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New surface treatment technologies for the adhesive bonding of lightweight aluminum-polypropylene hybrid joints in semi-structural applications

D. Gallant, F. Boudreault and V. Savard

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Introduction

Due to its interesting bulk properties, recyclability, low cost and lightweight, polypropylene (PP) is one of the most interesting thermoplastic materials for the design of stiff aluminum-PP hybrid structures. However, the widespread use of PP (as polymer or in composites) within adhesively bonded lightweight hybrid automotive structures is still a challenge. This situation can be explained by the low surface free energy of PP, which makes it difficult to bond using most commercially available structural adhesives that provide durable and highly reliable aluminum-based joints (i.e. epoxy, urethane and methacrylate). From a chemical point of view, this inherent problem comes from the fact that PP, as many thermoplastic materials, is made of hydrophobic and saturated polymer chains. Hence, to make it suitable for adhesive bonding, the surface of PP requires a pretreatment which introduces appropriate chemical polar functionalities and other surface features beneficial to adhesion phenomena.

Background

Over the past 50 years, various techniques have been suggested to make bondable PP-based materials (e.g., corona discharge, flame treatment, low-pressure plasmas, chemical-based treatments). However, many of these approaches present severe technical limitations that make them difficult to use in the automotive sector. As an example, low-pressure plasma requires a vacuum chamber that is restrictive in regard to the size of parts to be treated. Moreover, extended exposure time of the PP parts, as well as pump-down time, hold-time and re-pressurisation time must also be added to consider the duration of the whole plasma treatment process under low-pressure conditions, making it too slow for most manufacturing industries.

In order to overpass these intrinsic limitations related to the use of low-pressure plasmas, and in the aim to keep their well-known advantages (i.e. varied chemistry, highly reactive species, low temperature processes), atmospheric pressure plasma jet (APPJ) sources have recently been developed. These sources present virtually no limit to the nature, shape, size and thickness of parts to be treated, because they operate at ambient pressure and are almost zero-voltage. Furthermore, their automation using a robot represents an

important advantage allowing a highly efficient control of the processing parameters.

Objectives of the presentation

Within the context where new surface treatment technologies are emerging on the market, this presentation will focus on the following aspects:

- Provide the audience with a comprehension of the mechanisms governing adhesion phenomena of PP treated using APPJ sources: relative influence of the surface wettability and surface chemistry introduced to PP;
- Presentation of the influence of APPJ surface treatment parameters (power, exposure time, etc.) on the efficiency of adhesive bonding processes of PP;
- Comparison of surface features induced by APPJ sources and traditional flame treatment in terms of treatment lifetime and treatment efficiencies for the adhesive bonding of PP;
- Presentation of the mechanical properties of adhesively-bonded aluminum-polypropylene hybrid joints.

As a conclusion, the possibilities offered by emerging surface treatment technologies applied to adhesive bonding of lightweight materials will be summarized in the light of the requirements and limitations of the automotive industry.

Technical Session: Materials – Automotive Composites.

This session contains papers which describe the use of modern automotive composites in structural applications. Design, process, and analytical presentations are included, as well as papers presenting results of bonding strategies and techniques. Engineers involved in the design and use of advanced composites will find this session of particular value.

New Surface Treatment Technologies for the Adhesive Bonding of Lightweight Aluminum-Polypropylene Hybrid Joints in Semi-Structural Applications

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Aluminium Technology Centre of NRC

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ABSTRACT

Atmospheric pressure plasma sources are new devices dedicated to the modification of the surface condition of engineering materials such as thermoplastic and thermoset-based composites. Because they operate at ambient conditions, these plasma systems can advantageously be used on a production line as a pre-treatment solution prior to painting or adhesive bonding operations to significantly improve adhesion strengths. However, their efficient use in that matter requires a deep understanding on how they modify the surface state of materials and, by the same way, how these modifications can be detected and quantified in regard to their ability to provide adhesive joints with high strengths. Polypropylene, since it is one of the most difficult-to-bond thermoplastic polymer and in parallel, one of the most attractive polymer for the automotive industry (because of its low cost, widespread use in the formulation of composites, lightweight and recyclability), was used in this paper as a model polymer. Because adhesive bonding opens the door to the design of hybrid structures composed of virtually any combination of dissimilar materials, often impossible to esthetically marry otherwise, the efficacy of surface modifications brought to polypropylene using two plasma systems were tested within adhesively bonded aluminum-polypropylene hybrid assemblies. Once pre-treated using atmospheric plasma sources, the polypropylene surfaces were also deeply investigated using surface science techniques, namely contact angle measurements, attenuated total reflectance infrared spectroscopy and X-ray photoelectron spectroscopy. From the correlations established between the mechanical strength of adhesively bonded joints and surface features evidenced by the use of surface science approaches, the role of surface and adhesive chemistries in providing semi-structural adhesive joints were evidenced. Indicators of performance for adhesive joints, based on fast infrared spectroscopy analyses, were found to be efficient for the systematic identification of promising adhesive-surface treatment combinations. The adhesion mechanism of plasma-processed polypropylene is also presented.

INTRODUCTION

Due to its interesting bulk properties, recyclability, low cost and lightweight, polypropylene is one of the most interesting thermoplastic materials for the design of stiff aluminum-polypropylene hybrid structures. However, the widespread use of polypropylene (as polymer or in composites) within adhesively bonded lightweight hybrid structures is still a challenge. This situation can be explained by the low surface free energy of polypropylene, which makes it difficult to bond using most structural adhesives that provide durable and highly reliable aluminum-based joints (i.e. epoxy, urethane and methacrylate). From a chemical point of view, this inherent problem comes from the fact that polypropylene, as many thermoplastic materials, is made of hydrophobic and saturated polymer chains. Hence, to make it suitable for adhesive bonding, the surface of polypropylene requires a pretreatment which introduces appropriate chemical polar functionalities and other surface features beneficial to adhesion phenomena.

Over the past 50 years, various techniques have been suggested to make polypropylene-based materials bondable (e.g., corona discharge, flame treatment, low-pressure plasmas, molecular grafting, acid treatments). However, many of these approaches present severe technical limitations that make them difficult to use in the automotive sector. As an example, while it has many times been claimed as the most efficient treatment, low-pressure plasma requires a vacuum chamber that is highly restrictive in regard to the size of parts to be treated. Moreover, extended exposure time of the polypropylene parts, as well as pump-down time, hold-time and re-pressurisation time must also be added to consider the duration of the whole plasma treatment process under low-pressure conditions, making it too slow for most manufacturing industries. In order to overcome the intrinsic limitations related to the use of low-pressure

plasmas, and in the aim to keep their well-known advantages (i.e. varied chemistry, highly reactive species, low temperature processes), atmospheric plasma sources have recently been developed. These sources, which operate at ambient pressure, present virtually no limit to the nature, shape, size and thickness of parts to be treated. Furthermore, their automation using a robot represents an important advantage allowing a highly efficient control of the processing parameters. A comprehensive review on technical principles behind atmospheric pressure plasmas is given by Tendero et al. in Ref. [1].

Although evident and promising features are characterising atmospheric plasma sources, their use as unique surface treatment device for both aluminum and polypropylene materials for the design of engineering hybrid assemblies, has not been reported yet. Indeed, atmospheric plasma sources can be used in replacement of primers, organic solvents, and other chemicals traditionally used for the pre-treatment steps of both aluminum and thermoplastic materials. While studies concerning the plasma pre-treatment of aluminum are actually under progress, many results have already been obtained concerning the applicability of these technologies to the pre-treatment of polypropylene prior to its adhesive bonding. Therefore, the aim of this paper is to systematically present to which extent new plasma technologies can advantageously be applied to the treatment of polypropylene to make it bondable using adhesives that perform well with aluminum. For that purpose, the influence of processing parameters on the wettability and surface chemistry induced onto surfaces of plasma-processed materials is discussed. In order to overcome expensive and time-consuming X-ray photoelectron spectroscopy analyses of surfaces, the usefulness of attenuated total reflectance infrared (ATR-IR) spectroscopy in the assessment of surface treatment quality is investigated. Finally, ATR-IR spectroscopy is also used to state on the relative contribution to adhesion of surface chemistry and surface wettability.

EXPERIMENTAL DETAILS

MATERIALS AND SURFACE TREATMENTS

Materials

The polypropylene substrates (monomer: $\text{CH}_2=\text{CH}-\text{CH}_3$) with a tensile strength of 24 MPa, crystallinity percentage of 59% and density of 0.905 were obtained from McMaster-Carr (Los Angeles, CA).

Atmospheric pressure plasma jet treatments

Plasma treatments were performed using two different systems: Atomflo™ -250 plasma jet from Surfx® Technologies LLC (Culver City, CA, USA) and Openair® plasma technology from Plasmatrete (Mississauga, Ontario, Canada).

Atomflo™ plasma treatments

The Atomflo™ plasma was initiated and maintained by supplying an RF excitation frequency to the electrodes. He at a 30-L/min flow rate was used as primary gas, while O_2 and N_2 (water-free) were used as secondary gases at flow rates ranged from 100 to 500 mL/min. The RF power was adjusted depending on the gas mixture employed: 30 to 80 W for He/ N_2 and 70 to 150 W for He/ O_2 . The AH-250C plasma torch was precisely moved over the surface of the materials using a six-axis Motoman 3 kg payload robot (Yaskawa Motoman, Mississauga, Canada). Plasma exposure times ranging from 0.15 to 10 seconds were investigated, and samples were processed at a distance of 3 mm downstream of the showerhead. Figure 1 presents a photograph of the Atomflo™ torch during treatment of a polypropylene coupon.

Openair® plasma treatments

Openair® plasma treatments were carried out using a RD1004 nozzle controlled by a FG5001 plasma generator. The plasma was generated and maintained inside the Openair® rotation jet using a non-equilibrium discharge applied to air (excitation frequency of 21 kHz, operating at 300 V and 16.3 A). The 25° nozzle, in rotation at an angular speed of 2800 rpm, was filled with compressed air at an input pressure of 3 bars. The distance between the bottom part of the nozzle and the polypropylene coupons, set to 8 mm, allows the processing of polypropylene samples in a single pass. In contrast to treatments performed with the Atomflo™ system, coupons to treat were moved under the plasma head using the robot (the plasma head was kept stationary). Exposures to the plasma shower for durations ranging from 0.2 to 14 seconds were investigated. Figure 2 presents a photograph of the Openair® jet during treatment of a polypropylene part.

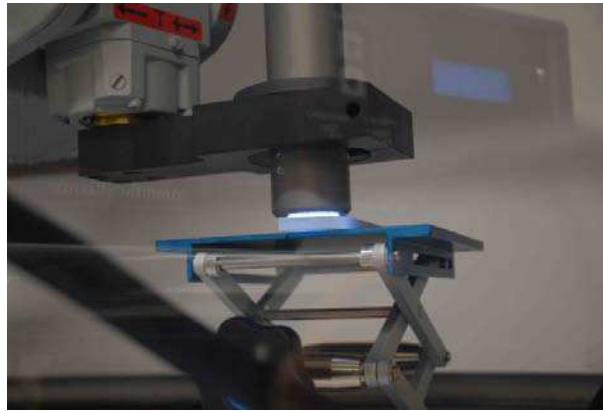


Figure 1 – Atomflo™250 plasma source moved over a polypropylene surface using the Motoman robot.



Figure 2 – Openair® plasma during the treatment of a polypropylene part.

Flame treatments

Flame treatment was carried out using the Dyne-A-Flame™ surface treater model DFE300 from Enercon Industries (Menomonee Falls, WI, USA). The polypropylene parts were processed in a single pass performed at 20 m/min through the flame. The distance between the visible blue tip of flame and the polypropylene surface was set to 5 mm. Ignition of the flame was accomplished by exposing an electric spark to a 230-L/min flow of filtered compressed air pre-mixed to a 22.1-L/min flow of natural gas. Considering the average volumetric composition of the natural gas delivered at ATC building, such a mixture contains a 10% excess amount of air (stoichiometric air-to-gas ratio of 10.4:1), resulting in an oxidizing flame. Under these conditions, the burner delivered a power of 52,000 Btu/h (or ~15,000 W).



Figure 3 – Enercon Industries Dyne-A-Flame™ DFE-300 flame treater.

SURFACE CHARACTERIZATION

Wettability and surface free energy measurements

Contact angles made by water on the polypropylene surface were measured on a Krüss DSA100 drop shape analysis system (Krüss USA, Matthews, NC). Figure 4 shows a typical liquid drop deposited on the surface of a solid material for contact angle measurements. For each sample treated with the plasma sources, static and dynamic (i.e., advancing and receding) contact angles were also determined. Advancing and receding contact angles are the critical angles at which the edge of contact starts to expand and contract, respectively. From advancing contact angles of water, diiodomethane and formamide, the surface free energy and its components were calculated according to Owens et al. theory [2,3]. Measurements were all carried out within 15 minutes after the surface treatment.

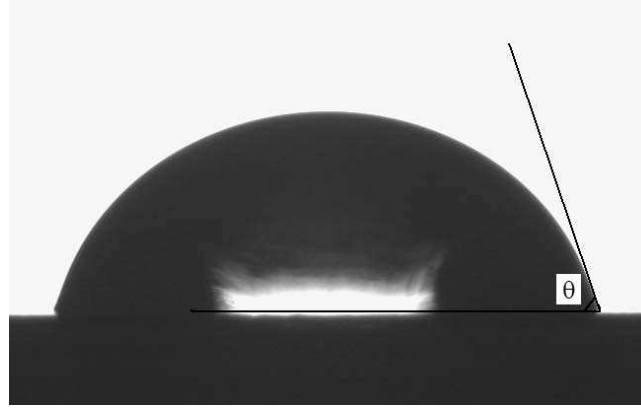


Figure 4 – Contact angle made by a liquid drop on a solid surface.

Overview of the surface free energy concept

In 1963-1964, Fowkes introduced the concept of additivity of intramolecular forces [4,5] and, in the same way, pioneered the surface component approach. He suggested that the geometrical mean of the dispersion force components across an interface ($\sqrt{\gamma_S^D \gamma_L^D}$, where γ_S^D is the dispersion component of the surface and γ_L^D is the dispersion component of the liquid wetting the surface) is a measure of the interaction energy caused by dispersion forces, as long as only dispersion forces are involved:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^D \gamma_L^D} \quad (1)$$

Owens and Wendt [2], and Kaelble and Uy [3] included, in 1969 and 1970 respectively, the polar interactions to the theory suggested by Fowkes:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^D \gamma_L^D} - 2\sqrt{\gamma_S^H \gamma_L^H} \quad (2)$$

where γ_S^H and γ_L^H represent hydrogen bonding terms for surface and liquid, respectively. The Owens et al. approach (sometimes called Kaelble method) then considers that both dispersive and non-dispersive interactions (i.e. polar interactions) contribute to interactions across interfaces:

$$\gamma^S = \gamma^D + \gamma^P \quad (3)$$

According to the Owens et al. theory, γ^D accounts for dispersive London interactions, while γ^P includes all of the non-dispersive forces, including H-bonding, acid-base, Keesom and Debye energetic contributions [6]. For polymeric materials, water and

diiodomethane are the two most frequently used liquids to determine γ^D and γ^P parameters from the Owens et al. theory [7]. Because the drop shape analysis system available for contact angle measurements allows a third liquid, formamide was used as the second polar liquid. In the past, liquid triplet water-diiodomethane-formamide was successfully used for surface free energy measurements of different materials [e.g.,7,8]. Moreover, it must be mentioned that the surface free energy calculation method suggested by Owens et al. is the most often applied method for polymeric materials [7].

As mentioned by Kwok et al. [9], on smooth but chemically heterogeneous solid surfaces, the contact angle to consider for surface free energy calculations is not necessarily equal to the thermodynamic equilibrium angle. Nevertheless, the experimental advancing contact angle can be expected to be a good approximation of the Young's contact angle. For this reason, in this study, the surface free energies were calculated from advancing angles even if the static and receding angles are also reported for wettability considerations.

Attenuated total reflectance infrared spectroscopy

The nature of the chemical modifications induced on the surface of polypropylene during atmospheric plasma treatments was studied using attenuated total reflectance infrared (ATR-IR) spectroscopy. Spectra were obtained with a Nicolet 6700 spectrometer (Thermo Scientific, Madison, WI) on a horizontally mounted internal reflection element (Smart iTR™ accessory, single-reflection germanium crystal, refractive index of 4.0 at 1000 cm⁻¹, 45° angle of incidence, 128 co-added scans with a 4 cm⁻¹ spectral resolution). In order to improve the detection sensitivity, a mid-IR liquid nitrogen-cooled mercury-cadmium-telluride (MCT-A) detector was used.

In the field of ATR-IR spectroscopy, the choice of crystal is a critical step. Indeed, the depth of penetration (d_p) of IR radiation within the material depends on the refractive index of the crystal used as a probe. The parameter d_p can be calculated using the following expression [10]:

$$d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2 \vartheta - n_2^2}} \quad (4)$$

where λ = wavelength of the light, ϑ = angle of incidence of the IR beam = 45°, n_1 = refractive index of the crystal = 4.0, n_2 = refractive index of the sample (for polypropylene: $n_2 = 1.49$). According to Eq. (4), with the Ge crystal used as reflection element, the penetration depth at 1000 cm⁻¹ is approximately 0.66 μ m. By comparison, the use of a diamond crystal ($n_1 = 2.4$) allows probing to a depth of 196 μ m at the same wavenumber. Thus, the use of a diamond crystal for the investigation of upper surface modifications attributable to plasma treatments would introduce numerous artifacts to ATR-IR spectra. Figure 5 presents ATR-IR spectra recorded for an acetone-degreased polypropylene coupon (no plasma treatment was performed on it). As shown, quite strong absorption bands, attributable to additives added to polypropylene during the molding process, are observed with diamond crystal. Since these absorption bands are not detected when the Ge crystal is employed, it is evidenced that diamond investigates at a far greater depth within the material than Ge does.

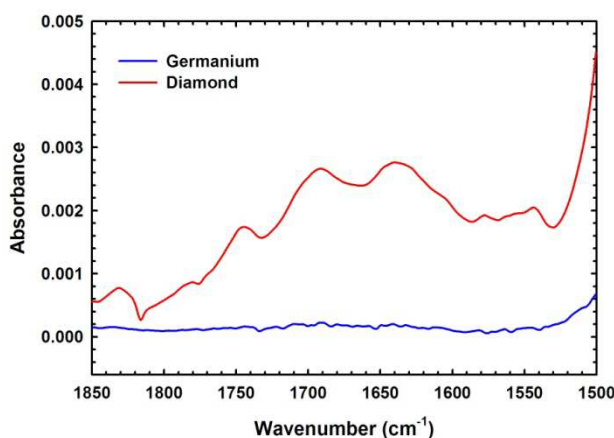


Figure 5 – Influence of the crystal on the ATR-IR spectra of polypropylene recorded in the carbonyl (C=O) region.

X-ray photoelectron spectroscopy

The surface composition of polypropylene was analyzed by X-ray photoelectron spectroscopy (XPS) before and after plasma treatment. XPS spectra were taken using the Al K α photon source ($h\nu = 1486.6$ eV; 300 W) of a Kratos Analytical (Manchester, UK) model Axis-Ultra spectrometer. The binding energies were calibrated with peaks Au 4f $_{7/2}$ at 83.95 eV, Ag 3d $_{5/2}$ at 368.20 eV, and Cu 2p $_{3/2}$ at 932.60 eV. For all samples, survey spectra were recorded with a 160 eV pass energy, while the high resolution spectra in the regions of interest (O1s, C1s and N1s peaks) were obtained with a 10 eV pass energy. Typically, XPS can characterize the first 5-10 nm of a surface. The underlying layers become accessible only if Ar $^{+}$ sputtering is practiced.

EVALUATION OF JOINT STRENGTH

Mechanical single lap shear (SLS) test procedure

Aluminum-polypropylene hybrid SLS specimens were prepared according to the geometry presented in Figure 6. The bondline thickness was 1.0 mm and an overlap 25 mm in length \times 25 mm in width was employed. Prior to SLS specimen assembling, aluminum 6061-T6 strips were acetone degreased, abraded using a 3M Scotch-Brite™ general purpose hand pad 7447B and primed using Cytec BR6747-1 primer. This surface preparation was found to be sufficient to avoid any aluminum-adhesive interfacial failure. In order to investigate the bondability of plasma modified polypropylene surfaces, a two-part amine cured paste epoxy adhesive was used (if not otherwise stated). SLS specimen testing was conducted on an electromechanical MTS Alliance RT/100 test system (MTS Systems Corporation, Eden Prairie, MN, USA), equipped with a 50 kN load cell. All tests were run at a 1 mm/min cross-head speed, and spacers helped to align the lap shear samples in the grips to make sure the load was parallel to the adhesive layer (see Figure 6).

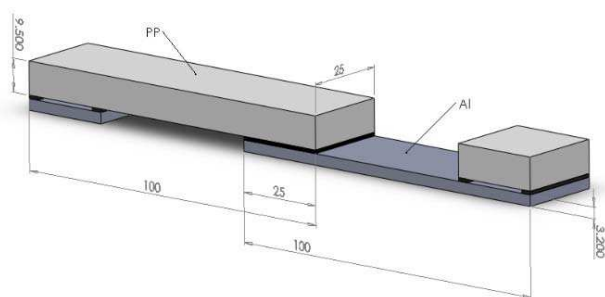


Figure 6 – Typical single lap shear assembly used to evaluate the joint strength of aluminum-polypropylene hybrid specimens (dimensions are in mm).

RESULTS AND DISCUSSION

INITIAL SELECTION OF THE ADHESIVE FAMILY TO INVESTIGATE

Although there exist today polyolefin bonders that can efficiently bond polypropylene and polyethylene with minimal surface preparation, these adhesives are not formulated for aluminum. In parallel to the development of polyolefin adhesives, during recent years, atmospheric plasma technologies have emerged and they are today increasingly used in many industrial sectors. Therefore, the approach proposed in this study is to put effort on surface preparation of polypropylene while keeping that of aluminum at a minimal point by the use of adhesive chemistries recognized for their ability to bond aluminum. In order to select the adhesive family the most relevant to investigate, flame treatment was performed on polypropylene coupons prior to their assembly to aluminum. Flame treating was first developed in the 1950s to improve the wetting and adhesion properties of polyolefin films. Therefore, there exists in scientific literature a large amount of data on the optimum flame processing parameters to use. Figure 7 shows the XPS spectra obtained for polypropylene before and after treatment with flame under the conditions described in the experimental details section. As demonstrated using a deconvolution procedure, the flame has introduced various oxidized carbon species (C-O, C=O, O-C-O, O=C-O) to the surface of polypropylene (Strobel et al. [11] proposed an oxidation mechanism for the flame in contact with polypropylene). Figure 8 presents the strength of SLS joints made of aluminum and flame-treated polypropylene, and assembled with 25 different adhesives which belong to three different families. All adhesives used are two component systems which crosslink at room temperature. An overview of these results shows that methacrylate adhesives provide very weak joints. While urethanes appear

to perform somewhat better than methacrylates, it is clear that epoxies are the most promising structural adhesives for the assembly of aluminum-polypropylene hybrid joints. Depending on the epoxy adhesive used, joint strengths ranging from 2.87 to 7.37 MPa were obtained. From these results, the next step was to systematically investigate atmospheric plasma treatment parameters that can allow an increased resistance of such bonded joints. Based on the results presented in Figure 8, the epoxy adhesive E1 was chosen for this purpose.

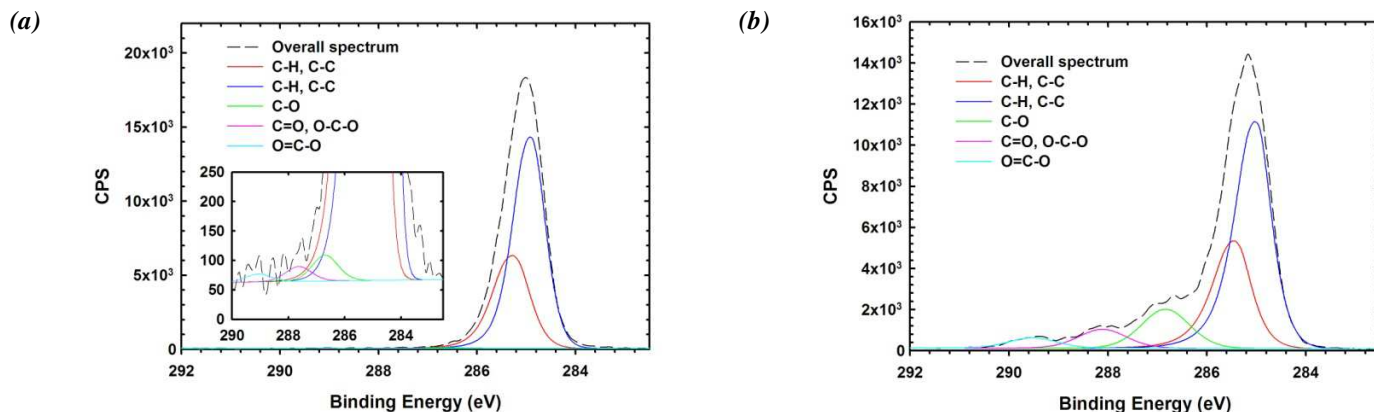


Figure 7 – High-resolution C1s XPS spectra for polypropylene (a) before and (b) after the flame treatment.

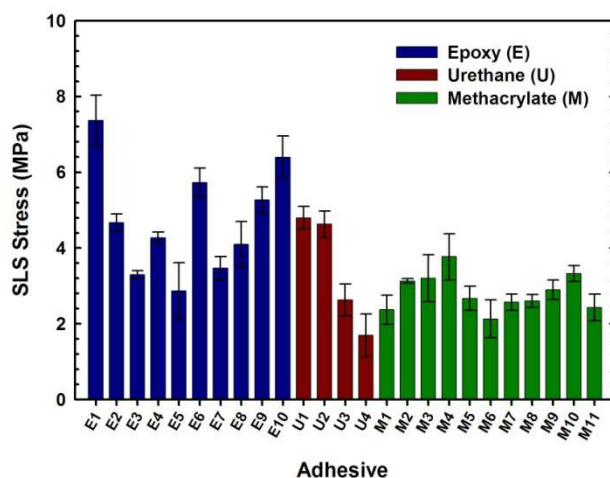


Figure 8 – Influence of the adhesive chemistry (epoxy, urethane, methacrylate) on the SLS stress measured for hybrid aluminum-polypropylene specimens (polypropylene coupons were flame treated).

METHODS FOR QUALITY CONTROL OF PLASMA PROCESSED SURFACES

Determination of optimal plasma treatment parameters from contact angle measurements

Plasma processed surfaces, before being assembled, must be submitted to a quality control inspection. As presented in previous paragraphs, in the field of adhesive bonding, the concept of surface free energy (and by extension the wettability phenomenon) is of paramount importance. Qualitatively, it can be argued that low water contact angles are generally representative of a high surface free energy which in turn can lead to high joint strengths. Although it is not the only condition that ensures the achievement of good quality joints, it is nonetheless known as one of the most critical.

With the purpose of determining the influence of plasma treatment parameters on the resistance of adhesive joints, contact angle measurements in static and dynamic (advancing and receding) modes were performed on the surface of polypropylene material plasma treated under different conditions. Figure 9 shows the influence of the Atomflo™ He/O₂ and He/N₂ plasmas power on such measured water contact angles. As presented, an increase in the plasma power decreases the water contact angles measured in static, advancing and receding modes. It is important to note that in parallel to power increases shown on the graph, the flow of secondary gas added to

the constant helium flow was also increased from 100 to 500 mL/min for both N₂ and O₂ secondary gases. Such a procedure is necessary to ensure the stability of the plasma generated. In all cases, polypropylene coupons were exposed to plasma during a short period of time, i.e. 0.5 second. As shown in Figure 9, for the two gas combinations investigated, the lowest contact angles (32° receding angles) were reached using the maximum plasma power allocated to each mixture (i.e. 80 W for He/N₂ and 150 W for He/O₂).

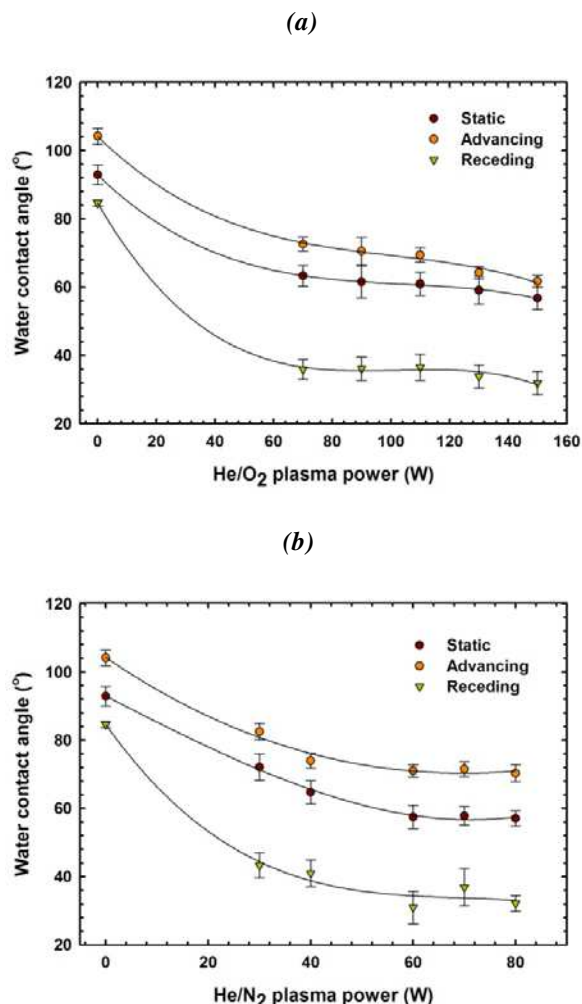


Figure 9 – Influence of the Atomflo™ (a) He/O₂; (b) He/N₂ plasma power on static, advancing and receding water contact angles (polypropylene parts were acetone degreased before the 0.5-s plasma exposure).

In the case of Openair® plasma, the most critical parameters are: (1) nozzle selection, (2) nozzle-to-sample distance and (3) exposure time to plasma. The nozzle and nozzle-to-sample distance were selected on the basis that the coupons had to be treated in a single pass. Regarding input air pressure and plasma voltage, they were kept constant (3 bars and 300 V, respectively) since their influence is intimately linked to that of the duration of coupons exposure to plasma. Thus, in this study, only the duration of exposure to the Openair® plasma was amended.

As presented in Figure 10, the water contact angles significantly decrease when the duration of treatment is increased from 0.2 to 2 seconds. Thereafter, a moderate decrease in advancing and receding contact angles is observed for durations of treatment ranging from 2 to 14 seconds, while advancing contact angles were virtually unchanged in that range. Interestingly, a 0.5 second exposure to Openair® plasma was found to give a receding contact angle of 34°, a value that is very close to corresponding angles measured following Atomflo™ He/O₂ and He/N₂ plasma treatments (i.e. 32°) performed using optimal conditions.

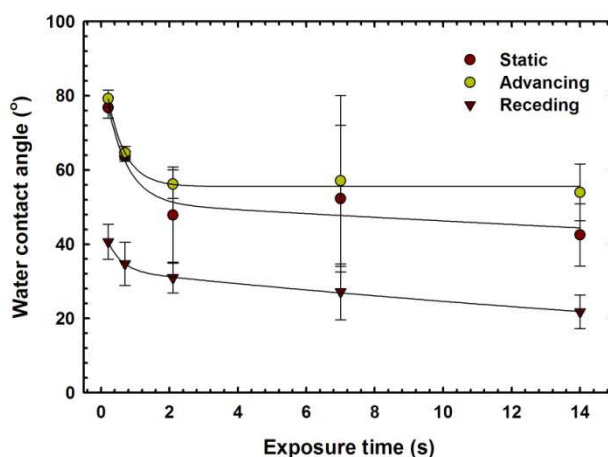


Figure 10 – Influence of the exposure time to Openair® plasma of polypropylene on static, advancing and receding water contact angles (polypropylene parts were acetone degreased before the plasma exposure).

The relevance of receding contact angles in the assessment of plasma-treated surfaces has been reported many times. In a paper published by Della Volpe and Siboni [12], it has been mentioned that receding contact angles are a better index of the high-energy portion of a surface. In the same way, advancing contact angles would be mostly indicative of the low surface free energy portion of a surface, and thus not necessarily representative of the plasma treated portion. Therefore, since plasma treatment performed using the following parameters were found to lead to similar receding water contact angles, they were selected for further investigations:

- Atomflo™ He/O₂ (30 L/min He & 500 mL/min O₂), P = 150 W, stand-off distance of 3 mm, treatment duration of 0.5 s;
- Atomflo™ He/N₂ (30 L/min He & 500 mL/min N₂), P = 80 W, stand-off distance of 3 mm, treatment duration of 0.5 s;
- Openair®, air at 3 bars, 300 V, stand-off distance of 8 mm, 25° nozzle, treatment duration of 0.5 s.

Surface chemistry of plasma processed polypropylene: relevance to adhesion

As discussed in the previous section, measurement of contact angles made by water droplets on the surface of polypropylene treated using plasma systems allows a preliminary selection of optimal treatment parameters. However, while it provides indications concerning global changes induced to a surface, the contact angle approach does not state about the nature of these modifications. For that purpose, attenuated total reflectance infrared (ATR-IR) spectroscopy was used. This technique allows a fast investigation (< 1 minute) of chemical organic functions present on the surface of a polymer. Contrary to X-ray photoelectron spectroscopy, it is practiced under ambient conditions and it is far less expensive.

Figure 11 presents the ATR-IR spectra recorded in the region of carbonyl and hydroxyl/amine functions. These functionalities are generally recognized as the main induced on the surface of polymers during an oxidative treatment, regardless of whether practiced by chemical or energetic means [13]. First, it is clear that plasma treatments of interest induce different chemical species on the surface of polypropylene. As shown in Figure 11a, Atomflo™ He/O₂ plasma mainly introduce esters (RCOOR') or carboxylic acids (RCOOH) groups (~ 1730 cm⁻¹), as well as a low amount of ketone (RCOR') or aldehyde (RCHO) (peak shoulder at ~ 1640 cm⁻¹). This ratio was found to be virtually inverted in the case of Atomflo™ He/N₂ plasma. A probable contribution of amide (RCNOR') groups is also expected for He/N₂ plasma. A different spectral signature is recorded for the Openair® plasma processed polypropylene surface for which a strong contribution from esters and/or carboxylic acids (~ 1700 cm⁻¹) as well as ketone, aldehyde or amide groups (~ 1640 cm⁻¹) is evidence in Figure 11a. The absorption peak observed at ~ 1560 cm⁻¹ shows that nitro groups (NO₂) were also introduced within polymer chains during Openair® plasma treatment of polypropylene. In Figure 11b, it is shown that plasma treatments have also introduced OH and NH functionalities onto the surface of polypropylene. According to relative intensities of absorption band observed, these species are found to a higher extent on the surface of polypropylene treated using Openair® plasma. It should also be pointed out that absorption bands detected in the 3800-3000 cm⁻¹ interval can evidence the presence of a variety of chemical functions, such as alcohols, carboxylic acids, and amines. However, the lack of resolution makes difficult a more precise assignment of vibration bands. Although contact angle measurements could lead to the belief that all plasma treatments lead to a quite similar surface

chemistry, ATR-IR measurements have shown this to be otherwise. However, it is unlikely that all species detected and roughly quantified contribute at the same extent to adhesion phenomena.

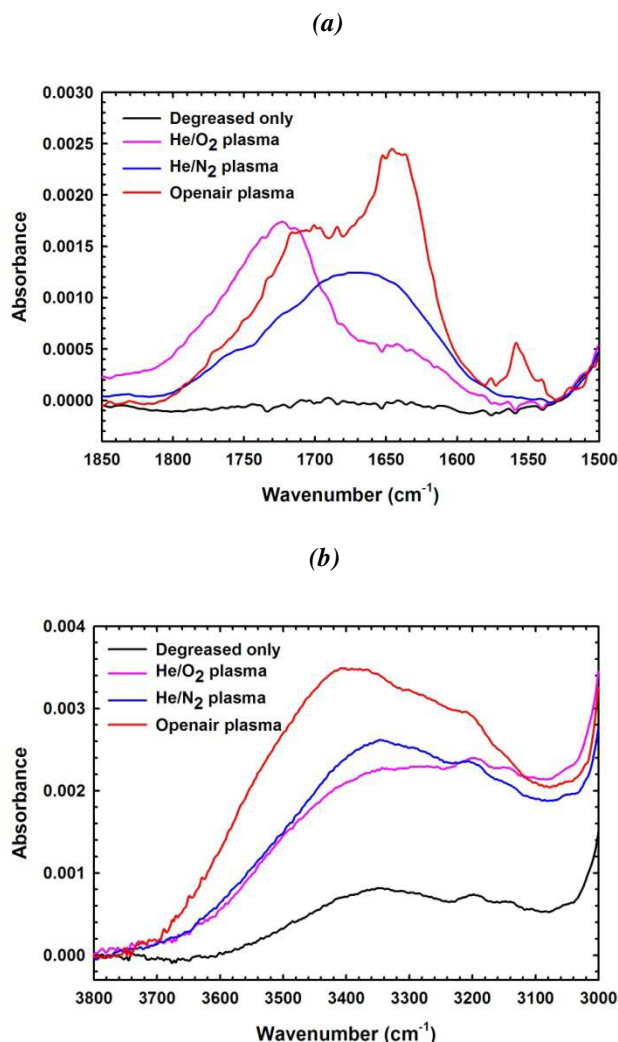


Figure 11 – ATR-IR spectra recorded in the (a) carbonyl region ($C=O$, $1850\text{-}1500\text{ cm}^{-1}$) (b) hydroxyl / amine region (OH , NH , $3800\text{-}3000\text{ cm}^{-1}$) for polypropylene following Atomflo™ He/O_2 , Atomflo™ He/N_2 and Openair® plasma treatments (pre-plasma treatment: acetone degreasing; post-plasma treatment: none) (plasma exposure time: 0.5 s)

Table 1 presents atomic percentages for C, O and N precisely quantified on the surface of polypropylene treated using Atomflo™ He/O_2 , Atomflo™ He/N_2 and Openair® plasmas. As shown, plasma treatments markedly increase the oxygen content on the surface of polypropylene. On the other hand, the nitrogen concentration found on the surface of polypropylene following plasma treatments was quite low, especially for coupons processed with Atomflo™ He/N_2 . Consequently, amine and amide groups were not importantly introduced to polymer chains during plasma treatments. Surprisingly, Atomflo™ He/O_2 plasma introduces more N atoms on the surface of polypropylene than Atomflo™ He/N_2 plasma does. It is thus likely that post-plasma reactions contribute to surface modifications observed [14]. The higher nitrogen content measured for polypropylene treated using the Openair® system is explained by the presence of nitro functionalities, clearly observed on the ATR-IR spectrum presented in Figure 11a.

Table 1 – XPS derived concentration of atomic C, O and N on polypropylene before and after plasma treatments.

Sample	Atomic Concentration (%)		
	C	O	N
Degreased only	99.22	0.51	---
Atomflo™ He/O ₂ plasma	87.02	11.73	0.66
Atomflo™ He/N ₂ plasma	90.61	8.09	0.31
Openair® plasma	84.3	13.35	1.62

Figure 12 presents the relationship established between the oxygen content of plasma processed coupons, as determined using XPS analyses, and the polar component of the surface free energy calculated for the same coupons by applying the Owens, Wendt, Kaelble, Uy theory to advancing contact angles measured for water, diiodomethane and formamide. Is also presented in this figure the relationship between the O content of polypropylene samples and the SLS stress measured for hybrid specimens bonded with E1 adhesive and made of aluminum and plasma processed polypropylene samples. Interestingly, it was found that an increase in oxygen content results in increased values of γ^P and stronger SLS aluminum-polypropylene assemblies. Therefore, in this case, the polar component of surface free energy, calculated from advancing contact angles, was found to be a better indicator of performance than receding water contact angles (32-34° for each treatment). However, quite large standard deviations associated to mechanical SLS results, especially for assemblies made of polypropylene treated with Atomflo™ He/O₂ plasma, makes believe that some surface contamination has negatively influenced bond performances. Since many precautions were taken during the plasma processing of parts as well as during their assembly, it is unlikely that an external source has brought contaminating agents to coupons. Therefore, it is suggested that loosely retained molecular fragments were generated on the surface of polypropylene during plasma treatments. In the case of polymers, such fragments are often identified as low-molecular-weight oxidized materials (LMWOM).

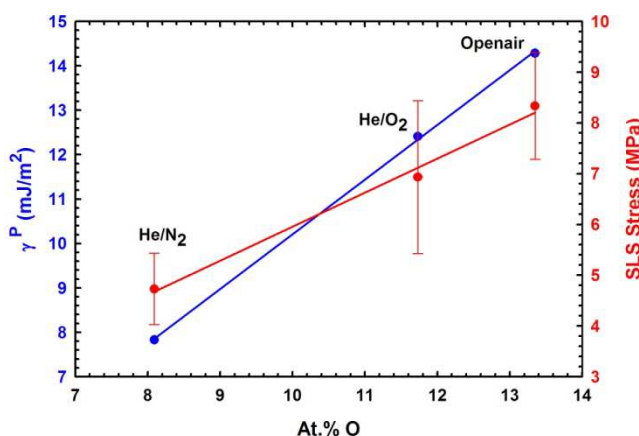


Figure 12 – Relationships γ^P vs. At.%O and SLS Stress vs. At.%O (derived from XPS experiments) for polypropylene plasma treated and adhesively bonded to aluminum (polypropylene degreased and plasma treated, no post-plasma treatment was used).

Methods to improve mechanical performance of adhesive joints made of plasma-treated polypropylene

In a recent paper, Gonzalez et al. [15] mentioned that low-molecular-weight polymer chains are soluble in methanol (MeOH). In order to determine if MeOH soluble species (that will be defined as low-molecular-weight polymer chains) are present on the surface of plasma treated polypropylene, a MeOH rinse step, followed by oven drying step at 60°C for 30 minutes to remove any remaining solvent trace, was practiced as post-plasma treatment. Also, to make sure acetone used to remove oils and greases from polypropylene substrates prior to plasma treatment does not negatively influence bond strengths, a drying step at 60°C was also included following acetone degreasing.

Figure 13 presents the effect of pre- and post-plasma treatments on the bond strengths measured for hybrid aluminum-polypropylene SLS specimens. First of all, it is relevant to mention that plasma treatments improve the bond strengths by more than one order of magnitude compared to untreated and simply degreased material. As shown, oven drying of polypropylene parts following acetone

degreasing and before plasma treatments slightly improve the resistance of SLS assemblies made of Openair® and Atomflo™ He/O₂ plasma treated polypropylene. In the case of Atomflo™ He/N₂ plasma, the average bond strength was found to be unchanged by the oven drying step, but the standard deviation on the calculated average was improved. The most relevant changes were observed for the last set of data presented in Figure 13. As seen, the complete treatment (acetone – oven – plasma – MeOH – oven) increases by more than 60% the joint strength made of Atomflo™ He/O₂ plasma processed polypropylene, and decreases by a factor of 5 the standard deviation on the average value calculated. A more modest improvement of 30% was observed for Atomflo™ He/N₂ plasma. In the case of Openair® plasma, the MeOH rinse was found to be detrimental to bond strengths. From the comparison of the 3rd and 4th data sets in Figure 13, it can be pointed out that the oven drying step following acetone degreasing seems to be essential (a research project is actually under progress to determine if the acetone degreasing step can be totally removed from all these treatment procedures). Finally, since a joint strength as low as 0.33 ± 0.35 MPa characterizes aluminum-polypropylene assemblies made of only degreased polypropylene, it is clear that plasma treatment is essential to obtain semi-structural bonds, regardless that pre- or post-plasma treatments are used or not.

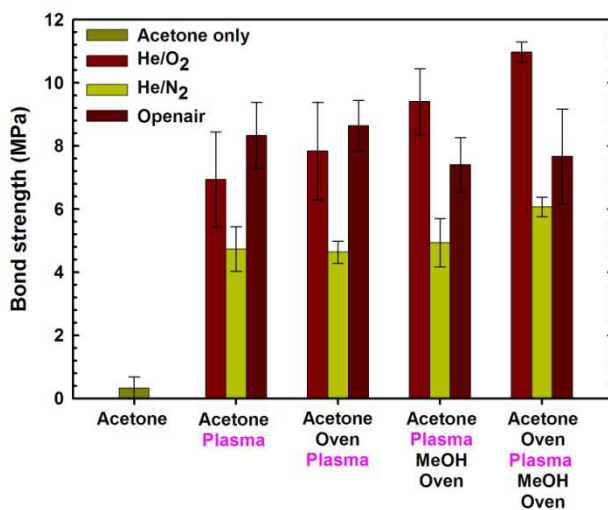


Figure 13 – Influence of pre- and post-plasma treatments on the bond strength of aluminum-polypropylene hybrid SLS assemblies.

At this point, it must be remembered that ATR-IR spectroscopy analyses (Figure 11) have revealed that plasma treated polypropylene surfaces are composed of numerous chemical species, although XPS experiments have shown the low relative concentration of N-containing ones. It was also pointed out that the participation to adhesion phenomena of all these species is unlikely. According to results presented in Figure 13, LMWOM species seem to be preferentially induced by Atomflo™ He/O₂ plasma treatment. Therefore, it is expected that the MeOH rinse contributed to the preferential removal of some of the species detected using ATR-IR spectroscopy, which were detrimental to adhesion because they were loosely retained to the surface. In counterpart, remained species have shown their efficiency in providing hybrid adhesive joints that could be characterized as semi-structural assemblies.

With the purpose of investigating chemical changes brought to the polypropylene surface by the MeOH rinse step, static, advancing and receding contact angles were measured for Atomflo™ He/O₂ plasma treated polypropylene having been submitted to pre- and post-plasma treatments. This specific plasma was selected since it was found to be the most impacted by pre- and post-plasma treatments. As shown in Figure 14, receding contact angles were virtually unaffected by MeOH rinse, while static and advancing angles measured for plasma treated materials were considerably increased by the MeOH rinse. This could be explained by the fact that receding angles are measured on a surface already wetted by water, which could have dissolved LMWOM species. Indeed, when the drop is retracted for receding angle determination, LMWOM species have already been removed from the surface. It is then suggested that static and advancing angles are more accurate indicators of the presence and removal of LMWOM species than receding angles. While they indicate that chemical changes have occurred at the surface of polypropylene during the MeOH rinse, the increased values of static and advancing contact angles cannot provide information about the chemical nature of these modifications.

Figure 15 presents ATR-IR spectra recorded for polypropylene treated using Atomflo™ He/O₂ plasma, before and after MeOH rinse. As shown in Figure 15a, MeOH has removed from the surface most of carbonyl species associated to ester and/or carboxylic acid species. Remained carbonyl species are attributable to MeOH insoluble ketone or aldehyde species. According to Shahidzadeh-Ahmadi et al.[16], O₂ containing plasmas do not importantly introduce ester functionalities within polymer chains. It is thus

reasonable to propose that removed carbonyl containing species were essentially carboxylic acids. Such a statement is in accordance with ATR-IR spectra recorded in the hydroxyl region and presented in Figure 15b. As evidenced, the MeOH rinse as improved the resolution of the OH band, probably by removing the OH groups associated to carboxylic acids. As a result, the remaining and well defined OH vibration band observed on the ATR-IR spectrum can be associated to alcohol functionalities.

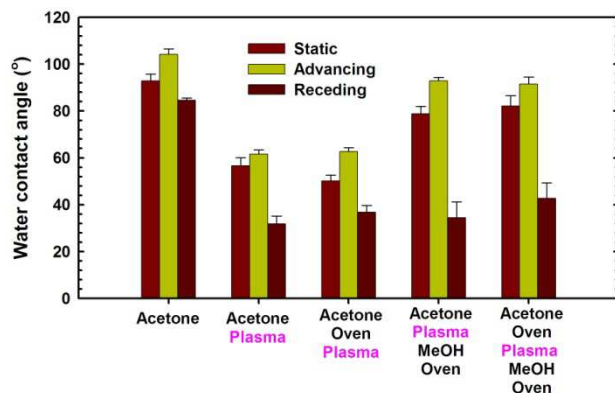


Figure 14 – Influence of pre- and post-plasma treatments on static, advancing and receding water contact angles for polypropylene treated with Atomflo™ He/O₂ plasma.

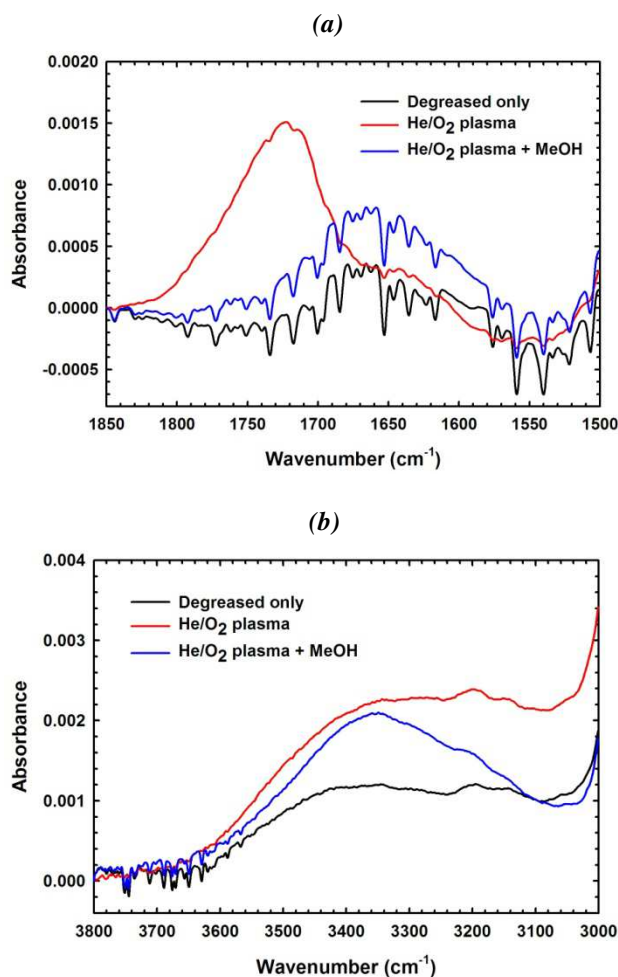


Figure 15 – Influence of MeOH rinse of polypropylene following Atomflo™ He/O₂ plasma treatment depicted from ATR-IR spectra recorded in the (a) carbonyl region (C=O, 1850-1500 cm⁻¹) (b) hydroxyl and amine region (OH, NH, 3800-3000 cm⁻¹).

MECHANISM OF ADHESION BETWEEN EPOXY ADHESIVE AND PLASMA PROCESSED POLYPROPYLENE

ATR-IR spectrum presented in Figure 15b supports the theory sustaining that -OH groups from alcohol functions introduced onto the surface of plasma processed materials are the main contributors to adhesion phenomena observed. Figure 16a presents ATR-IR spectra obtained from Openair®, Atomflo™ He/O₂ and Atomflo™ He/N₂ plasma treated samples following MeOH rinse. For comparison purposes, ATR-IR spectrum obtained from Atomflo™ He/O₂ plasma treated samples, without MeOH rinse, is also presented. Corresponding SLS stresses obtained from these materials within hybrid aluminum-polypropylene assemblies are presented in Figure 16b. As clearly seen, the strong OH band at ~ 3360 cm⁻¹ can be correlated to the high joint strength obtained using Atomflo™ He/O₂ plasma treatment, followed by a MeOH rinse. Interestingly, following MeOH rinse, all three spectra show similar band intensities in the carbonyl region at ~ 1650 cm⁻¹, reinforcing the idea that OH group from alcohol is responsible for the high joint strength reported for Atomflo™ He/O₂ plasma. Thus, carbonyl groups belonging to ketones and/or aldehydes also certainly contribute to adhesion of polypropylene, but without playing the key role assigned to alcohol functionalities. ATR-IR spectra recorded for other treatments exhibit similar features, which is consistent with corresponding mechanical results.

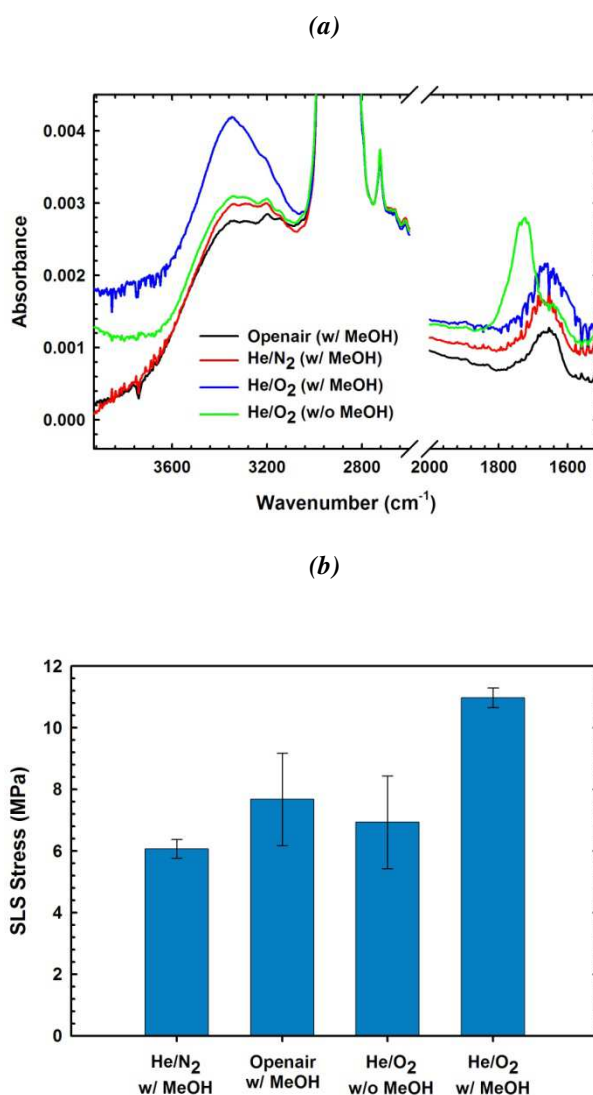


Figure 16 – (a) Influence of MeOH rinse on ATR-IR spectra of plasma processed polypropylene samples and (b) corresponding SLS aluminum-polypropylene joint strength measured.

The comparison of ATR-IR spectra shown in Figures 11 and 16b, especially in the carbonyl region, demonstrates that MeOH rinse removed LMWOM species from all three plasma processed samples, which is confirmed by XPS data presented in Table 2. However,

data presented in Table 2 do not allow identification of the chemical function responsible for the good adhesion behavior observed with Atomflo™ He/O₂ samples from which LMWOM species were removed. In order to confirm the molecular-level information obtained from ATR-IR spectra, high-resolution C1s XPS spectra were recorded and analyzed. Results are presented in Table 3 as $\frac{\text{C-O, C-OH}}{\text{O-C-O, C=O}}$ and $\frac{\text{C-O, C-OH}}{\text{O=C-O}}$ ratios. As can be seen, for all three plasmas, the $\frac{\text{C-O, C-OH}}{\text{O-C-O, C=O}}$ ratio was modified by the MeOH rinse. Indeed, a detailed examination of results shows that, following MeOH rinse, this ratio was slightly increased for samples treated with the Atomflo™ He/O₂ plasma, while it was observed to be decreased by the Atomflo™ He/N₂ plasma treatment and, more importantly, by the Openair® plasma treatment. These results are in good accordance with the relative $\frac{\text{OH}}{\text{C=O}}$ band intensities in ATR-IR spectra presented in Figure 16a. Also, the removal of carboxylic acid species from all plasma processed samples is evidenced from the increased $\frac{\text{C-O, C-OH}}{\text{O=C-O}}$ ratio values following MeOH rinse. Since MeOH rinse does not induce new C-O or C-OH species, it is then concluded that it removes carboxylic acid groups (O=C-O), resulting in increased values for the $\frac{\text{C-O, C-OH}}{\text{O=C-O}}$ ratio. Again, this result is in accordance with interpretation made of ATR-IR spectra.

Table 2 – XPS derived concentration of atomic C, O and N on polypropylene before and after MeOH rinse of plasma processed samples.

Sample	Atomic Concentration (%)		
	C	O	N
Degreased only	99.22	0.51	---
He/O ₂ plasma	87.02	11.73	0.66
He/O ₂ plasma & MeOH rinsed	96.61	2.97	---
He/N ₂ plasma	90.61	8.09	0.31
He/N ₂ plasma & MeOH rinsed	98.00	1.48	---
Openair plasma	84.3	13.35	1.62
Openair plasma & MeOH rinsed	95.56	3.74	---

Table 3 – C-O, C-OH / O-C-O, C=O and C-O, C-OH / O=C-O ratios calculated from C1s high-resolution XPS spectra recorded for polypropylene samples before and after plasma treatments.

Sample	Ratios $\frac{\text{C-O, C-OH}}{\text{O-C-O, C=O}}$	
	$\frac{\text{O-C-O, C=O}}{\text{C=O}}$	$\frac{\text{O=C-O}}{\text{C=O}}$
He/O ₂ plasma	1.74	1.42
He/O ₂ plasma & MeOH rinsed	1.85	3.51
He/N ₂ plasma	1.69	2.59
He/N ₂ plasma & MeOH rinsed	1.58	4.00
Openair plasma	1.94	2.69
Openair plasma & MeOH rinsed	1.68	5.05

While XPS and ATR-IR spectroscopy can be used to evidence the adhesion mechanism, surface free energy values calculated would certainly not be helpful in the prediction of joint strength for plasma processes samples and MeOH rinsed (Figure 16b). Indeed, based on the low polar component values of surface free energy (γ^p) reported in Figure 17, it would have been expected that these surface would poorly perform in terms of adhesion behavior, which was not the case. It is then clear that surface free energy values calculated from advancing contact angles of a series of liquids is not indicative of the adhesion performance of polypropylene treated using atmospheric plasma. At best, this technique shows that LMWOM species were introduced onto surfaces, but only once they are

removed. Therefore, by considering this conclusion for the analysis of results presented in Figure 12, it must be stressed out that the linear relationship observed between At.%O and SLS stress is not more than a coincidence.

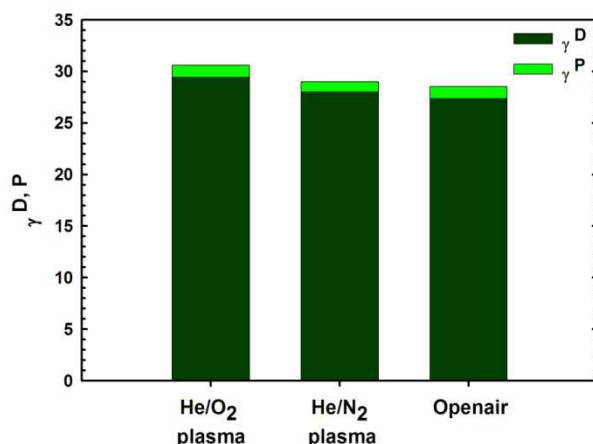


Figure 17 – Dispersive (γ^D) and polar (γ^P) components of the surface free energy ($\gamma^S = \gamma^D + \gamma^P$) calculated for plasma treated polypropylene materials following final MeOH rinse and drying steps.

In the case of metals, the significant chemical interactions that affect bond strength are believed to occur between the hydroxyl (OH) groups present on the metal oxide surface and OH groups present in the adhesive [17]. During the present study, the role of OH groups in adhesion of plasma treated polypropylene was evidenced from the use of ATR-IR spectroscopy practiced on different cured epoxy adhesives. As presented in Figure 18, ATR-IR spectroscopy has successfully demonstrated that there exists a linear relationship between the SLS stress measured for hybrid aluminum-polypropylene assemblies and the hydroxyl content of different epoxy adhesives once they are cured. Thus, hydrogen bonding interactions taking place between hydroxyl groups from plasma processed polypropylene surfaces and from the adhesive, as illustrated in Figure 19, would explain the high joint strengths obtained using the Atomflo™ He/O₂ plasma system.

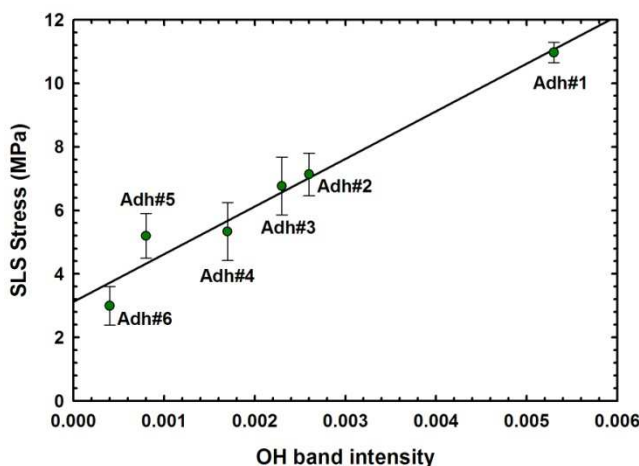


Figure 18 – Relationship between SLS stress determined for aluminum-polypropylene assemblies and the OH band intensity measured by ATR-IR at the surface of epoxy adhesives 1 to 6 (polypropylene was treated using Atomflo™ He/O₂ plasma, and MeOH rinsed).

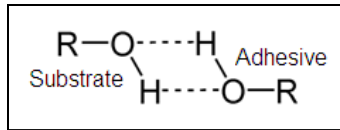


Figure 19 – Schematic of hydrogen bonding between OH groups from both the substrate and the adhesive.

INFLUENCE OF JOINT GEOMETRY

Although SLS specimens are useful for comparison purposes between different surface pretreatments, such specimen geometry is not recommended for studies aimed at the design of adhesively bonded joints. This can be explained by the fact that stresses are not uniformly distributed in a joint submitted to a shear stress, and the mechanical stress-based approach does not account for this non uniform distribution. As presented in Figure 20, when the length of overlap is increased, the maximum SLS stress measured for the assembly, i.e. upon joint failure, decreases. In parallel, the load applied to provoke the failure of the assembly was found to linearly increase with the length of overlap. For example, a quite low 6.2 MPa SLS stress was measured using a 51-mm overlap. However, a load as high as 8064 N was applied to this assembly to provoke its failure, which was found to be high enough to cohesively break the polypropylene substrate, while keeping the adhesive joint intact. Under such a loading condition, stresses corresponding to 99.2 MPa and 33.1 MPa were applied to aluminum and polypropylene substrates, respectively. Therefore, mechanical stresses measured and reported within the framework of this study must be interpreted with care and are certainly not directly applicable to existing designs.

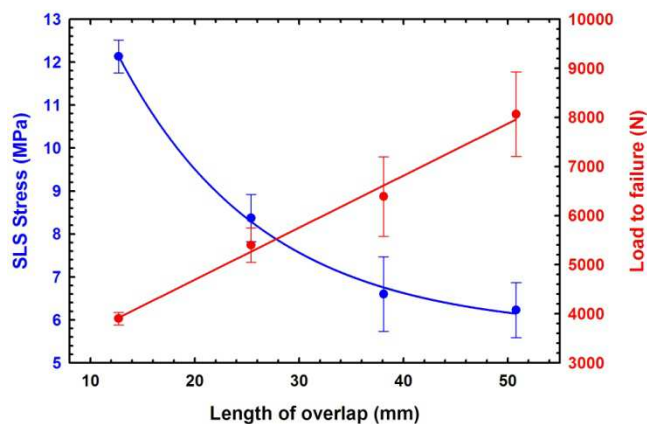


Figure 20 - Influence of the length of overlap on SLS stress and load to failure measured for aluminum-polypropylene joints (polypropylene was treated using Openair® plasma).

SUMMARY/CONCLUSIONS

This paper has shown that atmospheric plasma sources represent promising systems for the surface pre-treatment of polypropylene prior to its adhesive bonding to aluminum using an adhesive system that performs well with aluminum. While both plasma setups investigated present numerous advantages, this work has also demonstrated that the use of atmospheric plasma sources for the surface treatment of a difficult-to-bond thermoplastic material requires a structured R&D effort. Attenuated total reflectance infrared spectroscopy (ATR-IR) was found to be an efficient, fast and low-cost approach for the characterization of plasma treated polyolefin materials, that can also provide a good indication of the material (or adhesive) bondability. Findings described from the use of ATR-IR were in good agreement with X-ray photoelectron spectroscopy results. On the other hand, surface free energy calculations as well as contact angle measurements were sometimes found to be irrelevant for predicting performance of plasma treated materials. This work has globally shown that an improved comprehension of adhesion mechanisms from the use of surface analysis techniques is a mandatory step for the development of highly reliable adhesive joints made of a plasma treated material.

Research projects aimed at the atmospheric plasma treatment of a variety of thermoplastic materials, as well as aluminum substrates, are actually under progress at ATC. In parallel, studies dedicated to improve the effectiveness of atmospheric plasma treatments without the use of organic solvents during pre- and post-plasma treatments are also conducted. The main objective of these projects is to facilitate the use of atmospheric plasma sources for adhesive bonding activities in the automotive sector.

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DEFINITIONS/ABBREVIATIONS

ATR-IR	Attenuated total reflectance infrared spectroscopy
LMWOM	low-molecular-weight oxidized materials
MeOH	Methanol
SLS	Single lap shear
XPS	X-ray photoelectron spectroscopy