

*Research Article*

Strain-Rate-Dependent Behavior and Constitutive Modeling of Stereolithography-Printed Polylactic Acid and Hydroxyapatite Composites

Brilliant Dwinata^{1,5*}, Bagus Budiwantoro^{2**}, Muhammad Agus Kariem², Andi Isra Mahyuddin², Muhamad Naseh Sajadi Budi³, Wan Ismail Faisham⁴

¹Doctoral Program of Mechanical Engineering, Faculty of Mechanical and Aerospace Engineering, Institut Teknologi Bandung, Bandung 40132, Indonesia

²Department of Mechanical Engineering, Faculty of Mechanical and Aerospace Engineering, Institut Teknologi Bandung, Bandung 40132, Indonesia

³Department of Orthopaedic and Traumatology, Dr. Hasan Sadikin General Hospital, Bandung 40161, Indonesia

⁴Department of Orthopaedic, School of Medical Sciences, Universiti Sains Malaysia, Kelantan 16150, Malaysia

⁵Departement of Mechanical Engineering, Faculty of Manufacture Technology, Universitas Jenderal Achmad Yani, Cimahi 40513, Indonesia

*Corresponding authors: 33122301@mahasiswa.itb.ac.id

**Corresponding authors: budiwan@itb.ac.id ; Tel.: +62-22-2504243; Fax: +62-22-2534099

Abstract: Polylactic acid (PLA) reinforced with hydroxyapatite (HA) has attracted significant attention as a candidate biomaterial composite due to its biodegradability, bioactivity, and tunable mechanical properties. However, the strain-rate-dependent mechanical response of Stereolithography (SLA) 3D printed PLA+HA composites and its constitutive representation remain insufficiently explored, limiting predictive modeling for load-bearing applications. A simplified Zhu–Wang–Tang framework was employed to construct a constitutive model. This study presents an integrated experimental and constitutive modeling approach that combines quasi-static strain-rate characterization, simplified ZWT constitutive modeling, and complementary surface and microstructural characterization. PLA + HA composites containing 1, 5, 10, and 15 wt.% HA were fabricated by SLA and tested under compressive loading at strain rates of 10^{-4} s^{-1} and 10^{-3} s^{-1} . The experimental true stress–true strain data were used to identify the nonlinear elastic and Maxwell I parameters using a sequential fitting procedure. The simplified ZWT model successfully reproduced the strain-rate-dependent mechanical response of the investigated composites with a high agreement with the experimental results. Surface wettability measurements demonstrated improved hydrophilic behavior with increasing HA content, while scanning electron microscopy (SEM) revealed progressively increased particle clustering and localized micro-void formation at higher HA contents, providing direct microstructural evidence supporting the observed mechanical behavior. This study establishes a constitutive basis linking HA content, strain-rate-dependent mechanical response, and microstructural characteristics of SLA-printed PLA+HA composites, providing a foundation for future numerical simulations of polymer-based biomedical components.

Keywords: Polylactic Acid + Hydroxyapatite composites; Simplified Zhu–Wang–Tang constitutive model; Stereolithography 3D printing; Strain rate sensitivity; Viscoelasticity

1. Introduction

The mechanical behavior of soft materials, such as polymers, elastomers, and biological tissues, strongly depends on the loading rate. This strain rate sensitivity arises from intrinsic viscoelasticity, plasticity, and damage mechanisms, resulting in pronounced time-dependent stress–strain responses. Therefore, accurate constitutive models are for predicting the mechani-

cal response of these materials under dynamic loading conditions. The Zhu–Wang–Tang (ZWT) nonlinear viscoelastic constitutive model has demonstrated strong capability in capturing the mechanical response of polymers and other soft materials over a broad range of strain rates (Chen et al., 2025; Gao et al., 2024; Prot et al., 2016; Xu et al., 2018, 2019; Zhang et al., 2024b). However, its application to additively manufactured PLA+HA composites produced via stereolithography remains underexplored, particularly under quasi-static strain-rate-dependent loading conditions. To address this gap, a simplified ZWT framework was applied to characterize the quasi-static strain-rate-dependent compressive behavior of SLA 3D-printed PLA+HA composites for candidate biomaterial systems.

Bone implant development has progressed from metallic implants (Gide et al., 2022) and bioactive ceramics such as HA (Tamai et al., 2001), to biodegradable polymers such as PCL, PGA, and PLA (Abdulsalam et al., 2025). Consequently, increasing attention has been directed toward polymer-ceramic composites that combine the advantages of both material classes. PLA-HA composites combine these advantages, improving stiffness and bone-mineral similarity while retaining degradability (Custodio et al., 2021), and stereolithography (SLA) enables high-precision, smooth-finish fabrication of such composites (Tappa & Jammalamadaka, 2018).

The HA concentration and particle dispersion within the polymer matrix strongly influence the mechanical and structural performance of PLA/HA composites. Previous studies have shown that HA incorporation can enhance stiffness, compressive strength, and surface-related properties due to the ceramic reinforcement effect and the chemical similarity of HA to the mineral phase of natural bone. However, excessive HA loading may also introduce drawbacks such as particle agglomeration, increased porosity, poor interfacial bonding, reduced printability, and increased brittleness. Wu et al. (2020) reported that increasing the HA concentration in FDM-printed PLA/HA composites improved the stiffness-related properties but reduced the printing accuracy and structural integrity at higher HA contents. Similarly, Wang et al. (2021) and Zhang et al. (2021) observed that higher HA loading could enhance surface-related characteristics and stiffness while simultaneously deteriorating the overall mechanical stability and processing quality of printed structures due to inhomogeneous particle distribution and weak matrix particle interactions. These findings indicate that the selection of HA concentration requires careful optimization to balance mechanical performance, structural integrity, and manufacturability, particularly in PLA/HA composite systems that are additively manufactured.

The current mechanical assessment of PLA-based composite systems is still predominantly conducted under a single quasi-static loading condition, typically at strain rates around 10^{-4} s^{-1} . For instance, previous studies on SLA-fabricated PLA-based systems for orthopedic applications, particularly in spine cage design, have primarily relied on single compressive mechanical characterization to evaluate structural feasibility (Faadhila et al., 2022). However, due to their intrinsic viscoelastic and deformation mechanisms, polymers and polymer-based composites commonly exhibit strain-rate-dependent mechanical responses, which cannot be fully represented using a single loading rate. Variations in loading rate can significantly influence stiffness, strength, and deformation behavior, particularly in soft polymeric materials and their composites (Du et al., 2023; Long et al., 2024; Tang et al., 2023; Wang & Yue, 2010; Wang et al., 2014; Wang et al., 2007; Wu et al., 2023; Xu et al., 2019; Zhang et al., 2023; Zimmermann et al., 2014). At higher strain rates, restricted molecular mobility and delayed relaxation processes generally increase the material's clear stiffness and strength, whereas lower strain rates allow greater molecular rearrangement and more compliant mechanical responses. These nonlinear behaviors cannot be adequately represented using purely elastic or rate-independent constitutive models (Chen, 2016; Luo et al., 2021).

Neglecting strain rate effects from a constitutive modeling perspective may lead to inaccurate predictions of deformation behavior, load-bearing response, and energy dissipation under variable loading conditions. This limitation has motivated the development of viscoelastic constitutive frameworks capable of capturing the coupled influence of time, strain, and strain rate in polymer-based materials. Among these approaches, the Zhu–Wang–Tang (ZWT) nonlinear

viscoelastic constitutive model has demonstrated a strong capability in describing the rate-dependent response of polymers and polymer-based composites (Aghayan et al., 2022; Chen et al., 2023; Jiang et al., 2016; Lei et al., 2020; Luo et al., 2021; Ren et al., 2024; Wang & Yue, 2010; Wang et al., 2007; Wu et al., 2023; Xiao et al., 2023; Yao et al., 2024).

Existing studies have mainly evaluated the mechanical performance of SLA-printed PLA+HA composites through experiments, whereas the integration of experimental strain-rate characterization with constitutive modeling has rarely been reported. To address this gap, a simplified Zhu–Wang–Tang (ZWT) constitutive model is developed based on experimental data obtained at different quasi-static strain rates. This study aims to: (1) characterize the quasi-static strain-rate-dependent compressive behavior of PLA+HA composites with varying HA weight fractions; (2) develop a simplified ZWT constitutive model for the investigated materials; and (3) evaluate their preliminary surface wettability and fracture morphology relevant to candidate biomaterial applications. This study provides a unified understanding of the coupled influence of HA content and strain rate on the mechanical behavior of stereolithography-printed PLA+HA composites by integrating material fabrication, mechanical characterization, constitutive modeling, and complementary surface characterization. The proposed constitutive model provides a basis for improving the predictive accuracy of numerical simulations and facilitating the design optimization of polymer-based biomedical components subjected to different loading-rate conditions, where strain-rate-dependent mechanical behavior plays an important role.

2. Methods

This chapter presents the material preparation, SLA 3D printing technique, experimental characterization method, and constitutive modeling of the SLA 3D printed PLA+HA composites. This chapter establishes a clear experimental framework that supports the application of a simplified ZWT constitutive model within the quasi-static strain rate regime. To describe the strain-rate-dependent viscoelastic response within the quasi-static region of the bone implant composite system, the selected approach intentionally emphasizes controlled material preparation, additive manufacturing parameters, and mechanical testing, while also considering complementary wettability and microstructural properties relevant to polymer ceramic composites (Boyan et al., 2017; Sanati et al., 2025; Sawase et al., 2008).

2.1 Material Preparation

The base material used in this study was eResin-PLA, a bio-based photopolymer resin (eSUN Co., Ltd., Shenzhen, China) compliant with the EN71-3 safety standard. This resin was selected because of its biopolymer-based formulation, good printability in stereolithography (SLA) systems, and suitability for quasi-static mechanical characterization. Hydroxyapatite (HA) nanopowder was commercially procured from Hunan Songyuan Biotech Co., Ltd. (Changsa, China). The HA powder was used as a reinforcing filler to tailor the mechanical and surface properties of the PLA-based composite.

Four material formulations were prepared by varying the HA weight fraction at 1, 5, 10, and 15 wt% while, maintaining a constant resin volume of 125 mL for each batch. Prior to printing, the required amount of HA powder was gradually added to the liquid PLA resin and mixed using a magnetic stirrer for 1 h to promote the homogeneous dispersion of the ceramic particles within the polymer matrix. The prepared composite resin was then poured into the printer vat and immediately used for fabrication to minimize particle sedimentation.

All specimens were fabricated using a Phrozen Sonic Mighty 8K SLA 3D printer. After printing, the green parts were rinsed with isopropyl alcohol to remove residual uncured resin, followed by post-curing using a Phrozen UV curing unit for 15 min to ensure complete polymerization and mechanical properties stabilization. The SLA printing parameters were kept constant for all material formulations to ensure process consistency. The exposure time of the specimen body was set to 4.3 s with a layer thickness of 0.05 mm. A lift distance of 8 mm

and a lift speed of 60 mm/min were applied during the peeling process, followed by a retraction distance of 8 mm at a retraction speed of 150 mm/min. These parameters were selected based on preliminary trials to achieve stable printing quality and dimensional accuracy across all PLA+HA compositions.

Cylindrical compression specimens with a diameter of 12.7 mm and a height of 25.4 mm were printed, in accordance with ASTM D695-1, while the cylindrical specimen with a diameter of 10 mm and length of 10 mm was also printed for the hydrophilic test. The printing orientation and support strategy were kept consistent across all specimens to minimize geometric and process-induced variability.

2.2 Quasi-static Mechanical Testing for Characterizing the Effect of Strain Rate

Quasi-static experiments are essential for characterizing the mechanical behavior of soft materials under inertia-negligible loading, providing baseline properties such as elastic modulus, yield stress, and strain hardening coefficients that serve as foundational inputs for constitutive modeling (Li et al., 2022; Xu et al., 2019).

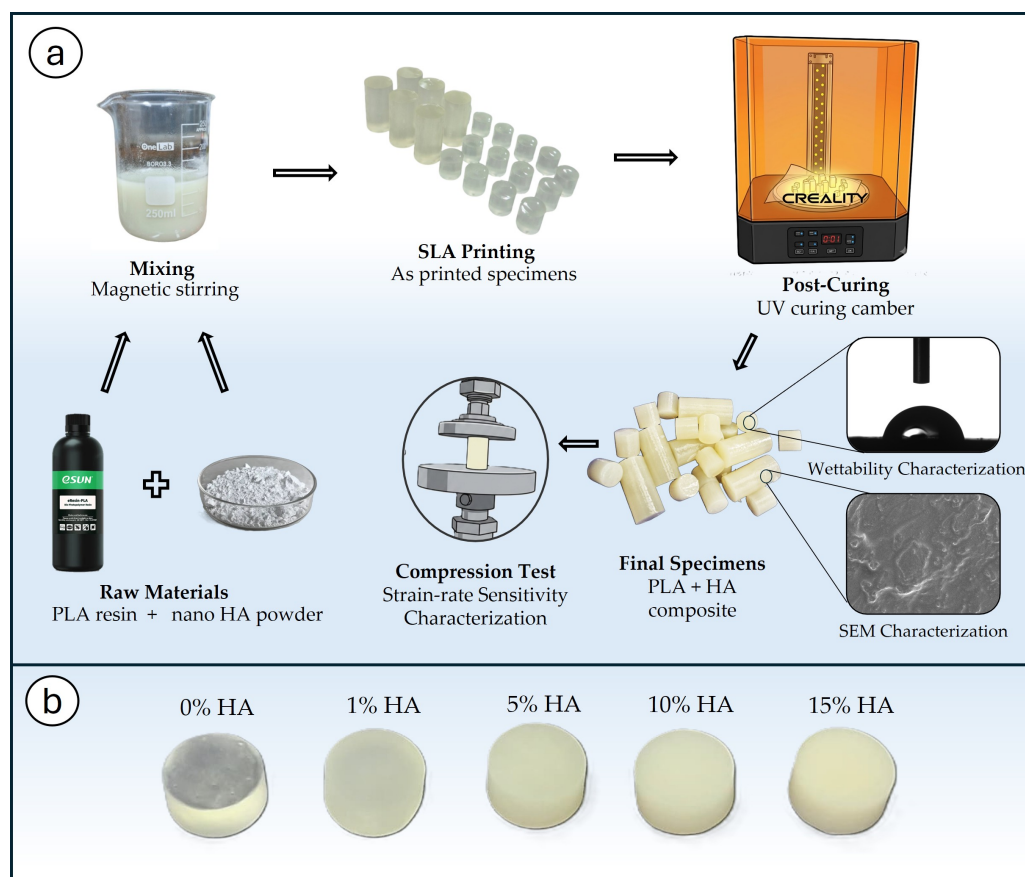


Figure 1 (a) Schematic illustration of specimen preparation and mechanical and physical characterization. (b) Final specimens of the PLA + HA composite at varying wt.% of HA

These tests are typically performed under tensile or compressive loading at strain rates of 10^{-6} – 10^{-3} s⁻¹ using universal testing machines, offering insight into viscoelasticity, plasticity, and damage evolution (Li et al., 2022; Luo et al., 2021; Wu et al., 2023). In the present study, compression was selected as the primary loading mode because it is the mechanically dominant condition in cancellous bone and porous bone-related structures, where trabecular architecture is optimized for compressive load transmission (Amira et al., 2022), and because a substantial portion of tibial loading during locomotion originates from compressive force generated by triceps surae contraction during propulsion (Yawar et al., 2026). Compressive characterization is therefore widely adopted for bone substitute and polymer-based scaffold materials, and pro-

vides an appropriate basis for calibrating the strain-rate-dependent simplified Zhu–Wang–Tang (ZWT) constitutive model adopted in this work (Chen et al., 2025; Lei et al., 2020; Tang et al., 2023).

The strain-rate-dependent constitutive studies generally employed at least two quasi-static strain rates, typically within 10^{-4} – 10^{-2} s $^{-1}$ — for example, epoxy resin, intervertebral disc, and Al/Ep/W composites tested across two or more discrete rates to resolve rate-dependent viscoelastic behavior (Gao et al., 2024; Liu et al., 2024; Luo et al., 2021), an approach valuable for calibrating time-dependent constitutive parameters such as those in the ZWT formulation. Following this precedent, the present experiments applied two quasi-static strain rates (10^{-4} – 10^{-3} s $^{-1}$) in compression; the resulting force–displacement data were converted to stress–strain form for consistent comparison across strain rates. In many strain rate-sensitive material studies, particularly for polymers and polymer-based composites, researchers commonly report material behavior using true stress true strain curves to better account for large deformations and evolving cross-sectional geometry during loading deformation (Cho et al., 2017; Drozdov & Dorfmann, 2001; Holmes et al., 2006). These data processing steps ensure consistency between the quasi-static experiments and the proposed constitutive modeling framework.

2.3 Simplified ZWT Constitutive Model: Formulation

The ZWT constitutive model is an advanced nonlinear viscoelastic formulation developed to describe the mechanical response of soft materials over a wide range of strain rates. Although rooted in the classical viscoelastic theory, the ZWT model extends the traditional linear formulations by incorporating multiple relaxation mechanisms, nonlinear elasticity, and damage-related effects. This extended framework enables accurate representation of material behavior under both quasi-static and dynamic loading conditions and has been widely adopted in polymer, elastomer, and soft composite studies (Chen et al., 2023; Dwinata et al., 2024; Gao et al., 2024; Li et al., 2024; Xu et al., 2018, 2019; Zhang et al., 2024a).

The ZWT model comprises three parallel-connected elements that collectively capture rate-dependent deformation mechanisms operating across different time scales from a rheological perspective. Element 0 is a nonlinear elastic spring representing the material's instantaneous, rate-independent response. Element I is a Maxwell-type viscoelastic component governing low strain rate behavior (approximately 10^{-4} – 10^1 s $^{-1}$), whereas Element II is a second Maxwell element responsible for high strain rate effects (approximately 10^1 – 10^3 s $^{-1}$). Each viscoelastic branch corresponds to distinct molecular relaxation processes with different relaxation times. This multi-mechanism configuration allows the model to decouple the elastic behavior of equilibrium from the dissipation of viscous and enables the independent calibration of the material response in quasi-static and dynamic regimes. A schematic representation of the rheological structure of ZWT is provided in Figure 2a.

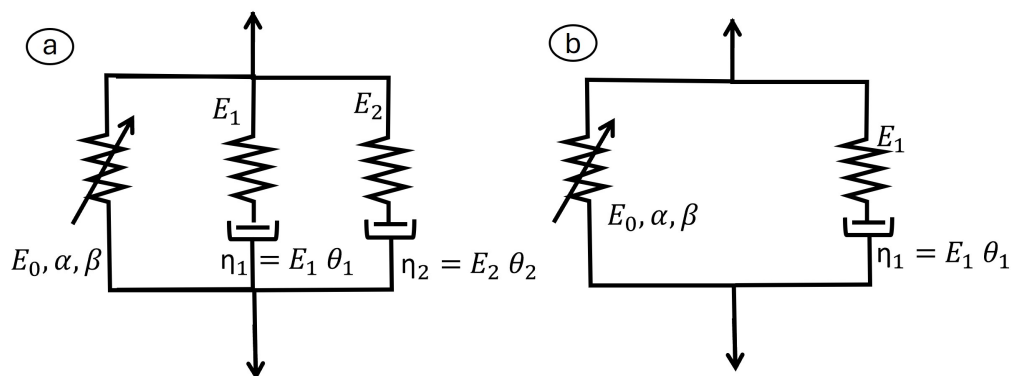


Figure 2 Rheological illustration of (a) ZWT constitutive model and (b) simplified ZWT model

Recent studies have demonstrated that the full ZWT constitutive formulation does not always need to be retained in its original form. In bone implant applications, the contribution of the high strain rate Maxwell element (Element II) becomes negligible, limited to quasi-static and intermediate strain rates where physical human body loading rates remain below the threshold required to excite high-frequency molecular relaxation. Element II introduces additional parameters that are weakly identifiable from experimental data and may unnecessarily increase model complexity without improving predictive accuracy. This simplification of the ZWT constitutive model has been adopted. Liu et al. (2024) investigated the strain-rate-dependent mechanical behavior of intervertebral discs under tension and compression. Their experimental program focused on low-to-moderate strain rates, where no dynamic relaxation processes associated with very short characteristic times were observed. Consequently, they reduced the ZWT formulation by neglecting the high-strain-rate Maxwell branch, allowing stable parameter identification while preserving the material response's essential viscoelastic features. A similar approach was employed by Dwinata et al. (2024) in the constitutive analysis of stereolithography printed PLA under varied quasi-static strain rates, where the exclusion of the high-rate viscoelastic element was justified by the absence of SHPB data. The resulting simplified ZWT model successfully captured the observed strain rate sensitivity using a reduced parameter set, achieving excellent agreement with the experimental stress vs. strain data.

The ZWT model provides a unified description of nonlinear elasticity and multi-timescale viscoelasticity. Numerous experimental studies have demonstrated its ability to reproduce the mechanical responses of soft materials across strain rates spanning several orders of magnitude, particularly in the range of 10^{-4} – 10^3 s $^{-1}$ (Gao et al., 2024; Wang, 2003; Xu et al., 2018). The ZWT model has become a widely used constitutive framework for impact analysis and high strain rate material characterization because of its flexibility and strong physical basis.

The experimental strategies and parameter identification procedures required to calibrate the ZWT model and its commonly adopted extensions are described in the following section.

2.4 The Parameter Identification Process

A structured parameter identification workflow is adopted to ensure a systematic and physically consistent identification of the Simplified ZWT constitutive parameters. Figure 3 presents a schematic flowchart of the sequential procedure used to extract elastic, viscoelastic, and rate-dependent parameters from much quasi-static experimental data. The workflow emphasizes the separation of deformation time scales, allowing the activation or suppression of individual model components according to the dominant loading conditions. This approach minimizes parameter coupling and enhances the robustness of the fitted ZWT parameters by integrating these quasi-static experiments tests within a unified identification framework. The flowchart serves as a concise roadmap for the parameter calibration process discussed in the following sections.

The ZWT model parameters are identified by separating two different quasi-static strain rates based on the characteristic relaxation time. Under quasi-static loading conditions, the Simplified ZWT constitutive equation becomes the following:

$$\sigma = E_0\varepsilon + \alpha\varepsilon^2 + \beta\varepsilon^3 + E_1 \int_0^t \dot{\varepsilon}(\tau) \exp\left(-\frac{t-\tau}{\theta_1}\right) d\tau \quad (1)$$

To identify the low strain rate viscoelastic parameters (E_1 , θ_1), the stress difference $\Delta\sigma$ between two quasi-static tests conducted at different strain rates is evaluated (Jiang et al., 2016). Assuming constant strain rates $\dot{\varepsilon}_1 > \dot{\varepsilon}_2$, the stress difference is expressed as follows:

$$\Delta\sigma = E_1\theta_1\dot{\varepsilon}_1 \left(1 - \exp\left(-\frac{\varepsilon}{\dot{\varepsilon}_1\theta_1}\right)\right) - E_1\theta_1\dot{\varepsilon}_2 \left(1 - \exp\left(-\frac{\varepsilon}{\dot{\varepsilon}_2\theta_1}\right)\right) \quad (2)$$

Here, $\Delta\sigma$ is obtained directly from the experimental stress–strain curves measured at two quasi-static strain rates, which are commonly selected within the range of 10^{-4} – 10^{-3} s $^{-1}$ in polymer studies. The parameters E_1 and θ_1 are determined by fitting Eq. (2) to the experimental $\Delta\sigma$

data using a nonlinear least squares optimization method, typically the Levenberg–Marquardt algorithm.

Once the viscoelastic contribution is identified, the quasi-static elastic parameters E_0 , α , and β are obtained by fitting the stress–strain response at the lowest strain rate to Eq. (1). This sequential identification strategy ensures physical consistency and minimizes parameter coupling across different deformation regimes.

In summary, simplifying the ZWT model is a sound engineering strategy when the experimental regime does not support its activation or calibration. Such simplification enhances parameter identifiability, reduces computational cost, and avoids over-parameterization while, maintaining consistency with the underlying physics of viscoelastic deformation. Therefore, this simplified ZWT formulation is adopted and applied in Chapter 3 to model the strain-rate-dependent behavior of the investigated material system within the experimentally relevant loading regime.

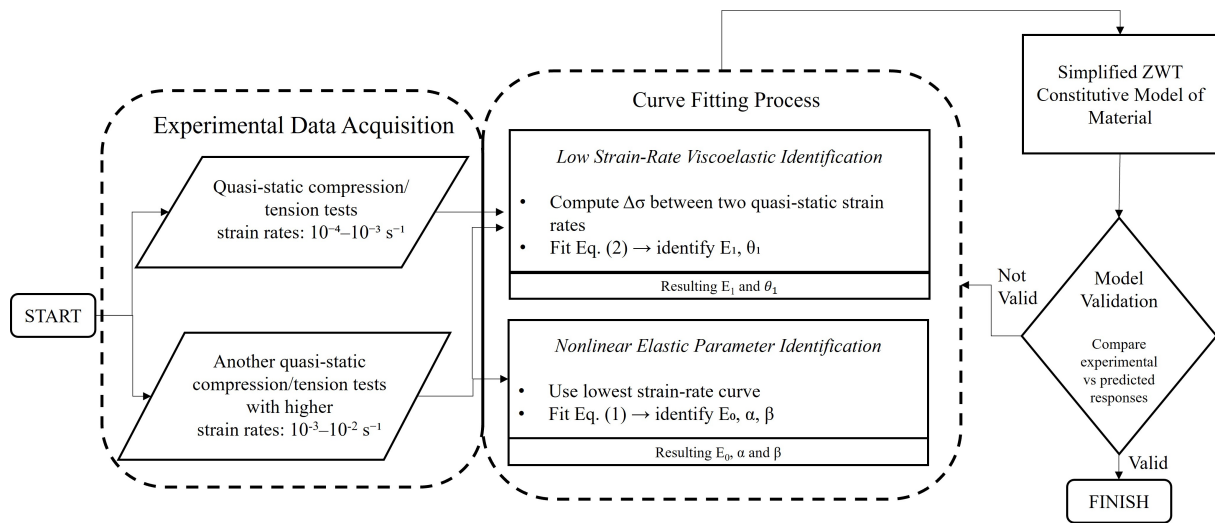


Figure 3 Flowchart of the ZWT parameter identification process

2.5 Wettability and Microstructural Characterization

The surface wettability and microstructural characteristics of the fabricated composites were evaluated in addition to mechanical characterization to provide complementary information regarding their potential suitability for biomedical applications. Surface wettability is an important factor influencing the early biological response of bone implant materials. In general, higher surface wettability promotes protein adsorption, osteoblast attachment, and cell proliferation, thereby supporting biomaterials' osteoconductivity and osseointegration (Zhao et al., 2005). Complementary microstructural observations were also performed to provide direct evidence of particle dispersion and fracture morphology associated with different HA contents.

The wettability of the SLA-printed PLA+HA composites was evaluated using a contact angle meter (Kyowa DM-CE1) based on the sessile drop method. The fracture-surface morphology of the composites was examined using SEM to complement the wettability characterization. The internal fracture surfaces of specimens fractured during the compression tests were selected to observe the internal morphological features. Before SEM observation, the specimens were sputter coated with a thin layer of gold to improve surface conductivity and minimize charging effects during electron-beam imaging. The fracture surfaces were examined using a Hitachi SU3500 scanning electron microscope (Hitachi High-Tech Corporation, Tokyo, Japan) operated in secondary electron mode at an accelerating voltage of 2–3 kV. SEM images were acquired at magnifications of 1000x and 5000x to comparatively evaluate fracture-surface morphology, particle dispersion, surface heterogeneity, and morphological changes associated with increasing

HA content.

3. Results and Discussion

This section presents the mechanical response of SLA 3D printed PLA + HA composites under quasi-static compressive loading, with particular emphasis on the influence of strain rate and HA content on the stress–strain behavior. Compression tests were conducted at two representative quasi-static strain rates, i.e., 10^{-4} s^{-1} and 10^{-3} s^{-1} . To clearly describe the material's rate-dependent viscoelastic characteristics, representative true stress true strain curves are first discussed for each HA composition. These curves highlight the differences in initial stiffness, nonlinear deformation response, and overall stress level arising from strain rate variations. Subsequently, the effect of HA content is examined by comparing the mechanical responses across different filler concentrations at identical strain rates, allowing the systematic assessment of the reinforcing role of HA particles within the PLA matrix. Finally, preliminary surface wettability characteristics relevant to candidate biomaterial applications were evaluated using hydrophilicity measurements.

3.1 Results of the Quasi-static Experiment

Quasi-static compression tests were performed following ASTM D695-15, which is specifically designed to determine the compressive mechanical properties of rigid plastics and polymer-based composites with relatively high elastic modulus. Thus, the 3D-printed PLA + HA specimen was suitable. All tests were conducted using an INSTRON 5985 Universal Testing Machine with a maximum load capacity of 250 kN, capable of both tensile and compressive loading. The loading platens were carefully aligned and maintained parallel to the specimen end surfaces during compression, with a maximum alignment tolerance of 0.025 mm as prescribed by the standard, to minimize bending effects and ensure uniform stress distribution. This testing configuration enabled the reliable acquisition of stress–strain responses under controlled quasi-static strain rate conditions. To assess the repeatability of the mechanical response, each testing condition, including HA content and applied strain rate, was evaluated using three independent specimens ($n = 3$).

Figure 4 illustrates the true stress true strain responses of selected SLA 3D printed PLA + HA samples with varying HA contents (1–15 wt%) tested under quasi-static strain rates of 10^{-4} s^{-1} and 10^{-3} s^{-1} . For all compositions, an increase in strain rate results in a consistently higher stress response over the entire strain range, indicating a clear strain rate sensitivity of the material. At a given true strain, specimens tested at 10^{-3} s^{-1} exhibit higher stiffness and stress levels than those tested at 10^{-4} s^{-1} , reflecting the reduced time available for molecular relaxation and viscous deformation mechanisms at higher loading rates.

This strain rate dependence is quantitatively reflected in the extracted mechanical parameters summarized in Table 1. For all investigated HA contents, both the elastic modulus and the compressive stress at 3% strain tend to increase with increasing strain rate. Similar trends are observed for higher HA contents, indicating that the strain rate effect remains observable regardless of the filler concentration.

Furthermore, at 3% strain, the higher HA concentration generally tends to increase both the elastic modulus and the compressive stress, suggesting that the incorporation of HA particles contributes to the stiffening and reinforcement of the PLA matrix under quasi-static compressive loading.

The standard deviation values are relatively higher for the elastic modulus of several low-HA specimens, particularly at 1 wt% HA. This variability is likely associated with the less stable initial deformation response and the occurrence of earlier nonlinear deformation behavior in several specimens, which increases the sensitivity of modulus extraction from the initial linear region of the stress–strain curves. In contrast, specimens with higher HA contents generally exhibited more stable compressive responses and reduced variability in the extracted stiffness

values.

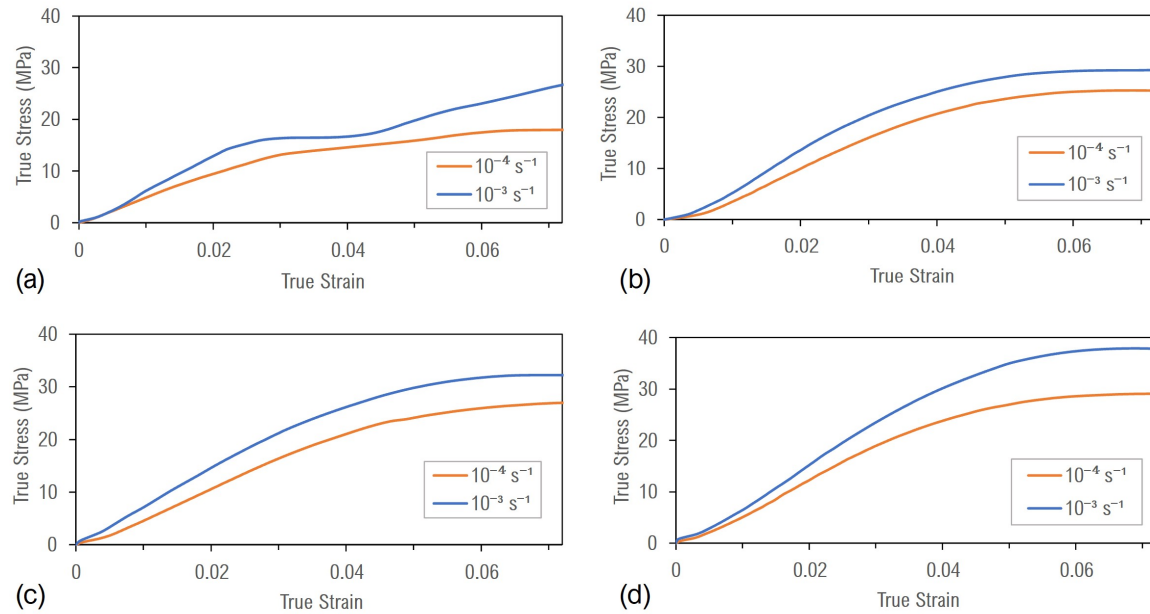


Figure 4 (a) True stress–strain curve of 1 wt% HA; (b) True stress–strain curve of 5 wt% HA; (c) True stress–strain curve of 10 wt% HA; (d) True stress–strain curve of 15 wt% HA

Table 1 Mechanical properties of SLA 3D-printed PLA+HA specimens. Values are presented as mean $\pm$ standard deviation ($n = 3$)

Strain Rate (s^{-1})	HA content (%wt.)	Young's Modulus $\pm$ SD (MPa)	Compressive stress at 3% Strain $\pm$ SD (MPa)
10^{-3}	1%	540.84 ± 127.50	15.47 ± 1.17
	5%	583.19 ± 34.65	18.67 ± 2.13
	10%	664.55 ± 70.68	21.26 ± 1.76
	15%	737.73 ± 93.20	22.55 ± 2.43
10^{-4}	1%	452.93 ± 103.23	13.80 ± 0.97
	5%	573.09 ± 54.34	17.58 ± 2.45
	10%	577.81 ± 18.14	18.02 ± 0.75
	15%	599.39 ± 103.39	18.09 ± 3.29

Figure 5 presents the true stress and true strain curves of PLA + HA specimens with different HA contents (1, 5, 10, and 15 wt%) tested at quasi-static strain rates of 10^{-3} s^{-1} and 10^{-4} s^{-1} . For both strain rates, a systematic enhancement in mechanical response is observed with increasing HA content. Specifically, higher HA concentrations lead to increased stiffness, higher stress levels at a given strain, and delayed onset of nonlinear deformation, indicating that HA has an effective reinforcing role within the PLA matrix.

Figure 5 also indicates a distinct early softening behavior in the 1 wt% HA specimens under both investigated strain rates. The 1 wt% HA composites exhibit an earlier deviation from the initial linear response followed by a relatively reduced hardening progression at intermediate strain levels compared with the higher-HA specimens. The observed response is consistent with the previously identified relatively higher variability in the extracted elastic modulus values for the low-HA specimens. In contrast, specimens containing higher HA concentrations generally exhibit smoother strain hardening behavior and more stable compressive responses throughout

the deformation process, suggesting that the reinforcing effect of the HA particles within the PLA matrix improved load transfer and deformation stability.

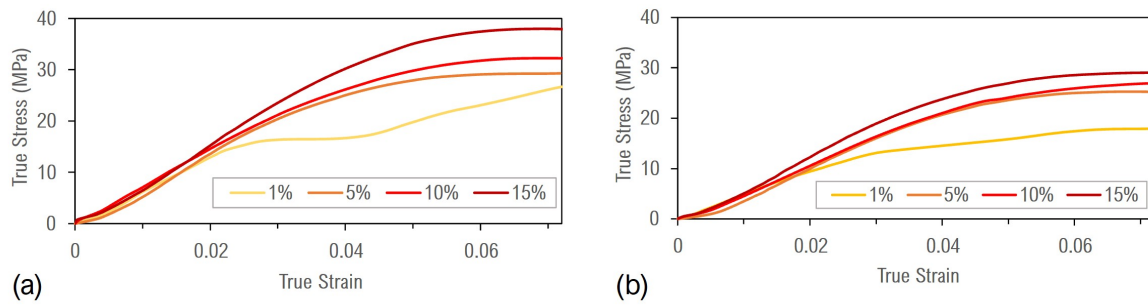


Figure 5 (a) True stress–strain curve of 10^{-3} s^{-1} strain rate; (b) True stress–strain curve of 10^{-4} s^{-1} strain rate

Notably, the reinforcing effect of HA is more pronounced at a higher strain rate of 10^{-3} s^{-1} , where the separation between curves corresponding to different HA contents becomes more significant. This observation shows a synergistic interaction between strain rate effects and filler reinforcement, in which the reduced time for viscous relaxation at higher loading rates amplifies the stiff HA phase's contribution. Such behavior is characteristic of viscoelastic composites and further supports the adoption of a rate-dependent constitutive framework.

The observed monotonic increase in stiffness and strength with HA content without abrupt changes in deformation mechanisms supports the applicability of a simplified ZWT formulation for the present quasi-static regime from a constitutive modeling perspective. The gradual, continuous hardening behavior indicates that the material response is predominantly governed by nonlinear elasticity and low-rate viscoelasticity, without the need to invoke high-strain-rate relaxation mechanisms. This observation provides a strong physical justification for excluding the high-strain-rate Maxwell element in the simplified ZWT model, as discussed in the subsequent section.

3.2 Formulation of the Simplified ZWT

This subsection presents the systematic identification of the constitutive parameters for the simplified ZWT model based on the results of the quasi-static compression test. As discussed in the previous sections, this study intentionally focuses on the low strain rate regime (10^{-4} to 10^{-3} s^{-1}), allowing the ZWT formulation to be reduced to a nonlinear elastic spring in parallel with a single Maxwell element (Maxwell I). Therefore, parameter calibration is conducted in two sequential stages to ensure physical consistency and numerical robustness.

The first stage is to determine the viscoelastic parameters that cause the sensitivity of the strain rate. The strain rate sensitivity is isolated by constructing the stress difference ($\Delta\sigma$) between the true stress true strain responses obtained at 10^{-3} s^{-1} and 10^{-4} s^{-1} , effectively filtering out the rate-independent nonlinear elastic contribution. The resulting $\Delta\sigma$ to strain curve is then fitted to the analytical expression of the Maxwell I element to determine the viscoelastic parameters, i.e., the elastic modulus E_1 and the relaxation time θ_1 . Figure 6(a,c,e,g) presents the fitting results for all representative cases. High determination coefficients were obtained, indicating that the Maxwell I element adequately captured the strain-rate-dependent viscoelastic response within the investigated regime. In the second stage, the nonlinear elastic parameters (E_0 , α , β) are identified by fitting the representative true stress–true strain curve at 10^{-3} s^{-1} , where the viscoelastic effects are minimized and the elastic response dominates. Nonlinear regression was performed to fit the experimental true stress vs. true strain curves. Figure 6(b,d,f,h) shows the fitting results for all specimens. The fitted model generally demonstrates excellent agreement with the experimental data up to the maximum strain investigated, confirming the

simplified ZWT formulation's validity under quasi-static loading.

The 1 wt.% HA specimen exhibits an earlier onset of softening behavior compared with the higher HA compositions, indicating a faster transition from stable elastic deformation toward localized nonlinear deformation and earlier damage mechanisms. This behavior becomes noticeable at relatively low strain levels and differs from the smoother and more stable compressive responses observed in higher HA-containing specimens. The strain domain used for constitutive parameter identification of the 1 wt.% HA specimen was restricted to a true strain of 3%, corresponding to the initial onset region of the softening behavior. This adjustment was introduced to minimize the influence of localized softening on the extraction of the viscoelastic parameter and to preserve the validity of the simplified ZWT formulation, which primarily assumes monotonic viscoelastic behavior. Following this refinement, the Maxwell I parameter fitting of the 1 wt.% HA specimen (Figure 6a) produced a good fit coefficient of determination (R^2) of approximately 0.931, whereas the remaining compositions exhibited R^2 values above 0.945.

Table 2 summarizes the extracted constitutive parameters of the simplified ZWT model together with their corresponding standard errors (SE) and goodness-of-fit metrics for all investigated PLA+HA compositions. Overall, the nonlinear spring component exhibits consistently good fitting accuracy, with R^2 values ranging from 0.992 to 0.999, indicating that the model's nonlinear elastic contribution adequately represents the composites' quasi-static compressive behavior. Similarly, the Maxwell I element demonstrates satisfactory fitting performance, particularly for higher HA compositions, where the R^2 values exceed 0.945. The relatively lower Maxwell fitting quality observed for the 1 wt.% HA specimen is associated with the occurrence of early softening behavior, which reduces the stability of viscoelastic parameter identification at larger strain levels.

Overall, the simplified ZWT constitutive framework is in good agreement with the experimental stress-strain responses of the investigated PLA+HA composites within the selected quasi-static strain rate range.

Table 2 Extracted ZWT parameters and R^2 values of the SLA 3D-printed PLA + HA specimens

%wt of HA	Nonlinear parameters of the spring element			Goodness of fit	
	$E_0 \pm \text{SE}$ (MPa)	$\alpha \pm \text{SE}$ (MPa)	$\beta \pm \text{SE}$ (MPa)	R^2	RMSE
1%	140.1 ± 4.5	31260 ± 462	-785900 ± 11400	0.999	0.107
5%	304.0 ± 14.8	11157 ± 655	-155709 ± 6940	0.992	0.835
10%	392.6 ± 5.5	7103 ± 246	-108200 ± 2602	0.999	0.313
15%	380.5 ± 7.3	10220 ± 324	-149000 ± 3427	0.998	0.412
%wt of HA	Maxwell I parameters		Goodness of fit		
	$E_1 \pm \text{SE}$ (MPa)	$\theta_1 \pm \text{SE}$ (s)	R^2	RMSE	
1%	258.4 ± 3.4	31.8 ± 2.2	0.931	0.352	
5%	393.6 ± 9.5	12.3 ± 0.4	0.945	0.294	
10%	434.1 ± 4.8	14.5 ± 0.2	0.985	0.182	
15%	271.8 ± 1.5	59.3 ± 1.2	0.992	0.262	

Note: SE: standard error; RMSE: root mean square error.

3.3 Hydrophilic Properties and Microstructural Characterization

In addition to mechanical performance, the surface wettability and microstructural characteristics of PLA + HA composites are relevant for potential biomaterial applications. The incorporation of hydroxyapatite (HA), which possesses intrinsically hydrophilic characteristics, may influence the surface interaction behavior of SLA 3D-printed PLA + HA composites. Therefore, contact angle measurements were conducted as a preliminary evaluation of the surface wettability behavior of the composites.

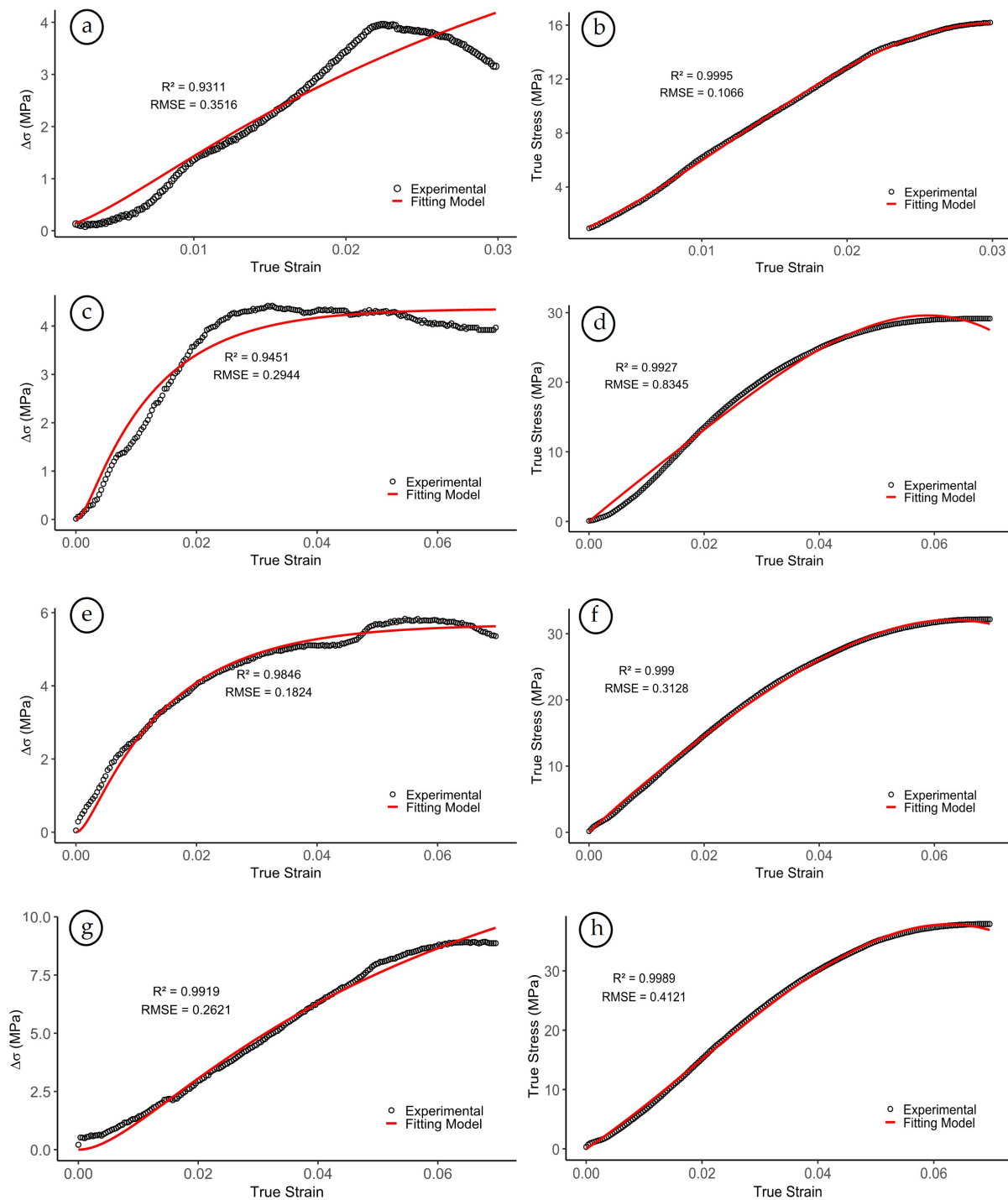


Figure 6 (a) Maxwell I fitting of the 1% HA specimen; (b) Nonlinear spring of the 1% HA specimen; (c) Maxwell I fitting of the 5% HA specimen; (d) Nonlinear spring of the 5% HA specimen; (e) Maxwell I fitting of the 10% HA specimen; (f) Nonlinear spring of the 10% HA specimen; (g) Maxwell I fitting of the 15% HA specimen; (h) Nonlinear spring of the 15% HA specimen

Table 3 summarizes the measured contact angle results and Figure 7 describes them. Pure PLA exhibited a contact angle of approximately 96.8° , indicating a relatively hydrophobic surface. The incorporation of HA progressively reduced the contact angle, indicating improved surface wettability with increasing HA content.

This behavior is primarily attributed to the intrinsically hydrophilic nature of HA, whose

surface contains polar hydroxyl ($-\text{OH}$) and phosphate (PO_4^{3-}) groups capable of interacting with water molecules through hydrogen bonding and electrostatic interactions, thereby increasing the surface affinity toward water. Furthermore, increasing the HA content increases the probability of HA particles being exposed at or near the composite surface, resulting in a greater contribution of these hydrophilic sites during CA measurements. The 15 wt.% HA specimen exhibited the lowest contact angle (approximately 77.7°) among the investigated compositions, indicating the highest surface wettability (Begum et al., 2024; Benziada et al., 2026; Zimina et al., 2020). The increased surface heterogeneity observed in the SEM images (Figure 8) at higher HA contents may also contribute to enhanced wettability by promoting water spreading over the composite surface. Similar reductions in the contact angle following HA incorporation have been widely reported for PLA+HA composite systems and are generally associated with the combined effects of HA surface chemistry and surface morphology (Shiroud Heidari et al., 2023).

Table 3 Hydrophilic ability of all PLA + HA specimens

Sample	Contact Angle ($^\circ$)	Wettability
Pure PLA	96.8	Hydrophobic
1 wt.% HA	90.3	Slightly hydrophobic
5 wt.% HA	89.5	Slightly hydrophilic
10 wt.% HA	92.7	Slightly hydrophobic
15 wt.% HA	77.7	Hydrophilic

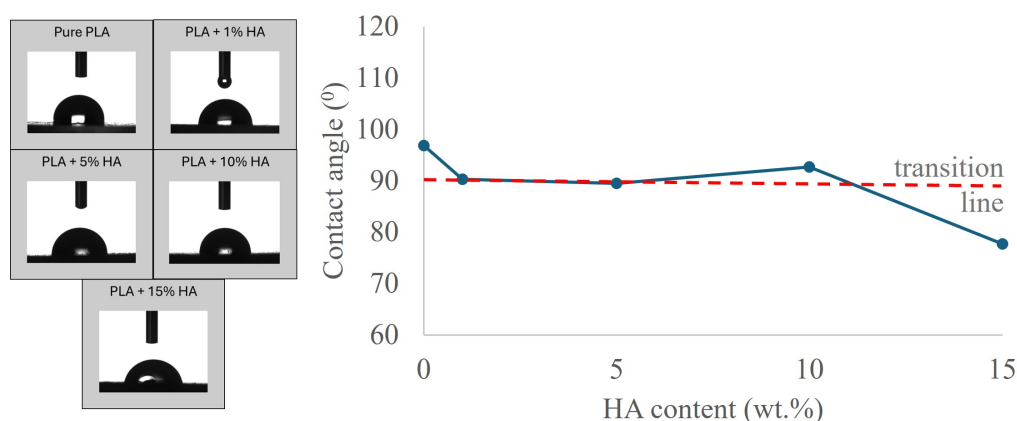


Figure 7 Images of water droplets on each specimen surface and static contact angle values for different HA contents

Although the overall trend indicates improved wettability with increasing HA incorporation, the measured CA did not decrease monotonically for every composition. The 10 wt.% HA specimen exhibited a slightly higher contact angle than the 5 wt.% HA specimen. Because the contact angle is highly sensitive to the local surface condition, this deviation may be associated with local variations in the exposure and distribution of HA particles, surface heterogeneity, or localized surface morphology rather than the nominal bulk HA content alone. The SEM observations in Figure 8 further indicates increasing surface heterogeneity and particle clustering with increasing HA content. This morphology leads to local variations in particle exposure across the fracture surface and consequently influence the measured CA. Nevertheless, the overall results consistently demonstrate that HA incorporation substantially improves the surface wettability compared with neat PLA, with the 15 wt.% HA specimen exhibiting the most hydrophilic behavior.

Figure 8 shows the SEM images of the fracture surfaces of pure PLA and PLA+HA composites at 1, 5, 10, and 15 wt% HA. The SEM observations reveal a progressive evolution of

particulate or agglomerate features on the fracture surface morphology with increasing HA content.

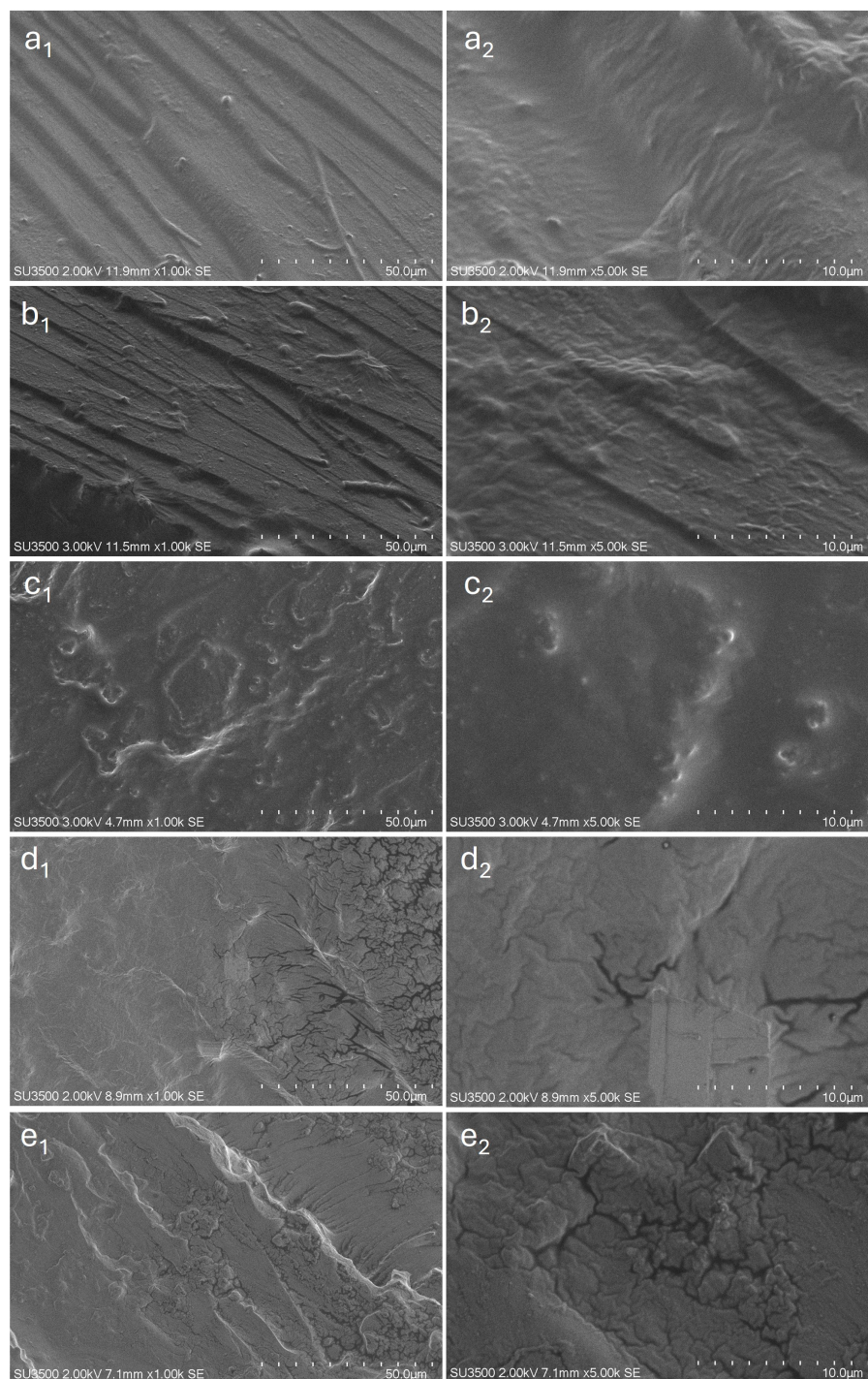


Figure 8 SEM micrographs of fracture surfaces for PLA+HA with various content of HA: (a) 0 wt.% HA; (b) 1 wt.% HA; (c) 5 wt.% HA; (d) 10 wt.% HA; (e) 15 wt.% HA

Pure PLA exhibits a smooth surface with less particulate fracture, providing a baseline image without HA incorporation. The 1 wt.% HA specimen exhibits sparse and distinct bright particulate features that are distributed relatively uniformly across the fracture surface. With increasing HA content, both the density and the degree of clustering of these particulate features increase progressively: at 5 wt% HA, particles begin to group into small local clusters; at 10 and 15 wt% HA, larger agglomerated regions are clearly visible, accompanied by localized micro voids consistent with agglomerate pull-out during fracture, and an overall increase in surface

roughness.

The observed morphological evolution is consistent with the increasing HA solid loading within the polymer matrix. At relatively low HA content, particles can be more uniformly dispersed and effectively bonded to the surrounding PLA matrix. However, the reduced interparticle spacing increases particle agglomeration as the HA content increases, resulting in localized heterogeneous regions that might act as stress concentration sites during deformation. Similar morphological characteristics have been reported in phase separation and extrusion-fabricated methods of PLA/HA composites, where increasing HA loading progressively increased particle clustering and fracture-surface roughness due to the polymer matrix's limited dispersion capability.

4. Discussion and Future Work

Further discussion of the microstructural characteristics can be supported by the porosity characterization of the SLA-fabricated PLA + 10 wt.% HA composite. The results indicate that HA incorporation reduced the effective scaffold porosity from approximately 52% in pure PLA to 46%–49% in PLA + 10% HA systems, indicating that HA particles partially occupied the internal void space and contributed to denser load-bearing pathways. Similar to the results of a previous study, porosity characterization can serve as an indirect evaluation of internal structural uniformity and material distribution in additively manufactured polymer-based systems (Asriyanti et al., 2022). The larger porosity variation observed in the HA-containing specimens may indicate localized dispersion heterogeneity, which may influence the strain localization behavior. The SEM evidence complements the porosity trend, providing a coherent multiscale microstructural picture. HA incorporation is associated with reduced effective porosity and a denser printed structure, whereas increasing HA content results in progressively heterogeneous, segmented, particle agglomeration fracture-surface morphologies at the local microstructural scale. These morphological changes demonstrate that HA incorporation progressively modifies the polymer matrix's continuity and local structure and promotes localized clustering at higher HA contents.

Table 4 summarizes representative investigations on PLA+HA composites to place the present findings in the context of previous studies. Previous studies have primarily focused on evaluating mechanical properties, scaffold architecture, or biological performance, whereas constitutive modeling has rarely been incorporated. This study extends those examinations by integrating quasi-static strain-rate-dependent mechanical characterization, constitutive modeling, and the alternative SLA fabrication method into a comprehensive experimental approach. Although the investigated processing routes and HA contents differ among studies, the observed improvements in stiffness and wettability following HA incorporation are generally consistent with the literature.

Overall, this work establishes a constitutive characterization framework for PLA+HA composites printed by stereolithography under quasi-static strain-rate conditions. This study provides a more comprehensive understanding of the coupled influence of HA content and strain rate on composite behavior by integrating experimental mechanical characterization, constitutive modeling, wettability evaluation, and SEM-based microstructural observations. In addition, a separate ongoing in vitro cytotoxicity study based on ISO 10993-5:2009 has demonstrated preliminary non-cytotoxic behavior for both pure PLA and PLA+HA systems, further supporting their biological safety potential. Nevertheless, additional in vitro, in vivo, and quantitative microstructural investigations are required. Therefore, future work will focus on detailed biological validation and the incorporation of damage-related constitutive mechanisms to further improve the predictive capability of the proposed model.

Table 4 Comparison of representative studies of PLA+HA composites and the present work

Reference	Fabrication Method	HA Content	Characterization	Main Findings
Zhang et al. (2021)	Fused deposition modeling	0; 30%; 50%	Compression; in vitro; in vivo; surface morphology; wettability	High nHA loading improved compressive strength and exhibited favorable osteogenic performance for bone tissue engineering.
Benziada et al. (2026)	Fused deposition modeling	40%	Compression; wettability; nanoindentation; tribology; XRD; Raman spectroscopy	HA addition significantly improved surface wettability, stiffness, and hardness, while auxetic PLA–HA structures maintained structural integrity after degradation.
Zimina et al. (2020)	Solvent casting and salt leaching	0%; 15%; 20%	Tension; FT-IR; EDX; morphology; wettability; in vitro; in vivo	HA addition improved wettability and biocompatibility while maintaining a porous scaffold with uniformly distributed HA particles suitable for bone tissue engineering.
Zhou et al. (2021)	Fused deposition modeling	0%; 50%	Compression; in vitro; in vivo; morphology	PLA/n-HA scaffolds demonstrated adequate mechanical performance and superior osteogenic capability compared with pure PLA.
Wu et al. (2021)	Fused deposition modeling	0%; 3%; 6%; 9%; 12%	Compression; wettability; in vitro; in vivo	Addition of hydroxyapatite significantly improved the strength, wettability, and osteointegration potential of PLA composites, also enhanced antibacterial properties.
Present Study	Stereolithography	0%; 1%; 5%; 10%; 15%	Compression (10^{-4} s^{-1} and 10^{-3} s^{-1}); constitutive modeling; wettability; SEM	Established a unified framework integrating quasi-static strain-rate characterization, simplified ZWT constitutive modeling, wettability evaluation, and SEM-based morphology analysis for SLA-printed PLA+HA composites.

5. Conclusion

The present study demonstrates that the simplified ZWT constitutive model adequately describes the strain-rate-dependent compressive behavior of SLA 3D-printed PLA + HA composites within the investigated quasi-static strain-rate range. The model successfully captured the rate-dependent stiffening behavior for most compositions under strain rates of 10^{-4} – 10^{-3} s^{-1} , yielding generally high goodness-of-fit for most compositions. The fitting process was most stable for the 5–15 wt.% HA specimens, whereas the 1 wt.% HA showed reduced stability due to early softening overlapping the nominal elastic region, requiring the fitting domain to be restricted to 3% true strain. Contact angle results further showed that increasing HA content improved surface wettability, with the 15 wt.% HA composite exhibiting the lowest contact angle and highest hydrophilicity, indicating that HA incorporation enhances both stiffness-related mechanical behavior and surface wettability relevant to candidate biomaterial applications.

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Author Contributions

B. Dwinata: Writing, original draft, conceptualization, data curation, investigation, formal analysis. **B. Budiwantoro:** Writing, review and editing, supervision. **M.A. Kariem:**

Writing, review, and editing, supervision. **A.I. Mahyuddin:** Writing, review and editing, supervision. **M.N.S. Budi:** Writing, review, and editing. **W.I. Faisham:** Review and supervision.

Conflict of Interest

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Declaration of AI

During the preparation of this work the author(s) used DeepL Translate and Grammarly in order to improve the quality of writing and its content in the manuscript. After using these tools/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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