



Scratch resistance of ‘fast-cured’ metal flake powder coatings[☆]

D. Bellisario^{b,*}, M. Barletta^a, N. Ucciardello^a

^a Università degli Studi di Roma Tor Vergata, Dipartimento di Ingegneria Meccanica, Via del Politecnico 1, 00133 Roma, Italy

^b Università degli Studi di Roma La Sapienza, Dipartimento di Meccanica ed Aeronautica, Via Eudossiana 18, 00184 Roma, Italy

ARTICLE INFO

Article history:

Received 20 June 2009

Received in revised form 27 July 2009

Accepted 11 September 2009

Keywords:

Powder coatings

IR pre-curing

Scratch response

Adhesion

ABSTRACT

The economy of high quality metal flakes powder coatings process is remarkably influenced by the curing procedure involving two cost and time consuming steps in convective oven. Significant savings can be achieved accelerating the baking process by IR pre-curing the outermost layers of the basecoat and following this with a conventional oven-baking of the whole coating system. In the present investigation, the IR pre-curing process of the basecoat was analyzed by studying the influence of the IR radiation intensity and exposure time on the adhesion strength and scratch resistance of the coating varying the contact load of the scratching indenter.

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1. Introduction

Metal flake powder coatings belong to a special class of metallic paint finishes [1]. They are typically deposited by a two-step procedure wherein a protective topcoat is electrostatically sprayed onto a decorative metal flake basecoat, leading to a bilayer coating. Each deposition step is followed by a curing process in convection oven for long enough time (at least, 10 min) at moderate or high baking temperature (~140 to 180 °C) [2]. Cooling of the coated surfaces at ambient temperature after the curing of the basecoat is always required to allow the further deposition of the topcoat. Therefore, the deposition process involves a multifaceted procedure which can last up to 1 h to deposit film of ~120 μm thickness [3]. This can strongly influence the overall economics of the painting process and, sometimes, can compromise its competitiveness in comparison to alternative technologies (i.e., base colour material moulded into shape) [4] or different coating procedures (i.e., those involving wet paints) [5,6].

All the cost-cutting measures conceivable with the paint appearance and protection therefore assume a crucial role for the success of the powder coaters and raw material manufacturers in the face of an economy characterized by rising costs and static prices. In this respect, powder coaters and manufacturers have always attempted to deal with the growing expenses by reducing the number of coats

in a system, or by reducing the thickness of one coat [7]. However, few, if any, manufacturers are prone to accept a lowering of the visual appearance and protection (coating performance) of the paint finishing due to the thinner coating thickness. Reductions in energy costs have also been pursued by decrease in baking time or temperature or change to less energy-consuming methods of cure (i.e., EBC, radiation and vapour cure) [4,7,8]. Yet, this often results in a modification or change to the basic material formulations, which might be more expensive in themselves and not always able to warrant the same performance of the customary paints [9–11]. Otherwise, changing the curing methods could lead to just ‘fairly’ or ‘poorly’ cross-linked materials, this severely compromising the final performance of the resulting coating system [12]. Finally, automation in painting processes can allow a close control of the coat weights and minimize paint losses or waste, thus determining significant savings related to the increase in transfer efficiency of the powder paints during the deposition process [1,2,5]. However, the introduction of automated painting lines is only for those manufacturers able to afford the capital investment [13].

The introduction of novel solutions to relieve the economic pressures is therefore of particular interest for powder coaters and paint manufacturers, this also in the light of the growing concerns for the even more stringent environmental and safety regulations, which are undeniable intensifying the drive against the pollution.

In the present investigation, a novel method to cure a bilayer of powder coatings consisting in a metal flake decorative basecoat and in a transparent protective topcoat is proposed. The new cure method, namely hybrid IR/oven-baking curing process, involves a ‘flash’ (that is, lasting <60 s) pre-curing step of the basecoat using IR radiations, followed by a customary oven-baking process of the bilayer after the deposition of the topcoat. Compared to the conven-

DOI of original article: [10.1016/j.porgcoat.2009.10.016](https://doi.org/10.1016/j.porgcoat.2009.10.016).

[☆] The Publisher regrets that this article was previously published in Progress in Organic Coatings, 67 (2010) 161–169, for citation purposes please use the original publication details.

* Corresponding author.

E-mail address: barletta@ing.uniroma2.it (D. Bellisario).

tional two-step curing procedure of the bilayer of powder coatings, such a novel cure method should allow to save a lot of time as the first curing step of the basecoats lasts only few seconds (rather than 10–20 min). Moreover, the cooling of the basecoats is spontaneous and very fast after the exposure of the coating to the IR radiation. Therefore, a designed *ad hoc* cooling section along the painting line is not required anymore before the application of the topcoat, thus allowing to save extra time (~10 min).

The change in the way in which heat is provided to the coated surfaces during the curing process could, of course, compromise the visual appearance and protective performance of the coatings. In particular, it is well known that the melt viscosity trend of a powder coating during the curing process is strictly heat rate dependent [14]. The heat rate imparted to the coating affects the steps by which the powders paint is progressively sintered and levelled onto the underlying substrate [14]. Poor levelling can often characterize powder coatings after an improper baking procedure. A rough morphology can compromise the visual appearance of the powder coatings apart from how many efforts have been produced and money has been spent to achieve a good-resembling finishing [15].

The melt viscosity trend is also strictly related to the kinetic of the curing reactions and, therefore, to the degree of conversion of the resin inside the coating [14,16,17]. Good levelling joined with poor or just fair degree of conversion of the resin is a phenomenon which is not unlikely to occur [16,17]. Similarly, any change in the way in which heat is provided to the powder coatings during the curing process can significantly affect the curing reactions and, therefore, the final properties of the coating. Low degree of conversion of the resin always leads to a coating with very poor protection performance, exhibiting scarce scratch resistance, adhesion strength and wear resistance [18].

For that reason, the present investigation was focused on to the evaluation of the appearance and performance of the bilayer of powder coatings baked according to the newly developed hybrid IR/oven-baking curing process. In particular, the morphology of the coatings was evaluated by combined field emission scanning electron microscopy and inductive probe profilometry, whilst the coating strength was checked by multi-parameters scratch tests varying both contact load and speed. Further, 3D deformation response of the residual scratch patterns was assessed by contact probe inductive profilometry and field emission scanning electron microscopy. The experimental findings proved how the novel curing procedure could lead to metal flake powder coatings with appearance quality and performance, at least, comparable with those of the coatings cured under the customary baking procedure. In particular, the results revealed how hybrid IR/oven-baking curing procedure could lead to smooth, well adherent and scratch resistant bilayer of powder coatings, whose properties are strictly related to the intensity of the IR radiation and exposure (irradiation) time.

2. Experimental

2.1. Materials and pre-treatments

Metal flake powder coatings were deposited on 1.5 mm thick metal sheet that had been previously cut down to 25 mm side square samples by fine blanking to limit the geometrical alterations of the substrates and warrant the most uniform starting surface morphologies.

The treatment of the metal substrate prior to coating included cleaning of the surface followed by application of an inorganic layer of a conversion coating. Washing of the sample surface was performed by dipping it in alkaline cleaners for ~3 min at moderate temperature. The cleaned substrates underwent subsequent rins-

ing operation in order to sweep the cleaning agents away. Zinc phosphate conversion coatings were deposited (~2.5 g/m²) at moderate temperature for ~3 min by immersion application method in acid solution containing zinc dihydrogen phosphate Zn(H₂PO₄)₂, zinc nitrate (i.e., accelerating agent) and additives for grain and coating weight control. Zinc phosphating was followed by a thorough surface rinsing in deionized water at ambient temperature to allow the removal of the active chemicals (in particular, of any unrinsed phosphating solution residue) and the neutralization of any residual water-soluble salts. After rinsing, the substrates were oven-dried to make them ready for the deposition process.

2.2. Coating preparation and curing procedures

Electrostatic spray deposition of the metal flakes decorative basecoat (epoxy-polyester, 20 μm mean diameter, 0.80 factor shape, PPG-Bellaria, Alessandria, Italy) was performed by setting voltage at 90 kV, feeding pressure (i.e., related to the amount of powder per unit of time which passes through the tip of the gun) at 1.5 bar, auxiliary pressure (i.e., related to how far the cloud of fine powders is spread from the tip of the gun) at 1.0 bar and exposure time at 6 s. A first set of samples was baked in convective oven for 20 min at 180 °C in agreement with the curing indications provided by powders manufacturers. After cooling at ambient temperature, the substrates were electrostatically sprayed using a transparent protective topcoat (polyurethane powder, 20 μm diameter, 0.80 factor shape, PPG-Bellaria, Alessandria, Italy) and the same deposition parameters. Re-baking of the whole coating system (i.e., transparent protective topcoat onto the pigmented decorative basecoat) was performed at 180 °C for 20 min in convection oven in agreement with the indications provided by the powder manufacturers.

The decorative basecoats of a second set of samples were 'flash' pre-cured inside an IR oven at varying power of the IR lamps (1.0–2.0 kW) and exposure time (10–60 s). The IR oven was equipped with a set of linear emitting halogen (94% of radiation in the IR range and the remaining 6% in the visible) lamps with low mass and short focus tungsten filaments (focus distance 50 mm and working temperature 2227 °C) and quartz envelopes. The internal surface of the IR oven was made from shined aluminium to avoid the dispersion of the radiations (more than 90% of radiations are reflected). The IR oven is also equipped with an air cooling system to keep the working temperature inside stable during the irradiation and to allow continuous baking operation. After 'flash' IR pre-curing of the basecoats, the samples were re-coated (without allowing them to cool) using a transparent polyurethane powder and the same deposition parameters. The whole coating systems were then re-baked at 180 °C for 20 min in convection oven.

Upon baking or 'flash' IR pre-curing, the coating thickness of each coating layer was measured with a standard gauge (MEGA-CHECK 5FN-ST) following the regulations ISO 2178 and ISO 2370. The coating thickness of the decorative basecoat was checked to be in the range of 70–80 μm. The coating thickness of the protective topcoat was checked to be in the range of 40–50 μm. The overall thickness of the coating was checked to be in the range of 110–130 μm. All the coatings failing to agree with this specification more than ±5% were discarded.

2.3. Characterization

The 3D morphology of the coatings was obtained with a Taylor Hobson Surface Topography System (TalySurf CLI 2000) using a non-contact 300 μm Chromatic Length Aberration (CLA) HE gauge. For the CLA profilometry, the substrates were located under the gauge and viewed optically, using the high-resolution camera built into the Surface Topography System. This enabled the choice of both

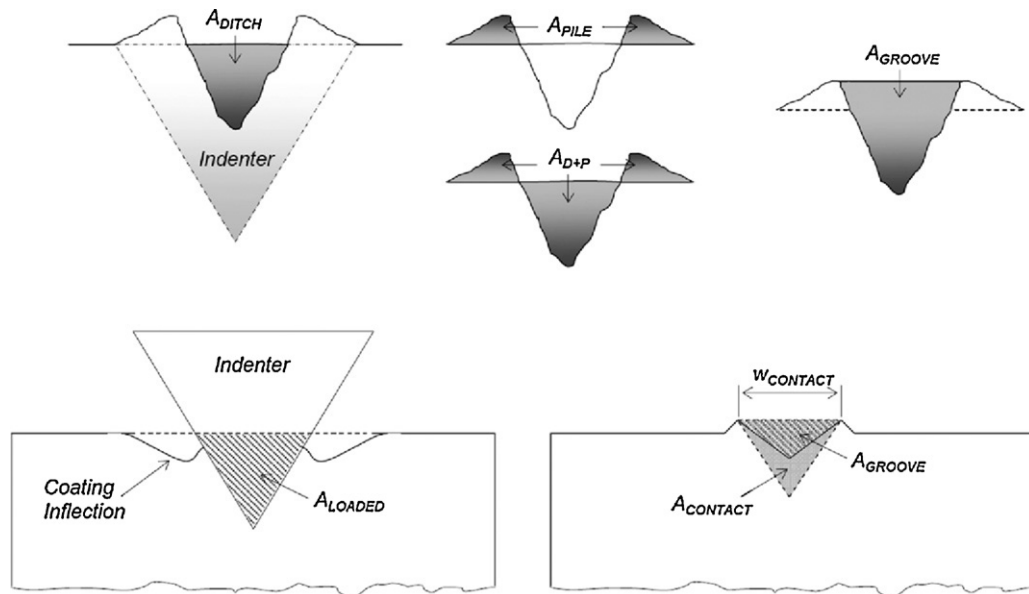


Fig. 1. Identification of dimensions of scratch during and after scratch indentation.

the measurement area and the rough focusing of the gauge. Using the CLA HE scanning mode, a number of patterns (1000), each 4 mm long, was recorded for each substrate so as to cover a representative area (16 mm²) of the entire surface structure. The surface morphology was then examined by using the TalyMap software release 5.0 and the trend of average roughness was reported.

Scratch tests were performed on the topcoats, being the tests aimed at investigating the scratch resistance of the whole coating system. Scratching procedures (C.S.M. Instruments Micro-Combi Tester) were carried out with a Rockwell C-type conical indenter with a rounded tip (200 μm tip radius), operating progressively (track 3 mm, scratch speed 1 mm/min, load 100 mN–30 N) at about 20 °C and 40% RH. Scratches were replicated to ensure data repeatability and the minimum distance between scratches was, at least, 4 mm in order to achieve data representative of the average response over greater surfaces. Normal and friction forces were monitored on-line and stored together with the starting profile, the current penetration depth, d_p , that is, the penetration depth during the application of the scratch load and the residual depth, d_r , that is, the profile of the residual scratch pattern immediately after the release of the scratch load. The surface imaging tool used to study magnitude and shape of residual deformation after scratch was the Field Emission Gun-Scanning Electron Microscope (FE-SEM Leo Supra 35) and the non-contact 3 mm CLA gauge (TalySurf CLI 2000). TalyMap software release 5.0 was used to calculate the key geometrical features of the residual scratch pattern. In particular, through the identification of the least square plane of the overall 3D film morphology, the volume of plastic pileup formations, V_{PILE} , scratch ditch, V_{DITCH} , their sum, V_{P+V} and complete scratch groove, V_{GROOVE} were accurately isolated and measured (Fig. 1).

3. Results and discussion

3.1. Analysis of the scratch response

Progressive load scratch tests were carried out to study the load dependent deformation response of the bilayer over a continuous range of loads. Fig. 2 reports the trends of the penetration depth vs. the normal force. The penetration depth shows a power-law like trend, with a decreasing branch at rather high penetration load (>20 N). Maximum penetration depths of 90–100 μm is achieved

during the tests and this means that the scratching indenter does not come in contact with the underlying metal substrate, because of the coating thickness of ~120 μm.

At lower scratch loads (<20 N), the bilayer coatings with the basecoats IR pre-cured 30 s or longer or oven-baked are the least penetration resistant. At higher loads (>20 N), all the samples show a decreasing trend of the penetration depth. The coatings keep on ductily deforming under the action of the advancing indenter and this results in an accumulation of material in front of the scratching geometry, which causes the decreasing branch at higher load. The experimental evidence agrees with the mechanisms formerly proposed by Briscoe [19,20] and, later on, by Jardret and Morel [21] for the ductile deformation of bulk polymers during scratch.

The samples submitted to shorter (<30 s) IR pre-curing of the basecoats are less prone to plastic deformation under the action of the indenter as the increasing branches of their penetration depth trends confirm (2.0 kW for 15 and 20 s; Fig. 2). Furthermore, their residual scratch patterns, i.e., the scratch pattern after the release of the scratch loads are definitely less deep (2.0 kW for 15 and 20 s; Fig. 3). On the contrary, the samples with the basecoat pre-cured for longer exposure time (>30 s) and whatever the intensity of the IR radiation as well as the oven-baked sample show a poorer response with a residual scratch pattern with a deeper average depth over

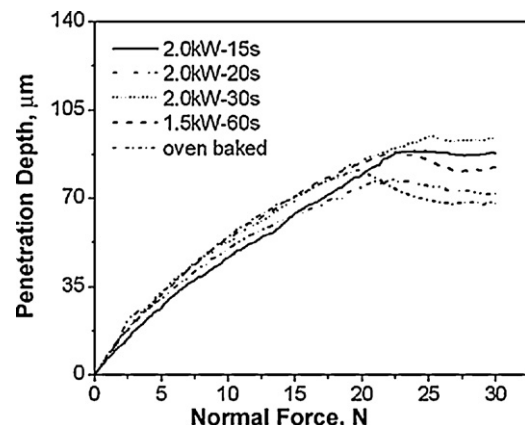


Fig. 2. Penetration depth vs. scratch load.

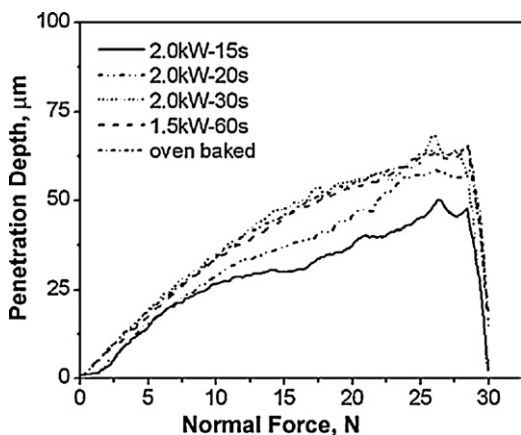


Fig. 3. Residual depth vs. scratch load.

the whole load range investigated (2.0 kW for 30, 1.5 kW for 60s and oven-baked; Fig. 3).

Fig. 4 summarizes the results arising from the analysis of the 3D deformation response [22–24] of the coatings after scratch tests and supports the previous considerations. In fact, the increase in pre-curing time when the intensity of IR radiations is set to 2.0 kW took to coatings less penetration resistant and affected by larger residual scratch pattern (complete scratch groove, V_{GROOVE}), whilst the increase in pre-curing time was found to be beneficial to the overall scratch response of the bilayers pre-cured at 1.5 kW. The discussion of the different mechanisms involved will be the matter of the next section. Here, it should be just emphasized that the way in which heat is provided to a powder coating during the curing process can certainly assume a crucial role and severely influence its resistance, quality appearance and the extent and kinetic of the curing reactions as results of the different viscosity trend the resins can get through.

The aforementioned considerations are supported by several experimental and theoretical findings reported in the pertinent literature. Manson and co-workers found a strict relationship between resin viscosity, degree of conversion and build up of the surface structure in epoxy-polyester and polyurethane-based powder coatings and Fig. 5 shows the typical viscosity trends when the resins are isothermally heated [14]. The trends are characterized by the presence of a minimum value of viscosity, which is found to decrease at any time the temperature (i.e., the heating rate)

is increased. Higher temperature means faster decreasing branch of the viscosity due to acceleration in the melting of the powder paints and sharper increase in the viscosity (increasing branch) after it approaches the minimum values due to the quicker activation of the curing reactions. Accordingly, faster heating rates cause shorter time to gel and time to dramatic increase in the resin viscosity (induction time) of the resin, with gelation being correlated to a decrease in the mobility of the growing polymeric chains. Andrei et al. showed for an acrylic-based powder coating how powder melting, coalescence and levelling could be related to the way in which the heating is performed and, more exactly, they define a prediction model of the final surface morphology of the coating given the rheological properties of the resin [17]. The relationship between the degree of conversion a resin is able to approach and the heating rate was discussed by Cadenato and co-workers for a polyester cross-linked with triglycidyl isocyanurate (TGIC) used in powder coatings [25]. Csuka et al. were able to study the reactivity of a TGIC promoted polyester resin, relating curing time, temperature, apparent viscosity and expected degree of conversion, showing how heating rate was of crucial importance in the establishment of the gelation curve and how resin reactivity could affect the visual appearance and the overall performance of the coating [26]. However, this result should not surprise as the strict bond between the resin reactivity with its rheological behaviour including the time to dramatic increase in the resin viscosity and the gelation time is well-known for various resins in styrene [27].

Lastly, Barletta et al. showed how the strict relation between the heating rate during the curing process with the resin viscosity and reactivity is an issue of crucial importance for the establishment of the mechanical response of the powder coatings. They found that different single layer and multi-layer powder coating systems are characterized by a scratch and wear response which is close function of the way in which the resin is cured [3,16]. In further investigations, Barletta et al. also showed how small changes in the settings of the operating parameters (mostly, curing time and temperature) of the curing process could lead to massive difference in the overall aesthetic and mechanical performance of the polymeric coatings, with their behaviour changing from purely elastic or ductile deforming to brittle failing through intermediate status of ploughing joined with local ruptures, mostly depending on time and temperature-dependent heating of the resin [18,23,24].

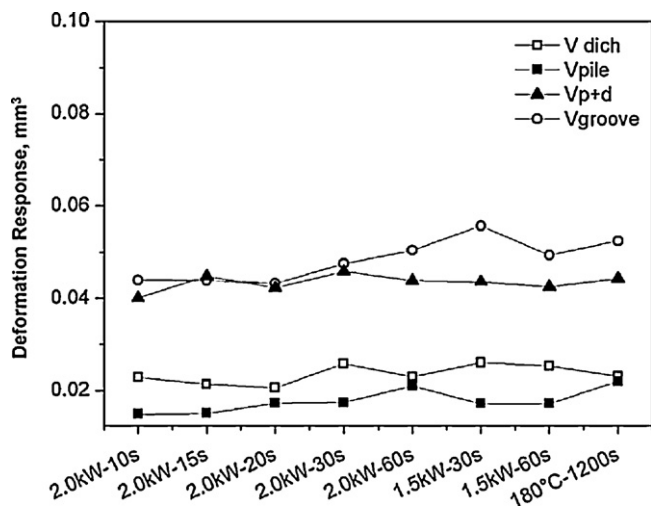


Fig. 4. Deformation response vs. pre-curing conditions.

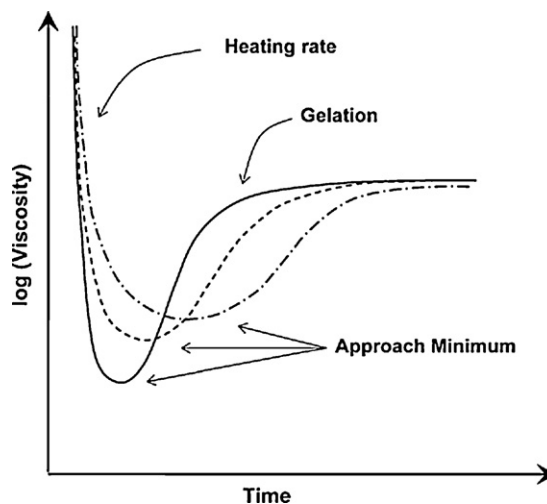


Fig. 5. Trend of the complex viscosity of a resin vs. the heating time with the heating rate.

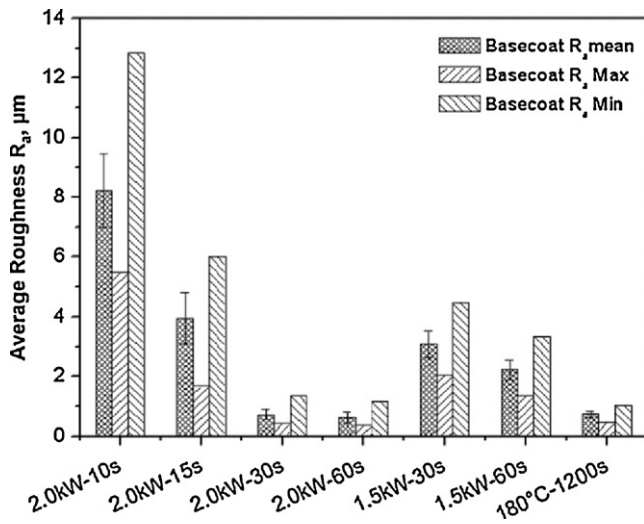


Fig. 6. Average roughness of the basecoat vs. IR power and exposure time.

3.2. Interpretation of the scratch results: surface morphology, resin viscosity and reactivity

The evaluation of thermal and rheological properties of powder coatings can be therefore extremely difficult [7] and the task is still more complicated when the heating of the powder paints (basecoat) is achieved by radiation. Under such circumstances, the resin is heated from the top and the heating rate is location dependent, i.e., it varies along the thickness. Therefore, the equipments for thermal and rheological measurements are not able to replicate similar heating process, leading, if any, to strongly discordant results.

However, the surface morphology of powder coatings is strictly related to the resin viscosity and degree of conversion as explained in the previous section. Therefore, the definition of a correlation between the scratch response of powder coatings and their morphology would allow yielding, with a certain degree of uncertainty, to analogous relationships with the viscosity and the extent of the curing reactions of the resin involved. This way, the scratch resistance would be indirectly correlated to the thermal and rheological properties of the powder paints and this would be of crucial relevance to support the interpretation of the mechanisms involved in the formation of the quality appearance and in the

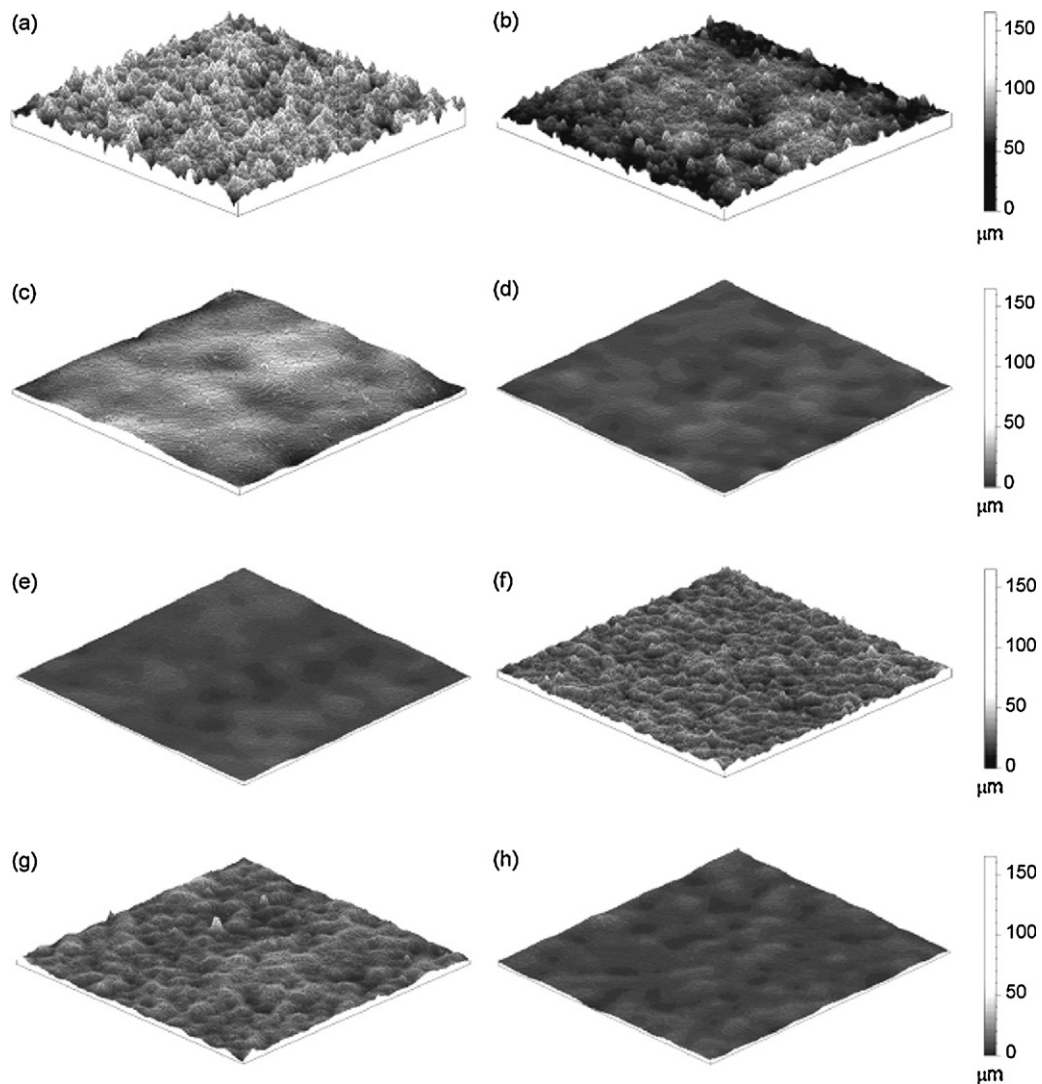


Fig. 7. CLA profilometry of basecoat: (a) 2.0 kW for 10 s, (b) 2.0 kW for 15 s, (c) 2.0 kW for 20 s, (d) 2.0 kW for 30 s, (e) 2.0 kW for 60 s, (f) 1.5 kW for 30 s, (g) 1.5 kW for 60 s and (h) oven-baked.

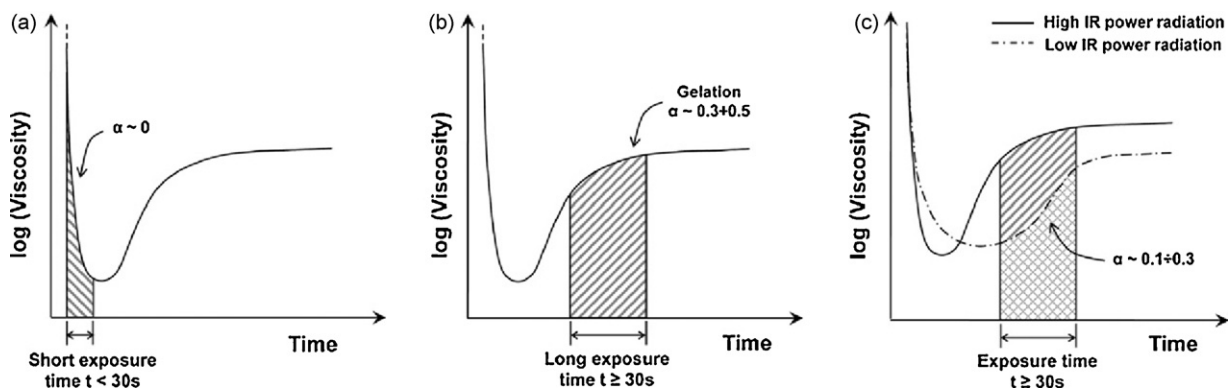


Fig. 8. (a) Trend of the complex viscosity of a resin pre-cured at 2.0 kW for $t \leq 20$ s. (b) Trend of the complex viscosity of a resin pre-cured at 2.0 kW for $t \geq 30$ s. (c) Trend of the complex viscosity of a resin pre-cured at 1.5 kW for $t \geq 30$ s.

build up of the overall mechanical properties of the coatings themselves.

In the present investigation, too short exposure time or insufficient heat supply during the pre-curing of the basecoats was always found to lead to poor levelling of the outermost layers of the coating material. This is the case of the basecoats pre-cured at 2.0 kW for <30 s, which approach R_a of ~ 8 and $4 \mu\text{m}$, respectively (2.0 kW 10 and 15 s; Fig. 6).

Poor levelling can be certainly correlated to the viscosity trend as formerly stated by Manson co-workers in their study about matt finish powder coatings [14]. In a more recent study, Barletta et al. closely correlated the viscosity trend, the degree of conversion (α) and the morphology of glossy finish epoxy-based thermosetting powder coatings [16]. They showed the achievable surface morphology was a close function of the heating conditions. They also showed how the average roughness established could be related to the degree of conversion of the resin and how progressively smoother finishes ($\sim 0.1 \mu\text{m}$ R_a) could be attained by progressively approaching degrees of conversion as high as 0.45–0.5, that, in terms of viscosity, means around the gelation point of the resin [16]. To the contrary, they found largely unsatisfactory finishes (R_a of $4 \mu\text{m}$ and higher) at any time the powder coatings were poorly cured, reaching degrees of conversion of 0.05 or less, which mean a corresponding resin viscosity averaging still over the decreasing branch of its trend (i.e., before the minimum viscosity value in Fig. 5).

The unsatisfactory finishes which were found to characterize the morphology of the samples with the basecoat IR pre-cured for short exposure times (<30 s) can be more likely ascribed to the aforementioned reason. The intensity of the IR radiation (2.0 kW) would be even high enough to promote a fast decrease in resin viscosity as a result of the high heating rate (Fig. 5). Yet, the exposure time is so short that the powder paints are not allowed to melt and flow for sufficient time, thus causing the build up of a very rough surface structure with poor visual appearance (Fig. 7a and b). In the light of the roughness values ($4 \mu\text{m}$ or more) measured after the IR pre-curing process, the resin viscosity can be supposed to remain in the decreasing branch of the typical viscosity trend, whereas it is still far from being gelled (Fig. 8a) and/or from approaching a sufficiently high degree of conversion. This hypothesis agrees very well with the experimental evidence reported by Manson and co-workers and Barletta et al. in their previous studies [14,16]. Accordingly, the extent of the curing reactions which occur inside the resin during the IR pre-curing for such short exposure times (<30 s) can be supposed nearly negligible with expected degree of conversion of 0.05 or lower. Under such circumstance, it can be supposed that the curing reactions are practically active neither in the bulk nor in the outermost layer of the basecoat.

After the deposition of the topcoat and re-baking in convection oven, the final average roughness of the samples with the basecoat IR pre-cured for short exposure times (<30 s) at 2.0 kW improves and $R_a \sim 0.3$ – $0.4 \mu\text{m}$ are achieved (2.0 kW 10 and 15 s; Fig. 9). In fact, the topcoat is always oven-baked at high temperature (200°C) and it tends to flatten the widespread peak-to-valley morphology of the rough basecoats. In particular, the observed flattening of the surface morphology can be better appreciated on the roughest basecoats (2.0 kW 10 s). Therefore, the overlying topcoats show good recover capability and rather flat morphologies could be always built up.

Re-baking after the deposition of the topcoat onto the basecoats IR pre-cured for short enough exposure time (<30 s) should easily reactivate the curing reactions over the whole coating system, including the poorly cured ($\alpha < 0.05$) outermost layer of the basecoat. The reactivation of the curing reactions should give rise to a bilayer of ‘coherently’ cross-linked material (Fig. 10a). Minor discontinuity inside the cured material could only affect the outermost layer of the basecoat and it should be ascribable to the IR pre-curing process, which, in a certain measure, could locally limit the mobility of the macromolecules and, therefore, worsen their reactivity [26,27]. However, if such an effect took place, it would be drastically restrained to an extremely thin layer of the basecoat at the very interface with the overlying topcoat. Accordingly, the inferred curing mechanism should promote bilayer coating with well established mechanical properties, thus supporting the pre-

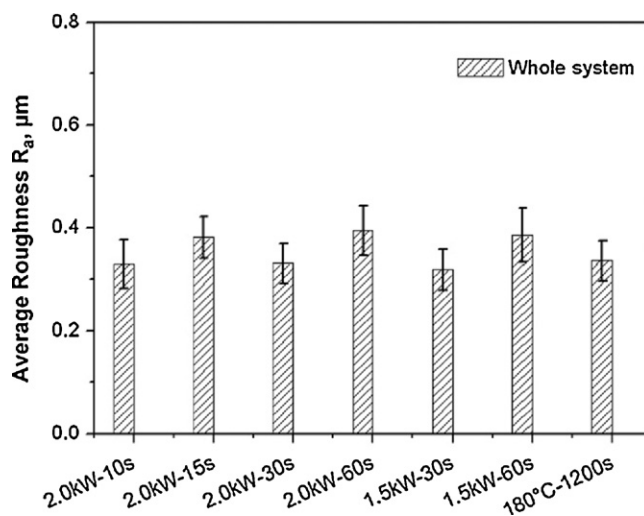


Fig. 9. Average roughness of whole coating system vs. IR power and exposure time. Low magnification SEM images of metal flake powder coatings with the basecoat pre-cured under varying conditions.

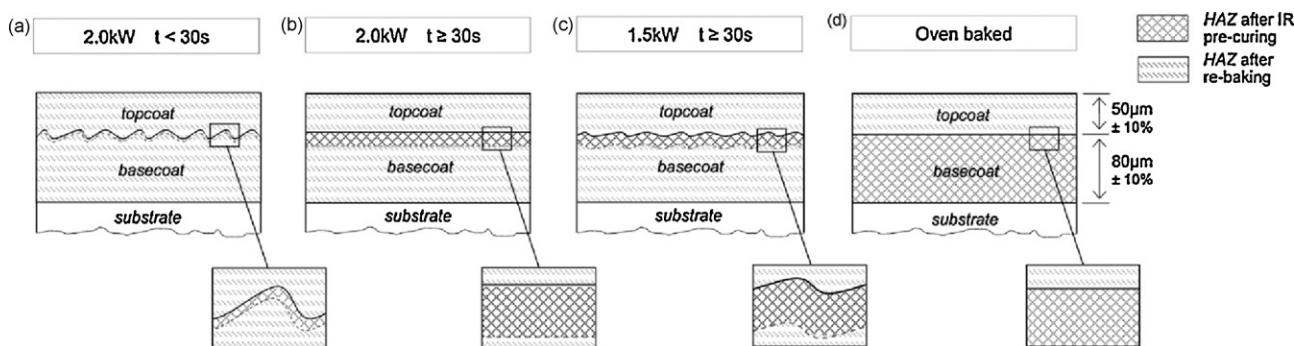


Fig. 10. (a) Structure at 2.0 kW for $t < 30$ s. (b) Structure at 2.0 kW for $t \geq 30$ s. (c) Structure at 1.5 kW for $t \geq 30$ s. (d) Structure oven-baked.

vious results of rather good penetration resistance (less deep penetration depth; Fig. 2) and recovery capability (better deformation response; Figs. 3 and 4) of the samples involving basecoats IR pre-cured for rather short time (10–20 s). During the scratch test, the whole coating system is supposed to behave like a monolayer, which withstands the action of the scratch geometry. Thus, the whole coating system exhibits a uniform behaviour without delaminations or clearly visible damages, as also confirmed by the corresponding SEM images (Fig. 11a).

Under IR radiation of high intensity (2.0 kW), longer exposure times (>30 s) were found to promote a fast drop and allow achieving very low minimum values in the resin viscosity (Fig. 5). Under such circumstances, the powder paints are provided with high power density and enough time to quickly melt and level, thus approaching high quality finishing (Fig. 6; $R_a < 1 \mu\text{m}$ —basecoats IR pre-cured at 2.0 kW for 30 s or longer). This result is in good agreement with the experimental findings of Andrei et al. on acrylic powder coatings, where levelling was found to be much increased at any time faster heating rate and enough time was provided during curing [17]. Barletta et al. found similar results on different powder coating systems and curing procedure [16,18,23,24]. They claimed that, at any time R_a of $1 \mu\text{m}$ or lower are measured, the expected degree of conversion of the resin is, at least, of ~ 0.3 to 0.5 and the corresponding viscosity averages the gelation point, or, at worst, it is located over the final part of the increasing branch of the viscosity trend [16]. Therefore, the relationship between the final surface morphology of the samples involving the basecoats after IR pre-curing at 2.0 kW and for long enough exposure time (30 s or more), the melt viscosity of the resin inside the outermost layer of the basecoat and the corresponding degree of conversion are exemplified by the 3D map in Fig. 7d and e and the sketch of the viscosity trend in Fig. 8b. Good finishes do correspond to high enough degree of conversion and viscosity range averaging the gelation point of the resin. Accordingly, the outermost layers of the IR pre-cured basecoats at 2.0 kW for longer exposure time (30–60 s) were expected to be close or beyond their gelation points, with an expected degree of conversion of, at least, 0.3 – 0.35 and, probably, much higher.

The resin reactivity could be compromised by the unexpectedly achievement of the gelation point inside the outermost layer of the basecoat [6]. As said before, when the resin approaches gelification, minimum mobility of the macromolecules is only allowed [27] and, accordingly, the speed at which curing reactions can occur are strongly limited. Therefore, when the whole coating system is re-baked after the application of the topcoat, the re-heating of the outermost layer of the basecoat is not able to effectively reactivate the curing reactions, as the resin is expected to be close to the gelation point or, at worst, in a status of severe gelification. Thus, the extent of the curing reactions inside the outermost layers of the basecoat remains very low with a degree of conversion which cannot proceed further. This phenomenon leads to a rather thick layer of material inside the basecoat and at the interface with the

topcoat with a limited expected degree of conversion ($\alpha \geq 0.4$ – 0.55 , that means close to those achieved during the pre-curing) and, consequently, with very poor mechanical properties (Fig. 10b). These considerations can explain the insufficient scratch response of the sample with the basecoat IR pre-cured at 2.0 kW for 30 s. In this case, the SEM image of the residual scratch pattern (Fig. 11b) shows the presence of significant damages and some local delaminations over almost the whole scratch length (that means, at rather low scratch load, too) and support the data about the limited penetration resistance measured during the loaded scratch scan (Fig. 2), the rather deep scratch pattern which was measured after the release of the scratch load (Fig. 3) and the overall poor 3D scratch response (Fig. 4).

Coatings pre-cured under lower heating rates, as those achievable with IR irradiation intensity with lower power (1.5 kW), display a fair finishing with average roughness of ~ 2 to $2.5 \mu\text{m}$ (Fig. 6). The heating rate of the powder coating is less fast and the viscosity drop is slower and expected to lead to a rather high minimum viscosity value in agreement with the expected trends of the resin viscosity for rather slow heating rate (Fig. 5). Therefore, the flow capability of the powder paints in the outermost layer of the basecoat is presumably limited and finishing results to be quite raw. The minimum value of the viscosity expected to be rather high would limit the mobility of the macromolecules and, accordingly, the curing reactions should be rather slow. The time to dramatic increase in the viscosity and the time to gel are, therefore, expected to be rather longer in agreement with the results reported in the pertinent literature [14,18]. The relationship existing among the surface morphology, the viscosity and the degree of conversion of the resin can be therefore well exemplified by the 3D maps in Fig. 7f and g and the sketch of the viscosity trend in Fig. 8c. Lower power density during IR pre-curing of the basecoat means lower heating rate of the powder paints. Their viscosity trend should fit the dot and dash trend in Fig. 8c. Keeping unaltered the curing time, a lower heating rate produces a resin whose viscosity averages the increasing branch of the typical trend, without approaching gelation. Furthermore, the expected degree of conversion should be less than 0.3 . This explains the reason why a rough morphology is still established, with R_a value widely larger than $1 \mu\text{m}$ (Fig. 6; 1.5 kW 30 and 60 s).

The expected degree of conversion ($\alpha \sim 0.1$ – 0.3) for the samples with the basecoat IR pre-cured at 1.5 kW for exposure time of 30 s and longer is lower than in the former case investigated where higher power of the IR radiation was involved. Thus, when the whole coating system is re-baked after the application of the topcoat, the re-heating of the basecoat finds a resin which is still far to be completely gelled and totally compromised. The mobility of the resin can be still reactivated and, accordingly, the curing reactions can progress again and in a more consistent way in comparison to the coatings pre-cured at higher intensity of IR radiation for longer exposure time. However, the rather longer exposure times could

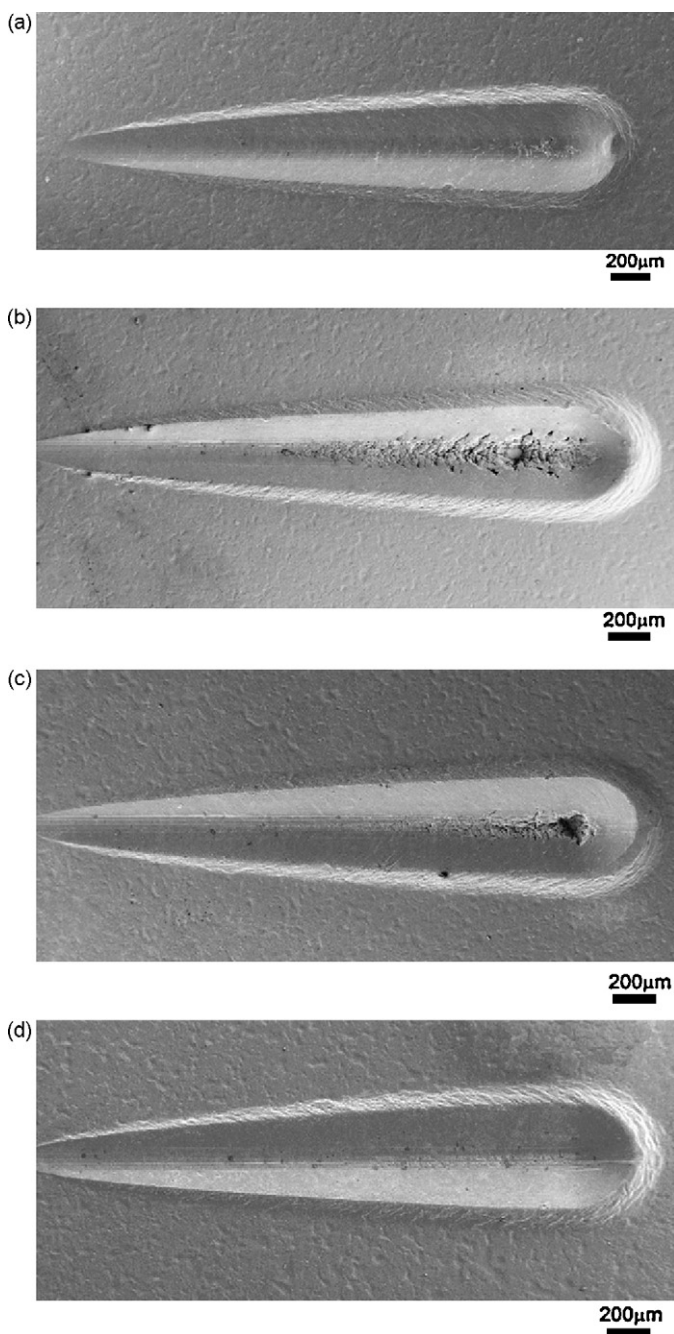


Fig. 11. SEM image of the residual scratch pattern of the metal flake powder coating: (a) basecoat IR pre-cured at 2.0 kW/10 s; (b) basecoat IR pre-cured at 2.0 kW per 60 s; (c) basecoat IR pre-cured at 1.5 kW per 60 s; (d) basecoat oven-baked at 180 °C/20 min.

partly compromise the reactivity of the outermost layers of the basecoat and allow the establishment of a layer with intermediate properties between the topcoat and basecoat (Fig. 10c), which is supposed to be the reason of the poor mechanical behaviour. The poor scratch resistance of the powder coatings baked under such conditions is supported by the SEM image of the residual scratch pattern (Fig. 11c), which display how damage of remarkable entity are spread over most of the scratch length.

The last case investigated involves samples with both the basecoat and topcoat oven-baked at 180 °C for 20 min. Actually, the oven-baked basecoat is expected to be completely cured as result of the longer curing time (20 min). Re-baking after the application of the topcoat should cure the topcoat, leaving unaltered

the already 'fully' cured basecoat. This can be supposed to lead to two different layers of 'properly' cured but presumably 'unmatching' coating material (Fig. 10d). The inferred discontinuity at the interface between the basecoat and topcoat, which was supposed to characterize the bilayer of the oven-baked and IR pre-cured samples for longer exposure time, could be a cause of major concern and could justify the slightly disappointing penetration resistance and coating recover capability (Figs. 2–4). Yet, the good degree of conversion, the resin with both the layers oven-baked can get through, takes to a bilayer with sufficient interfacial adhesion and to a topcoat characterized by a good ductility. In fact, even in presence of the larger deformations during the loaded scratch scan (Fig. 2) and/or of poor deformation behaviour after the release of the scratch load as summarized in Figs. 3 and 4, the coating with both basecoat and topcoat oven-baked does not show massive damages along the scratch pattern (Fig. 11d). The SEM image does not reveal the presence of massive cracks (through-thickness cracks). Only limited damages take place at the very bottom of the residual scratch pattern, which become perceptible only when more than 20 N load was applied.

4. Conclusions

The matter of the present investigation is the analysis of the scratch response of the metal flakes powder coatings after a hybrid IR/oven-baking curing process. The experimental evidences lead to the following conclusions:

- Scratch resistance of the coatings is related to the intensity and, mostly, to the exposure time of the IR radiations during the pre-curing of the basecoats.
- Samples with the basecoat pre-cured longer or oven-baked are less penetration-resistant and possess a reduced recover capability because of the inferred 'discontinuity' between the topcoat and basecoat.
- The coating with both topcoat and basecoat oven-baked is ductile enough to withstand higher deformations during the scratch tests without showing significant failures.
- Short exposure time and high IR radiation intensity does not affect the reactivity of resin inside the outermost layers of the basecoats.
- Basecoats pre-cured for shorter exposure time can be inferred to allow 'coherent' cross-linking pattern between basecoat and topcoat, which is supposed to lead to a better scratch resistance.

Finally, the surface morphology of the powder coatings under investigation could be strictly related to the resin viscosity and its degree of conversion. Therefore, the definition of a correlation between the scratch response of powder coatings and their morphology allows yielding to reliable relationships with the viscosity and the extent of the curing reactions of the base resin involved.

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