Article

Characterization of Cold-Spray Coatings on Fiber-Reinforced Polymers through Nanoindentation Tests

Alessia Serena Perna ^{1,2,*} , Antonello Astarita ¹ , Pierpaolo Carlone ³ , Xavier Guthmann ⁴
and Antonio Viscusi ¹

¹ Department of Chemical, Materials and Production Engineering, University of Naples “Federico II”, P.le Tecchio 80, 80125 Naples, Italy; antonello.astarita@unina.it (A.A.); antonio.viscusi@unina.it (A.V.)

² Department of Management, Information and Production Engineering, University of Bergamo, via Pasubio 7b, 24044 Dalmine, Italy

³ Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, Italy; pcarlone@unisa.it

⁴ Anton Paar TriTec SA, Vernets 6, 2035 Corcelles, Switzerland; Xavier.guthmann@anton-paar.com

* Correspondence: alessia.perna@unibg.it

Abstract: Polymer matrix composites are finding never-ending widespread uses in the last decades; one recent tendency is to metallize their surface to further widen their field of application. Cold-spray deposition is one of the most promising techniques that can be adopted to this aim. Cold-spray deposition on polymers is in its early stage and more experimental work is required to fully understand the phenomena ruling the deposition. In this paper, the results of nanoindentation measurements on cold-spray coatings on various substrates will be presented and discussed. Polypropylene was used as matrix while carbon and glass fibers have been used as reinforcement, both steel and aluminum have been used as feedstock material for the cold-spray deposition. Nanoindentations tests have been then carried out on all the different samples; the influence of the fibers and of the powders sprayed on the behavior of the coatings is discussed in light of the experimental outcomes.

Keywords: cold spray; metallization; nanoindentations; coating; composites; powders

Citation: Perna, A.S.; Astarita, A.; Carlone, P.; Guthmann, X.; Viscusi, A. Characterization of Cold-Spray Coatings on Fiber-Reinforced Polymers through Nanoindentation Tests. *Metals* **2021**, *11*, 331. <https://doi.org/10.3390/met11020331>

Academic Editor: Marcello Cabibbo

Received: 23 December 2020

Accepted: 9 February 2021

Published: 14 February 2021

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1. Introduction

In recent years, fiber-reinforced polymers (FRPs) have been increasingly used to replace metals as structural materials in several sectors, such as automotive, aeronautics, and space [1,2]. However, if on the one hand, these materials offer advantages such as lightweight, high strength-to-weight ratio, and design flexibility; on the other hand, they exhibit poor electrical and thermal properties, reduced electromagnetic shielding capabilities, flame resistance, and erosion and radiation protection. Surface metallization is addressed as an effective technique to enhance the abovementioned properties and then widen their applications [3–5]. To date, a lot of adapted techniques have been developed for coating deposition and surface metallization, such as vapour-phase deposition, thermal-spray deposition, electrodeposition, electroforming and electroless plating. Unfortunately, the abovementioned technologies suffer from a series of disadvantages: long production cycle and high cost of the mould for electroforming, distortion of the substrate surface resulting from the molten particles, and high-temperature flames in thermal spraying (TS) [6–8]. Compared to these techniques, cold-spray (CS) deposition provides intriguing advantages when spraying metallic particles on polymeric or FRPs substrates [9]: the deposition is made possible only by a mechanical interlocking mechanism, and no chemical reactions are required [10]. Moreover, compared with thermal spray processes, a less heat input is required in cold spray, therefore, the heat effects such as surface distortion, oxides, void, phase transformation, and residual stresses are considerably reduced in the coatings [11–15].

On these premises, cold spray appears to be a suitable technique to process temperature-sensitive materials, such as polymers and polymer-based composites, without reaching the melting or degradation temperature of the substrate material [9,10,16,17]. Although the deposition on metallic substrates has been widely studied, the deposition on polymeric surfaces is a relatively new branch of cold spraying. Some papers have been published in the last years, but some questions are still open and a lot of further experimental work needs to be carried out. Among other issues, the bonding mechanism between metallic particles and polymeric substrate, that is the key factor in each deposition technique, is not yet clearly understood, and several theories have been proposed by different authors [18–20]. Adhesion is governed mainly by the properties of the polymer used as a matrix for the FRP substrate. In particular, thermoplastics are more suitable for the process due to their ductility, while thermosets are subject to breakages during particle impact due to their fragile nature [10]. Moreover, the coating build-up and the formation of a thicker coating were proven to be very hard to achieve. In fact, when spraying metallic particles on FRP, the first layer of particles is sprayed on a polymeric surface but further layers are deposited on the metallic surface lying on polymers; unfortunately, the adhesion of the particles on a different materials takes place at different particle impact velocities resulting in a difficult growth of the coating. Such occurrence has been highlighted by several papers [10,21,22].

For this reason, the gap of knowledge on the bonding mechanisms between the particles and the substrate and the interface characteristics of the coating-substrate system (that could promote or hinder further layers of deposition) has yet to be filled. A very promising test scarcely addressed in the literature on metallized composite materials through CS that can help to better understand the mechanisms ruling the particles adhesion and the coupled behavior of the substrate/coating system is the nanoindentation test.

Therefore, aiming to fill this lack of knowledge, the scope of this paper is to release the first results regarding nanoindentation tests performed on cold-spray metallic coatings on FRP laminates and to give some insights on the interpretation of these results. The laminates analyzed consist of a polypropylene matrix, chosen due to the best coating adhesion performances obtainable through cold-spray technology on thermoplastics, as verified in previous works [23,24], and a glass and carbon fibers reinforcement that guarantees high values of mechanical parameters. To take into account the particular characteristics of the specimens analyzed in this activity, different models have been applied in order to study the load-penetration depth curves, characterizing the coating, and establish which indentation model can better fit the case studied. The paper is divided into four sections: (i) in the first one the experimental procedures will be described, (ii) then the results will be given and (iii) discussed, (iv) finally, as usual, some conclusions and future outlook will be included in a conclusive paragraph.

2. Material and Methods

Polymer composite laminates were realized using two different reinforcement materials, namely bidirectional glass and carbon fabrics, both with an areal density equal to 160 g/m^2 . In both cases, the matrix is made of polypropylene (with a melting point of about 160°C at a pressure of 0.1 MPa). The laminates were manufactured through compression molding, overlapping layers of fabric, and polymeric films to obtain the desired thicknesses. A total of 15 layers (seven fiber fabric layers and eight polymeric film layers) was chosen in order to obtain a thick, rigid laminate. The lay-up sequence chosen is shown in Figure 1.

The temperature was set to 230°C , according to the melting temperature point of the polymer under the constant pressure of 1.1 MPa applied for 15 min. The mold was then cooled down in the air, while the pressure was kept constant.

Afterwards, the metallization of the composite substrates was performed through the cold-spray technique by spraying both micron-sized aluminum (AlSi10Mg) and steel (AISI316L) powders on the polymer-based surfaces, both obtained through gas-atomization technology, by LPW South Group. The particle mean size was $22 \mu\text{m}$ (Figure 2). A low-

pressure cold-spray facility (Dymet 423) was used for the coating deposition using dry air as carrier gas.

Figure 1. Exemplificative sketch of the laminates build-up sequence.

Figure 2. SEM micrographs and granulometry of the aluminum powders (left) and AISI316L powders (right).

A 40 mm × 40 mm square-shaped coating was developed on the surface of both the polymer-based substrates by spraying the metallic particles. For this purpose, each laminate was mounted on a platform while CS spray gun was positioned vertically above the substrate. The deposition process was automated by a pantograph which was numerically and remotely controlled. The cold-spray nozzle was attached to a robot (HIGH-Z S-400/T CNC-Technik) to allow for control and repeatability of the coating deposition. The nozzle moved at a set speed (equal to 5 mm/s) and a set standoff distance when spraying onto the substrate. The metallization strategy was defined taking into account literature prescriptions and preliminary experimental trials [23,25]. In fact, different coating tracks were preliminarily produced by varying the process parameters in a wide range (inlet gas temperature: 100–600 °C, inlet gas pressure: 0.4–0.8 MPa, standoff distance (SoD): 10–80 mm).

In more details, the inlet gas temperature was defined, taking into account that the temperature of the gas flow on the target surface should be below the melting point of the polymeric matrix. Another parameter considered for the temperature choice was the

glass-transition temperature of the polymeric substrate: in order to ensure the softening and thus the penetration of the particles into the substrate, the gas-flow temperature should be above this glass-transition temperature. Concerning the gas pressure, the most suitable value was set assuming that the higher the pressure, the higher the substrate erosion due to the strong shot-peening effect of the particles. As for the standoff distance (SoD), its value should be low enough to guarantee adhesion while avoiding degradation of the substrate. In fact, larger values of SoD lead to lower momentum of the impinging particles, resulting in particle rebounding, thus in a poor and thin coating. This result was corroborated by the available literature [23].

The first set of samples was produced by setting a single pass of the spray gun for the coating deposition. An example of the coated laminate is shown in Figure 3; in particular, the figure reports the carbon-fiber-reinforced polymer-substrate coated with a single pass aluminum coating.

Figure 3. Real picture of carbon-fiber-reinforced polymer-substrate coated with a single pass of aluminum particles.

The second set of specimens was produced with the same process parameters and deposition strategy and with a double pass of the spray gun for the coating grow-up. A second pass may increase the continuity and the thickness of the coating, however, the upcoming particles may lead to a detachment of the first layer of the coating as proved in literature [26,27]. The reason is that the anchorage energy between the first layer and the polymeric substrate is smaller than the energy required by the second layer to adhere on the first one. The result is that the upcoming particles possessing relatively high impact energy destroy the first layer making the coating grow-up impossible. In order to investigate the anchorage mechanisms of the particles with the polymeric substrates and understand if a further sprayed layer could enhance or reduce the properties of the coating, nanoindentation tests have been conducted in this activity.

The most suitable CS process parameters were found and reported in Table 1. A square of each substrate without metal deposition was also prepared and considered as control samples in order to compare hardness and elastic modulus of coated and uncoated samples. The deposition efficiency (DE) was evaluated after the deposition. For aluminum-coated samples, the DE mean values settle around 10% while for steel-coated samples, around 1%. Those values are in good agreement with literature findings [3,28].

Table 1. Suitable CS process parameters used in this experimentation.

CS Parameter	Used Value
Gun travel speed [mm/s]	5
Powder mass flow [rpm]	5
Inlet gas temperature [°C]	160
Inlet gas pressure [MPa]	0.5
SoD [mm]	25

Microscopical observations were carried out through Hitachi TM 3000 SEM microscopy to analyse the cross-section of the samples and examine the particles deposition. For this purpose, the samples were incorporated in a thermosetting resin by a cold mounting process and then polished and metallized.

The surface characteristics of the laminates were analyzed by means of confocal Leica DCM3D Scan in order to evaluate the coating height, analyze the distribution of the powders on the substrate, and measure the surface roughness of the coated and uncoated samples. The results have been exported to LeicaMap Software for the profile extraction and the measurement of the roughness, which was estimated according to ISO 4287 standard. As summarized in Table 2, 10 different samples were analysed in this experimental campaign.

Table 2. Laminate characteristics examined in this experimental campaign.

Laminate	Substrate Material	Coating Material	Single or Double Pass (Average Coating Height [μm])
CFPP	Carbon fabric+Polypropilene	–	–
CFPP-Al ₁	Carbon fabric+Polypropilene	AlSi10Mg	Single pass (35)
CFPP-Al ₂	Carbon fabric+Polypropilene	AlSi10Mg	Double pass (60)
CFPP-AISI ₁	Carbon fabric+Polypropilene	AISI316L	Single pass (50)
CFPP-AISI ₂	Carbon fabric+Polypropilene	AISI316L	Double pass (70)
GFPP	Glass fabric+Polypropilene	–	–
GFPP-Al ₁	Glass fabric+Polypropilene	AlSi10Mg	Single pass (35)
GFPP-Al ₂	Glass fabric+Polypropilene	AlSi10Mg	Double pass (60)
GFPP-AISI ₁	Glass fabric+Polypropilene	AISI316L	Single pass (50)
GFPP-AISI ₂	Glass fabric+Polypropilene	AISI316L	Double pass (70)

Indentation tests have been performed on the samples reported in Table 2 using the nanoindentation Tester NHT3. During the test, the indenter tip with a known geometry is driven into a specific site of the material to be tested, by applying an increasing normal load with a loading rate of 300 mN/min. When reaching a maximum value, set to 5 mN, after a 5 s pause, the normal load was reduced until partial or complete relaxation occurred with an unloading rate of 300 mN/min. A differential capacitive sensor was used to monitor the position of the indenter relative to the sample after each repetition of the test.

The test was performed in a controlled temperature room, at 23 °C with a humidity of 24%. The indenter was chosen, which was a Berkovich type with a diamond tip, according to literature studies on similar specimens [29–31]. For each loading/unloading cycle, the applied load value is plotted with respect to the corresponding position of the indenter. The resulting load/displacement curves provide data specific to the mechanical nature of the material under examination. Established models in literature [32] were used to calculate quantitative hardness and elastic modulus values for such data.

Elastic modulus (E_{IT}), shown in Equation (1), was calculated according to the power law method developed by Oliver and Pharr [32]:

$$E_{IT} = \frac{\sqrt{\pi}S}{2\beta\sqrt{A_p(h_c)}} \quad (1)$$

where

- h_c is the depth of the contact of the indenter with the test piece at the maximum load.
- $A_p(h_c)$ is the projected area of contact of the indenter at distance h_c from the tip. The function is determined by a calibration of the indenter tip.
- β is a geometric factor depending on the diamond shape (circular: $\beta = 1$, triangular: $\beta = 1.034$, square: $\beta = 1.012$).
- S is the contact stiffness.

Hardness values (H_{IT}) were calculated through Equation (2), where F_{max} is the maximum load measured.

$$H_{IT} = \frac{F_{max}}{A_p(h_c)} \quad (2)$$

It is worth noting that the hardness and elastic modulus results were obtained by imposing the Poisson ratio of the material equal to 0.33, as this value is the most common for metallic materials.

3. Results and Discussion

The results from the SEM microscope observations of the cross-sections of the coated laminates are shown in Figure 4a,b for the specimens CFPP-Al₁ and CFPP-AISI₁, respectively, aiming to point out the influence of the soft/hard powders on the bonding mechanisms occurring at the interface between the first layer and the polymer substrate.

Figure 4. SEM micrographs of cross-sections of the specimens CFPP-Al₁ and CFPP-AISI₁. (a) CFPP substrate with aluminium coating, (b) CFPP substrate with steel coating.

It can be seen from Figure 4a that the softer aluminum particles are quite deformed and flattened upon impact with the substrate. On the other hand, harder steel particles keep their original shape. For this reason, the height of the aluminum coatings is lower than the height of the steel coating. However, it is known from the literature that the particle deformation is a key factor for bonding to occur [33–35], meaning that it is very difficult for the upcoming aluminum particles to remove the first layer as it remains firmly anchored to the polymer surface. Hence, the main result obtained is that for CFPP-Al₁, the coating deposition seems to be better than the AISI-based coating, and the particles seem to be bonded with the substrate, thus promoting the coating formation and grow-up. This is further confirmed by the micrographs of the double pass coatings, portrayed in Figure 5.

Figure 5. SEM micrographs of cross-sections of the specimens CFPP-Al₂ and CFPP-AISI₂. (a) CFPP substrate with aluminium coating, (b) CFPP substrate with steel coating.

It can be seen from the figure that the deformed aluminum particles produce a thick, continuous coating, where few voids are detected. On the other hand, the steel coating appears discontinuous, and only a few particles overlap. It is worth noting that SEM micrographs of the cross-sections of the specimens GFPP-Al₁ and GFPP-AISI₁ were not reported here for the sake of brevity as they show the same results. The reason is that, under the cold-spray deposition conditions used in this activity (see Table 1 for more details), the particles impacting on the top surface of the substrate do not feel the presence of the reinforcement fabric within the laminate and the bonding mechanisms are mainly ruled by the properties of the polymeric matrix, which is the same for both the samples typology (PP).

Aiming to further investigate the bonding mechanisms involved and analyze more in-detail the characteristics of the coated laminates in terms of hardness and elastic properties, nanoindentation tests were carried out. However, it is known from the literature that the measurements from indentation tests are affected by the surface finishing of the examined samples [36,37]. In fact, the surface of the metallic samples is prepared in agreement with ASTM metallographic methods for indentations [38]. In this case, no metallographic preparation has been carried on in order to assess the influence of the surface characteristics of the deposited coating. Confocal microscope analyses were conducted to characterize the surface of both coated and uncoated samples and point out the influence of the surface roughness on nanoindentation measurements. An exemplificative result from the confocal microscopy with the gaussian filter applied is reported in Figure 6 for CFPP-Al₁ sample.

The representative roughness profile of the uncoated area is quite smooth and characterized by relatively low values of the roughness depending on the composite manufacturing method used. As for the coated area, it can be observed that the roughness profile seems to be rougher due to the non-homogeneous nature of the coating (see Figure 4 for details), which was proved also by the authors in literature [39,40]. On the basis of these results, it is evident that the outcomes from the nanoindentation tests on the coated samples are expected to be affected by the relatively high value of the surface roughness.

As for the nanoindentation test results relative to the mean values of the elastic modulus and hardness calculated through Equations (1) and (2), the comparative charts are reported in Figures 7 and 8, respectively.

Figure 6. Confocal microscope results showing exemplificative roughness profiles for both coated and uncoated area of CFPP-Al₁ sample.

Figure 7. Elastic modulus (E_{IT}) comparative chart.

Figure 8. Hardness (H_{IT}) comparative chart.

For both the carbon and glass fiber-based substrates, an increase of the mechanical properties of the coated laminates compared to the bare ones (labeled as CFPP and GFPP in the figures) is observed when the coating is made of aluminum particles; moreover, this increment tends to increase for the double-pass configurations due to the more prominent contribution provided by the thicker metallic layer. The beneficial effect of the metallic coating and the surface metallization process is evident on both the hardness and the elastic modulus of the laminates examined, with an enhancement of the mechanical properties of the polymers. This is also a result of the intimate bonding occurring between the substrate and the particles which remain firmly anchored with the polymeric surface.

A different behavior was evidenced for the samples coated with steel particles. In particular, the hardness and the elastic modulus of the samples seem to decrease if compared to those obtained from aluminum coated laminates. Moreover, this reduction seems to be more prominent for the double pass configurations (see the results of CFPP-AISI₂ and GFPP-AISI₂). The reason may be that the steel particles were not firmly anchored with the substrates as they were not deformed and flattened, as shown above in Figure 4b. The result is that the steel particles tend to slip on the polymer during the indenter penetration without providing a significant contribution to the mechanical properties of the polymer substrates. The reduction effect is more pronounced when a second layer of particles is cold sprayed on the coated surface. In fact, the shot-peening effects of the upcoming particles tended to destroy and remove the particles of the first layer exposing the polymer substrate to possible deteriorations.

By looking more in-detail at Figures 7 and 8, it can be observed that the elastic modulus and hardness values show a very high scatter factor. However, measurements performed on the bare substrates without metal deposition showed a reduced scatter and high repeatability. As expected from confocal microscope results, the reasons of such behavior for bare laminates are due to their relatively high surface finishing, as proved by the smoothness of the roughness profile characterizing these laminates (see Figure 6), thus resulting in relatively high repeatability of nanoindentation results. By contrast, the larger values of the scatter factor for the coated laminates are due to the relatively high values of the surface roughness of the coating, which is non-homogeneous and discontinuous, thus resulting in high standard deviation values of both the calculated elastic modulus and hardness.

To further investigate on the cold-spray coating behavior under nanoindentation tests for a more detailed analysis of the mechanisms governing the bonding between the metal powder and the polymer-based substrate, the load (F_n)-versus-penetration depth (Pd) curves from nanoindentations were studied. For the CFPP bare laminate, the F_n vs. Pd curves are reported in Figure 9; each curve is representative of each indentation measurement performed in different points of the specimen (16 indentation points). As evident, the shapes of the curves are similar and tend to overlap each other due to the high repeatability of the results (the same trend was observed for GFPP laminates, and it is not here reported for the sake of brevity). The area enclosed by the region ABCD is the indentation work W_I , namely the elastoplastic energy required to indent the specimen. The mean value of the indentation work for CFPP samples was calculated, and it is about $W_I = 2.4 \times 10^{-7} \text{ J}$.

A different behavior of the F_n vs. Pd curves was observed for the coated samples; in particular, depending on the point of the coated specimen where the indentation was carried out, the load-penetration depth curves show different shapes, especially for the loading part. This is due to the non-homogeneous and powder-based nature of the coating (see Figure 4), resulting in relatively high values of the surface roughness (see Figure 6), with the penetration depth values of the indenter that vary with the point on the substrate surface where the test was performed. Examples of F_n vs. Pd curves from nanoindentation tests for a coated sample are reported in Figure 10 (the curves of CFPP-Al₁ and CFPP-Al₂ samples only are reported for the sake of brevity) highlighting the variability of nanoindentation measurements.

Figure 9. F_n vs. P_d curves for a CFPP bare laminate; (a) loading part of the curve, (b) unloading part of the curve. The insert highlights the indentation work. Sixteen curves are reported for each indentation point.

Figure 10. F_n vs. P_d curves for a CFPP- Al_1 laminate (a) and CFPP- Al_2 laminate (b); Sixteen curves are reported for each indentation point on both samples, highlighting the variability of the results obtained.

A deep analysis of the load-penetration depth curves from the nanoindentation tests performed on all the examined coated samples pointed out that it is possible to identify four different loading shapes (as for the loading part of the curve), reported in Figure 11, which are representative of four different behaviors of the tested materials. In these cases, the indentation work ranges between $1.2 \times 10^{-7} \div 2.3 \times 10^{-7} \text{ J}$ for the loading shapes, which is lower than the energy required to indent the bare laminates, proving the beneficial effects of the coating.

Figure 11. Different shapes of the load-penetration depth curves observed indenting the coated specimens.

By looking at the trend of the loading behavior of the curve referred as Shape 1 in Figure 11, the standard form of the indentation curves appears [41,42], which is very similar to that found from indentation of the uncoated specimens (see Figure 9). That suggests that the sprayed particles constituting the coating are well anchored each other and with the polymeric surface so that the mechanical properties of the laminates can be increased. This behavior was found mainly for CFPP-Al₂ and GFPP-Al₂ samples characterized by a double and thicker layer of aluminum particles. As previously discussed, in this case, the aluminum particles are deformed and entangled by the polymeric surface, thus promoting the bonding and the coating grow-up [25,43]. Hence, the beneficial effects of the double layer of aluminum particles are clear from the Shape 1 loading curve, also proven by the relatively high E_{IT} and H_{IT} values (and reduced standard deviation values) shown in Figures 7 and 8, respectively.

Shape 2 in Figure 11 is characterized by a larger area underlying the loading curve compared to Shape 1, caused by the additional work needed to create the indentation. This loading shape was found to be characteristics of CFPP-Al₁ and GFPP-Al₁ samples, namely; the Shape 2 behaviour has been detected in several indentation points of the above-mentioned laminates. It can be seen that starting from a given penetration depth value, a decrease of the slope of the loading curve occurs (highlighted by the red dashed line in the figure) meaning that the indenter tends to penetrate more easily within the tested material. The reason is that the thin layer of particles constituting the samples is not capable to give an effective mechanical contribution at such a penetration value of the indenter with the influence of the softer polymer on the performance of the coating that becomes more prominent.

The loading shape evidenced in Figure 11 as Shape 3 was mainly found for CFPP-AISI₁ and GFPP-AISI₁ samples. By looking at the trend of the loading curve, it can be seen

that after an initial resistance provided by the coating to be indented, the material tends to be penetrated for a constant value of the load, followed by a subsequent increase of the slope of the curve reaching the maximum load value. It is evident that the steel particles, which are not deformed and entangled by the polymeric surface (as shown in Figure 4), tend to slip on the substrate under the action of the indenter penetrating easily within the material, thus suggesting the presence of the plateau. After that, the penetration of the indenter within the polymeric matrix produces an increase of the slope of the loading curve, as pointed out in the figure.

The loading behavior of the curve referred as Shape 4 in Figure 11 was mainly observed from the nanoindentation tests carried out on CFPP-AISI₂ and GFPP-AISI₂ samples, for which the lowest values of both E_{IT} and H_{IT} values were calculated. The trend of this curve suggests that the indenter penetrates the material without an important resistance provided by the last. In this case, the steel particles constituting the second layer of the coating, which seem to be not well bonded to each other and to the first layer as discussed above, tend to move and slip during the nanoindentation test without opposing any significative resistance. After that, the slope of the loading curve strongly increases due to the beneficial effects of the first layer of particles. It is worth noting that the deviation standard values of E_{IT} and H_{IT} , for these cases, are high and are caused by the non-homogeneous nature of the AISI-based coating.

This kind of analysis proved that there exists a correlation between the shape of the loading portion of the indentation curves and the relative E_{IT} and H_{IT} values calculated through Equations (1) and (2); in fact, the experimental results shown in Figure 11 and discussed above are well in agreement with the results previously presented (see data reported in Figures 7 and 8). Moreover, an advance of knowledge of the mechanisms ruling the bonding between the cold-spray particles and the polymeric substrates was also provided.

4. Conclusions

The aim of this work was to provide preliminary results on nanoindentation tests on cold-spray laminates, comparing different substrates and powders. In fact, the study of the load-versus-penetration depth curves proved to be a viable means to rapidly understand the bonding behavior of coated specimens.

Therefore, on the basis of the experimental results discussed in the previous sections, the following conclusions could be drawn:

- For both CFPP and GFPP substrates, better results were obtained when spraying ductile aluminum particles, whereas steel particles remained undeformed after the deposition, hindering the anchoring of the coating in the substrate.
- Confocal analyses showed that uncoated samples were characterized by lower values of roughness compared to coated samples, due to the non-homogeneous nature of the coating. The high roughness of coated specimens affected the nanoindentations results, which presented high scatter factors.
- It was possible to observe an increase in mechanical properties, in terms of hardness and elastic modulus, of the coated samples compared to the bare ones. This increment was more evident for the aluminum-double-pass-coated samples, due to the thicker metallic layer. As for the steel-coated laminates, an overall reduction of the properties was evidenced due to the worse anchoring of the particles on the substrate.
- Observing the force-versus-penetration depth curves, it could be noticed that for bare samples the obtained curves tended to overlap due to the high repeatability of the results. Conversely, coated specimens portrayed different shapes of the loading portion of the indentation curves depending on the sprayed material, number of passes, and the areas where the tests were performed.
- Four different shapes of the loading portions of the indentation curves have been identified, and a correlation between the loading curve morphology and the elastic modulus and hardness values have been found.

On the basis of these conclusions some guidelines for the future research can be released:

- A new mathematical model to describe and interpret the data should be proposed; it is evident that these samples (made of a PMC substrate and cold-spray coating) deserve an ad hoc mathematical approach;
- The results of the nanoindentations tests should be compared with the results of adhesion tests; this to further investigate the link between the nanoindentations curves and the phenomena ruling the adhesion;
- The nanoindentation procedure itself may be customized for these samples, and some variations may be suggested;
- Definitely much more experimental data must be produced to address all the above points.

Author Contributions: Nanoindentation analyses, X.G.; coating characterization, A.A.; composites production and characterization, P.C.; data analyses and paper writing A.V. and A.S.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Acknowledgments: The authors want to acknowledge the Italian Ministry for University and Research for funding the research activity through the research grant “COSMEC” (2017N4422T), within the PRIN 2017 framework. The authors want also to thank Sophia High Tech for supporting the experimental activities related to the cold-spray deposition process. Moreover, the authors want to acknowledge Andrea Barone for his guidance in preparing the composite laminates.

Conflicts of Interest: The authors declare no conflict of interest.

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