Adhesion improvement of a polymer/stainless steel composites with a silane coupling agent by an atmospheric plasma process

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Abstract: 3-Aminopropyltriethoxysilane coatings have been deposited on stainless steel (SS) samples by means of an atmospheric pressure dielectric barrier discharge (AP DBD) as an adhesive promotion layer in polymer/ stainless steel composites. A thermal and a plasma post treatments was studied to enhance the Si-O-Si chain elongation and the siloxane networking, with a significant improvement of the adhesion strength.

Keywords: composites, plasma post treatment, silane, DBD, stainless steel

1. Introduction

Polymer-steel hybrids offer an interesting combination: the stiffness and strength of steel is combined with the low weight density and formability of polymers. These hybrid materials have several advantages over the metal alone thanks to an increased impact resistance, higher strength-to-weight ratio, resistance to corrosion, better dimensional stability and more design freedom.[1, 2] However the lack in adhesion at the SS/polymer interface is the main drawbacks of the hybrid combination.[3] One of the most promising solution is the use of silane as coupling agents in place of toxic chromate.

Application of silane coupling agents through wet deposition technique is a widely studied method, with some inherent limitations as being a multistep process involving use of solution and consequent waste flows.[4] Deposition of silane coupling agents using atmospheric plasma chemical vapor deposition could be an efficient and innovative alternative to wet deposition with the advantage of combining plasma cleaning a priori to the deposition in the same reactor. A plasma deposited siloxane layer can act as an interfacial modifier for improving adhesion and corrosion resistance creating chemical bonds between the siloxane and metal interface.[5]

The main goal of this study is to deposit a siloxane layer on a stainless steel surface through DBD process. 3-aminopropyltriethoxysiloxane was chosen as chemical precursor and various process parameters (plasma pre-treatment, power, treatment time and thermal and plasma post-treatment) were studied.

The effect of both thermal and plasma post treatment on the properties of the deposited film was studied. Contact angle (CA), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and SEM measurements were conducted to characterize the deposited film. The adhesion strength evaluation of different samples was done by using pull-off testing (dolly testing). Fracture surface of the different dolly samples were recorded and analyzed also to study the failure mode of the different samples.

2. Material and method

Bright annealed 304 stainless steel (mirror polished) 0.8 mm thick was provided by OCAS (Belgium) and used as substrates for plasma thin film deposition and dolly testing. For these purposes, the SS plates were cut in 30 mm x 30 mm samples and sonicated in an isopropanol bath (3510 BRANSON ultrasonicator, 70W) for 15 min. Mono/bi-sided lapped silicon and glass substrates were used for contact angle, FTIR and thickness measurements, respectively, after a proper cleaning in isopropanol ultrasonic bath.

3-Aminopropyltriethoxysiloxane (APS, ≥ 99% purity, CAS no: 919-30-2) provided by Sigma-Aldrich (Belgium) was selected as organic precursor for the plasma deposition. One weight% of bi-distilled water was added to pure APS to induce a pre-hydrolysis of the precursor. Different types of polymers, both thermoplastic and thermosetting, were used to investigate the efficacy on the method (epoxy resin, poly urethane, poly ammide). However the results reported in this paper are mainly related to a SS/epoxy resin composites. Aluminium dollies (20 mm in diameter), previously sandblasted and cleaned ultrasonically in acetone for 1 h, were used for pull-off testing.

The experimental deposition system is a typical parallel plate DBD reactor, PlasmaZone®, where the plasma discharge is generated between two metallic stainless steel electrodes both covered with 3.5 mm thick dielectric glass plate (Figure 1). The system is described more in details in a previous article.[6]

Figure 1. Picture of PlasmaZone® mounted on a X-moving table.

Prior to the plasma deposition, a plasma pre-treatment in N_2+ O_2 atmosphere was performed to remove impurities and to enhance the amount of hydroxyl groups on the surface able to link covalently to the siloxane film.[7]

Several experimental conditions were investigated to vary the chemical composition of the deposited coating in order to enhance the adhesion towards the polymeric layer. After the plasma deposition, a post treatment step was performed to build the siloxane network formation either by thermal (conventional oven for 4 h at 100°C) or plasma treatment in N_2+O_2 atmosphere. Note that this step is essential for the adhesion improvement: adhesion tests performed on plasma coatings without post treatment step showed an opposite effect with a breaking stress fracture strength lower than the untreated SS.

A multi-step analytical approach was used for the chemical evaluation of the deposited coatings (FTIR, XPS, SEM).

A dolly-plate-dolly (DPD) symmetric sample configuration was used (in accordance with ISO 4624:2003)[8] for the pull-off testing.

The sample preparation and the testing methodology is reported in Figure 2.

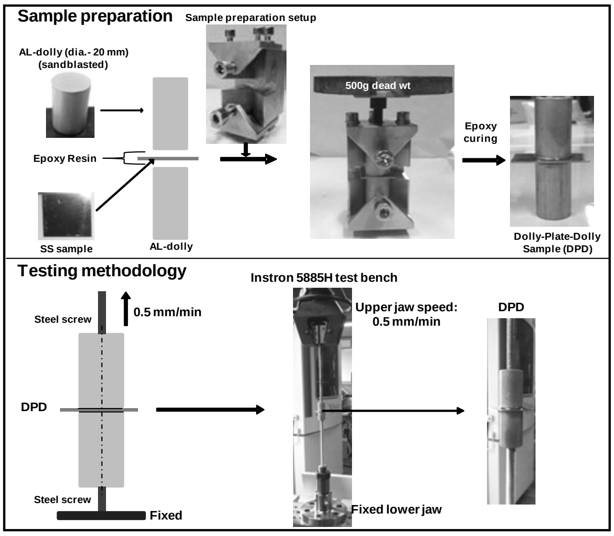

Figure 2. Schematic representation of dolly sample preparation and dolly testing methodology.

For these measurements, all the plasma treatments were repeated for both sides of the SS plates consecutively.

3. Results

The first step was the optimization of the coating deposition with regards to the retention of the APS chemical structure. In fact, the presence of ammine groups in the plasma deposited coating may encourage a the formation of chemical bonds at the interface with the polymeric matrix enhancing the adhesion strength in the final composite. The chemical composition of the deposited film has been carefully evaluated by means of FTIR analysis a priori to the mechanical pull-off testing.

FTIR spectra of plasma APS coatings deposited at two different powers, 200 W and 450 W are reported in Figure 3, where the most interesting peaks are highlighted.

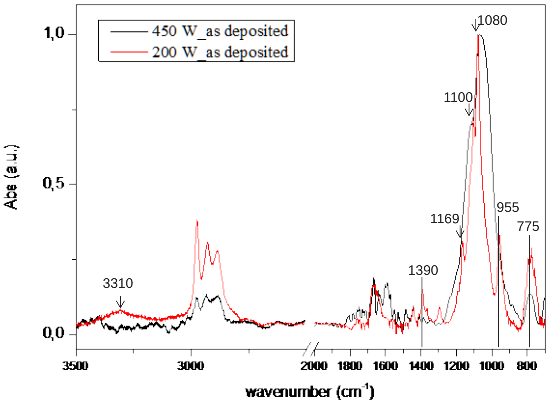

Figure 3. FTIR spectra of plasma deposited coating at 200 W and 450 W (Table 1, f= 1.5 kHz, N_2 $\Phi_{aerosol}$_APS+1%H_2O= 3 slm, N_2 $\Phi_{plasma\ gas}$= 20 slm, 48 s) without post treatment step.

The presence of peaks that are related to the precursor chemistry, such as NH_2 (3370-3230cm^{-1} and 1390cm^{-1}) and CH_2/CH_3 (2930-2830cm^{-1}) groups, is a strong evidence that the APS structure is more retained when a lower power is applied.

Therefore, the lowest possible power of 200 W to generate a plasma in nitrogen carrier gas was selected for the further coating development and adhesion improvement, as well as for the post treatment evaluation.

In order to evaluate the effect of the post treatment, the APS coating was deposited always in the same experimental conditions (f= 1.5 kHz, N_2 $\Phi_{aerosol}$_APS+1%H_2O= 3 slm, N_2 $\Phi_{plasma\ gas}$= 20 slm, 48 s, 200 W) for all the surface characterization performed.

The effect of the thermal post treatment (thermal PT) was studied for a fixed time and temperature (4 h, 100 °C), while more parameters were considered in case of the plasma post treatment (plasma PT), as the influence of the plasma power (200 W and 450 W), the oxygen percentage in the gas mixture (0.1%, 5%, 10, 20%) and the post treatment time (16s, 48s, 160s).

As main outcome, the post treatment step resulted in improved properties of the deposited coating as observed by the significant enhancement of the adhesion at the two interfaces plasma coating/ SS substrate and plasma coating/polymeric matrix.

The major chemical change observed after the post treatment is mainly related to the siloxane region 1200 – 1000 cm^{-1}. Indeed the FTIR spectra (Figure 4) showed the typical broad absorption band related to Si-O-Si/ Si-O-C stretching, confirmed also by the XPS analysis (data not shown).

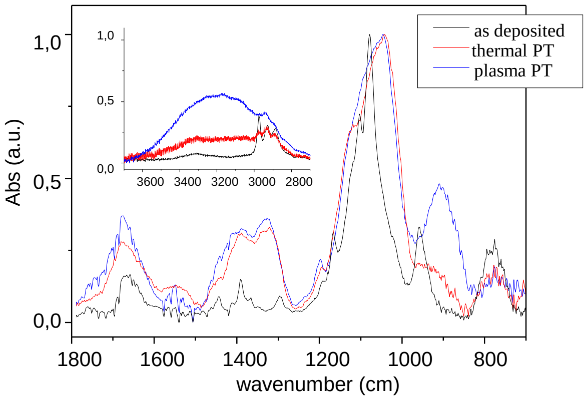

Figure 4. Effect of the post treatment on the chemical structure of the deposited coating: thermal (4h, 100°C) and plasma (16s, N_2+20% O_2) post treatments. Coating deposition condition: f= 1.5 kHz, N_2 Φaerosol_APS+1%H_2O= 3 slm, N_2 Φplasma gas= 20 slm, 48 s.

The improvement in the Si-O-Si networking and elongation thanks to the post treatment resulted in water stable coatings and in a significant increase of the adhesion strength at the interface in SS/ polymer composites. Compared to the native SS, the improvement of the fracture strength is of more than 20 MPa as measured in DPD pull-off test (Figure 5).

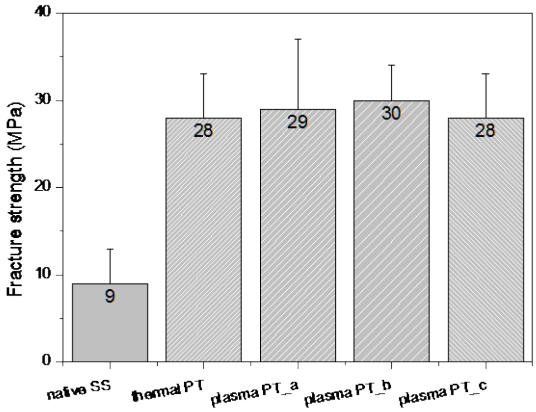

Figure 5. Improvement of the breaking stress fracture strength for thermal (4h, 100°C) and plasma post treatment (a. 450 W, 5% O_2, 48 s; b. 450 W, 10% O_2, 48 s; c. 450 W, 10% O_2, 16 s). Coating deposition condition: f= 1.5 kHz, N_2 $\Phi_{aerosol\_APS}$+1%H_2O= 3 slm, N_2 $\Phi_{plasma\ gas}$= 20 slm, 48 s.

4. Conclusion

In the present abstract atmospheric pressure plasma deposition of siloxane coatings is presented as a feasible and convenient alternative to conventional wet chemistry in terms of a sensible reduction of the overall process time and liquid waste as well as a versatile technology easy to be implemented in an existing production line. The chemical composition of the thin Si-O-Si plasma deposited film was optimized by a multi diagnostic approach by evaluating the effect of the main external plasma parameters (power, precursor, thickness and post treatment) in relation to the improved adhesion property. As main outcome, the positive effect of the post treatment step, either thermal or plasma, on the adhesion strength increase has been found. In both cases, an improvement of more than 20 MPa in stress at break fracture strength was reached when an applied power of 200 W and pre-hydrolyzed APS were used for the coating deposition.

Moreover, it is clear from this work that the post treatment after plasma deposition resulted in comparable adhesion strength with respect to the conventional thermal wet chemistry deposition. This leads to undoubted advantages over wet processes from the technological and industrial point of view.

On top of that, the versatility of the developed process is an another key issue for its implementation in production line: indeed the adhesion strength was significantly increased also for different SS/ polymer composites with the use of both thermoplastic and thermosetting polymers, as PU and PA (data not shown).

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6. References

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