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Tuning roughness and gloss of powder coating paint by encapsulating the coating particles with thin Al_2O_3 films

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ABSTRACT

In this work, we report a method to change the surface finish of a standard polyester-based powder coating paint, from gloss to matt, by depositing ultrathin films of Al_2O_3 on the powder coating particles. The coating experiments were performed in a fluidized bed reactor at 1 bar and 27 °C, using a gas-phase coating process of alternating exposure of the particles to the two precursors (trimethylaluminium and water), similar to atomic layer deposition (ALD). We varied the number of coating cycles (1, 2, 3, 5, 7 and 9 cycles) to obtain film thicknesses of the alumina shell ranging from 1 to 30 nm. The average growth per cycle of the process is 3.5 nm, significantly larger than the one for pure self-limiting ALD. When the average alumina shell was thicker than 6 nm, the shell prevented the flow of the core particles, even though the powder particles did soften above the glass transition temperature. With the particles morphology intact, this resulted in a rough and matte surface finish of the coating after curing. The surface roughness, with a value around 9 μm determined by surface profilometry, is associated to the alumina coated particles as observed with SEM and EDX analysis. In addition, the matte finish coating showed mechanical resistance similar to that of uncoated powder particles.

1. Introduction

A powder coating is a solvent-free powder-based type of coating used commonly to coat metals for a wide range of applications, such as in automotive industry. The surface appearance can be generally tuned by the addition of external additives to the powder formulation. Powder coatings have important advantages over liquid-based paints: being ease of application, high utilization by electrostatic spraying, environmentally friendly since they do not contain organic solvents, and showing excellent performance once applied. These strong points are also known as the *Four E's*, standing for ecology, excellence of finish, economy and energy [1–3]. These properties allow powder coatings to be used in a wide variety of applications, i.e. automotive, architectural, electronics and furniture amongst others [3]. A powder coating is composed of a resin, a catalyst, a cross-linker, pigments and additives such as flow modifiers and degassing agents, which define the properties of the final powder coating, including the surface finish (glossy or matte).

Glossy coatings reflect all the incident light in a mirror-like fashion, whereas a matte finish scatters part of the light, reducing the gloss level. The difference in gloss or matte appearance relies on the surface texture, whether it is highly smooth or it presents some roughness. Certain indoor applications require glossy paints, while for industrial and agricultural purposes, a matte paint is preferred to hide surface irregularities and damages. The gloss level of a powder coating can be reduced by the addition of a foreign compound, such as inorganic fillers or rheological additives, that can have different reactivity or curing temperature than the powder, by varying the size of the powder coating particles, by varying the humidity of the environment or by tuning the conditions during electrospraying [4–6]. Here we present a novel approach for gloss reduction that avoids the addition of foreign particles to the powder formulation, which may induce segregation or non-uniformities in the final product, but just relies on the surface modification of the primary powder coating particles to induce a transition in the surface appearance of the paint.

For that, we deposited ultrathin films of aluminium oxide (Al_2O_3) on the primary particles of a standard powder coating paint at ambient conditions by using gas-phase precursors. We evaluated how aluminium oxide films modified the flowing behaviour of the powder coating particles above the glass transition temperature, and whether that would induce roughness on the paint surface. The alumina films were deposited in a fluidized bed reactor (FBR) using a sequential exposure of precursors to the substrate, similar to the one in atomic layer deposition (ALD). A FBR allows processing large amounts of particles [7–11] while providing good mixing between gas and solids, that translates in the deposition of rather conformal alumina films. However, working

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at ambient conditions resulted in the deposition of thicker alumina films faster than in typical Al_2O_3 ALD processes [12,13].

ALD allows the deposition of inorganic films in a layer-by-layer growth mechanism based on two consecutive self-terminating reactions, with a purging step using an inert gas after each reaction [14,15]. The self-terminating feature of the ALD reactions ensures that the precursor molecules will only react where there is an active site available, preventing the growth of several layers of compound in each cycle [16–18]. Al_2O_3 ALD, using trimethylaluminium (TMA) and water as precursors, is commonly carried out at a range of temperatures between 33 and 170 °C and a few millibars of pressure, achieving a growth per cycle (GPC) of 0.1–0.2 nm [12,19–22]. In this work, the substrate used could not be heated to such temperatures, thus alumina films were deposited at ambient conditions, i.e. 27 ± 3 °C and 1 bar.

Working at atmospheric pressure and room temperature involves the accumulation of the unreacted precursor molecules on the surface of the substrate if they are dosed in excess above the saturation regime, inducing a chemical vapour deposition (CVD) type of reaction [23–25]. That would result inevitably in the deposition of multiple atomic layers of alumina during each cycle, depending on the amount of precursor molecules dosed to the reactor [13,26,27], producing a higher GPC than in a typical ALD process. Nevertheless, this can be beneficial to deposit thicker alumina films in a shorter time period.

Alumina ALD films have been used as passivating material, and in the production of membranes and catalysts amongst other applications [28–35]. In this work, thin Al_2O_3 films acted as physical barrier to confine the softened powder coating particles to tune the surface appearance of the cured powder coating paint. We investigated the influence of the thickness of the Al_2O_3 films on the flowability of the coated particles, and how this translated into different textures of the final paint. This experimental paper is a proof of concept for the applicability of an emerging gas-phase coating technology, such as ALD/CVD in a fluidized bed reactor, to modify the surface appearance of an industrial product, i.e. standard powder coating, while maintaining the same mechanical properties.

2. Experimental

2.1. Experimental setup and compounds

Al_2O_3 coating experiments were performed in a fluidized bed reactor similar to the one described previously [13,36], composed by a vertical glass column with a diameter of 26 mm and 500 mm in length which was located in a vertical vibration table to assist the fluidization [8]. Semiconductor grade TMA was provided by Akzo Nobel HPMO (Amersfoort, The Netherlands) in a 600 mL WW-600 stainless steel bubbler, which is kept at 30 °C during operation. Water, the second precursor, is kept in a similar bubbler, while nitrogen grade 5.0 is used as carrier and purging gas. A standard polyester powder coating paint was used as substrate. This powder coating paint is characterized by a fast and low-temperature cure, good flow and flexibility, and a gloss surface finish, ideal for architectural applications [37]. In each experiment, we coated 110 g of white standard powder coating particles provided by DSM Coating Resins (Zwolle, The Netherlands). The powder coating particles, with a Sauter mean diameter ($d_{3,2}$) of 33 μm, are composed of five components: resin, i.e. Uralac® P 3210, crosslinker, pigment, i.e. titanium oxide, flow control agent and degassing agent (more detail in [37] and *Supplementary information A*), all of them with different mass fraction in the final product. A flow of 0.4 L/min of nitrogen was used to fluidize the particles, which corresponds to a superficial gas velocity of 1.26 cm/s.

2.2. Coating experiments

The dosing times used in the coating experiments were 8–10–4–10 min for the sequence TMA–N_2–H_2O–N_2. To estimate the minimum dosing times, we used the maximum amount of aluminium atoms and methyl groups that can be allocated on the surface of a powder coating particle to obtain fully coverage. These values are 4 and 5 species per nm^2 of Al and CH_3, respectively [38,39]. The total surface area inside the column was 13 m^2 for the 110 g of powder used in each experiment, using the Sauter mean diameter of 33 μm, a particle density of 1500 kg/m^3 (*Supplementary information A*), and assuming that the particles are spherical and the calculated specific surface area of the powder is 0.12 m^2/g. The amount of precursor molecules dosed to the reactor was calculated using the vapour pressure of the precursors inside the bubblers and the ideal gas law, assuming that the TMA is a dimer at 30 °C [40,41], and that the saturation of the nitrogen bubbles inside the TMA bubbler is about 50% [42]. The theoretical dosing times to saturate the surface of the particles are respectively 0.25 and 0.24 min for TMA and water. In order to obtain thicker alumina films, we overdosed both precursors, fixing the dosing times in 8 and 4 min for TMA and water. At ambient conditions, we think that the unreacted molecules of water physisorb on the substrate surface [43–45], being involved in the following reaction with TMA molecules, also dosed in excess. The purging time of 10 min corresponds to approximately 13 times the residence time in the reactor. Using these times, we performed six coating experiments with different number of cycles, i.e. 1, 2, 3, 5, 7 and 9.

2.3. Characterization of the coated particles and sprayed panels

The influence of the alumina film thickness on the surface finish was first investigated on the individual powder coating particles. The film thickness and the growth per cycle were estimated from the mass fraction of aluminium on the samples measured by elemental analysis using ICP-OES (induced couple plasma – optical emission spectroscopy) as shown elsewhere [13]. Further, DSC (differential scanning calorimetry) was used to study whether the alumina films influenced the thermal properties of the coated particles, such as the glass transition temperature. The heat flow measured by the DSC device was normalized with the amount of powder used in each measurement, which ranged between 10 and 20 mg. Each DSC measurement consisted of a multistep program, composed by: (i) equilibration of the sample for 5 min at 25 °C, (ii) cooling from 25 to 0 °C, (iii) isothermal period of 5 min at 0 °C, (iv) heating from 0 to 130 °C, (v) isothermal period of 5 min at 130 °C, (vi) cooling from 130 to 0 °C, (vii) isothermal period of 5 min at 0 °C, (viii) heating from 0 to 170 °C, (ix) isothermal period of 10 min at 170 °C, and (x) cooling from 170 to 0 °C. All the heating and cooling steps were carried out with a rate of 10 °C/min. Steps (i), (ii) and (iii) were carried out so all the samples have the same thermal history. Steps (iv) to (vii) were carried out to have "enthalpic relaxation" of the powder, which typically occurs to amorphous resins during the glass transition [46]. Finally, steps (viii) to (x) were done to determine the glass transition temperature of the particles. With this approach, the samples were heated above the glass transition temperature during step (iv), but below the curing temperature, to prevent inducing irreversible changes on the powder coating particles. Finally, the completeness of the alumina films and its barrier performance were evaluated with a hot stage microscope and the pill flow test, which compares the flowability of the different alumina-coated powder coating particles down an inclined aluminium panel while heating the samples in an oven from room temperature to the curing temperature.

Subsequently, we sprayed the coated powders onto aluminium panels to study the influence of the alumina films on the appearance of the paints by using a corona-discharge gun and curing them in an oven at 160 °C during 10 min. The coated particles showed a poor adhesion to the panels during spraying, most likely produced by a reduction of the charge acquired by the powder while sprayed by the gun. To counteract the poor adhesion, we mixed, in a 1:1 mass ratio, the white Al_2O_3-coated powder prepared using TiO_2 as pigment with brown uncoated powder, prepared using a mixture of pigments and $BaSO_4$ as filler, in order to improve the adhesion and the contrast to facilitate