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Surface modification of a duplex stainless steel for plastic-metal hybrid parts

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ABSTRACT

Purpose: Of this paper is the evaluation of three different surface treatments on a duplex stainless steel, in order to improve its adhesive properties on a thermoplastic like polysulfone.

Design/methodology/approach: In order to improve the adhesion between stainless steel and polysulfone, shot-peening, acid (aqua regia) etching and atmospheric pressure plasma jet have been used. The topography and surface activation effects have been evaluated by means of SEM and contact angle measurements. Additionally, aging studies have been performed to evaluate the effect of storage time of parts on atmospheric plasma torch surface treatment. Finally, to test the effectiveness of the treatments, it has been carried out successfully shear strength tests by tension of adhesive assemblies previously modified with the treatments. It has been also examined rupture failures that have occurred in these assemblies.

Findings: Aqua regia and plasma torch treatments have reached the optimal surface modification condition under wettability criteria. Shear strength tests demonstrated that the improved surface adhesion provided on this substrate and the polysulfone is achieved by shot-peening and acid etching treatments.

Research limitations/implications: A deeper analysis varying several conditions like humidity could be suggested in order to evaluate the effectiveness of surface treatment.

Originality/value: Up to now there is no any study in the literature about the comparison of different surface treatment on duplex stainless steels and the subsequent evaluation of the adhesion of a polymer like polysulfone.

Keywords: Surface treatment; Duplex Stainless Steels; Engineering polymers

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

In many areas of Materials Science and Technology different process are used for surface modification of various materials. The modification can be done by different methods with a view to altering surface characteristics, such as: roughness, hydrophilicity, surface charge, surface energy and reactivity. These modification can be at micro and nanoscopic scale.

According to the formation mechanism of the modified layer on the material the surface treatments are classified into mechanical, chemical and physical methods.

Mechanical methods, such as machining, grinding polishing and shot-peening involve physical treatment, shaping, or removal of the materials. The goal of this method is to obtain specific surface topographies and roughness, remove surface contamination, and/or improve adhesion in subsequent bonding steps.

Chemical methods, like chemical treatment, electrochemical treatment (anodic oxidation), involve chemical or electrochemical reactions at the interface of the metal surface. In the case of chemical vapour deposition (CVD) chemical reactions between chemicals in the gas phase and the sample surface resulting in the deposition of a non-volatile compound on the substrate. It is different from physical vapour deposition (PVD), which typically employs techniques, such as evaporation and sputtering involving no chemical reactions.

Finally, in the case of the physical methods, chemical reactions do not occur. Several methods are included in this category, such as physical vapour deposition, ion implantation, thermal spray or plasma treatments. In the particular case of the last one, it has gradually increased due to its low cost and flexibility of a continuous process, furthermore the currently equipment allow to work in atmospheric condition, overcoming the drawback of vacuum processes. In general, plasma treatment produces hydrophobic or hydrophilic surfaces on metals, plastics, glasses or polymers. The surfaces could be activated for the adhesion enhancement on the metal–polymer or metal–metal combinations by atmospheric-pressure plasma jet (APPJ) system [1].

In the case of stainless steels, surface modification has been widely studied because it is a material used in many devices. The proper surface treatment expands the use of stainless steels in the biomedical fields.

Surface modification techniques are especially attractive in engineering applications because while retaining the bulk properties of the treated parts, they improve surface adhesion which may be critical for specific purposes. Surface cleaning of a metal is necessary in order to enhance the bonding strength. On the other hand, surface roughness and surface hydrophobicity are also considered to be important factors [3].

On the other hand, duplex stainless steels (DSS) combine some of the main characteristics of austenitic and ferritic steels [4]. The combination of these phases provides harder and more ductile steel than the austenitic and ferritic ones, respectively. From the microstructural point of view these steels are characterized by a structure consisting of approximately equal amounts of ferrite and austenite. These materials are widely used in industrial application due to its excellent corrosion resistance and superior mechanical properties [1]. In spite of surface modification of stainless steels has been reported and widely used in many biomedical devices, as mentioned before, we have not found any references about these kind of surface treatments for DSS.

The aim of this experimental work was to study three kinds of surface treatments performed on duplex stainless steel to improve the adhesion metal–polymer:

a) Mechanical: shot-peening.
b) Chemical: etching with acid solution.
c) Physicochemical: atmospheric pressure plasma jet.

Shot peening produces a modification of surface roughness which influences the fatigue life of component. Chemical actuations produce the removal of weak superficial layers, a selective corrosion, and the creation of polar groups on the substrate surface. Plasma is an active media constituted by energetic neutrals, ions and electrons which act on a surface modifying its physicochemical nature [5, 6]. Atmospheric pressure plasma torches (APPT) are devices which mainly produce cleaning by means of the breakdown of pollutants [6, 7], etching and surface activation [9, 10]. The latter is achieved by the introduction of different moieties of polar nature which significantly increase surface energy without affecting bulk properties of the material. Another interesting advantage of APPT is the relatively high density of energy of plasma, which favors a reduction in time treatment, thus a reduction in process costs.

2. Materials and methods

SAF 2205 duplex stainless steel was provided by Sandvik Materials Technologies. The composition of the steel is given in Table 1. The test specimens were

Table 1.
Composition of SAF 2205 (weight %)

Element	Cr	Ni	Mo	Mn	Si	S	P	C
wt %	22.32	5.22	3.16	0.78	0.47	0.0007	0.023	0.016

machined and electro-polished to obtain a high quality flat surface (Fig. 1). Polysulfone employed was Ultrason® PSU supplied by BASF.

Shot-peening experiments were carried out in a Norblast FN 31. The impact distance was 230 mm with a nozzle of 4 mm of diameter. The projection was assisted by a Protech 6918 employing a pressure of 2 bar. Aluminium oxide with an average particle size of 125 µm was selected for this process (Knoop hardness: 22500 N/mm²; Mohs hardness: 9; apparent density: 1.58 1.68 g/cm^3). After shot-peening, samples were cleaned with methyl-ethyl-ketone (MEK).

Fig. 1. Specimen of SAF 2205 stainless steel for surface treatments.

Chemical etching of samples was realized with aqua regia at different immersion times (1.5, 2.5, 3.5 and 5 min). After treatment, the reaction was stopped with water and finally the samples were cleaned with MEK.

APPJ was carried out in a Plasmatreat GmbH (Steinghagen, Germany). This equipment worked under a frequency of 17 kHz and a discharge voltage of 20 kV. By this torch, the plasma was expelled at a pressure of 2 bars. Thus, the variation of the effect of plasma on the surface from varying these parameters was studied.

In order to observe the influence of each parameter separately, a gap distance value and a reference scanning rate value was set. So, when the effect of scanning rate was studied, the gap of the nozzle with respect to the sample was always 14 mm, and in the case of studying the effect of the gap of the nozzle, the scanning rate of movement of the platform was set to 2 m/min.

Table 2.
Conditions of the APPJ treatment.

Gap of the nozzle (mm)	2	8	14	20	26
Scanning rate (m/min)	0.2	1	2	3	4

On the other hand, an aging experiment in order to know the durability of this superficial modification was realized at different times till 17 days. Samples were cleaned with MEK before plasma application.

Several characterization techniques were employed to evaluate the three superficial modifications carried out. Contact angle measurements were realized with a goniometer OCA 15Plus from DataPhysics (Neurtek Instruments) at 21ºC. The liquids selected were distilled water, diiodomethane and glycerol.

Roughness measurements were taken with a Hommel Tester T8000 perfilometer (Hommel Etamic France S.A.) along longitudinal and transversal directions of the specimens.

Surface microstructure of samples was studied employing a Philips XL30 scanning electron microscope equipped with SE and BSE detectors. In some cases, EDS analysis were used to determine compositions of some inclusion. These analyses were performed with an EDAX detector.

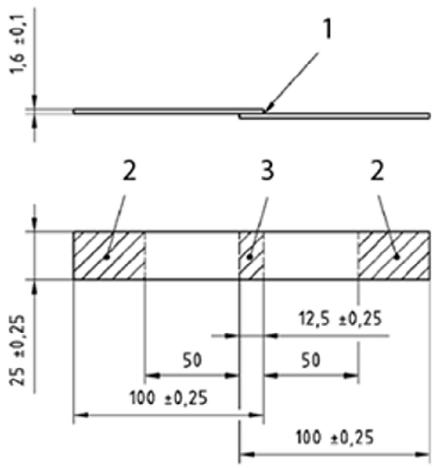


Fig. 2. Scheme of the shear test specimens (1: adhesive line; 2: grip area; 3: overlap area). Dimensions are given in mm.

Finally, the determination of tensile lap-shear strength of rigid bonded assemblies was carried out. To perform this type of direct adhesion assays we have followed the standard UNE EN 1465:2009. The preparation of joint specimens was carried out according to the scheme of Figure 2. In this case the adhesive will be the polysulfone and the substrate the duplex stainless steel.

To achieve adhesion of the samples, the system was pressed in a hot plate press for melting the PSU at 350ºC and applying 20 kN. Mechanical tests were realized in a Microtest universal machine with a load cell of 20 kN and a rate of 1 mm/min.

3. Results

3.1. Design of drop forging formed on TSFP

The roughness produced with the shot-peening treatment has not a preferential orientation; it appears uniform over the entire surface. These morphological changes were evaluated through scanning electron microscopy (Fig. 3). The roughness of the samples after shot-peening reaches 1.9 ± 0.2 µm. This huge value impedes to obtain reliable contact angle measurements. On the other hand, after treatment some alumina particles remain in the steel matrix.

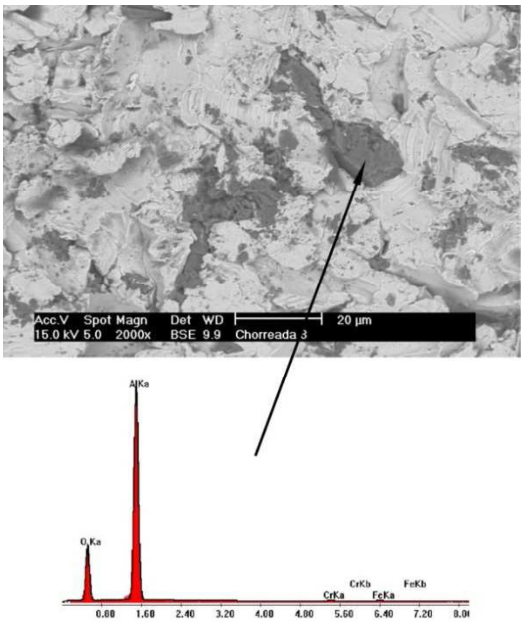


Fig. 3. Scanning electron micrograph of samples treated with shot-peening. Microanalysis of inclusion detected on the surface that corresponds with Al_2O_3

3.2. Aqua regia etching

Firstly, contact angle measurements were realized in samples that were etched with aqua regia at different immersion times. The results were compared with non-treated samples (NT). Contact angle decreases as the immersion time increases with all the liquids but is more pronounced in the case of water (Fig. 4). This fact indicates that the surface becomes more hydrophilic due to the formation of polar groups that increase their presence with the attack time.

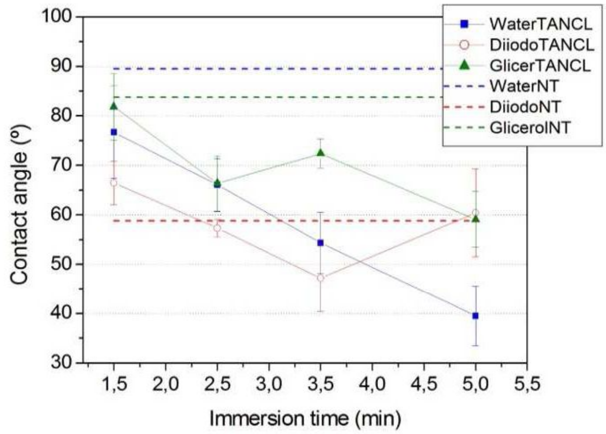


Fig. 4. Evolution of contact angle with immersion time of acid etched samples

Figure 5 shows the evolution of the surface roughness in both longitudinal and transversal directions of the test specimen. As expected, roughness increases with the immersion time and achieves a value of 0.2 µm.

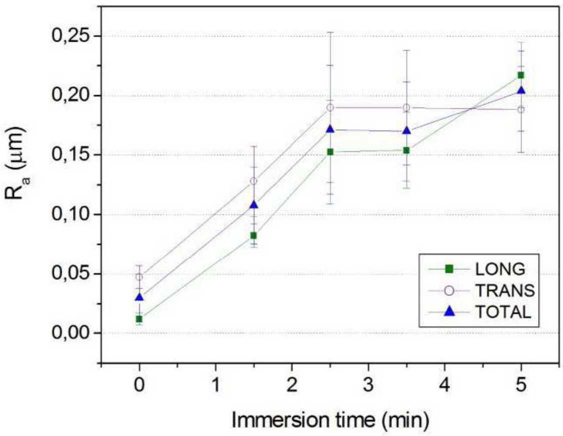


Fig. 5. Evolution of roughness with immersion time in aqua regia

The microstructure of samples was examined by SEM (Fig. 6). The grains are orientated due to a cold-rolled steel was selected to fabricate the samples. The increase on the roughness with etching time can be clearly observed. Besides, the morphology of etching is due to the different corrosion degree suffered by different regions of the microstructure.

a)
b)
c)

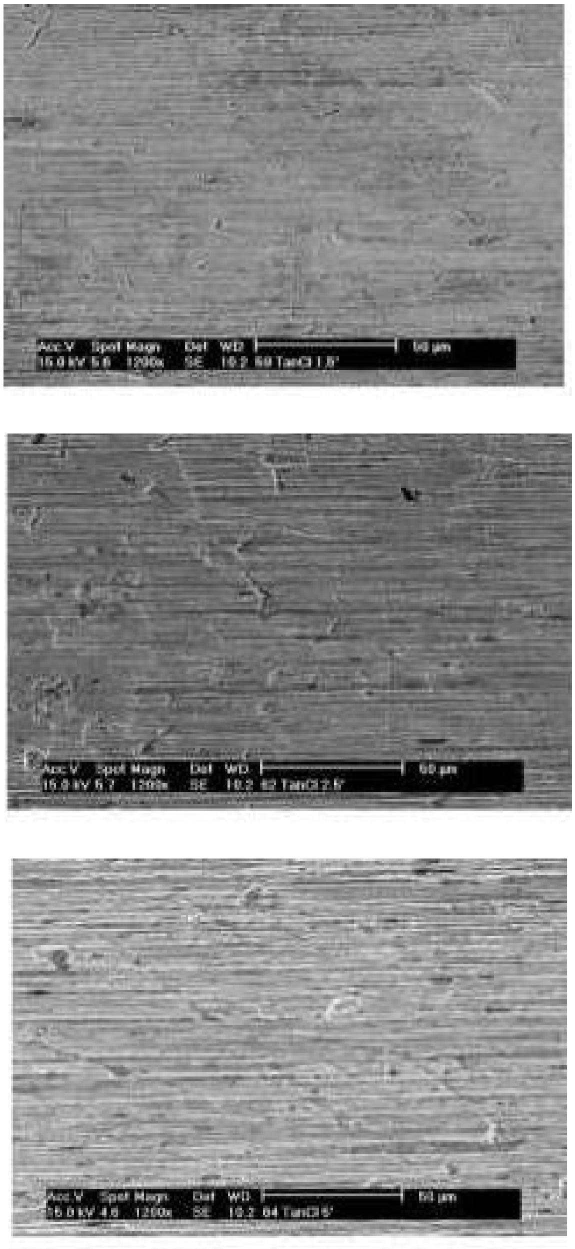


Fig. 6. SEM images of acid etched samples for 1.5, 2.5 and 5 minutes of immersion time

It is known that grain boundaries are preferentially etched, as well as ferrite when comparing with austenite. So, clear and dark contrast is associated to different phases of the microstructure.

3.3. APPJ

The third surface treatment carried out on duplex stainless steel was APPJ. Firstly, the results of contact angle of samples treated at different scanning plasma rates are presented in Fig. 7. On the other hand, the results obtained varying the height of plasma torch from steel surface are shown in Fig. 8. The results were compared with non-treated samples (NTP).

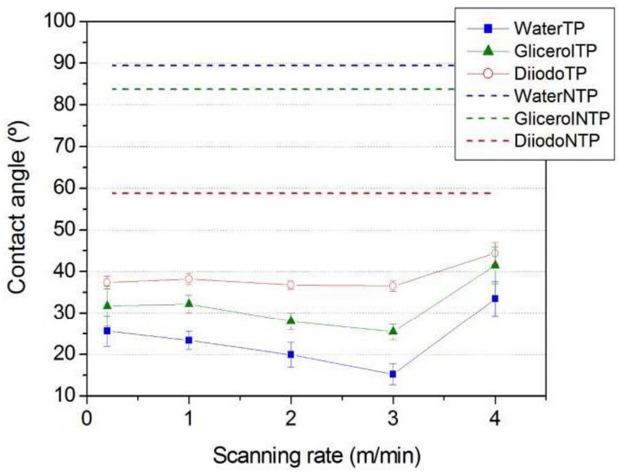


Fig. 7. Variation of contact angle with scanning rate

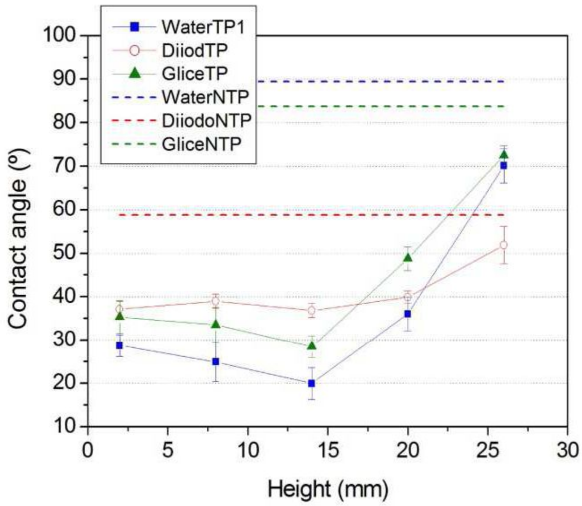


Fig. 8. Variation of contact angle with plasma torch height

A significant drop of contact angles with the three liquids respect to the untreated surface is observed in Fig. 7 and 8. A slight decrease of this effect is observed when the treatment conditions are more aggressive. Besides, a smooth decrease of contact angle takes place from a scanning plasma rate of 0.2 to 3 m/min. In the case of the height of the plasma torch the lowest contact angle is found at 14 mm. At higher height values the contact angle drastically increases.

So, it is estimated that the optimal condition by APPJ surface modification occurs at a speed of displacement of the probe under the plasma of 3 m/min, and a nozzle gap distance of about 14 mm from the sample surface.

In Fig. 9a the roughness results of samples non-treated (NTP) and treated with APPJ are shown. We can observe that the micro-roughness measured in the transversal direction of the work piece is greater than in the longitudinal direction of the sample, both treated and untreated. Besides, the roughness of the samples did not change after treatment. The SEM images show that no significant changes in the surface can be perceived after applying this technique (Fig. 9b). In conclusion, plasma treatment does not cause changes in the roughness of the samples that could be detected by SEM.

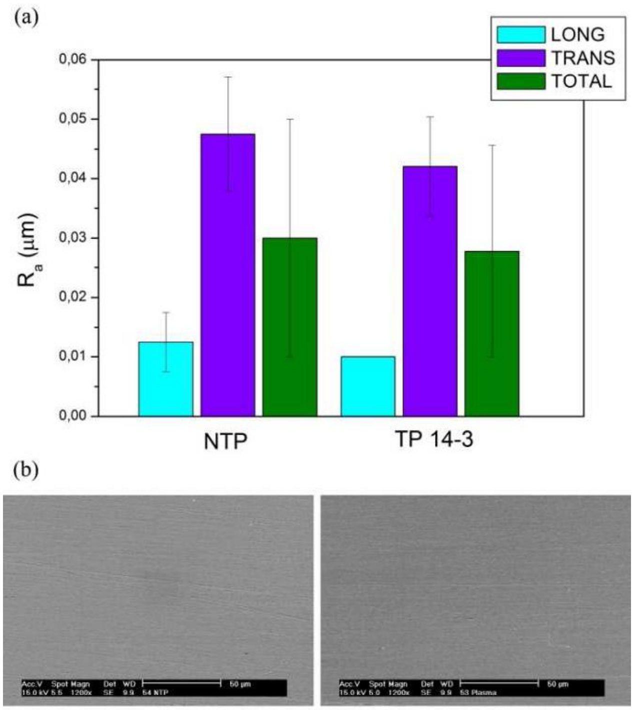


Fig. 9. (a) Surface roughness in both longitudinal and transversal directions of the test treated (TP 14-3) and untreated (NTP) specimens. (b) SEM images of treated and untreated samples

Finally, we conducted a study of the effect of aging by direct measurement of the contact angle over 17 days. In this case, for measuring the surface durability, distilled water was used as test fluid. Fig. 10 shows the evolution of contact angle with aging time.

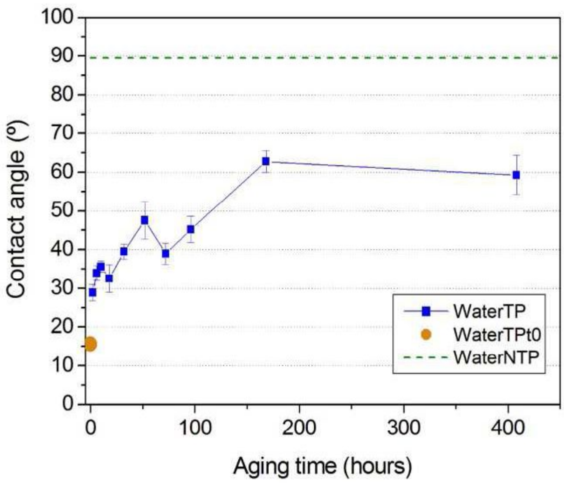


Fig. 10. Evolution of contact angle with aging time after APPJ

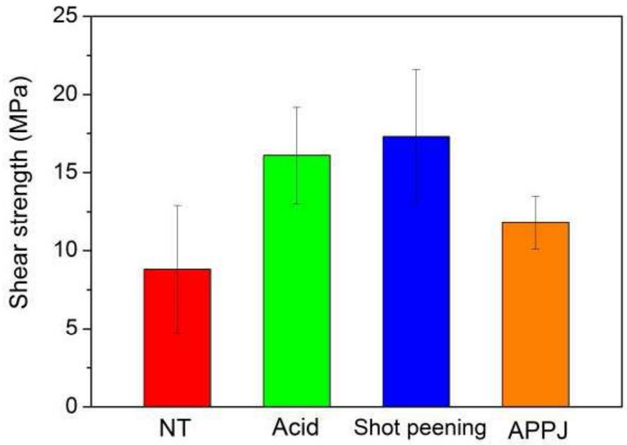
The results show a progressive deactivation of the treated surfaces with APPJ. After 17 days of storage, there was an increase in the contact angle of 66% of the initial value. And this result indicates a relative high durability of the treatment.

Finally, the tensile lap-shear strength of rigid bonded assemblies was determined. The samples were prepared employing the treatment in its most aggressive condition: some samples were etched with aqua regia over 5 minutes long, and for which modified with plasma the conditions were the optimal (14 mm and 3 m/min). Specimens without any surface treatment were also prepared for using as reference (NT). The results obtained are shown in Fig. 11a.

Scanning electron micrographs of lap joint after mechanical testing are shown in Figure 11b as an example (the images were taken with BSE detector). PSU appears in black contrast. Non- treated as well as treated samples showed that the failure mode is mixed with a high degree of adhesive character.

Therefore, according to tests, it was demonstrated that the improved surface adhesion provided on this substrate and the polysulfone is achieved by shot-peening and etching treatments. It could also be concluded that the increase in shear strength, both shot-peening and etched with acid surfaces, is attributed to the surface roughness, since this is more pronounced compared to surfaces treated with plasma.

a)



b)

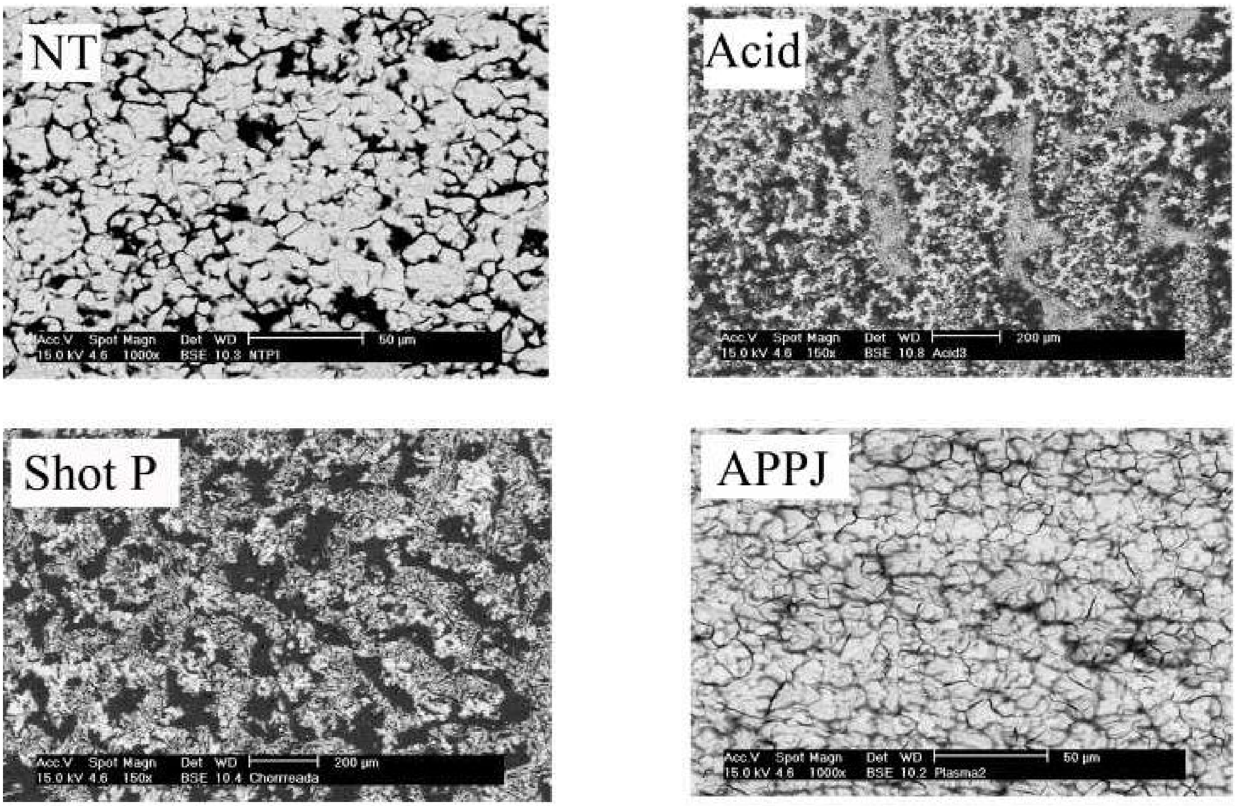


Fig. 11. (a) Shear strength and (b) micrographs of rupture failure of treated and untreated samples

4. Conclusions

Different surface treatments have been performed successfully on duplex stainless steel, to find the appropriate surface modification method of ensuring satisfactory integration between the metal and a thermoplastic polymer like polysulfone.

In the case of plasma treatment, from the results of contactangle of different liquids, it has been observed the surface activation increasing interactions between solid and liquid. Regarding to the modification of the surface topography no significant changes were seen to micron level. In addition, the effect of aging is sufficiently long that the steel parts that have been subjected to this treatment can be stored for long periods of time.

The etching with acid solution of aqua regia increases the surface roughness in both longitudinal and transversal directions with the immersion time and achieves a value of 0.2 μm.

The roughness produced with the shot-peening treatment has not a preferential orientation, appears uniform over the entire surface. The roughness of the samples after shot peening increases till 1.9 μm.

The shear strength tests demonstrated that the improved surface adhesion provided on duplex stainless steel and the polysulfone is achieved by acid etching and shot-peening treatments.

Acknowledgements

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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