Composite Finishing for Reuse

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Abstract Coating processes are emerging for new applications related to remanufactured products from End-of-Life materials. In this perspective, their employment can generate interesting scenarios for the design of products and solutions in circular economy frameworks, especially for composite materials. This chapter would give an overview of coating design and application for recycled glass fiber reinforced polymers on the base of the experimentation made within the FiberEUse project. New cosmetic and functional coatings were developed and tested on different polymer composite substrates filled with mechanically recycled End-of-Life glass fibers. Afterwards, recycled glass fiber reinforced polymer samples from water-solvable 3D printed molds were successfully coated. Finally, new industrial applications for the developed coatings and general guidelines for the coating of recycled glass fiber reinforced polymers were proposed by using the FiberEUse Demo Cases as a theoretical proof-of-concept.

Keywords Glass fibers · Polymer composites · Surface finishing · Physical vapor deposition · Thermal spray coatings · Indirect 3D printing

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1 Introduction, Motivation and Objectives

1.1 Re-processing and Post-processing for Recycled Composite Materials

Composites, as a whole, are in a vivid and challenging market. A big portion of the market is composed by established and standardized production and processes which are responsible for the bigger production volume. In Europe, glass fibers reinforced plastics (GFRPs) accounts for over the 90% of reinforced composites production, and the 85% of the GFRPs market is covered by construction, transport and electronic sectors. Over the past 20 years, resin transfer molding (RTM) and reinforced thermoplastic composites represent the two most significant segments of GFRPs market for the flexibility of the process and for the particular interest gained for large-scales series production, respectively [1].

In particular, boat hulls and wind turbine rotor blades account for most of the End-of-Life (EoL) GFRPs products. Because of their thermosetting matrix, the recovery of the original components is impossible, and the amount of GFRPs wastes is expected to raise significantly considering the increased use of wind energy. Very recently, a work shows the possibility to exploit the high strength, high water resistance of EoL GFRPs products by keeping the composite structure intact but sectioning the structure in smaller parts, strips or flakes suitable for the production of simple shape profile, beams or plates. Thanks to this methods, structural reuse of EoL thermoset composite has been successfully proven with infra-structural demonstrator such as retaining walls and crane-mats or bridge decks [2].

The composite substrates, in general, can be coated for two main reason: the reduction of their surface roughness, or the protection against corrosion and erosion. Gelcoats are used for the roughness reduction particularly for hand-made components, which are quite frequent in composite industry. At the same time, gelcoats assume a key role for wind blades. As a matter of fact, their protection against corrosion and erosion is essential, given their exposure to harsh environment [3]. However, literature does not provide specific information for the coatings for re-processed composites.

Using a coating is not only advantageous from the mechanical and durability point of view, but also for the possibility to cover imperfection and in homogeneities of recycled material. As a consequence, coatings could produce a beneficial effect on the perception of the recycled material, giving more confidence on the properties of the material.

1.2 Research Goal: Coatings for Reprocessed Composite Materials

The development of a new circular economy model is becoming not only a significant objective in global economy, but also an ethical duty. In fact, the growing costs linked to the disposal of EoL parts are no longer sustainable, as well as the environmental footprint of wastes. Nevertheless, EoL composite products are still landfilled. Considering the heterogeneity of these kinds of materials, this method is considered as the fastest and cheapest solution [4].

The attention on the remanufacturing and reforming of new products starting from EoL composites has grown significantly. In this scenario, new products obtained from recycled GFRP can be remanufactured relying on circular economy models. But their surface finishing may not satisfy the aesthetic standards of potential end-users. Functionality and aesthetic could be extremely affected by the finishing of these reformed products [5]. Therefore, the use of rGFRP for real industrial applications could be more challenging.

Accordingly, the main research goal was to investigate methods and solutions to provide aesthetic (i.e. bright chrome finishing) or functional improvements (i.e. anti-bacterial, anti-scratch, self-cleaning properties) to the final reformed product in order to increase its perceived quality. For this reason, the work was mainly focused on the development of cosmetic and functional coatings for rGFRP.

Subsequently, the aim focused on the implementation of some of the developed coatings on 3D objects with a particular shape and geometry, to observe the advantages and the limitations of the processes under investigation on more complex surface and realistic context. At the end, some industrial applications and theoretical links with the FiberEUse demo-cases are given, in order to close the gap related to the development of real products made with rGFRP.

2 Positioning of the Solution

2.1 Composite Coatings

Surface finishing of GFRPs parts or products obtained by using recycled glass fibers are often of low quality [6]. However, a surface coating can be desirable not only for aesthetic purposes but also for protection against environmental erosion. An example of this protective effect against rain erosion is the use of polyurethane coatings applied on GFRP airfoils to damp the stress waves induced by the impact of water droplets and therefore to reduce the stress transmitted to the substrate [7].

An enhanced level of resistance to water droplet erosion was also studied for GFRPs coated with various electro-deposited metal layers, such as chrome and nickel with an intermediate Cu layer [8]. The impact resistance of GFRPs with metallic coatings was found to increase by more than 20 times when compared to the resistance of the uncoated material. Taking into account that composite materials obtained with recycled glass fibers can find probably applications in the building construction and sanitary ware industry, erosion protection coatings against damage caused by liquid impact can be advantageous even for this case. Moreover, an epoxy-based coating was recently developed and studied to enhance the erosion resistance of GFRPs in the marine environment. This erosion-resistant polymeric coating demonstrated to reduce the surface abrasion of epoxy glass laminate composites induced by the impact with sand particles in marine simulated conditions [9].

As already mentioned before, the recycling of EoL GFPRs is becoming a big environmental issue. Only a better understanding of the relationships between the processing, the formulations and the properties of GFRPs filled with recycled composites can promote the actual reuse of composite wastes. For example, a lower level of hardness and therefore a higher wear rate was observed for composites only filled with mechanically recycled GFRPs and an increase of wear resistance was obtained with the introduction of virgin glass fibers together with recycled GFRPs [10].

In light of the above, the development of functional and protective coatings can be very helpful for fostering the recycling and the reuse of GFRPs. A thorough literature search highlighted that there are no examples of coatings on GFRP filled with mechanical recycled GFRPs. Only one paper about the development of a surface layer on a structural composite reinforced with recycled glass fibers was reported very recently [11]. This surface layer was composed of a polyester matrix filled with small particles of calcium carbonate ($CaCO_3$, size up to 2 μm). The thickness of the surface layers seems quite variable. However, this surface showed a homogeneous morphology without cracks, contributing to the protection of the underneath porous composite.

2.2 Limitations and Needs

As shown in the previous paragraph, only one paper showing the study of surface layers applied on composite substrates reinforced with recycled GFRPs was found. This clearly suggests the need to investigate new polymeric and metallic coatings for composite substrates obtained reusing GFRPs. A finishing material or coating can boost the aesthetic properties of GFRPs obtained by recycling EoL products. Moreover a protective function can be surely identified for coatings applied on composites, which find outdoor applications and therefore the study of coating resistance against atmospheric agents by hardness and abrasion tests emerges as a crucial factor. Few examples of works regarding the characterization of hardness for composite coatings are present in literature, but no previous studies like these were found for coatings applied on recycled GFRPs. Moreover, the level of adhesion between the substrates and coatings can be of a fundamental importance for a functional coating and this is another missing point in literature regarding the coatings of GFRPs.

Excellent mechanical and physical properties can be achieved when using reinforced polymer material. Among these low manufacturing costs, excellent resistance to corrosion, and low weight together with relatively high strength can be found. Wear resistance can be good enough, but it can be significantly improved by coating the surface with a wear resistant coating material. Moreover, thermal and electrical conductivities can be improved by coating polymer-based composite. In addition to this, the surface coatings can aim at imparting new added-value functionalities to rGFRPs. These added-value functionalities can be, for instance, anti-scratch resistance, antibacterial properties and self-cleaning abilities.

When thermal spray coating methods are used to produce coatings on the polymer-based composite surfaces, anti-scratch resistance can be introduced for example by thermally sprayed hard metal coatings containing tungsten and chromium carbides. Antibacterial properties can be obtained with thermally sprayed thick metallic coatings (e.g. silver, copper, zinc, nickel–chromium, bronze), and self/easy-cleaning surfaces with titanium oxide coatings.

The composite surfaces can be therefore modified by coatings to have desired properties. It is evident that these type of coating procedures can be also applied on the surfaces of recycled composites as it will be presented below in this chapter.

3 Methods and Workflow

3.1 Approach and Workflow

The main workflow of the experimentation can be resumed in Fig. 1. Two different kinds of mechanically recycled glass fibers (rGF) were used as a filler for the reformed composite substrates. The first one derived from EoL wind blade, while the second one was mainly composed by internal waste scraps of corrugated GFRP sheet production. Starting from them and optimizing the process parameters, two different kinds of samples were obtained: epoxy-based substrates with EoL wind blade rGF, and unsaturated polyester-based (UP-based) substrates filled with internal waste rGF. After that, two different approaches were defined for the surface optimization of the developed substrates:

1. appearance improvement aiming at the increase of the aesthetic appeal for design products (cosmetic coatings);
2. functional improvement aiming at the increase of the value-added features of the reprocessed composite products (functional coatings).

The first approach provided for the liquid deposition of UV- or thermally-curable primers on the substrates, followed by the coating deposition of a thin chrome layer by means of PVD (Physical Vapor Deposition) sputtering process. Methods and parameters were optimized specifically for rGFRP materials.

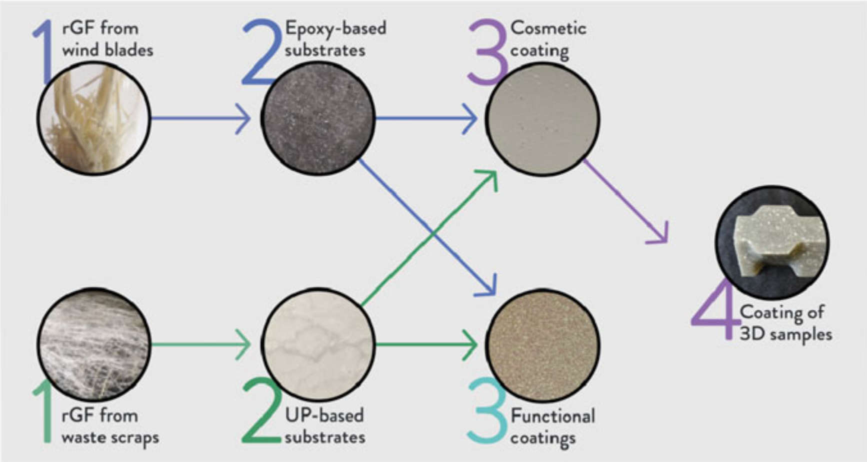

Fig. 1 Workflow of the experimentation from the development of new coatings for rGFRP composites to their preliminary implementation on 3D samples with complex surfaces

In the second approach, new functionalities were implemented on the substrates through the deposition of thick metal coatings with thermal spray processes for new anti-bacterial, anti-scratch and self-cleaning properties. Finally, samples obtained from water-solvable 3D printed molds were coated with PVD, implementing this surface finishing on components with a complex shape.

3.2 Substrates

Mechanically rGFs were used as a reinforcement for the reprocessed GFRP samples, employed as substrates for coating tests. These rGFs were provided both by Rivieresca (RIV), recovering RIV's ground GFRP internal waste, and by STIIMA-CNR (Istituto di Tecnologie Industriali e Automazione-Consiglio Nazionale delle Ricerche), grinding EoL wind turbine blades (Siemens Gamesa Renewable Energy S.A.).

UP-based samples with rGFs provided by RIV were composed by a mixture of virgin glass fibers and rGFs combined with an orthophthalic unsaturated polyester resin. These substrates contain approximately 44 wt% of recycled waste, and they were coated with a chrome layer deposited by PVD, using either a UV-curable solvent-less acrylic primer or a two-component acrylic primer with solvent.

As for rGFs from wind blades, the resulting fibers had a maximum size of around 4 mm, after the processing through grid holes with this dimension. An epoxy-based resin (commercial resin name: Araldite BY158, Huntsman, BY158 for brevity) was used for substrates filled with the rGFs obtained from EoL wind blades. BY158, which was composed of an epoxy-terminated bisphenol-A-based oligomer and 1,4-butanediol diglycidyl ether, was crosslinked with a curing agent (Aradur 21, Huntsman) using a weight ratio of 100/28 between BY158 and Aradur 21. The rGFs were added to the resin and mixed for 15 min by a mechanical stirrer (50 rpm). A nominal percentage of rGFs ranging from 40 to 60% wt. with respect to the mixture of BY158 and Aradur21 was used. The real content of glass fibers in samples prepared with a nominal 60wt% of rGFs was found to be 51.3 ± 5.9wt% by thermogravimetric analysis (TGA). The resulting mixture was subjected to a low vacuum level for 15 min and processed by compression molding for 24 h at room temperature with a post-curing at 100 °C for 1 h. These substrates were employed to develop a UV-curable or thermo-curable epoxy-based primer for a consequent chrome deposition.

3.3 Cosmetic Coatings

A PVD process was employed to obtain a decorative bright chrome finishing on rGFRP substrates. Prior to PVD sputtering deposition, the application of a primer was necessary to provide a smooth surface and improve the hardness and brightness of the coating. The absence of Cr^{6+} and Cr^{3+} compounds and the possibility to use a solvent-less primer make this process a more sustainable option to electroplating.

Two different commercial primers were initially used in the experimentation. The first one is a UV-curable solvent-less primer commonly used in PVD coating of injection molded parts (Cromogenia Units SA., Spain). It is composed by a blend of different acrylates and a mixture of two different photoinitiators with range of absorption of 255–380 nm. The second one is a two-component solvent-based acrylic primer (Lechler S.p.A., Italy), suitable for composite substrates. For PVD, chrome target with purity 99.95% was used.

Araldite BY158 was employed for the development of the thermally-curable epoxy-based primer. Aradur 21 was added as curing agents to increase the crosslinking with a weight ratio of 100/28. Epoxy-resin primer formulations were cured following the same procedure used for the epoxy-resin substrates.

Four different methods for surface preparation were tested. Degreasing with acid solution took place in pre-treatment spray tunnel, and the parts were sprayed with a phosphoric acid based solution at 60 °C for 4 min. Samples were then rinsed using demineralized water of 5 μS/cm of conductivity. Finally, a drying phase was carried out in oven at 60 °C for 30 min. Degreasing was carried out manually with an isopropanol moistened cloth rubbing the surfaces, and followed by 10 min of drying at room temperature. Surface sanding was carried out manually or with a sanding machine, using P100 and P120 grit sandpaper.

Plasma surface activation was carried out in a vacuum chamber equipped with two electrodes, a power source up to 6 kW, a turbo-pump allowing 10^{-3} mbar vacuum and a flow-controlled gas inlet. The treatment was performed for 40 s with a power of 4 kW. The processing gas used in the experimentation was oxygen.

Primer was applied both with manual and automatic equipment. UV-curable solvent-less primer was applied in the painting booth by anthropomorphic robot equipped with rotary bell atomizers. UV-curing was carried out in a station equipped with 26 microwave-powered bulbs, delivering a peak irradiance up to 500 mW/cm^2 and an energy density up to 2600 mJ/cm^2.

The steps of the PVD sputtering and its parameters were set according to the standard process, which is already consolidated for injection molded plastic parts. The chrome layer was deposited using four chrome target at 10 kW of power and 120 s of takt time (240 s of total deposition time). The tests were mainly focused on the optimization of the methods and the process parameters in order to improve the process ability of rGFRPs surfaces.

Adhesion properties of the chrome coating were tested performing manual cross-cut test according to ISO2409:2013 [12]. A linear Taber equipment was used to test abrasion resistance with a H1 felt (total weight of 1 kg and 60 cycles/min). Abrasion test results are expressed in 5 levels depending on the surface area of coating removed by abrasion. In detail, 0 means no abrasion, and level 5 means more than 50% of area was affected by removal. Chrome layer thickness was measured using a Helmut Fischer Fischerscope X-RAY XDL spectrometer.

3.4 Functional Coatings

Thermal spray coating onto polymer-based base materials are defined as the application of thermal spray processes to deposit metallic, ceramic or polymeric feedstock materials (powder or wire) onto the surface of a polymeric composite base material.

According to the primary energy source used for particle acceleration and heating, thermal spray coating processes can be categorized into four groups: cold spraying, flame spraying, electric arc wire spray and plasma spraying [13, 14]. In this experimentation, all these processes were used for the deposition of functional coatings. However, the most suitable thermal spray processes to deposit heat sensitive substrates, such as polymer composites, are electric arc spraying and wire flame spraying. Other processes are possible, but they often require the preparation of the surfaces to make the substrates more heat resistant.

To improve the adhesion of thermal spray coatings, different kinds of primers were studied, such as low melting polymer (melting region of 80–120 °C), metallic layer (aluminium, nickel–chromium and WC–CoCr powders, chromium or aluminium oxides). The thickness of the primer layer was controlled by adding some quartz particles with a size of 200–600 μm, when the primer layer was applied between the base material and the PTFE plate.

Experiments were carried out with different materials and equipment, according to the specific thermal spray technology. For low-pressure cold spray (LPCS) trials, a Dymet cold spray unit was used to produce copper and aluminium coatings, that were sprayed using a thin low melting polymer layer on the rGFRP surface.

Table 1 List of thermal spray treatment for the characterization of the rGFRP samples

Coating method	Substrates	Primer	Coatings
Cold spray (Dymet)	Composite	80 °C melting polymer	Cu, Al, or AlZn
Flame spray (Castodyn DS 8000)	Composite	80 °C melting polymer	Diam 4008, Amp. 481.002, Amp 481.003, or LDPE
Flame spray (Master Jet)	Epoxy + Cr_2O_3, Epoxy + WC–CoCr, Epoxy + Al, Epoxy + NiCrSib	RODCUR 6740, NiChrome, Chroma Supra, or TI-Elite	NiCrBSi + 40%WC, 80%Ni + 20%Cr, Cr_2O_3, or Al_2O_3 + TiO_2
Plasma spray (Technik A3000 S)	Composite	None	Diam 2001
Arc spray (Sulzer Metco Smart Arc)	Composite, Epoxy	None, or Zn	Zn wire, or Cu + 10Al + 1Fe

Powder flame spraying equipment Castodyn DS 8000 was used with LDPE polymer powder. The coating was sprayed directly on slightly sand blasted surfaces. Wire flame spraying equipment Saint-Gobain Master Jet was used for metallic coatings with RODCUR 6740 (60% NiCrBSi with 40% WC) and NiChrome (NiCr) wires. Ceramic TI-Elite (Al_2O_3 + TiO_2) coatings were also made using this method, and prepared on WC–CoCr, Cr_2O_3 or NiCrBSi filled epoxy based precoated surfaces.

Electric arc spraying equipment Sulzer Metco Smart Arc was used for arc spraying. Zinc wire was sprayed directly on slightly sand blast composite surfaces, whereas aluminium bronze coatings were sprayed on the composites and on the zinc precoat surface. Plasma Technik A3000 S unit was used for atmospheric plasma spraying with Diamalloy 2001 (NiCrSiB) as feed material.

To better understand the quality and real thicknesses of the coatings, polished cross-section specimens cast were prepared and studied using scanning electron microscopy (SEM) equipped with an Energy-dispersive X-ray spectroscopy (EDX) analyser. The list of the thermal spray treatments and the kinds of substrates, primers and coatings used during the experimentation are shown in Table 1.

3.5 *Surface Finishing Implementation on 3D Complex Shapes*

To evaluate the surface finishing on more complex substrates, two different 3D samples were designed. The samples were obtained by casting the epoxy-based rGFRP (40wt% of wastes) in water-solvable 3D printed molds. The final pieces were then treated with the PVD sputtering process.

In this work, Fusion 360 (Autodesk, San Rafael, California, US) and Rhinoceros (Robert McNeel & Associates, Seattle, WA, USA) were the CAD software used for the design of the samples and molds. Afterwards, the water-solvable molds were produced with a BVOH (butane diol vinyl alcohol copolymer) filament (Verbatim Italia S.p.A., Cassina de Pecchi, Italy) through a Prusa i3 MK3S Fused Deposition Modeling (FDM) 3D printer (Prusa Research, Prague, Czech Republic). The Gcode files were created with the open source software Prusa Slicer from the same manufacturer.

The epoxy-based composite was prepared following the procedure previously described, and poured into the molds. After the first curing phase (24 h at room temperature), the molds were immersed in a beaker with water. To easily dissolve BVOH, the beaker was heated at 60 °C for 2 h on a magnetic stirrer. The 3D samples were manually washed to remove the residues of BVOH, and a layer of the thermally-curable epoxy-based primer was applied on the surface with a soft-bristled brush. The curing treatment was accomplished following the same steps for the epoxy-based flat substrates.

Finally, the PVD treatment was performed according to the process parameters set for the flat samples. In Table 2, the main features of the two 3D samples are shown, whereas the appearance of the casted pieces and of the molds is visible in Fig. 2.

Table 2 Main parameters for the brick, surface tile samples for the PVD sputtering process

3D sample shape	Dimensions (mm)	Mold layer height (mm)	Filler content (% wt.)	Number of samples (−)
Brick	58 × 25 × 30	0.15	40	6
Surface tile	40 × 40 × 18	0.10	40	6

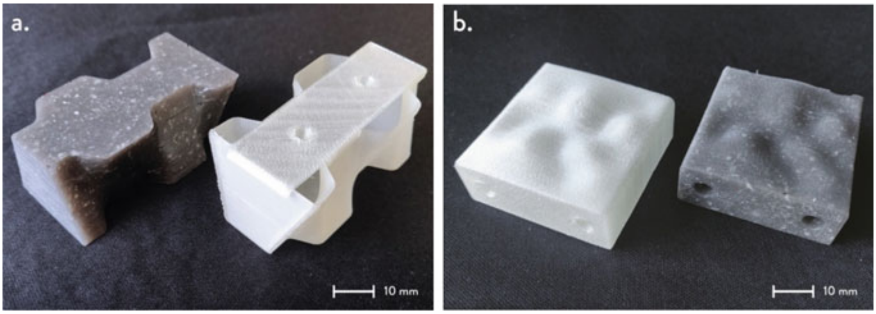

Fig. 2 3D Samples for the PVD cosmetic coating with the corresponding water-solvable 3D printed mold: brick shape (**a**), surface tile shape (**b**)

4 Coating Results and Validation

4.1 Cosmetic Coatings

In first test, the UP-based samples were divided into two groups, on which two different surface preparation methods were applied: acid degreasing on the former group, isopropanol cleaning on the latter. Both groups were coated with a UV-curable solvent-less acrylic primer applied by robots equipped with rotary atomizers. For levelling the rough surface of the samples, the primer flow-rate was increased from the standard values of 15–35 μm to 60–80 μm. As a consequence, the samples were cured with 100% of UV power.

Since it was not possible to further increase the primer thickness, the final result was highly dependent on the substrate roughness, which showed an uneven surface with several cavities as visible in Fig. 3. In this case, the adhesion level between the primer and the substrate was found to be equal to 5, which means that more than the 65% of the cross-cut area was affected by detachment. This represented a primary issue to be solved, since the standard level for furniture and creative products must be at least equal to 1 (less than 5% of cross-cut area affected).

Poor adhesion can be linked to the chemical incompatibility between the primer and the matrix of the substrate. Therefore, further rGFRP samples made with different resins were tested, and other methods to improve adhesion were investigated.

According to Table 3, machine sanding significantly improved the adhesion levels of the coating. In addition, the abrasion level was satisfactory for machine-sanded UP-based substrates, since less than 1% of the coating was removed at 1000 strokes. Nevertheless, the adhesion level should be furtherly increased to fulfill the minimum requirements of the industrial sectors.

Fig. 3 UP-based sample before (on the left) and after the chrome coating using (on the right) UV-curable primer

Table 3 Adhesion and abrasion level tests of the UP-based and vinylester coated samples

Samples	Adhesion level test		Abrasion test
	Manual sanding	Machine sanding	Machine sanding
UP-based	5	3	1
Vinylester	N.A	2	2

Two-component acrylic primer. Since an alternative solvent-less UV-curable primer was not available, a two-component acrylic primer for PVD process on composite surfaces was then chosen, and manually applicated with an handgun.

As visible in Fig. 4, the use of this alternative primer did not change the aesthetical appearance of the chrome coating with respect to the previous tests on the UP-based substrates. On the contrary, the adhesion level was equal to 1, which is generally enough for most of the technical applications for indoor furniture and home appliances. However, the abrasion level was inadequate if compared to the substrates treated with the UV-curable primer, since the chrome layer was fully removed at 500 strokes. For this reason, this primer could be used for surfaces that are not subjected to frequent mechanical stresses (i.e. reflective surfaces of lightning appliances).

Primer development for epoxy-based composites. Considering the low adhesion level observed with a standard UV-curable acrylic primer on epoxy-based matrix, a new primer should be developed for this kind of rGFRP. To minimize the surface tension differences, a thermally-curable primer formulation with the same composition of the substrate matrix (BY158 and Aradur 21) was tested. As observed after the deposition, the overall quality of the primer coating was better with respect to the UV-curable commercial solutions, and the cratering effect almost disappeared as shown in Fig. 5a. Accordingly, the samples were coated with PVD sputtering deposition process. The result after the chrome deposition is visible in Fig. 5b.

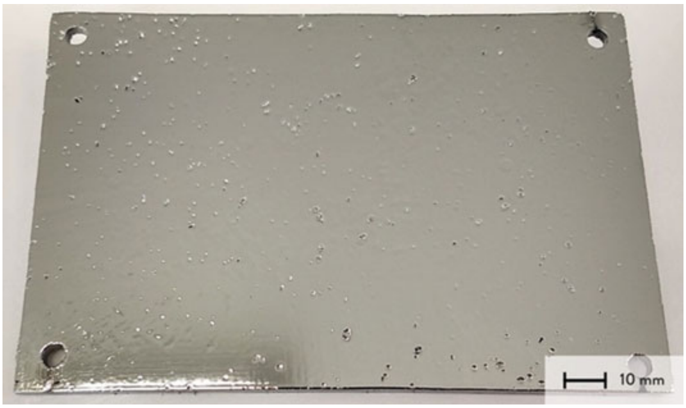

Fig. 4 UP-based sample after chrome coating using solvent-based acrylic primer

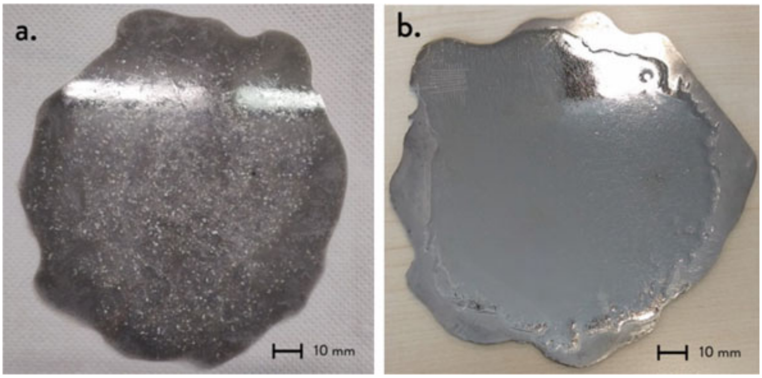

Fig. 5 Epoxy-based sample before (on the left) and after (on the right) the chrome deposition on the thermally-curable primer formulation

Since no detachment occurred, the adhesion level was equal to 0. On the contrary, the abrasion resistance was low. As a matter of fact, the chrome layer was almost entirely removed at 100 strokes.

4.2 Functional Coatings

At first stage, the quality of the formed coatings were visually evaluated. As mentioned before, the adhesion of thermal spray coatings was improved by developing several kinds of pre-coatings. Initially, the layer consisted in a low melting polymer layer, but it was too soft especially for cold sprayed coatings. Consequently, the next step was to use a metallic or ceramic powder primer (aluminium, nickel–chromium and WC–CoCr or chromium and aluminium oxides) as pre-layers under the thermal sprayed coating. Their use seemed promising, since grow and adhesion of the coating was found to be improved especially for flame spraying methods.

Cold spraying. To test cold spray technology to form coatings on polymer composite surface low pressure cold spray Dymet cold spraying equipment was used. Cold spraying method was also tried directly on the composite surface without any precoat layer. However, the high-speed coating material particles hitting the surface were only removing the composite material, and the coating was not growing on the base material surface. Accordingly, a pre-coat layer is needed.

Coating materials used for these experiments were Cu and Al–Zn powders sprayed on low melting polymer primer layer. Mainly, it was found that the primer layer had too low melting point, and was too soft. As a result, formed coatings were not uniform and dense, even though individual feed particles were stick on the surface forming metallic colored layer.

Flame spraying. Two flame spraying methods were used within the experiments. At first Castodyn DS 8000 flame spray gun was used. Two Ni–Al coating materials were utilized: Diamalloy 4008 and Amperit 281.002 on low melting polymer primer layer.

Also in this case, no uniform metallic coating layer was formed on the composite surface. It is obvious that the primer used is too soft to form dense thermal sprayed coating layer. Therefore, the process with this kind of soft bonding layer was not suitable for the coating of rGFRPs. This primer layer was used only because the metallic coating did not deposit directly on the surface with this flame spray technology.

Recycled GFRPs can also be coated with polymer layers. Of course there are several suitable polymers to choose as the coating material, but in this case low melting LDPE powder was used. The adhesion of the LDPE coating on the sand blasted composite surface was good. On the interface between the coating and base material, some porosity was observed in the cross-sectional specimens. Thickness of the coating layer was measured to be between 250 and 300 μm.

Using the Saint-Gobain Master Jet unit, metallic and ceramic coatings were made on the recycled composite surface. For the first trials, the selected coating material was RODCUR 6740. The coating was mainly sprayed on slightly sand blasted composite surface and thin coating layer formed. Metallic NiChrome (Ni + Cr) and ceramic Ti-Elite ($Al_2O_3 + TiO_2$) were successfully sprayed on recycled composite surfaces, as can be seen in Fig. 6. Also epoxy-based precoat layers filled with metallic or ceramic powder were obtained on the rGFRP surface. Thanks to this kind of precoat layer, the coating can easily grow on the surface, improving the adhesion. According to the EDX analysis map measured from the cross-sectional RODCUR 6740 presented in Fig. 7, the coating is well built on the rGFRP surface.

To sum up, Powder flame spraying coating was sprayed directly on slightly sand blasted composite surface with great success. Different kinds of coating materials could be used with this technology, and there are several filler materials for the precoat to be tested. In this work, only some were tested with promising results.

Plasma spraying. For the plasma spraying experiments, Diamalloy 2001 powder was used as coating material. The coating was sprayed directly on the rGFRP surface or on thermally sprayed HDPE precoat. A uniform layer was not formed with this latter method. The polymer precoat layer should be more heat resistant and harder to

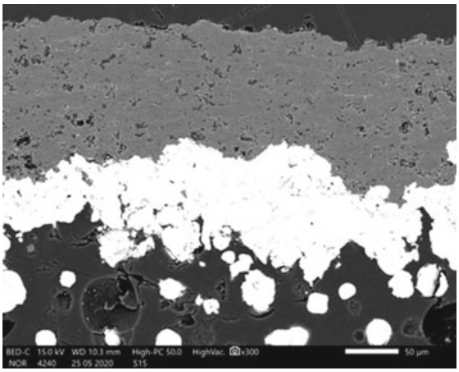

Fig. 6 Cross-section of ceramic $Al_2O_3 + TiO_2$ coating on the rGFRP surface with the NiChrome precoat (light) under the ceramic coating sprayed using Saint-Gobain Master Jet unit

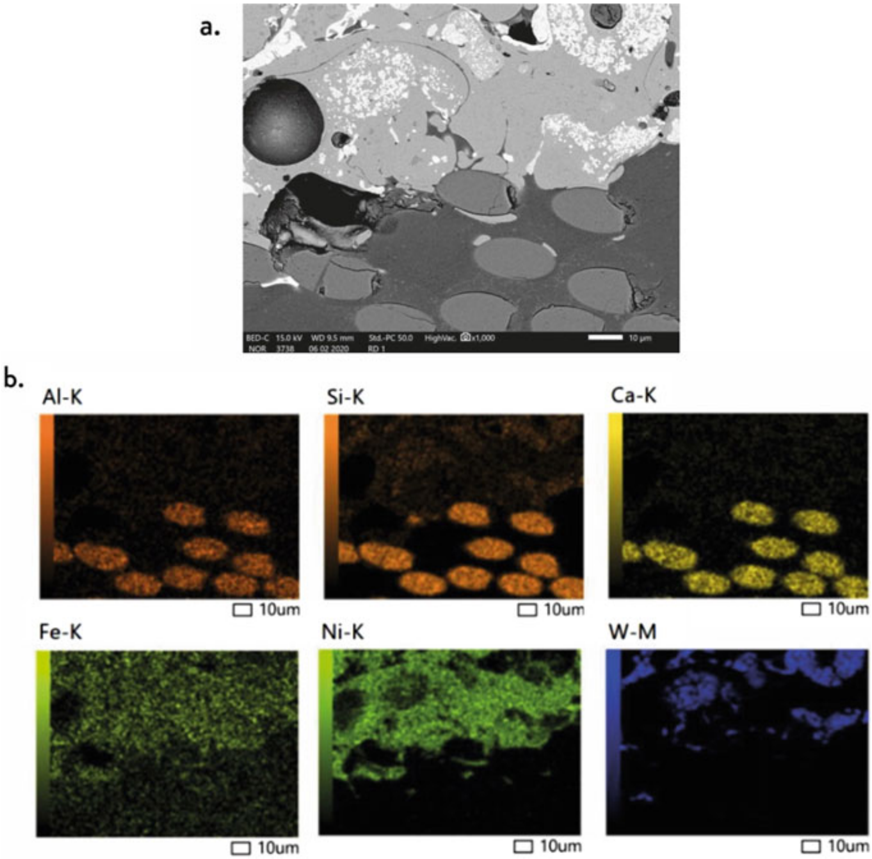

Fig. 7 Cross-section of Saint-Gobain MasterJet flame spray coating on the recycled composite surface with RODCUR 6740 layer (**a**) and EDX elemental maps (**b**)

last to the melt coating particles hitting the surface. As shown in Fig. 8, dense coating was formed on sand blasted rGFRP surface. As a conclusion, plasma spraying has potential for composites. Material processed with plasma spraying has good wear resistance and it was sprayed successfully directly on softly sand blasted recycled composite surface. Moreover, other suitable coating material could be used.

Arc spray coatings. Coating materials chosen for these experiments were zinc and bronze wires sprayed. Thick and dense coatings were achieved especially with zinc as coating material. Zinc was used also as a precoat under the bronze layer to improve the adhesion. The coating surfaces are visible in Fig. 9a and b, whereas cross-sectional image and elemental maps measured from the zinc-bronze construction cross-section are presented in Fig. 10. According to the results, aluminum was oxidized during the process, forming an antibacterial coating primarily made of copper, and the most promising results were obtained with the zinc as a precoat. Similarly, other coating materials could be potentially obtained with this technology.

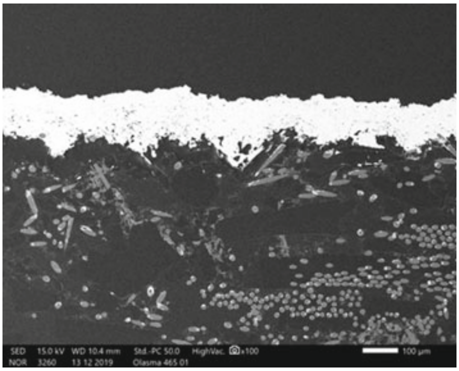

Fig. 8 Cross-section of the plasma sprayed Diamalloy 2001 coating on the rGFRP surface

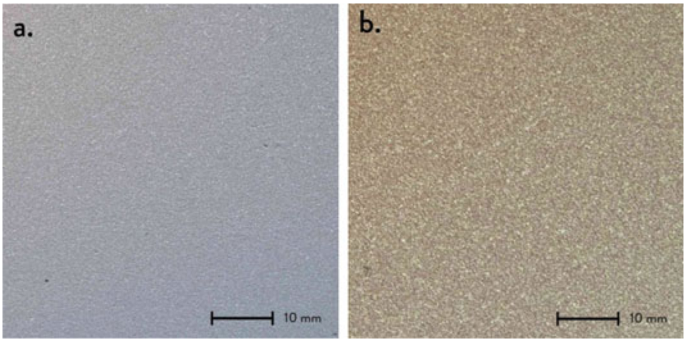

Fig. 9 Arc sprayed zinc coating on the sand blast epoxy based rGFRP surface (**a**), and antibacterial bronze coating sprayed on zinc precoat (**b**)

4.3 Surface Finishing Implementation for New Applications

As described in the previous paragraphs, the surface finishing for reformed composite substrates with rGF was deeply investigated in the FiberEUse context. However, the application of these coatings should be done at larger scales in order to promote their real application. From literature, the importance of the material surface finishing for the definition of new products is a well-established concept. This is especially true in the field of industrial design, since surface finishing strongly affects the technical properties of a new product and its expressive-sensorial qualities [15, 16].

For these reasons, after the development on new cosmetic and functional metal coatings for reprocessed GFRPs on flat substrates, an ad-hoc experimentation on 3D samples was carried out for PVD processes to give the possibility not only to validate the surface finishing process but also directly experience expressive-sensorial qualities. As seen in a previous experimentation with PVD sputtering onto 3D printed surfaces, the choice of a proper shape of the samples was crucial. On the

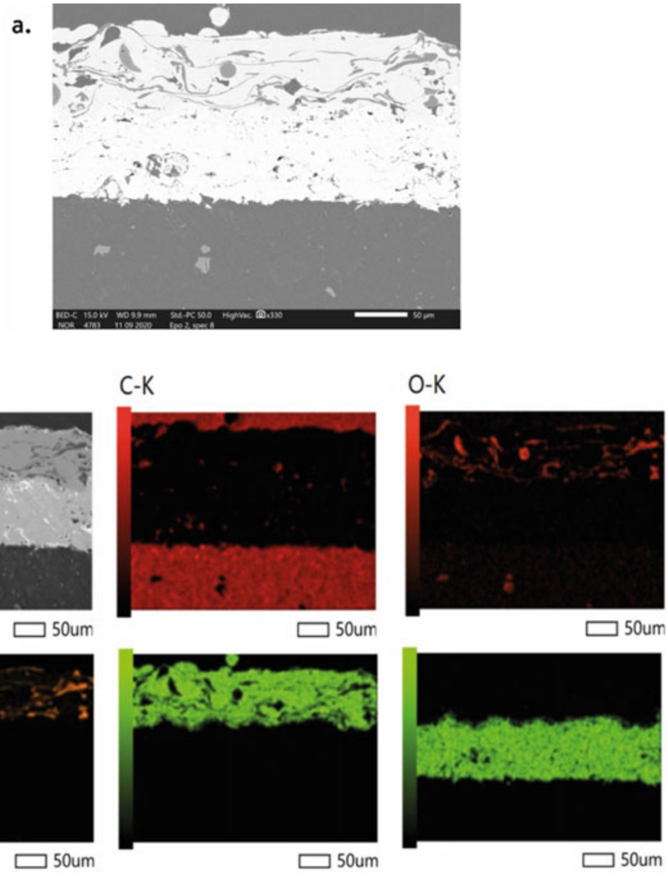

Fig. 10 Cross-section of arc sprayed antibacterial coating of zinc and bronze on the rGFRP epoxy based composite surface (**a**) and EDX elemental maps (**b**)

one hand, the shape itself could affect the surface perception. On the other hand, a more complex surface could simulate the coating application on new reprocessed products, showcasing the achievable results from the designer and manufacturer perspectives [17].

As mentioned, the samples were produced by pouring the epoxy-resin based composite in water-solvable 3D printed molds. From literature, this process is known as "Indirect 3D Printing". Accordingly, the final piece is not directly 3D printed, but its shape is defined by means of 3D printed tooling such as molds or inserts. A wider range of materials can be processed, including thermosetting resins and composites. Moreover, solvable molds allow the production of parts with complex overhangs. At the moment, this approach is mainly adopted in electronics, bioengineering or medical fields [18, 19], but it could be suitable for all those applications that need high-performance composite pieces, complex shapes or heat resistance properties [20].

Two different shapes were designed to evaluate the PVD coating on a planar ("Brick" sample) and on a complex curved surface ("Surface Tile" sample). Mainly, molds were designed to avoid resin leakages after casting. At the same time, one of the goal was to minimize the amount of 3D printed solvable material for each mold.

First, a batch of six brick samples was successfully produced. After the application of the thermally-curable epoxy-based primer, the surface of the bricks did not show cratering effect except for the area near to the sharp angles, as shown in Fig. 11a. Moreover, no marks on the primer surface related to the FDM process are visible. After the PVD, the appearance of the chrome layer is similar to the previous planar substrates made with the epoxy-based rGF composite. The final appearance of the bricks is shown in Fig. 11b.

Afterwards, the PVD coating was performed on six Surface Tile samples following the above-mentioned steps. In this case, the primer tended to accumulate in the surface lows of the shape, as visible in Fig. 12a. This is mainly due to the polymerization time needed for the primer curing, that does not allow to obtain a uniform thickness. Nevertheless, no cratering effects was visible on the surface.

The chrome coating emphasized the inhomogeneities related to the thickness of the primer. According to Fig. 12b, the 3D printing extrusion marks were clearly visible in all those points where the primer layer was thinner. As expected, no signs were found in the surface lows. However, some cracks on the chrome surface were detected in correspondence of the highest thicknesses of the primer layer. Even though the chrome layer was successfully deposited, other efforts should be done for the optimization of the primer application, since it negatively affects not only the performances of this coating, but also its expressive-sensorial qualities.

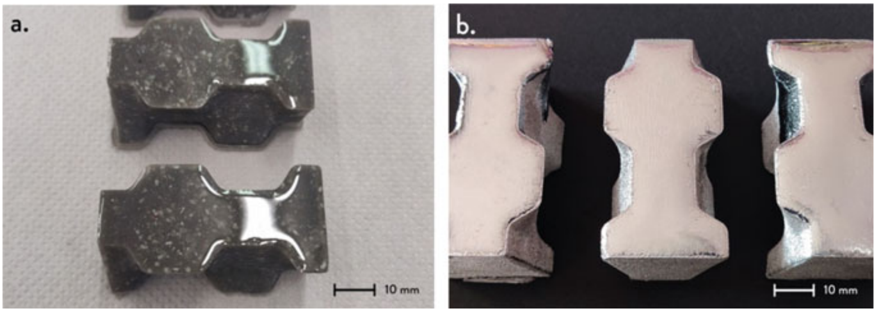

Fig. 11 Brick samples for surface finishing evaluation: samples after the primer application (**a**), and after the PVD cosmetic coating (**b**)

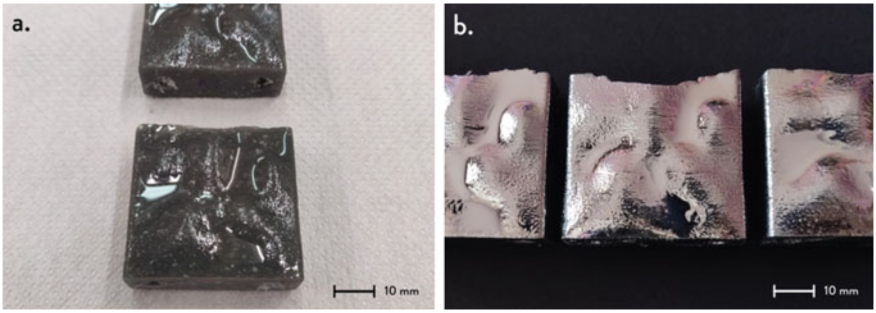

Fig. 12 Surface Tile samples for surface finishing evaluation: samples after the primer application (**a**), and after the PVD cosmetic coating (**b**)

5 Fields of Application

5.1 Surface Coatings for Industrial Application

Cosmetic Coatings. The most potential industrial applications of chrome coating on rGFRPs are represented from all those fields with a high relevance of the expressive-sensorial qualities. Mainly, these coatings are able to enhance end user perceived quality. Moreover, they can give unique finishing characteristics to rGFRPs that are not commonly linked to these kinds of recycled composites. As a consequence, their use perfectly fits for the design of new products in the furniture and interior design sectors. More in detail, UP-based and epoxy-based substrates could be used at this purpose, since high levels of abrasion resistance are not required. For these reasons, design-driven products from the FiberEUse Demo Cases could extremely benefit from the application of this kind of coating.

Other fields of application could considered once the functional features will be optimized, and the current limits will be overcome (i.e. outdoor products, automotive). Thanks to the promising results of the adhesion test, UP-based rGFRPs could also be suitable for technical applications for indoor furniture and home appliances. Similarly, epoxy-resin based rGFRPs could be considered for the same sectors after fixing the current issues related to the primer development and deposition. Further opportunities could be then explored by including additional properties in the surface treatment (i.e. antibacterial power or wear-resistant features), or taking into account rCFs products. Therefore, Automotive Demo Cases as well as products from Additive Remanufacturing could be potentially considered for future developments.

Functional Coatings. Improvement of wear resistance and better visual appearance can be achieved using thermal spraying methods for rGFRP surfaces. Moreover, improving the thermal and electrical conductivities of the coated rGFRPs could lead to new technical high-performance application. Accordingly, Automotive Demo Cases seem to be the most promising application within the FiberEUse framework.

Protective and antibacterial functions could also be implemented for outdoor applications (i.e. against the weathering). Moreover, antibacterial coating should be considered in those contexts where a specific product gets in contact with several users.

Further novel applications could be detected after the development of new functional coatings, since their coating can give new properties to the rGFRP surface.

5.2 *Guidelines for Reformed Composites Coating*

Cosmetic Coatings. The results of the experimental phase underline the importance, for the coating of recycled composites, of surface pre-treatment of the substrate before proceeding with PVD deposition. When using UV primers, best results have been achieved by machine sanding the surface with sandpaper 100–120 grit. It is therefore necessary that all surfaces to be coated are easily accessible to sanding operations.

For solvent-based acrylic primer instead, accurate surface cleaning with isopropanol is sufficient. After the application, it is important to follow the curing times indicated on the technical datasheet in order to assure a complete cross-linking before proceeding with PVD deposition. Otherwise, defects like cracking lines may occur on the surface after the chrome layer deposition.

PVD deposition is carried out in vacuum environment. This requires that all parts are completely humidity-free and used resins are fully polymerized in order to avoid degassing during the process. This could lead to defects such as darker color, iridescent shades and thickness of chrome layer lower than expected.

Since temperature during PVD process can reach 70 °C, the parts need to be sized to avoid deformation. Deposition power and time can be set to reduce the process temperature. However, this would negatively impact layer thickness and productivity.

Since the PVD process takes place in a closed chamber, parts must be designed taking into account the maximum size which can be processed by the plant.

Functional Coatings. There are several thermal spray technologies, which can be utilized when making functional coatings on the recycled composite surface. Each of them is giving different qualities to the formed coating, since feed materials are different. Therefore, several coating methods can be used for different needs. Coatings can be sprayed successfully on the rGFRP surface using several technologies. In general, the sand blasting of the rGFRP surface can significantly improve the adhesion and the quality of the coating. This is also true for the deposition of the precoat.

For powder flame spray with Ni–Al, the polymer primer was too soft to form dense coating layer. Accordingly, the process with this kind of soft bonding layer is not suitable for coating of polymer composites, even though that layer was used only as a precoat layer for the metallic coating on the rGFRP surface. Nevertheless, polymer coating could be possible, as demonstrated thanks to the good adhesion of LDPE coating on composite surface.

By changing the flame spray technology, metallic and ceramic coatings are possible on the rGFRP surface. In this case, an epoxy based precoat filled with metallic or ceramic powders is recommended, since it makes the coating to grow easier on the surface. Moreover, it could improve the adhesion on the composite surface.

Through plasma spraying, the coating can be sprayed directly on the sand blasted composite surface without the need of a precoat. Therefore, this technology has potential for coatings on rGFRP surfaces, also considering the suitable coating powders.

Similarly to plasma spraying, it is possible to directly spray Zn and aluminium bronze wires sprayed on the sand blasted rGFRP surface with arc spraying. Zinc can be use both as coating material and as precoat layer under the bronze layer. In the first case, thick and dense coatings can be achieved, whereas the adhesion of the bronze layer improves in the latter one. Consequently, it is worthful to use more demanding coating materials with this technology.

6 Conclusions and Future Research Perspectives

6.1 Cosmetic Coatings

Best results with solvent-less UV-curing primer were obtained on UP-based and vinyl-ester substrates treated with sandpaper machine. The chrome coating showed a good abrasion resistance on UP-based, fulfilling the requirement from the industrial sectors of 1000 linear Taber strokes without detachment. However, the adhesion requirement was not met in this work.

In terms of adhesion, the most promising results were achieved with the alternative solvent-based primer. Anyway, the use of solvent-based primer limits the environmental benefits prospected at the beginning of the experimentation. If compared to typical requirements for furniture and design products, the adhesion of solvent-based primer proves to be satisfactory on UP-based. The abrasion resistance of the top chrome layer is not satisfactory if compared to the requirements of the industrial sectors. Nevertheless, results may be adequate for lighting design.

Regarding the developed epoxy-based primer, very high level of adhesion between the primer and the rGFRP substrates was achieved. However, the adhesion between the chrome layer and the epoxy-based primer seems not enough satisfactory according to the abrasion tests. Therefore, this coating can be successfully employed for design-driven applications, which do not require high levels of abrasion resistance.

6.2 Functional Coatings

Most promising results during the studies were obtained with plasma spraying, arc spraying and flame spraying methods. With these technologies tailored coatings was formed also directly on the slightly sand blast composite surface. However, deposition of composites often requires some sort of pre-treatment, or actually a precoat layer, in order to prepare the coatings successfully with adequate coating adhesion to the composite substrate and proper microstructure. Thin epoxy-based coatings mixed with fine metallic or ceramic particles were used successfully in this purpose.

To highlight some results, it can be concluded that wear resistant tungsten carbide containing coatings can be deposited on the recycled composite surface. Also, other metallic coatings such as copper, bronze or zinc can be made on the composite surface giving metallic properties and appearance for the recycled composite surface.

Ceramic coatings sprayed on precoat layer were also made on the recycled composite surface using flame spaying technology, e.g. for providing wear and scratch protection and for visual appearance. Also, LDPE polymer coatings were sprayed successfully directly on the slightly sand blast recycled polymer composite surface using conventional flame spray technology.

For the first time in literature, chrome coating from PVD was successfully deposited on rGFRP pieces obtained from water-solvable 3D printed molds. Two different kind of samples were manufactured in order to test the primer application and the PVD coating both on planar and curved surfaces. Even though cratering effect was not detected, some issues occurred, mainly related to the primer thickness. As a matter of fact, its inhomogeneity negatively affected the overall aspect of the chrome layer.

In the light of the above, further work would be done to improve the quality of the coated surface and its aesthetic properties. At this purpose, different application methods for the epoxy-based primer should be investigated, such as airbrush deposition or dip coating. Alternatively, other primer formulation could be developed to reduce the polymerization time. These solutions may lead to a more accurate control of the primer layer thickness, improving the final outcome. Furthermore, more complex 3D samples could be developed in order to test this coating onto different surface features, i.e. embosses or engraves, with a view to new design-driven applications.

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