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Development and Durability of PLA Composites with HAp Nanoparticles as an Additions for Improved Bone Fracture Fixation Rods and Screws

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Abstract **-** A fracture fixation procedure is primarily designed to stabilize fractured bones, promote rapid bone healing, and restore the fractured extremity to full mobility and function. Fractures can be fixed externally or internally. With biodegradable implants, there is no need to remove hardware that has been attached to traditional metallic implants after treatment. Polylactic Acid (PLA) is commonly used in bone fixation due to its excellent biocompatibility, biodegradability, and mechanical strength. The objective of this study is to manufacture a biopolymer rod and screw for bone fixation using the PLA biopolymer. The potential of incorporating hydroxyapatite (HAp) powder into PLA rod and screw was also studied using mixed matrix composite technique. As a result of the degradation study, it was found that PLA rods and screws could withstand 70°C for over a month without losing significant weight. The pH rapidly dropped from around 6.5 to 2.1 by the end of the degradation study, unequivocally demonstrating the successful degradation of PLA in the synthetic saline solution. Thermal/chemical stability characteristics of PLA and PLA/HAp rods and screws have been examined by both DSC and TGA, highlighting the advantages of incorporating HAp into PLA rods/screws. This study demonstrates the promising durability and enhanced properties of PLA and PLA/HAp biopolymer rods and screws, offering a potential breakthrough in fracture fixation technology with implications for sustained stability and improved patient outcomes.

Keywords**:** Bone, Fractures, Polylactic Acid (PLA), HAp, Composite, Biodegradability.

1. Introduction

Skeletons serve as a number of essential functions for an organism. They are a means of support, a means of protection, a means of locomotion, a means of buoyancy, a means of feeding, and a means of breathing [1]. Vertebrates have two major skeletal systems: the endoskeleton and exoskeleton. The endoskeleton is located inside the body and is made up of cartilage and bone. The exoskeleton is located outside the body and is made up of bone and cartilage. [2]. Broken bones are defined medically as fractured bones. The severity of a fracture de-pends on the position, cause, and type of fracture [3]. To ascertain the position of the frac-ture, the physician assesses which specific bone is affected and considers the circum-stances leading to the injury. Various types of fractures exist, including open or closed, displaced or non-displaced [4-6]. Usually, bone fractures occur as a result of trauma, such as falls, car accidents, sports injuries or by medical conditions such as osteoporosis. Athletes, in particular, are suscep-tible to injuries due to the physical stress associated with training [7].

There are several types of fractures, and the choice of treatment method depends on what type of fracture it is. In terms of treatment options, there are both surgical and non-surgical options available [8]. As a result of surgical intervention, the bone is fixed in its proper position by using internal support equipment such as rods and pins in order to maintain the bone's position [9]. Unlike surgical treatment, non-surgical treatments in-volve repositioning the bone to its original alignment without the need for surgery to be performed in order to achieve the desired results. As a result, the bone is usually stabilized by the use of a splint or another piece of supportive equipment.

The surgical treatments include open reduction, external fixation, and internal fixa-tion [10]. External fixation is employed to stabilize the broken bone for repair. It is also uti-lized prior to internal fixation in cases where patients cannot endure the prolonged dis-comfort of a complex procedure. For high-degree fractures, the surgeon employs open re-duction and internal fixation [11]. This involves the insertion of plates, screws, nails, rods, and wire pins made from durable and robust materials like stainless steel or titanium, as illustrated in Figure 1. Screws and plates are utilized to maintain the alignment of bone pieces, while wires and pins secure smaller fragments. In the central region of the bone, rods or nails are implanted [12].

A non-surgical treatment for this problem involves the use of traction and cast im-mobilization, on the other hand [13]. Casts, commonly used to immobilize and protect patients with fractures, support bone realignment and healing by maintaining the bone's position during the repair process, though not all fractures require this supportive measure [14]. In orthopedic fixation applications, materials such as metals and polymers are used because of their properties, which make them suitable for these applications [17]. As a re-sult of their superior advantages as compared to metallic based materials, polymers are nowadays the most popular choice when it comes to treating bone fractures as compared to metals [18-20]. Among the biodegradable polymers employed in orthopedic implants, polyester stands out as the most widely used [21]. As polyester degrades, it loses strength, mass, and molecular weight due to ester bonds. A polymer's degradation rate can be influenced by its monomer ratio, molecular weight, and structure [22]. There are several types of polymers that been showing high potential to be used for medical related applications, but the most common and important are aliphatic polyesters, such as polylactic acid (PLA), polyglycolic acid (PGA), and polycaprolactone (PCL) [23].

Bone is composed of natural calcium apatites called hydroxyapatite (HAp), which explains the bone's osteoconduction and osseointegration capabilities [24]. Carbonate ap-atite is an important component of bone minerals and other substances, such as dental enamel [25]. Stiff tissues also contain HAp. Furthermore, HAp is an inorganic and bio-compatible material [26]. During polymer degradation, HAp plays a role in stabilizing the pH of its surroundings, thereby enhancing osseointegration [27]. In clinical orthopedics, HAp composites have been utilized to fill or space bone defects due to their non-immunoreactive properties and the absence of postoperative morphological changes or volume loss [28].

The objective of this study is to produce a biodegradable rod and screw based on PLA biopolymer. The chosen PLA biopolymer is anticipated to exhibit several key properties, including ease of fabrication, relatively low cost, corrosion resistance, superior thermal and chemical stability, as well as bio-absorbability and biocompatibility with the human body. Additionally, the polymer's degradation period aligns with the recovery period from the injury, thereby avoiding the need for the patient to undergo two separate surgeries. Furthermore, the study investigates and assesses the impact of incorporating hydroxyap-atite (HAp) particles as an additive into PLA, focusing on aspects such as processing and chemi-cal/thermal stability.

2. Materials and Methods

2.1. Materils

A PLA polymer 213T has been purchased from Shanghai Hengsi New Material Sci-ence & Technology Company Limited for the purpose of this project. The calcium hy-droxyapatite (HAp) used in this study was purchased from a local market. A positive mold is made of epoxy compound (m-seal) because it can withstand higher temperatures than a negative mold made of silicon.

2.2. Design of Rod and Screw Mold

A 3D-printed positive mold was used to create a negative mold for rod manufacturing. The negative mold, made of heat-resistant M-seal epoxy, was formed by applying the epoxy to the powdered positive mold and allowing it to cure. This negative mold was designed to withstand the heat of the PLA material used in the subsequent rod manufacturing process. Baby powder facilitated the removal of the M-seal negative mold from the 3D-printed positive mold.

2.3. Manufacture of Rod and Screw

PLA rods/screws were fabricated by melting PLA at approximately 200°C for 20-30 minutes and pouring it into 3D molds (detailed in Supplementary Figures S2 and S3). For HAp-incorporated PLA rods/screws, a 1:8 weight ratio of HAp was added to the molten PLA before molding. The mixture was then poured into the molds, which were removed after approximately two minutes, and holes were created. The resulting rods and screws, both pure PLA and HAp-incorporated, are shown in Figure 1.

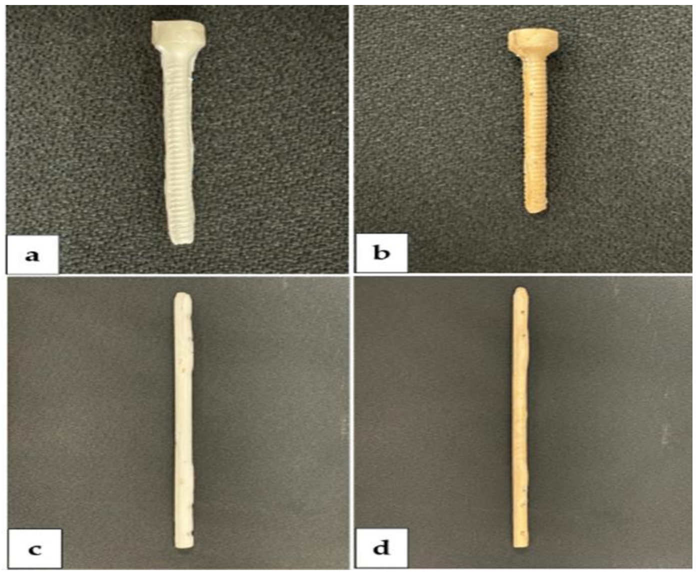

Fig. 1: Manufactured rods and screws. (a) Manufactured pure PLA screw, (b) manufactured PLA/HAp composite screw, (c) manufactured pure PLA rod and (d) manufactured PLA/HAp composite rod.

2.4. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to analyze the thermal behavior of PLA-based rods, measuring heat flow associated with transitions. The DSC analysis determined the glass transition temperature (Tg), crystallization temperature (Tc), and melting temperature (Tm) for both pure PLA and PLA/HAp composite rods. This technique helps understand how the materials behave thermally.

2.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted on pure PLA and PLA/HAp composite rods and screws, heating samples from room temperature to 600°C at a rate of 10°C/min under a 40ml/min nitrogen flow. The study analyzed thermal stability by calculating the temperatures at 5% weight loss (T5) and 50% weight loss (T50), with T5 representing the onset of significant PLA decomposition. These values were determined from TGA data to evaluate the impact of the HAp composite on PLA's thermal degradation.

2.6. Biodegrdation Test

Biodegradation of PLA-based rods was tested using a synthetic solution mimicking human body conditions, with an accelerated degradation study performed at 70°C instead of 37°C due to time constraints. A 0.9% saline solution (9g table salt in 1000mL distilled water, pH 6.5) was used, stirred at 1000 RPM for 30 minutes. Sample mass and solution pH were measured throughout the test, with mass loss percentage calculated using the following formula, where M0 is the initial mass and Mt is the mass at time t. PLA degradation was also assessed by monitoring pH changes due to lactic acid release.

$$\text{Mass loss (\%)} = \frac{M_0 - M_t}{M_0} \times 100$$

3. Results and discussion

3.1. DSC Analysis

DSC analysis was conducted to examine the thermal behavior of both pure PLA and PLA/HAp composite rods and screws. As detailed in Table 3 and illustrated in Figure 2, the observed increase in melting temperature indicates an enhancement in the thermal properties of the composite sample. The results in Table 3 from the DSC test reveal a sig-nificant rise in melting temperature when comparing the pure PLA sample to the PLA with HAp composite at an 8:1 ratio, increasing from 156.3 °C to 172.82 °C. This suggests that the addition of HAp enhances the thermal properties of the sample. Furthermore, the incorporation of HAp into PLA has decreased the crystallization temperature, allowing PLA to crystallize at a lower temperature. Specifically, while pure PLA has a crystalliza-tion temperature (Tc) of 85.2 °C, the inclusion of HAp has reduced it to 75.7 °C. The accuracy of DSC data is contingent on the quality of the input data. Potential errors may arise from noise in DSC sensor readings or/and sample moisture contents variation, which could minor affect the overall precision of the results.

Table 3. DSC results of pure PLA and HAp/PLA composite sample.

Sample	Tg (°C)	Tc (°C)	Tm (°C)
PLA	47.9±0.5	85.2±2.5	152.3±2.1
HAp/PLA	-	75.7±1.7	171.5±2.3

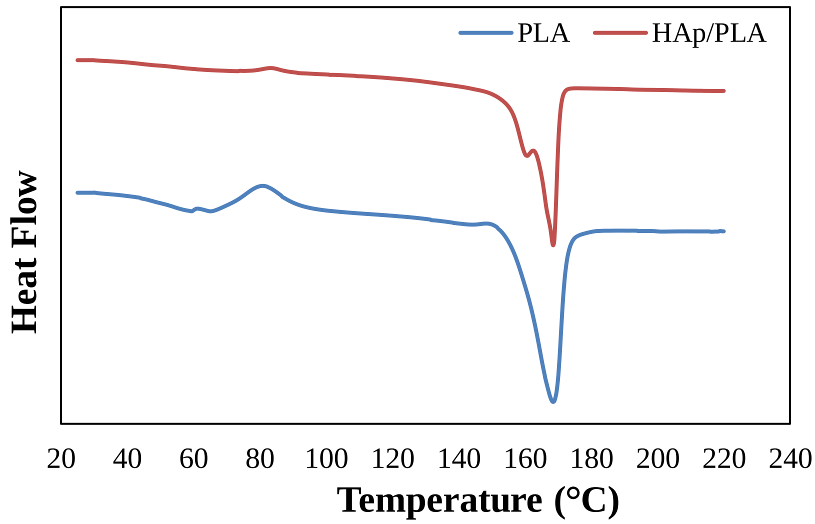

Fig. 2: Thermal behavior of pure PLA and HAp/PLA composite obtained via DSC.

3.2. TGA Anlysis

TGA analysis was conducted to investigate the thermal and chemical stability of both pure PLA and PLA/HAp composite rods and screws. As illustrated in Figure 3 and de-tailed in Table 4, the manufactured pure rod/screw exhibited an initial degradation tem-perature of 296.0 °C at 5% weight loss and maintained stability up to 354.7 °C before los-ing 50% of the initial weight. The incorporation of HAp into PLA positively shifted the T5 and T50 values to 303.5 and 360.2 °C, respectively, indicating the successful integration of HAp into the PLA matrix.

Our findings align with a study where an HAp/PLA composite scaffold was 3D printed with varying percentages of HAp into PLA ranging from 2.5 to 30 wt.% [30]. They reported a reduction in thermal stability at low HAp weight percentages (2.5 and 5), while stability significantly improved at 10, 20, and 30 wt.%. Another study explored the ther-mal stability of HAp/PLA composite matrix nanocomposites prepared by the intercalation technique at PLA loadings of 10, 20, and 30 wt.% [31]. Their observations indicated an enhancement in the thermal stability of the matrix with the addition of HAp. Table 4 summarizes the TGA results of our study alongside findings from various studies that incorporated HAp into PLA.

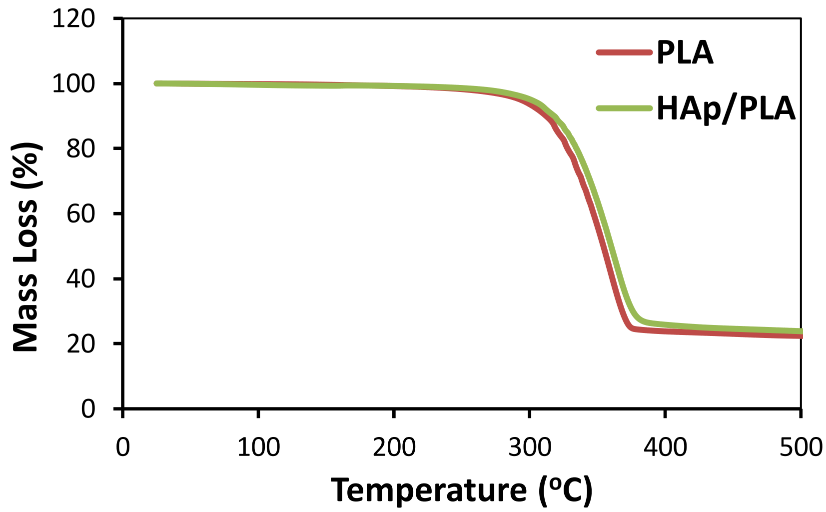

Fig 3: Thermal stability of pure PLA and PLA/HAp composite obtained via TGA.

3.3. Biodegrdation study

Biodegradation tests (Figure 4) showed an initial weight increase in the sample from day 0 to 7, likely due to water absorption by its hygroscopic, microporous structure. A subsequent weight decrease until day 16 indicated hydrolysis, where PLA reacted with water. Around day 16, mechanical loss was also observed.

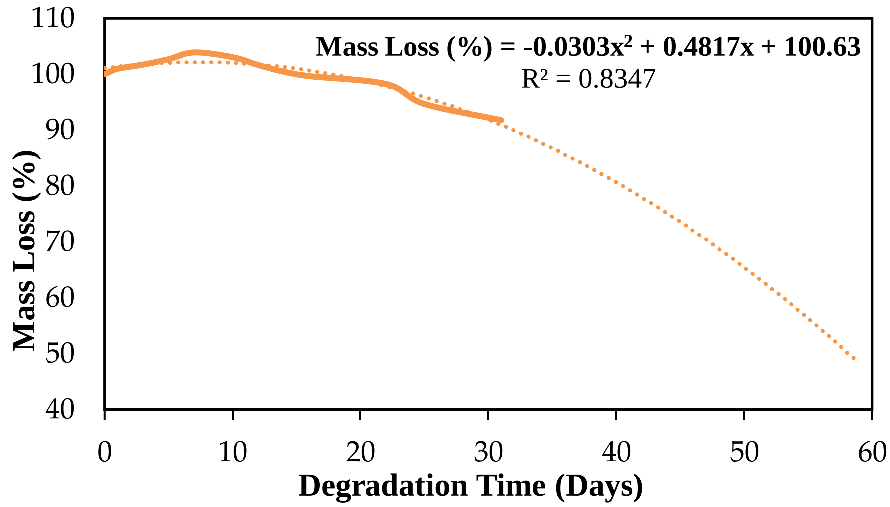

Fig 4: The mass loss for PLA with time during degradation at 70 °C.

A biodegradable rod/screw was immersed in a 0.9% saline solution at 70 degrees Celsius (to accelerate degradation) with a pH of 6.5, mimicking the human body environment (normally 37 degrees Celsius). The sample's weight initially increased over 7 days, then decreased until day 16, marking the start of mass loss recording due to a hydrolysis reaction between the PLA and water molecules. Mechanical loss was also observed around day 16.

Based on the biodegradation results, it is evident that the natural behavior of PLA involves absorption of water when exposed to a solution containing H2O. In the initial days, the PLA sample exhibited an increase in mass, rising by 0.96% on day 1 and peak-ing at 0.45% on day 16. Subsequently, around day 16, the mass loss began, indicating a decline of 0.35%.

This pattern aligns with a study conducted by Reda Felfel (2013) on pure and composite PLA degradation, where an increase in mass was observed [32]. As the sample started losing mass, its mechanical properties were affected, attributed to the breaking of bonds between PLA molecules by water (H2O); thus, the sample weakened over time. Our findings were compared to a study conducted by Cedarville University (2021) on a biodegradable test, where their results also demonstrated both mass and me-chanical properties loss in their samples [33]. At the end of the degradation test, the measured pH of the PLA sample was 2.1, an anticipated result given the acidic nature of PLA molecules.

3.4. pH study

PLA's mechanical properties during degradation testing are significantly impacted by several factors. Molding techniques introducing uneven pressure can create bubbles or voids, while the temperature of the polymer above its melting point also plays a crucial role. Furthermore, the pH of the degradation environment is critical, as PLA degradation begins at a pH of 6.5.

A 30-day degradation study of PLA showed a 10% mass decrease and a significant pH drop from 6.5 to 2.1, indicating advanced degradation (Figure 5). Weight loss measurements on rods and screws confirmed consistent and predictable degradation over time. This suggests uniform and predictable degradation of the rods and screws.

According to a study conducted by Georgiopoulos (2014), the pH of the degradation environment at 7.4 prevented the initiation of PLA degradation [33]. Conversely, for envi-ronments that induced degradation, the pH became acidic, and the acids rapidly disinte-grated the PLA. Another factor is the nature of the acidic solution, which may not maintain the same pH as the human body. Similar to the study by Reda Felfel (2013), where the substance was placed in a PBS solution with properties that maintain a constant pH, re-sulting in minimal pH change [32]. The non-medical grade PLA used in this study, potentially degraded by high manufacturing temperatures, showed mechanical property loss. However, degradation experiments in saline solution confirm the rods' and screws' controlled biodegradability, indicating promise for temporary bone fixation applications. It is important to note here that when dealing with degradation and pH studies, there are always potential measurement errors. In this study we have attempted to minimize those errors by making the study under controlled testing environments; however they can still occur.

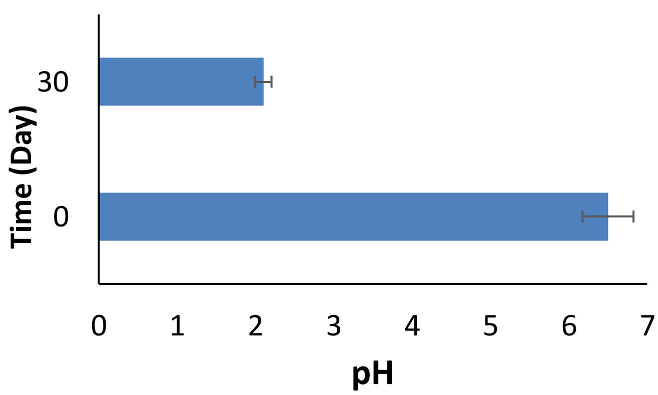

Fig 5. Degradation time versus pH value.

4. Conclusions

PLA polymer offers a promising solution for bone fracture treatment, particularly femur fractures, by streamlining the process compared to traditional metal implants that require two surgeries. Incorporating HAp into PLA rod/screw surfaces improves bone tissue bonding and accelerates healing. PLA's biocompatibility, biodegradability, non-toxicity, non-carcinogenicity, and fatigue resistance, along with controlled mold manufacturing, make it ideal for in-body applications. Thermal tests (DSC and TGA) confirm increased stability with HAp, and biodegradation studies show the PLA rods/screws maintain mechanical properties for 16 days at 70°C and exhibit weight loss over 30 days.

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