

Accepted Manuscript

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PII: S0257-8972(19)30315-9

DOI: <https://doi.org/10.1016/j.surfcoat.2019.03.047>

Reference: SCT 24460

To appear in: *Surface & Coatings Technology*

Received date: 6 November 2018

Revised date: 23 February 2019

Accepted date: 20 March 2019

Please cite this article as: C. Mandolino, Polypropylene surface modification by low pressure plasma to increase adhesive bonding: Effect of process parameters, *Surface & Coatings Technology*, <https://doi.org/10.1016/j.surfcoat.2019.03.047>

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Polypropylene surface modification by low pressure plasma to increase adhesive bonding: effect of process parameters

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Abstract

The purpose of this study is to evaluate the effect of a cold plasma surface treatment of polypropylene substrates with the aim of increasing their adhesion characteristics.

These substrates were treated with plasma, using different process parameters such as power, time and working gas. The effect of the treatment has been studied through a surface characterization, analyzing the chemical species created on the topmost layer of the substrates thanks to the plasma treatment and evaluating the surface energy, through contact angle measurements.

Then, untreated and plasma treated samples with various parameters were used to create single overlapping bonded joints and evaluate the effect of the surface treatment on the mechanical characteristics of the joints.

Experimental results show that plasma treatment is an effective treatment for the surface preparation of polypropylene adhesive bonding. In fact, the increase in surface energy and the formation of chemical bonds between oxygen and carbon have favored the adhesion, thus increasing the mechanical strength of the joint.

Keywords: cold plasma treatment; adhesive bonding; polypropylene; surface energy; XPS.

1. Introduction

In recent years, thermoplastic polymers have been widely used in a variety of industrial manufacturing applications [1]. Polypropylene (PP) is a versatile polymer due to its low cost, good workability and good mechanical properties; it is used in many applications such as membranes, fibers, slit strips, packaging, interior furnishings for vehicles [1], [2]. The polypropylene structure is responsible for its chemical inactivity; for this reason, polypropylene is strongly hydrophobic and poses difficulties for surface modification.

Structural bonding is one of the most effective methods for joining polymeric components, where it is necessary to guarantee good mechanical strength, both static and dynamic, thus minimizing weight. On the other hand, polymers are usually more difficult to bond compared to metal substrates because they are characterized by a low surface energy. However, even with these potential difficulties, adhesive bonding can be an easy and reliable method of fastening one type of plastic to itself, to another plastic, or to a non-plastic substrate [3][4].

Several characteristics of thermoplastic resins can affect their joining capability. For instance, additives and mold release agents are often used in the formulation, the properties of the surface, such as surface energy and crystallinity, may be different from the bulk and thermoplastics are very influenced by the environmental conditions. This is especially true of the crystalline thermoplastics such as polyolefins, linear polyesters, and fluoropolymers. With the growing interest in bonding technology, therefore, changing the surface characteristics of materials has become a central theme in a wide variety of industrial manufacturing. Thus, physical or chemical modification of the surface is sometimes necessary to achieve acceptable bonding [5].

Wettability and adhesion characteristics are among the most studied research topics, since these factors strongly affect the success of a surface treatment prior to bonding, for the short-term and long-term performance of the joints. Wettability and surface energy of the substrates with respect to the adhesive is critical for the formation of secondary bonds in adsorption theory. In fact, it has been theoretically verified that for complete wettability (i.e., for a contact angle equal to zero), the surface energy of the adhesive must be less than the surface energy of the substrate [6][7]. Therefore, the primary objective of a surface treatment is to increase the surface energy of the adherend as much as possible.

This leads to the need for surface treatment of the pieces to be joined and cold plasma plays a significant role in this. It is often used to improve the quality of polymers through cleaning processes (removal of surface contaminants) and activation (formation of new surface chemical groups), increasing adhesion and wettability [7]–[14].

A number of surface preparation methods, including flame, chemical, plasma, and primer treatments are in use. In particular, the chromic acid etch method, similar to the sulfuric-chromic acid (FPL) etch developed for treating aluminum, had been recognized as one of the most effective ways of surface treating polyolefin parts [15]. Recently, plasma treatment has been recognized as an effective surface treatment for polyolefins when high bond strength is required [16]–[20].

Concerning this aspect, ASTM D2093 [21] (reference standard for surface preparations of polymeric substrates before bonding) advises a mechanical abrasion or a chemical treatment with sulfuric dichromate acid for polyolefins.

The opportunity to use a physical and non-chemical method, such as low-pressure plasma (LPP), also allows the undoubted advantage of complying with the strictest environmental policies. Many studies have been carried out on the effects of plasma on the surface characteristics of polypropylene substrates [13], [22]–[24], but little is known about the correlation between these characteristics and the shear strength of the bonded joints, which is the most common stress present during adhesive-joint exercise. In particular, no statistical correlation has been established between the surface characteristics and the mechanical characteristics of shear strength of bonded joints between rigid substrates.

This paper presents an in-depth experimental and statistical study that evaluates the effect of a LPP treatment of polypropylene substrates with the aim of increasing the mechanical properties of adhesive bonded joints. LPP was chosen because it allows a better control of the processing parameters, and this guarantees high consistency and reproducibility in results. For this purpose, untreated and plasma treated samples with various parameters were used to create single overlapping bonded joints and evaluate the effect of the surface treatment on the lap shear strength of the joints.

The effect of the variation of the main treatment parameters on mechanical characteristics was correlated to a surface characterization, analyzing the chemical species created on the topmost layer of the substrates through an X-ray Photoelectron Spectroscopy (XPS) analysis and evaluating the surface energy, through contact angle measurements.

2. Materials and methods

The purpose of this study was to investigate the effects of LPP parameters on the mechanical behavior and adhesion characteristics of polypropylene (PP) samples. In particular, the correlation between shear strength of bonded joints and surface modification provided by the plasma to the above samples, was assessed through a lap-shear test analysis along with the evaluation of the contact angle and a survey of the chemical composition of the surface of the substrates.

2.1. Materials

The study focused on a neutral polypropylene as substrate, therefore without any additives, 2 mm-thick, provided by Total Petrochemicals with the trade name of PPC 5560 and from now on reported as PP. Table 1 reports the main mechanical and thermal characteristics of the substrates.

Mechanical properties	PP
Yield stress (MPa)	25
Elongation at break (%)	6
Tensile modulus of elasticity (MPa)	1300
Charpy impact strength (kJ/m ²)	13
Rockwell hardness (R scale)	85
Thermal properties	
Melting point (°C)	165
Heat deflection temperature (°C)	50

Table 1. Mechanical and thermal properties of the substrates used for the tests [25]

A two-component epoxy adhesive, 3M™ DP490, was used to manufacture the adhesively bonded joints, Table 2 lists some of its main technical characteristics.

	Base	Accelerator
Specific Gravity	1.00	1.00
Consistency	Non-sag paste	Non-sag paste
Mix Ratio By Weight	100	50
By Volume	100	50
Colour	Black	Off - White
Work Life	1.5 hours at 23°C	
Time to Handling Strength	4 to 6 hours at 23°C	
Time to Full Strength	7 days (test to full performance at one week)	
Shelf Life	15 months from date of despatch by 3M when stored in the original carton at 21°C (70°F) & 50 % Relative Humidity	

Table 2. Technical data of the epoxy adhesive used for bonding

2.2. Surface treatment

The entire surface of each adherend was first cleaned with acetone and then differently treated with plasma, except for one set of degreased-only control samples (nominated as S in the following graphs), which were employed as a reference for mechanical and surface evaluations. As regards the PP samples treated with Low Pressure Plasma (LPP), a Tucano (Gambetti Kenologia, Italy) plasma device, powered by an RF generator operating at a frequency of 13.56 MHz, was used. Such preparation was carried out varying the main working parameters, i.e. power, time and process gas. In particular, two extreme and one intermediate values were selected for both power and treatment time, in order to carry out a detailed analysis of the effects of the plasma as the treatment parameters changed. In this investigation, air and oxygen were used as process gases: indeed, air is the most economic choice, whereas oxygen is well known for its strong activating properties towards polymers [26], [27]. The gas flow rate was kept constant at 0.025 SLM, as was the process pressure, set at 0.1 mbar. Table 3 shows a summary of all the treatments performed.

Surface treatment	Description		
Degreasing (S)	Acetone wiping		
Plasma	Acetone wiping + LPP (with different set-up parameters)		
Set-up parameters	Power input (W)	Exposure time (s)	Gas
	50, 125, 200	5, 180, 300	Air, Oxygen

Table 3. Surface treatment performed in this study

2.3. Bonding procedure and lap shear test

Rectangular specimens of dimensions 100 mm × 25 mm × 2 mm were first cleaned using acetone. Then the various surface preparations described in table 3 were performed. The specimen geometry and test conditions followed the ASTM D3163 standard [28]. Adhesive was applied to the faying surface of each substrate, covering an area of 12.5 mm × 25 mm (figure 1). To align the test samples during the assembly, comb polytetrafluoroethylene equipment was used. The same equipment ensured a constant adhesive-layer thickness equal to 0.5 mm. After bonding, each sample was subjected to a uniform pressure of 1300 Pa over the entire surface in order to maintain the flatness required during the curing of the adhesive. Excess adhesive was removed from the edges. Then, a 7-day cure time was performed at room temperature, as suggested by the manufacturer, to ensure complete cross-linking and maximize the mechanical characteristics. Lap shear tests were performed to evaluate the influence on mechanical characteristics of bonded joints due to adhesion-property variations caused by plasma treatment. The test was performed using an Instron test machine at a test speed of 1.3 mm / min. For each set of treatment conditions, five measurements were performed and the mean value was taken as shear strength.

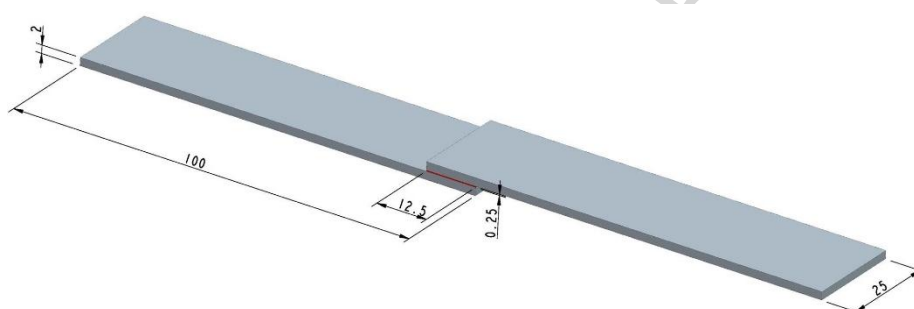


Figure 1. Single overlap joint configuration according to ASTM D3163

Each shear strength value was calculated by referring to the real bonding area of each sample. To understand the repeatability of plasma treatment, the percentage standard deviation was also calculated.

2.4. Evaluation of contact angle and surface energy

The surface free energy (SFE) of the adherends was estimated by measuring the contact angle formed on the substrates by two probe liquids, deionized H₂O and diiodomethane (CH₂I₂), whose γ_{lg}^p (polar component) and γ_{lg}^d (dispersive component) are reported in table 4.

Liquid	γ_{lg}^d [mN/m]	γ_{lg}^p [mN/m]	γ_{sg} [mN/m]
Water	21.8	51	72.8
Diiodomethane	50.8	0	51

Table 4. Characteristics of the two liquids used for static contact angle evaluation

The angle was measured by projecting an image of a sessile drop deposited on the substrate surface using a THETA LITE optical tensiometer (Attension - Biolin Scientific). Once the sample has been placed on the support, a droplet of constant volume (3 μ l for H₂O and 2 μ l for CH₂I₂) was deposited on the substrate surface by means of a micro-syringe. The image was processed by using the affiliated software, OneAttension, which provided a view of the distension of the drop on the substrate and the values of the angles in real time.

For each sample, ten readings were taken at different portions of the top surface and an average was determined.

A correlation between contact angle and surface energy of the substrate was obtained using Wu's energy model [6].

$$\gamma_{lg}(1 + \cos \theta) = \frac{4 \cdot \gamma_{sg}^d \cdot \gamma_{lg}^d}{\gamma_{sg}^d + \gamma_{lg}^d} + \frac{4 \cdot \gamma_{sg}^p \cdot \gamma_{lg}^p}{\gamma_{sg}^p + \gamma_{lg}^p} \quad (1)$$

The total SFE is the sum of the dispersive γ_{sg}^d and the polar γ_{sg}^p contributes, which can be deduced using two different probe liquids, having both the polar and dispersive components of γ_{lg} known, and measuring the respective contact angle formed on the surface studied: from the system of equations obtained, thus, it is possible to find the two components sought and, consequently, the total surface energy of the sample.

2.5. X-ray Photoelectron Spectroscopy (XPS)

The surface functionalization of the plasma modified PP substrates was analyzed using X-ray photoelectron spectroscopy (XPS). The XPS Kratos Axis UltraDLD instrument was used to perform the analyses. It is equipped with a monochromatic Al K α source (1486.6 eV), operating at 15 kV and 20 mA. For the correct insertion into the vacuum chamber, samples of dimensions 10 mm x 10 mm were made. The area actually subjected to the survey was 700 μm x 300 μm .

Through the software CasaXPS, the spectra were acquired in survey mode, i.e. at low resolution, over the entire range of available energies. All spectra were calibrated with reference to the peak C1s, which was centered at a value of E_b equal to 284.8 eV (C-C bond). During data acquisition, a Kratos charge neutralization system was used.

Since the objective of the study is an optimization of the plasma treatment to increase mechanical properties of adhesive bonded joints, the surface investigation focused on the most significant samples, selected on the outcome of the other tests. The only-degreased sample was used as a reference to evaluate the surface chemical modifications brought about by LPP treatment.

2.6 Statistical analysis through Pearson correlation coefficients

Pearson correlation coefficient [29], [30] is often used in statistic to establish relationship among variables. It could be calculated as:

$$PCC = \frac{cov(\alpha, \beta)}{\sqrt{var(\alpha) \times var(\beta)}}$$

Where $cov(\alpha, \beta)$ is the covariance, $var(\alpha)$ is the variance of α and $var(\beta)$ is the variance of β .

The values that this coefficient can assume are between -1 and 1, and in particular, the extreme values represent a perfect inverse (-1) or direct (1) correlation. On the contrary, when 0 or values close to it are found, the correlation is very weak and therefore the two variables can be considered independent.

In this study, Pearson correlation coefficients, were used to understand the influence of the different parameters on the shear strength values. In particular, quantitative correlations between the main process parameters and surface wettability were assessed. Furthermore, the effect of surface changes (mainly surface energy and chemical state) on lap-shear tests results were established, in order to understand the significance of those changes.

3. Results and discussion

3.1. Effects of plasma parameters on shear strength

In Fig. 2, shear-strength trend is plotted as a function of power and treatment time, for the two process gases; error bars indicate the standard deviations of the results. Table 5 reports the increase in shear strength for each parameter set and a focus on the failure mode observed in the tested samples.

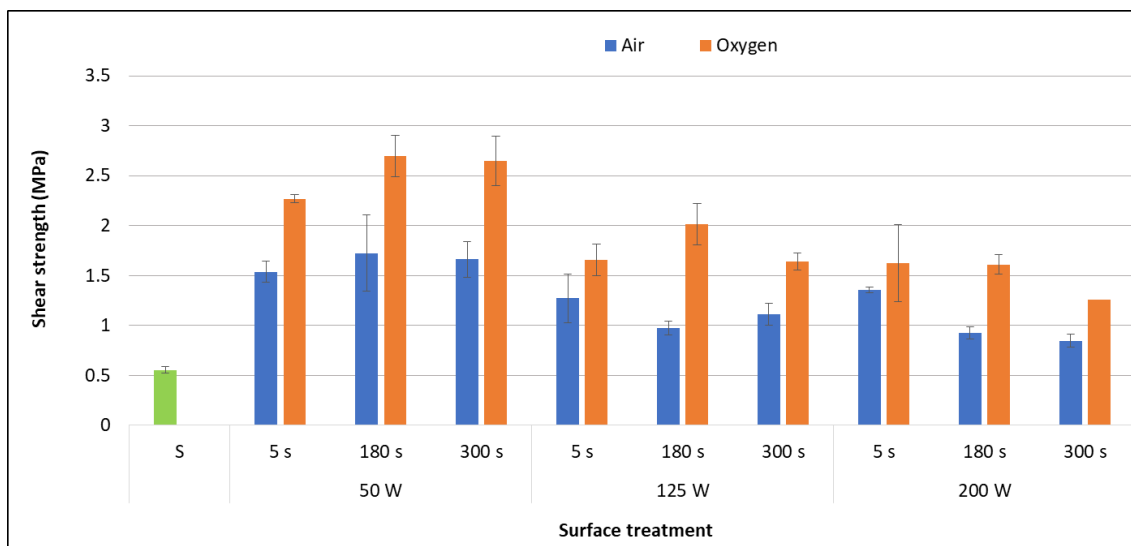


Figure 2. Shear strength as a function of the different plasma-treatment parameters

Surface treatment		Shear strength increasing (%)	Failure mode	
Degreasing		Reference (0)	Adhesive	
Plasma treatment				
Air	50W 5s	177	Partially cohesive	
	50W 180s	211	Cohesive	
	50W 300s	200	Cohesive	
	125W 5s	129	Partially cohesive	
	125W 180s	76	Adhesive	
	125W 300s	100	Adhesive	
	200W 5s	144	Partially cohesive	
	200W 180s	67	Adhesive	
	200W 300s	53	Adhesive	
	Oxygen	50W 5s	309	Substrate
		50W 180s	387	Substrate
		50W 300s	378	Substrate
125W 5s		199	Cohesive	
125W 180s		263	Cohesive	
125W 300s		196	Cohesive	
200W 5s		193	Partially cohesive	
200W 180s		190	Partially cohesive	
200W 300s		127	Partially cohesive	

Table 5. Increase in shear strength and failure mode for each parameter set

As shown, independently from the process gas used, shear strength of the adhesive-bonded joints made after plasma treatment on the PP substrate is significantly higher than that obtained from joints with only-degreased surfaces. However, statistical analysis - performed by using Pearson correlation coefficients and reported in Table 6 - demonstrated that, for both air and oxygen, power input is the most influential parameter on the shear strength. In particular, an inverse relationship between the treatment power and mechanical performance of the bonded joints exists: considering the air-case, maximum resistance was obtained using a 50W-power input, for any treatment duration, producing an improvement of the mechanical response to shear of more than 200%. On the contrary, when the maximum power input (200W) was adopted, the lowest values were

obtained, although they were still higher (+53% in the worst case) than that presented by the reference (0.56 MPa). A similar trend was also detected when oxygen-plasma was adopted, for which the maximum increment in the shear strength (+387%) was obtained with the 50W-180s parameter set. A possible explanation could be that high values of power input lead to saturation of chemical bonds; despite having, as shown in the following paragraphs, a large number of polar groups, they present less open bonds available to the interaction with the adhesive.

Parameter	Working gas	
	Air	Oxygen
Power input	-0.798	-0.894
Time	-0.257	0.028

Table 6. Pearson correlation coefficients on shear strength

Moreover, observation of the fracture areas confirmed that mechanical performance of the joints differently treated is strictly related to the failure mode presented: generally, the best mechanical results were obtained where a complete cohesive failure occurred, meaning that strong adhesive conditions (i.e. strong chemical bonds) were generated between the PP-adherend and the resin. Effectiveness of LPP treatment was particularly emphasized by a low-powered oxygen-plasma, whose adoption resulted in a substrate failure, proving that the overall adhesive-system resistance did overcome the intrinsic strength of the adherend material.

Similar results on polypropylene, both in terms of shear strength improvement and failure mode were obtained by Encinas et al. [31] using an atmospheric plasma (APPT): lap-shear strength on adhesive bonded joints revealed an important enhancement of tensile strength of about 500%, when the APPT treatment was employed.

The study by Pandiyaraj et al. [24] on polypropylene films confirms the expected use of a vacuum plasma to increase T-peel and lap-shear strength.

3.2. *Effects of plasma parameters on surface wettability and surface energy*

Surface wetting and adhesion properties are related aspects, especially for polymer surfaces. Evaluating wettability properties of both the untreated and plasma-treated PP-surfaces, it is possible to state that neither deionized H₂O nor diiodomethane exhibited low contact angles on the control surfaces. These results are indicative of the non-polar, hydrophobic behavior of the polyolefin, which is the main cause of the poor-adhesion problems associated with this type of polymers.

As expected, any kind of plasma treatment, for both air and oxygen, made the PP substrate more wettable, consequently decreasing contact angle and increasing surface free energy, as fig. 3 reports.

The values obtained by plasma treatment are between a minimum of 112% up to a maximum of 251% compared to the surface energy of the control sample. Furthermore, the moderate standard deviation, represented by the error bars in fig. 3, confirms the reliability of the process.

However, the two gases present different trends. Using air as process gas, significant results could be obtained mainly increasing the power input to 200W. Use of oxygen significantly increases the surface energy for low power input values, while, for 200W of power input, the improvement reached is slight if compared to untreated samples.

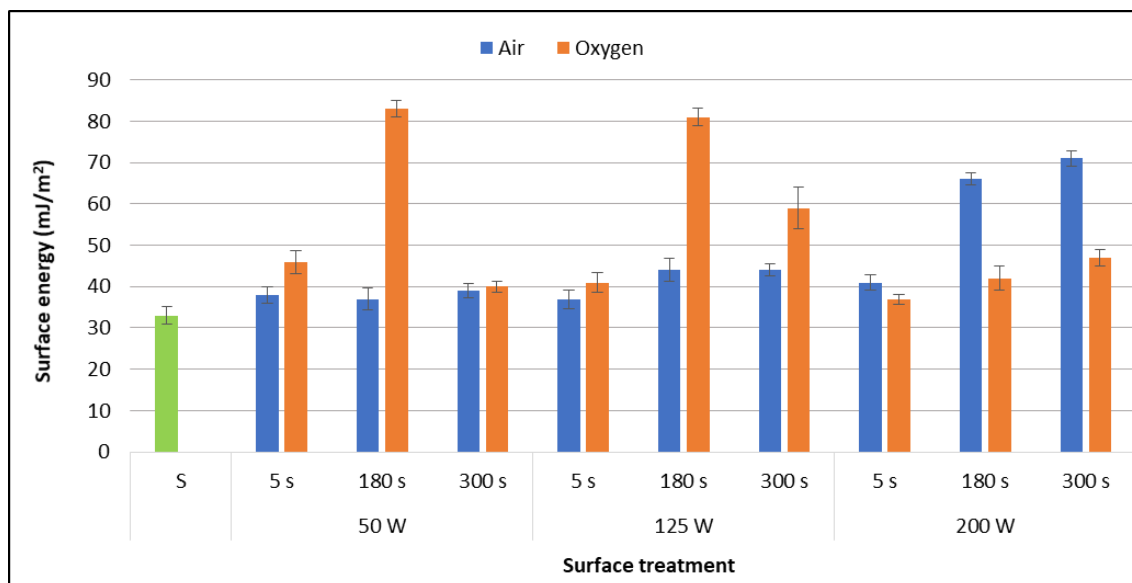


Figure 3. Surface energy of different plasma treatment

The values of SFE obtained are in agreement with the results previously reported for other polymers, using both vacuum [32] and atmospheric pressure plasma [13], [16], [33].

Table 7 reports the statistical analysis performed to understand the influence of process parameters on surface energy. According to that observed for shear strength of bonded joints, the most effective parameter is the power input, especially using air as process gas.

Parameter	Working gas	
	Air	Oxygen
Power input	0.716	-0.351
Time	0.439	0.250

Table 7. Pearson correlation coefficients on surface energy

Also in this case the behavior of the gases is different: using air, power input has a direct proportionality, while oxygen requires low power input values, as highlighted by the inverse proportionality.

The enhancement in surface energy is usually correlated to chemical changes on the topmost layer of the polypropylene due to plasma treatment, which makes the surface hydrophilic relative to the untreated one. This is found to be an effect of plasma treatment on several polymers [34][35][36]. In particular, the forces regulating the wetting behavior of organic substrates do not originate only from the chemical composition as it is, but rather from the surface groups created with plasma treatment.

For this reason, a further investigation of the chemical species originated on the samples was carried out, focusing on the effect of power input, which has proved to be a key factor for both shear strength and surface energy, keeping the exposure time fixed.

3.4. XPS investigation

The XPS technique was used to elaborate the results obtained by contact angle measurement and lap shear tests. A quantitative evaluation of the changes in the atomic concentration in the PP surfaces as a function of exposure time is summarized in Table 7.

As mentioned above, chemical analysis of the plasma-treated samples was carried out on the substrates exposed to the plasma at different powers for the same treatment time, equal to 180 s.

Treatment			Elemental ratio	
Power Input (W)	Time (s)	Gas	O/C ratio	N/C ratio
0	0	0	0.062	0.046
50	180	Air	0.220	0.125
50		Oxygen	0.156	0.087
125	180	Air	0.164	0.083
125		Oxygen	0.142	0.059
200	180	Air	0.137	0.078
200		Oxygen	0.131	0.048

Table 8. Surface elemental composition and elemental ratio of the plasma-treated polypropylene substrate for different process parameters.

The quantitative data confirm that plasma treatment with both gases caused an increase in the oxygen and nitrogen contents and a simultaneous carbon-content decrease. This shows that oxygen and nitrogen components are introduced into the PP surface after plasma treatment. In particular, table 8 reports the elemental ratio of O1s/C1s and N1s/C1s of the untreated and plasma-treated PP substrates.

These ratios have increased in treated samples, and their maximum was reached with the lowest power input, which actually corresponds to the highest values of surface energy. This could be attributed to the increase in the newly formed functional groups by the LPP, as clear from the data derived from high resolution XPS spectra of PP substrates, reported in table 9.

Power Input (W)	Contribution of C1s components (%)											
	C-C / C-H		C-N / C-OH		C-O		C-O-C		O-C=O		C=O	
	Air	Oxy	Air	Oxy	Air	Oxy	Air	Oxy	Air	Oxy	Air	Oxy
0	95.7		-	-	-	-	-	-	-	-	4.3	
50	67.31	67.1	16.01	16.48	7.48	6.98	2.04	3.21	3.11	2.75	4.05	3.48
125	73.81	67.45	10.85	14.44	5.69	7.39	3.33	3.65	3.07	3.24	3.26	3.83
200	71.56	67.18	13.24	15.57	5.3	7.76	3.24	3.82	3.47	2.56	3.19	3.11

Table 9. Relative intensity data of the C1s level spectra of control and plasma treated samples for different power inputs

From the analysis of the high resolution spectra it is noticed that the chemical composition of the treated-samples surface is very different from that of the untreated; in fact, all the treated samples present several new peaks between 285.5 and 289 eV compared to the untreated: these peaks describe the presence of various C-O groups on the surface [37]. These results suggest that plasma treatment introduce oxygen-containing functional groups into the molecular chain of PP surface. These polar groups contribute to increasing surface hydrophilicity of the PP substrates [24], [31]. All the treated samples investigated present similar XPS spectra. In particular, fig. 4 compares the spectra of the untreated and the plasma-treated samples, which gave the best results in terms of shear strength.

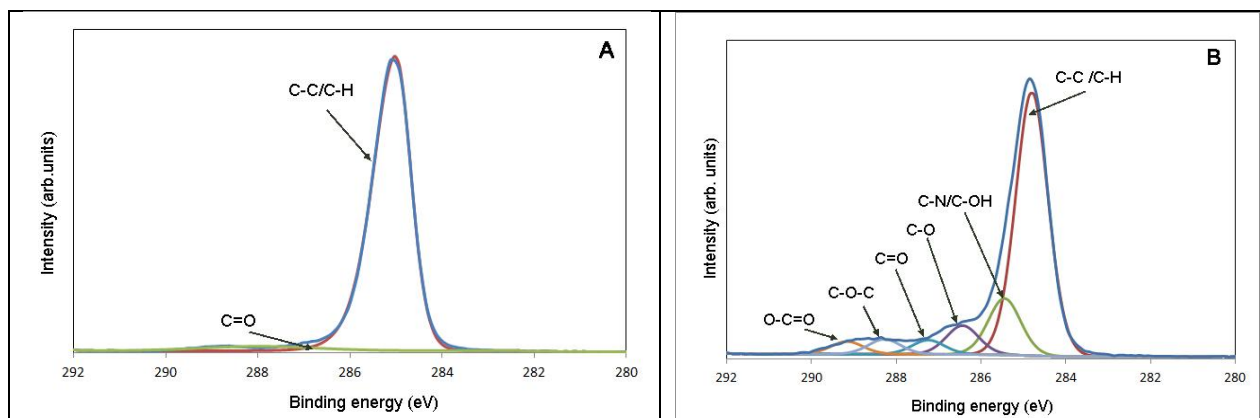


Figure 4. High-resolution C1s spectra of untreated (A) and 50W-180s oxygen treated (B) samples

A statistical analysis, carried out to deepen the influence of the presence of polar groups on surface energy, has made it possible to establish that it is not so much the increase of O1s or N1s values that entail an increase in the wettability of the surface (intimately linked to surface energy), but the creation of some new chemical bonds between oxygen and carbon.

In fact, only a weak correlation relates the increase in O1s or N1s with the surface energy created on the polypropylene surface, as reported in table 10.

Surface characteristic	Pearson correlation coefficients
O/C ratio	0.103
N/C ratio	0.006

Table 10. Pearson correlation coefficients on the surface energy as a response

On the contrary, the influence of the different groups is quite marked (table 11): in particular, the main aspect responsible in surface energy changes are the C-O-C group (when air is used) and O-C=O (when oxygen is used).

The inverse proportionality of the C-C/C-H and C=O groups was quite expected, in fact, these bonds are contained in high percentages on the substrate before the plasma treatment and, as a result of the treatment itself, they are split to give rise to the other bonds.

C1s components	Air	Oxygen
C-C / C-H	-0.460	-0.685
C-N / C-OH	0.450	0.681
C-O	0.322	0.630
C-O-C	0.707	0.602
O-C=O	0.629	0.771
C=O	-0.822	-0.201

Table 11. Pearson correlation coefficients on the surface energy as a response

The relationship between chemical composition and surface energy indicates that plasma treatment, efficiently imparts polar functionalities on the surface, which are strongly correlated to the improvement in SFE increase, reported in a previous paragraph.

The functionalization of polymeric substrates is often reported as an advantage in terms of mechanical behavior, for the beneficial effect on shear [24], [31], [35], T-peel [24], [35] and pull-off tensile strength [38].

3.5. Statistical analysis considerations

Further statistical analysis was then carried out to correlate the plasma-induced surface modification, with the shear strength values.

Table 12 reports the correlation strength between the main surface characteristics (chemical species and surface energy) and the shear strength of the bonded joints as a response, using Pearson correlation coefficient.

Surface characteristic	Pearson correlation coefficients
O/C ratio	0.479
N/C ratio	0.301
SFE	0.238

Table 12. Pearson correlation coefficients on the shear strength as a response

The chemical insertion of oxygen-containing groups is most notably directly proportional resulting in a great effect on the mechanical characteristics of adhesively bonded joints. Moreover, slower correlation strength was exhibited for both the N/C ratio and the surface energy. In particular, as shown in table 13, the main groups, which contribute to the shear strength increase, are C-N and C-OH. The weakest relationship is reported by C-O-C bond, which was the main aspect responsible for surface energy increase. This reminds us how important it is to consider the bonded joint as a system, in which we cannot disregard the various elements involved: not only the surface energy and the substrate chemistry, but also the rheological and polarity characteristics of the adhesive used.

This aspect implies that for this specific adhesive system, made up of polymer substrates, the insertion of polar species creates the optimal interface condition with epoxy adhesive.

C1s components	Pearson correlation coefficients
C-C / C-H	-0.715
C-N / C-OH	0.749
C-O	0.718
C-O-C	0.504
O-C=O	0.716
C=O	-0.111

Table 13. Pearson correlation coefficients on the shear strength as a response

4. Conclusions

Primarily, the tests carried out in this study have highlighted the critical issue of obtaining valid joints by bonding untreated polypropylene pieces, due to the inadequacy of a simple solvent degreasing. Indeed, low surface energy and poor adhesion properties make it necessary to submit the pieces to be joined to accurate surface preparations in order to obtain joints presenting good mechanical performance.

Regarding the results of the wetting analysis, surface free energy and wettability of all the treated samples was therefore greater than that of the untreated sample, from a minimum of 112% (Oxygen – 200W-5s) to a maximum of 251% (Oxygen – 50W – 180s).

The increase in surface wettability is related to the action of the plasma that promotes chain scission on the topmost layers of the polypropylene substrate and this forms free radicals which act as interlock points for polar groups. XPS survey shows that functionalization occurs by insertion of oxygen-based species for both working gases and high O/C ratios.

The increase in wetting properties and surface free energy produces a remarkable increase in mechanical performance of polypropylene bonded joints with an epoxy adhesive. In particular the power input acts as the most effective parameter.

It can be concluded that plasma treatment proved to be an effective solution to obtain good shear strength of joints, especially with the use of oxygen. For certain treatment parameters, failure of the substrate occurred, indicating that the forces involved in the adhesion were greater than the resistance of the substrate itself, which means high plasma efficiency.

Acknowledgments

A special acknowledgment to Dr. Mirko Prato and all at the IIT for the scientific and technical support in the analysis of the polymeric surfaces studied.

The author wishes to thank Dr. Silvia Vicini and Dr. Maila Castellano for their scientific support in the wettability issue.

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

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Highlights

- Plasma treatment proved to be extremely effective on the surface tension, even using low power input.
- In treated samples C-O bonds were identified, absent on the untreated sample.
- ~~Statistical correlation between the different process aspects were established~~
- Statistical correlations between process parameters and surface properties were established.
- Oxygen is a particularly effective working gas.

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