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Metallization of Vitrimers by cold spray: A preliminary study

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Abstract. Cold spray is a promising solution for the production of metallic coatings on polymer substrates. However, the adhesion mechanism between the impacting particle and the polymer in cold spraying depends on the chemical structure of the polymer itself. In this scenario, the emerging vitrimer polymers, which were proved to combine enhanced mechanical and chemical performances with abilities to be healed, welded, reprocessed, and recycled and that show a ductile behavior when exposed to given operating temperatures, can be particularly suitable for being functionalized by cold spray. Therefore, the aim of this work is to experimentally prove the feasibility of the metallization process via cold spray of epoxy vitrimer substrates. For this purpose, an epoxy vitrimer formulation was studied and experimentally characterized. Vitrimer-based panels were manufactured and used as substrates for the surface metallization. A low-pressure cold spray facility was used for the deposition of aluminum alloy particles. Microscope analyses were carried out for the characterization of the samples.

Introduction

It is known from literature that the relatively new additive cold spray technique (CS) is the best solution for the manufacturing of metallic coatings on polymer-based substrates [1]. Compared to traditional thermal spray technologies, cold spray offers benefits in terms of efficiency in the use of resources which generate economic and environmental advantages contributing to sustainability [2,3]. Some special characteristics such as electrical and thermal conductivity, erosion and radiation protection, wear and poor flame resistance can be enhanced through metallization of polymers [4,5].

When cold spraying metal on polymer, the only possible bonding mechanism between the particle and the substrate is the mechanical interlocking and the adhesion depends on the chemical structure of the polymer itself [6,7]. In this regard, Ganesan et al. [8] found that the particles can bond with the surrounding polymer material only when they penetrate the thermoplastic substrate profoundly. On the contrary, the fragile behavior of thermosetting substrates makes coating formation and growth difficult, if not impossible. In the case of thermosets, the coatings process

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is even more challenging since degradation rather than softening happens at elevated temperatures. Several solutions were proposed in literature with the scope to overcome this issue for thermosets, the interlayer concept [9], or the PLA treatment [10] represent the promising methods; however, none of these solutions are based on new formulations for thermoset polymers fitting the cold spray requirements.

In this scenario, the emerging class of vitrimers combines the structural performances and thermal stability of thermosets with the flow ability of thermoplastics. Epoxy vitrimers and their composites have the ability to be reprocessed, welded and easily recycled [11], therefore they are ideal candidates to be functionalized by cold spraying. In fact, epoxy vitrimers exhibit different behavior at specific temperatures: below the topology freezing transition temperature (T_v) behave like traditional thermosets, with good mechanical and thermal properties. While above the T_v, they can flow like viscoelastic fluid due to the topology rearrangement induced by dynamic exchange reaction (i.e. transesterification reactions) [12,13]. The occurrence of the transesterification reaction is governed by the addition of a catalyst; several catalysts, including organocatalysts and metal-containing compounds, have been implemented to promote transesterification in epoxy vitrimer production [14]. Zinc ions (Zn^{2+}) significantly accelerates esterification by opening anhydride ring and yielding monoester and carboxylic acids [15].

Based on these premises, the aim of this work is to experimentally prove the feasibility of the metallization process via cold spray of epoxy vitrimer substrates. In other words, since the cold spray deposition on thermosetting material was proved to be difficult, if not impossible today, the possibility to coat epoxy vitrimer polymers was investigated. To achieve the scope, an epoxy vitrimer was formulated modifying a commercially available epoxy system by adding zinc acetate ($Zn(Ac)_2$) and the chemical-physical properties of the vitrimers were studied. Vitrimer-based panels were manufactured and used as substrates for surface metallization. A low-pressure cold spray facility was used for spraying aluminum alloy particles. Microscope analyses were carried out for the characterization of the samples.

Materials and methods

In this section, the materials, the methods, and the technologies used to produce both the epoxy vitrimer panels, used as substrates, and the aluminum coatings, will be presented; the experimental tests used for the characterization of the samples proving the feasibility of the process developed, will be also described.

The resin used in this study consists of a mixture of Bisphenol A diglycidyl ether (DGEBA) epoxy resin, curing agent tetrahydro-methyl phthalic anhydride (THMPA), and of a 2,4,6-tris (dimethylaminomethyl)phenol as catalyst, all provided by Huntsman Corporation. The standard epoxy system has been modified by adding anhydrous zinc acetate $Zn(Ac)_2$ as transesterification catalyst, to promote the vitrimeric behavior.

The formulation has been prepared whit a stochiometric ratio of epoxy/acyl equals to 1, and a 10% wt. of $Zn(Ac)_2$ with respect to the total acyl groups. The manufacturing process is illustrated in Fig. 1: (i) hand-mixing of epoxy resin and $Zn(Ac)_2$ fine powder; (ii) adding of cross-linking Anhydride and mixed by a planetary centrifugal mixer (THINKY mixer ARV 310) under vacuum at room temperature; (iii) addition of the accelerator (Amine) and further mixing in the THINKY to obtain a homogenous mixture; (iv) casting in Teflon molds and (v) cured in the oven at 120°C for 1 h 30 min and then post cured at 140°C for two hours.

The coating was produced by using micron sized AlSi10Mg powders with a particle mean size of 25 µm, provided by LPW South Group. The low-pressure cold spray facility (DYMET 423) fed by nitrogen as carrier gas was used for the deposition. The spray gun was attached to a cartesian robot for the control and the repeatability of the deposition process.

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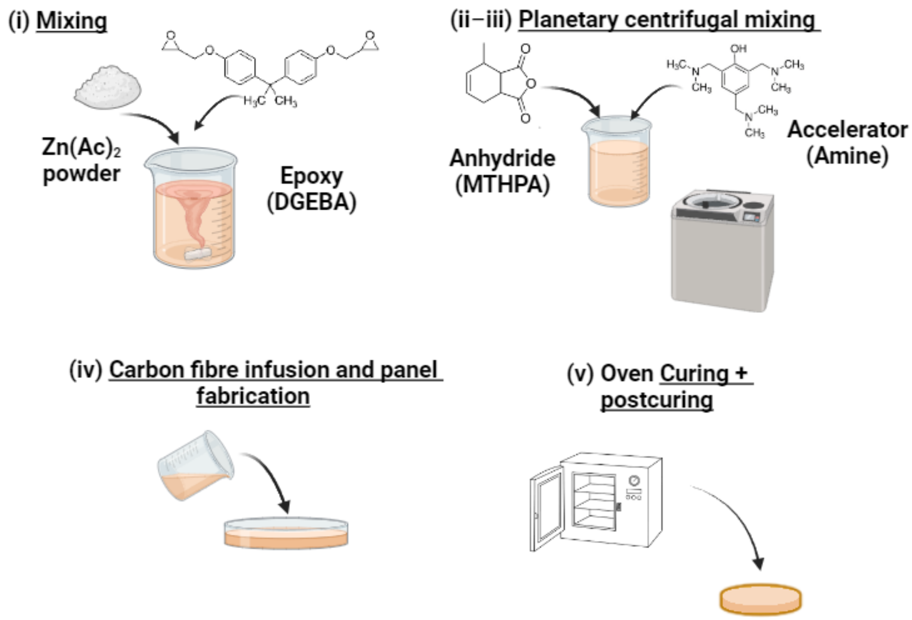

Fig. 1. Manufacturing process of vitrimeric epoxy resin [15].

To analyze the interaction between the cold sprayed particles and the epoxy vitrimer substrate, only one layer was sprayed on the panel [16] producing a 50 mm length metallic track. Different tracks of aluminum coatings were produced on vitrimers to set the proper cold spray process parameters.

The nozzle to substrate standoff distance (SoD) was varied between 45 and 100 mm [6,17], and then set to 70 mm after a preliminary experimental test. The gas pressure and the gun traverse speed were kept constant in all the experiments and set equals to 6 bar and 1 mm/s, respectively.

The inlet gas temperature was found to be a key factor for the deposition on polymers [18]. If on one hand it affects the particle velocity, on the other it was proved to have a noticeable influence on the physical behavior of the polymeric substrate when impacted by the particles, due to the temperature reached by the gas flow on the target surface. Two values of inlet gas temperature were chosen in this activity (T_1=200°C, T_2=300°C) in agreement with previous authors' research and literature data [6], so resulting in two types of coated vitrimeric samples (here referred as V_{T1} and V_{T2}). The main cold spray process parameters used are reported in Table 1.

Table 1. Main process parameters in cold spraying AlSi10Mg particles on epoxy vitrimer substrates.

Sample	Inlet gas temperature [°C]	SoD [mm]	Gas pressure [bar]	Gun traverse speed [mm/s]
V_{T1}	200	70	6	1
V_{T2}	300	70	6	1

The epoxy vitrimer was characterized through creep tests performed using the DMA Q800 from TA Instrument equipped with the tension film (TF) clamp. Rectangular specimens of 10x5.5x2 mm^3 were tested, at different temperatures between 70°C to 220°C, at 25°C steps to evaluate the strain rate variation from the glassy to the rubbery state.

The surface morphology of the vitrimeric panels was observed by means of confocal Olympus OLS5100 microscope in order to analyze the surface characteristics and chose the most appropriate face upon which the deposition can be carried out effectively. Note that the terms back face and front face will be used here to indicate the "as-is" and "to be coated" surface of the vitrimeric panel, respectively.

The metallized samples were observed through Hirox ST-AS microscope to show the coating obtained and analyze in more details the mechanisms ruling adhesion during deposition of aluminum particles on epoxy vitrimer substrates.

Results and discussion

The vitrimeric behavior of the resin can be highlighted by discussing the results from the creep experiments shown in Fig. 2. In contrast with the epoxy standard behavior, the vitrimeric system displayed a significant increase in the strain rate under a constant load at temperature above 170°C, which can be identified as the topological vitrimeric transition temperature (T_v).

Inset pictures reproduce the creep test for the standard epoxy and the vitrimer at two characteristic temperatures, 95°C and 170°C. The temperature has been chosen as representative of the dynamic change in the vitrimer and as an evidence of the actual flow happened. At 95°C both the systems act as a thermoset, the deformation rate is negligible, while at 170°C the standard epoxy keeps its behavior conversely the vitrimer starts to flow (deformation rate increases).

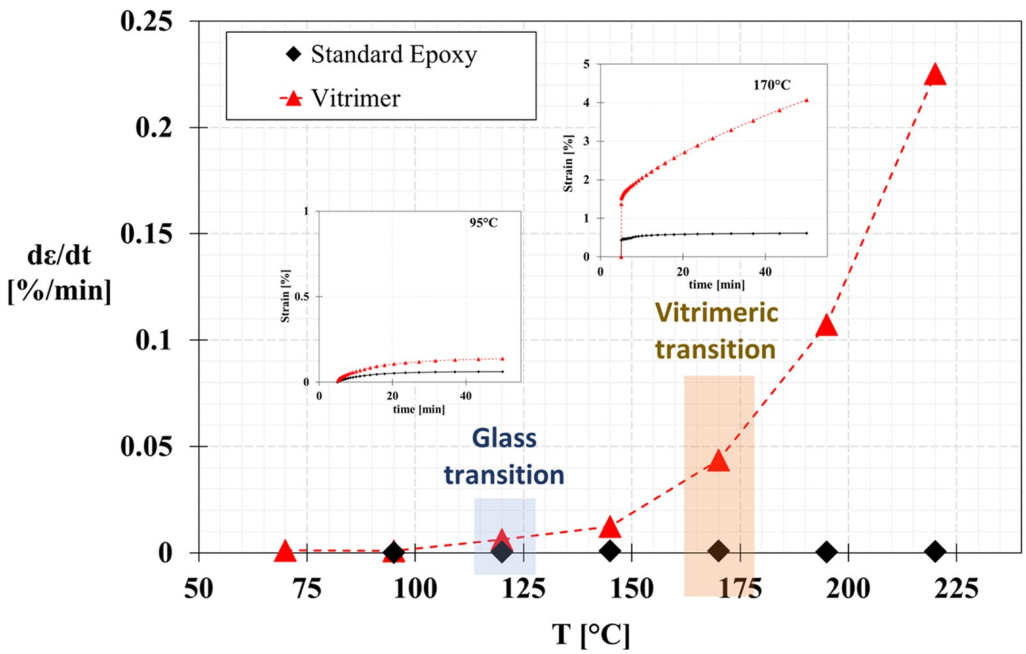

Fig. 2. Creep curves at different temperatures of the standard epoxy (black diamond shape) and vitrimeric system (dotted red line).

The results from the confocal microscope observations relative to back (which is the face in contact with the Teflon mold in Fig. 1) and front face of the vitrimeric panel are reported in Fig. 3 and Fig. 4, respectively. In particular, the scope of this preliminary analysis was to study the surface morphology of the target surface and identify the most suitable face to be cold sprayed.

It can be observed from Fig. 3a that the morphology of the back face is characterized by deep craters and grooves that are much larger than the mean diameter of the feedstock particles. These characteristics should not promote the sticking of the particles impacting the substrate. In fact, as known from literature, it seems to be necessary that the valleys of the surface texturing of the polymer used as substrate had a comparable dimension to the feedstock powder diameter [19], this is a key factor for the particle interlocking between the substrate and the powders, as the latter may impinge into the valleys becoming entangled. The sketch in the right side of the figure (Fig. 3b) clearly show that the particle does not impact normally to the substrate under these surface conditions, without promoting the mechanical interlocking, so rebounding from the target surface. This mechanism is known from literature in cold spraying [20].

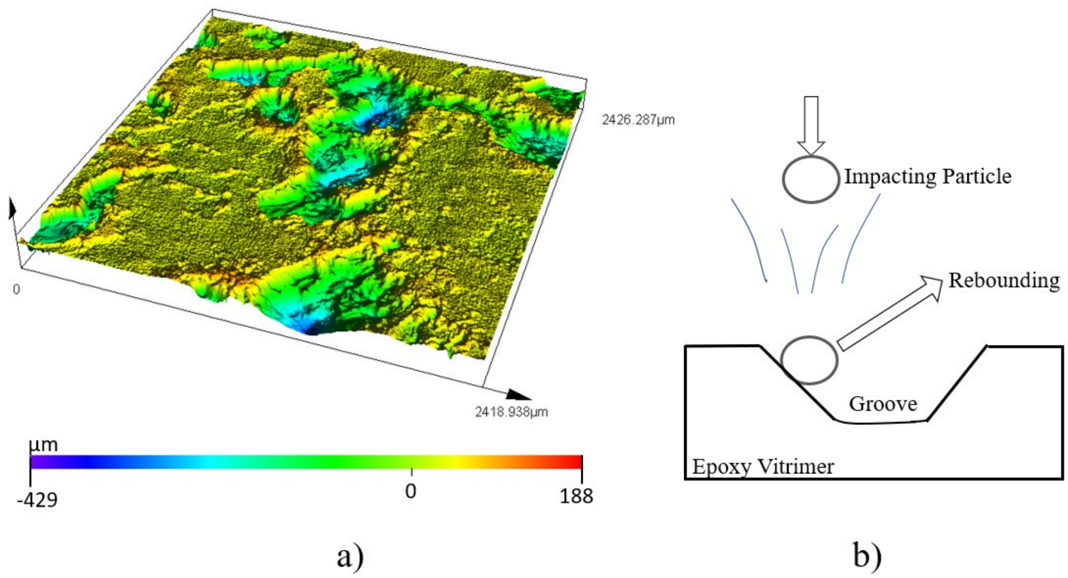

Fig. 3. a) Surface morphology of back face of vitrimeric panel. b) Illustrative sketch of particle rebounding mechanism.

Based on the results above, the powders have been cold sprayed on the front face of the panel to benefit the effects of the smoothed surface, as shown in Fig. 4a. An exemplificative picture of the coated epoxy vitrimer sample is displayed in Fig. 4b.

The metallized samples were observed through Hirox microscope, and the results obtained are discussed below. A specimen of the coated epoxy vitrimer, labelled as V_{T2} in Table 1, is shown in Fig. 5.

Firstly, it can be observed that the feasibility of the process was proved with the metallic particles adhered the polymeric surface. This result shows that an epoxy-based polymer can be effectively coated by cold spraying aluminum particles when using a given vitrimeric formulation. However, some considerations need to be carried out regarding the set of the proper cold spray process parameters.

When cold spraying at T=300°C, the temperature of the gas, which expands through the nozzle, reduces, and can achieve also 200°C onto the substrate (as measured via k-type thermocouple), under the set process conditions. It is clear that the temperature on the surface of the polymer remains much higher than the vitrimeric transition temperature (see the Fig. 2 above), the material tends to soften and deform like thermoplastics [21]. The result is that the material flows and the particles impacting with relatively high velocity stick with the polymeric substrate due to the mechanical interlocking mechanism [22]. However, the softened material showed an extensive groove on the area interested by the spray deposition characterized by a depth larger than 25% of the panel thickness, that may affect the mechanical properties of the panel. This is clearly visible by looking both the macrograph and the relative profile in Fig. 5a and 5b, respectively. The observed phenomenon is related to high temperature of the impinging gas that results in a significant shoot peening effect of the upcoming particles impacting at relatively high velocity on a very soft polymer, causing possible defects and erosion of the substrate.

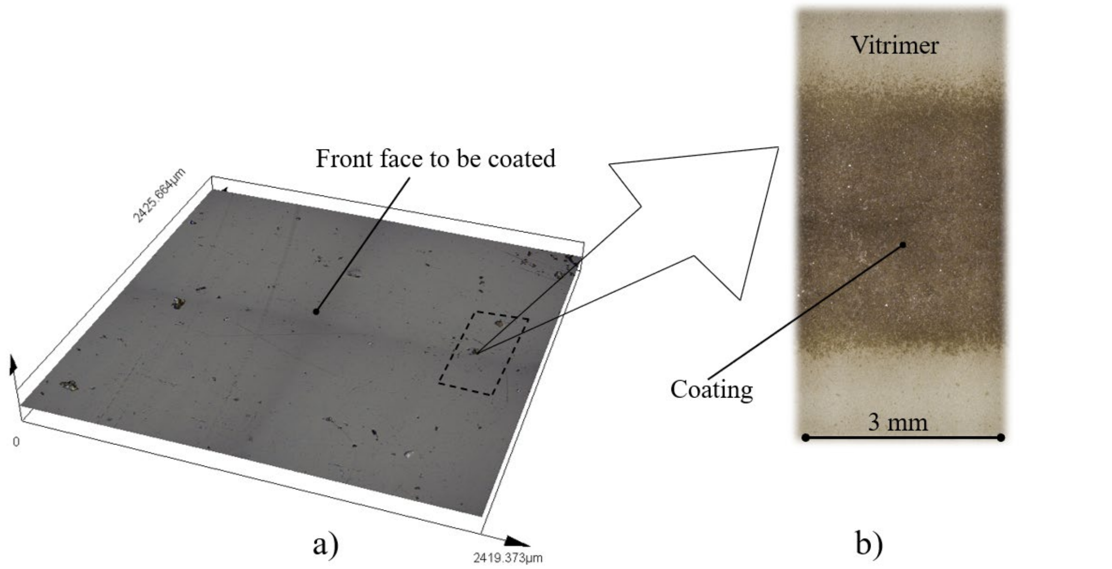

Fig. 4. a) Result from confocal microscope scan of front face of vitrimeric panel. b) Specimen of cold sprayed epoxy vitrimer.

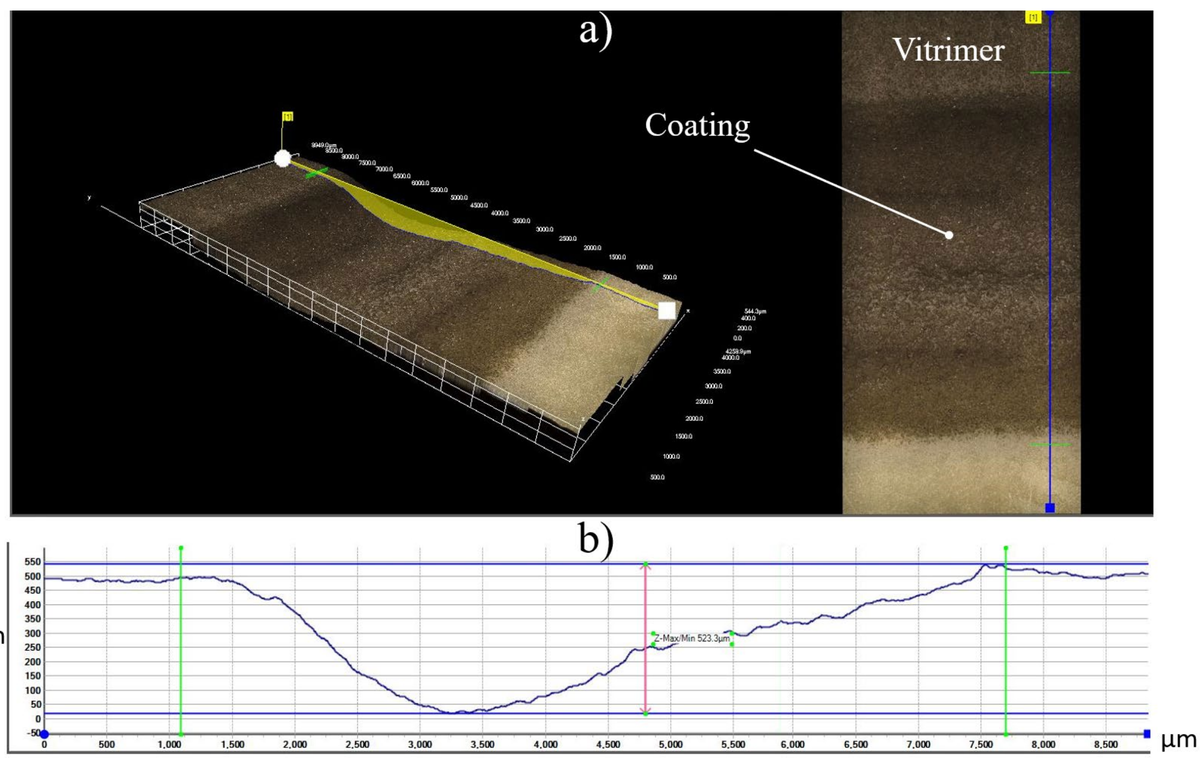

Fig. 5. Results from Hirox observations with the large groove highlighted in yellow: a) macrograph of V_{T2} coated panel; b) measurement of height profile.

The results of the deposition process at T=200°C on epoxy vitrimer sample (V_{T1}) are shown in Fig. 6. It can be observed the single layer of AlSi10Mg particles proving the effectiveness of the deposition process (Fig. 6a). Contrary to V_{T2} sample, the groove left by the spraying process is negligible, being about 4% in depth of the panel thickness (Fig. 6b). The reason is that, under these spraying conditions, the temperature of the gas at the impact surface (which was measured to be about 140°C) is a little below the vitrimeric transition temperature, with the epoxy polymeric material that starts to behave like thermoplastics (see the Fig. 2 above). The result is that the particles impact the relatively rigid surface and penetrate the like-thermoplastic substrate promoting adhesion, without inducing significant defects and grooves within the material.

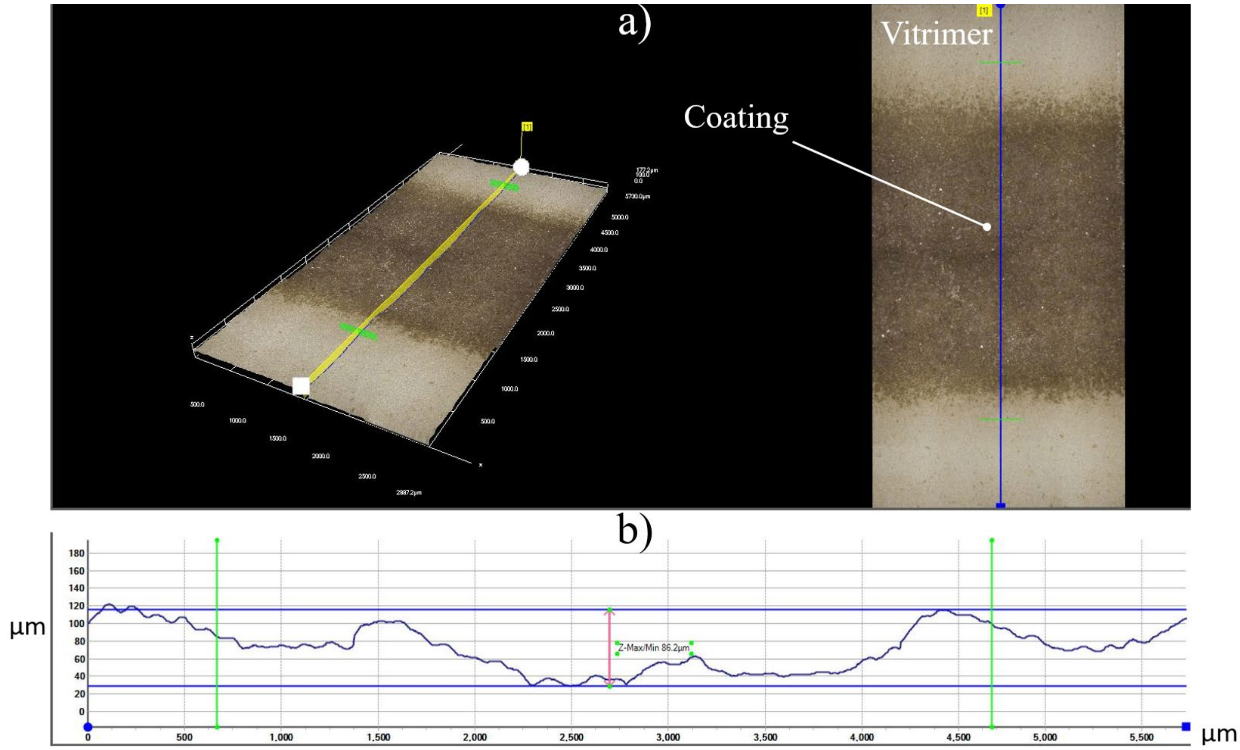

Fig. 6. Results from Hirox observations with the negligible groove highlighted in yellow: a) macrograph of V_{T1} coated panel; b) measurement of height profile.

Conclusions

Based on the experimental results presented and discussed in the previous sections, the following conclusions could be drawn:

- Firstly, the cold spray deposition process was proved to be an effective technique for the metallization of epoxy vitrimers if the spraying parameters are properly set (T=200°C, SoD=70 mm, Gas pressure=6 bar).
- The epoxy vitrimer was proved to be a promising polymer to be metallized via cold spray thanks to its thermoplastic-like behavior above the T_v, maintaining the mechanical and thermal characteristics of the thermosetting below this temperature.
- The surface morphology of the vitrimer was proved to affect the cold spray deposition process. Particularly, it is necessary that the valleys of the surface texturing of the polymer used as substrate had a comparable dimension to the feedstock powder diameter, so promoting the mechanical interlocking mechanism.
- The inlet gas temperature was found to be a key factor for an effective deposition on vitrimers. Particularly, the temperature of the gas at the impact surface of vitrimer should be close to the vitrimeric transition temperature. Relatively higher gas temperature values may lead to defects and grooves within the material.

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