Manufacturing of hybrid thermoplastic-thermoset fiber reinforced composite and metallization by cold spray technique

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Abstract. Polymer and polymer matrix composites (PMCs) have found applications in aerospace sector. Thermosets (TS) possess higher corrosion resistance, shape retention and durability. Thermoplastics (TP) are easier for remolding in comparison to the former. Surface metallization is one of the recently applied trends for electrical and thermal properties improvement. In different metallization methods, primary restrain is the thermoset surface degradation, whereas thermoplastics have been found to be favorable for metallization. The presented article is part of continuous study aiming the cocuring of thermoset-thermoplastic resin with fibrous reinforcement. The composite manufacturing stage consisted of resin infusion (RI) process route for realizing the composite. Main objective of this stage was the through thickness and linear direction impregnation of thermoset to ensure the sound composite comprising contact between thermoplastic layer as well as fiber reinforcement. Fiber reinforcement combined with the resin infusion auxiliary materials were placed over the thermoplastic material prior to the vacuum bagging stage. Catalyzed thermoset resin impregnation in the vacuum bagged preform was conducted under the cocuring cycle. The composite panel was subsequently metallized via low-pressure cold spraying technique. The coating formation was analyzed with process parameters variation. Qualitatively, coating formation on such hybrid composite substrate was observed. However, the substrate manufacturing was found to have influence on the coating quality. Adhesion pull-off test displayed detachment zone directly in the coating substrate interphase. Presence of voids and less thermoset resin was noticed in the case of coating attempts varying process parameters such as traverse speed and standoff distance. Higher adhesion was noted with lowest selected 1 mm/s traverse speed and 10 mm standoff distance.

Introduction

Recent industrial sectors advances are aided by advanced materials and manufacturing technique development in order to ensure improved performance [1-7]. Specifically, in the aerospace sector, there has been an increase in the usage of polymer and PMCs to exploit the weight reduction as well as the high strength to weight ratio advantages. Reduced electrical and thermal conductivity are main limitations for the polymeric and PMC materials system, which have been addressed by using various techniques. Metallization is one amongst them, with primary focus on electroless plating, chemical vapor deposition (CVD), physical vapor deposition (PVD), which depicts their inherent process drawbacks [8]. Besides that, thermal spray processes suffers from substrate surface deterioration in high temperature conditions as well as high temperature induced flames [9]. On the other hand, since cold spray is the low processing temperature method, it is feasible to metallize polymer and PMCs [10,11]. Literature suggests adapting low pressure cold spraying

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(LPCS) process for metallizing thermoplastic polymer substrate [12-14]. Major investigations comprised of deposition attempts of Al [8], Ti [15], Sn [16], Cu [13] and also formation of interlayers [13]. The focus of the cold spray (CS) study was in determining processing parameters influence on coating performance for the substrate materials such polymers and glass fiber reinforced polymer (GFRP), carbon fiber reinforced polymer (CFRP), and carbon fiber-polyetheretherketone (CF-PEEK) reinforced PMCs [17,18]. Conversely for the thermoset based composites, easier metallization is not feasible owing to the challenges including erosion of brittle matrix, fiber breakage, and exposure of fibers [19]. Che et al. attempted Al high pressure cold spraying (HPCS) study for CFRP substrate yielding substrate removal and fiber breakage [20]. In case of Cu deposition on thermoset epoxy substrate, presence of erosion and reduction in deposition efficiency (DE) was observed [12]. Several diverse strategies have been applied for mitigating the issues arising in thermoset metallization.

The “co-curing” strategy was described in literature in which placement of thermoplastic coupling layer over the thermoset substrate are subjected to the cure together to manufacture a hybrid composite [21]. During co-curing, diffusion of thermoset precursors in the thermoplastic species is intended to provide a reaction induced phase separation and interphase. The resultant heterogeneous morphology can exhibit the TP and TS mechanical interlocking [22]. Some investigations applied this approach for welding the TP and TS surfaces. The employed welding processes ranged from resistance welding, induction welding to ultrasonic welding [21,23,24].

Under the resin infusion process, the presented work contains a co-curing concept for manufacturing of thermoset-thermoplastic composite and LPCS process for metallization. The investigation is concentrated on realizing the co-cured hybrid composite and studying the effect of the CS process parameters variation on the coating quality. For manufacturing purposes, resin infusion process has been employed. A microstructural analysis was followed by the CS campaign. Adhesion between the coating and the substrate being important criteria, was assessed by the adhesion peel-off test. The article includes findings of this campaign and discussion based on it.

Materials and Methods

The material selection for the presented work was conducted focusing on advanced aerospace applications point of view. A high Tg (217°C) temperature amorphous thermoplastic PEI (ULTEM 1000) film was used with the resin infusion stack to form TS-TP composite. The high-density aerospace application grade RTM6 epoxy resin was selected for realizing a thermoset resin infused composites.

Vacuum assisted resin infusion (VARI) from the out of autoclave (OoA) manufacturing route was employed for the composite manufacturing. The RTM6 epoxy resin flow in the reinforcement was induced under VARI action (Fig. 1 a). Progressing flow front towards the spiral outlet is visible in the image. Placement of PEI layer bellow CF reinforcing layers and auxiliary materials is followed by vacuum bagging operation of the preform maintaining the vacuum inside the vacuum bag cavity. Two stage curing cycle was opted for facilitating the co-curing of the TS-TP inside the CF reinforcement. The designated curing temperature 180°C was considered for the Epoxy resin curing stage (also evidenced in literature for PEI-Epoxy interphase generation). As a primary stage, resin and mould preheating and beginning of resin infusion was initiated at 90°C temperature. Total two hours of dwell time was dedicated at the 180°C curing temperature with the intermediate hold at 160°C temperature.

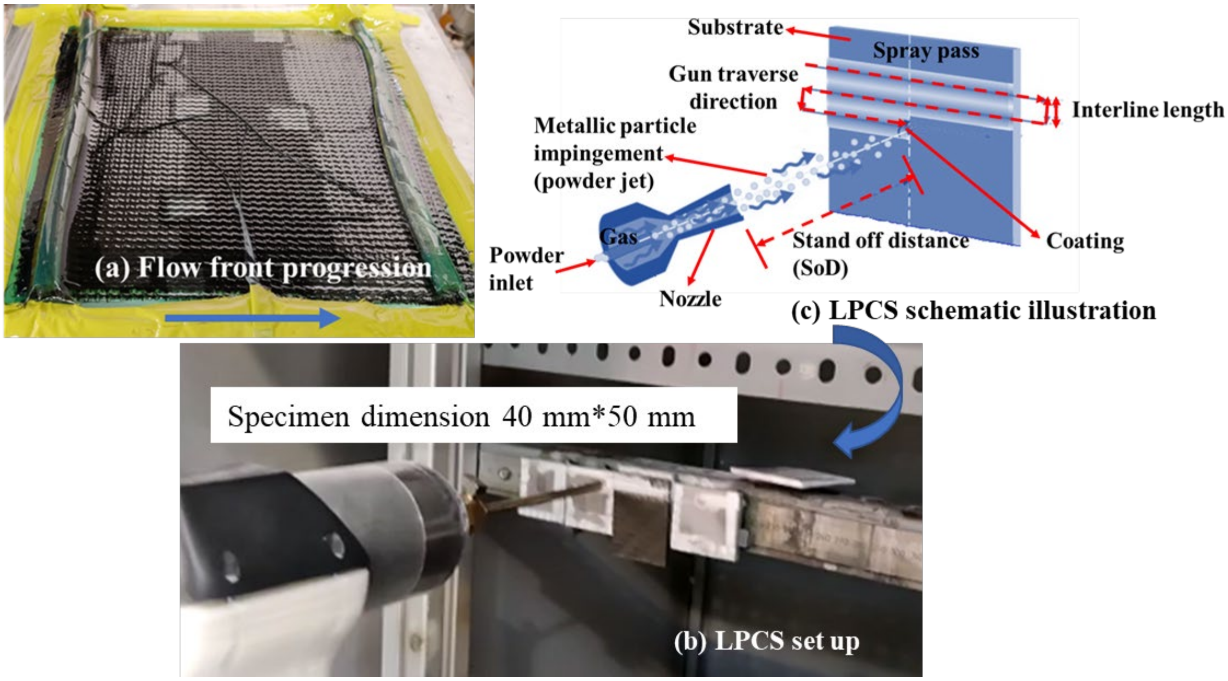


Fig. 1. (a) Resin infusion set-up for hybrid composite manufacturing consisting of 8 CF layers (b) LPCS metallization set-up (c) LPCS process schematic with general process parameters illustration.

The experimental scheme of process parameters for the LPCS of the manufactured composite panels is indicated in the Table 1. Fig. 1 (c) depicts illustrative view on the cold spraying process and highlights the relative process parameters while the actual set-up is included in Fig. 1(b). Processing parameters namely, traverse speed and stand-off distance (SoD) were varied while keeping constant interline length 3 mm and air flow 383 L/m. Al plus Al_2O_3 (min 1%) powder was utilized for the composite surface metallization. The cold spray gas temperature and chamber pressure were maintained constant at 360°C and 6 bar for each variation respectively. The total approximate spray duration to coat the composite sample (40*50*3) was 106 s. The manufactured reference case and metallized composite panels were subjected to the microstructural analysis by the optical microscopy (OM). Prior to the OM observation, the samples were subjected to the metallographic specimen preparation according to the standard prescribed procedure. The samples were cut by the abrasive disc cutter and polished with the abrasive rough paper grades and fine polished subsequently.

Table 1. Cold spraying processing parameters conditions.

Sample identification code	Gun Traverse Speed (mm/s)	SoD (mm)	Interline length (mm)
CS05	1	10	3
CS06	2	10	
CS07	1	30	
CS08	2	30	
CS12	2	20	

Adhesion peel-off test was conducted for determining the adhesion strength of the coated composite specimens. During the peel-off test, the Araldite (industrial grade) adhesive was applied over the sample surface and the test stub (dolly) with 10 mm diameter. Required force for the complete debonding of the specimen and the stub was recorded for each combination. The failure surface observation of coated and uncoated surfaces was undertaken to understand the mode of failure and adhesion behavior of the coating-composite.

Results and Discussions

Analysis of manufactured hybrid composites.

In the primary stage of manufacturing a direct resin infusion step is conducted as opposed to the hybrid interlayer method [25] where hot pressing action is necessary. The presence of distribution media aided in the uniform distribution of the epoxy resin through the fiber bundles. The uniform pressure distribution due to the vacuum bagging operation resulted in the close contact between three interacting constituents beyond the preheating temperature of 90°C. The resin viscosity was decreased upon the preheating operation prior to the RI step. This step facilities reduction in the voids as well as smooth flow of the RTM6 through the spiral inlet and beginning with the linear flow front movement plus the transversal flow of the rein through reinforcing stack. A close contact between the PEI thermoplastic layer and the reinforcement stack being infused with the thermoset resin is established under vacuum. The flow front movement in all associated trials were found to be linear. The visual inspection of coated hybrid composite panel in the cross-sectional view indicated close contact of coating with the substrate. Fig. 2 (a) presents the coated hybrid panel which is further elaborated in Fig. 2 (b) and (c). The in-plane and through thickness percolation of the RTM6 Epoxy resin through the fiber tows during the RI process is highlighted in the Fig. 2 (b). A clear distinguishing presence of both the PEI and RTM6 resin was detected in the OM images acquired after the etching operation. In the micrograph Fig. 2, light-orange areas are highlighted as the PEI film and dark-orange areas corresponded to the RTM6 infused in the reinforcing fiber tows. Light areas are fibers and metallic particles. The empty spaces between the fiber tows, the inter-tow regions are filled with majorly RTM6 in the remaining substrate.

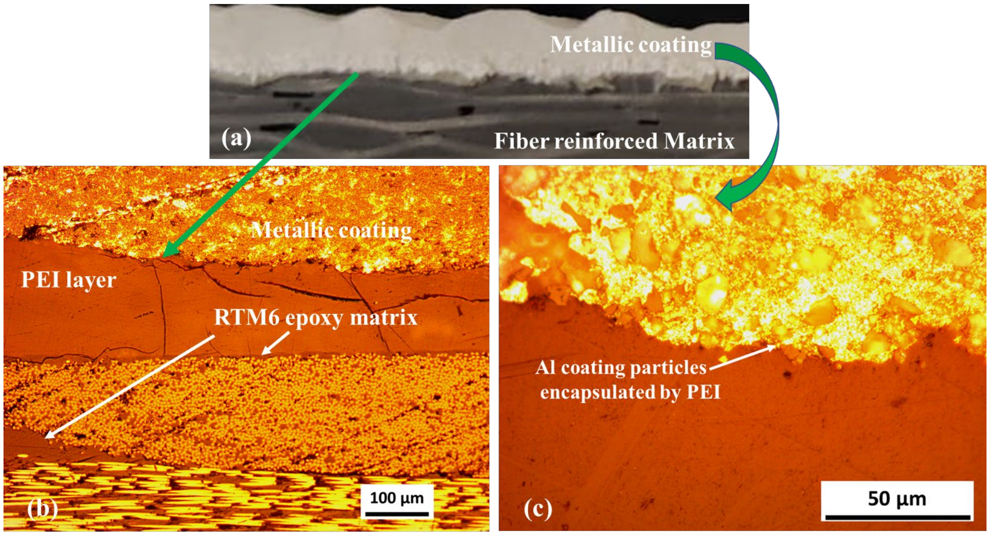
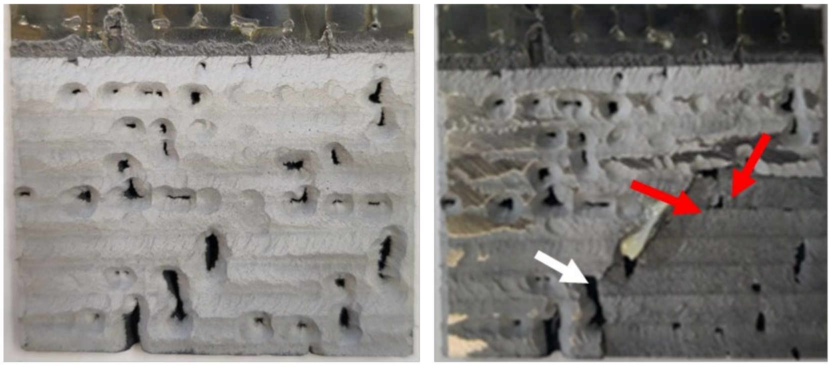


Fig. 2. The cross-sectional optical micrograph after the resin infusion depicting (a) hybrid composite panel cross sectional view (b) Presence of Epoxy resin in the inter-tow region and PEI-RTM6 close contact, magnification 10x. (c) PEI-coating region, magnification 50x.

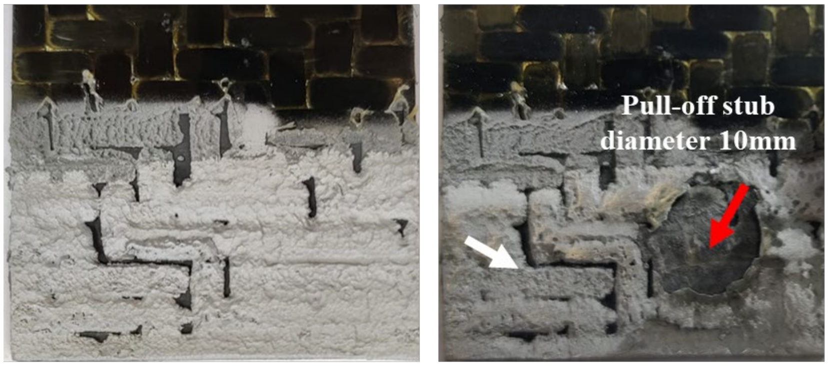
The main area of interest is the interphase created at the top surface where PEI and Epoxy are said to have been experienced inter-diffusion in the curing stage. The dwell time of the 2 h was sufficient for cocuring of PEI-RTM6 constituents upon inter-diffusion.

Analysis of metallized hybrid composites.

The cold spray process parameters variation and its influence on the hybrid composite coating was assessed. The experiments were conducted at constant N_2 gas temperature and chamber pressure. The interline length after a preliminary campaign was determined to be 3 mm for each trial for covering the entire available surface area. The spray gun was facing the substrate side with PEI layer adhered to the composite substrate. Al (plus Al_2O_3) Coating was formed in each process parameters variation indicating the suitability of the gas temperature of 360°C for the PEI polymer softening. As indicated in Fig.2 (c), the softened PEI formed a close contact with imparting Al particles, also some amount of particle-particle bonding can be expected. The high velocity impact (also including the variation in the traverse speed and SoD) resulted in the adherent coating as confirmed in the visible inspection. The Fig. 3 left side images are representative sample top coating surface.



1 mm/s, 10 mm SoD, before adhesion test **1 mm/s, 10 mm SoD, after adhesion test**



2 mm/s, 20 mm SoD, before adhesion test **2 mm/s, 20 mm SoD, after adhesion test**

Fig. 3. LPCS panels with processing parameters variation and subsequent adhesion pull-off test coupons. The images contain top surface view to highlight the coating pattern and positioning of defects.

Visible voids extending from the coating through the TP layer and eventual up to the fiber reinforcing material was created in process of cold spraying. The formed coating top surface carried the impression of the fiber tows intertwined in the substrate reinforcing layers, where the voids appeared only in the inter-tow cites. Such occurrences are highlighted by means of the white arrows. The primary reason can be the substrate condition, which is favorable for the substrate excessive softening and cracking in the substrate while the particle impact impinges the coating particles into the substrate surface. Such abrupt occurrences are noted between the consecutive passes and is the combined result of the manufacturing and coating processes. Overall, the coating thickness in the range of 0.3 mm to 1.5 mm was achieved. In comparison, lower traverse speed 1 mm/s in combination with SoD 10 and 30 mm achieved improvement in the coating thickness as compared to the cases with faster traverse speed of 2 mm/s. The possible reason for such attribute can be the greater exposure of the spray gun over the allocated surface locations of the substrate. Also, another process parameter SoD plays important role, where the intermediate 20 mm value with the higher traverse speed yielded thinner and less adherent coating on the substrate surface. Increase in the SoD generally promotes scattering of the impinging coating particles in the spray path and loss of coating material or loose bonding. Similarly, a faster nozzle speed can be insufficient for the bonding of the metallic particles with the available softened TP surface. Thirdly, as previously mentioned, the effect of the overall substrate manufacturing condition i.e., voids in the panel, voids between the TP layer and the fiber reinforcement, non-uniform contact between the TP and TS constituents, can affect the coating quality. In the opportune condition of optimum balance between the manufacturing and spraying condition, uniform and more adherent coating can be realized.

Adhesion test.

The adhesion pull-off tests were undertaken for the coated samples with different coating conditions. Referring to the Fig. 3 top left side image, the topography of the coating top surface was not flat. The pull off test necessitates a stronger attachment between the flat coating surface and the pull off stub (dolly) prior to the test. The coated samples were hence roughly grinded on the 320-mesh abrasive paper and were subjected to the application of the adhesive on the dolly and substrate surface. The circular impression of the stub was remained on the coated substrate post failure (highlighted with red arrows in Fig. 3). A complete detachment of the stub from the glued substrate surface and presence of any mode of failure i.e., adhesive or mixed mode was considered as the success of the test.

The obtained adhesion strength values for each condition of processing parameters are reported in the Fig. 4. Fracture surface observation (Fig. 3) indicated the presence of adhesive mode of failure, where certain portion of coating was detached from the substrate. Some loosely bonded Al particles are visible around this impression.

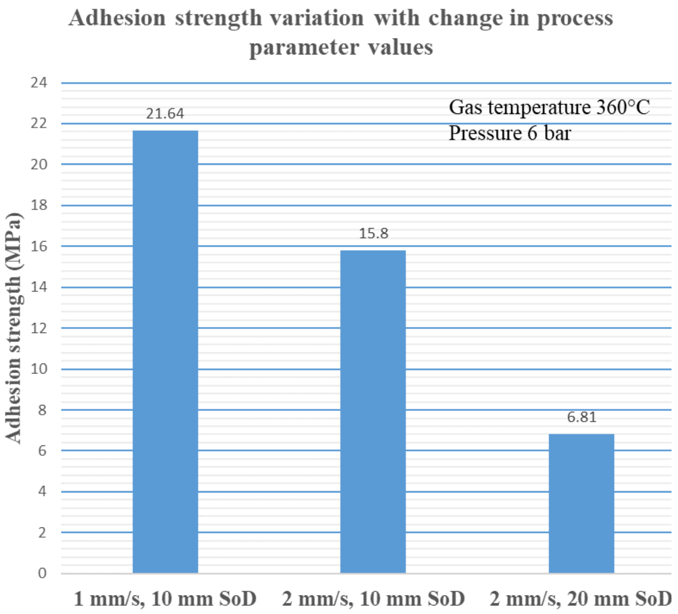


Fig. 4. obtained adhesion strength trend corresponding to the various cold spray conditions.

The inferior coating condition of 2 mm/s, 20 mm SoD also yielded a void and crack passing through the substrate in the circular impression. This again can be linked to the combination of manufacturing condition and spraying parameters influence. There is also a trend of reduction in adhesion strength with faster traverse speed, which in combination with SoD changes derives loosely bonded coatings with the substrate. The case of lowest SoD on the other hand provides a direct exposure of coating particle stream avoiding the particle scattering and less availability of the contact area surface in each time interval. These worked as the favorable working conditions for the interlocking of the impinging metallic particle in the softened PEI matrix. The designated

Tg for PEI is 220°C, and the provided gas temperature of 360°C can also in a way induce the substrate heating. This could be the primary condition for each of these coatings to be formed on the RI manufactured composite panels. The reinforcing fiber and encompassing RTM6 resin was well adhered to the PEI top layer, since the failure images show few cases of the substrate damage and fiber pluck out. Further research on the remaining CS condition is underway for determining the adhesion behavior of the coatings.

Summary

Hybrid thermoset-thermoplastic composite manufacturing was feasible by implementing resin infusion route. The manufacturing condition affected the coating deposition. In the cold spraying of PEI-CF- RTM6 epoxy composites, a clear influence of processing parameters traverser speed and SoD was found. Highest adhesion strength was obtained with lower values of traverse speed and SoD. Increase in SoD resulted in weaker bonding. Microstructural observations exhibited particle -particle bonding and coating particle encapsulation by means of PEI softened matrix during CS.

References

[1] P. Boisse, R. Akkerman, P. Carlone, L. Kärger, S. V. Lomov, J.A. Sherwood, Advances in composite forming through 25 years of ESAFORM, Int. J. Mater. Form. 15 (2022) 39. https://doi.org/10.1007/s12289-022-01682-8

[2] R.M.F. Paulo, F. Rubino, R.A.F. Valente, F. Teixeira-Dias, P. Carlone, Modelling of friction stir welding and its influence on the structural behaviour of aluminium stiffened panels, Thin-Walled Struct. 157 (2020) 107128. https://doi.org/10.1016/j.tws.2020.107128

[3] F. Rubino, M. Pisaturo, A. Senatore, P. Carlone, T.S. Sudarshan, Tribological Characterization of SiC and B4C Manufactured by Plasma Pressure Compaction, J. Mater. Eng. Perform. 26 (2017) 5648-5659. https://doi.org/10.1007/s11665-017-3016-9

[4] F. Rubino, P. Poza, G. Pasquino, P. Carlone, Thermal spray processes in concentrating solar power technology, Metals 11 (2021) 1-30. https://doi.org/10.3390/met11091377

[5] H. Parmar, T. Khan, F. Tucci, R. Umer, P. Carlone, Advanced robotics and additive manufacturing of composites: towards a new era in Industry 4.0, Mater. Manuf. Process. 37 (2021) 483-517. https://doi.org/10.1080/10426914.2020.1866195

[6] F. Tucci, P. Carlone, A.T. Silvestri, H. Parmar, A. Astarita, Dissimilar friction stir lap welding of AA2198-AA6082: Process analysis and joint characterization, CIRP J. Manuf. Sci. Technol. 35 (2021) 753-764. https://doi.org/10.1016/j.cirpj.2021.09.007

[7] F. Tucci, R. Bezerra, F. Rubino, P. Carlone, Multiphase flow simulation in injection pultrusion with variable properties, Mater. Manuf. Process. 35 (2020) 152-162. https://doi.org/10.1080/10426914.2020.1711928

[8] M.R. Rokni, P. Feng, C.A. Widener, S.R. Nutt, Depositing Al-Based Metallic Coatings onto Polymer Substrates by Cold Spray, J. Therm. Spray Technol. 28 (2019) 1699-1708. https://doi.org/10.1007/s11666-019-00911-y

[9] X.L. Zhou, A.F. Chen, J.C. Liu, X.K. Wu, J.S. Zhang, Preparation of metallic coatings on polymer matrix composites by cold spray, Surf. Coatings Technol. 206 (2011) 132-136. https://doi.org/10.1016/j.surfcoat.2011.07.005

[10] M. Grujicic, C.L. Zhao, W.S. DeRosset, D. Helfritch, Adiabatic shear instability based mechanism for particles/substrate bonding in the cold-gas dynamic-spray process, Mater. Des. 25 (2004) 681-688. https://doi.org/10.1016/j.matdes.2004.03.008

[11] H. Parmar, F. Tucci, P. Carlone, T.S. Sudarshan, Metallisation of polymers and polymer matrix composites by cold spray: state of the art and research perspectives, Int. Mater. Rev. 67 (2021) 1-25. https://doi.org/10.1080/09506608.2021.1954805

[12] A. Ganesan, M. Yamada, M. Fukumoto, Cold spray coating deposition mechanism on the thermoplastic and thermosetting polymer substrates, J. Therm. Spray Technol. 22 (2013) 1275-1282. https://doi.org/10.1007/s11666-013-9984-x
[13] A. Ganesan, J. Affi, M. Yamada, M. Fukumoto, Bonding behavior studies of cold sprayed copper coating on the PVC polymer substrate, Surf. Coatings Technol. 207 (2012) 262-269. https://doi.org/10.1016/j.surfcoat.2012.06.086
[14] A. Małachowska, M. Winnicki, M. Stachowicz, M. Korzeniowski, Metallisation of polycarbonates using a low pressure cold spray method, Surf. Eng. 34 (2018) 251-258. https://doi.org/10.1080/02670844.2016.1277843
[15] M. Gardon, A. Latorre, M. Torrell, S. Dosta, J. Fernández, J.M. Guilemany, Cold gas spray titanium coatings onto a biocompatible polymer, Mater. Lett. 106 (2013) 97-99. https://doi.org/10.1016/j.matlet.2013.04.115
[16] H. Che, X. Chu, P. Vo, S. Yue, Metallization of Various Polymers by Cold Spray, J. Therm. Spray Technol. 27 (2018) 169-178. https://doi.org/10.1007/s11666-017-0663-1
[17] V. Gillet, E. Aubignat, S. Costil, B. Courant, C. Langlade, P. Casari, W. Knapp, M.P. Planche, Development of low pressure cold sprayed copper coatings on carbon fiber reinforced polymer (CFRP), Surf. Coatings Technol. 364 (2019) 306-316. https://doi.org/10.1016/j.surfcoat.2019.01.011
[18] F. Rubino, F. Tucci, V. Esperto, A.S. Perna, A. Astarita, P. Carlone, A. Squillace, Metallization of Fiber Reinforced Composite by Surface Functionalization and Cold Spray Deposition, Procedia Manuf. 47 (2020) 1084-1088. https://doi.org/10.1016/j.promfg.2020.04.353
[19] J. Affi, H. Okazaki, M. Yamada, M. Fukumoto, Fabrication of aluminum coating onto CFRP substrate by cold spray, Mater. Trans. 52 (2011) 1759-1763. https://doi.org/10.2320/matertrans.T-M2011807
[20] H. Che, P. Vo, S. Yue, Metallization of carbon fibre reinforced polymers by cold spray, Surf. Coatings Technol. 313 (2017) 236-247. https://doi.org/10.1016/j.surfcoat.2017.01.083
[21] E. Tsiangou, S. Teixeira de Freitas, I. Fernandez Villegas, R. Benedictus, Investigation on energy director-less ultrasonic welding of polyetherimide (PEI)- to epoxy-based composites, Compos. Part B Eng. 173 (2019) 107014. https://doi.org/10.1016/j.compositesb.2019.107014
[22] B. Lestriez, J.P. Chapel, J.F. Gérard, Gradient interphase between reactive epoxy and glassy thermoplastic from dissolution process, reaction kinetics, and phase separation thermodynamics, Macromolecules 34 (2001) 1204-1213. https://doi.org/10.1021/ma0012189
[23] C. Brauner, S. Nakouzi, L. Zweifel, J. Tresch, co-curing behaviour of thermoset composites with a thermoplastic boundary layer for welding purposes, Adv. Comp. Lett. (2020). https://doi.org/10.1177/2633366X20902777
[24] F. Lionetto, M.N. Morillas, S. Pappadà, G. Buccoliero, I. Fernandez Villegas, A. Maffezzoli, Hybrid welding of carbon-fiber reinforced epoxy based composites, Compos. Part A Appl. Sci. Manuf. 104 (2018) 32-40. https://doi.org/10.1016/j.compositesa.2017.10.021
[25] H. Parmar, A. Gambardella, A.S. Perna, A. Viscusi, R. Della Gatta, F. Tucci, A. Astarita, P. Carlone, Manufacturing and metallization of hybrid thermoplastic-thermoset matrix composites, ESAFORM 2021. (2021). https://doi.org/10.25518/esaform21.2727