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Development of improved polypropylene adhesive bonding by abrasion and atmospheric plasma surface modifications

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ABSTRACT

The present work deals with the problematic adhesive bonding of substrates with low surface energy. Different approaches have been explored with the aim of creating adequate adhesive joints based on polyolefinic substrate and polyurethane adhesive. The selected material under study was polypropy lene (PP) as adherend, and a commercial Sikaflex® 252 polyurethane one component based structural adhesive (PU) as joint fluid. Among the diverse pre treatments typically used to prepare surfaces prior to bonding, mechanical abrasion with emery paper of 80 grain size, the use of a chemical primer and atmospheric pressure air plasma torch (APPT) were the selected methods to facilitate the application of the PU by means of surface energy enhancement as well as to create a correct mechanical interlocking of the adherent adhesive interface. Changes in the wettability of the polymer were evaluated by contact angle measurements following the UNE EN 828:2010. Surface energy was calculated both in terms of Owens approximation and acid base considerations, leading to the possibility of determining a relationship between changes in surface energy and adhesion. Changes in the chemical composition of the surface were studied by X ray photoelectron spectroscopy (XPS), electron diffraction X Ray (EDX) probe and attenuated total multiple reflection mode infrared spectroscopy (ATR FTIR). Morphological modifications were investigated with scanning electron microscopy (SEM). Variations in the strength of single lap PP PP joints with the treatments were evaluated by lap shear tests following the UNE EN 1465:2008 standard. Experimental evidence supports the superiority of the APPT treatment to increase wettability and adhesion of polyolefinic surfaces, especially when combined with the use of a primer.

1. Introduction

The application of polymeric materials in automotive or aircraft industries results in systems, which offer many benefits, like lightweight, good thermomechanical bulk properties, low cost and recycling [1 4]. These materials are often presented as bonded components [5] enabling to avoid the use of mechanical methods (welding, riveting), which generally lead to stress and failure problems, or surface degradation. In the context of automotive industry, polyurethane based (PU) structural adhesives offer high performance, including chemical resistance, gap filling capability, vibration damping or short curing time [6 8]. PU are known to be one of the most versatile type of polymers, used as foams, coatings, adhesives or elastomers, for example. They are formed by the reaction of isocyanate with hydroxyl, amine, urea/urethane or allophanate groups [9], yielding urethane based compounds, which generally cure under moist conditions to generate elasto meric materials. Tyczkowski et al. [10] presented the main mechanisms involved in the process of sticking polymers, includ ing mechanical adhesion (due to interdiffusion of the adhesive into the polymer), chemical adhesion (based on the creation of covalent bonds) and thermodynamic adhesion, which relied on the surface energy of the substrates [11]. Adhesion on polymeric substrates is hindered by their low surface energy and hydrophobic nature [12 15]. Many approaches on surface treatments based both on chemical or physical modifications have been developed in the recent years [2,16 18]. Physical methods based on mechanical abrasion are supposed to create an extended bonding area as they generate grooves and valleys, but cause a large damage to the treated specimens [12]. On the other hand, chemical treatments are typically used with the aim of modifying both morphology, by means of surface etching or grafting, and the chemical structure of polymers, but they present serious problems of environmental contamination, which have provoked the investigation on the industrial substitution of these processes [13].

In this context, plasma sources represent a fast and environ mentally friendly method to modify polymeric surfaces without affecting bulk properties [19 22]. The action of plasma onto a surface is basically focused on three effects: (a) cleaning by means of pollutants' breakdown, (b) surface etching due to the impact of

the flux and (c) introduction of new functionalities, thanks to the rupture of bonds in the polymers' outermost layer and further reactions with active species (molecules, ions, radicals) existing in plasma. These moieties may also induce a crosslinking process.

Interfacial interactions are an important factor in the prediction of adhesion. The surface energy can be described as a sum of a polar and a dispersion contribution

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

This treatment was considered to obtain the Owens Wendt Rable Kaelble (OWRK) [24] calculation method (Eq. (2)), which enables the determination of the contributions to the total surface energy due to London type forces (dispersion) and the rest of interactions existing in the liquid solid interface such as hydrogen bonding and dipole dipole interaction (polar). In this expression, θ represents the test liquid contact angle onto the surface, γ_l and γ_s are the liquid surface tension and the surface energy, respectively. The superscripts D and P are referred to the dispersive and polar fractions contribution, respectively, to the γ_l and γ_s parameters:

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

A deeper understanding of the adhesion process will be achieved by calculating the thermodynamic work of adhesion required to separate a unit area of two phases in contact [25]. The combination of the Dupré expression [26], which assumes that there is negligible liquid surface area change upon adhesion to a solid surface [27], and Young's equation [28] leads to an expression (Eq. (3)), which allows the prediction of the bonding characteristics of a surface through two experimentally measurable parameters, the liquid tension and its contact angle onto the solid surface [29]:

$$W_A = \gamma_{lv} + \gamma_{sv} \quad \gamma_{sl} = \gamma_{lv}(1+\cos\theta) \approx \gamma_l(1+\cos\theta) \qquad (3)$$

where W_A is the work of adhesion, γ_l is the surface tension or energy of the liquid and θ is referred to the value of the liquid contact angle on the solid surface.

On the other hand, Good et al. [30 32] took the surface energy as the sum of two different fractions, acid base and Lifshitz van der Waals (Eq. (4)), related to specific and non specific interactions, respectively:

$$\gamma_T = \gamma_s^{LW} + \gamma_s^{AB} \qquad (4)$$

While the γ_s^{LW} term comprises three additive parameters (London dispersion, Debye induction and Keesom dipole dipole forces), the term γ_s^{AB} is referred to an electron donor (γ^-) and an electron acceptor (γ^+) factors, which follow the relation shown below

$$\gamma_s^{AB} = 2\sqrt{\gamma^-\gamma^+} \qquad (5)$$

By substitution in the Young Dupré equation [26 29], the total surface energy between a liquid and a solid surface can be expressed as follows (Eq. (6)):

$$\gamma_l(1+\cos\theta) = 2\sqrt{\gamma_l^{LW}\gamma_s^{LW}} + 2[\sqrt{\gamma_l^+\gamma_s^-} + \sqrt{\gamma_l^-\gamma_s^+}] \qquad (6)$$

It is necessary to achieve contact angle data of three liquids, two polar and one of non polar nature in order to obtain the values of the required parameters.

As Dillingham et al. described [33], it is possible to assume a relationship between the acid base interactions and the work of adhesion, thus to predict the functionalities responsible for adhesion by means of contact angle and wettability measurements.

In this paper, single lap joints of PP substrates bonded with a thixotropic PU adhesive (Sikaflex® 252) were obtained by subjecting polymer to treatments of abrasion, application of a chemical primer (Sika Primer® 215), APPT and combination of methods (APPT and the use of primers), in order to achieve an adequate bonding area. The evaluation of the chemical changes achieved by contact angle, EDX, ATR FTIR and XPS measurements showed the special effectiveness of APPT to enhance the surface energy, thus the work of adhesion and the joints' shear strength. Results suggested that the most suitable treatment to improve the adhesion capability of the studied polyolefin was the combination of a primer and APPT.

2. Experimental

2.1. Materials

Experiments were carried out on the surfaces of PP, provided by Ketersa (Spain). Every treatment was preceded by a cleaning process with methylethylketone (MEK) in order to eliminate any possible grease or pollutant particle existing on the surfaces. The selected adhesive was a Sikaflex® 252 (Sika S.A.U., Spain) with one component as PU chemical base. Supplier specifications list a curing speed of approximately 12 h under 23 °C and 50% relative humidity conditions, with a low shrinkage rate (about 6%).

2.2. Surface pre treatments

Mechanical abrasion was performed using emery paper of 80 grain size (hereafter denominated S80). After abrading, an exhaustive cleaning step was necessary due to the amount of detached particles from the sandpaper generated in the process. Plasma treatment was achieved using an APPT set up, described in detail elsewhere [23]. Briefly, the air plasma species were generated by a non equilibrium high tension discharge of 20 kV at a frequency of 17 kHz and expelled through a rotating torch situated at 6 mm distance to the samples. The system speed was set at 0.2 m/s.

Finally, an adequate primer for polymeric surfaces (Sika Primer® 215) was used under three different conditions: (i) application after surface wiping with MEK, (ii) deposition of the primer after subjecting surfaces to APPT and (iii) APPT treatment followed by primer use and further fast curing of the promoter under APPT.

2.3. Calculation of surface energy and work of adhesion through contact angle

The selection of the liquids for the contact angle measurements was done considering a wide range of polarities, including deionised water, glycerol, nitromethane, diiodomethane and 1,5 pentanediol.

Measurements were performed with an OCA 15 plus device from DataPhysics (Neurtek Instruments, Eibar, Guipúzcoa, Spain) using the sessile drop method and following the UNE EN 828:2010 standard.

Electron acceptor and donor characteristics of the surfaces were obtained by substitution of water, glycerol and diiodo methane data in Eq. (6) (Table 1).

Table 1
Surface energy components of the acid–base test liquids.

Liquid	γ_T (mJ/m²)	γ^{LW} (mJ/m²)	γ_i^+ (mJ/m²)	γ_i (mJ/m²)
Deionised water	72.8	21.8	25.5	25.5
Glycerol	64.0	34.0	3.9	57.4
Diiodomethane	50.8	50.8	0.0	0.0

2.4. Morphological and chemical study of the treated surface

The topography of the PP surfaces before (both pristine and treated) and after lap shear tests was analysed with a Philips XL 30 FEI EUROPE SEM microscope (Eindhoven, Holland) with electron beam energy of 20 kV.

Chemical modifications on the outermost surface layer on the pristine and APPT treated samples were analysed both by X ray photoelectron spectroscopy (XPS) and attenuated total multiple reflection infrared spectroscopy (ATR FTIR). The devices are described elsewhere [23], but briefly, they consist of a VG Scientific Microtech Multilab (VG Scientia, Hastings, United Kingdom) spectrometer using a Mg K_{α} X ray source (1253.6 eV) and a Brucker Tensor 27 (Brucker Optik GmbH, Madrid, Spain) spectrometer.

Finally, an elemental analysis of the specimens was performed using the energy dispersive X Ray probe provided in the SEM device.

2.5. Lap shear test

The scheme of the sample geometries used for the tensile single lap shear tests is shown in Fig. 1. The EN 1465:2008 standard was followed, and experiments were carried out with
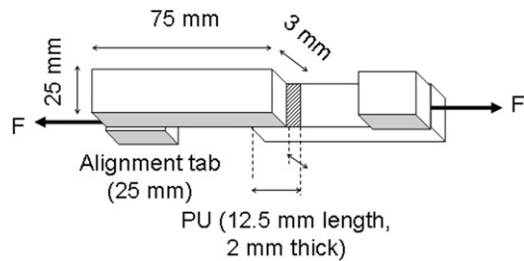

Fig. 1. Single lap joint geometry.

Table 2
Variation of surface energy components (OWRK method) with treatment.

Surface	γ_T (mJ/m^2)	γ_D (mJ/m^2)	γ_P (mJ/m^2)
Untreated	23.01	22.82	0.19
S80 abraded	23.45	22.04	1.40
APPT treated	50.29	21.24	29.05

a 1 kN load cell test machine setting a test speed of 1 mm/min, yielding the lap shear strength results.

3. Results and discussion

3.1. Effects of pre treatments on surface energy

Results of the effects of both mechanical abrasion and APPT treatment on the PP surfaces are published elsewhere [23,34]. Briefly, attending to data shown in Table 2, the S80 sanding process allowed an increase in surface energy of just 2% compared to pristine PP, with an almost negligible variation of the polar fraction. In contrast, when the samples were subjected to APPT, an almost three times higher surface energy was obtained. In this case, changes in total energy were accompanied by an extra ordinary improvement in the polar fraction by a factor of approximately two. Dispersion fraction, due to London type forces, did not suffer remarkable variations.

When the W_A parameter was studied on the as received surface (Fig. 2), results varied in a range of approximately (± 20) mJ/m^2, with an upper value for the almost purely dispersive diiodomethane of 75.9 mJ/m^2, and lower value for glycerol of 57 mJ/m^2. This was in agreement with the non polar character previously described for these types of surfaces, as well as the lower W_A results (all of them located around 60 mJ/m^2) found for the more polar liquids. A very similar situation was achieved when subjecting specimens to mechanical S80 abrasion, with the only difference of the relatively gathered results of W_A corresponding to water, glycerol, nitromethane and 1,5 pentane diol. As it could be inferred from the estimated surface energies (Table 2), the APPT treatment led to materials, which present higher W_A, correlated with higher difficulties to separate a unit area of the liquid solid interface, in other words, better wett ability and thus, adhesion properties. Calculated W_A results for APPT treated samples showed an in line behaviour with the decreasing order of liquid tensions from water to nitromethane. In addition, liquids with greater tension and polar character (water and glycerol) were grouped at the top of the chart, while a difference of approximately 20 mJ/m^2 separated the diiodo methane, 1,5 pentanediol and nitromethane W_A values.

In order to illustrate the type of mathematical relation existing between the surface energy and the W_A data previously shown,
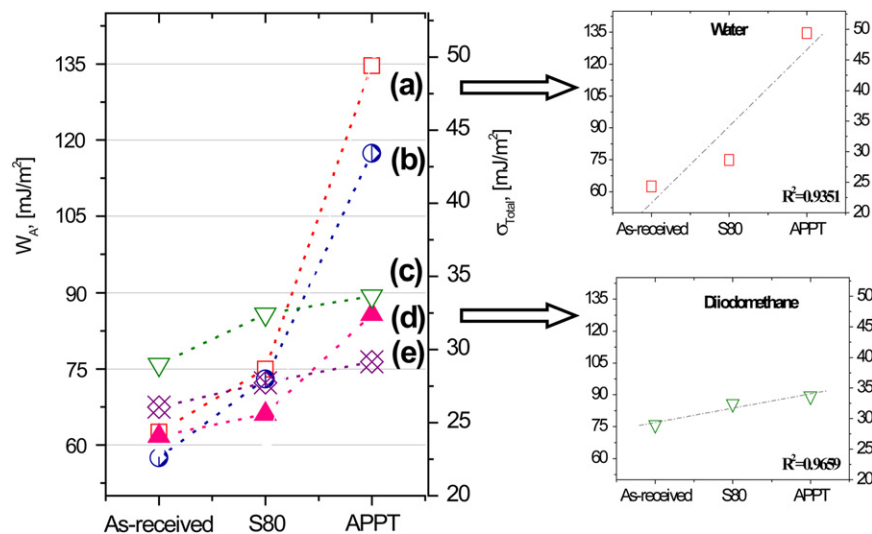

Fig. 2. Estimation of the changes in W_A due to the surface treatments for (a) deionised water, (b) glycerol, (c) diiodomethane, (d) 1,5-pentanediol and (e) nitromethane. Linear relationship between W_A and surface energy of (a) water and (b) diiodomethane is presented in detail.

3

the energy necessary to separate liquid droplets from PP surface under the test conditions (pristine material, S80 abraded and APPT treated) as a function of the surface energy is also shown in detail in Fig. 2 for two liquids, deionised water and diiodo methane. The linear fitting of the plotted data led to correlation coefficients next to one, corresponding to a non diverted and directly proportional relationship, as it was expected.

Previous works of this research group, involving SEM and mechanical profilometry analysis, have shown the impact of diverse surface pre treatments on the morphology of polyolefinic materials [23,34]. While sanding caused a high rate of material pull off, the APPT treatment derived in an affected surface due to plasma etching, with an enhancement in the average arithmetic roughness (defined in the DIN 4768 regulation) from (0.08 ± 0.03) μm to (0.14 ± 0.02) μm. It was also observed that the existence of precipitates containing C, O and Ti attributed to plasma oxidation and catalysts of the materials processing.

FTIR ATR analysis of PP is shown in Fig. 3, marking the band corresponding to each type of functionality by black and white coloured squares and circles. The spectrum of the untreated material exhibited typical polypropylene bands [35], such as the CH_2 and CH_3 stretching vibration mode (white circle, 2831 2949 cm^{-1} zone), CH_3 symmetric and asymmetric bending modes (white square, 1373 and 1462 cm^{-1} zones, respectively) and vibration modes associated to the C C bondings (black square, 1178 848 cm^{-1} zone). After APPT exposure, a new broad band arose (black circle), located at 1718 cm^{-1}. This peak corresponded to carbonyl moieties [36], the appearance of which was indeed in agreement with the APPT enhanced polar energy (Table 1).

The XPS study of the chemical composition of the samples (Table 3) confirmed the insertion of oxygen and nitrogen atoms due to the activation of the PP surface via rupture of C C/C H linkages and further reactions with plasma and environmental species. The great increase of the polar fraction, thus the total component, of the surface energy lies in these radical type processes.

According to the appearance of peaks at binding energies corresponding to the existence of oxygen and nitrogen containing groups, acid base character of the surface was supposed to be modified by APPT. Fig. 4 illustrates the range of values of each component of the PP surface energy, both calculated by the OWRK (Eq. (1)) method (dispersion, polar and total) and obtained by the acid base (Eq. (6)) approximation (acidic, basic and Lifshitz van der Waals). Results of the as purchased surfaces implied the existence of an almost purely dispersive PP (about 1% polar

Fig. 3. FTIR-ATR spectra of PP surface (a) untreated and (b) subjected to APPT.

Table 3
Assignment of XPS C 1s and N 1s core levels of both as-received and APPT treated PP.

Surface condition	Binding energy (eV)	Corresponding chemical group
Untreated	284.6	[–(C–C)–], [–(C–H)–]
	285.6	[–(C–N)–], [–(C–OH)–]
	399.7	[–(R–CN)–]
APPT	284.6	[–(C–C)–], [–(C–H)–]
	285.6	[–(C–N)–], [–(C–OH)–]
	287.7	[–(CO_2)–], [–(C=O)–]
	288.7	[–(C–C(=O)-OH)–], [–(C–C(=O)–OR)–]
	399.7	[–(R–CN)–]
	401.6	[–(N–O)–]
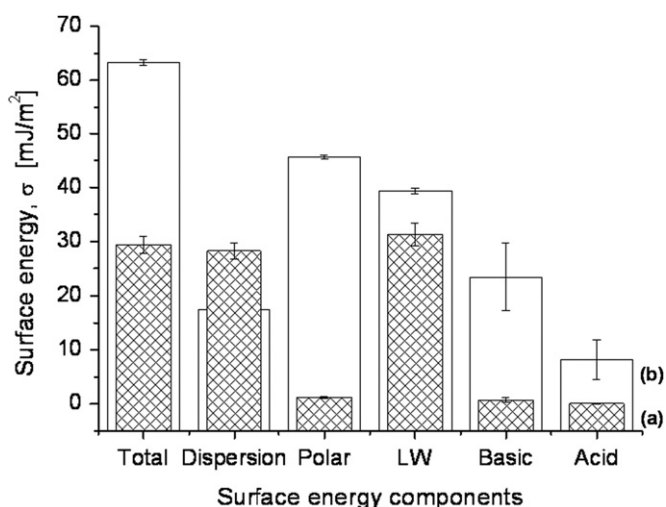
Fig. 4. OWRK and acid–base fractions of the surface energy for a (a) pristine and (b) APPT treated PP.

contribution to the total surface energy), with low wettability and low electron donor and electron acceptor values (0.71 and 0.06 mJ/m^2, respectively). Attending to the principles of wetting and adhesion, it was possible to predict that pristine PP would not yield adhesive joint with PU, due to its lack of active sites susceptible for bonding.

When the samples were treated with APPT, every component related to specific interactions (polar, acid and base) suffered an outstanding improvement of about one order of magnitude. Comparing these results with the ones obtained by XPS (Table 3), it was confirmed that the insertion of [(C=O)], [(C C(=O) OR)], [(R CN)] and [(N O)] type moieties, responsible for the enhancement in wettability, was achieved. Although the electron acceptor fraction of the APPT samples was two orders of magnitude higher than the as received result, surfaces developed an important electron donor character This indicates that most of the groups created by APPT are amine, imine, ketone, ester, ether or alcohol functionalities, which is in agreement with the XPS results (Table 3).

3.2. Lap shear strength tests

3.2.1. Effect of APPT treatment

Once a chemical and physical study of the samples was carried out, a shear tensile test of polyolefinic single lap joints using a PU adhesive (with the characteristics shown in Fig. 1) was per formed. Results of the mean lap shear strength measurements
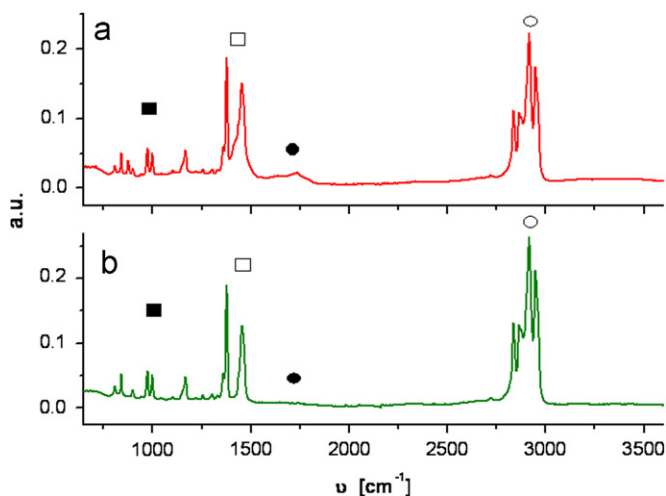
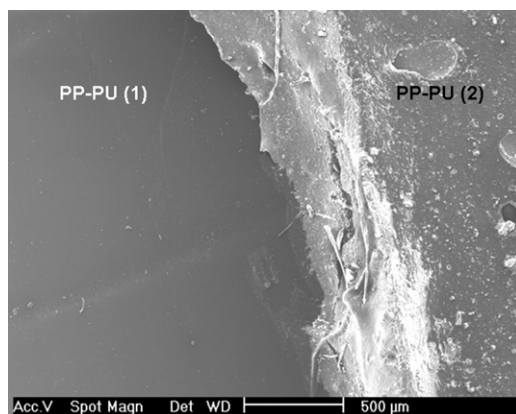for the different pre treatments of the surfaces are shown in Table 4.

The untreated materials showed almost negligible shear values. These data were in concordance with the existence of too few surface anchoring sites due to both the very low surface energy they exhibited and the smooth topography and low porosity of the specimens. The combination of these facts led to the impossibility of the PU adhesive to properly wet the surfaces, thus, create an adequate interlocking between the bonded parts.

An increase in surface roughness was usually associated to a better adhesive strength due to larger anchoring area. Never theless, results showed the inefficiency of mechanical abrasion to enhance adhesion between the PU adhesive and the PP substrates [12], leading to very low values close to the ones found for the untreated samples. In conclusion, mechanical abrasion on PP was dismissed as a surface treatment prior to adhesion.
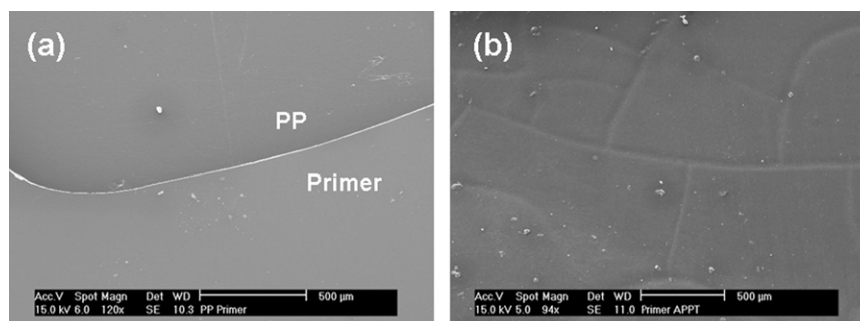
The comparison between the shear strength of each adhesive bonding when using the APPT treatment revealed an important enhancement of tensile strength of about 500%. This increase was associated to the combination of two positive factors: (i) the formation of new moieties of polar nature, which was responsible for surface energy and wettability enhancement, and (ii) the

achieved basic behaviour due to electron donor groups, such as amines or alcohols, which are capable of establishing primary hydrogen bonds, acting as catalysts in the crosslinking curing reaction of PU [10,30].

Therefore, attending to the experimental data, it was possible to conclude that the driving force of the adhesion of PU to polyolefinic surfaces was based more on chemical interactions (especially those related to specific dipole dipole and hydrogen bondings) than on physical interlocking considerations.

3.2.2. Effect of combined surface treatment

Further attempts to develop higher tensile shear strength results were carried out. Tested conditions were (i) deposition of a chemical primer PU solvent based on the pristine surfaces, (ii) application of the primer on the APPT treated samples and (iii) curing under APPT conditions of a primer film placed on an APPT treated surface.

It is necessary to highlight the great improvement in the adhesive bonding strength obtained using both APPT and primer, which enabled the achievement of values three orders of magni tude larger than the ones found for pristine surfaces. This enhance ment of the joint strength was accompanied by a cohesive failure mode, more desirable due to the possibility of prediction (Fig. 5).

Although the primer was selected attending to the specifica tions of the material to bind (PP) and the type of adhesive (PU), its use led not only to the peel off of the PU, but also to the separation of the primer itself from the samples (Fig. 6a). This behaviour was supposed to be a consequence of both the low surface energy of the polymeric substrate and the incompatibility with the chemical primer.

This debonding process was not observed when the primer was applied onto an APPT treated PP surface. The effect of a fast curing under plasma conditions of the chemical adhesion promoter (pri mer) applied on a previously APPT treated sample was the creation of a quartered topography, thus rougher surface (Fig. 6b). The subtle increase of shear strength from the APPT (Sika Primer® 215) to the APPT (Sika Primer® 215) APPT treated PP specimens (7%) sug gested that the existence of a rougher adherend surface was exerting a positive secondary effect (larger bonding area) on adhesion.

3.3. Study of the adhesive failure

To conclude this study, EDX analysis of the surfaces was performed. Data are shown in Table 5. Pristine PP surface presented a hydrocarbon composition, which was predictable according to its (C_3H_6)$_n$ general formula, and a certain amount of oxygen, which derived from an already oxidised surface of the polyolefin in the delivery state. The application of the primer led to the appearance of a silicon and sulphur content, which are part of one of the primer components, the 3 trimethoxysilylpropane 1 thiol. An enhancement of the oxygen content and a decrease in

Table 4
Variation of maximum tensile strength and failure mode with surface treatment.

Surface treatment	Shear strength (kPa)	Failure mode
Untreated	37.5 ± 1.8	Adhesive
Abraded (S80)	42.0 ± 2.1	Adhesive
Sika Primer®-215	> 0.3	Peel off
APPT	232.1 ± 1.4	Cohesive
APPT+(Sika Primer®-215)	714.3 ± 1.5	Cohesive
APPT+(Sika Primer®-215)+APPT	764.3 ± 1.2	Cohesive

Fig. 5. SEM micrograph of the cohesive failure of a tested joint.

Fig. 6. SEM micrographs of (a) pristine PP–primer interface of separation and (b) quartered primer due to a fast curing process under APPT conditions.

Table 5
Chemical composition (%wt) of the studied surfaces.

Surface	C	O	Si	S	Cl	Al	Ti	Ca
Pristine PP	82.3	17.7	–	–	–	–	–	–
PP Primer	69.9	22.7	2.9	4.5	–	–	–	–
APPT–Primer–APPT	71.4	23.1	2.3	3.2	–	–	–	–
PP–PU (1)	80.9	19.3	–	–	–	–	–	–
PP–PU (2)	66.1	15.4	3.7	–	6.9	2.7	3.2	1.8

carbon percentage were found with the APPT treatment. This fact corroborates the C C/C H bond scission and further insertion of oxidised polar moieties on the PP surface, thanks to the reaction with plasma active species.

Compositional test of a sample presenting cohesive failure (Fig. 5) was achieved both on the naked PP area (labelled PP PU (1)) and the one with rest of PU (PP PU (2)). Approximately the same composition of pristine PP was obtained for the PP PU (1) zone, as it was expected. When the PP PU (2) was analysed, a new atomic percentage of silicon, chlorine, aluminium, titanium and calcium content arose. The existence of these elements was in agreement with the formulation of a PU adhesive, which, besides the paraffin base (carbon, hydrogen and oxygen), presents small amounts of diverse elements used as conditioners, lubricants or stabilisers.

Malucelli et al. found high tensile strength results for these types of PP PU adhesive bondings [37], by subjecting adherends to sulfochromic oxidation process. The main difference of our study is the use of a technology, which avoids both the use of toxic chemical reagents and the generation of environmental waste, being more suitable for the legislation currently in force.

On the other hand, the previous works of our group described an incredible durability of plasma treatment on PP surfaces [23], up to 9 months, against flame, corona and even air plasma, which are much short lived effects [38 39]. This fact enables to transport materials and postpone the joint process.

4. Conclusions

The present work focused on the attempts to develop high strength adhesive bonding between a polymeric material (PP) and a PU using abrasion, primers and plasma surface preparation methods. Results showed that APPT treatment appears to be the most suitable way to enable good adhesion of PP, whereas mechanical abrasion leads to an adhesive failure even prior to the realisation of the lap shear tests. This fact was demonstrated to be due to both the low surface energy, hence poor wettability of polyolefins, and the impossibility of the adhesive to fill the large number of groves and valleys generated on the surfaces by the abrasion treatment. The higher tensile strength values obtained by plasma (240 kPa) were achieved by means of the increase of the total and polar components of the surface energy from 23.01 and 0.19 mJ/m^2 to 50.29 and 29.05 mJ/m^2, respectively, as a result of the introduction of hydrophilic moieties on the polymeric surfaces. Acid base components of the surface energy were also estimated, determining fundamentally electron donor PP behaviour with APPT.

The combination of the APPT technology with the use of chemical primers enabled the achievement of almost three times better tensile strength values in the single lap joints (varying from 4 kPa for the pristine PP to 715 764 kPa with APPT and primer), which was in agreement with the acid base and the XPS results; the creation of a higher density of electron donor functionalities, such as amine, ketone, ether, etc., enhanced the possible creation of hydrogen type bonding involved in the PU curing mechanism.

Attending to the results of this work, we have been able to create adequate and reliable bonding with PU, and developed an optimum surface treatment, which combines the activation of PP surfaces with plasma and the application of an adhesion promoter (primer). The activation by plasma encompasses not only a fast and green friendly technology, but also develops an effect on PP remaining almost constant for large periods, which enables the storage and transport of materials.

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