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THERMAL BEHAVIOR OF COATED BIO-POLYMERS

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Abstract: Thermal behavior in plastic materials has a strong influence on their performance. In the current research, scientists are using different equipment that highlights the calorimetric behavior of parts by the identification and localization of transitions and exothermic/endothermic reactions that take place during material heating. The paper aims to characterize from a thermal point of view a lignin-based polymer (Arboblend V2 Nature) coated with three distinct micro-ceramic powders: two based on chrome oxide - Cr_2O_3, Cr_2O_3 - $xSiO_2$ -$yTiO_2$ (commercial name Amdry 6420 and Metco 136F) and one based on zirconium oxide - ZrO_2 $18TiO_2$ $10Y_2O_3$ (commercially known as Metco 143). The samples to be covered were obtained by injection in the mold and the coating technique used was a thermal – APS (Atmospheric Plasma Spray). After thermal analysis, all three coated samples reviled thermal stability up to 230°C, the degradation of the lignin matrix taking place around 345°C. Thus, based on this important data the recommendation to be used in practical applications can be made. So, the Arbobelnd V2 Nature bio-polymer coated with ceramic micro-particles works in normal working parameters for temperatures not exceeding 200°C. The paper also highlights in the beginning part the systemic analysis of the coating process in order to underline the factors that significantly influence the output parameters as: structure, morphology, mechanical, tribological, and thermal behavior.

Key words: coating, micro-ceramic powders, lignin-based polymer, thermal behaviour, systematic analysis.

1. INTRODUCTION

A global effort to create biodegradable polymers and biodegradable bio-composites has been made recently as a result of expanding environmental consciousness reading the ecological issues (waste management). Currently, both companies and the government are focusing on biodegradable polymers, bio-based materials, and composites, [1, 2]. The synthetic thermoplastic polymers (nylon, polystyrene (PS), polyethylene (PE), and polypropylene (PP)) made from petroleum resources have often been employed in the plastic industries in the last century. These polymers, however, are difficult to break down in the natural environment, which causes a variety of environmental contamination in the eco-system, [3].

Additionally, plastic wastes are an unwanted pollutant in the ocean, rivers, and soil. They have a tendency to build up in the natural environment as a result of their resilience to microbial attack, [4]. In place of traditional plastic materials, the use of ecologically benign, biodegradable polymers and materials is being investigated as a solution to these issues. Natural fibers and flours have gained popularity in recent years as reinforcing fillers in both non-biodegradable polymer and biodegradable polymer composite materials in order to provide favorable environmental benefits, [5-7]. In comparison to inorganic fillers like calcium carbonate, carbon black, zinc oxide and talc, bio-composites made with natural fillers have a number of advantages, including low CO_2 emission, biodegradability, low mass and cost, low manufacturing energy, easy availability, renewability and the absence of associated health risks, [8, 9].

The main drawback of employing biodegradable polymers in high-strength applications is that they easily decay when exposed to high humidity condition and do not withstand high operating temperatures. The hydrolysis/thermal resistance qualities of biodegradable polymers and bio-composites need to be improved in order to boost their utilization. The biodegradability of biodegradable polymers and bio-composites has mostly been researched recently in relation to the biological activity that is brought on by bacteria in the soil, fungi, microorganisms, and enzymes from compost soil, lakes, and marine environments, [10]. By depositing tiny ceramic layers, the goal of this research is to improve the thermal stability of Arboblend V2 Nature lignin-based polymer. Thermal analysis is an experimental analytical method that can be used to determine the thermal properties and structural degradation of materials, in this case biodegradable polymer – as and micro-powders – as coating, [11]. The breakdown of biodegradable polymers can be studied using a variety

of thermo-analytical techniques, including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA).
The main objective of this study was to conduct a and Thermal Gravimetric Analyze – TGA, between (30 - 700)°C, on the coated lignin-based polymer. Three ceramic layers have been used in order to enhance the surface and thermal characteristics of the bio-based polymer: two based on chrome oxide (Cr_2O_3, Cr_2O_3-$xSiO_2$-$yTiO_2$) and one based on titanium and zirconia oxide (ZrO_2 $18TiO_2$ $10Y_2O_3$).

2. MATERIALS AND METHODS

The selected thermoplastic material to be coated with ceramic micro-particles was Arboblend V2 Nature, a lignin/polylactic acid - based polymer according to the information provided by the producers (Fraunhofer Institute for Chemical Technology and Tecnaro company) and the specialized literature [12, 14]. Obtaining the samples to be coated was achieved through injection molding on a SHEN ZHOU SZ-600H equipment (Zhangjiagang, China), with dimensions of (70x50x10)mm^3. Melting temperature was -165°C, injection speed was 80m/min, injection pressure was 100MPa, and cooling time was 30s.
Atmospheric plasma spray (APS) technology was used on an SPRAYWIZARD-9MCE (Sultzer-Metco, Westbury, New York) equipment with a USA/9MB spraying gun to coat the injected samples. The employed technological coating parameters were: spray distance – (137-145)mm, 5 passes – obtaining micro-layers, direct current – 400A, powder dispenser air pressure – 1.4bar, gas - hydrogen and nitrogen, carrier gas flow – (5.1-5.5)NDPL, amount – (126-144)g/min.
For the coating, three ceramic micropowders from the Oerlikon Metco manufacturer (Bella Vista, New South Wales, Australia) were used: Amdry 6420 (Cr2O3), Metco 143 (Cr_2O_3-$xSiO_2$-$yTiO_2$), and Metco 136F. (ZrO_2 $18TiO_2$ $10Y_2O_3$), [15].
The used equipment for analysing the thermogravimetric behaviour of the coated samples was Mettler Toledo TGA/SD with the STARe SW 9.10 software. The testing conditions were as follows: mass of samples – (2.9-3.9)mg, air atmosphere, flow rate - 20cm^3/min, testing temperature (25–700)°C, heating rate - 10°C/min. The drawing of three types of curves was pursued differential thermal analyses (DTA), derived thermogravimetric curves (DTG) and thermogravimetric curves (TG).
The aim of the manuscript was to obtain a new material with improved properties that can then be used successfully as a substitute for synthetic plastics in the automotive industry but not only. Given this objective, the biodegradable material Arboblend V2 Naure was chosen, for which the research team previously studied the properties. The thermal analysis aimed to determine the degradation interval (from calorimetric point of view) of the polymer after the coating with ceramic micro-particles. Also, it was followed to identify the residue that results from the test because it gives us important information about the amount of ceramic material incorporated but also about the constituents of the biodegradable material that have not been charred until that temperature.

2.1. Systemic analysis of the coating process with ceramic/metallic particles

The use of thermal spray technology, are often obtained surfaces with structural, electrical, tribological and anti-corrosive characteristics if the input parameters are set to the optimal values. In order to identify the main parameters involved in the ceramic powder coating process (thermal spray method), a systematic analysis was performed, Figure 1. The analysis has balanced the input parameters, hard controllable factors and the output parameters of the process in order to establish their influences on the good development of the coating process but first of all on the quality of the resulting samples.
Following the specialized literature, a series of input parameters have been identified that significantly influence the surface characteristics of the samples obtained by material deposit:
- *selection of the spray material* has a fundamental role in determining the surface properties of the sample/part, but also on the obtained thick layer - parameter. The dimensions and shapes of micro/nano-particular are very variant depending on the chemical structure of the selected compound for coating. Thus, a coarse granulation powder will lead to a rusty layer while a fine powder granulation will provide a more uniform and compact layer, [16]. Also, another feature that can be improved according to the type of raw material used is the surface hardness, which has the role of protecting against the substrate wear (polymer in the case of this study), [17].
- *selection of the substrate* depends on the type of application in which the parts/ sample are to be used. It is known that metal materials are slightly corrosive and also have a high mass compared to any other material used in the industry. Thus, its replacement with the plastic in certain situations/applications is an extraordinary alternative because, the plastics are much more resistant to the action of the corrosive agents, are good electrical insulators, have a reduced mass, low acquisition costs and do not involve thermal treatments in order to control/correct the structural morphology of the substrate, [18].
- *intensity of the spray current*: with the careful increase of this variable parameter the specific structures of the ceramic deposits (splates) become less porous so, the coating being more uniform, [19]. This is due to the fact that the particles have more energy when leaving the plasma flame, these being

melted in a higher number than in the use of a lower intensity. Of course, depending on the coating and substrate material the values of this parameter differ.

- *spray distance* - the greater the spray distance the thermal influence of the melted particles (the splashes) sent to the substrate is smaller. However, with the increase of this input parameter decreases the density of particles deposited on the substrate thus needing a greater number of passes to make a complete and uniform coating, [20].

- *number of passes* necessary to obtain a homogeneous layer is as mentioned in the previous paragraph in close connection with the spray distance. The adhesion resistance is strictly influenced by the uniformity of the deposited layer and the existence or lack of defects, [19, 21-23]. However, if the number of passes is too high then the substrate deterioration appears, especially in the case of plastics that are so thermally sensitive, due to their low melting point compared to that of metal or ceramic materials, [18].

- spray temperature - the plasma flame has an extremely high temperature, while the raw materials are exposed in the perimeter of the flame for a very short time. Micro/nano-particles rapidly solidify on the substrate (heated or most often unheated) with a solidification speed > 100 K/s, due to the thermal differences between the two materials that come in contact, [19, 24-29]. However, due to the rapid cooling (caused by the low temperature of the substrate) of the particles, the upper layer has obvious defects in the form of holes or pores, which are suitable for the characteristic literature (by the APS method). During the cooling process it is possible to form micro cracks attributed to the contraction of the melted particles, which have released the tensions from the coatin during the thermal cycle. Also, the effect of the uncontrolled spray temperature through the other input parameters leads to the destruction/impairment of intermolecular bonds due to the overheating/carbonization of the substrate material. For the correct selection of parameters that mitigate the thermal effect, a study is carried out to the thermal behavior of the substrate material, by DSC analysing (differential scanning calorimetry), DTA (differential thermal analysis), which reveals the transitions suffered by the material during heating, transitions associated with the melting/softening point.

- *coating speed* must be moderate so that the largest amount of micro/nano particles are deposited on the substrate but large enough to not carbon the substrate. Depending on the type of substrate, recommendations of this parameter are made: polymer - high spray speed (correlated with a sufficient number of passes), metal- average spray speed (lower number of passes), [19, 30].

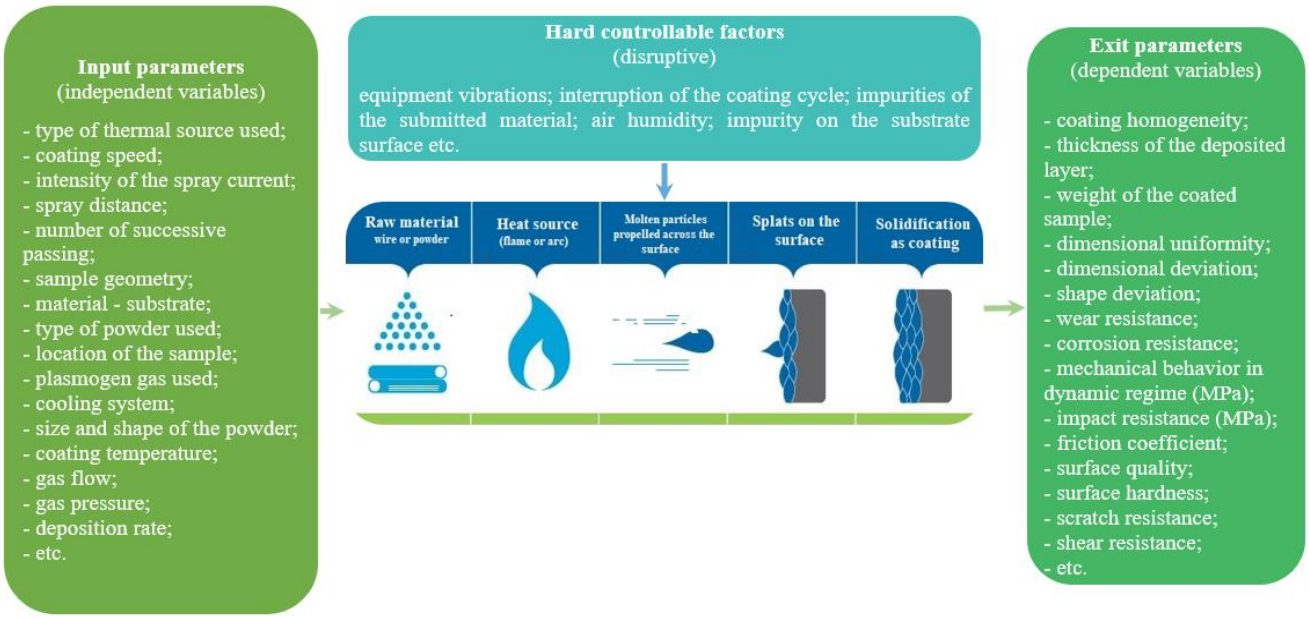

Fig. 1. Factors that influence the coating process

A judicious choice of the substrate (biodegradable polymer in this case), of the deposited powder, of the coating technique and of the manufacturing parameters can lead to high performance coatings with improved properties. Thus, according to the mentioned ones, it is appreciated that the parameters that significantly influence the quality and functionality of a coated sample in applications that involve various tribological and/ or corrosive actions are: spray distance, spray time (speed, number of passes) and intensity of the spray current. These coating parameters were taken into account when coating samples with micro-ceramic powders was realized.

3. RESULTS AND DISCUSSION

Thermal stability becomes essential during the practical use of materials in different applications especially when it comes to applications that involve harsh operation conditions. Thus, the knowledge of the degradation interval of the coated Arboblend V2 Nature becomes mandatory.

To track the thermal stability of the new created material (composite), the thermogravimetric analysis was realized. The thermogravimetric (TG), derived thermogravimetric (DTG), and differential thermal (DTA) curves for the three samples coated with ceramic layers made from five successive passes are shown in Figure 2 (notations: P1 - Cr_2O_3-xSiO_2-yTiO_2, P4 - Cr_2O_3, P7 - ZrO_2 18TiO_2 10Y_2O_3)

According to the DTG curves, Figure 2b, two decomposition stages were pointed out, toking place in close temperature intervals for the three analyzed samples, the differences being very small and influenced by the quantity of ceramic micro-particles (different size and shape) deposited on each sample surface. The first stage was recorded at around 340°C, with largest mass loss - over 85%: caused by the pyrolysis of the Arboblend V2 Nature bio-polymer that has lignin and/ PLA matrix, [12]. According to the specific literature, PLA and pure lignin degrade completely at temperatures around 500°C, [31-34].

In the second stage the mass loss was about 10%, the temperature range being (410-436)°C. The mass loos can be attributed to the thermal oxidation of carbonic residue remained from PLA and/or lignin and also the degradation of other natural constituents introduced by the manufacturer of Arboblend V2 Nature as binders such as wax and resin, [35]. Regarding the residual mass obtained from the thermal degradation of the three samples up to 700°C, it was observed that the sample coated with Cr_2O_3 (P4-6420) ceramic powder highlight the highest percentage of residue, about 6.5% the result being correlated again with the quantity of micro-powder that has been incorporated on the biopolymer surface. The lowest residual mass was in the case of Cr_2O_3-xSiO_2-yTiO_2 (P1-143), which highlighted problems of adhesion to the substrate, [36]. The compounds considered to be part of the residue mass besides the ceramic powders that have not yet reached their degradation temperature (over 3000 °C) can be inorganic substances that are structural parts in the composition of the studied biopolymer, [15, 37].

On the differential thermal curves (DTA), Figure 2c, a small inflexion can be observed around the temperature of 170°C which corresponds to the Arboblend V2 Nature melting temperature, [36].

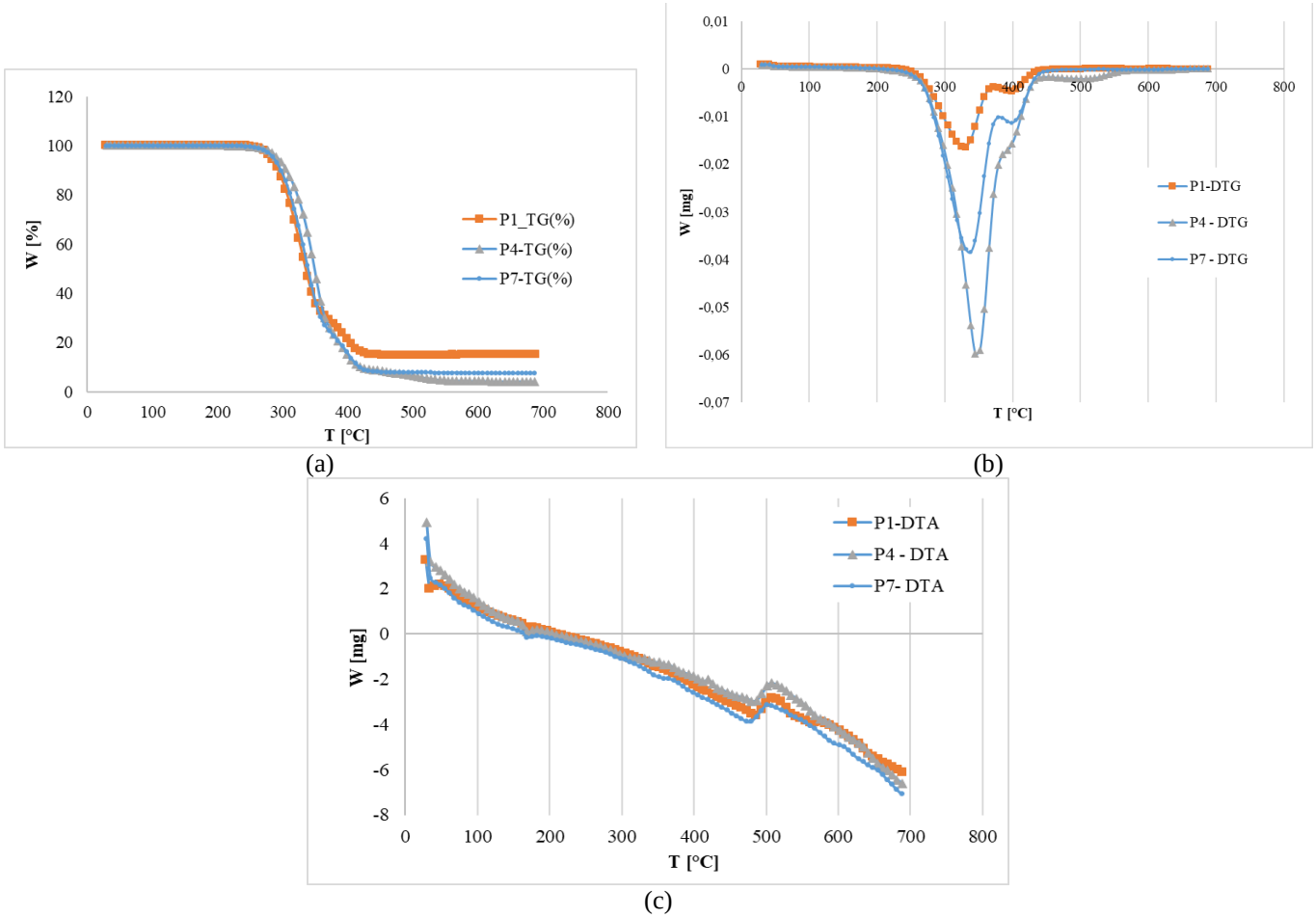

Fig. 2. Thermogravimetric curves of the coated samples: (a) TG, (b) DTG and (c) DTA

4. CONCLUSIONS

Systemic analysis performed before obtaining the samples coated with micro ceramic powders made it possible to obtain thermally non -graded samples, an essential quality aspect in practice, demonstrated following the thermographic analyzes performed.

The coating of bio-based polymers has gained the attention of researchers worldwide. The purpose of coatings with various layers, be they ceramic, metal, etc., as well as with reinforcements, the goal is to improve the properties of the base material. so that it responds better to certain industrial applications and can even replace a certain material, such as metal. The coatings were developed in order to improve the thermal characteristics of the Arboblend V2 Nature samples (thermal resistance), making them suitable for use in applications requiring harsh working conditions, particularly in the automotive industry. The following results were obtained after coating the sample with ceramic microlayers:

- A slight increase in the melting point, from 172℃ (base material [14, 36, 38]) up to 174℃, varying depending on the thickness of the deposited layer. The thickness value is closely influenced by the micro-particles size that constitute the ceramic powder. As a result, the larger the micro-particles, the greater the thermal resistance of the coated material.
- No significant differences were observed in terms of temperature range and mass loss during thermal degradation, and the differences were attributed in this case to the size of the ceramic micro-particles.

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