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Research Article

## Effect of ZrO<sub>2</sub> on morphological and adhesion properties of hydroxyapatite reinforced poly- (lactic) acid matrix hybrid coatings on Mg substrates

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### Abstract

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The study aimed to reduce the high biodegradability of magnesium (Mg) as well as local infections due to the hydrogen gas formation because of pH increase around biological tissues. Composite coatings of poly- (lactic acid)/hydroxyapatite (PLA/HA) are commonly employed, although their adhesive strength to the metallic substrates are insufficient. In this study, PLA/HA-zirconia (ZrO<sub>2</sub>) hybrid coatings were successfully coated on Mg surfaces by means of dip-coating method to enhance this insufficient adhesion strength at the coating - Mg substrate interface with desired surface morphology. Scanning electron microscopy (SEM) micrographs were used to examine the surface morphologies of the coatings, both energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analyses to characterize them elementally and phase formation, respectively. Micro-Vickers hardness measurements were taken on coatings and tape tests were carried out following ASTM D3359 standard to reveal the adhesion strengths. The agglomeration size on the coating surfaces decreased as the ZrO<sub>2</sub> reinforcement increased, and the Mg surface was entirely sealed with 30 wt% ZrO<sub>2</sub> reinforcement, according to the SEM micrographs. The presence of both HA and ZrO<sub>2</sub> in the coating was confirmed by XRD analysis, which also demonstrated that it was crystalline. Adhesion strengths were determined 1B, 3B, 4B, and 5B for HA, HA-10%ZrO<sub>2</sub>, HA-20%ZrO<sub>2</sub>, and HA-%30 ZrO<sub>2</sub> reinforced hybrid coatings, respectively. As a result, it was concluded that hybrid coatings which reinforcements of ZrO<sub>2</sub> particles to the PLA/HA composite coatings reduced agglomeration and enhance the coating - substrate adhesion at the interface.

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## 1. Introduction

Materials, used in a living environment, are expected to be able to withstand mechanical reactions (muscle movements and body weight), chemical interactions (corrosion and degradation), factors originating from temperature and radiation, and osseointegration (interacting with tissues) properties. In this way, biomaterials can be defined as any material that is safe, harmless, economically, and physiologically acceptable to the body during use as a part of the body [1]. They are also in contact with the surrounding living tissues from the moment they are placed in the body and fulfil the task of the missing limb. Biocompatibility is also another important term that can be defined as the chemical interaction of this biomaterials with body fluids during use in the body and whether the physiological consequences of these interactions cause harm to the body [2]. For this reason, it is a prerequisite for the biomaterial to be accepted by the environment in which it is defined as biocompatible.

Metals and their alloys are frequently used in biomedical fields as biomaterials. Today the most commonly used metallic biomaterials are titanium and its alloys (such as commercially pure titanium, Ti6Al4V), stainless steels (such as 316L), and cobalt-chromium (such as Co-Cr) alloys [3]. They are used in the body in many places such as hip prostheses, orthopaedic applications, heart valves, stent applications, and dental implants [4]. These materials also have a high load-carrying capacity with sufficient wear and corrosion properties [5,6]. Thus, the plastic deformation of the metallic biomaterials will be delayed and their life cycle can be extended in the body. On the other hand, two features have come to mind in terms of compatibility with the surrounding tissues. The first one is structural compatibility, which means the most suitable adaptation of the material to the mechanical behaviour of body tissues. When we consider the structural integrity, it is necessary to mention the Young's modulus mismatch (Wolf's law) between the implant and the bone. As Wolf's law mentioned, when Young's modulus (also known as the Stress-Shielding effect) between bone and metallic biomaterial is increased, osteoporosis which is inadequate regeneration of bone can occur [7,8]. The second one is surface compatibility: it means that a biomaterial should have physically, chemically, and tribologically suitable for tissues. Magnesium (Mg) and its alloys are preferable among metallic biomaterials for low density, lower Young's modulus, and high specific strength features [9]. On the other hand, Mg and its alloys are not very advanced in terms of surface compatibility due to their high biodegradability properties. One of them can be explained with its high corrosion tendency. As a result of corrosion that may occur on the Mg implant, the material loss may occur which will reduce the strength of the implant, and more importantly, the interaction of metal ions with the surrounding tissues may lead to undesirable results [10]. On the other hand, the high degradation rate of Mg in the physiological environment is encountered as a significant drawback in clinical applications [11]. Some reactions occur because of the interaction of Mg with the surrounding tissues which most important one is the formation of H<sub>2</sub> gas ( $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$ ) resulted in undesired interactions at implant-tissue interface [12]. Furthermore, the formability of this reaction increased with implant-tissue interaction with body fluids, because of this reason, it is very important to seal Mg and its alloys from surrounding tissue with biological compounds. However, as a result of recent studies, especially coating with organic polymers, these desired surface compatibilities can be increased [12-15].

Polymer coatings are preferred in many applications to ensure that the interface to be formed between the implant material and the living tissue has the desired properties [16]. Thin and enhanced adhesion properties of polymeric coatings not only isolate the material against direct contact with body fluid but also provide the desired biological response. For this reason, choosing the right polymer coating can both improve the corrosion behaviour of the Mg and prevent any complications during the application. Poly- (lactic) acid (PLA) has received considerable attention due to its controllable properties such as biodegradability - biocompatibility, well-defined formulation techniques, easy handling, thermal barrier properties, and high machinability with traditional technologies (extrusion, injection moulding, compression moulding, and blow moulding) [17,18]. Certain properties such as poor mechanical properties of PLA can be increased with composite blending, co-polymerization, etc. [19]. Owing to these advantages of PLA, absorbable fixation components have been studied for decades experimentally before clinical use [20]. The mechanical properties and bioactivity of PLA materials are decisive for bone regeneration and degradation rate [17]. On the other hand, as a result of PLA's high hydrophobic properties, adequate wettability cannot be achieved during implant-tissue interaction [21]. For this reason, researchers have generally been carried out on PLA-hydroxyapatite (HA: Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) composites [22]. Owing to its similarity to bone structure in terms of calcium: Ca- and phosphor: P- with the Ca/P ratio (1.67), HA is frequently used in biomaterial applications, especially to increase the biocompatibility of

coating applications [23–25]. Studies conducted by many researchers aim to use the advanced biocompatibility features of HA together with the high corrosion resistance and adhesion strength of PLA in coatings. Nowadays, researchers have widely investigated hybrid composites to further improve these properties by addition of various reinforcements to PLA/HA coatings [11,26,27]. Zirconia ( $ZrO_2$ ) ceramics have been commonly used as coating reinforcements due to its non-cytotoxicity to the human body (except for an acidic environment like an oral cavity), non-degradable *in-vivo* conditions, high fracture toughness, and chemical durability [16].

The method used in the surface coatings should be selected by taking into consideration of thickness, surface roughness, crystallinity, price of the equipment, and safety. Recently, many methods commercially used for surface coatings on metallic materials such as plasma spray [28], cold spray [29], magnetron sputtering [30], electrochemical deposition [31], and dip-coating [23,24]. The dip-coating method is notable among them since not dependent on the shape, high purity and homogeneity can be obtained, and inexpensive [32]. The dip-coating method can be defined as immersing the substrate material to be coated into the prepared solution under certain atmospheric conditions and speed and then removing it again. When the material is withdrawn from the coating liquid, a stable liquid film is carried along with the material surface due to surface tensions. To obtain a thin film on the material surface, the thin liquid film must be evaporated without allowing any chemical reaction. Normally, post-treatments such as curing or sintering are required to obtain thin coatings [33]. With the dip-coating method, the coating can be obtained in a few seconds depending on the volatile components. In this way, the method is frequently used in industrial and laboratory applications due to its simple processing stages, and high coating quality.

As stated a recent study conducted by Harb *et al.* [34], suggested that poly (methyl methacrylate) (PMMA)- $TiO_2$  and PMMA- $ZrO_2$  reinforcement to organic-based additives such as HA and  $\beta$ -tricalcium phosphate ( $\beta$ -TCP) could enhance implants surface features. They stated that the surface roughness, hydrophilicity, surface free energies, and corrosion resistance were increased with HA reinforced PMMA- $ZrO_2$  coatings. While no adhesion test was performed in the study, the effect of the  $ZrO_2$  fraction was also not investigated. Unlike the aforementioned study, PLA/HA- $ZrO_2$  hybrid coatings were successfully coated on Mg substrates as a possible candidate for biomedical applications in this study. Investigation of both morphological and adhesive effects of  $ZrO_2$  in PLA/HA composite coatings on Mg substrates was investigated in detail. In this way, it was aimed that the hybrid composite coatings which were reinforced with both HA and  $ZrO_2$ , prolonged the lifetime of the implant.

## 2. Materials and Methods

### 2.1. Substrate and Coating Preparation

In all coated specimens, high purity (99.9%) Mg was employed as the coating substrate (Merck, 7439-95-4). Cylindrical specimens were cut from rod-shaped Mg with a precision cutter machine (Metkon, Micracut 152) in dimensions of  $12.7 \times 3$  mm. All substrates were sandblasted (Mikrodental, MKK975) with  $250 \mu m$  sized  $Al_2O_3$  particles at 6 bar for 1 min to promote adhesion at the coating-substrate interface [32]. A series of ultrasonic surface cleaning in distilled water and ethanol for 15 min each was applied for degrease and remove sand particles from the substrates. Chloroform has been used in coating procedures to dissolve PLA. While the size of irregular shaped and agglomerated HA powders ranges from 3–5  $\mu m$ , sharp-edged  $ZrO_2$  powders have a maximum size of 49  $\mu m$  and a purity of 99.7% (Fig. 1). PLA was first dissolved in chloroform at room temperature for 2 h. To synthesize PLA/HA composite coatings HA reinforcement was held constant at

50% by weight. On the other hand, 10, 20, and 30 wt%  $ZrO_2$  reinforcement to HA balanced of 50 wt% (Table 1). Both possible delamination and sedimentation occurrence were effective in using the 50 wt% PLA fraction in the coatings. The hybrid mixture was stirred for another 2 h to ensure uniform dispersion of the reinforcement powders (HA and  $ZrO_2$ ) in the PLA. To avoid particle agglomeration, it was then homogenized for 5 min in an ultrasonic homogenizer (MTI, MSK-USP-3N). The coating was carried out by using the dip-coating method, substrates kept in hybrid mixtures for 5 s, and pulled up at  $45^\circ$  to prevent clumping at the corners of Mg substrates. Finally, to prevent absorbing moisture from the atmosphere, coatings were stored in a desiccator containing silica gel at room temperature until the tests were carried out. On behalf of clarification, the abbreviations for PLA/HA and 10, 20, and 30 wt%  $ZrO_2$  reinforced PLA/HA- $ZrO_2$  coatings will be used as PH, PHZ1, PHZ2, and PHZ3, respectively (Table 1).

Table 1. Abbreviations and compositions of coatings

Substrate	Coatings	Abbreviation	Composition (wt%)		
			PLA	HA	$ZrO_2$
Magnesium	PLA/HA	PH	50	50	0
	PLA/HA- $ZrO_2$ 10 wt%	PHZ1	50	40	10
	PLA/HA- $ZrO_2$ 20 wt%	PHZ2	50	30	20
	PLA/HA- $ZrO_2$ 30 wt%	PHZ3	50	20	30

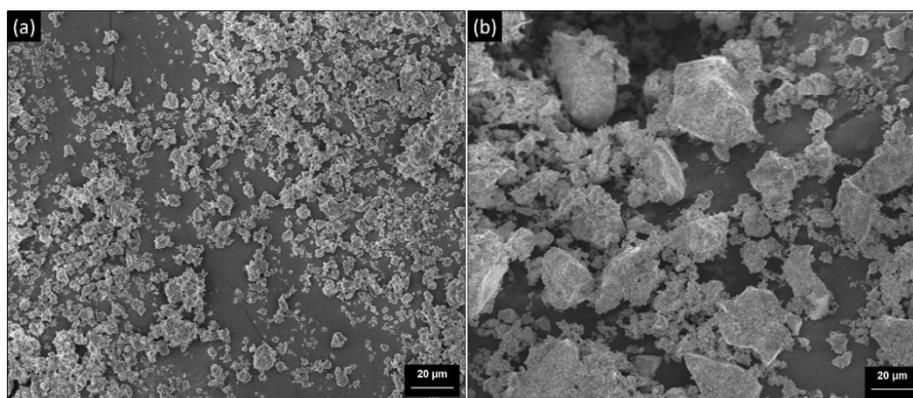


Fig. 1 SEM morphologies of the (a) HA and (b)  $ZrO_2$  powders

## 2.2. Characterization

The morphological changes on coatings were investigated by scanning electron microscopy (SEM, Zeiss Sigma 300). In SEM morphological investigations, a thin Au-Pd coating was applied to coatings to increase the electrical conductivity of coatings for better observation. Energy dispersive spectroscopy analysis (EDS, Oxford INCA) was used for the elemental evaluation of coated Mg substrates which attached to the SEM. The phase analysis of hybrid composite coatings was determined using X-ray diffraction (XRD, PANalytical Empyrean) analysis. XRD analysis was carried out with a K-tube and a step rate of 0.02 at a wavelength of 1.5406 (between  $25$  and  $55$   $2\theta$  angles). Following adhesion tests, optical microscopy (OM) was used to better clarification of the adhesive behaviour of coatings.

### 2.3. Micro-Vickers and Adhesion Tests

The micro-Vickers hardness (DMHV100EDV, HARDWAY) device was used to determine the hardness values of the coatings. In the hardness measurements, a load of 100 gf (HV.0,1) was applied for 20 seconds and the hardness value was measured from five different regions. Adhesion testing was conducted according to ASTM D3359 [35]. In short, the test method covers the evaluation of the adhesion strength of the coatings on the substrate, using pressure-sensitive tape with several scratches. Adhesion tests were conducted with method B which claimed that firstly lattice patterns with numerous scratches (preferably more than 6) in every 90° directions were made on a coated substrate then pressure-sensitive tape (Elcometer 99, Elcometer, USA) is applied over scratches, finally removed from coated specimens. Adhesion resistance was evaluated by comparison with local delamination of coatings as visually. According to the separation rate of coatings from substrates as spatially, less than 0%, 5%, 5-15%, 15-35%, 35-65% and greater than 65% were defined as 5B, 4B, 3B, 2B, 1B, and 0B, respectively.

### 3. Results and Discussion

In Fig. 2a-d, SEM surface morphology images of PH, PHZ1, PHZ2, and PHZ3 coatings are presented, respectively. The first striking point of the SEM surface morphologies is the presence of agglomeration structures on all surfaces. While this agglomeration size is large in the PH coating, it is seen that the agglomeration size decreases with the increase of ZrO<sub>2</sub> reinforcements to PLA/HA composite composition (Fig. 2b, c). Moreover, with the 30% ZrO<sub>2</sub> (PHZ3) reinforcement, it was determined that these agglomerations were considerably reduced and were almost completely covered with PLA. Similar surface morphologies have been obtained by other researchers [12]. Considering the general morphology, it is predicted that while the smaller size of agglomeration is a desirable morphology for implant-tissue interaction in the biomedical usage of coatings, the biodegradability may increase but the adhesion strength of the coatings, which important parameter for coatings, may decrease. On the other hand, it has been stated in other studies that these properties will increase in PHZ3 coatings as a result of both the reduced agglomeration size and the fact that PLA completely covers the Mg surfaces [12]. It was concluded that ZrO<sub>2</sub> decreased the agglomeration rate between PLA/HA as a result of the increasing weight fraction. It is thought that the total agglomeration on the surface decreases as a result of the particle size of ZrO<sub>2</sub> is quite large compared to HA and resulted in HA agglomeration around the ZrO<sub>2</sub> particles. The main reason for this is thought to be inorganic - organic interactions between ZrO<sub>2</sub> and HA [36]. The increase in the tendency of this interaction with the increasing ZrO<sub>2</sub> fraction may have resulted in SEM morphologies which are presented in Fig. 2b-d. It can be said that morphological changes in PLA, HA, and ZrO<sub>2</sub> composition are highly affected by the components and their fractions. On the other hand, it is thought that the decrease in micropores on the surface together with the increasing ZrO<sub>2</sub> reinforcement will increase the stability of the coatings in the body fluid, thus increasing the service life of the implant (Fig. 2a-d). According to a study conducted by Jin *et al.* [11], similar surface morphology was obtained with the increasing PLA fraction in the coating, while it was mentioned that the completely sealed Mg would increase the possible corrosion resistance. Unlike the aforementioned study, it is thought that the similar coating morphologies obtained with the increase of the ZrO<sub>2</sub> fraction rather than increasing the PLA fraction will be more effective on the adhesion strength.

The EDS analyses carried out to reveal the elemental compositions in the coatings are given in Figs. 3a-b. As seen in Fig. 3a, in the analysis of the point indicated by the white square, no elemental finding was found for the base material Mg, while Ca and P elements were found due to their HA structure. In Fig. 3b, in EDS analyses taken from a surface similar to the PHZ morphology (Fig. 2d), the Zr element was also found in addition to Ca and P.

Among these findings, the presence of Ca, P, and Zr in the structure as well as the absence of Mg substrate and the fact that the coatings are crack-free and homogeneous can be presented as proof that the coatings can be successful in use as implant material.

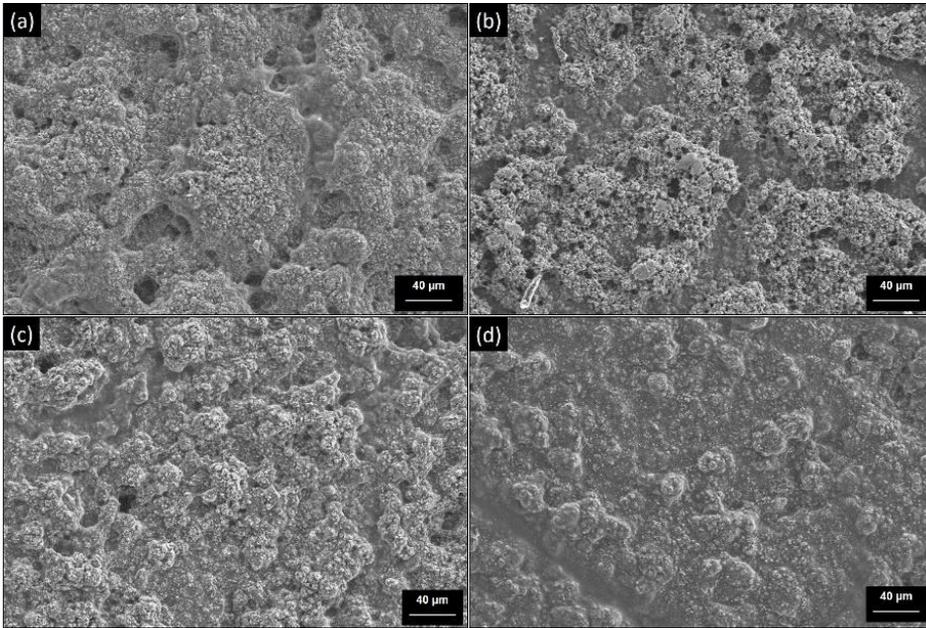


Fig. 2 SEM surface morphologies of coatings with different compositions: (a) PH, (b) PHZ1, (c) PHZ2, and (d) PHZ3

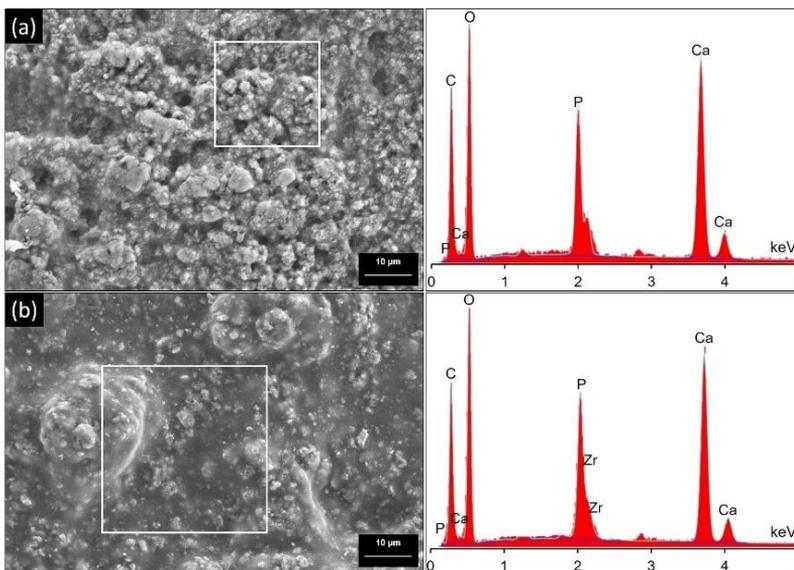


Fig. 3 EDS elemental analysis of (a) PH and (b) PHZ3 coatings

The elemental composition of the coatings on Mg substrates is given in EDS elementally. However, the results of XRD analysis carried out to investigate the presence of these elements formed in the HA phase are presented in Fig. 4. As indicated by the black line in

Fig. 4, characteristic HA peaks were encountered in the 30–32 2θ angle range in PH coatings and the accuracy of the HA phase in the structure was revealed (ICDD: 01-074-9780). It is well known that compared to other Ca–P bio ceramics (such as TCP: Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>), HA exhibits lower solubility as a result of its high crystallinity. Due to these features, the coating dissolves more slowly and is more stable in the body, and increases the service life of the implant material. On the other hand, the presence of ZrO<sub>2</sub> in PHZ coatings was found at ~30.4, ~31, 31.2, and ~35.1 2θ angles (JCPDS: 81-1314), respectively, as shown by the red line in the figure [37]. Unlike the study by Yuan *et al.* [26], the crystallinity of the HA phase is quite high, although no heat treatment was applied to the coatings. As a result, since HA will reduce the dissolution rate of the coatings, it provides controllability of the implant service time [38].

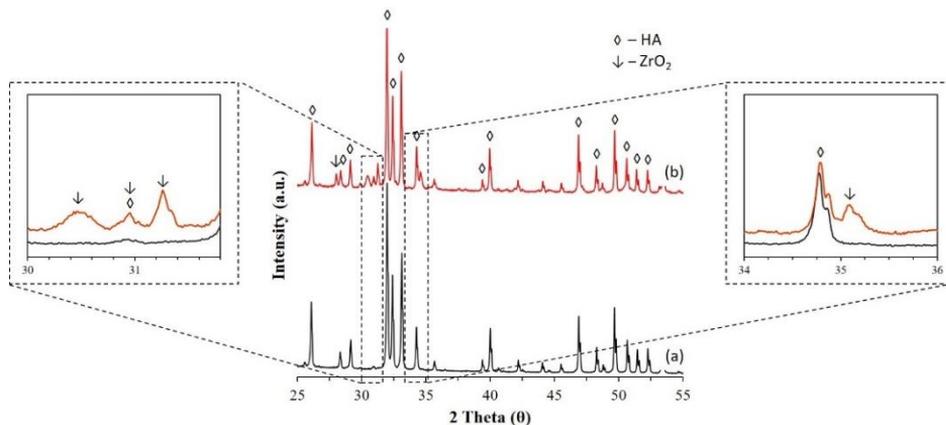


Fig. 4 XRD analysis results of coatings: (a) PH and (b) PHZ, with detailed peaks at 30-31.8 and 34-36 2θ degrees

In Table 2, the micro-Vickers hardness and thickness results of the coatings are presented with standard deviations. It is seen that the hardness increases with the increasing ZrO<sub>2</sub> fraction ratio. The reason for this is thought to be due to the higher hardness value of ZrO<sub>2</sub> compared to HA. On the other hand, it is noteworthy that the coating thickness increased with ZrO<sub>2</sub> 10 wt% reinforcement, but remained almost constant with 20 wt% and 30 wt% reinforcements, but the standard deviation decreased. With such a decreasing standard deviation, it can be said that the coating thickness was found to be the most stable in the PHZ3 coating. The surface morphologies in Fig. 2 confirm this change in coating thickness. As it is known, the increase in coating thickness is an important factor that will decrease the adhesion strength between the substrate and the coating film. However, as can be seen from Figs. 5-6, the adhesion strength of the coatings increased with the addition of ZrO<sub>2</sub>. It is predicted that this may be the result of both ZrO<sub>2</sub> preventing agglomeration and the higher affinity of ZrO<sub>2</sub> to Mg than HA.

Table 2. Micro-Vickers hardness and thickness of coatings

Coatings	Hardness (HV)	Thickness (μm)
PH	135.6 ± 3.8	74 ± 14
PHZ1	219.8 ± 4.1	94 ± 11
PHZ2	241.4 ± 2.6	97 ± 9
PHZ3	279.2 ± 4.7	96 ± 4

Undoubtedly, it is very important for the coating to remain on the substrate for a long time after any coating on Mg alloys, in protecting the Mg from the physiological environment against aggressive media. Accordingly, the coatings must be firmly attached to the substrate (advanced adhesion property). Tape test results, which are an indication of the adhesion strengths performed in this direction, are given for PH, PHZ1, PHZ2, and PHZ3 coatings in Fig. 5a-d, respectively. In the figure, the black areas represent the substrate material (Mg), while the orange areas represent the presence of coatings. The first finding that draws attention after the adhesion tests is the coating structure that occurs in PH coatings and deforms completely in some parts in various areas (Fig. 5a). On the other hand, partial black coating removal was observed around the scratches on the PHZ1 coating (Fig. 5b). In Fig. 5c, black areas were found on the scratches on the PHZ2 coating, and no coating remained around the scratch. As a result of the increased  $ZrO_2$  reinforcement fraction, on the PHZ3 coating, there were no areas of the substrate material either on the scratch or around the scratches (Fig. 5d). In some studies, a similar adhesion strength increase was observed with increasing PLA fraction [11]. Based on this, it has been revealed that the adhesion strength is not only affected by the PLA fraction, but also by the agglomeration of PLA matrix composite coatings. Briefly, it is thought that high adhesion strength can be obtained as a result of the smoother surface morphology and lack of agglomeration with the increased  $ZrO_2$  reinforcement in this study.

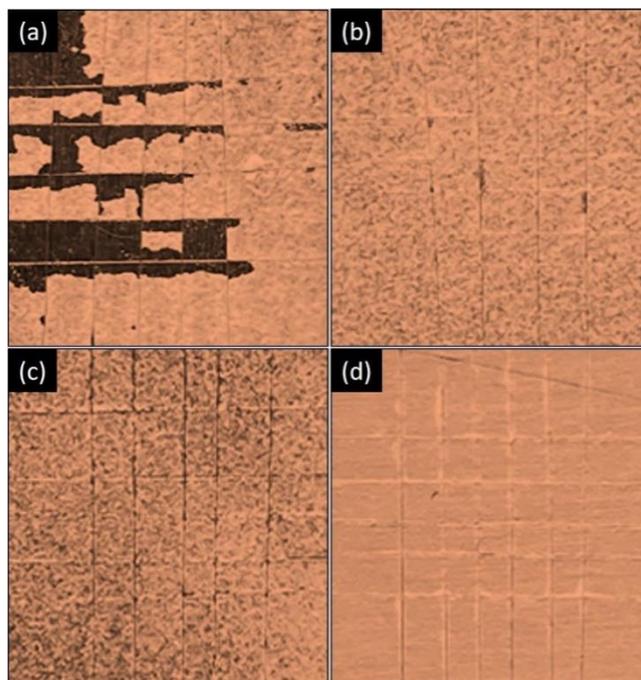


Fig. 5 Tape test results of (a) PH, (b) PHZ1, (c) PHZ2, and (d) PHZ3 coatings, respectively, in accordance with ASTM D3359 standard

In Fig. 6a-d, OM images are presented to reveal the behaviour of the PH, PHZ1, PHZ2, and PHZ3 coatings, especially around the scratches, after the adhesion tests, respectively. Based on this, the adhesion strength of the coatings, as specified in the ASTM D3359 standard, is 1B, 3B, 4B, and 5B for PH, PHZ1, PHZ2, and PHZ3, respectively [35]. In Fig. 6a, the presence of both substrate and partial coatings in the PH coating is shown. The partial coating in the middle of the scratches is thought to have higher strength in the middle part

of the coating. The reason for this result is that the adhesion strength is weak in the sharp corners close to the scratch traces. Although the traces of scratches are not fully visible in Fig. 5b, c, these traces are visible in Fig. 6b, c, so it has been determined that the scratch traces have reached the base material. It is thought that increased adhesion strength with the increased reinforcement fraction of  $ZrO_2$  may be the result of the decreased agglomeration presented in Fig. 2. Another factor is that the polymer and ceramic structures of PLA and HA have less affinity with the metallic substrate (Mg), and metal-polymer/ceramic bonding may have increased with the reinforcement of metal oxide ( $ZrO_2$ ). The last phenomenon that increases the adhesion strength is thought to be the result of decreasing PLA/HA agglomeration with increasing  $ZrO_2$  fraction and increasing the contact angle between PLA and HA- $ZrO_2$  reinforcement.

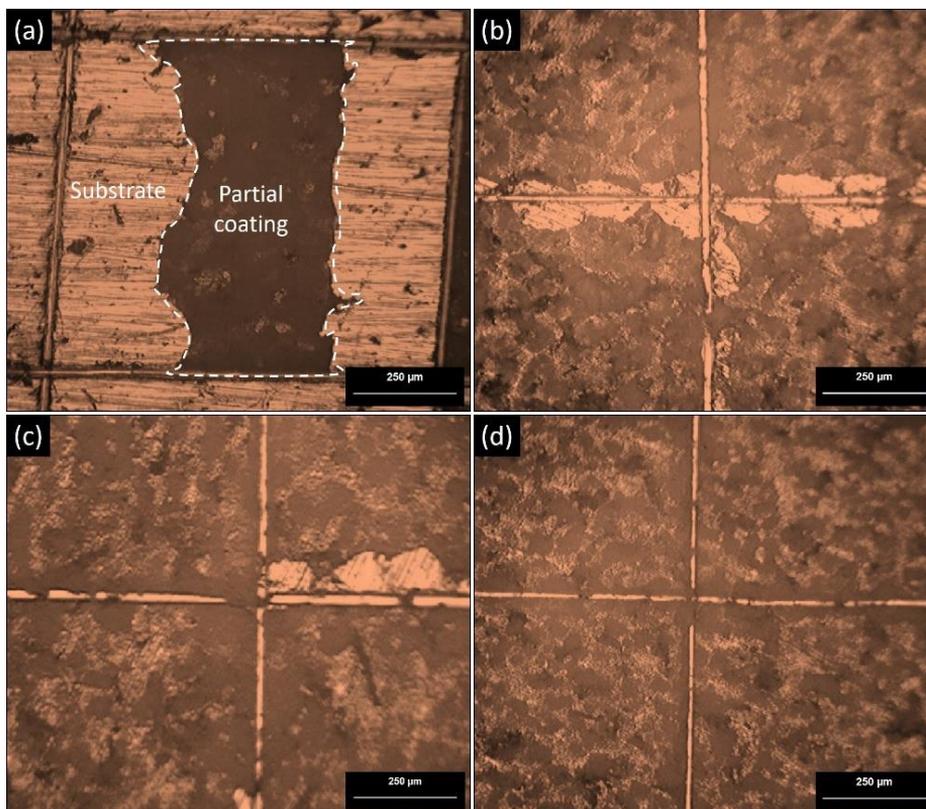


Fig. 6 OM microphotographs of (a) PH, (b) PHZ1, (c) PHZ2, and (d) PHZ3 coatings for the examination of adhesion scratches, respectively

In Fig. 7, a mechanism is proposed for the relationship of coatings with different compositions and fractions to the proposed surface morphology, such as morphology, possible implant-tissue interface interaction, solubility, and adhesion behaviour. A smoother surface was obtained as seen in Fig. 7 with  $ZrO_2$  reinforcement (also can be seen in Fig. 2d). As a result of the proposed mechanism, there are agglomerations and micro porosities in PLA/HA coatings that will increase the implant-tissue interaction. However, this surface morphology can also lead to fast biodegradability and low adhesion strength of coatings. On the other hand, it has been determined that the decrease in the size of these agglomerations as a result of increasing  $ZrO_2$  contribution and the fact that the coatings are increasingly smooth and homogeneous lead to an increase in the biodegradability and

adhesion strength of PLA/HA-ZrO<sub>2</sub> coatings. Similar surface morphology and coating interface were reported by Chen *et al.* [39], which can be said that the high adhesion strength obtained has a similar mechanism.

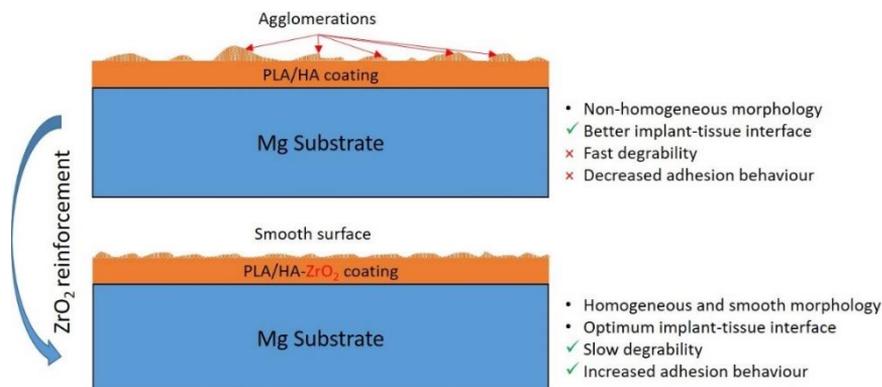


Fig. 7 The proposed mechanism for the effects on the surface morphology and coating structure as a result of ZrO<sub>2</sub> reinforcement

## 5. Conclusions

The morphological and adhesion properties of poly- (lactic) acid/hydroxyapatite-zirconia (PLA/HA-ZrO<sub>2</sub>) coatings were successfully proven within the scope of the study, with the goal of both limiting the rapid biodegradation process of Magnesium (Mg) biomaterials and minimizing the H<sub>2</sub> gas formation. To investigate the ZrO<sub>2</sub> reinforcement in PLA/HA-ZrO<sub>2</sub> hybrid coatings, 10, 20, and 30 wt% ZrO<sub>2</sub> doped coatings, were successfully coated on Mg using the dip-coating method. In SEM surface morphologies, a large agglomeration was observed in PLA/HA coating, it was observed that these agglomerations' sizes decreased with increasing ZrO<sub>2</sub> reinforcement (10 and 20 wt%). Furthermore, it was discovered that the surface has a smooth structure and entirely seals the Mg substrate with the 30 wt% ZrO<sub>2</sub> reinforcement. Additionally, EDS analyses confirmed the presence of Ca, P, and Zr in the coating. XRD analysis revealed the HA and ZrO<sub>2</sub> phases, confirming that the elemental presence of Ca and P in the coatings is HA and revealing their amorphous-crystalline characteristics. It was found that HA did not decompose into different structures such as TCP as a result of not applying heat treatment in the production of coatings. While the hardness values of the coatings increased with the ZrO<sub>2</sub> reinforcement, they increased further with the increasing ZrO<sub>2</sub> fraction. On the other hand, it was concluded that the coating thicknesses did not change much with the increasing ZrO<sub>2</sub> fraction, but the roughness on the surfaces of the coatings decreased, also confirmed by the decrease in the standard deviation in thickness. As a consequence of the adhesive strength, which is arguably the most expected feature of all biomedical coatings, it has been discovered that the adhesion strength of the coatings increased with the increase of ZrO<sub>2</sub> reinforcement (1B, 3B, 4B, and 5B for PH, PHZ1, PHZ2, and PHZ3, respectively). The OM examinations performed after the adhesion tests corroborated these findings. The study found that adding a third-phase reinforcement to PLA/HA composite coatings can modify the physical properties of the coating. High biodegradability and H<sub>2</sub> gas evolution, which limit the use of Mg in biomedical applications, are prevented by polymer-based hybrid composite coatings on it, and its prevalence is assumed to rise.

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