

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

2011-01-0217

Published
04/12/2011

Danick Gallant and Véronique Savard
Aluminium Technology Centre

doi:10.4271/2011-01-0217

ABSTRACT

Atmospheric pressure plasma sources are new devices for modifying the surface condition of engineering materials such as thermoplastic and thermoset-based composites. Because they operate at ambient conditions, these plasma systems can be used on a production line as a pre-treatment solution prior to painting or adhesive bonding to significantly improve adhesion strength. However, their efficient use requires sound understanding on how they modify the surface state of materials and, by the same token, how these modifications can be detected and quantified as regards their ability to provide high-strength adhesive joints. Polypropylene, since it is one of the most difficult-to-bond thermoplastic polymers and, at the same time, one of the most interesting polymers for the automotive industry (due to 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 polypropylene surface modifications using two plasma systems was tested on adhesively bonded aluminum-polypropylene hybrid assemblies. Once pre-treated using atmospheric plasma sources, the polypropylene surfaces were also analyzed 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 using surface science approaches, the role of surface and adhesive chemistries in providing semi-structural adhesive joints was

determined. 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 mechanisms of plasma-processed polypropylene are also presented.

INTRODUCTION

Due to its 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 must be pretreated, which provides appropriate chemical polar functionalities and other surface features that enhance 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 have technical characteristics that limit their use in the automotive sector. For example,

although often claimed as the most efficient treatment, low-pressure plasma requires a vacuum chamber, which limits the size of parts that can be treated. Moreover, the extended exposure time of the polypropylene parts, as well as pump-down time, hold-time and re-pressurization time make the full plasma treatment process under low-pressure conditions too slow for most manufacturing industries. To overcome the intrinsic limitations related to the use of low-pressure plasmas, and aiming to maintain 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, have virtually no limits as to the nature, shape, size and thickness of parts. Furthermore, their robotic automation is a major advantage yielding efficient control of the processing parameters. A comprehensive review of the technical principles behind atmospheric pressure plasmas is found in Tendero et al. [1].

Although atmospheric plasma sources possess evident and promising features, their use for the surface treatment of both aluminum and polypropylene materials in engineering hybrid assemblies has not yet been reported. Indeed, atmospheric plasma sources can be used to replace primers, organic solvents, and other chemicals traditionally used in the pre-treatment steps of both aluminum and thermoplastic materials. Ongoing studies on the plasma pre-treatment of polypropylene have already produced results concerning the applicability of these technologies as pretreatment solutions prior to adhesive bonding. Therefore, the aim of this paper is to systematically describe to which extent new plasma technologies can be applied to polypropylene to make it bondable using adhesives that perform well with aluminum. To this end, the influence of processing parameters on the wettability and surface chemistry induced onto surfaces of plasma-processed materials is discussed. To overcome expensive and time-consuming X-ray photoelectron spectroscopy surface analyses, the usefulness of attenuated total reflectance infrared (ATR-IR) spectroscopy for assessing surface treatment quality is investigated. Finally, ATR-IR spectroscopy is also used to determine the relative contribution to adhesion of surface chemistry and surface wettability.

EXPERIMENTAL METHOD

MATERIALS AND SURFACE TREATMENTS

Materials

The polypropylene substrates (monomer: $\text{CH}_2=\text{CH}-\text{CH}_3$) with 24 MPa tensile strength, 59 % crystallinity percentage, and 0.905 density were acquired 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 treatment

The Atomflo™ plasma was initiated and maintained by supplying an RF excitation frequency to the electrodes. The primary gas was He at a 30-L/min flow rate, while O_2 and N_2 (water-free) were used as secondary gases at flow rates ranging from 100 to 500 mL/min. The RF power was adjusted according to the gas mixture: 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 used, and samples were processed 3 mm downstream from the showerhead. Figure 1 shows a photograph of the Atomflo™ torch during treatment of a polypropylene coupon.

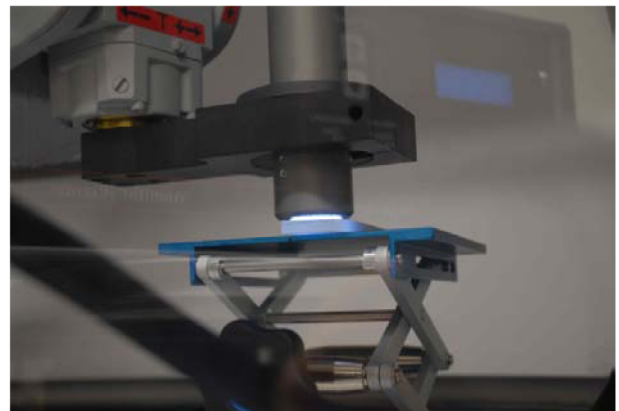


Figure 1. Atomflo™-250 plasma source moved over a polypropylene surface using the Motoman robot.

Openair® plasma treatment

Openair® plasma treatments were carried out using an RD1004 nozzle controlled by an 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 processing polypropylene samples in a single pass. In contrast with the Atomflo™ system treatments, the coupons were moved under the plasma head using the robot (the plasma head was kept stationary). Exposure to the plasma

shower ranged from 0.2 to 14 seconds. [Figure 2](#) shows a photograph of the Openair® jet during treatment of a polypropylene part.



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

Flame treatment

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 through the flame at a rate of 20 m/min. The distance between the visible blue tip of the flame and the polypropylene surface was set to 5 mm. The flame was ignited by exposing a pre-mixed 230 L/min of filtered compressed air with 22.1 L/min natural gas flow to an electric spark. Considering the average volumetric composition of the natural gas delivered at the ATC building, such a mixture contains 10 % excess 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).

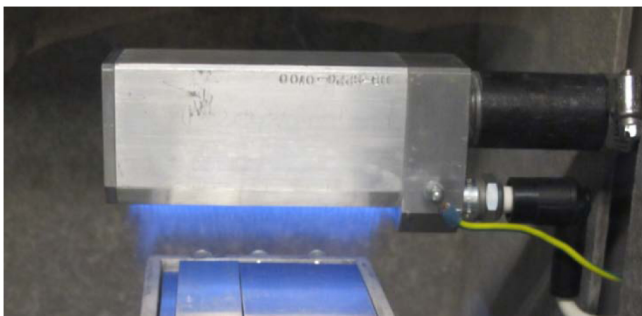


Figure 3. Enercon Industries Dyne-A-Flame™ DFE-300 flame treater.

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 the 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 of the surface treatment.

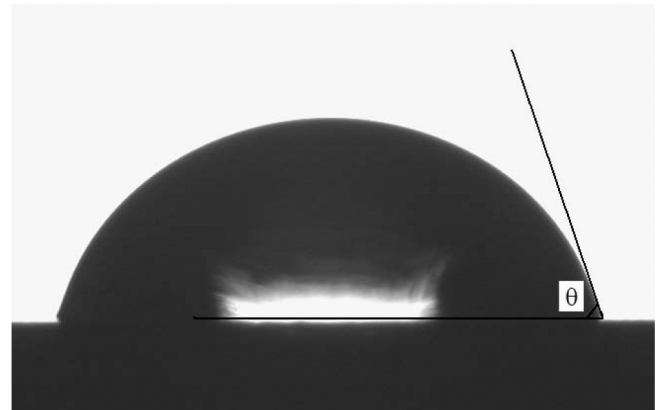


Figure 4. Contact angle made by a liquid drop on a solid surface.

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, and 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 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 one most often applied to 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 advancing contact angle can be expected to yield 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). 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]:

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

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 μm. By comparison, the use of a diamond crystal ($n_1 = 2.4$) allows probing to a depth of 196 μm at the same wavenumber. Thus, using a diamond crystal for the investigation of upper surface modifications attributable to plasma treatments would introduce numerous artifacts to the ATR-IR spectra. Figure 5 shows ATR-IR spectra recorded of an acetone-degreased polypropylene coupon (non-plasma-treated). As shown, quite strong absorption bands, attributable to additives added to polypropylene, are observed with the diamond crystal. The fact that these absorption bands are not detected with Ge crystal reveals that diamond reaches a far greater depth within the material than Ge.

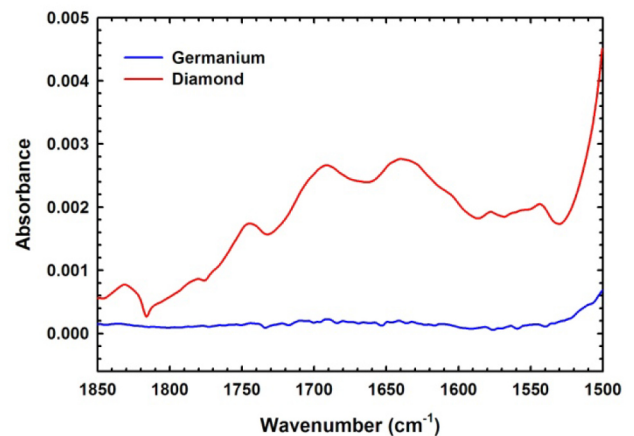


Figure 5. Influence of the crystal on the ATR-IR spectra of polypropylene recorded in the carbonyl (C=O) region.

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 bond line thickness was 1.0 mm and a 25 mm long × 25 mm wide overlap was employed. Prior to SLS specimen assembling, aluminum 6061-T6 strips were acetone degreased, abraded using a 3M Scotch-Brite™ 7447B general purpose hand pad, and primed with Cytec BR6747-1. This surface preparation was found to be sufficient to inhibit aluminum-adhesive interfacial failure. 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](#)).

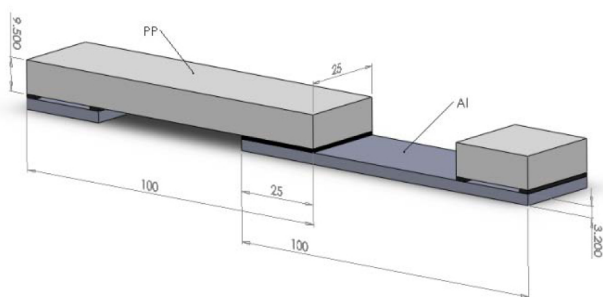


Figure 6. Typical single-lap-shear assembly used to evaluate the joint strength of aluminum-polypropylene hybrid specimens (dimensions are in mm).

RESULTS AND DISCUSSION

INITIAL SELECTION OF THE ADHESIVE FAMILY TO INVESTIGATE

Although polyolefin bonders that can efficiently bond polypropylene and polyethylene with minimum surface preparation exist today, these adhesives are not formulated for aluminum. Parallel to the development of polyolefin adhesives in recent years, atmospheric plasma technologies have emerged and are today increasingly used in many

industrial sectors. Therefore, the approach proposed in this study is to concentrate on polypropylene surface preparation while keeping that of aluminum at minimum using adhesive chemistries recognized for their ability to bond aluminum. Polypropylene coupons were flame treated prior to their assembly to aluminum to select the most relevant adhesive family for this study. Flame treating was first developed in the 1950s to improve the wetting and adhesion properties of polyolefin films. Therefore, there is a large amount of data in the scientific literature on the optimum flame processing parameters. [Figure 7](#) shows the XPS spectra obtained for polypropylene before and after flame treatment under the conditions described in the Experimental Method Section. As demonstrated using a deconvolution procedure, the flame introduced various oxidized carbon species (C-O, C=O, O-C-O, O=C-O) to the polypropylene surface (Strobel et al. [11] proposed an oxidation mechanism for the flame in contact with polypropylene). [Figure 8](#) shows the strength of SLS joints made of aluminum and flame-treated polypropylene, and assembled with 25 different adhesives belonging to three different families. All adhesives used are two-component systems that 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 involved systematically examining atmospheric plasma treatment parameters that can increase the strength of such bonded joints. Based on the results in [Figure 8](#), the epoxy adhesive E1 was chosen for this purpose.

METHODS FOR QUALITY CONTROL OF PLASMA-PROCESSED SURFACES

Determination of optimum plasma treatment parameters from contact angle measurements

Plasma-processed surfaces, before being assembled, must be subjected to a quality control inspection. As described above, in the field of adhesive bonding, the concept of surface free energy (and by extension the wettability) 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 to achieve 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 plasma treated under different conditions. [Figure 9](#) shows how the power of Atomflo™ He/O₂ and He/