



Scratch response of high-performance thermoset and thermoplastic powders deposited by the electrostatic spray and 'hot dipping' fluidised bed coating methods: The role of the contact condition

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ABSTRACT

The scratch performance of powder-coated substrates depends on many factors, including the coating material and thickness, the deposition techniques, and the characteristics of the baking processes. In the present investigation, two thermoplastic (PPA571, an alloy of acid-modified polyolefins) and thermoset (TGIC-free, transparent, bronze-pigmented polyester) organic powders were deposited onto flat aluminium substrates by the 'hot dipping' fluidised bed and electrostatic spray coating technologies. In the former technology, the metal substrates were pre-heated to 300 °C before being dipped in the fluidised bed and powder coated. In the latter technology, after electrostatic painting, the coated substrates were submitted to a curing process for 20 min at 170 °C to allow the formation of continuous films.

The resulting coatings differed in morphology, thickness and adhesion strength. The scratch responses of the coatings were evaluated by progressive-mode scratch tests. Different contact conditions between the scratching geometry and the coating surface were analysed using three conical (Rockwell C) diamond indenters with tip radii of 100, 200 and 800 µm.

Electrostatically sprayed thermoset coatings showed a better overall scratch resistance with minor deformation events and damage of a lesser extent compared to the thermoplastic coatings. On the contrary, the thermoplastic coatings displayed very singular scratch properties regardless of the deposition process, having the largest deformation events and most massive interfacial rupture.

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1. Introduction

The adhesion strength of organic coatings is of paramount importance in a wide range of manufacturing processes, including paints for automotive and aeronautics parts, housings for consumer electronics, domestic appliances, and indoor and outdoor furniture [1,2]. One of the most widespread techniques to quantitatively assess the adhesion strength and scratch resistance of organic coatings is the scratch test [3]. During the scratching procedure, the organic coatings are usually submitted to the action of an advancing conical or spherical indenter with a diamond or metal tip at either a constant or progressively increasing load [4]. The scratch loads, sliding speeds and contact conditions between the advancing indenter and the coating surface can be varied to better evaluate the adhesion strength and scratch resistance of the organic coatings under different loading conditions [5–8]. Briscoe et al. were the first to systematically investigate the scratch hardness and the deformation mechanisms

for several plastics using cones and spheres of various size under a number of contact conditions (i.e., applied normal load, strain, scratch velocity) [5]. The various damage regimes such as ironing, ploughing, and brittle cracking were introduced and the role of the important contact mechanical variables was described. A number of 'scratch' or damage maps were also provided to illustrate the types of material which might be derived and portrayed using this approach [6]. Xiang et al. attempted to correlate the scratch behaviour of a broad range of polymers under constant and progressive load scratch test and basic material properties, such as the Young's modulus, yield stress, and tensile strength [7]. Later on, Krupicka et al. investigated the use of contact scratch tests on polymer coatings, studying the influences on the material deformation response from test parameters such as scratch speed, contact geometry and load [8]. These operating parameters allow the modulation of the stress state induced in the coating material during the scratch, as well as the magnitude and distribution of the stress field, the contact strain and the strain rate inside the scratched material. In particular, the scratching geometries (i.e., the indenter geometries) have a very crucial role with respect to the imposed effective strain and, therefore, to the effective loading conditions to which the coating is submitted [8–11]. In this respect,

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Krupicka et al. mapped the scratch response of a one-layered flexible powder coating and a two-layered ductile solvent borne coating, emphasising how the contact load and the contact strain influence the magnitudes of the total scratch deformation and the onset of the damage mechanisms [8]. Barletta et al. investigated the relationship between the actual loading conditions during scratch tests and the scratch deformation response of single layer and bi-layer electrostatically sprayed powder coatings [9,10]. More recently, Pelletier et al. reported on the relationship between contact geometry and the deformation response during scratch tests of two amorphous (i.e. thermoset and thermoplastic) polymers, demonstrating clear correlations between the average plastic strain and the geometrical parameters used to describe the geometry of the contact area [11].

Indeed, the effective strain that an indenter with a spherical tip is able to apply on the coating material is directly related to the penetration depth and is linearly proportional to the ratio of the radius of efficient contact, a , and to the radius of the spherical tip, R , according to the following formula:

$$\varepsilon_s \propto \frac{a}{R}. \quad (1)$$

On the other hand, a purely conical indenter applies a theoretical effective strain on the coating material that is not dependent on the penetration depth (because the angle between the indenter and the coating surface is constant regardless of the penetration depth), provided that the coating material is thick enough to avoid direct contact between the indenter and the underlying substrate. Indeed, the effective strain that a conical indenter is able to apply depends on the semi-cone angle θ according to the following formula:

$$\varepsilon_s \propto \tan \theta. \quad (2)$$

The suitability of Eq. (2) to model the contact conditions between a conical indenter and the coating surface depends on the perfection of the cone tip. Conical indenters are characterised by a certain tip radius. In general, the real contact between the conical indenter and the coating surface is limited to the spherical tip at the extremity of the conical indenter, provided that a large enough tip radius is chosen ($>100 \mu\text{m}$). Under those circumstances, Eq. (1) can be used to predict the effective contact strain induced on the coating material, even in the case of a conical indenter.

In light of the previous considerations, the role of the contact conditions, and therefore of the effective contact strain, is of utmost importance in understanding the scratch resistance of polymeric coatings. The contact conditions are strongly influenced not only by the contact geometry but also by the penetration depth inside the coating material during the scratching procedure.

In this respect, different coating materials and deposition techniques can lead to either more or less penetration-resistant coatings during the scratching procedure. This is the case of the thermoplastic and thermoset resins that were investigated. In particular, in the present work, thermoplastic polyphthalamide (PPA571, an alloy of acid-modified polyolefins) and thermoset polyester (TGIC-free, transparent, bronze-pigmented polyester) powder paints were deposited by the hot dipping fluidised bed [12,13] and electrostatic spray coating methods [14,15] onto flat aluminium substrates. The resulting coatings can differ in morphology and thickness and can possess extremely different mechanical properties according to the chosen material and the implemented deposition techniques. Each deposition technology also plays a crucial role in determining the characteristics of the coatings, with the hot dipping fluidised bed coating process leading to thicker and more ductile coatings, whilst electrostatic spraying to thinner but somewhat brittle coatings.

In this context, the present work examines the differences in the scratch performance of hot dipping fluidised bed- and electrostatic

spray-coated flat aluminium substrates coated by thermoplastic polyphthalamide (PPA571) and thermoset polyester resins. The scratch resistance of the organic coatings investigated was analysed by progressive mode scratch tests at a constant sliding speed and by imposing different contact conditions between the scratching geometry and the coating surface. In particular, three conical (Rockwell C) diamond indenters with tip radii of 100, 200 and 800 μm were used to simulate three distinct conditions of effective contact strains. In this way, the scratch behaviours that the coatings exhibited at variable contact strains were systematically investigated.

2. Materials and methods

2.1. Powder paints

Polyphthalamide PPA 571 H (Plascoat Systems Limited, Farnham, Surrey, UK) is a halogen-free blend of acid-modified polyolefins and additives. It is supplied in the form of a finely divided powder (granulometric distribution mean of $\sim 150 \mu\text{m}$), and it has been specifically designed to provide a long-lasting, tough coating for exterior applications to metal substrates including aluminium alloys. PPA 571 H is resistant to stress cracking, detergents, salt spray and typical airborne pollutants. It provides improved weatherability, and it maintains excellent adhesion to the metal substrate without the need for a separate primer. It also provides good electrical insulation and resistance to abrasion and impact.

The polyester resin (PPG Industries Inc., Pittsburgh, Pennsylvania, USA) is a triglycidyl isocyanurate-free (TGIC-free), transparent, pigmented (bronze) polyester powder. It is supplied in the form of a loose powder with a mean granulometric distribution of $20 \mu\text{m}$ and a shape factor of ~ 0.9 – 0.95 . It is designed to achieve good adhesion to metal substrates, elevated corrosion resistance and a high exterior durability.

2.2. Coating procedure

The thermoplastic and thermoset powder paints were deposited onto metal substrates by means of two different application techniques: (i) 'hot dipping' fluidised bed coating and (ii) electrostatic spray deposition. The fluidised bed coating system is described elsewhere [13]. The coating system consists of a fluidised bed, a blower and an integrated convective furnace. The fluidised bed is comprised of two superimposed chambers, the fluidisation column (250 mm in diameter and 500 mm in height) and the homogenisation section (250 mm in diameter and 200 mm in height), and a porous plate distributor between them. Fluidisation air is supplied from the blower to the homogenisation section, which allows for uniform distribution over the cross section of the chamber and up through the porous plate distributor. As soon as the fluidisation air reaches the fluidisation column, it exerts an aerodynamic compressive force on the powder particles, which are, consequently, suspended in the airflow. When in a suspended state, i.e., fluidisation [16], the powder/air mixture assumes a liquid-like behaviour [16], thereby allowing the coating process to successfully take place upon dipping of a pre-heated metal substrate [17].

To that end, flat aluminium substrates ($30 \times 30 \times 3 \text{ mm}^3$) were first pre-heated at $\sim 300^\circ\text{C}$ and then dipped for ~ 3 – 4 s inside the fluidisation column, which had been pre-loaded with the thermoplastic polyphthalamide and thermoset polyester powder paints. The suspended powder paints that come into contact with the hot metal surface at a temperature well above their softening points tended to melt, coalesce and adhere to the metal, thereby forming continuous films.

The thermoplastic and thermoset powder paints were also deposited onto metal substrates by electrostatic spray (ES) deposition. The ES deposition system that was used in the present investigation

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