International Journal of Manufacturing Economics and Management
ISSN 2784-1278 ISSN-L 2784-1278, Vol. II, No. 1 / 2022
https://doi.org/10.54684/ijmem.2022.2.1.35

SURFACE CHARACTERIZATION OF ARBOBLEND V2 NATURE COATED WITH CERAMIC MICRO PARTICLES

Alina Marguță[1], Simona-Nicoleta Mazurchevici[1], Ramona Iuliana Popa[1], Marcelin Benchea[2]

[1]"Gheorghe Asachi" Technical University of Iasi, Faculty of Machine Manufacturing and Industrial Management, Department of Industrial Engineering, Blvd. Mangeron No. 59A, 700050, Iasi, Romania
[2]"Gheorghe Asachi" Technical University of Iasi, Faculty of Mechanical Engineering, Department of Mechanical Engineering, Mechatronics and Robotics, Str. Prof. Dr. Doc. Dimitrie Mangeron, No. 43, Iasi, 700050, Iasi, Romania

Corresponding author: Simona-Nicoleta Mazurchevici, simona0nikoleta@yahoo.com

Abstract: The paper aims to investigate the behavior of Arboblend V2 Nature biopolymer samples covered with three ceramic powders, Amdry 6420 (Cr_2O_3), Metco 143 (ZrO_2 18TiO_2 10Y_2O_3) and Metco 136F (Cr_2O3-xSiO_2-yTiO_2). The coated samples were obtained by injection molding, and the micropowder deposition was achieved by using the Atmospheric Plasma Spray (APS) method, with varied thickness layers. The present study will describe the results for nine, seven and five-layer deposition. It was observed that with the increase of the number of deposited layers the surface quality and mechanical/thermal characteristics such as wear and hardness are also increased. The followed determinations were conducted: the adhesion strength and hardness on a microscopic scale by micro-indentation. The samples' crystalline structure as well as the presence of the Cr_2O_3 compound significantly influenced the micro-indentation and scratch analysis responses. The novelty of this study is given by itself the coating of the Arboblend V2 Nature biopolymer (as base material), with ceramic microparticles as the micropowder coating material. Following the under-taken study, the increase in the mechanica and tribological characteristics of the samples recommend all three coated biopolymer samples as suitable for operating in harsh conditions, such as the automotive industry, in order to replace plastic materials.
Key words: biodegradable thermoplastic, coating, Amdry 6420, Metco 143, Metco 136F, hardness, adhesion.

1. INTRODUCTION

In the last three decades, plastic materials have become increasingly popular in lightweight components due to strengths like machinability, simple formation, low density, weldability and so on, [1]. However, all these advantages come at package with a great disadvantage, that of world health, whether it is living or environmental beings. The engineering industrie, aerospace, aviation and automotive, due to the increasing demands and technological advancement currently needs weight reduction, superior corrosion resistance and structural flexibility, [2]. In this sense, the composite material industry has greatly developed. But even so, it is quite difficult to reach the functional performance of metal materials because polymers have weak electrical conductivity, low thermal resistance, low modulus and strength, low corosion resistance and high sensitivity to ultraviolet damage, [3]. A technique called Atmospheric Plasma Spray (APS), in which a ceramic layer is formed on the surface of polymeric parts, diminishes these deficiencies and extends the applicability of polymers. The ceramic layers based on zirconium and chromium chemical elements are widely spread materials in engineering applications. Like any other coating technology, it has some weaknesses as isolation inhomogeneity, residual stresses, micro-cracks, [4]. Other polymer surfaces coating methods, among which we can list: physical vapor deposition (PVD), thermal spray (TS), chemical vapour deposition (CVD), [5].
It is well known that the addition of ceramic particles on polymers substate provides a combination of properties of these types of materials: biopolymer matrices and ceramic reinforcement components. This may result in the improvement of the physical and mechanical properties of the resulted composite material, [6]. Deposition of coatings on polymer-based substrates by using the thermal spraying process is a challenging task due to the thermal sensitivity of polymer materials and the high temperatures involved in the spraying processes. Thus, selection of the process parameters (spraying distance, spraying temperature, speed, pressure) is a key factor in obtaining good coating, meaning surface quality - uniformity of the deposited layer, minimum defects, [7].
In the present manuscript, the authors have analysed three types of APS coatings (ceramic micropowders). The coatings were made on a biodegradable thermoplastic - Arboblend V2 Nature as substrate materials with the

purpose of increase the material surface characteristics in order to replace the conventional plastic materials from applications that involve harsh operating condition.

2. MATERIALS AND METHODS

The polymer selected as substrate for coating with ceramic microparticles was Arboblend V2 Nature. This thermoplastic according to the scientific literature, [8 - 11] have as base matrix the lignin compound, but also it can contain polylactic acid, cellulose, bio-polyamides, natural additive added in order to ease the processability, [12, 13].
The coated samples (70 x 50 x 10) mm^3), were obtained by injection moulding, on SZ-600H equipment, the tehnological parameters being as fallow: melting temperature of material — 165°C, injection speed—80m/min, injection pressure — 100MPa and cooling time—30s.
The coating of the injected samples was performed using Atmospheric Plasma Spray (APS) technology, SPRAYWIZARD-9MCE equipment. The tehnologica plarameters used during the coating process: spraying distance – 145mm; gun type – 9MB; gases – N_2 and H_2; electric DC – 400A/70-80V, carrier gas flow 5.1NLPM. The microparticles deposition rate of was constant. Thickness of the deposited ceramic layers was of the micrometers order.
Three ceramic micro-powders were used from Oerlikon Metco manufacturer: Metco 143 (Cr_2O_3-$xSiO_2$-$yTiO_2$), Amdry 6420 (Cr_2O_3) and Metco 136F (ZrO_2 $18TiO_2$ $10Y_2O_3$). In order to observe how the number of layers and implicitly thickness influence the sample surface characteristics, the following passing numbers were made: 5, 7 and 9 passes for each powder.
For the scratch and microindentation tests a CETR UMT-2 microtribometer was used. The main testing conditions for scratch analysis were as follows: blade tip - 0.4 mm; vertical force – 10 N NVIDIA blade, testing distance - 10 mm, testing timp - 60 s, test speed - 0.167 mm/s. In Case of microintentation test the following parameters can be specified: indenter - Rockwell type; vertical force - 10 N; loading time — 30 s; holding time — 15 s; unloading time — 30 s; sensor of (0.2–20) N. Microindentation tests involved testing three samples for each type of ceramic powder in order to confirm experimental repeatability. The average values were obtained by calculating the arithmetic average, and the standard deviation highlights the variation in a set of numbers compared to the calculated average value.
In order to facilitate the pursuit of the manuscript, was realized a table, Table 1, which summarizes each type of sample analyzed, depending on the powder type (chemical elements, commercial name) and the pass number made on each surface.

Table 1. Analised coated samples - abbreviations

Commercial name	Chemical composition	Number of passes	Abbreviation in manuscript
Metco 143	ZrO_2 $18TiO_2$ $10Y_2O_3$	5	S1
		7	S2
		9	S3
Amdry 6420	Cr_2O_3	5	S4
		7	S5
		9	S6
Metco 136F	Cr_2O_3-$xSiO_2$-$yTiO_2$	5	S7
		7	S8
		9	S9

3. RESULTS AND DISCUSSION

3.1 Scratch Analysis

To observe the adhesion of the ceramic layers on the Arboblend V2 Nature biopolymer substrate, a scratch analysis was performed on all nine samples, three for each microceramic powder type. The obtained data are highlighted in Table 2 and refers at apparent friction coefficient (A-COF) – average and maximum value, moment of maximum A-COF.
In what concern the A-COF the sample coated with chromium(III) oxide (S4, S4, S5) recorded the highest value of 0.34±0.16 for the sample with 5 passes, 0.34±0.16 – sample with 7 passes, and 0.56±0.42 – sample with 9 passes. So, the A-COF for this type of material is increasing with the number of passes. For samples, S4 and S6 are registered two moments of maximum A-COF one at the beginning of the test and one when the test is stopped. The reason why the first value is taking place is related to the deposition granulation, which, according

to the literature, [10], it has larger dimensions (9–30 µm) than the other two types of powders. Also, it is possible that the tip of the cutting tool has hung a micro-particle of the deposited powder with a large granulation. The second moment of maximum apparent coefficient is normal, was normal, as we expect, as in the case of the other samples, with the number of layers increase the accession of the coated layer to become even better.

Table 2. Values of apparent coefficient recorded by samples coated with ceramic layers

Sample	*A-COF Medium*	*A-COF Maximum*	*Time of maximum A-COF [s]*
S1	0.33±0.18	0.88	60
S2	0.30±0.06	0.41	51
S3	0.29±0.16	0.53	50
S4	0.34±0.16	0.55/0.76	11/60
S5	0.28±0.12	0.67	60
S6	0.56±0.42	1.62/1.37	3.0/60
S7	0.35±0.10	0.6	60
S8	0.21±0.09	0.49	60
S9	0.18±0.08	0.37	60

Analysing the Figure 1, it is observed that one sample, number 6, reflect a better adhesion between the deposited fine layers and the substrate due to the Cr_2O_3 powder presence.

The medium value A-COF registered for the samples coated with Metco 136F (S7, S8, and S9) are very close to that of the substrate (injected sample from Arboblend V2 Nature) which has a 0.16 value for rotational determinations and 0.13 for oscillation method, [14]. The quite low values highlight the fact that the adhesion of the ceramic layer is low. Another aspect to note is that with the increase in the number of layers, the apparent friction coefficient decreases, which denotes again the poor adhesion of the Cr_2O_3-xSiO_2-yTiO_2 powder on the polymer substrate.

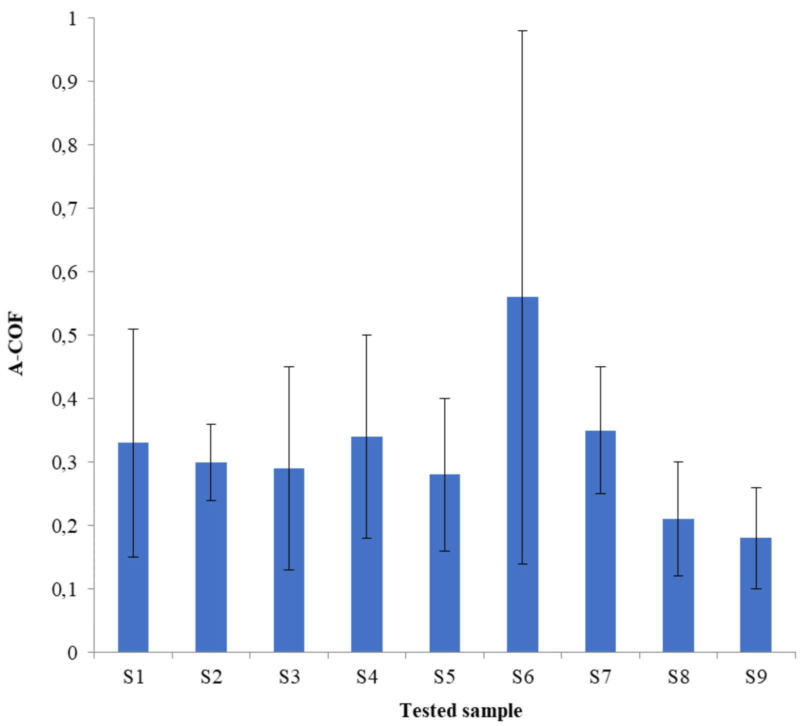

Fig. 1. The apparent friction coefficient of the screech analysed samples

In case of ZrO_2 18TiO_2 10Y_2O_3 coating (S1, S2 and S3) both A-COF values and their standard deviations reflect a uniform adhesion of the ceramic layer, so, a uniform deposition of the layer, also confirmed by the SEM (Scanning Electron Microscopy) analysis of these samples, [10]. The good results were certainly influenced by the chemical composition of the micropowder, which favored the good adhesion to the polymer substrate but also by the particles size (1 - 27 µm.) much smaller and unvariated as shape (spherical form), [10], than in the case of the other to micropouder who did not meet these features.

3.2 Microindentation Test

For the micro indentation tests, three samples for each type of ceramic powder were tested, with the objective of finding the hardness of the created surfaces by depositing ceramic microparticles and observing the experimental stability. These two aspects are visible in Table 3 which summarizes the mechanical analysis results at the micro-level. Through the used analysis software, UMT Test Viewer, 2.16 version, it was possible to determine both the microhardness values and Young's modulus. These values are presented in Table 3. The lowest dispersion of the results was obtained in the case of ZrO_2 $18TiO_2$ $10Y_2O_3$ coating, most likely due to the fact that the deposited ceramic layer was uniform. In addition, the other tested samples did not present large differences.

Table 3. Results obtained by micro indenting the samples coated with ceramic micro powders

Sample	Test	Max load (N)	Max Depth (µm)	Young's modulus (GPa)	Micro Hardness (GPa)
	1	8.98	73.18	1.75	0.11
S1	2	9.03	62.5	2.05	0.14
	3	8.99	59.96	2.24	0.14
Average		*8.99±0.03*	*65.21±7.02*	*2.02±0.25*	*0.13±0.02*
	1	8.95	66.35	2.53	0.12
S2	2	8.99	61.45	4.22	0.12
	3	8.95	60.00	3.06	0.13
Average		*8.96±0.03*	*62.60±3.33*	*3.277±0.86*	*0.12±0.01*
	1	8.99	73.55	1.51	0.11
S3	2	8.97	72.78	1.56	0.11
	3	8.98	73.02	1.48	0.11
Average		*8.98±0.01*	*73.12±0.40*	*1.52±0.04*	*0.11±0*
	1	8.98	70.43	1.543	0.12
S4	2	8.99	58.14	1.94	0.16
	3	8.98	63.8	1.85	0.14
Average		*8.98±0.00*	*64.14±6.15*	*1.77±0.21*	*0.14±0.02*
	1	8.96	54.74	3.18	0.15
S5	2	8.98	58.70	3.13	0.14
	3	8.95	57.79	2.98	0.14
Average		*8.96±0.01*	*57.08±2.07*	*3.09±0.10*	*0.14±0.01*
	1	8.99	66.64	1.75	0.13
S6	2	8.98	71.70	1.83	0.11
	3	8.98	71.02	1.99	0.11
Average		*8.98±0.01*	*69.79±2.75*	*1.86±0.13*	*0.12±0.01*
	1	8.98	68.19	1.84	0.12
S7	2	8.99	65.09	2.05	0.13
	3	8.99	60.06	2.31	0.14
Average		*8.99±0.01*	*64.45±4.10*	*2.06±0.23*	*0.133±0.01*
	1	8.96	53.45	2.88	0.16
S8	2	8.97	54.07	2.78	0.16
	3	8.92	55.73	2.78	0.15
Average		*8.95±0.02*	*54.42±1.18*	*2.81±0.06*	*0.16±0.00*
	1	8.99	53.77	3.04	0.16
S9	2	8.99	53.08	2.80	0.17
	3	8.97	50.42	3.05	0.17
Average		*8.98±0.01*	*52.42±1.77*	*2.96±0.14*	*0.17±0.01*

Taking into account both the above table data and the graphical representation of the obtained microdurities, Figure 2, it can be stated that the samples coated with Cr_2O_3-xSiO_2-yTiO_2 powder show the highest hardness values, despite the fact that the deposition it wasn't very uniform and the adhesion as could be observed suffered. For instance, S9, the sample with the highest hardness value, 0.17 ± 0.01 GPa, recorded as expected the lowest value of maximum indentation depth, 52.42 ± 1.77 µm.
Comparing the obtained results with those of the Arboblend V2 Nature polymer, an improvement of the hardness is observed by deposition of ceramic layers, since the average value of its hardness is 0.12 GPa, [15].

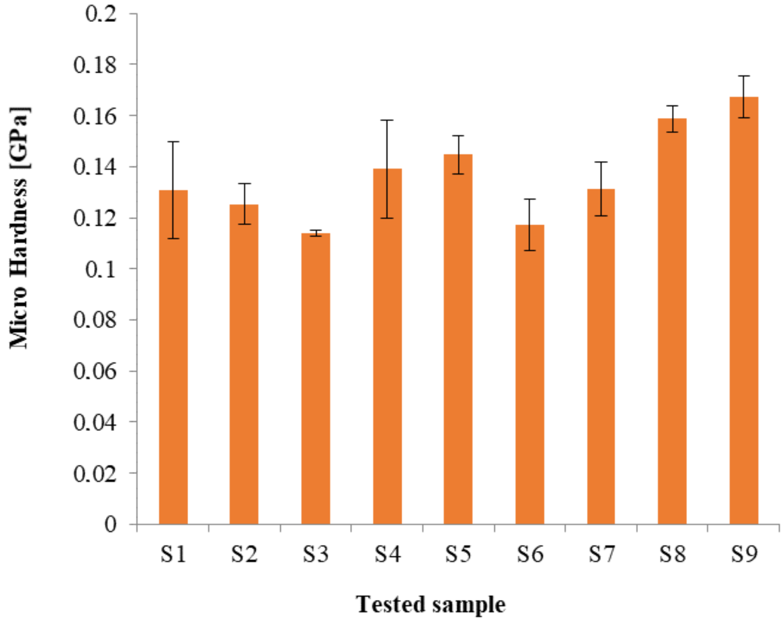

Fig. 2. Micro hardness of the tested samples

The behaviour of the tested samples from maximum penetration depth poin of view captured in Figure 3. The samples that allowed the deepest penetration of the indentor were those coated with Metco 143 - ZrO_2 18TiO_2 10Y_2O_3, due to the thin deposited layer. It is also observed that with the increase in the number of layers, the deposited layer resist to pressing force, allowing allowing less and less penetration of the indenter, the case of samples: S1 - S2, S4 - S5 and S7 - S8 - S9. Deviations from this rule can be attributed to non-uniformity of the analyzed areas.

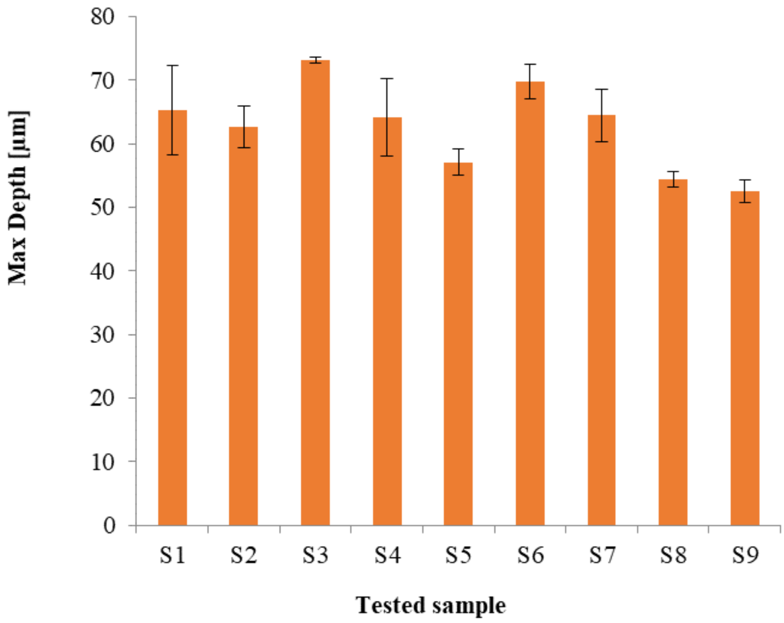

Fig. 3. Maximum depth of the tested samples

4. CONCLUSIONS

The obtained coated samples highlighted surface characteristics (micro hardness, scratch resistance thru A-COF) superior to the uncoated polymeric material, Arboblend V2 Nature. The coating of the sample with ceramic microlayers led to the following results:

- Compared to the zirconium-based ceramic coating (Metco 143), the chromium oxide coatings have a higher hardness (Amdry 6420, Metco 136F), which can be justified through the thin deposited layer which is based on small ceramic microparticles.
- In what concern the scratch analise, according to the obtained results the adhesion of the ceramic layers on the substrate surface it was mostly pretty good, presenting strong chemical bonds at the interface between the deposited layers polymer.

In conclusion, the purpose of the manuscript has been achieved, the characteristics of the base material were increased and can face the challenges of industrial applications, coping with and even being able to substitute conventional materials such as fossil-based polymers, wood, and metals.

5. REFERENCES

1. Hsissou, R., Seghiri, R., Benzekri, Z., Hilali, M., Rafik, M., Elharfi, A., (2021). *Polymer composite materials: a comprehensive review*, Compos. Struct. **262**, 113640, https://doi.org/10.1016/j.compstruct.2021.113640.
2. Senthilkumar, K., Karthikeyan, S., Ismail, S.O., (2019). *An overview of burst, buckling, durability and corrosion analysis of lightweight FRP composite pipes and their applicability*, Compos. Struct. **230**, 111419, https://doi.org/10.1016/j.compstruct.2019.111419.
3. Brinson, H.F., Brinson, L.C., (2008). *Polymerization and classification*, Polymer Engineering Science and Viscoelasticity, Springer, Boston, MA, pp. 99–157, https://doi.org/10.1007/978-0-387-73861-1_.
4. Melentiev, R., Yu, N., Lubineau, G., (2021). *Polymer metallization via cold spray additive manufacturing: A review of process control, coating qualities, and prospective applications*, Additive Manufacturing **48**, 102459, https://doi.org/10.1016/j.addma.2021.102459.
5. Gariboldi, E., Rovatti, L., Lecis, N., Mondora, L., Mondora, G.A., (2016). *Tribological and mechanical behaviour of Cr3C2–NiCr thermally sprayed coatings after prolonged aging*, Surf. Coat. Technol., **305**, 83–92.
6. Rajkovic, A., Uyttendaele, M., Deley, W., Van Soom, A., Rijsselaere, T., Debevere, J., (2006). *Dynamics of boar semen motility inhibition as a semi-quantitative measurement of Bacillus cereus emetic toxin (Cereulide)*, J. Microbiol. Methods, **65**, 525–534.
7. Ashrafizadeh, H., Mertiny, P., McDonald, A., (2014). Determination of temperature distribution within polyurethane substrates during deposition of flame-sprayed aluminum–12silicon coatings using Green's function modeling and experiments, Surface & Coatings Technology **259**(2014) 625–636.
8. Nedelcu, D., Marguta, A., Mazurchevici, S., Munteanu, C., Istrate, B., (2019). *Micro-structural and morphological analyses of coated 'liquid wood' samples by ceramic particles*. Mater. Res. Express, **6**, 085326.
9. TECNARO–The Biopolymer Company. Available from: https://www.tecnaro.de/en/, Accessed: 10/05/2022.
10. Mazurchevici, S.-N., Marguta, A., Istrate, B., Benchea, M., Boca, M., Nedelcu, D., (2021). *Improvements of Arboblend V2 Nature Characteristics through Depositing Thin Ceramic Layers*, Polymers, **13**, 3765, https://doi.org/10.3390/polym13213765.
11. Mazurchevici, S.-N., Mazurchevici, A.-D.; Nedelcu D., (2020). *Dynamical mechanical and thermal analyses of biodegradable raw materials for additive manufacturing*, Materials, **13**, 1819.
12. Broitman, E., Nedelcu, D., Mazurchevici, S., Glenat, H., Grillo, S., (2019). *Tribological and nanomechanical behavior of liquid wood*, J. Tribol., **141**, 022001.
13. Nedelcu, D., Santo, L., Santo, A.G., Plavanescu Mazurchevici, S., (2015). *Mechanical behaviour evaluation of arboform material samples by bending deflection test*, Mater. Plast., **52**, 423–426.
14. Nedelcu, D., Comaneci, R., (2014). *Microstructure, mechanical properties and technology of samples obtained by injection from arboblend*, Indian J. Eng. Mater. Sci., **21**, 272–276.
15. Nedelcu, D., Ciofu, C., Lohan, N. M., (2013). *Microindentation and differential scanning calorimetry of ''liquid wood''*, Composites: Part B, **55**, 11–15, https://doi.org/10.1016/j.compositesb.2013.05.024.

Received: March 05, 2022 / Accepted: June 15, 2022 / Paper available online: June 20, 2022 © International Journal of Manufacturing Economics and Management