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The effect of substituted poly(*p*-xylylene) on the quality of bonded joints when used as a primer replacement

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ABSTRACT

Organic coatings are widely used in the aerospace industry as corrosion protective coatings or as primers in improving the adhesive bond in structural adhesive joints. However, these organic coatings may become unstable under exposure to high temperatures or in extreme hostile environments. This article presents a method to successfully coat metallic surfaces with an environmentally friendly and easy to apply coating which resists high temperatures. The coating consists of derivative of poly (*p*-xylylene) (PPX) polymers (so-called poly(*o*-amino-*p*-xylylene-*co*-*p*-xylylene) (amppx)). The surface modification after application of an amppx coating and the adhesion strength of bonded joints (on titanium, aluminium and stainless steel) were verified by means of contact angle, roughness measurements and interfacial shear strength tests. The adhesion of the amppx coating to three surfaces was compared with other surface treatment methods such as chromic acid anodising and atmospheric plasma in terms of adhesive bond strength performance. Lap-shear test results show that the strength of adhesive bonded titanium specimens, which were grit blasted and coated with an amppx coating is almost as good as after a chromic acid anodising treatment. The failure mode of the specimens is 100% cohesive. The method presented in this study opens new possibilities for the use of PPX and their derivative coatings for aerospace applications.

1. Introduction

The adhesion of coatings to metals or polymers as well as the adhesion strength of bonded joints depends to some extent on the surface conditions of the parts to be coated or bonded. For example, a pre-treatment process, which creates a fresh oxide layer or increases the roughness/porosity of the surface, leads to a considerable increase in the adhesion strength of coatings [1,2].

Electrochemical processes based on chromic, sulphuric and phosphoric acid solutions or their combinations result in an increase of the surface porosity of the material. For example, chromic acid anodising of aluminium alloys is widely used and provides an excellent surface to be primed both for painting and adhesive bonding. However, the chromic acid anodising solution contains chromium (VI) or hexavalent chromium, which is highly toxic and carcinogenic [3]. Another frequently used technique to remove the old oxide layer formed during exposure of the metal to air is grit blasting [4,5]. Grit blasting is a process where abrasive particles (such as aluminium oxide) are accelerated and forcefully blown onto the surface of a material. Atmospheric plasma irradiation of metal surfaces has been recently used to remove the organic contaminations, activate the surface and thus increase the adhesion of organic coatings [6–8].

Many attempts have been done to develop an organic coating, which in combination with a suitable surface treatment secures good adhesion between the organic/inorganic materials. Furthermore, in order to be suitable for aerospace applications, the coating should protect against corrosion, be resistant to high temperatures and environmentally friendly. Silane coupling agents are widely used as organic coatings in industry due to their capability to provide chemical bonding between an organic and an inorganic material [9]. Unfortunately, these organic coatings are not resistant to temperatures such as 500 °C or even higher.

Poly-*p*-xylylene (PPX) polymers are aromatic polymers whose molecular structure consists of a benzene ring and two methylene groups in the para-position (see Fig. 1). They are obtained after pyrolysis at high temperature of [2.2]paracyclophane [10]. These polymers and especially their derivatives present excellent electrical properties, high crystallinity, good mechanical properties and are resistant to high temperatures (up to 780 °C) [11–14]. They show no creep and stress relaxation phenomena. Moreover, they have low permeability, are non-biodegradable and biocompatible [15,16]. These properties attribute to the

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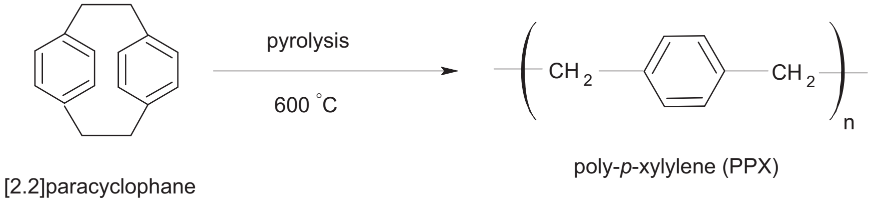

Fig. 1. PPX formation from pyrolysis of cyclophanes.

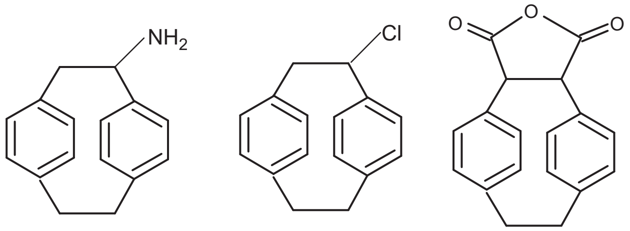

Fig. 2. Amino, anhydride and chlorine PPX derivatives.

successful implementation of PPX polymers and their derivatives in various technologies such as printed boards, integrated circuits or microelectronics. A number of different PPX derivatives have been developed, e.g. amino-, anhydride- or chlorine-PPX substituted ones [17], see Fig. 2.

The poor solubility of PPX derivatives in organic and inorganic solvents below 150 °C [18] does not allow their preparation following common polymerisation techniques but they can be prepared by chemical vapor deposition (CVD) process. Advantages of the CVD technique compared to spraying, dipping or brushing lies in the fact that the solid coating is directly formed from the gaseous phase without an intermediate liquid state. The CVD polymerisation of PPX and substituted PPX appears to be an excellent method to coat metallic surfaces [19], zinc-coated steel [20] or low-density polyethylene [21] with a very good control over the layer thickness and homogeneity.

In spite of the excellent properties of PPX polymer coatings, their strength and durability on adhesive bonds have not been systematically studied. Organosilane coupling agents coated on the surface of a silicon wafer during or before the adhesion of PPX leads to an increase in the adhesion strength as determined by 180° peel tests [22]. It is known, however, that organosilane coupling agents degrade when exposed to high temperatures. Therefore, application of such a system in aerospace materials is limited.

This study aims to investigate the possibility of using PPX-derivative coatings, poly(*o*-amino-*p*-xylylene-*co*-*p*-xylylene) (amppx), to improve the adhesive strength of bonded joints. The ability of the amppx layer to improve the adhesion between metal surfaces is determined by lap-shear tests.

2. Experimental

2.1. Materials

Sheet metal of 316L stainless steel (SS), unalloyed titanium (Ti) (ASTM grade 2 purity level 99.2% Ti and limited amounts of C, H, Fe, N and O) and aluminium 2024-T3 non-clad (Al) with a thicknesses 1.4, 1.5 and 1.6 mm, were cut into 60 mm × 15 mm test specimens. A cleaning fluid called power formula quick dry (PFQD) (an environmentally friendly multipurpose solvent of PT Technologies Europe, Ireland) was used to secure a reproducible clean surface. The adhesive primer Cytec BR 127 and epoxy adhesive film Cytec FM 73 were used to bond the specimens.

2.2. Surface treatment

Prior to further surface treatment and coating application, dust particles and finger print grease were removed from all test specimens by using the PFQD fluid.

The surface of the specimens was treated prior to the application of the amppx coating either by grit blasting or by abrasion. These two methods were studied to determine the influence of the surface properties on the adhesion of the amppx coating.

Grit blasting (*GB*) was performed in a grit blast cabinet using Corublast Super Z-EW α-Al_2O_3 particles (corundum), type FEPA no. 100 (grain size 0.10–0.15 mm). After the grit-blasting treatment the surfaces were cleaned again with PFQD to remove remaining dust particles. The role of the α-Al_2O_3 particles is to remove the old oxide layer formed during the exposure of the metal to air and also to increase the surface roughness.

Mechanical abrasion was done by using 180 grade emery paper followed by cleaning with PFQD. After the sand paper treatment, an increase in the surface roughness and surface contact angle was observed.

Chemical vapor deposition process (*CVD*) was performed after the above-mentioned pre-treatments of the specimens. The amppx coating was applied in the self-designed equipment of DWI (German Wool Research Institute at the RWTH Aachen) that allowed variable process parameters. The monomer 4-amino[2.2]paracyclophane was synthesized from [2.2]paracyclophane by the method described before [16]. The monomer was first vaporized at 200 °C and subsequently pyrolysed for 30 min at 750 °C at a pressure of 20Pa 2×10^7 Pa and a monomer stream flow of 15 sccm (standard cubic centimeter per minute). Finally, it was polymerised and condensed at 7 °C on the surface as poly(*o*-amino-*p*-xylylene-*co*-*p*-xylylene) (amppx) as shown in the reaction Scheme 1.

The CVD process resulting in the amppx layer was compared to other techniques and coatings such as chromic acid anodising and atmospheric plasma in terms of adhesive bond strength performance.

Chromic acid anodising (*CAA*) of titanium was carried out in a chromic acid solution (40 g/L, 50 °C). The voltage was increased progressively from 0 to 15 V during 4 min and maintained at 15 V for another 36 min. Prior to the CAA treatment, the specimens were degreased in an alkaline cleaning bath.

Atmospheric plasma treatment (*PA*) was performed with a Plasma-Blaster (Tigres GmbH, Rellingen, Gemany) instrument equipped with three separate plasma guns. Plasma is generated and controlled by a 300 W power generator. The pressure needed to produce stable and uniform plasma is 4×10^5 Pa at a gas consumption of 17 L/min. The gas used for treatment is laboratory air. The degreased specimens were placed underneath the plasma guns at a distance of 2 cm and irradiated during 1 min. To assure a complete and homogeneous surface activation, the specimens