Biodegradable polymer properties through ceramic coatings

Alina Marguta [1], Simona-Nicoleta Mazurchevici[1] [0000-0002-6452-7413], Constantin Carausu[1] [0000-0002-4501-7370] and Dumitru Nedelcu [1,2*] [0000-0002-6023-5544]

[1] "Gheorghe Asachi" Technical University of Iasi, Department of Machine Manufacturing Technology, Blvd. Mangeron, No. 59A, 700050, Iasi, Romania
[2] Academy of Romanian Scientists, Str. Ilfov, Nr. 3, Sector 5, Bucharest, Romania
*dnedelcu@tuiasi.ro

Abstract. Coating of bio-based polymers with ceramic layer has attracted interest recently, the research topic raising difficulties regarding the technology of obtaining layers that involve very high working temperatures. The study aims to analyses the mechanical, tribological and structural characteristics of the Arboblend V2 Nature biodegradable polymer after the deposition of ceramic microlayers. The micro powders used were Amdry 6420 (Cr_2O_3), Metco 143 (ZrO_2 $18TiO_2$ $10Y_2O_3$) and Metco 136F (Cr_2O_3-xSiO_2-yTiO_2). The coated samples were obtained by injection molding and the deposition was achieved by using Atmospheric Plasma Spray (APS) method. The results of the related analyses showed that, in general, the deposits of ceramic micro particles increased the material surface characteristics (hardness, scratch resistance, apparent friction coefficient), due to the uniformity of the ceramic coating on the polymeric substrate. Based on these, it was possible to recommend the use of coated bio-based polymer - Arboblend V2 Nature in harsh operating conditions, such as the automotive industry.

Keywords: lignin-based polymer, coating, micro powders, wear, adhesion.

1 Introduction

The world market of plastic materials, at the beginning of 2020, registered 650 billion dollars and it is estimated that it will grow by 5% in the next five years [1]. In the last two decades, plastic has penetrated all fields of activity due to its special qualities compared to conventional materials (as metal and wood), low mass, low density, machinability, weldability, corrosion resistance, and so on [2]. However, due to the need of continuous improvements, the automotive, aviation and aerospace industries are constantly interested in reducing the weight of components [3].

The thermal coating process of polymer materials finds its applicability in fields such as automotive, aerospace and marine industries, in order to improve the corrosion resistance, wear resistance and service life of parts such as cylinders, turbine blades, valves, pistons [4 -6]. One of the most common thermal deposition techniques is plasma jet deposition (APS), widely spread in mechanical applications [7]. The main disadvantages of these coatings are given by micro-cracks, inhomogeneity of insulation and residual stresses (appears during the cooling process) [8].

Plasma jet deposition (APS), is part of TS - thermal spraying technology [9]. The APS process involves introducing of particulate feedstock into the plasma jet to accelerate and fuse them. The process is based on the formation of a plasmatic gas when is dissociated and ionized by a high-power electric arc (about 80kW) between a cathode and a tubular anode. The generated rate of gas flow is high, of the order of 1000m/s, because on the jet exit, the gas tends to return to the normal energy state (lowest energy) forming again a strongly exothermic reaction [9]. The main objectives of APS technology are closely related to the improvement of the surface characteristics: resistance to wear (abrasion, erosion and friction); resistance to corrosion/ oxidation; electrical conductivity/ insulation; thermal or magnetic conductivity; biocompatibility; and so on.

Regarding the coating of polymers, whether they are biodegradable or not, it is necessary to investigate the surface characteristics of the obtained samples, more precisely, their roughness and topography. It is well known that the roughness has a significant influence on the suitability of a surface in various applications that require functional characteristics - offered by the ceramic layers, more than that the texture of a sample/part recommends it for various sectors of activity.

Surface analysis of the coated samples has brought enormous contributions in the field of adhesion science as it has allowed the investigation of the adhesion between the deposited layer and the polymeric substrate by using modern technologies such as XPS - X-ray Photoelectron Spectroscopy, SEM - Scanning Electron Microscope, ATR - Attenuated Total Reflection, AFM - Atomic Force Microscopy, RAIR - Reflection-Absorption Infrared Spectroscopy, etc. These methods provide data regarding the composition of the polymer surface, the nature of the reactions that occur at the interface between the deposited layer and the substrate, the inclusion of particles in the substrate, the lack of adhesion bonds, the mechanisms responsible for the failure of adhesion bonds, specific defects of ceramic coatings (cracks).

The aim of the surface coating presented in this manuscript was to improve the wear and hardness but also to increase the anti-corrosion characteristics of Arboblend V2 Nature. The novelty of the study consists in achieving a coating with APS on a thermally sensitive substrate - biodegradable polymer (low melting temperature approximately 170°C) [10].

2 Materials and methods

The selected to improve biopolymer was Arboblend V2 Nature. This one it is produced and marketed by the German company Tecnaro [11]. Arboblend V2 Nature® is a lignin-based biopolymer [12, 13], but also containing other biodegradable constituents such as bio-polyamides, polylactic acid, cellulose and natural additives (waxes, resins, oils) to improve the adhesion between the component elements and the processability of the newly formed polymer.

The coating was made on rectangular samples (70 x 50 x 10) mm^3 obtained by injection molding, SZ-600H industrial equipment. The injection process parameters were selected based on the experience of the team that carried out this research, as follows: melting temperature — 165°C, injection pressure - 100MPa, injection speed - 80m/min and cooling time - 30s. The thermal spraying technology available for this study was the Atmospheric Plasma Spray (APS) type - SPRAYWIZARD-9MCE equipment. The working parameters set before coating can be listed: gun type - 9MB, carrier gas flow - 5.1NLPM, spraying distance – 145 mm; deposition rate – constant; gases – N_2 and H_2 and electric DC – 400 A/70-80 V.

The selected micro-powders were purchased 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). Different numbers of layers (five, seven and nine) were deposited in order to observe how the thickness of the layer influences the surface characteristics of the coated samples. At the same time, the adhesion of the upper layers to the biopolymer substrate was monitored. However, in this manuscript, only the results regarding the micro layers obtained through five passes will be presented, in order to easily observe if a reduced number of layers is sufficient to improve the surface properties of the Arboblend V2 Nature samples.

In order to observe the surface topography and the roughness of the coated samples, an AFM (Atomic Force Microscopy) analysis was carried out, on the Nanosurf easyScan 2 equipment, which also has a Nanosurf Easyscan 2 data representation program. The analyzed area was approximately (49.5x49 .5) μm^2.

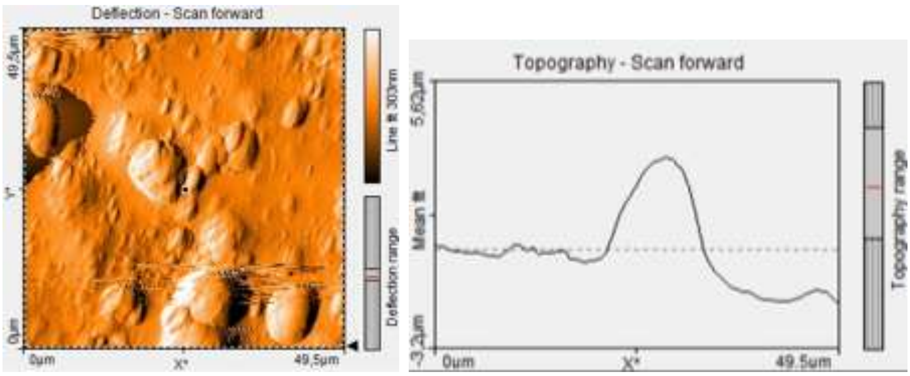
A CETR UMT-2 microtribometer was used for the scratch and microindentation tests. The main testing conditions for scratch analysis were as follows: vertical force – 10 N NVIDIA blade, test speed - 0.167 mm/s; testing distance - 10 mm; testing time - 60 s; blade tip - 0.4 mm. For the micro-indentation test the following process parameter were set: indenter type – Rockwell; sensor of (0.2–20) N; force - 10 N (vertical type); loading time — 30 s; holding time — 15 s; unloading time — 30 s. In the case of micro-indentation tests, on each sample were performed three tests in order to highlight the experimental repeatability as a consequence of deposited layer uniformity. The average value of the three micro-indentation tests performed for each sample were obtained by calculating the arithmetic average.

3 Results and discussions

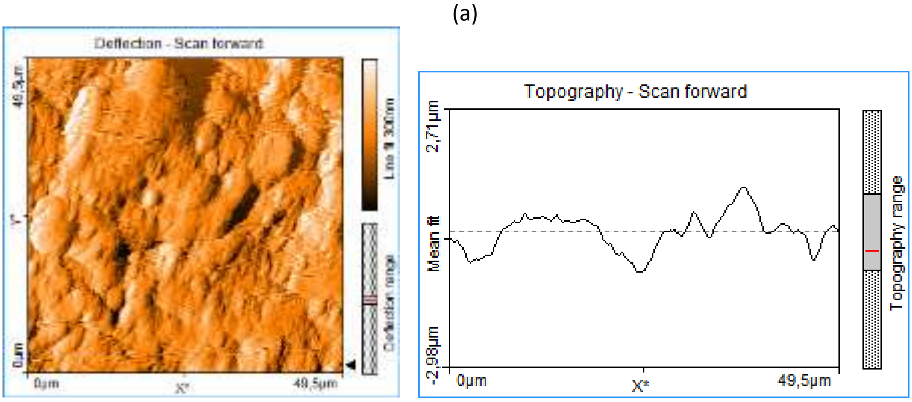
3.1. AFM analysis

In the first part of the determination of the surface characteristics of the coated samples, the AFM analysis was performed on the surface of the coated samples with the three types of ceramic powders, with five passes, in order to better observe the possible problems related to the adhesion of the particles to the polymer substrate.

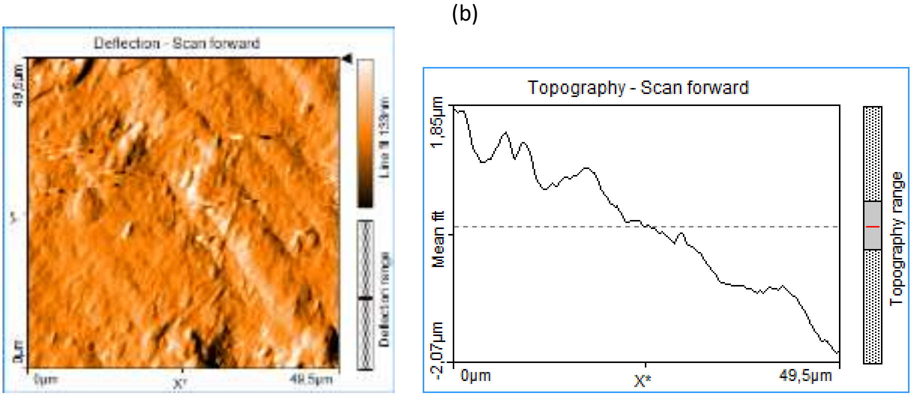
Fig. 1(a) shows the topography of the Arboblend V2 Nature sample coated with Metco™ 143 (ZrO_2 18TiO_2 10Y_2O_3) micro-powder. It is noted that the micro particles are uniformly distributed on the surface of the analyzed area (49.5μm^2). Moreover, the micro particles kept their spherical shape, due to the fact that they came into contact with the unheated substrate, but some of them were incorporated into the biopolymer mass. For the sample coated with chromium(III) oxide, Fig. 1 (b), the arrangement of the rectangular micro particles is in patches inhomogeneous and, just like in the case of the sample coated with ZrO_2 $18TiO_2$ $10Y_2O_3$, the smaller, spherical micro particles were embedded in the surface polymer structure.



(a)



(b)



(c)

Fig. 1. AFM analyses of the coated samples: (a) Metco 143 (ZrO_2 $18TiO_2$ $10Y_2O_3$), (b) Amdry 6420 (Cr_2O_3), (c) Metco 136F (Cr_2O_3-$xSiO_2$-$yTiO_2$).

The last sample, Fig. 1 (c), also coated with a compound containing chromium(III) oxide, Cr_2O_3-xSiO_2-yTiO_2, reflects the fact that the coating is even more uneven. Thus, the samples covered with Amdry 6420 and Metco 136F it seems to present lack of micro particles substrate adhesion, which can be attributed to the chromium oxide that came into contact with the polymer substrate and did not adhere to it, most likely due to structural incompatibility but also to the process parameters.

Thickness of the deposited ceramic layers is of the order of micro meters. According to Table 1, the value of *Sa*, a parameter that usually together with *Sq* evaluates the roughness of the surfaces, has the highest values for the coating with ZrO_2 18TiO_2 10Y_2O_3 because the micro ceramic particles created multiple bonds with the polymer substrate over the entire surface of the sample, while the other two types of coatings also highlighted the existence of some portions where the particles actually did not stick to the substrate. The *Sp* parameter also recorded the highest value for the sample coated with micro ceramic power based on zirconium oxide, 664.91nm.

Table 1. Surface roughness parameters.

Sample	Area (nm^2)	Sa (nm)	Sq (nm)	Sp (nm)
Metco 143 ZrO_2 18TiO_2 10Y_2O_3	2.47	104.78	116.9	664.91
Amdry 6420 Cr_2O_3	2.47	102.14	108.07	416.73
Metco 136F Cr_2O_3-xSiO_2-yTiO_2	2.47	100.25	103.19	305.9

where: *Sa* (arithmetical mean height) - average surface roughness; *Sq* (root mean square height) - Standard deviation of the height distribution, or RMS surface roughness; *Sp* (Maximum peak height) - Height between the highest peak and the mean plane.

3.2. Scratch Analysis

This type of analysis was carried out in order to observe the adhesion of the (hard) ceramic micro-layers to the polymeric substrate - Arboblend V2 Nature, but also the resistance to wear, through the A-COF parameter - apparent friction coefficient.

Fig. 2(a) shows the scratch behavior for the sample with an upper layer based on ZrO_2 18TiO_2 10Y_2O_3. It is observed that the tendency of the curve is to increase throughout the testing. The most important aspect to mention is the fact that there are several peaks in the variation of the apparent friction coefficient, quite wide, from where we can draw the conclusion that the scratch resistance and adhesion between the two layers is good.

For the sample coated with Cr_2O_3 micro powder, Fig. 2 (b), it can be observed the appearance of a large number of peaks with high amplitude, which are attributed to the very good adhesion of the micro particles on the polymer surface. The trend of the curve is increasing, which means that the test pin dislodged micro particles that were then deposited as residues on the sample coated surface, thus increasing the A-COF.

The sample coated with Cr_2O_3-xSiO_2-yTiO_2, Fig, 2 (c), appearance of a very large peak at the beginning of the test, the first 18 seconds, can be attributed to the greater granulation of the constituent particles. The wear resistance of the sample is lower than in the case of the other sample that has chromium(III) oxide in its composition, primarily due to the lower adhesion of the particles as it can be seen that during the testing there are not many and wide fluctuations of A-COF. The trend of the curve is still increasing, as in the case of the other two previously tested samples.

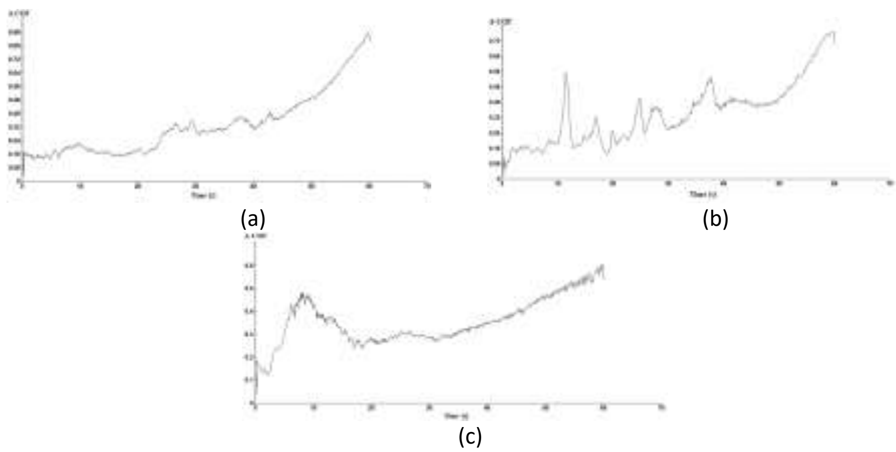


Fig. 2. Variation of apparent COF with test time for the coated samples: (a) Metco 143 (ZrO_2 $18TiO_2$ $10Y_2O_3$), (b) Amdry 6420 (Cr_2O_3), (c) Metco 136F (Cr_2O_3-$xSiO_2$-$yTiO_2$).

3.3. Microindentation Test

The microindentation tests presented in this paper will be for the samples coated with the three types of ceramic powders and with a number of 5 passes, to observe the improvement of the surface characteristics - the hardness in the moment in which a thin layer of ceramic particles is deposited.

In Fig.3(a), it can be seen the specific curve of the microindentation test, load - depth of penetration, for the sample coated with a layer based on zirconium oxide, which records the lowest dispersion of the results, due to the uniform distribution of the micro particles on the substrate surface. The other two coatings, Fig. 3 (b)-(c), have a slightly higher dispersion of the registered results, a fact that can be correlated with the slight lack of uniformity of the ceramic layers based on chromium (III) oxide, Amdry 6420 (Cr_2O_3) and Metco 136F (Cr_2O_3-$xSiO_2$-$yTiO_2$).

Regarding the penetration depth, contrary to expectations, the layer based on ZrO_2 $18TiO_2$ $10Y_2O_3$ allowed a slightly higher penetration, approximately 65 µm, although the layer was uniform. The other two samples recorded values of 64 µm - Amdry 6420 and 64.5 µm - Metco 136F, most likely due to the higher hardness of chromium oxide, which, being a matrix, is found in abundance in their composition. The hardness of the samples will also be lower for the sample that allowed greater penetration.

The results recorded for the analyzed samples can be compared with those obtained under the same conditions on the same samples but for nine passes [10, 14]. Thus, it could be concluded, as expected, that with the increase in the number of passes from five to nine, the characteristics improve significantly, but the trends are the same [10, 14].

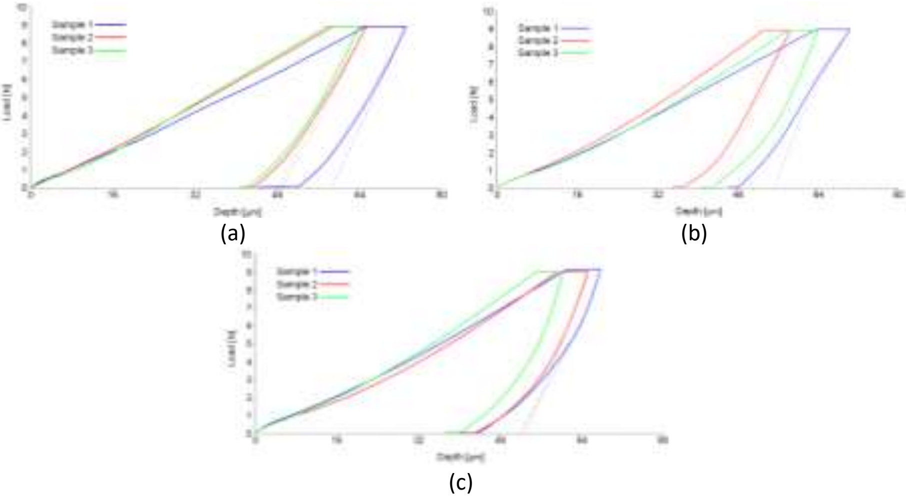


Fig. 3. Microindentation test results for: (a) Metco 143 (ZrO_2 $18TiO_2$ $10Y_2O_3$), b) Amdry 6420 (Cr_2O_3), (c) Metco 136F (Cr_2O_3-$xSiO_2$-$yTiO_2$).

4 Conclusions

After the surfaces analyses, AFM, scratch and microindentation tests on the three types of ceramic coatings, an improvement of the characteristics was observed with the deposition of ceramic micro particles on the biopolymer substrate - Arboblend V2 Nature, as follows:

- the coating based on zirconium oxide showed, according to AFM, the highest uniformity of the deposited layer. The layers based on chromium(III) oxide were relatively uniformly distributed on the surface of the samples;
- after the scratch tests, the samples coated with Metco 136F (Cr_2O_3-$xSiO_2$-$yTiO_2$) behaved the best, presenting multiple variations of A-COF, which correspond to a high wear, scratch resistance. The coating with ZrO_2 $18TiO_2$ $10Y_2O_3$ also recorded variations, but not as large as the sample coated with Metco 136F;
- the wear resistance of samples based on chromium(III) oxide is closely related to the penetration resistance (hardness) of the samples. Thus, although the coating with a micro layer of ZrO_2 $18TiO_2$ $10Y_2O_3$ was uniform, resistant to wear and implicitly the adhesion between the layers (bio polymeric substrate - ceramic top layer) was not as strong as in the case of the samples coated with Cr_2O_3 particles and respectively Cr_2O_3-$xSiO_2$-$yTiO_2$;
- with the increase in the number of passes, the surface characteristics of the samples also increase, making them suitable to be used in industrial applications that require special operating conditions - wear and not only.

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