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ANALYSIS OF BIODEGRADABLE COMPOSITES MATERIALS

BY

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Abstract. This study highlights the use of biodegradable materials in the medical field for the prevention and repair of fractures, ruptures, and vascular or bone blockages. Various studies have been analyzed, demonstrating that these degradable biomaterials, when alloyed with different materials such as magnesium, zinc, and iron, have the ability to degrade in a controlled manner within the biological environment, facilitating tissue regeneration without leaving behind residues that could be harmful to the body after the resolution of medical issues. However, research results indicate that these materials have limited applicability due to their restricted degradation rate and the rapid loss of mechanical properties. To enhance their applicability, reinforcement elements such as biodegradable ceramic materials, nanodiamonds, metallic fibers, and advanced composites are integrated into the biodegradable matrix.

Keywords: biodegradable, biomaterials, metallic, medical.

1. Introduction

The development of society and the establishment of new living standards have led to an improvement in quality of life. Researchers are

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developing new materials and technologies for the production and implementation of implantable elements with superior clinical properties. In the tissue healing process, the short-term use of a support structure is necessary to prevent certain medical issues such as bone fractures or vascular blockages (Yang J. *et al*., 2018). This support is composed of a degradable biomaterial, allowing the implant to begin the degradation process after tissue healing is complete. The concept of biodegradation has long been present in medical treatments (e.g., sutures containing polymers), but degradable implants introduce a new approach, as they are made from metals and other materials, following the principle that "metallic biomaterials must be corrosion-resistant" (Yang H. *et al*., 2018).

The definition of biodegradable metals (BM) is expressed as follows: Biodegradable metals are those metals that, in a biological environment, tend to gradually corrode, generating an appropriate physiological response to the resulting corrosion products. Once they fulfill their role in supporting tissue regeneration, they completely dissolve without leaving residual implant traces (Liu *et al*., 2019). Therefore, BM must primarily contain essential metallic elements capable of being metabolized by the human body and exhibit a degradation rate compatible with the biological environment. Currently, biomedical devices are made of metallic materials in a proportion of 70–80%. These biomaterials play a major role in the medical field, primarily in supporting tissues subjected to mechanical loads, as well as in orthopedic, dental, and cardiovascular applications. Choosing the right material for a specific medical problem represent a key point in healing solutions of human wounds, Fig. 1.

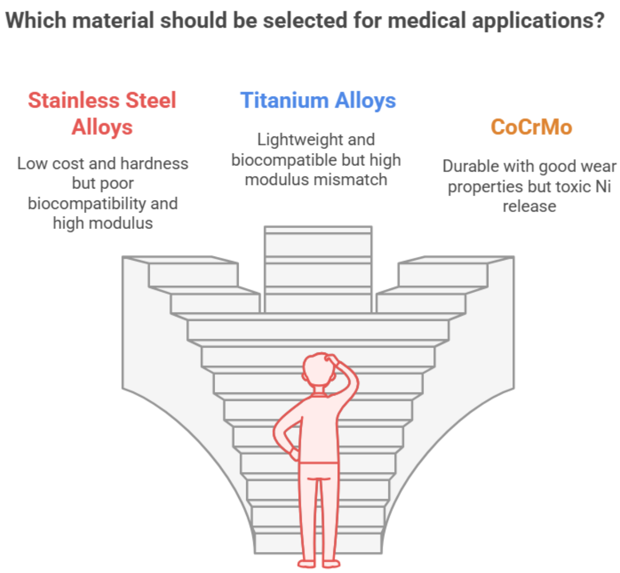

Fig. 1 – Choosing the proper solution for medical implants materials.

In 2007, attention was drawn to zinc alloys as a form of biodegradable biomaterial. Experiments began on Zn-Mg alloys containing between 35% and 45% magnesium. Various mechanical properties were analyzed, as well as their degradation behavior. During the investigations, it was concluded that pure Zn implanted in a blood vessel exhibits excellent corrosion resistance, making it a promising candidate for use in stents. Tests were conducted on Zn-based alloys in both controlled environments (in vitro) and biological systems (in vivo). The results showed that the mechanical properties were superior to those of magnesium- and iron-based alloys (Yang H. *et al*., 2018).

Yang and his colleagues analyzed the degradation behavior of a pure zinc stent in an abdominal aorta model in rabbits. The results showed that this type of stent exhibits excellent biocompatibility, with no significant inflammatory reactions, no platelet activation, no blood clot formation, and no vascular wall thickening. All these findings confirm that zinc can be a suitable material for biodegradable stents. In another animal experiment, it was discovered that by adding HA (hydroxyapatite) to pure zinc, the bone formation process was enhanced, and the implant's lifespan was extended (Yang H. *et al*., 2018).

Zinc-based materials have been developed to overcome several disadvantages associated with biodegradable magnesium- and iron-based materials. For example, magnesium-based materials tend to degrade too quickly, making them less effective in providing the necessary mechanical support. Additionally, they can lead to unwanted hydrogen gas accumulation around the implantation site. On the other hand, iron-based materials degrade much more slowly and form large corrosion deposits, which the human body struggles to eliminate. Over time, these deposits can become toxic to the organism. Furthermore, the ferromagnetic properties of iron-based materials make MRI investigations impossible after implantation (Li *et al*., 2014).

Compared to these materials, zinc-based materials exhibit an optimal degradation rate and excellent biocompatibility, making them a highly promising option for biodegradable implants. For this reason, zinc and its alloys have become a widely studied topic in the field of biodegradable metallic biomaterials (Li *et al*., 2014).

Due to their high biocompatibility and corrosion resistance, zinc-based materials are among the most widely used and sought-after options. Zinc is an essential element for the human body in specific amounts. It plays a crucial role in stimulating and maintaining bone mass, supporting enzymatic functions, promoting human growth and development, and contributing to reproductive genetics, immune functions, and endocrinology, among other physiological processes.

However, pure cast solidified zinc exhibits the following mechanical properties: (i) a tensile strength of 20 MPa and (ii) an elongation of 0.2%. Due to specific standards regarding the mechanical properties of materials used in the development of orthopedic implants, the mechanical values of pure zinc are considered suboptimal, ranking lower in terms of strength and toughness.

Li and his team reported that adding alloying elements such as Mg, Ca, and Sr can enhance the tensile strength of zinc alloys; however, the resulting elongation remained below 10%. These studies demonstrate that while alloying contributes to increasing the mechanical strength of zinc, its plasticity is considerably reduced, which limits the material's applicability (Li *et al*., 2014).

Nanostructured reinforced materials, such as graphene nanoplatelets (GNS), consist of graphene layers bonded through covalent bonds and van der Waals forces between adjacent carbon atoms. These materials exhibit a mechanical strength of 130 GPa while also demonstrating high biocompatibility in contact with the human body.

Biodegradable materials serve as a fundamental support for host tissues undergoing regeneration, as they naturally degrade within the physiological environment and dissolve entirely after sufficient tissue healing, in contrast to non-degradable biomaterials. Furthermore, biodegradable materials contain essential trace elements, without which the human body cannot sustain its biological functions.

Iron (Fe), zinc (Zn), and magnesium (Mg)-based materials have been extensively studied as biomaterials (BM) due to their high potential in the field of orthopedics. The microstructure of zinc alloys consists of a predominant matrix phase (α-Zn) along with secondary phases, commonly referred to as intermetallic phases, which are generally characterized by high hardness and pronounced brittleness.

The mechanical properties of zinc alloys are significantly influenced by the presence of intermetallic phases, as well as their volumetric fraction, size, and distribution within the Zn matrix. Additionally, the microstructural characteristics of these alloys are directly dependent on the manufacturing and processing methods employed.

A potential solution to this challenge could be the use of metal matrix composites (MMC) based on magnesium alloys. Over the past decade, MMCs have gained considerable interest, particularly in the automotive and transportation sectors, due to their superior specific stiffness, high tensile and creep resistance, and reduced susceptibility to galvanic corrosion (Jia *et al*., 2020).

Mechanical properties such as Young's modulus, tensile strength, and corrosion resistance provide various advantages for the use of metal matrix composites.

The most commonly used natural bone component, due to its low solubility in the human body, is hydroxyapatite (HA). These HA particles are employed as reinforcement elements in ceramic matrix materials based on zinc (Witte *et al*., 2007).

2. Types of matrices used in biodegradable composite materials

The most commonly used matrix materials for biodegradable composite materials are magnesium (Mg), zinc (Zn), and iron (Fe), due to their mechanical properties and biocompatibility.

Magnesium has a low density and mechanical properties similar to those of bone but degrades rapidly. Zinc exhibits a stable degradation rate, whereas iron has high mechanical strength but a relatively slower degradation rate (Yang H. *et al.*, 2018).

In a study conducted by Yu and his collaborators, zinc-based composites reinforced with nanodiamonds (ND) were developed, representing a novel type of zinc-based metal matrix composite (BMMC) for biomedical applications. These composites were fabricated using powder metallurgy techniques, employing pure zinc and nanodiamond powders, which were sintered under various conditions to achieve distinct structural effects (Yu *et al.*, 2014).

According to the standard electrode potential values – Mg (2.37V) > Zn (0.763V) > Fe (0.440V) (relative to SHE) – zinc exhibits a higher corrosion rate than iron but a lower rate than magnesium. Given that magnesium-based metal matrices require a slower degradation rate, while iron-based matrices require an accelerated degradation rate, zinc-based metal matrices are considered the "rising stars" of biodegradable biomaterials (Jia *et al.*, 2020).

The alloys used for the development of biodegradable composite elements are exemplified as follows:

1) **Mg-Ca, Mg-Zn, Mg-Sr, Mg-RE** (These alloys are used due to their mechanical properties and biocompatibility. Alloying elements enhance mechanical strength and corrosion resistance, making them ideal for orthopedic applications (e.g., magnesium matrix alloys, particularly the AZ91D alloy) (Li *et al.*, 2014).

2) **Fe-Mn, Fe-W, $Fe\text{-}Mn_{30}\text{-}Si_6$** (Iron is combined with other alloying elements to improve its degradation rate and mechanical properties. Iron-based alloys are ideal for biodegradable stents due to their high strength and ductility (Li *et al.*, 2014).

3) **Zn-Mg** (Zinc plays a crucial role due to its biocompatibility and controlled degradation properties. These alloys are promising for biomedical applications, such as temporary implants (Li *et al.*, 2014).

4) **Mg-Zn** alloys (Magnesium-zinc alloys are used to control the degradation rate and enhance mechanical properties (Haghshenas *et al.*, 2017).

5) **Mg-Ca** alloys (Magnesium-calcium alloys are used to achieve excellent biocompatibility and stimulate bone formation (Haghshenas *et al.*, 2017).

6) **Mg-REE** alloys (Magnesium alloys with rare earth elements (REE), such as yttrium (Y), cerium (Ce), and lanthanum (La), are used to stabilize the metallic structure and control the corrosion rate (Haghshenas *et al.*, 2017).

Studies have shown that galvanized zinc coatings are susceptible to degradation under various environmental conditions, including industrial and marine environments. Additionally, galvanized steel is often painted, and proper preliminary treatments are required to ensure optimal paint adhesion.

In this context, numerous attempts have been made to optimize the composition of zinc coatings to enhance their durability. Alloying zinc with other elements, such as cobalt (Co), nickel (Ni), iron (Fe), and manganese (Mn), has proven to be an effective method for increasing the protective effect of these coatings.

Table 1

The most common materials for orthopedic (Hussain *et al.*, 2022)

Material	Applications	Advantages	Disadvantages	Challenges
Stainless Steel Alloys	Support rods, nails, plates, screws, wires, pins, fixation elements, and cables	Low cost, excellent hardness, and mechanical strength	High modulus, mismatch of mechanical properties with bone, reduced biocompatibility	Improving biocompatibility, wear resistance, and corrosion resistance
Titanium Alloys	Rods, support rods, nails, plates, screws, wires, pins, and fixation elements	Low weight, acceptable biocompatibility, and corrosion resistance	High modulus, mismatch of mechanical properties	Enhancing biocompatibility, wear performance, and mechanical property stability
Cobalt-Chromium-Molybdenum (CoCrMo)	Contact surfaces, plates, and wires	High durability, acceptable biocompatibility, and improved wear and corrosion properties	Poor machinability, mechanical property mismatch, and biological toxicity due to Ni release	Improving biocompatibility, wear performance, and metal friction resistance
Alumina/Zirconia Composite	Contact surfaces	High biocompatibility and good wear properties	Poor machinability and high fracture rate	Improving ductility
Polyethylene/UHMWPE	Contact surfaces	Acceptable biocompatibility and good wear properties	Reduced biocompatibility, low mechanical properties, and wear debris	Enhancing durability and longevity

In addition to alloying, surface modification has also been adopted to enhance the corrosion resistance of the zinc coating, primarily through the use of chemical conversion coatings and organic layers. Representative surface modification methods for zinc-based alloys used in industrial applications are illustrated in Fig. 2 (Yuan *et al.*, 2022).

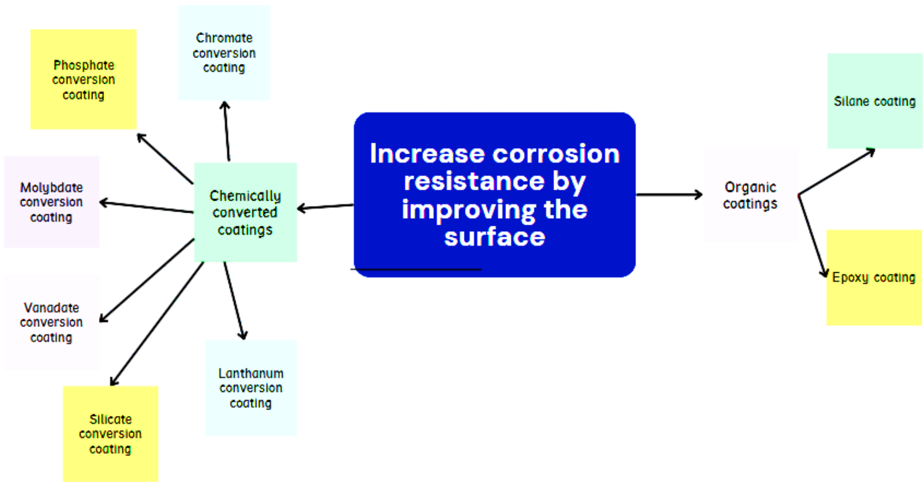

Fig. 2 – Representative surface modification methods for industrial Zn-based alloys (Yuan *et al.*, 2022).

3. Main reinforcement elements used in the development of biodegradable composite materials

The biodegradable metallic composite materials analyzed in this study use magnesium (Mg), zinc (Zn), and iron (Fe) as matrices. These materials are utilized due to their biocompatibility, their ability to degrade in a controlled manner within the biological environment, and their role in facilitating tissue regeneration without leaving harmful residues after the implant fulfills its function (Yang J. *et al.*, 2018). However, the applicability of these materials is limited by their high degradation rate and the rapid loss of mechanical integrity. To counteract these disadvantages, reinforcement elements are integrated into the biodegradable metal matrix, contributing to the improvement of mechanical properties, biocompatibility, and corrosion resistance. These reinforcements include biocompatible ceramic materials, nanodiamonds, metallic fibers, and advanced composites, each playing a crucial role in optimizing the performance of these materials.

By employing various processing techniques, such as powder metallurgy, cold pressing, or sintering, complex materials are obtained, capable of meeting current biomedical requirements. Research findings demonstrate the high performance of reinforcement processes in developing safe and efficient implants tailored for orthopedic applications. These solutions provide viable alternatives for the regeneration of fractured or lost tissues, presenting a promising and advantageous option compared to conventional transplants or various traditional interventions (Yang J. *et al*., 2018).

Biocompatible ceramic materials:

Hydroxyapatite (HA), Zinc Oxide (ZnO), TiO_2: These materials are added to enhance the mechanical properties and corrosion resistance of biodegradable materials, reducing the degradation rate and increasing compatibility with biological tissues. Hydroxyapatite, being a mineral component of bone, improves osseointegration.

Metal powders (e.g., Mg) are mixed with ceramic materials using powder metallurgy technology, followed by compacting the mixture at a low temperature and sintering it in a controlled atmosphere to form a solid composite. This process results in increased hardness, improved corrosion resistance, and enhanced biocompatibility (Hussain *et al*., 2022).

Magnesium-based composites with HA have been produced using powder and sintering techniques, with HA concentrations of 5%, 10%, and 15%. Among these, Mg-5% HA demonstrated the best corrosion resistance due to its porous structure. For example, Mg-HA with 5% HA exhibits superior corrosion resistance compared to pure Mg. Composite materials are reinforced with hydroxyapatite (HA) particles in a 20% volume fraction. The uniform distribution of HA particles helps improve the mechanical properties and corrosion behavior of the composites.

Specifically, a 30% HA weight fraction can be used to enhance the biocompatibility and osteoconductivity of composite materials. This percentage creates a balance between the mechanical strength of the composite and its ability to promote bone formation around the implant, leading to better integration with surrounding tissues while ensuring corrosion resistance (Hussain *et al*., 2022).

Additionally, using 20% ZnO in combination with magnesium can form an Mg-MMC composite through an in-situ reaction. This composite has shown improved corrosion resistance and superior mechanical properties due to grain refinement. The addition of TiO_2 and MgO in Mg/HA/TiO_2 composites further enhances corrosion resistance and ductility (Yang H. *et al*., 2018).

Nanodiamonds (ND): In terms of the manufacturing process, Zn powder is combined with nanodiamonds through mixing, with the mixture being cold-pressed and sintered to obtain a compact structure. Reinforcement with metallic fibers, such as Mg alloy fibers (e.g., AZ31) integrated into composites, is employed to improve tensile strength and material elasticity. These fibers neutralize acidic byproducts resulting from the degradation of adde. To enhance mechanical strength and material stability, the fibers are embedded in a biodegradable polymer matrix (e.g., PLA or PLGA), compacted, and subjected to thermal treatments to bond the fibers to the matrix (Yang J. *et al*., 2018).

Reinforcement using multiple nanocomposites, such as Mg/HA/TiO_2 and Mg-Zn intermetallics, enables the combination of various materials to create reinforcements with superior properties, such as high strength and controlled degradation behavior. From a technological perspective, these materials are processed through high-energy milling, followed by multi-stage compaction and sintering to obtain composites with enhanced strength and improved biocompatibility, such as Mg-MMC, which exhibits significant corrosion resistance (Yang H. *et al*., 2018).

MgO and MgZn Intermetallics, Fe_2O_3, ZnO: These reinforcements are used to enhance mechanical strength and reduce the corrosion rate. MgO contributes to increased corrosion resistance by forming a protective layer on the surface of the metallic matrix (Liu *et al*. 2019).

Nano-graphene, Carbon Nanoparticles, Sr, Ca, Mn, and other inorganic reinforcements: These also include graphene particles or other nanometric particles to enhance durability and electrical properties. They are used to improve mechanical properties and increase wear resistance (Krishnan *et al*., 2022). Nano-graphene is utilized to enhance mechanical strength and provide good electrical conductivity to the material (Yang H. *et al*., 2018).

The percentage of elements such as Mn ranges between 0.1% and 1%. Manganese has been added in varying proportions to zinc alloys to improve mechanical properties and biocompatibility. Concentrations of 0.1%, 0.4%, and 0.8% by weight were used. The results showed that the addition of manganese improved the elongation of the zinc alloy, reaching 83.96% in the case of the alloy containing 0.8% Mn. The addition of calcium in alloys such as AZ91Ca and AZ61 enhances the formation of calcium phosphates on the alloy surface, which improves corrosion resistance (Yusop *et al*., 2012).

Zinc Oxide (ZnO) nanoparticles and glass fibers: These reinforcements are used to enhance hardness and mechanical strength. ZnO nanoparticles have been added in small proportions, typically below 2%, to achieve significant improvements in mechanical properties and to control degradation.

Tri-Calcium phosphate (β-TCP): Used to enhance biocompatibility and mechanical strength. For example, an Mg-Zn_2-$Ca_{0.5}$ composite was reinforced with 1% β-TCP, resulting in an 18% increase in hardness.

Calcium Polyphosphate (CPP): CPP is a ceramic reinforcement with good biocompatibility and osteoconductivity, used in weight proportions of 2.5%, 5%, 7.5%, and 10%. At concentrations above 5%, particle agglomeration and the formation of porosity were observed (Haghshenas *et al*., 2017).

Fluorapatite (FA): Fluorapatite has been used to reinforce AZ91 composites in volume fractions of 10%, 20%, and 30%. FA particles were relatively uniformly distributed within the matrix and contributed to an overall increase in the composite's hardness (Haghshenas *et al*., 2017).

Cellulose Nanocrystals (CNC) and Other Metallic Nanoparticles: (such as TiO_2 and Ag nanoparticles) are often incorporated to ensure compressive strength and corrosion stability (Livesey *et al*., 2023).

Graphene Nanosheets (GNS) as Reinforcement for the Zinc Matrix: Graphene, a two-dimensional carbon nanomaterial with a hexagonal honeycomb structure, is used due to its excellent mechanical properties and its ability to enhance both strength and plasticity, as well as the overall composition of the material. The GNS content was varied to study its effects on the mechanical and structural properties of the composites: 0.3% and 0.7% volume fractions of GNS were used to reinforce the zinc matrix. These values were optimized to balance increased mechanical strength while maintaining adequate plasticity (Krishnan *et al.*, 2022).

4. Conclusions

There is a significant potential for improving the properties of biodegradable iron-, zinc-, or magnesium-based alloys by reinforcing their matrices with non-metallic, ceramic, or metallic elements. The role of these reinforcements includes:

- Stabilizing the degradation rate;
- Enhancing the corrosion resistance of magnesium-based matrices or reducing the corrosion resistance of iron-based ones;
- Improving the mechanical properties of zinc matrix alloys;
- Optimizing composite hardness through the uniform distribution of fluorapatite particles;
- Enhancing durability through the use of nanographene;
- Maintaining plasticity and mechanical strength due to the addition of graphene (0.3% and 0.7%) in the reinforcement process of the zinc matrix.

The use of advanced processing technologies such as cold pressing, sintering, reinforcement techniques, and powder metallurgy demonstrates the ability to develop complex materials tailored to modern biomedical requirements. These materials contribute to reducing risks and shortening the healing process. By optimizing these materials, a high-quality and safe alternative can be established, leading to new and innovative research directions in advanced medical fields.

REFERENCES

Haghshenas M., *Mechanical characteristics of biodegradable magnesium matrix composites: A review,* Journal of Magnesium and Alloys, 5, 189-201, (2017).

Hussain M., Khan S.M., Al-Khaled K., Ayadi M., Abbas N., Chammam W., *Performance analysis of biodegradable materials for orthopedic applications*, Materials Today Communications, 31, 103167, (2022).

Jia B., Yang H., Han Y., Zhang Z., Qu X., Zhuang Y., Wu Q., Zheng Y., Dai K., *In vitro and in vivo studies of Zn – Mn Biodegradable metals designed for orthopedic applications*, Acta Biomaterialia, 108, 358-372, (2020).

Krishnan R., Pandiaraj S., Muthusamy S., Panchal H., Alsoufi M.S., Ibrahim A.M.M., Elsheikh A., *Biodegradable magnesium metal matrix composites for biomedical implants: synthesis, mechanical performance, and corrosion behavior - a review*, Journal of Materials Research and Technology, 20, 650-670, (2022).

Li H., Zheng Y., Qin L., *Progress of biodegradable metals*, Progress in Natural Science: Materials International, 24, 414-422, (2014).

Liu Y., Zheng Y., Chen X.H., Yang J.A., Pan H., Chen D., Wang L., Zhang J., Zhiu D., Wu S., Yeung K.W.K., Zeng R.C., Han Y., Guan S., *Fundamental Theory of Biodegradable Metals—Definition*, Adv. Funct. Mater., 29, 1805402, (2019).

Livesey T.C., Mahmoud L.A.M., Katsikogianni M.G., Nayak S., *Metal–Organic Frameworks and Their Biodegradable Composites for Controlled Delivery of Antimicrobial Drugs*, Pharmaceutics, 15, 274, (2023).

Witte F., Feyerabend F., Maier P., Fischer J., Stormer M., Blawert C., Dietzel W., Hort N., *Biodegradable magnesium–hydroxyapatite metal matrix composites*, Biomaterials, 28, 2163-2174, (2007).

Yang H., Qu Z., Lin W., Wang C., Zhu D., Dai K., Zheng Y., *In vitro and in vivo studies on zinc-hydroxyapatite composites as novel biodegradable metal matrix composite for orthopedic applications*, Acta Biomaterialia, 71, 200-214, (2018).

Yang J., Guo J.L., Mikos A.G., He C., Cheng G., *Material Processing and Design of Biodegradable Metal Matrix Composites for Biomedical Applications*, Annals of Biomedical Engineering, 46, 9, 1229-1240, (2018).

Yu M., George C., Cao Y., Wotton D., Zhou J., *Microstructure, corrosion, and mechanical properties of compression-molded zinc-nanodiamond composites*, J. Mater. Sci., 49, 3629-3641, (2014).

Yuan W., Xia D., Wu S., Zheng Y., Guan Z., Rau J.R., *A review on current research status of the surface modification of Zn-based biodegradable metals*, Bioactive Materials, 7, 192-216, (2022).

Yusop A.H., Bakir A.A., Shaharom N.A., Abdul Kadir M. R., Hermawan H., *Porous Biodegradable Metals for Hard Tissue Scaffolds: A Review*, International Journal of Biomaterials, (2012).

ANALIZA MATERIALELOR COMPOZITE BIODEGRADABILE

(Rezumat)

Acest studiu evidențiază utilizarea materialelor biodegradabile în domeniul medical pentru prevenirea și repararea fracturilor, rupturilor și blocajelor vasculare sau osoase. Au fost analizate diverse studii care demonstrează că aceste biomateriale degradabile, atunci când sunt aliate cu diferite materiale precum magneziu, zinc și fier, au capacitatea de a se degrada într-un mod controlat în mediul biologic, facilitând regenerarea țesuturilor fără a lăsa în urmă reziduuri care ar putea fi dăunătoare organismului după rezolvarea problemelor medicale. Cu toate acestea, rezultatele

cercetărilor indică faptul că aceste materiale au o aplicabilitate limitată din cauza ratei limitate de degradare și a pierderii rapide a proprietăților mecanice. Pentru a le spori aplicabilitatea, în matricea biodegradabilă sunt integrate elemente de armare precum materiale ceramice biodegradabile, nanodiamante, fibre metalice şi compozite avansate.