographs showed no paint detachment on the edges of the scratch, neither for the polyurethane paint (Figure 4a), nor for the epoxy base (Figure 4b). In this substrate, a load of 3 kg for the EP coating and 4 kg for the PU coating was used.



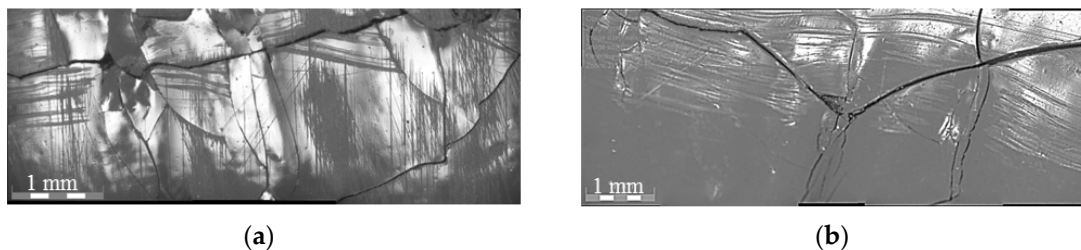
**Figure 3.** Scratch test on acrylonitrile-butadiene-styrene (ABS): untreated and painted with polyurethane (PU) and epoxy (EP) ((a,b) respectively); with APPT painted with PU and EP ((c,d) respectively). Scratch test on polydimethylsiloxane (PDMS): untreated and painted with PU and EP ((a',b') respectively), with APPT painted with PU and EP ((c',d') respectively).



**Figure 4.** Scratch test on ABS: Micrographs with polyurethane (a) ABS + APPT/PU and epoxy (b) ABS + APPT/EP after treatment.

Generally, it is known that silicones present problems with coatings, due to their bad adhesion with them. In the case of PDMS, both PU (Figure 3a') and EP (Figure 3b') paints tore and detached

from the untreated polymer (untreated samples were tested with 2 kg), as expected. On the contrary, no clear paint removal was observed after the scratch test of APPT-modified surfaces. PU (Figure 3c') and EP (Figure 3d') presented a good level of adhesion, and passed the test. To analyse the scratch, opto-digital microscopy provides more information than electronic microscopy, since the magnification is lower. Figure 5 shows OM images where good adhesion between APP-treated samples and PU (Figure 5a) and EP (Figure 5b) coatings were observed. The loads used for scratch test on treated PDMS were 2 kg for the EP coating and 3 kg for the PU coating. Cracks on the coating do not depend on the paint, but on the difference of flexibility with the substrate. They are caused by the difference in deformation among the flexible PDMS and the more rigid coating during the test. The standard does not consider the case of flexible substrates.



**Figure 5.** Scratch test on PDMS: Images by opto-microscopy after (APPT) with polyurethane (a) PDMS + APPT/PU and epoxy (b) PDMS + APPT/EP.

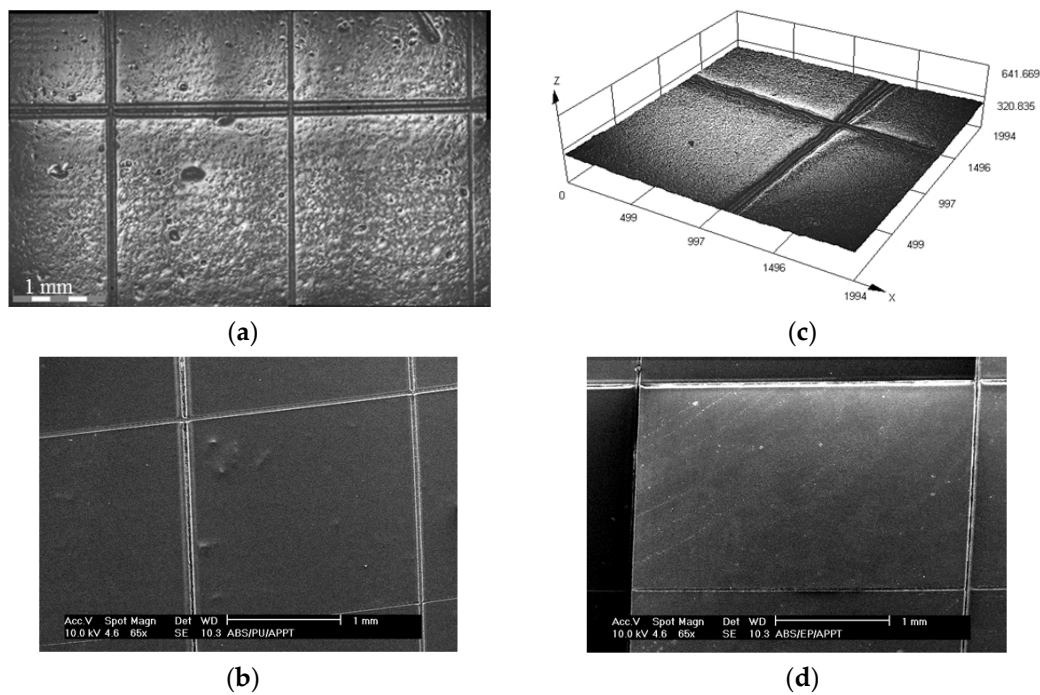
According to the standard, the scratch test was passed for both the ABS and PDMS with APPT treatment. With regard to the untreated samples, only ABS with the PU coating passed the scratch test.

#### 3.4. Cross-Cut Test

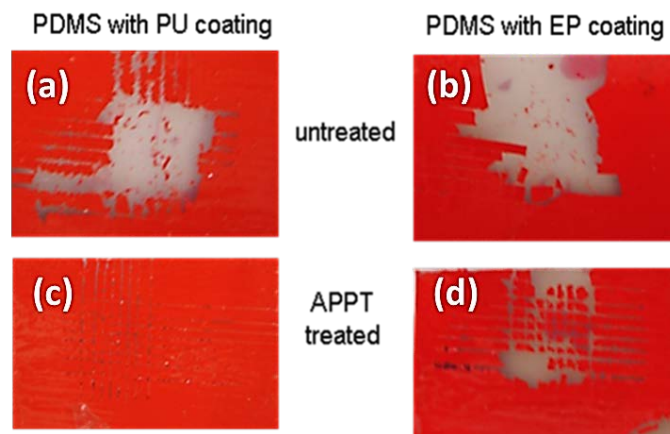
This test was more aggressive than the previous one. The results of these tests were practically qualitative and allowed for an idea of the quality of the paint adhesion. A cross-test on painted ABS did not show any differences. In all cases, the paint did not come off the substrate, regardless of whether ABS was untreated (Figure 6a,b) or treated (Figure 6c,d), and the kind of painting, PU (Figure 6a,c), and EP (Figure 6c,d).

In the case of the PDMS substrate (Figure 7), it was easily deformed upon contact with the test blades, so that after the cross-cut test, the mark could be well observed on the coatings, as they were more rigid. In the treated specimens, partial detachment (60%) of the EP coating occurred (Figure 7d), whereas the PU coating did not come off (Figure 7c); therefore, a better compatibility with the substrate was defined.

Figure 8 shows in more detail the cross-cut test on the PDMS. In the sample painted with polyurethane (Figure 8a), the lattice was observed, but the sides were not significantly detached. Some cracks on the coating were found, due to the different deformation of the substrate compared with the coating. Similar cracks were observed on the scratching test (Figure 5a). In the case of epoxy coating (Figure 8b) a clear detachment was found, and no cracks were observed, as they were more rigid and directly detached when PDMS was deformed.

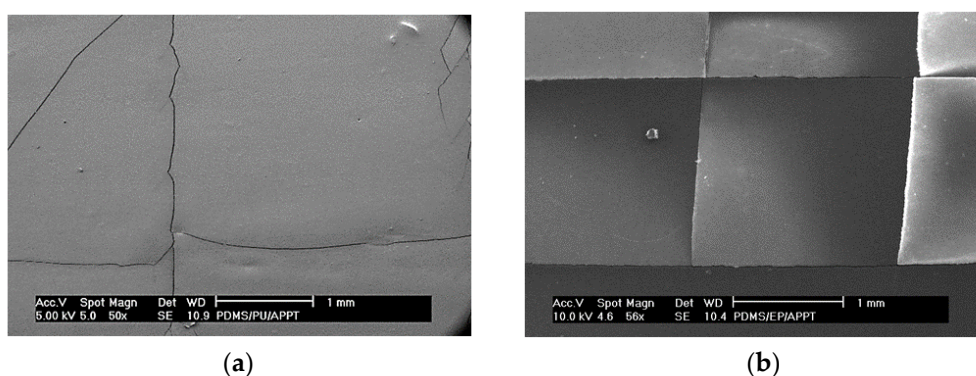


**Figure 6.** OM micrographs after the cross-cut test on ABS: (a) ABS + PU, without APPT treatment and PU paint; (b) APS + APPT/PU, without APPT treatment and EP paint. Scanning electronic microscopy (SEM) micrographs after the cross-cut test on ABS: (c) ABS + EP, with APPT treatment and PU paint and (d) APS + APPT/EP, with APPT treatment and EP paint.



**Figure 7.** Cross-cut test on PDMS: (a) without APPT painted with PU, (b) without APPT painted with EP, (c) with APPT painted with PU, and (d) with APPT painted with EP.





**Figure 8.** SEM micrographs of the cross-cut test of treated PDMS with polyurethane (a) PDMS + APPT/PU and epoxy (b) PDMS + APPT/EP.

Following the standard classification, the percentage of detachment was determined by visual inspection. The results are shown in Table 3. It is important to highlight that the standard was presented in terms of acceptable values 0, 1, and 2. As a consequence, untreated ABS with epoxy failed the test, passing it with the treatment. The same was observed for PDMS with the polyurethane-based paint.

**Table 3.** Classification of paint loss on the cross-cut test.

Substrate	Paint	Treatment	Classification	% Detached
ABS	Epoxy	Untreated	5	>65
		APPT	0	0
	Polyurethane	Untreated	0	0
		APPT	0	0
PDMS	Epoxy	Untreated	5	>65
		APPT	4	≈50
	Polyurethane	Untreated	5	>65
		APPT	2	<10

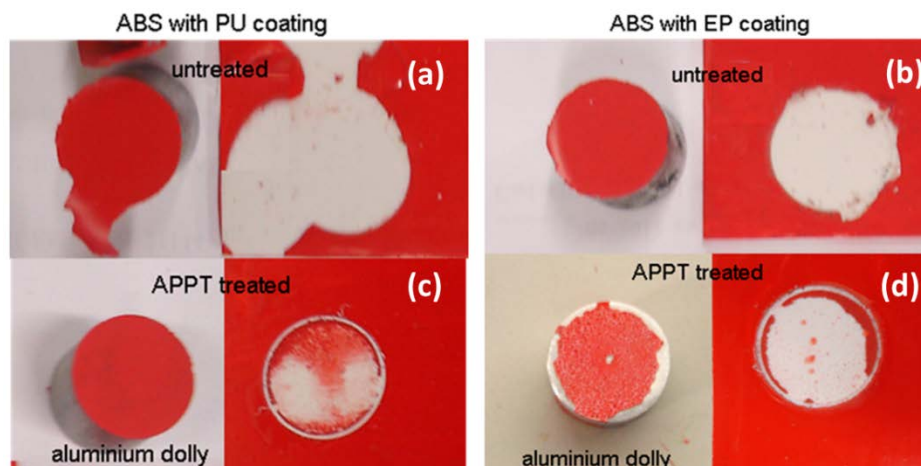
### 3.5. Adhesion Pull-Off Test

In this test, adhesion may be studied quantitatively and qualitatively. It provides the force that is needed for breaking the joint, and the type of failure. Table 4 summarizes the adhesion results. ABS–PU painted systems (Figure 9a) shows the adhesive failure before pre-treatment, although certain adhesion strengths (59 kPa) are obtained. Upon APPT pre-treatment (Figure 9c), the adhesion is 10-fold augmented (577 kPa), showing a mixed failure rate (adhesive + cohesive) at around 50%, as Figure 10a shows. For other substrates, greater adherence after plasma treatments has also been found [31–33].

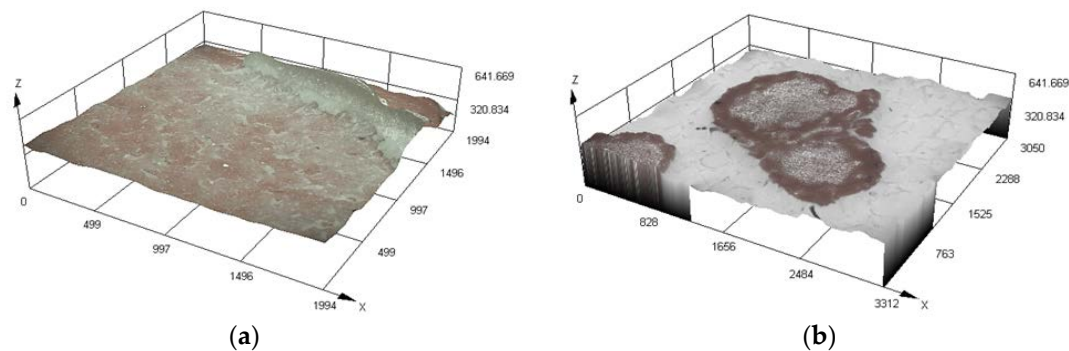
In the case of the ABS–EP system, adhesive failure occurs on untreated substrates (Figure 9b), whereas cohesive failure through ABS itself takes place after plasma modification (Figure 9d). ABS rests adhere to the paint on the dolly surface, having a substrate failure, as seen in Figure 10b in more detail.

**Table 4.** Adhesion strength (kPa) by adhesion pull-off test.

Coating	PDMS		ABS	
	APPT-treated	Untreated	APPT-treated	Untreated
EP	37 ± 2	–	1025 ± 10	–
PU	199 ± 5	–	577 ± 5	59 ± 4

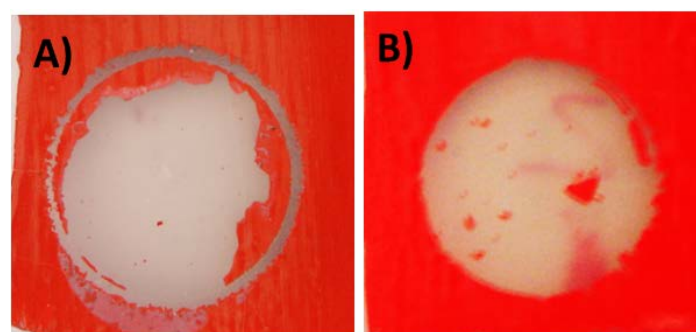


**Figure 9.** Adhesion pull-off tests: failure of untreated ABS with polyurethane (a) and epoxy (b) coatings, and treated ABS with PU (c) and EP (d).



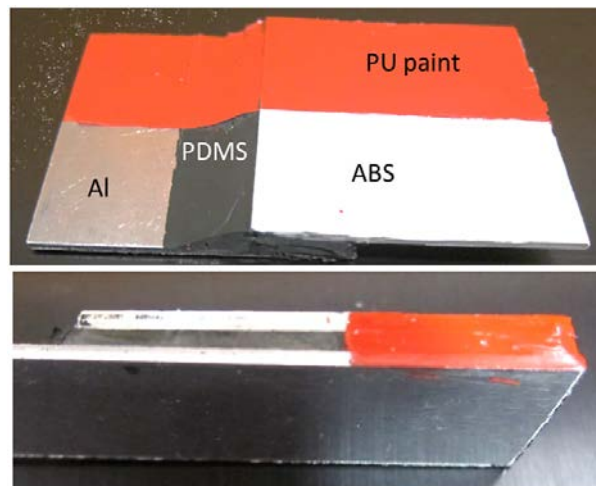
**Figure 10.** Detail of pull-off failures of treated ABS–PU and treated ABS–EP. (a) APS + APPT/PU; (b) APS + APPT/EP.

PDMS presented no adhesion under the pull-off test for both adhesives without surface modification. After the APPT hydrophilic modification, adhesive failure with a higher resistance for the polyurethane-based paint (Figure 11A) compared to the epoxy-based paint (Figure 11B) was found.



**Figure 11.** Adhesion pull-off test of treated PDMS coated with PU (A) and EP (B).

This work is focused on the application of PDMS as an adhesive in dissimilar unions between aluminium and ABS, which is typical in the automotive industry (Figure 12). This work shows that it is possible to paint the whole set with the same paint, since the versatility and ease of automation in the industry of the plasma torch allows for this set-up in assembly line. Besides, considering the favorable properties that the current structural silicones present; these kinds of joints could be introduced easily in other industries, such as construction or transport.



**Figure 12.** PU-based painted ABS–aluminium joined by PDMS (silicone).

#### 4. Conclusions

In this work, atmospheric pressure plasma torch treatment (APPT) has been used to increase the wettability through hydrophilic modification of ABS and PDMS surfaces, with the aim of improving paint ability with epoxy- and polyurethane-based fluids. It is observed the aesthetic features of the materials were preserved (no physical surface damage), but with enhanced surface energy and nano-roughness. Therefore, an improved coating or paint adhesion was expected.

On the ABS substrate, APPT hydrophilic modification is effective after at least 336 h of storage. Along with the increased nanoroughness (18%) of the surfaces, better wetting and mechanical anchoring of the coatings is expected, as well as the proper storage/transport of the samples at least 14 days after treatment.

On the contrary, PDMS undergoes rapid hydrophobic recovery, allowing for a coating-active window after APPT treatment of approximately 5 min.

The high strength of the ABS–PU after the treatment is especially important, and it has been multiplied by a factor of 10, changing from an adhesive failure to a mixed one. In addition, the ABS–EP bond has risen from zero to very high strength, with failure by the substrate once treated.

The good compatibility obtained in the PDMS–PU bond is of great importance, due to the applications that can be found as much in the field of paints as in that of adhesives. In this case, joint strength is also obtained after the treatment.

As a final conclusion, ABS should pass the tests with both coatings used when it is treated, but when untreated, it is only the PU coating that passes the tests. Furthermore, the PDMS would only pass the test when it is treated and the coating is PU.

The possibility of painting this dissimilar joint allows it to extend their applications, especially to the habitat industry, enabling more innovative designs.

**Author Contributions:** Conceptualization, J.A.; Methodology, S.L.d.A.; Validation, J.A. and M.A.M.; Formal Analysis, J.A.; Investigation, M.A.M. and S.L.d.A.; Data curation, J.A.; Writing—Original Draft Preparation, J.A.; Writing—Review and Editing, S.L.d.A. and M.A.M.; Supervision, M.A.M.; Project Administration, M.A.M.; Funding Acquisition, M.A.M.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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