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Enhancing the characteristics of bio-based polymers coated with ceramic particles

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Abstract. Biodegradable plastics have been a primary concern for all experts in the sector due to the negative effects that plastics have on the environment. The current study is going to examine the samples after coating using the aid of SEM and EDX investigations. As foundation materials for the ceramic particle coating approach, the Arboform L, V3, Arboblend V2, and Arbofill Fichte have all been considered in the research. Injection molding was employed to construct the samples, and the coatings were applied utilizing the atmospheric plasma spray technique at the SPRAYWIZARD 9MCE facility. The intermediate layers were composed of Ni 78W 14Mn 6Al₂, Ni 55W 26Cr 13F 6, and W 49Ni 44Cr 6Mn 1, while the final ceramic layer was composed of Al₂O₃. The final layer might contribute to the improvement of mechanical properties like wear resistance, hardness, and higher thermal resistance. The results of the study suggest adopting these coated materials in fields with demanding working conditions, such the automotive industry. Given the successful results, it is reasonable to assume that the currently used biodegradable material has better features that meet technological requirements, enabling it to gradually replace plastic in important activity areas.

Keywords: bio-polymer, coating, ceramic particles.

1. Introduction

In contrast to the predominant plastic usage tendency, certain individuals continue to favor ceramic or glassware, despite their relatively higher cost and fragility. This preference stems from the fact that plastics have a tendency to degrade over time when exposed to food, resulting in the development of odors, deterioration in appearance, and even color alteration. Nano-ceramic coatings provide the ability to

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mitigate these limitations while preserving the benefits associated with plastic, as the coating alone modifies the plastic's surface, [1]. A diverse range of coating deposition techniques exists, including physical vapor deposition (PVD), chemical vapor deposition (CVD), spin coating, dip coating, chemical synthesis, vacuum deposition, flame and arc spraying, electrolytic deposition, and electro less coating. Nevertheless, it should be noted that methods such as PVD, CVD, and thermal spraying are characterized by elevated deposition temperatures, which can occasionally surpass the melting point of plastic substrates [2-10].

Plasma provides the application of several coatings to temper components. The characteristics of a coat are determined by the selection of the base materials, which include hydrophobic (water-repellent) or hydrophilic (water-attracting/wetting) properties, scratch protection, corrosion protection, barrier or diffusion barrier properties, anti-friction coatings, nonstick coatings, adhesion promoters, primers, water or steam barriers, and metallization, among others [11-24].

Ceramic coatings have the potential to be sprayed onto plastic surfaces. There are various advantages associated with this practice, including enhanced surface durability and endurance, heightened resistance to scratches and stains, improved chemical protection, and simplified cleaning processes. Furthermore, ceramic coatings can enhance the aesthetic appeal of plastic surfaces by providing a glossy finish, enhancing the material's shine and luster. Ceramic coatings have the potential to be applied to a range of plastic materials, such as PE (polyethylene), PET (polyethylene terephthalate) PP (polypropylene), lignin based polymers, and ABS [3, 11, 12, 25-34]. In the majority of instances, the application of ceramic coating is feasible for a wide range of plastic materials, provided that they exhibit minimal flexibility or bending tendencies.

These coatings are designed to form a durable and resilient protective layer, safeguarding plastic surfaces against potential harm. Moreover, it confers enhanced surface protection against scratches and chemical harm, while additionally offering supplementary defense against the detrimental effects of UV radiation, which can lead to fading and discoloration over an extended period. Moreover, ceramic coatings exhibit exceptional resistance to stains and possess a high degree of ease in terms of cleaning. Through meticulous preparation and skillful implementation, ceramic coatings offer a viable solution for rejuvenating plastic surfaces, effectively restoring their original appearance [1, 35, 36].

In order to apply a ceramic coating onto polymeric substrates, it is imperative to commence the process by carefully preparing and cleaning the surface. Prior to commencing the application process, it is imperative to eliminate any particles of dust, dirt, or debris. After the cleansing of the surface, it is advisable to apply a primer in order to facilitate the appropriate adhesion of the ceramic coating. Following the process of priming, the selected ceramic coating can be administered in several successive thin layers utilizing a spray gun [4, 35, 36].

The main goal of the present study was to acquire a novel material exhibiting enhanced characteristics, which might be effectively employed as an alternative to synthetic plastics in various applications, including the automobile industry. In light of the stated purpose, the selection of biodegradable materials, namely Arboblend V2 Nature, Arboform L, V3, and Arbofill Fichte, was made based on prior investigations into their respective qualities. The subsequent procedure involved the application of an intermediary metallic layer to enhance the adherence of the subsequent ceramic layer (upper layer) using the APS method. Subsequently, an analysis of the metrological characteristic was conducted. The current study is unique and not found in previous research of other authors. Therefore, the proposed research, which incorporates both technological advancements and experimental findings, possesses a distinctive characteristic.

2. Materials and methods

The coatings were made on lignin-based polymers (as substrate), Arboform L, V3, Arboblend V2 and Arbofill Fichte, developed and commercialized by Tecnaro Company, [37]. The samples (3 from each material) to be coat were injected in the mold by using the SZ-600H equipment. The dimensions of the injected samples were ($150 \times 40 \times 10$) mm³.

The samples were secured using metallic bands, and subjected to blasting in order to attain an ideal level of roughness and eliminate surface contaminants. Subsequently, the samples underwent degreasing using ethyl alcohol.

On these samples were deposited various metallic/ceramic coatings by using APS (atmospheric plasma spray) facility, SPRAYWIZARD-9MCE, Sultzer-Metco, USA/9MBspraying gun. The powders size was between (15–150) µm, according to the manufacturer [38].

The deposition process was conducted at a distance of 150mm from the support, with six consecutive passes done at a consistent speed. The thickness of the layers was on the order of micrometers, and the samples were subjected to continuous measurement using a laser pyrometer in order to regulate the melting temperature of the biodegradable materials.

The deposition process resulted in the creation of three intermediate layers of metallic powder coating: Ni78W14Mn6Al2 (named next 1st powder), Ni55W26Cr13Fe6 (named next 2nd powder), W49Ni44Cr6Mn1 (named next 3rd powder), and one ceramic powder as final layer, Al₂O₃ (ceramic alumina - named next 4rd powder).

The role of the intermediate layer was to help strengthen the bond between the final layer and the polymeric substratum. The ceramic layer might have a growing influence in terms of the mechanical qualities wear, hardness, and an increase in heat resistance. One potential drawback is that the samples will become more fragile with time, which will also decrease their ability to biodegrade.

The technological parameters used for the APS coating were: carrier gas flow - 13.5 (SCFH); air pressure -20 (psig); Rate -4 - 5.5 (lb/h); gases - Ar and H₂.

On a scanning electron microscope known as a SEM Quanta 200 3D DUAL BEAM that was also fitted with an EDX detector, a large field detector (LFD) and

a dual backscattered detector (dual BSD) were used, respectively, to analyses the morphology and the microstructure of the samples.

Scanning electron microscopy (SEM) examinations were carried out at a range of magnification powers using the Low Vacuum mode of the instrument with 20 kV, a spot size of 4.5, magnification (100–5000)X, a working distance of 15 mm, an inclination angle (tilt) of 0 degrees, and a pressure of 60Pa inside the microscope chamber.

3. Results and discussions

3.1. EDX analysis

Table 2 displays the results of an EDX (Energy-dispersive X-ray) study that were used to reflect the percentages of aluminium oxide present in the support/base materials.

On the surface of the samples, the three distinct types of material exhibited varying degrees of deposition in a manner that was uniform. Because of the differential in their melting points, the coated Arboform LV3 Nature base material was found to have the largest concentration of aluminium oxide (78%) compared to the other two support materials. As a consequence, it made possible the inclusion of ceramic and metallic particles in a greater quantity.

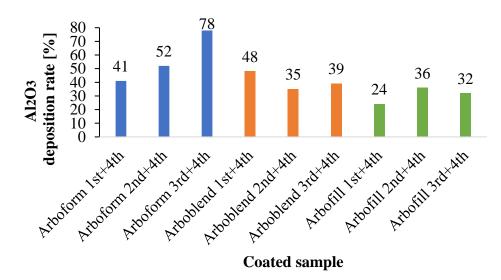


Fig. 1. Aluminium oxide embedded in the lignin-based substrates' surface.

Analyses of the microstructure and morphology, SEM and EDAX analyses, show that the deposition for Arboform LV3 is uniform and complete. In the case of Arboform LV3 Nature coated with Ni-W-Cr-Mn powder, the percentage by weight of the final ceramic layer (aluminium oxide) was 78%. For the Arboform LV3

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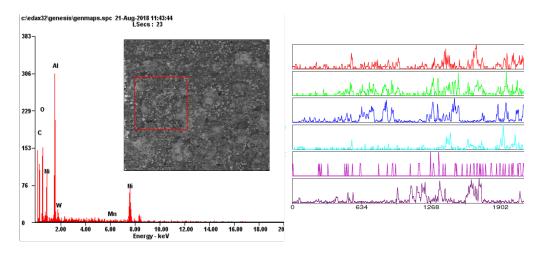
Nature material that was coated with the Ni55W26Cr13Fe6 powder, the deposition layer of ceramic was reconstituted in a proportion of 52%, whereas for the Arboblend V2 material, the value was 48%. The final coating of aluminium oxide is quite homogeneous in appearance thanks to different melting points and the morphologies of both Arboblend V2 Nature and Arbofill Fichte.

Figure 2 present two different types of EDX analyses, one performed in line and one on the surface of the coated samples, in order to determine the proportional distribution of chemical elements. Carbon, oxygen and aluminium are the three chemical elements that make up the majority of the coated samples and their proportions change based on the relative energy peaks.

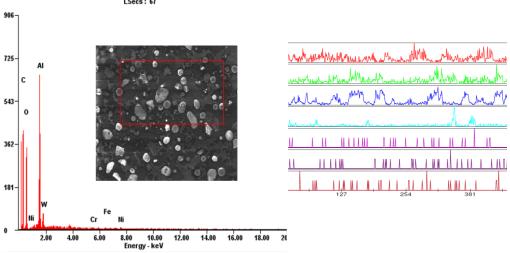
The chemical composition of coated samples is what determines whether or not there is carbon present in significant amounts. Based on the findings of prior scientific research [11–13, 18, 19], the EDX analysis determined that the chemical composition of all three fundamental elements consists of approximately (55–60) % carbon and the remaining percent is oxygen.

In this study

Results of the SEM and EDX analyses performed on the Arboform L V3 Nature coated with powder 1 and 4; Arboblend V2 Nature coated with powder 2 and 4; Arbofill Fichte coated with powder 3 and 4 samples are going to be presented in this study. This selection of the three samples was realized with the objective of being able to demonstrate the effectiveness of the deposition (polymer substrate + intermediate metallic layer + upper ceramic layer).

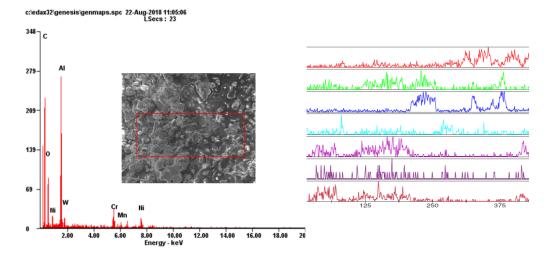


Arboform L V3 Nature+ 1st and 4rd powders



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Arboblend V2 Nature $+ 2^{nd}$ and 4^{rd} powders



Arbofill Fitcher + 3rd and 4rd powders

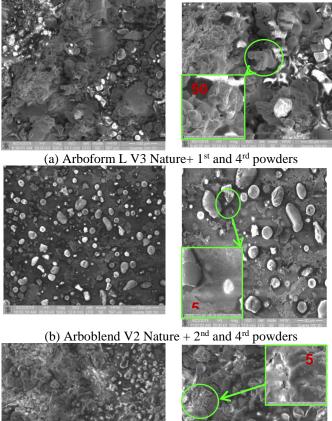
Fig. 2. In lines and for an area EDX an alysis of the coated sample surface.

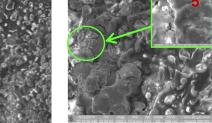
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The EDX analysis, which is used for elemental analysis and for determining the chemical characteristics of samples that have been coated with aluminium oxide, verifies that the microparticles are arranged in a manner that is approximately uniform over the surface of the polymers substrates.

3.2. SEM analysis

Surface analyses performed using the SEM technique are shown in Figure 3 for the selecte samples. The images were scaled up by a factor of 500X, 1000X, and respectively 5000X.





(c) Arbofill Fitcher + 3^{rd} and 4^{rd} powders

Fig. 3. SEM analysis of the coated sample surface.

According to the present analyse on the surfaces of the samples, depending on the coating powder, parallelepiped shapes were found in the case of ceramic powder (aluminium oxide), whilst elliptical or spherical shapes were found in the case of metallic powder coating (intermediate layer). The presence of coating powders on the surface of the samples was further confirmed also by the EDX study performed on the layer.

In figure 3(a), it is easy to observe the homogenous layer of Al_2O_3 that has been incorporated into the structure of the base material (Arboform LV3 Nature) more as a result of its higher deposition temperature and lower deposition rate. The morphology of particles that are uniformly dispersed is depicted in figure 3(b). The unique splat of aluminium oxide ceramic coating can be observed in figure 3(c) due to the overlapping melting of the ceramic particles, which led to the formation of a splat type structure.

The fact that the particles remain partially unmelted in the base materials proves that the temperature wasn't higher than the melting points of the materials and powders. Some samples had local melting of particles that generated a ceramic splat structure peculiar to this kind of coating.

4. Conclusions

The process of applying a thermal coating on polymeric materials finds application in industries such as the automotive industry, the aerospace industry, and the naval industry in order to improve the corrosion resistance, abrasion resistance, and lifespan of various components (such as cylinders, turbine blades, pistons, and piston liners). One of the most common techniques for applying a thermal deposit is known as deposition with a plasma spray (APS), and the coatings obtained from zirconium and chromium are typically spread over a wide area for mechanical applications. The most significant drawbacks of these covers are that they are susceptible to micro-fissures, precarious isolating, and residual tensions (which manifest themselves during the cooling process).

According to the obteined results of the microstructural and morphological studies (SEM and EDX), the Arboform LV 3 deposition appears to be both uniform and comprehensive. In the cases of Arboblend V2 and Arbofill Fichte coated with aluminium oxide, the examinations confirm that the micro particles are arranged on the surface of the samples in a manner that is approximately uniform.

The topmost coating of ceramic may have a role in boosting the mechanical qualities of wear and hardness, as well as the material's resistance to thermal expansion and contraction. One potential drawback is that the samples may become more fragile and lose some of their capacity to degrade naturally. Based on the findings of this research, it is recommended that coated materials be utilized in industries that have particularly demanding working circumstances, such as the automotive industry.

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