

Improving the adhesion strength of polymers: effect of surface treatments

Hamdi, Marouen; Saleh, Mohamed Nasr; Poulis, Johannes A.

DOI

[10.1080/01694243.2020.1732750](https://doi.org/10.1080/01694243.2020.1732750)

Publication date

2020

Document Version

Final published version

Published in

Journal of Adhesion Science and Technology

Citation (APA)

Hamdi, M., Saleh, M. N., & Poulis, J. A. (2020). Improving the adhesion strength of polymers: effect of surface treatments. *Journal of Adhesion Science and Technology*, 34(17), 1853-1870. <https://doi.org/10.1080/01694243.2020.1732750>

Important note

To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

Green Open Access added to TU Delft Institutional Repository

'You share, we take care!' – Taverne project

<https://www.openaccess.nl/en/you-share-we-take-care>

Otherwise as indicated in the copyright section: the publisher is the copyright holder of this work and the author uses the Dutch legislation to make this work public.



Improving the adhesion strength of polymers: effect of surface treatments

Marouen Hamdi, Mohamed Nasr Saleh & Johannes A. Poulis

To cite this article: Marouen Hamdi, Mohamed Nasr Saleh & Johannes A. Poulis (2020): Improving the adhesion strength of polymers: effect of surface treatments, Journal of Adhesion Science and Technology, DOI: [10.1080/01694243.2020.1732750](https://doi.org/10.1080/01694243.2020.1732750)

To link to this article: <https://doi.org/10.1080/01694243.2020.1732750>



Published online: 12 Mar 2020.



Submit your article to this journal [↗](#)



Article views: 5



View related articles [↗](#)



View Crossmark data [↗](#)



Improving the adhesion strength of polymers: effect of surface treatments

Marouen Hamdi , Mohamed Nasr Saleh  and Johannes A. Poulis 

Faculty of Aerospace Engineering, Department of Aerospace Structures and Materials, Group of Structural Integrity and Composites, Delft University of Technology, Delft, The Netherlands

ABSTRACT

To improve their adhesion strength, polymeric surfaces are usually modified through different treatments. This study investigates the effect of mechanical, chemical, and energetic treatments on the bonding strength of ethylene propylene diene methylene (EPDM), polyvinyl chloride (PVC), and acrylonitrile butadiene styrene (ABS) materials. Three adhesives based on different chemical compositions, namely silicone, polyurethane, and modified-silane (MS) polymer, were considered. Results show that the effect of the applied treatments on the adhesion strength of EPDM surfaces is insignificant. Only a slight improvement is obtained in the case of polyurethane-based adhesive, while the failure modes remained adhesive. As for PVC, most treatments were effective in the case of the silicone-based adhesive, especially grit blasting, primer, and UV/ozone treatments. Only UV/ozone treatment improved the adhesion strength and altered the failure mechanisms of this material when polyurethane and MS-based adhesives are used. The adhesion of ABS increased and the failure modes changed from adhesive to cohesive for most treatments. Particularly, a significant improvement is obtained when primer coating and UV/ozone radiation are applied. This comparative study paves the way for the design of polymeric joints with highly enhanced adhesion performance.

ARTICLE HISTORY

Received 4 December 2019
Revised 11 February 2020
Accepted 12 February 2020

KEYWORDS

Surface treatment; adhesion strength; EPDM; PVC; ABS

1. Introduction

Polymers are known for their low surface energy and adhesion strength compared to other materials like metals. This is mainly due to their weak boundary layers caused by (1) impurities arising during the polymerization process, (2) low molecular weight tails at the surface, (3) additives such as antioxidants and slip agents, (4) external processing aids like mold release agents and (5) post-fabrication contaminants [1,2]. Therefore, different treatments are often applied to polymeric surfaces to improve their adhesion performance [3]. They can be categorized into mechanical treatments affecting mainly the surface topography (e.g. grit blasting, peel ply), chemical treatments involving

CONTACT Marouen Hamdi  m.hamdi@tudelft.nl  Faculty of Aerospace Engineering, Department of Aerospace Structures and Materials, Group of Structural Integrity and Composites, Delft University of Technology, Delft, The Netherlands

chemical substances (e.g. solvent cleaning, primers, ultrasonic cleaning), and energetic treatments targeting mainly the surface free energy (e.g. plasma, corona discharge, flame, UV/ozone) [2]. Moreover, they can be classified into passive treatments that only clean and remove the weakly bonded layers of the surface without changing its chemistry (e.g. solvent cleaning, mechanical abrasion), and active treatments that alter the surface chemistry (e.g. plasma, primer coating) [2].

The mechanical treatments consist mainly in abrasive techniques to remove weak surface layers and increase the contact area with the adhesive [4]. The adhesion theory associated the most with these treatments is the *mechanical theory* where the adhesive and the adherends are mechanically interlocked [2]. Higher surface roughness usually leads also to higher contact area and an increased number of molecular interactions between the adherent's surface and the adhesive. Some of the most commonly-used surface abrasion techniques are sand papering, grit blasting, and Scotch-Brite abrasion. Previous studies found that grit blasting is effective in improving the adhesion strength of glass reinforced polymer (GRP) [5] and polyetheretherketone (PEEK) [6]. Cleaning is generally required before and after mechanical treatments to remove the abrasion-induced debris from the surface.

As for chemical treatments, the adhesion theory that is more linked to this category is the *chemical bonding theory*, in which covalent chemical bonds are promoted across the interface [2]. This mechanism depends on the presence of mutually reactive functional groups, such as hydroxyl and carboxyl, in the adhesive and the adherends. The simplest chemical treatment is surface cleaning which removes contaminants such as process oils, dirt, waxes, mold release agents, and plasticizers [4]. Effective cleaning solvents include methyl ethyl ketone (MEK), acetone, and methanol. The chemical resistance of the polymer should be considered to prevent its degradation [4]. The most widely-used chemical treatments are primers and adhesion promoters. These multifunctional chemicals provide a "molecular bridge" between the adhesive and the substrate by adding a new bi-functional layer at the interface [2,7]. Primers usually have lower viscosity than adhesives, which allows them to fill in porous and rough surfaces. They are applied only on the substrate whereas adhesion promoters can be either used on the substrate or incorporated in the adhesive formulation [2]. Care should be taken when primers and adhesion promoters are applied to the substrate. They should have low thickness to reduce the risk of becoming the weakest part of the joint [2].

The main objective of energetic treatments is to remove organic contaminants, trigger oxidation processes, and increase the polarity and wettability of polymeric surfaces [4]. Although these treatments may change the polymer topography by removing weak cohesive layers [8], they still may have much less effect on the surface features compared to mechanical treatments. For instance, Oosterom et al. found that UV/ozone, corona discharge, and low-pressure plasma treatments did not significantly change the roughness of ultra-high-molecular-weight polyethylene (UHMWPE) surfaces [9]. One of the major energetic treatments applied to polymers is UV/ozone radiation. Previous studies showed that this treatment significantly improves the adhesion strength of several polymers [1,8]. Another example is (atmospheric) plasma treatment which is extensively used in a wide range of industrial sectors. Plasma is produced by exciting a gas with electrical energy to make it highly reactive [10]. This technique is highly

effective to etch, cross-link, and activate polymeric surfaces [11]. Three reactions may occur between the gas plasma and the treated surface: (1) the reactions between the surface species or between the gas species and the surface chemical groups (2) the plasma-induced polymerization where the plasma gas acts as a monomer forming a thin surface layer, and (3) the creation of volatile surface products by removing surface material by chemical reactions and physical etching [10]. There are two major plasma techniques, namely, low-pressure (vacuum) plasma and atmospheric plasma. The latter is more common thanks to its relatively low cost and easy integration in production lines [10,12,13]. Previous studies found that atmospheric plasma treatment improved the adhesion strength of polyethylene (PE), polyethylene terephthalate (PET), polyamide (PA), polyvinylidene fluoride (PVDF), polypropylene (PP), and high-density polyethylene (HDPE) [10,13,14]. However, the effectiveness of this treatment is still dependent on the properties of the treated materials and several processing parameters such as the plasma gas, treatment speed, and nozzle-surface distance [11,14]. For instance, Hegemann and coworkers found that argon plasma treatment promoted the chain scission and decreased the hardness of a propylene foil while helium plasma treatment promoted its crosslinking and increased its hardness [11].

In most of the previous studies, the impact of each surface treatment on the adhesion strength of polymeric systems was investigated separately. However, a comprehensive analysis comparing a wide range of treatments should be conducted to gain a better insight. In this study, a campaign of commonly-used mechanical, chemical, and physical treatments is performed on three types of polymers, namely flexible ethylene propylene diene methylene (EPDM) rubber, flexible polyvinyl chloride (PVC), and hard acrylonitrile butadiene styrene (ABS). The impact of these treatments on their adhesion performance is investigated. Besides, three types of adhesives based on different chemical compositions, namely silicone, polyurethane, and silane-modified, were considered. The effectiveness of the applied treatments for each material and adhesive is discussed. This study opens avenues for the design of adhesive bonds with enhanced adhesion performance and durability.

II. Experimental

1. Model systems

Three model systems were examined in this study, namely flexible EPDM, flexible PVC, and hard ABS, with thickness values of 1.1 mm, 1.2 mm, and 4 mm, respectively. They were provided by Vink Kunststoffen (Netherlands), Firestone Building Products (USA), and Royal Roofing Materials (Netherlands) companies, respectively. Flexible EPDM and PVC foils are commonly used as roofing materials. Hard ABS is an impact-modified styrenic polymer which usually contains light stabilizers and antioxidants to reduce its susceptibility to ultraviolet (UV) radiation [15].

2. Surface treatment

Table 1 summarizes the surface treatments applied in this study. They are classified into mechanical, chemical, and energetic treatments depending on how they change

Table 1. Applied surface treatments.

Treatment	Type	Parameter	Layout	Activity
Grit blasting	Mechanical	Pressure: 2, 4, 6 bar	GB2, GB4, GB6	Passive
Scotch-Brite	Mechanical	with / without	SB	Passive
Solvent cleaning	Chemical	with / without	C	Passive
Primer	Chemical	with / without	PR	Active
UV/Ozone	Energetic	Time: 3, 10 min	UV3, UV10	Active
Atmospheric plasma	Energetic	with / without	PL	Active

the materials surface. Moreover, when the material chemical composition is changed, the treatment is considered ‘active’ [2]. The main experimental parameters and abbreviations of the treatments are presented in the table and will be considered throughout the paper. The combined treatments are beyond the scope of this study. Untreated samples are labelled as “NoT” in the paper. More details about each of these treatments are presented below.

a. Mechanical treatments

The mechanical treatments applied in this analysis are twofold: grit blasting and Scotch-Brite surface abrasion. These treatments affect mainly the surface roughness of the model systems. The first treatment was applied using Pulsar III grit blasting cabinet manufactured by Clemco Company (Missouri, USA). The chamber is equipped with a self-contained, sealed glove box for powder recycling. Corundum (Al_2O_3) grit particles (Leering, The Netherlands) with a grain size range of 0.59–0.84 mm were used. The samples were treated for approximately five minutes under pressures of 2 bar (GB2), 4 bar (GB4), and 6 bar (GB6). The blasting angle was 90° and the distance between the samples and the cabinet nozzle is about 5 cm. At least three samples were considered in each treatment condition for more representative results. The samples were cleaned before and after the treatment to remove debris and grit particles. The abrasive treatment was performed using a Scotch-Brite paper supplied by 3M (Minnesota, USA). The samples were cleaned, scraped with a sharp blade to remove upper weak layers, and then cleaned again to eliminate debris.

b. Chemical treatments

The first chemical treatment consists in simply cleaning the samples with methanol according to ASTM D2093 standard [16]. The samples were cleaned at room temperature and left in a clean room to dry for at least 20 min. The second treatment is primer coating. The primer appropriate for each adhesive was selected based on the recommendations of the manufacturers. The primer was carefully applied on the surface to maintain a low thickness and avoid becoming the weakest part of the joint [2].

c. Energetic treatments

All the samples were cleaned before applying the energetic treatments to remove any surface debris. The first energetic treatment consists in the exposure to UV/ozone

Table 2. Properties of the applied adhesives.

	Adhesive 1 (Ad-Si)	Adhesive 2 (Ad-PU)	Adhesive 3 (Ad-MS)
Chemical base	Silicone	Polyurethane	Silane-modified polymer
Components	Two-components	One-component	One-component
Curing process	Polycondensation	Moisture curing	Moisture curing
Tensile strength (ISO 37) (MPa)	2	6	3
Elongation at break (ISO 37) (%)	250	500	250
Shore-A-hardness (ISO 868)	45	55	55
Application temperature (°C)	5 to 40	5 to 40	5 to 40
In-service temperature (°C)	−40 to 150	−50 to 90	−40 to 100

radiation. The samples were isolated in an in-house built apparatus and exposed to UV light in combination with ozone gas for 3 (UV3) and 10 (UV10) minutes at room temperature. Only ambient air was used and no oxygen concentrator, fan, or air pump was employed. The box is equipped with three ozone generating UV disinfection lamps with a power of 35 watt each, emitting UV light with wavelengths of 185.49 and 253.742 nm. The distance between the samples and the UV lamps is about 35 mm.

The second energetic treatment is atmospheric pressure plasma treatment. It was applied using a plasma jet system manufactured by Tigres GmbH (Marschacht, Germany), equipped with three nozzles, for a wider application, and a computer-controlled displacement table. The process was operated with air, at an input pressure of 4 bar, a flow rate of 51 lpm, and a power of 600 W per nozzle. While appropriate treatment leads only to outer chain scission, higher treatment intensity or longer duration causes physical etching, which leads to inner chain scission and polymer degradation [11]. To minimize these plasma-induced degradation and ageing effects, the treatment speed and the sample-nozzle distance were carefully adjusted. Preliminary tests showed that no significant physical etching is observed at a distance of 30 mm and a speed of 25 mm/s. The samples were bonded immediately after the plasma treatment to minimize the ageing effect.

3. Surface roughness measurements

The effect of grit blasting on the surface roughness of the model systems was determined. Measurements were conducted using a high-resolution KEYENCE VR-5200 LED scanning confocal microscope. Root-mean-square roughness (Rq) is frequently used for fine surfaces in scientific measurements because it is more sensitive to peaks and valleys than arithmetic average roughness (Ra) [17,18]. Therefore, this parameter was employed for accuracy purposes. To obtain more representative results, five roughness measurements, each over an area of 1 mm², were conducted for each treatment condition. This instrument was also employed to show the topography of the bonded surfaces after adhesion tests and highlight the effect of the surface treatment on the failure mechanisms.

4. Adhesion test

To conduct more comprehensive tests, three adhesives with different chemical compositions were used in this analysis. Table 2 highlights the major mechanical and

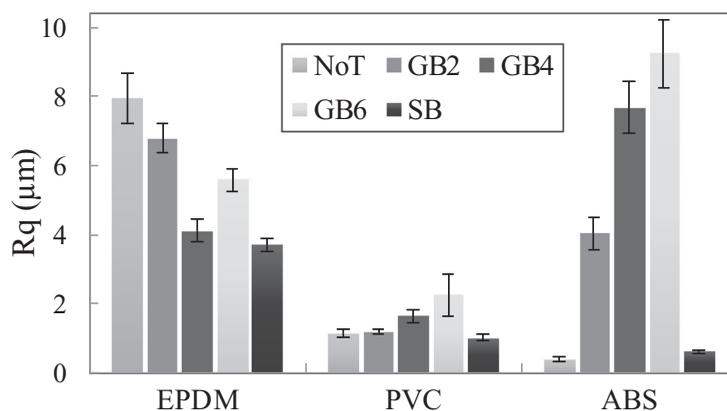


Figure 1. Effect of the mechanical treatments on the surface roughness of the model systems.

chemical properties of the adhesives as indicated by the manufacturers. They are based on silicone (Ad-Si), polyurethane (Ad-PU), and silane-modified polymer (Ad-MS). Only Ad-Si is a two-components adhesive and cures through a polycondensation process. The other two adhesives are one-component and cure using moisture. A mixture of adhesives can also be considered in future studies [19].

To maintain a uniform and consistent thickness across the bond-line without affecting the performance of the bonded joints, the adhesives were first mixed with 1 wt.% of glass beads provided by Sigma Aldrich (St. Louis, USA) with a diameter range of 212–300 μm [9,20–22]. Then, the samples were bonded using a curing schedule of approximately one week at room temperature. To determine the adhesion strength of flexible EPDM and PVC samples, T-peel tests were conducted according to ASTM D1876 standard at a crosshead speed of 254 mm/min [23]. Similarly, lap-shear tests were performed on rigid ABS samples according to ASTM D3163 standard at a crosshead speed of 1.27 mm/min [24]. These tests were executed using a Zwick Roell tensile test instrument (Ulm, Germany) coupled with a 10 kN load cell.

III. Results and discussion

1. Mechanical treatments

The mechanical treatments affect mainly the surface morphology of the samples. Figure 1 shows the variation of Rq roughness with increasing grit blasting pressure. It is observed that the roughness of untreated EPDM surface is initially higher than that of untreated PVC and ABS. At lower pressures of 2 and 4 bar, the blasting process contributes to the polishing and smoothing of EPDM. At a sufficiently high pressure of 6 bar, EPDM roughness increases from 4.1 to 5.6 μm reflecting a roughening mechanism. Unlike EPDM, higher grit blasting pressure lead to a slight and significant increase in the roughness of PVC and ABS surfaces, respectively. The abrasion of the samples using Scotch Brite decreased the roughness of EPDM but did not significantly affect that of PVC and ABS.

The adhesion mechanism which is more related to mechanical surface treatments is the mechanical interlocking [2]. However, these treatments might also affect other

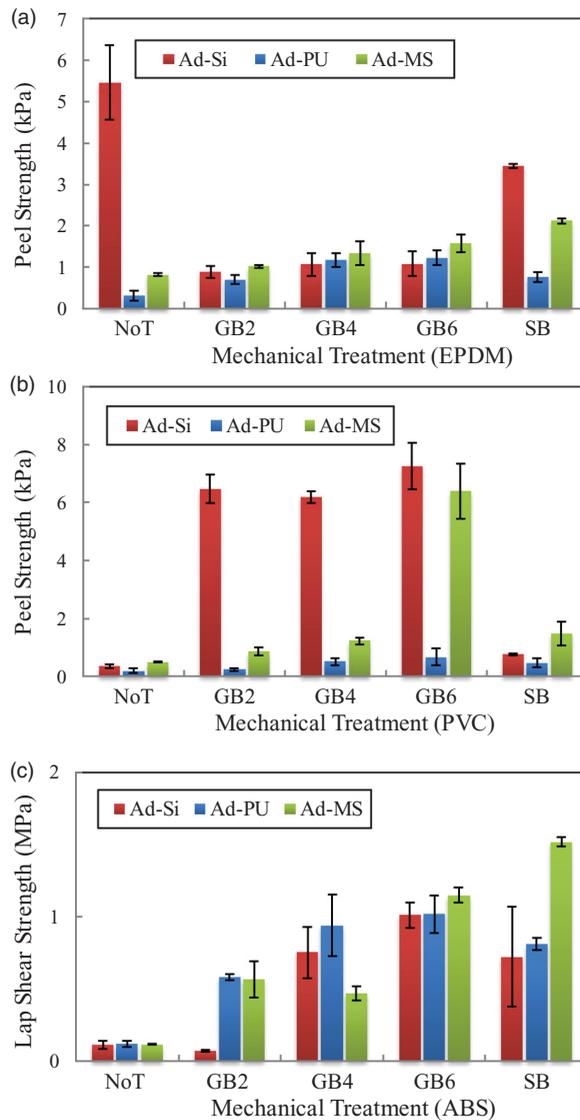


Figure 2. Effect of the mechanical treatments on the adhesion strength of (a) EPDM, (b) PVC, and (c) ABS.

adhesion mechanisms by the exposure of a fresh layer of the samples to the adhesive, thus changing the adhesive-substrate chemical/physical bonding. The effect of the mechanical treatments on the adhesion strength of the examined systems is presented in Figure 2. Figure 2(a) shows that the silicone-based adhesive (Ad-Si) is initially much more effective for the adhesive bonding of EPDM than the polyurethane-based (Ad-PU) and silane modified-based (Ad-MS) adhesives. After grit blasting treatment, a significant decrease is observed in Ad-Si results. A similar observation is made for the Scotch-Brite (SB) treatment. This can be attributed to the decrease in EPDM surface roughness after treatment as discussed previously in Figure 1. The results obtained using Ad-PU and Ad-MS adhesives improved slightly after the mechanical treatments

despite the decrease in EPDM roughness. This might be caused by the enhanced chemical bonding with the newly- exposed surfaces, which may counteracted the effect of EPDM smoothing. [Figure 2\(b\)](#) shows the results of PVC material. Similar adhesion strength was initially obtained using the three adhesives. The grit blasting treatment significantly improved Ad-Si results even at low pressures (2 bar) where the adhesion strength increased from 0.34 to 6.47 kPa. The effect of this treatment is insignificant for Ad-PU adhesive, and significant only at high pressure (6 bar) when R_q is sufficiently high for Ad-MS adhesive. The effect of SB treatment on PVC adhesion strength is insignificant compared to GB treatment. As for ABS material, [Figure 2\(c\)](#) shows that its adhesion strength is generally increased with higher grit blasting pressure. This is explained by the increase in ABS roughness after grit blasting treatment ([Figure 1](#)). SB treatment was also successful in improving the adhesion performance of this material.

The overall results presented in [Figure 2](#) show that the bond strength is highly dependent on the nature of the applied adhesive. As discussed earlier, the mechanical treatment removes the upper weak layers, and thus improves the bonding mechanisms with the adhesive. The effectiveness of each adhesive depends on its response to these mechanisms. Moreover, the variation of the surface roughness may affect the bonding strength depending on the applied adhesive. For instance, in the case of Ad-PU adhesive, insignificant changes were obtained for EPDM and PVC after surface treatment ([Figure 2\(a,b\)](#)). [Figure 1](#) shows that the surface roughness of these two materials slightly changed after treatment. However, the bonding strength of ABS increased significantly after surface treatment ([Figure 2\(c\)](#)). [Figure 1](#) indicates that the surface roughness of this material increased considerably with higher grit blasting treatment. This suggests that Ad-PU adhesive is more sensitive to the change in the surface roughness. However, a significant change is observed in Ad-Si results even when R_q did not change (e.g. GB2 in PVC). This suggests that this adhesive is more related to the chemical/physical bonding with the newly-created surface.

2. Chemical treatments

The adhesion mechanism associated the most with these treatments is the *chemical reaction theory*, where the adhesion strength is mainly caused by the chemical bonds [2]. The effect of these treatments on the adhesion of the model systems is presented in [Figure 3](#). The figure shows that the impact of solvent cleaning on the adhesion of the samples is insignificant for all the adhesives.

The effect of the primers depends on the chemical structures of the treated material and the applied adhesive. An improvement in the adhesion strength indicates that the primer is successful in enhancing the adhesive-substrate chemical bonding. In the case of Ad-Si adhesive, the primer decreased the adhesion strength of EPDM ([Figure 3\(a\)](#)), but improved that of PVC ([Figure 3\(b\)](#)) and ABS ([Figure 3\(c\)](#)). These results suggest that this adhesive is more sensitive to the chemical adhesion mechanism compared to mechanical treatments presented previously. As for Ad-PU and Ad-MS adhesives, the effect of the primers is insignificant in the case of EPDM and PVC but highly significant for ABS. The results of the mechanical and chemical treatments show that ABS adhesion strength was improved considerably with grit blasting and primer treatments.

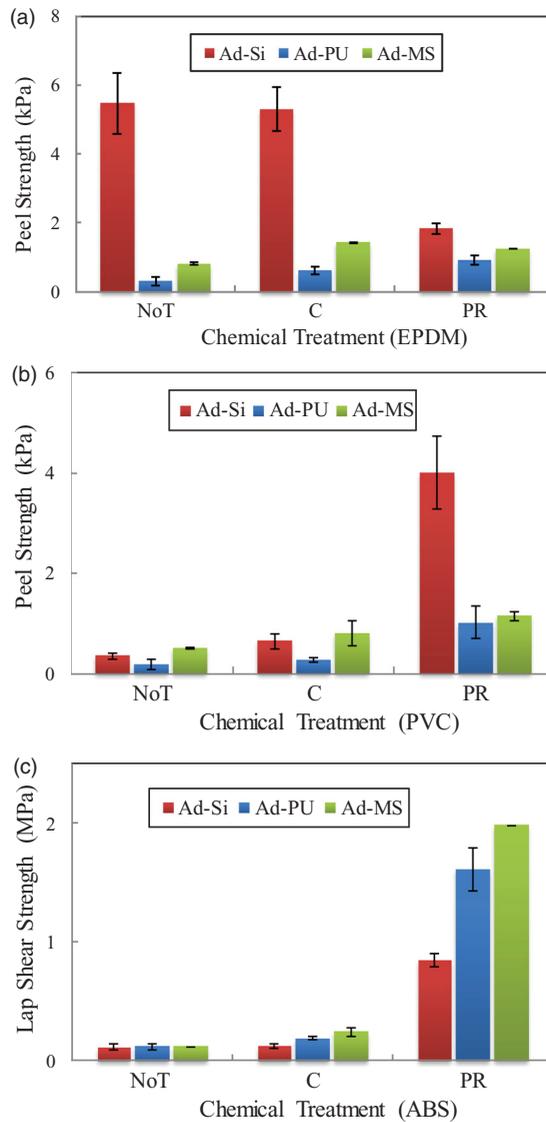


Figure 3. Effect of the chemical treatments on the adhesion strength of (a) EPDM, (b) PVC, and (c) ABS.

A combination of these two treatments is expected to give even stronger ABS bonding as was shown in previous investigations [25,26].

3. Energetic treatments

The impact of the energetic treatments on the adhesion strength of the model systems is summarized in Figure 4. Particular attention should be given to the duration of UV/ozone treatment. Long durations promote chain scission and lead to the production of weakly bonded fragments with low molecular weight (M_w) [8,9]. For instance, a previous study showed that the optimal treatment duration for PE and PEEK polymers

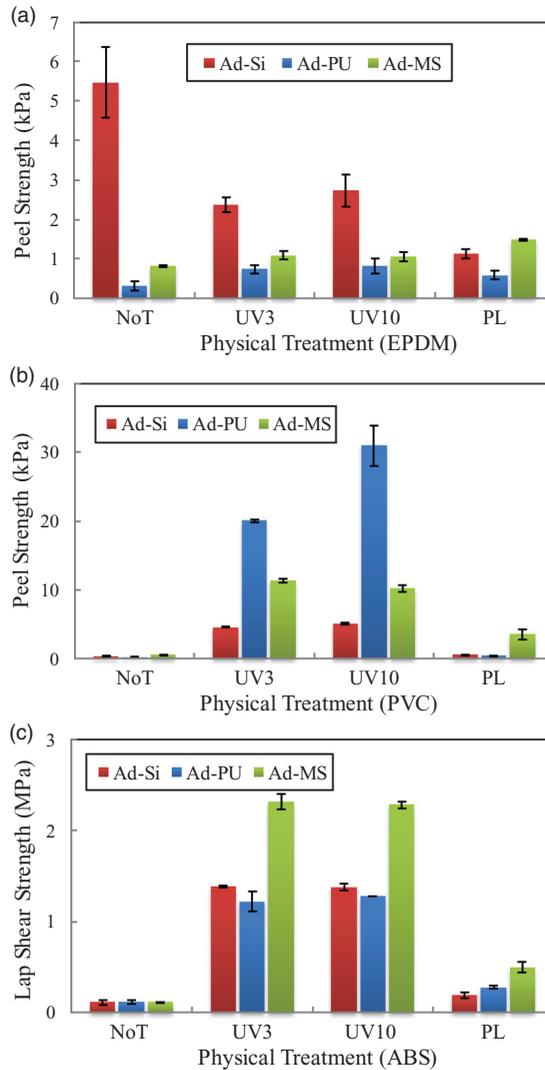


Figure 4. Effect of the energetic treatments on the adhesion strength of (a) EPDM, (b) PVC, and (c) ABS.

is as low as one minute [8]. Longer UV/ozone exposure decreased the PEEK adhesion strength and did not significantly improve that of PE. First, tests were conducted to determine the optimal duration of UV/ozone treatment at room temperature. Preliminary results showed that a maximum duration of 10 min should be considered to avoid the degradation of the studied materials.

Figure 4 shows that, for almost all the materials and adhesives, 10 min of UV/ozone treatment (UV10) gave similar adhesion results compared to 3 min (UV3) of treatment. This indicates that a UV radiation of 3 min is sufficient to activate the surfaces. Figure 4(a) shows that UV/ozone treatment adversely affected the adhesion strength of EPDM in the case of Ad-Si, without a significant effect on the two other adhesives. Figure 4(b,c) show that the treatment considerably improved the adhesion strength of PVC

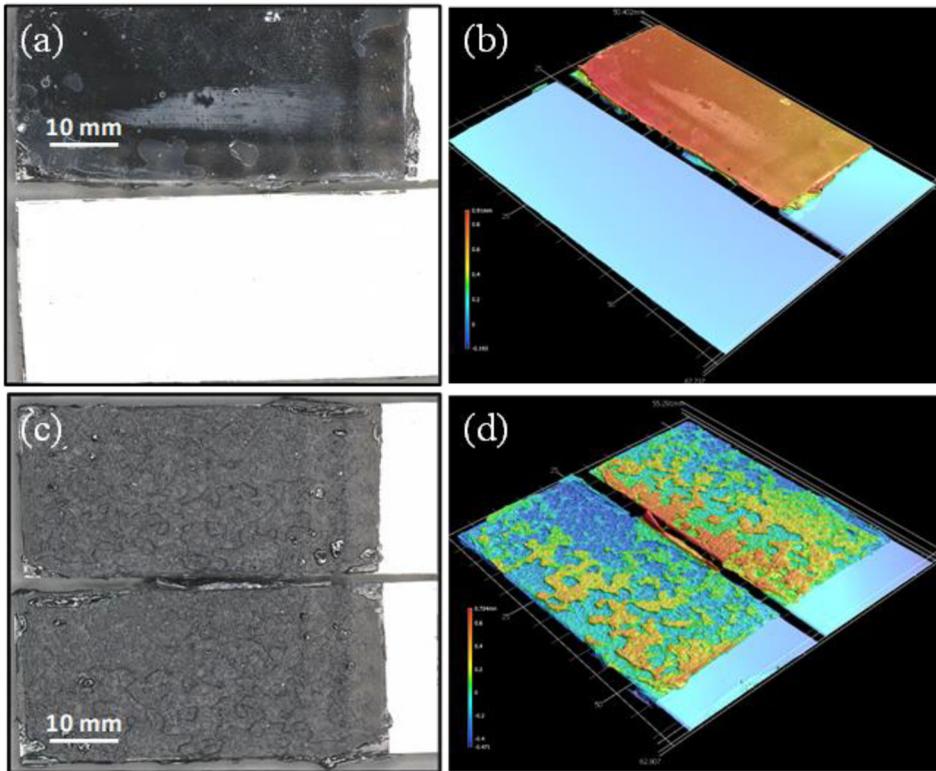


Figure 5. Optical and 3D images of ABS joints (a,b) neat and (c,d) UV-treated for 10 min.

and ABS for the three applied adhesives. Furthermore, UV/ozone treatment changed the failure mechanisms of the three applied adhesives on PVC and ABS surfaces from adhesive (failure at the interface) to cohesive (failure within the adhesive) mechanisms. For instance, [Figure 5](#) shows optical and 3D images of failed ABS joints before and after UV/ozone treatment. The figure clearly highlights the adhesive failure of neat ABS joints and the cohesive failure of those treated using UV/ozone for 10 min.

To have a deeper understanding of the mechanisms induced by UV/ozone treatment, the changes of the chemical and morphological properties of the treated surfaces were previously investigated [27]. The chemical changes of polymeric materials can be effectively detected using Fourier Transform Infrared Spectroscopy coupled with Attenuated Total Reflection accessory (FTIR-ATR) [28,29]. [Figure 6](#) shows the FTIR-ATR spectra of neat and UV-treated surfaces [27]. The figure shows that UV/ozone treatment caused insignificant changes in the chemical structures of the studied materials. The changes in EPDM spectra are insignificant which can be explained by either its chemical stability or the effectiveness of the added fillers such as light stabilizers and carbon black. Likewise, PVC spectra changed slightly with an insignificant increase at the absorbance band of $3100\text{--}3500\text{ cm}^{-1}$, which corresponds to the stretching of the hydroxyl region ($-\text{OH}$) [30,31]. As for ABS spectra, only the peaks within the absorbance bands of $2800\text{--}3100\text{ cm}^{-1}$ were slightly attenuated. These bands are associated

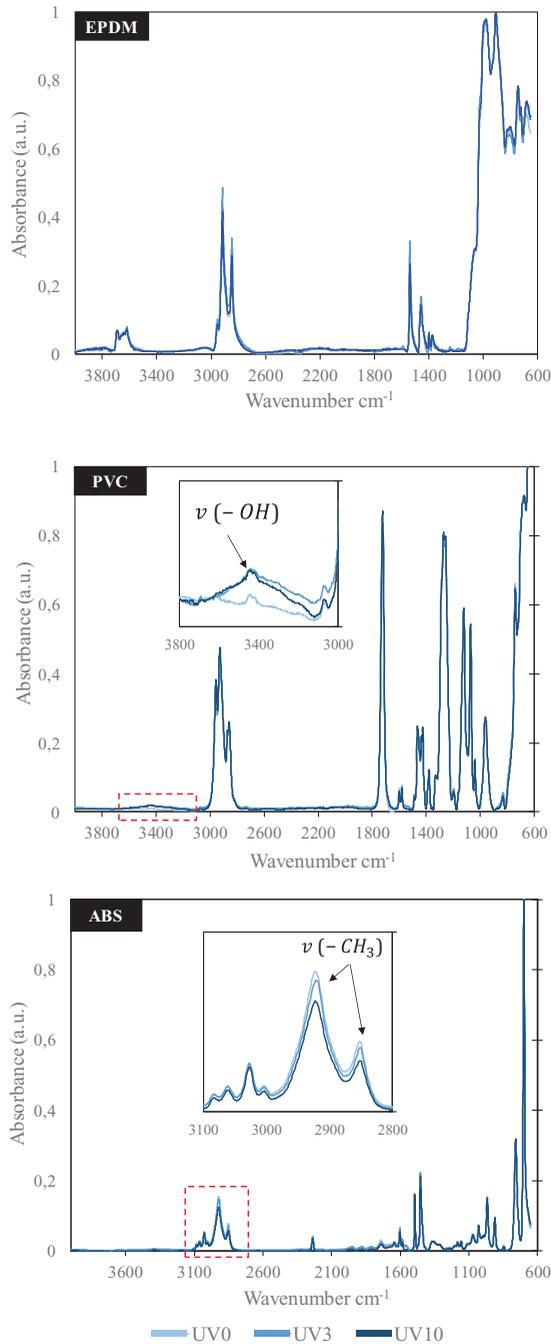


Figure 6. FTIR-ATR spectra of untreated and UV-treated samples for 3 and 10 min. ν = stretching vibrational mode [27].

with the stretching mode of $C-H$ groups [30,31]. A similar effect of UV treatment on the chemical bonds of carbon/epoxy composite was previously found [32].

In addition, the effect of UV/ozone treatment on the surface morphology of the model systems was previously investigated by performing Scanning Electron

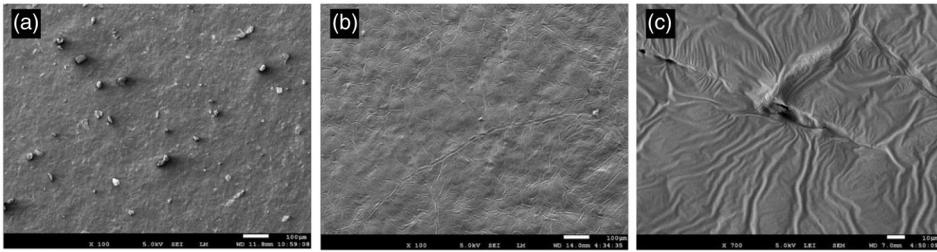


Figure 7. SEM micrographs of PVC surfaces (a) untreated (b,c) UV-treated for 10 min [27].

Microscopy (SEM) observations [27]. **Figure 7** shows the features on PVC surfaces before and after 10 min of UV/ozone treatment. First, impurities are observed on neat PVC surfaces (**Figure 7(a)**). The treatment removed these impurities and made the surface cleaner (**Figure 7(b)**). Also, the morphology of the treated surfaces is significantly changed by the creation of many small wrinkles (**Figure 7(c)**). Some wrinkles were developed into microholes, indicating the violent degradation of one of the material inorganic additives (**Figure 7(c)**) [33]. Other SEM observations showed that these microholes increase in size and number with higher durations of UV/ozone treatment. Similarly, **Figure 8** shows the creation of micropores with a diameter of approximately $0.1\ \mu\text{m}$ on ABS surface after UV/ozone treatment. Other SEM observations not shown in this paper indicated that the size of the pores increases with higher treatment duration. These UV-induced morphological features explain the improvement of the adhesion strength of PVC and ABS surfaces shown in **Figure 4**. The adhesive fills the microholes and microcracks created on PVC surface and the microporous structure of ABS surface, which significantly increases the contact area and enhances mechanical interlocking [34,35]. No similar morphological features were observed on the treated EPDM surfaces, which explains the ineffectiveness of UV/Ozone treatment in improving its adhesion strength [27].

The second energetic treatment is the plasma treatment. Similar to previous treatments, the efficiency of this treatment depends on the chemical structure of both the material and the adhesive. Previous studies showed that plasticizers with small chains are more susceptible to be leached out from PVC surface, after oxygen and argon plasma treatment, compared to more stable long-chain plasticizers [36].

Figure 4 shows that this treatment is less effective than UV/ozone treatment in improving the adhesion strength of the model systems, especially PVC and ABS. During the treatment, two competing processes occur on the polymer surface, namely chain scission and crosslinking [11]. Therefore, the effect of plasma treatment on the adhesion strength depends on the dominant process. The results found in this study suggest that plasma treatment is more associated with the chain scission phenomenon. Also, the effectiveness of plasma treatment can be hindered by some post-treatment phenomena. During the post-treatment ageing, the surface energy of the polymer is decreased until a thermodynamically stable state is reached. This process is highly affected by external factors such as the contaminants of the atmosphere [11]. As a result, the functionalities of the newly-treated surfaces, and thus their wettability, are reduced [14]. Therefore, the limited effect of plasma treatment in improving the

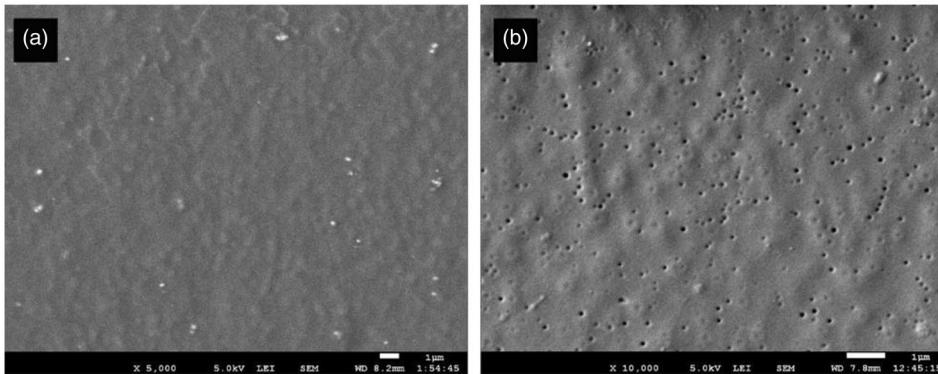


Figure 8. SEM micrographs of ABS surfaces (a) untreated (b) UV-treated for 10 min [27].

adhesion strength might be caused by the contamination of the treated surfaces during the ageing effect.

4. Summary

The role of each category of treatments was discussed separately. However, a better understanding is gained by comparing the results of all the treatments. Table 3 summarizes the impact of the surface treatments on the adhesion strength and the failure mechanisms of the studied materials. For each material, the corresponding color indicates the increasing factor of the adhesion strength for the applied adhesive. The factors correspond to *diminishing* (<0.5), *insignificant* (0.5–2), *slight* (2–5), *good* (5–10), *significant* (10–20), and *highly significant* (20<) effect on the adhesion strength. Also, the failure mechanism is described as *adhesive* (A), *cohesive* (C), *mixed* (M), or *broken adherents* (B) for each material-adhesive-treatment combination.

The upper part of Table 3 corresponds to EPDM samples. When Ad-Si adhesive is applied, most treatments have *diminishing* effect and the failure mode changed from *mixed* (M) to *adhesive* (A). In the case of Ad-PU and Ad-MS adhesives, mostly *insignificant* and *slight* effects were obtained, respectively and the failure modes remained *adhesive* (A). These results show the difficulty of improving the adhesion strength of EPDM through surface treatment as previously discussed [26]. They also suggest that a combination of grit blasting and UV/ozone (or primer) treatment may provide good results.

The middle part of Table 3 summarizes PVC results. The applied treatments are most effective in the case of Ad-Si adhesive. The effects of the treatments are *significant* (e.g. grit blasting and primer, and UV/ozone), and even *highly significant* (factor higher than 20) in the case of GB6 grit blasting. This was not the case when the two other adhesives Ad-PU and Ad-MS were applied: only UV treatment has a *highly significant* effect and changed the failure mode from *adhesive* (A) to *mixed* (M) or even *cohesive* (C). Most of the other treatments are *insignificant* or *slight* without having an effect on the failure modes. Therefore, a combination of UV/ozone and high-pressure grit blasting treatments will most likely give even better adhesion results for PVC [9].

Table 3. Summary of the effect of the conducted treatments on EPDM (top), PVC (middle), and ABS (bottom).

	NoT	GB2	GB4	GB6	SB	C	PR	UV	PL
Ad-Si	M	A	A	A	M	M	M	M	A
Ad-PU	A	A	A	A	A	A	A	A	A
Ad-MS	A	A	A	A	M	A	A	A	A

	NoT	GB2	GB4	GB6	SB	C	PR	UV	PL
Ad-Si	A	M	C	C	A	A	M	C	A
Ad-PU	A	A	A	A	A	A	A	M	A
Ad-MS	A	A	A	M	A	A	A	C	A

	NoT	GB2	GB4	GB6	SB	C	PR	UV	PL
Ad-Si	A	A	M	M	A	A	M	C	A
Ad-PU	A	A	A	A	A	A	B	A	A
Ad-MS	A	A	A	A	M	A	C	C	A

< 0.5	0.5-	2-5	5-10	10-	20 <
-------	------	-----	------	-----	------

A: adhesive C: cohesive M: mixed B: broken

Finally, the lower part of Table 3 summarizes ABS results. Most treatments improved the adhesion strength of this material. The mechanical treatments had generally *good* effect, and sometimes *significant* in the case of Ad-MS adhesive. The treatments that were most effective are the primer and the UV/ozone treatments. Similar to almost all the previous cases, cleaning and plasma treatments were not as effective as the other treatments. Therefore, a combination of Scotch Brite abrasion or high-pressure grit blasting with UV/ozone treatment is expected to highly increase the adhesion strength of ABS materials.

IV. Conclusion

This study investigates the effect of mechanical, chemical, and physical surface treatments on the adhesion strength and failure mode of EPDM, PVC, and ABS materials. To make this study more comprehensive, three adhesives with different chemical bases, namely silicone, polyurethane, and silane- modified (MS) polymer were applied. The effect of each treatment is strongly dependent on the investigated material and the applied adhesive. Results show that EPDM is the least responsive to the surface treatments. Only a slight improvement is obtained when the polyurethane-based adhesive is applied, and the failure modes remained adhesive. As for PVC, the treatments were mostly effective for the silicone-based adhesive where grit blasting, primer, and UV/ozone treatments had significant and in some cases highly significant effect. In the case of the two other adhesives, only UV/ozone treatment improved the adhesion strength

and the failure modes changed from adhesive to mixed or cohesive. Finally, the applied surface treatments were most effective on ABS for the three adhesives. Particularly, the primer and UV/ozone treatments had a considerable effect, and the failure modes became cohesive in some cases. This study provides insight on the appropriate adhesive and surface treatment that should be applied for the studied materials. It can be extended to other materials, combined surface treatments, and mixed adhesives in future research efforts. Moreover, the ranking of the applied treatments and adhesives can be quantified using statistical tools such as multidimensional scaling analysis, which unveils the most important relationships and inferences [37].

Acknowledgements

Special thanks are also given to Frans Oostrum from the Delft Aerospace Structures and Materials Laboratory (DASML) at the Faculty of Aerospace Engineering of Delft University of Technology for his insight and assistance.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The authors would like to acknowledge the generous financial support of the project partners and the Rijksdienst voor ondernemend Nederland (the Netherlands Enterprise Agency).

ORCID

Marouen Hamdi  <http://orcid.org/0000-0001-8615-9896>

Mohamed Nasr Saleh  <http://orcid.org/0000-0002-0725-5319>

Johannes A. Poulis  <http://orcid.org/0000-0003-3041-5285>

References

- [1] Brewis DM, Briggs D. Adhesion to polyethylene and polypropylene. *Polymer* (Guildf. 1981;22(1):7–16.
- [2] Petrie EM. Handbook of adhesives and sealants. 2nd ed. New York, United States: The McGraw-Hill Companies, Inc., 2007.
- [3] Nagi SM, Omar N, Salem HN, et al. Effect of different surface treatment protocols on the shear bond strength of perforation repair materials to resin composite. *J Adhes Sci Technol*. 2020;34(4):417–426.
- [4] Ebnesajjad S. Material surface preparation techniques. In: Surface treatment of materials for adhesive bonding. New York, United States: William Andrew Publishing; 2014. p. 95–138.
- [5] Chamochin R, De Santayana MC, Abenojar J, et al. The effect of surface treatment on the behavior of toughened acrylic adhesive/GRP(epoxy) composite joints in. *J Adhes Sci Technol*. 2010;24(11–12):1903–1916.
- [6] Hamdan S, Evans JRG. The surface treatment and adhesive bonding of polyetheretherketone. Part I. Adhesive joint strength. *J Adhes Sci Technol*. 1987;1(1):281–289.

- [7] Wang X, Wang C, Zhang L, et al. Influence of priming time and primer's concentrations on bovine enamel bond strengths. *J Adhes Sci Technol*. 2013;27(23):2558–2570.
- [8] Mathieson I, Bradley RH. Improved adhesion to polymers by UV/ozone surface oxidation. *Int J Adhes Adhes*. 1996;16(1):29–31.
- [9] Oosterom R, Ahmed TJ, Poulis JA, et al. Adhesion performance of UHMWPE after different surface modification techniques. *Med Eng Phys*. 2006;28(4):323–330.
- [10] Ebnasajjad S. Plasma treatment of polymeric materials. In: *Surface treatment of materials for adhesive bonding*. New York, United States: William Andrew Publishing, 2014. pp. 227–269.
- [11] Hegemann D, Brunner H, Oehr C. Plasma treatment of polymers for surface and adhesion improvement. *Nucl Instruments Methods Phys Res Sect B Beam Interact Mater Atoms*. 2003;208(1–4):281–286.
- [12] Tendero C, Tixier C, Tristant P, et al. Atmospheric pressure plasmas: a review. *Spectrochim Acta Part B Spectrosc*. 2006;61(1):2–30.
- [13] Lommatzsch H, Pasedag U, Baalman D, et al. Atmospheric pressure plasma jet treatment of polyethylene surfaces for adhesion improvement. *Plasma Process Polym*. 2007;4(S1):S1041–S1045.
- [14] Noeske M, Degenhardt J, Strudthoff S, et al. Plasma jet treatment of five polymers at atmospheric pressure: surface modifications and the relevance for adhesion. *Int J Adhes Adhes*. 2004;24(2):171–177.
- [15] Santos RM, Botelho GL, Cramez C, et al. Outdoor and accelerated weathering of acrylonitrile-butadiene-styrene: a correlation study. *Polym Degrad Stab*. 2013;98(10):2111–2115.
- [16] ASTM International. *D2093-03(2017) Standard Practice for Preparation of Surfaces of Plastics Prior to Adhesive Bonding*. West Conshohocken, PA; ASTM International, 2017. doi: [10.1520/D2093-03R17](https://doi.org/10.1520/D2093-03R17)
- [17] Hamdi M, Puopolo M, Pham H, et al. Experimental and FEM analysis of scratch behavior on polypropylene thin films: Effect of film orientation and ethylene monomer content. *Tribol Int*. 2016;103:412–422.
- [18] Hamdi M, Zhang X, Sue H-J. Fundamental understanding on scratch behavior of polymeric laminates. *Wear*. 2017;380–381:203–216.
- [19] Jairaja R, Naik GN. Strengthening of the adhesive bond using a mixture of adhesives between dissimilar adherends in a single lap joint. *J Adhes Sci Technol*. 2020;34:579–598.
- [20] Kozowyk PRB, Poulis JA, Langejans GHJ. Laboratory strength testing of pine wood and birch bark adhesives: a first study of the material properties of pitch. *J Archaeol Sci Reports*. 2017;13:49–59.
- [21] Severijns C, de Freitas ST, Poulis JA. Susceptor-assisted induction curing behaviour of a two component epoxy paste adhesive for aerospace applications. *Int J Adhes Adhes*. 2017;75:155–164.
- [22] Kozowyk PRB, Langejans GHJ, Poulis JA. Lap shear and impact testing of ochre and beeswax in experimental middle stone age compound adhesives. *PLOS One*. 2016;11(3):e0150436.
- [23] ASTM International. *D1876-08(2015)e1 Standard Test Method for Peel Resistance of Adhesives (T-Peel Test)*. West Conshohocken, PA; ASTM International, 2015. doi: [10.1520/D1876-08R15E01](https://doi.org/10.1520/D1876-08R15E01)
- [24] ASTM International. *D3163-01(2014) Standard Test Method for Determining Strength of Adhesively Bonded Rigid Plastic Lap-Shear Joints in Shear by Tension Loading*. West Conshohocken, PA; ASTM International, 2014. doi: [10.1520/D3163-01R14](https://doi.org/10.1520/D3163-01R14)
- [25] Li Y, Li J, Huang M, et al. Effect of combined surface treatment on the adhesion performance of aluminium-lithium alloy. *J Adhes Sci Technol*. 2019;33(16):1821–1835.
- [26] Ebnasajjad S. Surface preparation of thermoplastics, thermosets, and elastomers. In: *Surface treatment of materials for adhesive bonding*. New York, United States: William Andrew Publishing; 2014. pp. 185–226.

- [27] Hamdi M, Poulis JA. Effect of UV/ozone treatment on the wettability and adhesion of polymeric systems. *J Adhes.* 2019;1–21.
- [28] Hamdi M. Fundamental understanding of scratch and mar behavior of polymers [Dr. Diss.]. Texas, United States: Texas AM Univ; 2016.
- [29] Hamdi M, Sue H-J. Effect of color, gloss, and surface texture perception on scratch and mar visibility in polymers. *Mater Des.* 2015;83:528–535.
- [30] Lambert BJ, Shurvell FH, Cooks RG. *Introduction to organic spectroscopy.* Macmillan, 1987.
- [31] Munajad A, Subroto C, Munajad, SA. et al. Fourier Transform Infrared (FTIR) spectroscopy analysis of transformer paper in mineral oil-paper composite insulation under accelerated thermal aging. *Energies.* 2018;11(2):364.
- [32] Kim JM, Kim JK, Lee DG. Ultraviolet surface treatment for adhesion strength improvement of carbon/epoxy composite. *J Adhes Sci Technol.* 2003;17(11):1523–1542.
- [33] Novis Y, De Meulemeester R, Chtaïb M, et al. XPS and SEM study of UV laser surface modification of polymers. *Brit Poly J.* 1989;21(2):147–153.
- [34] Venables JD. Adhesion and durability of metal-polymer bonds. *J Mater Sci.* 1984;19(8): 2431–2453.
- [35] Pastor-Blas MM, Sanchez-Adsuar MS, Martin-Martinez JM. Surface modification of synthetic vulcanized rubber. *J Adhes Sci Technol.* 1994;8(10):1093–1114.
- [36] Zhang X, Zhang C, Hankett JM, et al. Molecular surface structural changes of plasticized PVC materials after plasma treatment. *Langmuir.* 2013;29(12):4008–4018.
- [37] Hamdi M, Manica D, Sue H-J. A multidimensional scaling analysis of surface perceptual parameters on scratch and mar visibility resistance in polymers. *SAE Int J Mater Manuf.* 2017;10(2):94–106.