

Plasma functionalization and texturing of poly(ether ether ketone) (PEEK): correlation of the surface physicochemistry and topography on the metal-polymer adhesion

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Abstract: This study shows that low or atmospheric pressure oxidative plasma improve the wettability by an increase in the surface free energy, and the adhesion of metallic thin films. These improvements are correlated to the increase of the polar component of the surface, as measured by XPS. This study also shows that the modification of both surface chemistry and the surface topography at the same time further improves the practical adhesion of the metallic thin films. Indeed, we verified that dense patterns etched by an infrared femtosecond laser allow good practical adhesion of the metallic thin films on the substrate.

Keywords: Plasma functionalization, adhesion, surface chemistry, wettability, PEEK

1. Introduction

In the transportation industry, compromises have long been made to reach good mechanical resilience while ensuring the lightness of the structural materials. This objective is still of concern nowadays to further lower energy consumption of transportation means. The replacement of metallic structures implies using polymer composites. Many composites are made of thermosetting resins such as epoxy resins; yet, they present low mechanical and chemical stability, and are hard to recycle. This is why engineering thermoplastic composites gain more interest to replace them, especially the poly(aryl ether ketone) (PAEK) family. This study focuses on one of the PAEK matrixes, the poly(ether ether ketone) (PEEK).

However, PEEK is no exception to other polymers and is endowed with poor surface free energy. Thus, PEEK surface presents poor wettability and poor adhesion for a vast variety of coatings, such as organic or inorganic thin films. To solve this poor surface property, polymer surfaces undergo physical or chemical treatments to enhance the spreading of liquids[1–3] for dyeing, painting or gluing,[4] or to enhance the strength of assemblies[5] and the adhesion towards solid coatings[6,7].

The goal of this study is to define the optimal surface chemistry that has to be aimed to enhance the adhesion of metallic thin films, deposited by thermal evaporation. An effective way to modify the surface chemistry is via plasma treatment. For this study, two plasma functionalization methods were compared: an atmospheric pressure plasma and a low pressure plasma. The modification of the surface chemistry obtained by plasma treatment was extensively surveyed by X-ray photoelectron spectroscopy. As surface roughness is

known to improve adhesion, the influence of the surface topography on adhesion was also studied.

2. Materials and methods

Surface chemistry, wettability and adhesion of metallic coatings were studied in the case of Victrex® PEEK 450 G, after plasma functionalization or laser etching.

Plasma functionalization was compared and studied for two plasma technologies in oxidative conditions. The first plasma is an atmospheric pressure blown arc (Ultra-Light System from AcXys™). The efficiency of the functionalization by the air plasma was finely tuned by varying the scan speed, the number of scans and the nozzle-surface distance. The other plasma system used for this study is a low pressure plasma sustained by a microwave generator, using an Electron Cyclotron Resonance configuration; influence of the plasma parameters on surface properties was also studied, for several compositions of the introduced gases; admixtures of argon, oxygen and nitrogen were used.

In the case of the low pressure plasma, two surface-treatment modes were considered: a “low energy” mode, where the polymer surface was functionalized by the activated neutral gaseous species in the plasma phase and diffusing to the surface; and a “high energy” mode, where negative voltage was applied on the substrate to accelerate ions towards the surface, allowing ionic interaction on top of the chemical activation by neutral species.

In the case of the high energy mode, significant surface texturing was obtained. In order to characterize the influence of the surface topography obtained by plasma on the surface properties, it was compared to a more defined surface texture. A geometrical pattern was obtained via laser etching, for which minimal surface chemistry alteration was assumed.

To assess the modification of the surface chemistry, X-ray photoelectron spectroscopy was used, on the one hand

to quantify the oxidization degree as measured from low resolution spectra by calculating the oxygen-to-carbon ratio, on the other hand by calculating the functional groups proportions added on the surface from the C 1s components fitting.

Surface wettability was studied by calculating the surface free energy as described by the Owens-Wendt method [8], from Equation (1).

$$\gamma_{lg}(1 + \cos \theta) = 2\sqrt{\gamma_s^D \gamma_l^D} + 2\sqrt{\gamma_s^P \gamma_l^P} \quad \text{Equation (1)}$$

Contact angle of diiodomethane and water sessile drops were measured to quantify respectively the non-polar and polar components of the surface free energy.

Practical adhesion of 1 μm metallic thin films was measured by the pull-off test. Aspect of the interface was also characterized to have more information on the fracture mechanisms of the assemblies.

3. Results and discussion

In this study, we showed that both plasmas in oxidative conditions allowed the grafting of ketones (C=O), acidic and ester groups (COO), and ethers (C-O-C) was highlighted thanks to XPS measurements; the proportion of these functional groups showed a certain sensibility to the plasma parameters. Thus, the proportions varied, (i) for ether groups from 17 to 25 %, (ii) the ketone from 2 to 14 % and (iii) the acid/ester groups from 0 to 8 %.

Measurements of the surface free energy and the practical adhesion of metallic thin films showed that these surfaces characteristics had similar dependencies on the plasma parameters, as observed for the variation in surface chemistry. Thus, we show that a strong correlation is observed between the wettability (through surface energy) or metallic coatings adhesion, and the proportion in the C=O (ketone) and COO (acid/ester); however low, if nonexistent correlation was brought to the light between C-O-C (ether) and surface wettability or adhesion.

Yet, even if similar surface oxidation was observed for both plasmas, several differences were observed between both plasma treatments.

First, atmospheric pressure plasma showed the role of adsorbed water on the surface before plasma treatment. Indeed, adsorbed water on the polymer surface acts as a barrier to the plasma functionalization. Thus, to optimize the efficiency of the plasma activation, drying the surface is needed before treatment. If the surface is not prepared that way, two scan of the surface are needed, where the first pass of the plasmas has the main role of desorbing the water from the surface, as shown in our work[9].

Second, low pressure plasma is more efficient in the activation process than the atmospheric pressure plasma, as quicker saturation of the surface energy and adhesion of metallic thin films (Fig. 2) was observed. That higher efficiency is attributed to higher density and wider variety of activated species in the low pressure plasma phase.

Third, adhesion characterization showed different rupture modes between both plasmas (Fig. 1). In the case of the low pressure plasma, all ruptures were adhesive. In the case of the atmospheric pressure plasma, rupture modes evolved from adhesive, to cohesive (metal layer failure) and up to a cohesive failure with the rupture of the substrate.

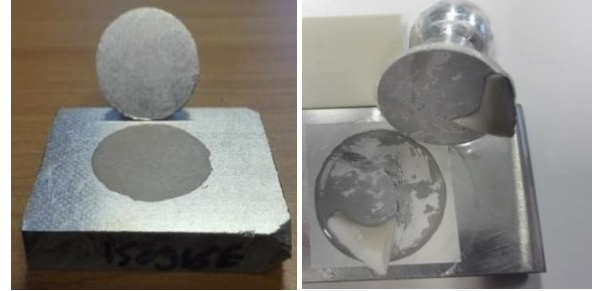


Fig. 1. Pictures of the interface aspect after separation. Left: adhesive rupture; right cohesive rupture with substrate failure.

These differences in the rupture processes were attributed to a quicker increase of the surface temperature in the case of the atmospheric pressure plasma treatment, causing a thermal shock, altering the mechanical stability of the assembly.

When substrate polarization is used in the case of the low pressure plasma (high energy mode), surface texturing (10-100 nm scale) appears. This surface roughness, coupled with the chemical activation, further increase the adhesion of metallic coatings (Fig. 2), from 3 to 4 MPa (chemical-only effect) up to 8 MPa (chemical and texture). However, the rupture mode evolved from adhesive, to cohesive when texture appears. These observations imply (i) a cumulative effect of chemical interactions between functional groups and metal atoms and mechanical anchoring, but (ii) some limitation of the maximal level of adhesion attainable with this kind of treatment. To explain the impact of surface texture on the adhesion mechanism, laser etching was studied. It was shown that densification of surface textures increases the mechanical anchoring and thus the practical adhesion (Fig. 2), but quick saturation was observed because of the cohesive rupture of the assembly. This limitation of the mechanical resilience of the assembly when surface texture is formed is attributed to local build-up of tensile stresses during the pull-off test. Indeed, surface texturing could induce uneven distribution of the tensile strength, or induce the appearance of a weak boundary layer.

Several secondary effects of the surface treatments could thus induce a limitation of the strength of the assembly, especially by weakening the polymer substrate. In this work, thermal shock and formation of a weak boundary layer was observed. To assess this weakening effect, a mechanical model was developed with the ABAQUS software. This model showed the stress dynamics occurring through the interface. Good agreement was attained with the experimental tensile

strengths measured, and the aspect of the interface after the rupture. This model indeed showed how and why substrate rupture could occur.

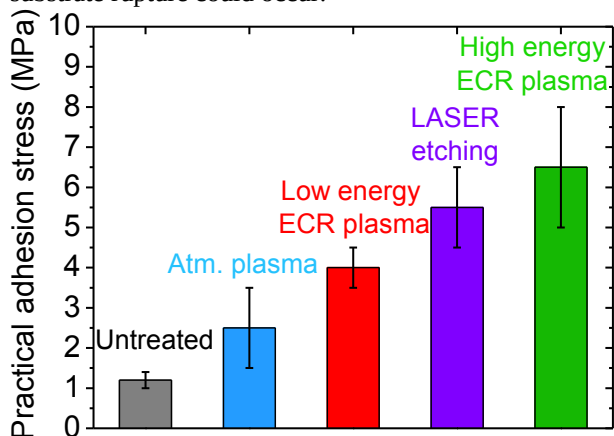


Fig. 2. Comparison of the variation spans in the practical adhesion stresses obtained for the different surface treatments.

4. Conclusions.

This work shows how plasma functionalization induces a modification of the surface chemistry of PEEK, and how it is possible to modify the surface topography. In particular, the control of the surface chemistry obtained by plasma treatment shows that the increase in the polarity of the surface increases the wettability and metal adhesion onto polymer substrates. The combined effect of the texture and chemistry of the surface can optimize the adhesion properties of polymers, if the mechanical behavior of the coating-substrate assembly is taken into account.

5. References

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