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Plasma Treatment of Crosslinked Polyethylene Tubes for Improved Adhesion of Water-based Paints

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Cold plasmas fed trichloromethane-argon mixtures were used to treat cross-linked polyethylene (PE) to improve the adhesion of water-based paint. The effects of the plasma treatment undertaken at different percentages of $CHCl_3$ in the plasma feed, C_{Cl}, were investigated using Infrared Spectroscopy in Diffuse Reflection (DR) mode, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS), goniometry for surface contact angle measurements, profilometry for roughness measurements, and paint adhesion tests. All the treatments modify the surfaces by introducing chlorine. Oxygen is present in the bulk and on the surfaces of the treated and untreated material. The treatments do not alter the bulk, but tend to increase the surface roughness and contact angle. When $CHCl_3$ is present in the plasma subsequent paint adhesion is improved from a very poor classification of 4 to an excellent classification of 0 (assessed according to the appropriate Brazilian standards (BS EN ISO 2409:2007 and BS 3900-E6:2007A)). Surface roughness is not increased at low C_{Cl} but improved paint adhesion occurs for all $C_{Cl} > 0$. Although the causes of the improved paint adhesion with the plasma treatment are unclear, they may be related to the plasma activation of unsaturated carbon and oxygen functionalities.

Keywords: *paint, roughness, cold plasma, trichloromethane, adhesion.*

1. Introduction

Plasma treatment is well established for the surface modification of diverse materials [1]. For example, air cold plasmas have been used to improve the adhesion of acrylic paint to 2024 aluminum alloy [2], which is used in aircraft manufacture and therefore has to resist harsh conditions, such as the presence of moisture, organic materials, and wide temperature fluctuations. Such treatments allow the elimination of an otherwise essential surface-cleaning step and a reduction in the amount of primer needed, potentially reducing the overall painting time and the paint weight, the latter being an important consideration for aircraft. Plasma-deposited films have also been used as promoters for the adhesion of alkyd paint to titanium alloy (Ti-6Al-4V) substrates [3]. Several silanes were used as monomers, improving the adhesion of the paint under monomer-deficient conditions. Improved adhesion in the cases mentioned here are attributable to increases in surface roughness and decreases in surface contact angle induced by the treatments, which lead to increased covalent, van der Waal's or hydrogen bonding [4].

Wolkenhauer et al [5] examined the adhesion of paints (and adhesives) on wood-plastic composites following atmospheric dielectric barrier discharge plasma treatment in air. Contact angle measurements, atomic force microscopy and tensile bond strength testing were applied. These revealed that the polar component of the surface energy and the roughness increased under treatment. The treatments also improved adhesion of water-borne, solvent-borne and oil-based paints.

The efficacy of improving urethane paint adhesion to a polypropylene car bumper using oxygen, water, and acetylene plasmas instead of a primer has been reported [6]. Each treatment increased the adhesion strengths, as assessed by lap-shear tensile strength values, in dry conditions but the treatment in acetylene was more robust when subsequently exposed to wet conditions. The improved adhesion in the presence of acetylene is attributed to the existence of reactive unsaturated hydrocarbons and oxidized hydrocarbons in the deposited film.

Irradiation of poly(ethylene glycol-co-1,3/1,4 cyclohexanedimethanol terephthalate (PETG) using H_2 and CF_4 plasmas typically increased surface roughness and decreased surface contact angles as measured by profilometry and goniometry, respectively [4]. Paint adhesion was strongest

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when wettability and work of adhesion were increased. (Work of adhesion is defined as the reversible thermodynamic work that is needed to separate the interface from the equilibrium state of two phases to a separation distance of infinity).

As summarized elsewhere [7], chlorine-containing plasmas have been employed to modify the surfaces of polymers. For example, when polypropylene is treated in CCl_4 plasmas or $CHCl_3$ plasmas, chlorine and often also oxygen is introduced into the treated surface, changing the surface roughness and surface contact angle. Such treatments are simple, one-step, rapid, dry, almost pollution free, and may readily be automated and scaled-up as required.

In the present study, the use of cold $CHCl_3$ - Ar plasmas to improve the adhesion of water-based paint to crosslinked polyethylene material used in fuel gas installations is investigated. The motivation for this is to be able to use these tubes for external use. Obtaining good paint adhesion is difficult but necessary for such outside use, which is a common requirement in Brazil. Infrared Spectroscopy in Diffuse Reflectance (DR) mode, Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS), were used to investigate the chemical structure and composition of the treated polymer. Scanning Electron Microscopy (SEM) was used to confirm surface morphologies. Goniometry, profilometry, and a Brazilian standard paint-adhesion test were employed to reveal surface contact angles, surface roughness, and quality of adhesion, respectively.

2. Experimental

2.1 Plasma treatment

Plates of rough dimensions 12 mm x 7 mm x 1mm were produced by cutting, opening out, and flattening pieces of high density cross-linked polyethylene tube, PE-Xc (HENCO, Doorn, Netherlands).

The substrates were cleaned by immersion in an ultrasonic bath containing 50% water and 50% detergent (DET LIMP S32) for 8 minutes, then rinsed in running water, immersed in an ultrasonic bath of distilled deionized water for 8 min., rinsed again in running water, and finally treated in an ultrasonic bath of isopropyl alcohol for 8 min. and dried in a hot air current.

Treatments were undertaken in a Radiofrequency PECVD system consisting of a cylindrical stainless-steel chamber equipped with internal circular, horizontal electrodes. Power (60 W) was fed to the lower electrode from a 13.56 MHz power supply (TOKYO HY-POWER, MB-300) via a capacitance matching box; the upper electrode was earthed. Cleaned plates were placed on the powered electrode for treatment. Initially the chamber was evacuated to a pressure of ~ 10 mTorr. Mixtures of argon and tricloromethane were used for the treatments. Trichloromethane vapor was introduced to the chamber from glass vials containing liquid trichloromethane via needle valves (EDWARDS, LV10-K). Argon (99.99% pure, WHITE MARTINS, Brazil) was supplied from a cylinder via an electronic flowmeter (DATAMETRICS, USA). During treatments the chamber was evacuated continuously using a rotary vane pump (EDWARDS E2M18). Mixtures of argon and trichloromethane were used at a total pressure of 100 mTorr. The partial pressure of chloroform expressed as a percentage of the total pressure, C_{Cl}, was varied from 0 to 100%. The C_{Cl} value of 0% represents the untreated sample. Pressures were monitored using a Pirani gauge (AGILENT TECNOLOGIES LTDA). A treatment time of 15 min. was used throughout. Figure 1 shows the treatment system.

2.2 Characterizations

A JASCO FTIR-410 spectrophotometer was used for the diffuse reflectance (DR) infrared spectroscopic analyses for wavenumbers in the 4000 to 400 cm^{-1} range. Each spectrum comprised 128 scans; a resolution of 4 cm^{-1} was achieved.

Surface morphology of the treated surfaces was studied using a JEOL JSM-6010 scanning electron microscope equipped with a secondary electron detector. Micrographs were obtained using the secondary electron signal at an accelerating voltage of 3 kV. Chemical composition of the material was studied using Energy Dispersive X-ray Spectrometry (EDS).

X-ray Photoelectron Spectroscopic (XPS) analyses obtained using a VG Microtech-ESCA 3000, which employs a beam of MgK_α radiation of 1253,6 eV at an incidence angle of 45º, provided additional compositional information. A resolution of ~0.8 eV was achieved. Shirley background correction was employed.

Surface wettability was determined from contact angle (θ) data taken using a RAMÉ-HART 100-00 goniometer. To obtain a mean value and its uncertainty, a total of 30 measurements were made on three drops of deionized water (0.2 μL) placed at different regions of the sample surface.

Surface roughness, R_a, i.e. the arithmetic average of the absolute values of the profile height deviations from the mean line, was calculated using ten points from each of three 250 mm-long linear scans obtained using a profilometer (VEECO, Dektak^{3}ST).

Paint adhesion tests were carried out on the untreated and treated substrates using the procedures given in the internationally accepted Brazilian standards BS EN ISO 2409:2007 and BS 3900-E6:2007A. White premium acrylic paint (FORTY DUBAI IND E COM DE TINTAS E VERNIZES LTDA, Brazil) for interior and exterior use was applied to the substrates.

The paint was homogenized with 20% water (by mass in relation to the original paint mass). An initial coat of paint was applied using a polyethylene roller. The painting was repeated after 4 and after 8 hours. On the following day the adhesion tests were undertaken.

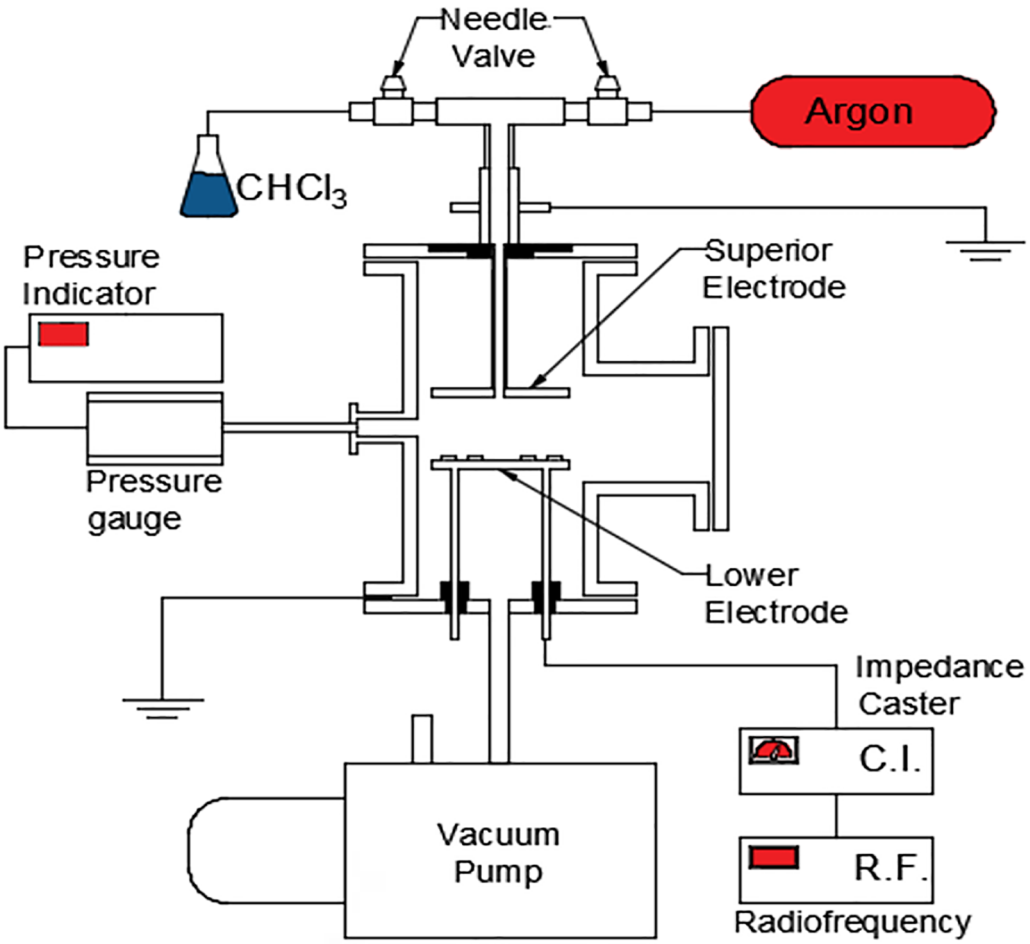

Figure 1. The plasma treatment system.

Cuts along square grid lines were made using a sharp knife. Any excess paint was then lightly brushed off. A standard tape was pressed to the painted surface uniformly using a rubber eraser. The tape was then removed at an angle of 60º between it and the surface of the sample at a constant rate. This procedure was triplicated for each sample.

3. Results and Discussion

Figure 2 shows the diffuse reflectance (DR) infrared spectra of the untreated and treated PE. As DR is not a strictly surface technique, surface changes produced by the plasma treatments are not evident in the sequence of spectra. Absorptions owing to the presence of CH symmetrical and asymmetrical stretching modes in CH_2 and CH_3 groups at around 2923 cm^{-1} and 2852 cm^{-1} are seen. The band at around 3600 cm^{-1} is attributed to stretching vibrations in hydroxyl groups. Two absorptions at about 2020, 1896 cm^{-1} may be due to vibrations in carbonyl groups or C=C=C structures. The absorption at about 1700 cm^{-1} is attributed to stretching in carbonyl groups. There are similar attributions to peaks

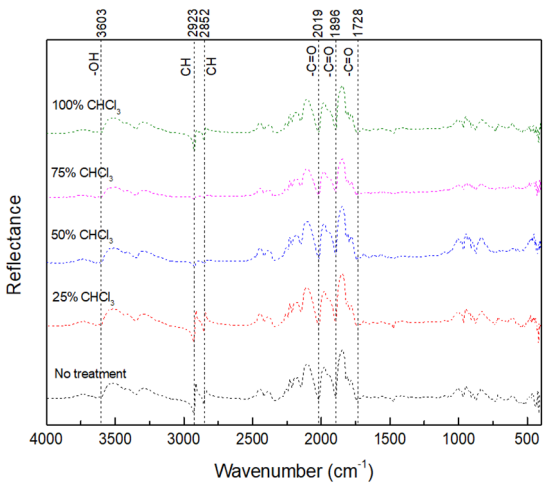

Figure 2. DR spectra in the 400 to 4000 cm^{-1} range of the PE treated at different C_{Cl}.

in infrared spectra of, for example, untreated low density PE in the literature [8]. No absorptions due to C-Cl_x groups

are detected in the spectra of the treated material. This is accounted for by the relatively great sampling depth and the expected low sensitivity of C-Cl_x absorptions.

Figure 3 shows scanning electron micrographs of the treated and untreated PE. There is an apparent tendency to rougher surfaces at high values of C_{Cl}, especially at $C_{Cl} \geq 75\%$. Some free chlorine is expected to be produced in plasmas containing $CHCl_3$, thus surface etching by chlorine may account for the increased roughness.

As shown in Figure 4, the elemental composition (C, Cl, O), estimated using EDS, varies with C_{Cl}. The relative carbon content decreases while that of chlorine increases. In thin films produced by PECVD with a source of chlorine in the plasma feed the chlorine film concentration typically increases with increasing C_{Cl}[7,9]. Similarly, for treatment in $CHCl_3$ plasmas, holding other system parameters constant (e.g. applied power and treatment time) it is anticipated that the chlorine content of the surface increases with increasing C_{Cl}, unless saturation occurs. Polypropylene, for example, has been chlorinated in $CHCl_3$ plasmas [10].

As indicated by the infrared analyses (Fig. 2), the untreated PE contains some oxygen. Figure 4 shows that [O] varies roughly over the range 3 to 6 at.%. Some post-deposition incorporation of oxygen as a result of reactions between radicals in the film and ambient oxygen or water or both is

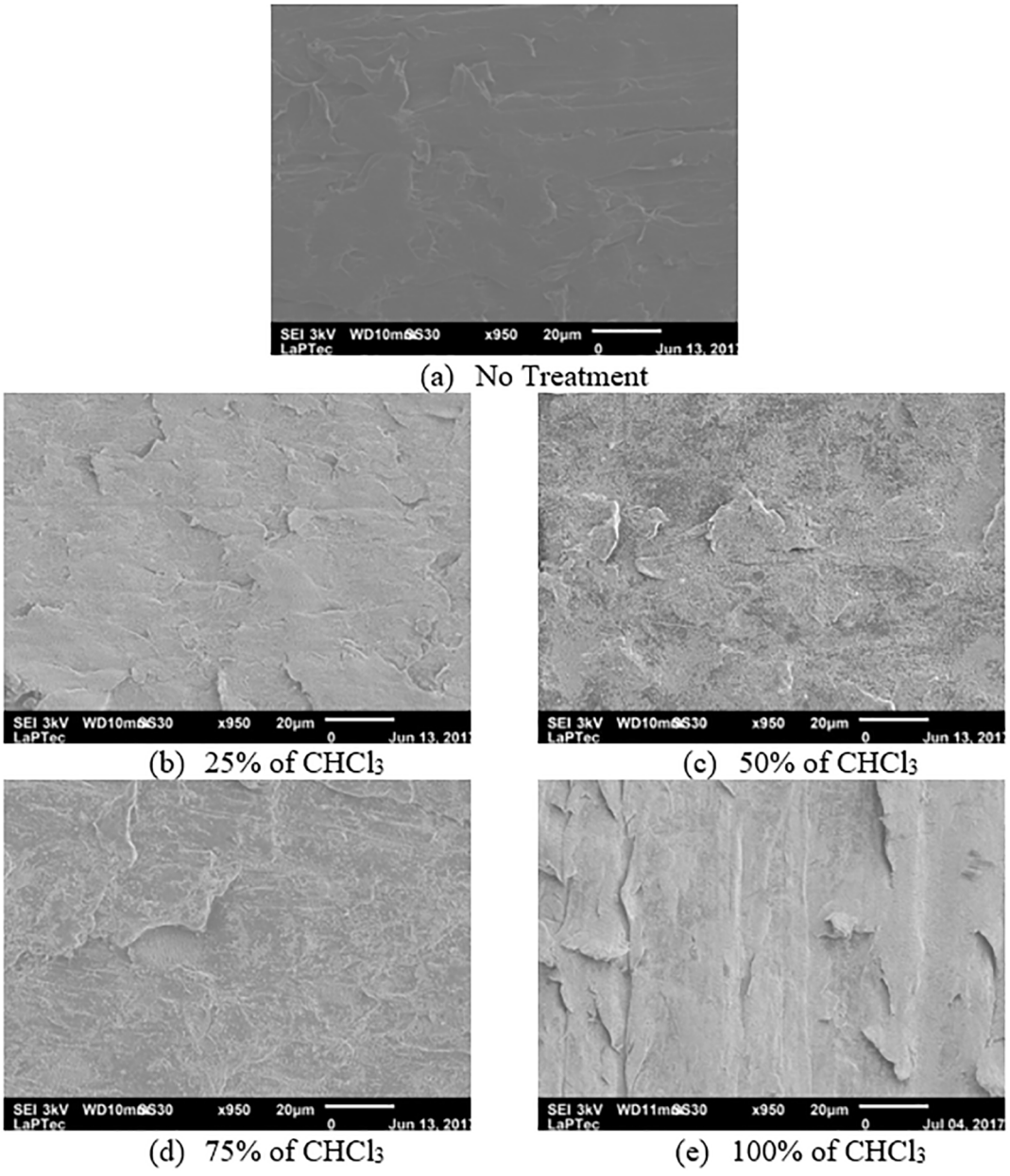

Figure 3. Scanning electron micrographs of PE treated at C_{Cl} = 0%; (b) C_{Cl} = 25%; (c) C_{Cl} = 50%; (d) C_{Cl} = 75%; (e) C_{Cl} = 100%.

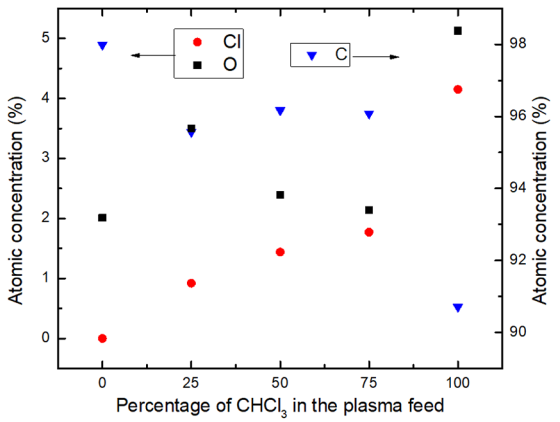

Figure 4. Elemental composition determined using EDS as a function of C_{Cl}.

well-known for plasma polymers [11]; similar interactions may explain the slight increase in [O] observed with increasing C_{Cl}.

The untreated and treated samples were also analyzed using XPS but quantification of the elements present was limited by the following factors: (i) insufficient resolution did not allow quantification based on the 2p3/2 and 2p1/2 peaks; (ii) the presence of a few extraneous elements such as Si and Na made the deconvolution of the C1s peaks unreliable; (iii) chlorine could not be quantified without the Cl 2s peak, which was only detectable when chlorine was present above a minimum concentration. This occurred for the surfaces for which C_{Cl} was 50% or greater; the results were as follows. For C_{Cl} of 50%, 75% and 100%, respectively, Cl passed from 38.7 to 49 to 46.8 at.%; C passed from 40.4 to 36.9 to 46.9 at.%; O passed from 20.8 to 14.1 to 6.3 at.%.

Figure 5 shows XPS survey spectra of the untreated and treated polyethylene. The tendencies in the peak heights show higher values of Cl and lower values for O as C_{Cl} is increased.

EDS measurements generally reflect the elemental concentrations in the bulk but can detect, for example, surface Cl when it is present at a sufficiently high concentration. The bulk PE contains oxygen. Therefore the [O] measured by EDS may indicate small variations in the concentration of this element in the bulk, while the XPS values (where available) indicate surface concentrations. Thus oxygen is present in both the bulk and the surface of all the films. The role of oxygen is important and merits future study. For example, atmospheric moist air plasma treatment of steel can reduce contact angles by about 20º and potentially improve paint adhesion [12]. Oxygen surface cleaning and oxidation also play key roles in the increased hydrophilicity of the treated surfaces. Similarly, surface cleaning and activation are responsible for reducing surface contact angles on aluminum exposed to an atmospheric plasma from 87º to 8º [13].

The trends in [Cl] as a function of C_{Cl} observed by EDS and XPS are compatible on the assumption that on the surface Cl tends to displace O. Thus at high C_{Cl} the surface is chlorinated at the expense of oxygen, while the bulk contains oxygen but no chlorine.

Figure 6 shows the water surface contact angle, θ, as a function of C_{Cl}. As C_{Cl} increases, θ increases by only about 20 degrees over the whole range of C_{Cl}. Figure 7 shows the surface roughness as a function of C_{Cl}. Roughness tends to increase as a function of C_{Cl}. This increase is compatible with the surface morphologies shown previously (Fig. 3). Roughness,

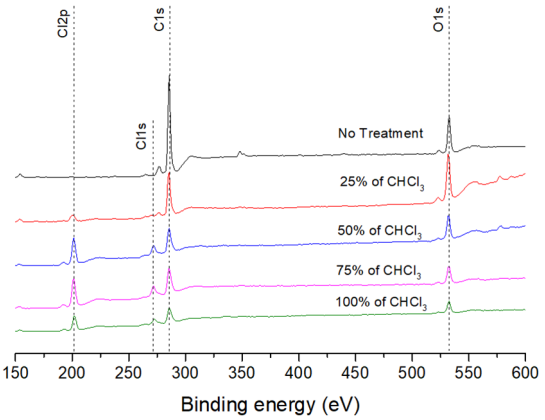

Figure 5. XPS survey spectra of the untreated and treated polyethylene.

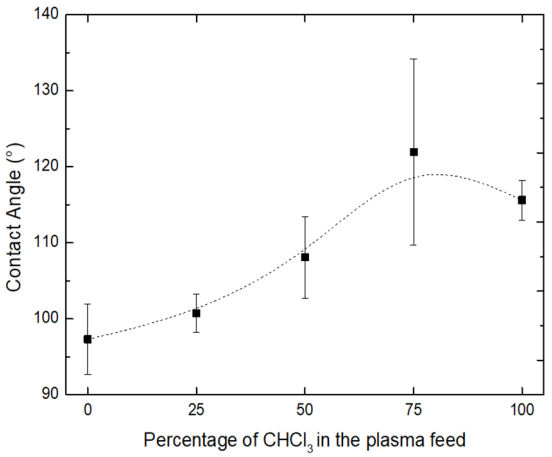

Figure 6. Surface contact angle as a function of C_{Cl}.

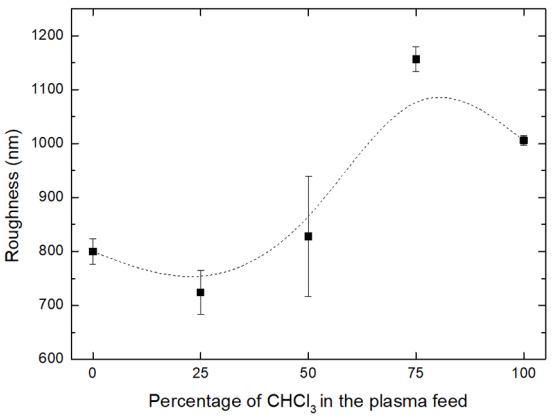

Figure 7. Surface roughness as a function of C_{Cl}.

chemical composition, and structure influence θ. Increased roughness correlates roughly with increased θ.

While greater values of θ may tend to impede paint adhesion, greater roughness may improve it. Figure 8 (a,b,c,d,e) shows the results of the paint adhesion tests for the untreated and treated PE. All of the treatments are highly effective independently of C_{Cl} ($C_{Cl} > 0$). For C_{Cl} = 25%, θ increases and roughness decreases with respect to the untreated

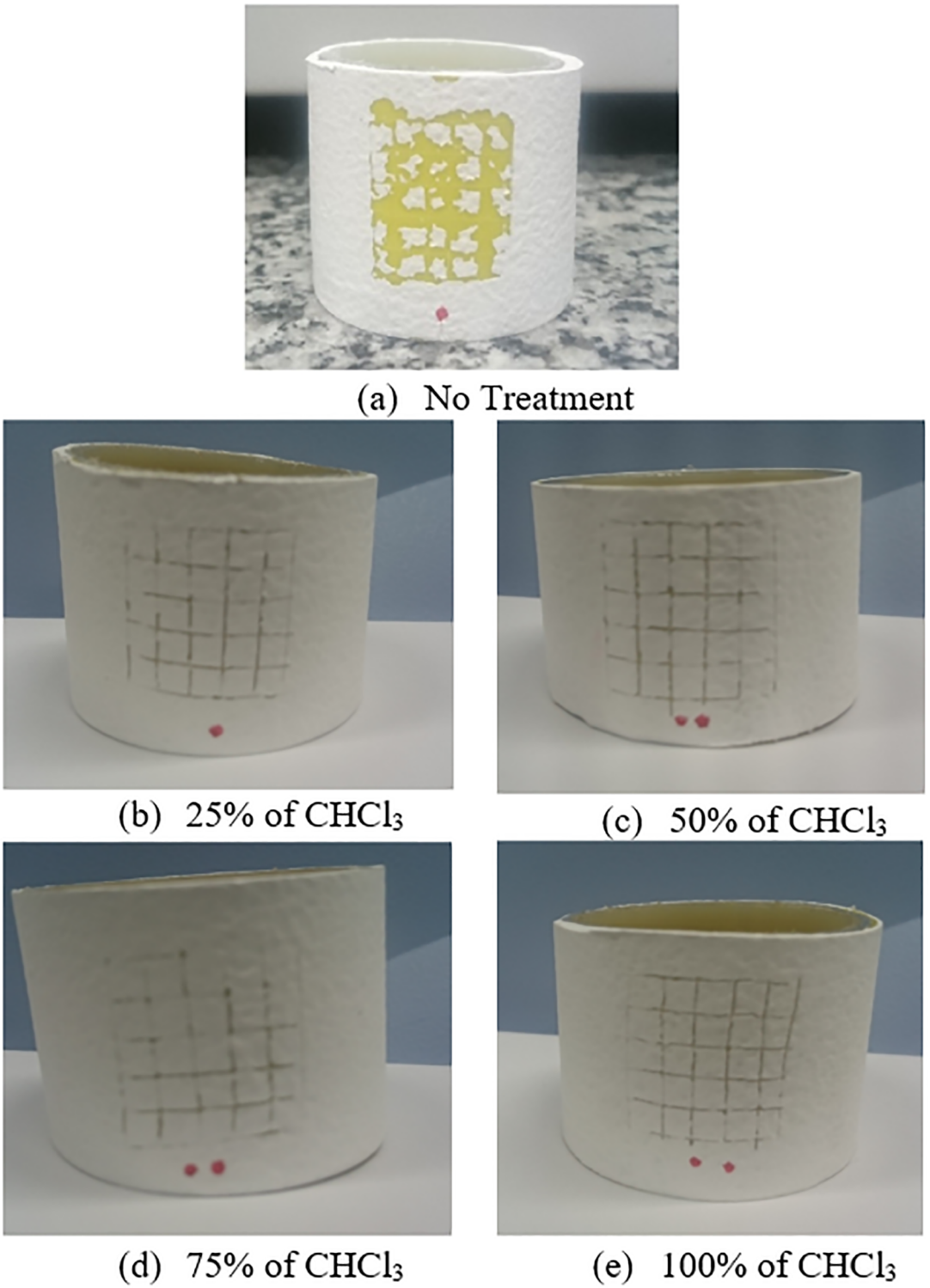

Figure 8. Photographs of the paint adhesion tests on PE treated at C_{Cl} = 0% (untreated); (b) C_{Cl} = 25%; (c) C_{Cl} = 50%; (d) C_{Cl} = 75%; (e) C_{Cl} = 100%.

materials. Both effects are expected to reduce paint adhesion but this is not observed. Therefore, for this case the cause of the improved adhesion must lie elsewhere; for example, in the presence of Cl or the combination of chemical structures present on the treated surface. Regarding the latter, the untreated material contains unsaturated carbon bonds and oxygenated functionalities, which may be activated and altered by the treatment, producing free radicals and dangling bonds as well as new oxygen-containing species. These then possibly react with the acryloyl, $H_2C=CH-C(=O)-$, components of the paint.

Table 1 shows the classification of the adhesion test results according to the Brazilian standards (BS EN ISO 2409:2007 and BS 3900-E6:2007A). The results obtained by painting the untreated PE clearly correspond to classification 4, which represents an extremely poor performance. In contrast, for all of the plasma-treated PE samples paint adhesion at level 0 is obtained.

4. Conclusions

Trichloromethane-argon plasma treatment of high density crosslinked PE over a wide range of partial pressures greatly improves water-based paint adhesion. The treatment modifies the surface oxygen content and produces surface chlorination, which is greater at greater C_{Cl}. The improvement in adhesion is not readily explained by the changes in surface contact angle or roughness induced by the treatment, but

Table 1. Classification of test results

Classification	Description	Appearance of surfasse of cross-cut from which flaking has occurred(Example for six parallel cuts)
0	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	-
1	Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not greater than 5% is affected.	
2	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5%, but not greater than 15%, is affected.	
3	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area greater than 15%, but not greater than 35%,is affected.	
4	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area greater than 35%, but not greater than 65%, is affected.	
5	Any degree of flaking that cannot even be classified by classification 4.	-

incorporation of chorine and activation of unsaturated carbon groups and oxygen-containing functionalities may play a role. However, the improved adhesion results are robust and have obvious application.

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