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Experimental Evaluation of Metallic Coating on Polymer by Cold Spray

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Abstract

Cold spray (CS) is an emerging coating technology that makes use of a converging/diverging nozzle, a high pressure and a heated gas source to create a high-velocity gas flow. Coating deposition occurs at relatively low temperatures compared to other spray technologies, therefore the sprayed particles remaining in the solid-state. The process can produce dense coatings when the process parameters are optimized. Despite the incredible advantages of CS and the established knowledge of CS considering metal substrates, some questions like the bonding mechanism and the adhesion/cohesion strength of the coating with polymeric substrates remain an open research topic. In this paper, a metal coating (AlSi10Mg) was deposited on a plate in polypropylene by cold spray in order to increase the properties of the surface. Metallic particles, in the range of 20-40 µm, were injected into gas flow and propelled to supersonic velocities. Polymers require a deposition technique in which the substrate remains at relatively low temperatures during the whole process in order to avoid plastic deformation or degradation. Determination of the mechanical properties of thin films on substrates by indentation has always been difficult because of the influence of the substrate on the measured properties. In order to evaluate the local properties of the deposited coating, microindentation tests and DMA were carried out. In particular hardness values by microindentation tests and values of elastic modulus by DMA were calculated.

Keywords: Cold spray; Aluminum coating; Polymer substrate; Microindentation; DMA.

1. Introduction

The Cold Gas Dynamic Spray, or generally referred as cold spray (CS), is a relatively new additive coating technique developed a few decades ago by the Russian professor Papyrin [1]; the coating is made by exposing a metallic or non-metallic substrate to bombardment of fine particles (typically in the range 1-50 µm) [2], which are dragged and accelerated by a compressed gas stream (air, argon, nitrogen) to velocities on the order of 300 to about 1200 m/s [3]. The propellant gas (also called carrier gas) at high pressure and temperature conditions is accelerated to supersonic velocities through a converging-diverging de Laval nozzle [4]. When the particles exit the nozzle and impinge on the target surface, they undergo significant plastic deformations resulting from collisions and bonds to the substrate [5].

In contrast to the traditional thermal spray technologies (HVOF, wire flame, plasma), in CS processes the particles are heated in the gas stream only to a fraction of their melting temperature, remaining entirely in a solid-state prior to impacting the substrate [6]. The main result is that CS can minimize effects of oxidation, melting, evaporation and other common problems suffered in thermal spraying [7]; moreover, the critical thermal deterioration phenomena as well as the structural variations of the substrates taking place in thermal spray processes, can be strongly reduced by CS [8]. Therefore, as a low-temperature based technique, the cold spray candidates as a potential method to develop metal coatings on sensitive-temperature materials such as composites or plastics [9].

The surface metallization of polymeric substrates, with or without the fibre reinforcement, is growing of interest in the last years because of the need to enhance their surface properties; in

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fact, the polymer-based materials are increasingly using in several sectors of engineering such as automotive, aerospace and construction replacing metals for different applications [10]. However, if on one hand, these materials offer advantages such as lightness, high strength to weight ratio and flexibility in designing shapes and forms, on the other hand, it could be useful to improve some of their properties such as the electrical ones, electromagnetic shielding capabilities, thermal conductivity, flame resistance, and erosion and radiation protection, in order to further widen the fields of application of these materials. In this regard, the surface metallization is considered to be an effective technique to enhance the above-mentioned surface properties and then expand their engineering application fields [11].

To date, several research papers were carried out on CS process for metal/metal depositions [12–16], several theories were proposed in the literature explaining the intriguing bonding mechanisms taking place between the particle and the substrate [17,18]. Low attention was devoted to CS deposition of metal particles on polymer-based substrates and a lot of experimental tests will have to be done, as it remains still an open research topic [19,20]. For instance, Ganesan et al. [21] studied the influence of the substrate polymer's typology on the bonding mechanisms finding that the particles can adhere on the thermoplastic surface thanks to ductile behaviour of the polymer; on the contrary, the particles merely attach on fragile thermosets resins that are subject to breakages during impact. Further, the coating build-up was proved to be very difficult on polymers due to the shot peening effect of the upcoming particles that can destroy the first layer, if it is not firmly anchored to the substrate [22]. It is clear that some questions like the bonding mechanism and the adhesion/cohesion strength of the coating with polymeric substrates need to be better analysed. Few papers were found in the literature on this topic [23,24].

Interesting results on the mechanical properties of coating structures can be found thorough indentation tests. In fact, microindentation hardness experiments are widely used to measure the plastic flow resistance of materials in small volumes, such as thin films. It has been shown repeatedly that the microindentation hardness of crystalline materials displays a strong size effect with spherical, conical or pyramidal indenters.

In order to evaluate local mechanical properties of thin film, polymer blends, composites and other, micro and nano indentations have been developed and employed [25,26].

Nanoindentation tests are affected by many problems due to zero point determination, instrument frame compliance, effective indentation area; furthermore, compared to hardness, it is very difficult to evaluate the mechanical properties of a thin film on a substrate by indentation response because of the influence of the substrate on the properties [27]. This is because the elastic field under the indenter is not confined to the film itself; rather it is a long-range field that extends into the substrate, especially when the film thickness is small.

The properties measured by indentation are a complex function of the elastic and plastic properties of both film and substrate.

The principal characteristics in microindentation tests are the hardness H, contact stiffness S (dF/dh) at the beginning of unloading and elastic modulus E, determined from a load-unload cycle by Oliver and Pharr [28]. Hardness is defined as the mean contact pressure (P_m) under the loaded indenter (Eq. 1).

$$H=P_m=F/A \tag{1}$$

Where F is the load and A is the projected contact area, determined from the contact depth h_c for a spherical indenter of tip radius R and small depth of penetration (Eq. 2).

$$A=2\pi Rh_c \tag{2}$$

In Eq. (2) h_c is calculated from the total penetration h, indenter load and contact stiffness S (dF/dh) at the beginning of the unloading cycle.

In some researches, nanoindentation tests with dynamic mechanical analysis (DMA) were carried out [29,30], in particular, the possibility to merge DMA and microindentation was studied in [31] investigating four types of polymer, including polypropylene (PP).

Therefore, aiming to better investigate the adhesion mechanisms between the sprayed powders and the polymer-based substrates, micron-sized aluminium particles (AlSi10Mg) were cold sprayed on a thermoplastic plate in polypropylene; both microindentation and DMA tests were performed on the manufactured coated samples for hardness and elastic modulus calculations, respectively.

The outcomes provided interesting results on the adhesion mechanisms and the surface characteristics of the metal-coated polymeric surface.

2. Materials and methods

The polymeric substrates were manufactured through the compression moulding technique, by overlapping PP film layers. PP thermoplastic polymer was chosen, taking into account the best coating adhesion performances obtainable, as proved in literature [32,33]. The curing temperature was set to 210° C in accordance with the melting temperature of the polymer by imposing a pressure of 1.1 MPa for 15 minutes. The mould was then cooled down in the air, while the pressure was kept constant.

Dymet 423 equipment was used for surface metallization. It is a low-pressure cold spray facility with a spray gun, two powder feeders and a control unit. Control unit includes fluid pressure and fluid temperature control and powder feeders switch with powder feed rate regulators (Fig. 1).

In this research activity, the deposition process was automated by means of a pantograph which is numerically controlled remotely; in fact, 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.

Compressed air was used as carrier gas as a consequence of the low velocities required when spraying on polymeric substrates.

Micron sized powders of aluminium alloy AlSi10Mg (particle mean size of 40 μm) were used for the spraying process. The SEM image of powders is shown in Fig. 2.

Fig. 1. Dymet 423 low-pressure cold spray facility.

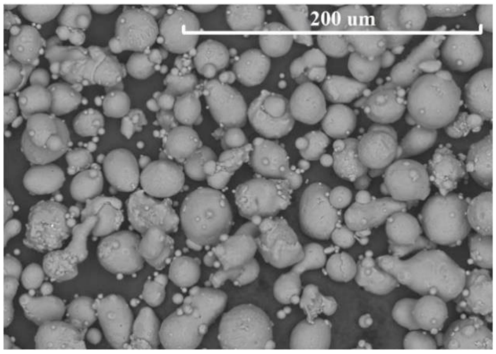


Fig. 2. SEM image of AlSi10Mg powders used in this experimentation.

A preliminary experimental campaign, which is not here reported for the sake of brevity, was carried out in order to determine the range of the optimal process parameters to be adopted for the next experimentation step, namely for the coating deposition on PP polymers. Different coating tracks, 40 mm long and 5 mm width, with a travel speed of the spraying gun of 500 mm/min were produced by varying the process parameters in a wide range (inlet gas temperature: 150-600 °C, inlet gas pressure: 0.4-0.8 MPa, stand-off distance (SoD): 10-80 mm), in agreement with the literature data [9]. This was done to select the best process parameters to be used for the next experimental step.

As for the inlet gas temperature, its value was chosen by taking into account that the temperature of the gas flow on the target surface was below the melting point of the polymeric material and, at the same time, greater than the glass-transition one; this was done in order to avoid the deterioration phenomena of the substrate and ensure the softening so that the metallic particles can penetrate the polymeric surface [22,24]. Concerning the gas pressure, the correct value was set taking into account that the higher the pressure, the higher the substrate erosion due to the strong shot peening effect of the particles [24]. Finally, as for the stand-off distance, the larger values of SoD, the lower the momentum of the particles upon impact with the substrate, resulting in particles rebounding, thus in a poor and thin coating [33].

After a first visual inspection, the coated samples were observed through SEM microscopy (Hitachi3000) for the cross-section analyses in order to highlight the morphology of the coating, thus to set the best CS process parameters. For this purpose, specimens were cut, mounted and prepared according to the international ASTM standards for the metallographic observations.

On the base of these premises, the optimal CS process parameters were found and reported in Table 1.

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

CS parameter	Used value
Inlet gas temperature [°C]	150
Inlet gas pressure [MPa]	0.6
SoD [mm]	25
Travel speed gun [mm/min]	500

Quasi-static and dynamic microindentations were performed in a standard compression mode by TDMA (RSA III TA). Spherical indenter in HSS with a diameter of 2 mm was employed in quasi-static microindentation, while a flat cylindrical punch in tungsten carbide with a diameter of 0.8 mm was used in dynamic tests.

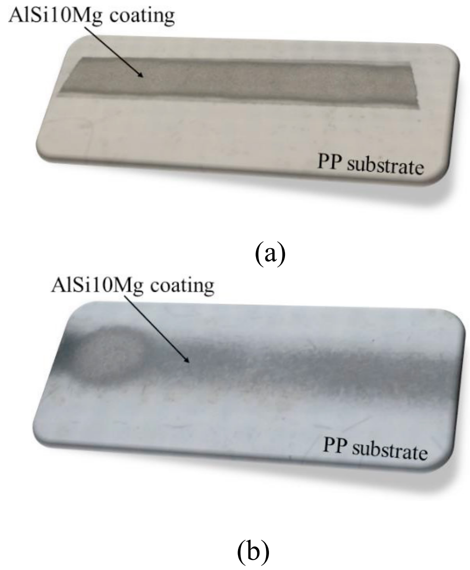
Dynamic tests were performed in a standard compression mode at environmental temperature applying a preload of 2 N and a deformation amplitude varying from 0.03% to 0.4% with a frequency of 1 Hz at room temperature. Three specimens were tested for each kind of sample to verify the repeatability of the results obtained. In order to verify the current value of the modulus of the polymer, DMA test using three-point flexural bending mode was carried out.

3. Results and discussion

The macrograph of the top view of the coated sample obtained by using the selected CS protocol is reported in Fig. 3(a). By visual inspection, it can be seen that the coating seems to be almost continuous with an effective deposition of the particles. On the contrary, when the process parameters are not properly set, the metallic coating appears discontinuous and poor of particles, as shown by the exemplificative picture in Fig. 3(b). These results are in agreement with the available literature [33], for which a lower momentum of the particles leads to the formation of a poor coating.

More in details, the SEM images of the cross-sections of the coated samples for both the CS conditions are reported in Figs. 4(a) and (b).

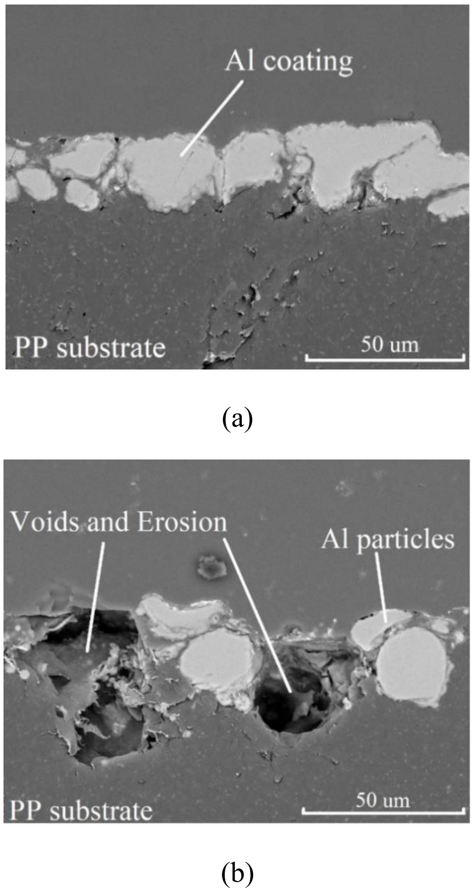
By looking at Fig. 4(a), it is noticeable that the coating is thicker, more compact, denser and more homogeneous than the coating shown in Fig. 4(b), which was obtained by using the following CS parameters: gas pressure=0.4 MPa, gas temperature=150° C and SoD=70 mm.



(a)

(b)

Fig. 3. Metallised PP substrate: (a) by using the optimal CS parameters and (b) when the process parameters are not properly set (gas pressure=0.4 MPa, gas temperature=150° C and SoD=70 mm).



(a)

(b)

Fig. 4. SEM image of the cross-section of coated sample: by using the optimal CS parameters and (b) when the process parameters are not properly set (gas pressure=0.4 MPa, gas temperature=150° C and SoD=70 mm).

Before of quasi-static and dynamic microindentation tests, a conventional DMA test was carried out adopting the three-point flexural bending mode in order to evaluate the bulk modulus (later referred as E' in the text) of the PP used in the experimental campaign; from this test, a value of 1.21 GPa was measured.

In Fig. 5, the comparison between the curve obtained by microindentation tests on the surface of neat PP and the coated substrate (PP_Al) is shown. In the right side of the same figure, the insert shows a magnification of a part of both the curves in order to point out the different behavior of the investigated polymers.

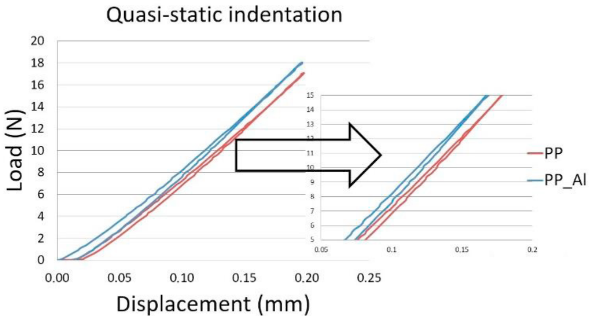


Fig. 5 Quasi-static microindentation of investigated polymers.

In Fig. 6, the curves of storage modulus as a function of the deformation are reported.

Take note that an exemplificative curve was used for this purpose due to the good repeatability of the experimental results.

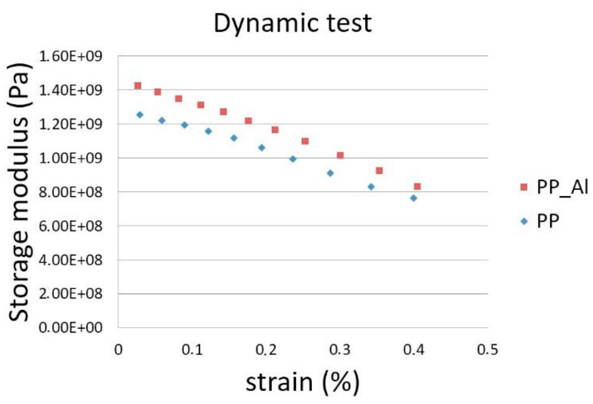


Fig. 6 Variation of storage moduli in dynamic microindentation tests

In Table 2, the values of stiffness obtained from quasi-static tests and storage modulus measured by dynamic tests along with the dispersion of data are reported.

It is possible to note an increase of mechanical properties for the coated PP, this increase is less than 10% for the stiffness while it is about 15% in the case of dynamic tests. Probably on the stiffness, some effects due to the different types of deformation could influence the measure, such as both the preload applied and the test frequency.

Table 2. Values of stiffness and moduli for the investigated specimens.

	dF/dh	E'[GPa]
PP	111 (3.36)	1.21 (0.020)
Al_coated_PP	118 (3.53)	1.42 (0.030)

The difference in modulus for the PP and coated PP decreases as the strain increases, tending to assume the same values for high values of strain. In fact, in order to increase the strain, the amplitude of the oscillation increases and the tip penetrate into the material making the influence of surface properties negligible.

4. Conclusions

The aim of this work was to investigate more in details the local properties of the coating/substrate system made by cold spraying aluminium particles on polymer-based substrates (PP) through microindentation and dynamic mechanical analysis tests. Therefore, on the basis of the experimental results discussed in the previous sections, the following conclusions can be drawn:

- The cold spray process was proved to be an effective technique to develop an aluminium coating on PP thermoplastic substrate if the process parameters are properly set;
- The outcomes from microindentation and DMA tests proved that the metal coating enhanced the mechanical behaviour of PP substrate, in terms of stiffness and elastic modulus.

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