Assessment of atmospheric plasma treatment cleaning effect on steel surfaces

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ABSTRACT

The present study deals with the ability of an atmospheric pressure air plasma torch (APPT) treatment to remove lubricant pollutants coming from machining processes on steel surfaces. This effect has been characterized by contact angle measurements, gravimetric analysis and reflection absorption infrared reflectance spectroscopy (RAIR-FTIR). Attending to the initial results of the investigation, further surface analysis has been done by means of X-ray photoelectron spectroscopy (XPS). In order to define the benefits of cleaning for adhesive bonding processes, pull-off tests were performed on all the coupons. Experimental data show the effectiveness of APPT to achieve not only a high rate of surface lubricant layer elimination, thus cleaning the metal samples by means of a solvent free and fast treatment, but also a remarkable improvement on the substrate adhesive bonding strength.

1. Introduction

Surface cleaning is a key step in most industrial manufacturing procedures. Metal sheets are generally coated by oils with the purposes of friction reduction during metal-forming or corrosion protection. These organic natural layers have to be removed before achieving further surface finishing (coating, painting or adhesion) steps of the metals sheets [1]. For a good attachment of the coating, the oil has to be eliminated from the metal surface, due to the fact that it is a low cohesion layer. Thus, surface cleaning of a metal is necessary in order to enhance the bonding strength.

Removal of oils and waxes from metallic surfaces is usually accomplished by a combination of wet chemical treatment and mechanical brushing. The chemical condition is often performed in alkaline or acid treatment baths. Those baths have to be monitored and adjusted to obtain consistent cleaning results [2]. These wet processes present several problems from the viewpoint of environmental and economic impact. Attending to this fact is the 1989 Montreal Protocol which states that substances that deplete the ozone layer require the cessation of chlorofluorocarbon substances by 2020. Moreover, the use of organic solvents may cause environmental pollution due to volatile organic compounds (VOCs), and the removal of waste solution incurs significant expense. As a result, the development of a cleaning technique with a low environmental impact is desired. Plasma is an active media constituted by energetic neutrals, ions and electrons which act on a surface modifying its physicochemical nature [3–11]. Depending on the way it is activated and their working power, it is possible to distinguish between cold or non-local thermodynamic equilibrium (non-LTE) plasmas [9] and thermal or local thermodynamic equilibrium (LTE) plasmas [8]. Non-LTE plasmas usually reach low temperature of heavy particles compared to electrons [7], so they can be used for applications like coating, cleaning or surface activation without producing a hazardous effect on the substrates. Atmospheric pressure plasma torches (APPT) [7,11] are non-LTE devices which mainly produce cleaning by means of the breakdown of pollutants [12–17], etching and surface activation [18–22]. 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.

The aim of this paper is to study and optimize an APPT procedure that will replace the traditional chemical degreasing process that takes places today in the manufacturing process of metal sheets, focusing on the performance of further adhesion processes. Economic and environmental benefits are expected to arise due to the rejection of chemical use in this cleaning step.

2. Experimental procedure

2.1. Materials and sample preparation

The experiments were carried out on commercial steel surfaces (70 mm × 25 mm × 1 mm). The selected surface conditions were a control as-received sample (CC) degreased with methyl ethyl ketone (MEK); coupons were coated with industrial lubricant and APPT treated. The selected lubricant was an evanescent oil based commercial lubricant, Trenoil 320, developed and marketed by Fuchs Lubricantes S.A. (Castellbisbal; Spain).

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2.2. Atmospheric pressure plasma torch (APPT) treatment

The APPT device used in this study was developed by Plasmatreat GmbH (Steinhagen, Germany).

The setup operated at a frequency of 17 kHz and a high tension discharge of 20 kV, and it was provided with a rotating torch ending in a nozzle (1900 rpm) through which plasma was expelled [23]. The system contained an electronically speed-controlled platform where the samples were placed. The air plasma was generated at a working pressure of 2 bars inside the rotating nozzle by a non-equilibrium discharge and expelled through a circular orifice onto the samples. The speed of the platform was set at 1, 5 and 10 m/min, and the distances between the sample and the nozzle were 2, 4, 6, 8, 10 mm.

2.3. Contact angle test and surface energy calculation

Contact angle was measured on the samples under all the tested conditions by using an OCA 15 plus device from Data Physics (Neurtek Instruments, Eibar, Guipúzcoa, Spain) following the normative UNE EN 828:2009 [24].

The samples were placed into an isothermal chamber at (24 ± 2) °C previously saturated with vapor of the corresponding liquid for at least 10 min before placing the drops. Contact angle was measured within 3 min after the liquid drop of deionized water, diiodomethane and glycerol (Table 1) was attached to the surface. At least twelve drops per sample were measured and averaged by using the sessile drop method. Each component of surface energy was calculated by means of the Owens–Wendt–Rabel–Kaelble (OWRK) [25,26] method (Eq. (1)). This calculus method allows to obtain dispersive (due to London type forces, γ_D) and polar (related to the dipole–dipole and hydrogen bonding interactions, γ_P) additive contributions to total surface energy, which derives from the Fowkes expression [27].

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

In this expression, θ represents the test liquid contact angle on the surface, and γ_l and γ_s are the liquid surface tension and the solid surface energy, respectively. The superscripts D and P are referred to the dispersive and polar fraction contribution to the surface tension and γ_s parameters.

2.4. Analysis of lubricant mass loss

The lubricant elimination of the sample surface was characterized as a function of weight change by gravimetric analysis, using a Gibertini E 42S-B balance (Gibertini Elettronica, Milan, Italy). The removed lubricant percentage was calculated by means of Eq. (2). Five measurements were performed and averaged for each condition.

$$\%_{Lubricant} = \left[\left(\frac{W_{Lubricant} - W_{plasma}}{W_{Lubricant} - W_{clean}} \right) \right] * 100. \tag{2}$$

In this expression, the parameters represent the weight of the samples with lubricant ($W_{Lubricant}$), after performing APPT (W_{plasma}) and oil free (W_{clean}), respectively.

Table 1
Test liquid surface tension. The three OWRK fractions are shown.

Liquid	γ_T (mJ/m^2)	γ_D (mJ/m^2)	γ_P (mJ/m^2)
Water	72.80	21.80	51.00
Glycerol	63.40	37.00	26.40
Diiodomethane	50.80	50.80	0.00

2.5. FTIR experiments

A Bruker Tensor 27 (Bruker Optik GmbH, Madrid, Spain) spectrometer was used to obtain the infrared spectra of both untreated and APPT treated samples and the lubricant itself. The reflection absorption infrared mode (RAIR) was used to analyze the surface chemical modifications and the effectiveness of the cleaning process. The incident angle was 80°. RAIR spectra were recorded with 128 scans at a resolution of 4 cm^{-1} in the wavenumber region of 4000 to 400 cm^{-1}. For the Trenoil 320 qualitative analysis, an attenuated total multiple reflection mode (ATR) was used, working with a diamond prism and an incident angle of the IR radiation of 45°. Thirty two scans with a resolution of 4 cm^{-1} were obtained and averaged. Spectra were recorded from 600 to 4000 cm^{-1}.

2.6. XPS analysis

Chemical modifications on the outermost surface layer (about 5 nm) on the APPT treated samples were analyzed by VG Scientific Microtech Multilab (Vg Scientia, Hastings, United Kingdom). The analysis was performed on 1×1 cm^2 surfaces at a residual pressure below 5×10^{-8} Torr. A survey scan encompassing the 0–1200 eV region was obtained for each sample. High resolution spectra were obtained in a 20 eV range. All binding energies were referred to the C (1s) core level spectrum position for C–C/C–H (hydrocarbons) species at 285 eV. Atomic concentrations were calculated using a VGX900-W system.

2.7. Adhesion pull-off test

An adhesion electromechanical EM1/FR Microtest device (Microtest S.A., Instruments, Madrid, Spain) equipped with a 1 kN load cell was selected to evaluate the improvement in adhesion of composites surfaces using steel studs of 20 mm diameter and a silicone based CAF® 99 AXAD adhesive (Bluestar Silicones, Lyon, France). Ten samples per condition were tested and averaged under the UNE-EN ISO 4624:2003 standard.

3. Results and discussion

3.1. Working rate optimization. Surface energy calculation

Contact angle measurements are a good predictable method to assess the cleaning of a solid surface and the effectiveness of a treatment, as stated by Adams [28].

In this study upper and lower results (Table 2) were found for the CC (around 68° for deionized water) and lubricant coated surfaces (42° for deionized water), in agreement with previously reported data by Tang et al. for 1% HCl cleaned steel samples. This fact was explained by the surface tension of the organic residue layer, which was calculated by pendant drop measurements to be 50 mJ/m^2 and a 40% polar contribution to the total fraction for the lubricant fluid, corresponding to a highly hydrophilic behavior. Attending to Young's definition of a liquid drop on a solid surface [25], lubricated samples showed the highest surface energy, while the removal of the pollutant layer achieved by solvent cleaning (CC) led to an almost three times lower polar contribution (7.7 mJ/m^2 compared to the 20.7 mJ/m^2 exhibited by the coated metals).

Surface energies of the three surface states (lubricant coated, CC and APPT modified under the selected conditions) are shown in Fig. 1. After subjecting the lubricated samples to the 1 m/min speed, it was possible to confirm a certain removal of the organic layer due to the achievement of surface energy values close to the cleaned CC sample for the five tested nozzle-sample gaps (below 50 mJ/m^2). The surface energy polar fraction suffered a decrease of 40% after APPT cleaning, thus the lubricant elimination was taking place. All the surfaces treated with the