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THE MAIN CHARACTERISTICS OF THE BIOMATERIALS COMPONENTS AND THE EXTRUSION METHOD MANUFACTURING TECHNOLOGY FOR PLA/HA BIOCOMPOSITE

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Abstract: *The PLA/HA biocomposite material is a medical composite made of biomaterials in which the matrix is made of the biopolymer polylactic acid (PLA) and the bioceramic reinforcement (HA). Since the biopolymer (PLA) is completely bioresorbable and the bioceramic (HA), under normal conditions, is not degradable, the PLA/HA biocomposite is considered partially bioresorbable. The paper presents the main characteristics of the two biomaterial components of the PLA/HA biocomposite, PLA biopolymer and bioceramics (HA), their fields of use in various medical applications and the manufacturing technology of the PLA/HA biocomposite, by the "extrusion" method.*
Key words: *biocomposite, biodegradable, biopolymer, PLA, extrusion, mechanical properties.*

1. INTRODUCTION

Dorozhkin [1], [2] synthetically defined the term "biocomposite" or "biocomposite material" as the non-toxic composite used in medical applications which, through good interaction with the living organism, in vivo, has the possibility and quality to stimulate, with one or several components, the process of healing and absorption of the existing artificial surgical implant in the body. Examples of surgical implants made of polymeric biocomposites are presented by Ramakrishna et al. [3].

The PLA/HA biocomposite is a synthetic polymer-ceramic biocomposite with the matrix from biopolymer polylactic acid (lactic acid) (PLA), known as one of the most popular biopolymers used in medical applications and the reinforcement from the HA hydroxyapatite bioceramic, known to be used, first of all, as a covering layer for the various constructions of surgical implants made of biomaterials [4], [1], [2], [3].

Combining the properties of the two PLA and HA phases proved very promising. This combination is used in variously healthcare applications such orthopedic and cardiovascular implants, orthopedic interventions etc. [3], [5].

The PLA/HA biocomposite is partially bioresorbable [3].

2. CHARACTERISTICS OF THE BIOPOLYMER POLYLACTIC ACID PLA

Polylactic acid or polylactide PLA [6] is a synthetic biopolymer obtained from the monomer of lactic acid (LA), a naturally occurring organic acid [4], [6], [8].

Due to the chiral configuration offered by the lactic acid monomer from which it originates [6], [7], [8], PLA is presented in three forms of stereoisomers abbreviated as poly-L-lactic acid (PLLA), poly-D-lactic acid (PDLA) and poly-DL-lactic acid (PDLLA), with different properties, and where L and D are the enantiomers L- and D-lactic acid of Lactic Acid [7], [6], [8].

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The properties of polylactic acid such as physical properties, chemical properties, mechanical properties, etc. have been well documented in numerous investigations in recent years, [6], [7], [8].

PLA is highly versatile, thermoplastic and complete biodegradable and fully compostable synthetic polyester [6], [7], [8], [9].of Poly(lactic acid) PLA has numerous and interesting biological properties, such as good biocompatibility with host tissue [7], [9], [10], bio-absorbable [8], [9], [11] and non-toxic [9] and with little or no carcinogenic effects in local tissues [9], [10], [11].

The mechanical properties of polylactic acid are generally considered good [13] being favorable for load-bearing medical applications [10]. The different types of PLA such as (PLLA), (PDLA) and (PDLLA) have different mechanical properties [12], [14], [15] corresponding to the degree of crystallization and the molecular weight of each type of PLA polymer [14].

The PLA biopolymer also has disadvantages such as it is very fragile, it has a low elongation at break, it has a low hardness and tenacity [15].

The commercial biodegradable biopolymer PLA can be processed by extrusion and injection molding [16], [17].

The properties of PLA biopolymer are favorable for its use in numerous medical applications [10] such as bone graft substitute [10], orthopedic applications and interventions such as fixation of fractured bones with plates, pins, screws etc. [8], [14], [11], [10], resorbable prostheses [7], [10], scaffolds [10], osteotomies [9], [14], [11], oral and maxillofacial surgery [8], [11], articular cartilage repair [11], meniscus repair [10], drug delivery systems (DDS) [9], [11], cancer therapy [10].

PLA has been approved by the Federal Drug Administration FDA, USA and European regulatory authorities [9].

The commercial biodegradable biopolymer PLA can be processed through several technological possibilities such as extrusion, thermoforming [15], [16] and injection molding [17].

3. CHARACTERISTICS OF HA HYDROXYAPATITE BIOCERAMICS

Hydroxyapatite bioceramics, with the abbreviation HA, HAp or OHAp [1] can be of biological origin, derived from animal bones, seaweed, etc. [18] or of synthetic origin with the chemical formula Ca10(PO4)6(OH)2 [1], [12]. Hydroxyapatite is available in different physical forms such as granules/powders, solid blocks and scaffolds [18], with dense physical structure "Dense hydroxyapatite" [18], [19] or porous "Porous hydroxyapatite" [18], [20] .

Synthetic hydroxyapatite, is a typical component of the calcium phosphate (CaP) group with a molar ratio of 1.67 Ca/P, stoichiometric HA [1], [2] and has two important structural characteristics, namely crystallography and chemical composition are almost similar with natural bone and teeth for the human and animal body [1], [2], [19], [20].

Hydroxyapatite has an excellent biological behavior in living tissue characterized by properties such as, it is bioactive, if it is sintered at high temperature [19], it is biodegradable, if it is sintered at low temperature [19], excellent biocompatibility in bone contact [1], achieves excellent processes of osteoinduction [21], [22], [23], osteoconduction [24], [19], [25] and osseointegration [25], non-immunogenic and non-inflammatory behavior.

In general, hydroxyapatite has relatively good mechanical properties [26] with indicative values such as tensile strength 100-900 [MPa] [27], compressive strength 300-600 [MPa] [26] or 400-900 [28], flexural strength 60-115 [MPa] [26] or 115-200 [28] and high Young' modulus 35-110 [GPa] [27], 40-120 [GPa] [26], 80-110 [GPa] [28] , [29]. HA has Vickers hardness (HV) 600 [29], it is a fragile material [4] and with low fracture toughness [27]. Certain mechanical characteristics, such as tensile strength of an inappropriate value level and especially the brittle characteristic, limit the use of hydroxyapatite in the bulk form or in load-bearing orthopedic clinical applications [4], [27], [29]. LeGeros, R. and LeGeros, J. [18] report an improvement of some mechanical properties of hydroxyapatite, such as resistances and modulus of elasticity to compression and bending, with the increase of the sintering temperature of the ceramic material, but also a worsening of these properties together with the increase of the microporosity of the ceramic material. At the same time, the mechanical properties of hydroxyapatite worsen as the material's microporosity, grain size and amorphous phase increase. These reports are also supported by Fiume et al. [30].

Artificial hydroxyapatite can be obtained through different techniques/technological methods such as dry methods [18], [26], [30], wet chemical methods, [30], [26], [18], [30] and hydrothermal routes [26], [29], [18], [30].

HA and nano-HA bioceramics have a number of important clinical applications, but non-loadbearing [29], [4], such as bone and tooth repair [31], bone regeneration osseous defect [18], filling and repair of orbital floor fractures [30], [31], orthopedic and dental metal implants coating [32], [33], [18], maxillofacial and dental surgery [31], [34], [35], vertebrae replacement [32], that scaffold for bone tissue engineering applications [31], [35], implantable drug delivery systems [30], [31].

At the moment, several techniques are used for the manufacture of PLA/HA biocomposites such as extrusion process, extrusion and injection molding [36], solvent casting, hot pressing and 3D printing [5].

Mohamed [37] reports that following the combination of biological, mechanical, etc. advantages. of the PLA biopolymer with those of the HA bioceramic, PLA/HA biocomposite materials can be obtained with good biocompatibility, bioactivity, biodegradability and mechanical behavior that can be monitored for the intended purposes.

4 PLA/HA BIOCOMPOSITE MANUFACTURING BY EXTRUSION

4.1 Materials

Biocomposites PLA/15 mass% HA were produced from PLA Ingeo™ Biopolymer 6201D, from NatureWorks (Minnetonka, MN, UUSA), a pellet form having the characteristics [Jlbr], density of 1.24 g/cm3, melt index (g/10 min) 15-30, crystalline melt temperature [0C] 160-170, glass transition point Tg = 55-60 [0C], tenacity (g/d) 2.5-5.0 [17], [7], [36], [38] and from hydroxyapatite HA Sigma-Aldrich, Steinheim, Germany, in powder form (Fig. 1), with minimal controlled impurities, reference p.a., ≥ 90% (as Ca3(PO4)2, KT), product no. 101625633, [39]. In the case of the current research, in the PLA/HA mixture, hydroxyapatite was dosed in a mass proportion of 15% (Fig. 2).

Fig. 1. Dosing mass percentage 15% hydroxyapatite,

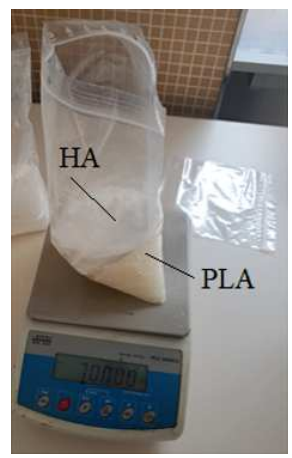

Fig. 2. Dosing mixture 15 mass% HA/PLA.

4.2 Preparation of PLA/HA composites

The PLA/15 mass%HA biocomposite was manufactured using the melt extrusion technique (viscous flow) of the mixture formed by PLA polymer and hydroxyapatite, in the established proportion.

A compounding extruder with two screws with four temperature control zones was used for extrusion (Fig. 3).

The technological process to manufacture the PLA/15 mass% HA biocomposite included the following main work stages:

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Fig. 3. Twin screw extruder.

- dosing mixture hydroxyapatite/polylactic acid in the proportion of PLA/15 mass% HA;
- thorough extruder cleaning;
- extruder preparation and adjustment: screw rotation speed 60 rpm; adjustment of working temperatures: 190°C (hopper), 195°C, 185°C and 200°C (mould);
- feeding the machine's hopper with the PLA/15 mass% HA mixture;
- extrusion mixture PLA/15 mass% HA;
- obtaining the PLA/15 mass% HA biocomposite material in melt form, and after cooling in the form of sticks (Fig. 4).

The PLA/HA biomaterial can later be processed by injection in order to make components/specimens.

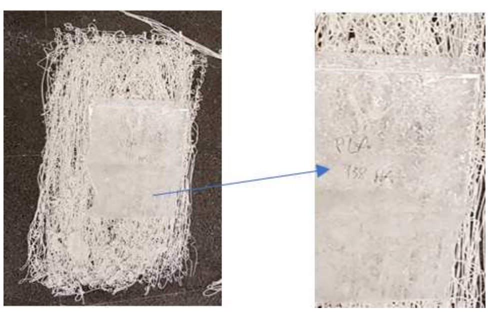

Fig. 4. Biocomposite material (compound) 15 mass% HA/PLA in the extruded state, in the form of sticks.

5. CONCLUSION

The PLA/HA biocomposite is made up, in certain quantitative proportions, of the biomaterials biopolymer polylactic acid PLA and bioceramic hydroxyapatite HA. These two biomaterials have excellent biological properties, good mechanical properties and good processing capabilities. The manufacturing technology by extrusion of the PLA/HA biocomposite allows the preservation of the characteristics of the two biomaterials, it is simple and does not require pretentious processing equipment, being able to be used in laboratory conditions as well as rigorous experimental research.

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Principalele caracteristici ale componentelor biomaterialelor și metoda de realizare prin extrudare pentru biocompozitele PLA/HA

Rezumat: Materialul biocompozit PLA/HA este un compozit medical format din biomateriale la care matricea este din biopolimer polilactic (PLA) și ranforsare din hidroxiapatită (HA). Cum PLA este complet bioresorbabil și bioceramica HA, în condiții normale, nu este biodegradabilă, biocompozitul PLA/HA este parțial bioresorbabil. Lucrarea prezintă principalele caracteristici a celor două componente ale biomaterialului PLA/HA: biopolimerul PLA și bioceramica HA, domeniile lor de utilizare în diferite aplicații medicale și tehnologia de realizare prin extrudare.

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