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Physicochemical Properties of Soft Polylactic Acid Biocomposites Reinforced with Rice Husk and Titanium Dioxide Nanoparticles for Orthopedic Insole Applications

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Abstract

This study investigated the physicochemical properties of virgin biodegradable soft polylactic acid (SPLA) and SPLA biocomposites reinforced with rice husk (RH), titanium dioxide (TiO₂), and RH/TiO₂ hybrid fillers for orthopedic insole applications. The study was motivated by the need for more sustainable insole materials with tunable weight, hardness, and moisture response. Hybrid filler biocomposites are already known in the broader polymer-composite literature, but comparatively fewer studies have evaluated RH-filled, TiO₂-filled, and RH/TiO₂-filled soft PLA systems side by side in the specific context of orthopedic insole materials. The objective was therefore to determine how natural, inorganic, and hybrid fillers influence apparent density, water absorption, hardness, and fracture morphology in soft-PLA-based materials. The composites were prepared by two-roll milling followed by compression moulding at 160 °C and 3.5 MPa for 5 min. RH-filled formulations were designated R1, R2, and R3 for 10, 20, and 30 wt% RH, respectively; TiO₂-filled formulations were designated T1, T2, and T3 for 1, 3, and 5 wt% TiO₂, respectively; and hybrid formulations were designated H1, H2, and H3 for 11, 23, and 35 wt% combined RH/TiO₂ filler. Apparent density, water absorption, Micro Vickers hardness (Vickers hardness number), and scanning electron microscopy (SEM) were evaluated. T2 exhibited the highest apparent density (1.076 g/cm³), whereas R2 showed the lowest apparent density (0.845 g/cm³). Hardness increased in all filled systems relative to virgin SPLA, with T3 showing the highest hardness (65.4 HV) and virgin SPLA the lowest (46.3 HV). Water absorption was highest in virgin SPLA (62.230%) and lowest in T1 (0.031%). Unless independently verified as equilibrium values, the reported final water-absorption values represent the 7-day measurements rather than confirmed saturation values. SEM revealed formulation-dependent differences in fracture morphology, visible voids, pull-out cavities, and micron-scale heterogeneity. However, SEM was interpreted conservatively and was not used to claim nanoscale TiO₂ dispersion or confirmed interfacial bonding. Overall, RH reduced composite density, whereas TiO₂ increased hardness and apparent density. TiO₂-rich SPLA systems appear more suitable for relatively rigid orthopedic insoles, while RH/TiO₂ hybrid systems may provide a balance between stiffness, reduced mass, and sustainability.

Keywords: soft polylactic acid; rice husk; titanium dioxide; hybrid biocomposite; orthopedic insole; water absorption; hardness; SEM

1. Introduction

Sustainable polymer materials are receiving increasing attention in orthopedic and biomedical applications because they offer a pathway to reduced environmental impact while maintaining useful engineering performance. Among these materials, polylactic acid (PLA) remains one of the most widely studied bio-based polymers because it is biodegradable, renewable, relatively easy to process, and suitable for composite development (Bajpai et al., 2012; Bajpai et al., 2018; Rajeshkumar et al., 2021). In orthopedic insole applications, however, the matrix alone is rarely sufficient; density, hardness, moisture behavior, and durability must all be tailored to the functional demands of underfoot support and cushioning (Butler et al., 2003; Melia et al., 2021).

The mechanical role of an orthopedic insole depends strongly on material stiffness and deformation behavior. Softer materials can improve conformity to plantar contours and promote redistribution of peak plantar pressure, whereas harder materials are typically more suitable for structural support, stabilization, and motion control (Che et al., 1994; Melia et al., 2021; Peng et al., 2023). The optimum balance is application-specific. A material that is too soft may bottom out under repetitive loading, but a material that is too hard may increase discomfort or localized pressure. This functional trade-off makes materials selection particularly important in orthopedic insole development (Rome, 1991; Tsung et al., 2004).

Natural fillers and inorganic fillers are commonly used to tailor the performance of PLA-based composites. Rice husk (RH) is attractive because it is an abundant agricultural by-product, lightweight, inexpensive, and compatible with sustainability goals. As a lignocellulosic resource, RH can reduce material cost and potentially lower composite density, which is advantageous in weight-sensitive applications (Faruk et al., 2012; Siakeng et al., 2018). Titanium dioxide (TiO₂), by contrast, is a rigid inorganic filler with higher density and ceramic character, making it attractive where increased hardness, stiffness, and improved resistance to deformation are desired (Dua et al., 2023; Mehmood et al., 2023). A hybrid RH/TiO₂ system could therefore offer a useful balance between lower weight, increased surface resistance, and broader sustainability.

In addition to its environmental and economic advantages, rice husk (RH) possesses several material characteristics that make it a promising reinforcement for orthopedic insole applications. Rice husk is a lightweight lignocellulosic material containing a naturally occurring silica-rich outer layer, which can contribute to stiffness enhancement while maintaining relatively low composite density (Ranjan et al., 2022; Kazushi et al., 2026). For orthopedic insoles, reducing material weight is particularly important because lighter insoles improve user comfort, reduce fatigue during prolonged walking, and may enhance patient compliance. Furthermore, the incorporation of RH into biodegradable polymer matrices has been reported to modify the balance between stiffness and flexibility, allowing the development of semi rigid materials capable of providing mechanical support without excessive hardness. Such characteristics are desirable in orthopedic devices intended to redistribute plantar pressure and improve gait biomechanics.

Despite the growing interest in RH-reinforced biocomposites, limited information exists regarding their suitability for orthopedic insole applications, where density, moisture behavior, hardness, and

microstructural integrity must be carefully balanced. Excessively rigid materials may compromise comfort, whereas overly compliant materials may fail to provide adequate support and pressure redistribution. Consequently, there remains a need to identify sustainable filler systems capable of tailoring these properties for orthopedic use. In this study, it was hypothesized that alkali-treated RH would reduce the density of soft polylactic acid (SPLA) composites while providing sufficient reinforcement for semi-rigid insole applications. Titanium dioxide (TiO_2) nanoparticles were expected to enhance hardness and structural stability, whereas RH/ TiO_2 hybrid systems were anticipated to provide an optimized balance between lightweight characteristics, mechanical support, and moisture resistance suitable for orthopedic insole development.

Existing literature has already shown that hybrid biocomposites are an active area of polymer-composite research. The present study does not claim novelty merely because hybrid fillers are used. Rather, the unique contribution lies in the application-specific comparison of RH-only, TiO_2 -only, and RH/ TiO_2 hybrid reinforcement in a soft PLA matrix intended for orthopedic insole relevance, all prepared under the same general processing route. In particular, comparatively fewer studies have compared how these three filler strategies influence apparent density, moisture behavior, hardness, and fracture morphology within the same SPLA system and then interpreted those trends in terms of rigid versus semi-rigid insole design.

Accordingly, the aim of this study was to evaluate the physicochemical properties of compression moulded SPLA biocomposites reinforced with RH, TiO_2 , and RH/ TiO_2 hybrid fillers for orthopedic insole applications. The specific objectives were to: (i) determine the effect of filler type and loading on apparent density, water absorption, and Micro Vickers hardness; (ii) compare fracture morphology using SEM; and (iii) identify formulation trends relevant to the design of rigid and semi-rigid orthopedic insole materials.

2. Materials and Methods

2.1 Materials

The materials used in this study were soft polylactic acid (SPLA), rice husk (RH), titanium dioxide (TiO_2) precursor materials, polyethylene glycol (PEG), sodium hydroxide (NaOH), and chromic acid. Rice husk was sourced from Abakaliki rice mill, Nigeria, while SPLA was obtained from the open market. NaOH, used for RH treatment, and chromic acid, used for pH adjustment during TiO_2 synthesis, were sourced from NILEST. Titanium tetraisopropoxide (TTIP), used as the TiO_2 precursor, was obtained from Steeve Moore Chemicals Ltd., Zaria, Nigeria. Terminalia catappa leaves used during TiO_2 synthesis were collected from the Department of Metallurgy and Materials Engineering garden, Ahmadu Bello University, Zaria. Polyethylene glycol (PEG, molecular weight 4000 g/mol) was used as a plasticizer.

2.2 Pretreatment of Rice Husk

A starting quantity of 186 grams of rice husk, was subjected to thorough washing using distilled water. This washing step was necessary to eliminate the surface impurities such as sand particles, dust, and other impurities that are typically present in agricultural residues. Distilled water was employed intentionally in order not to introduce any other contaminants during washing.

Following the washing process, sun drying for one hour and thirty minutes at environmental conditions typical for the Harmattan period, where the ambient temperature was approximately 39°C, was applied to the rice husk. The mellow drying was intended to reduce surface moisture content without compromising the integrity of the fibers' structure, setting the husk out for further chemical treatments. Upon drying, the weight of the husk was reduced slightly to 182.5 grams, showing that washing and drying removed water and soluble impurities.

To further improve the chemical and physical characteristics of the rice husk fibers and promote their compatibility with the polymer matrices, alkaline treatment was performed. In particular, the dried rice husk was immersed in 2000 milliliters of sodium hydroxide (NaOH) solution. This alkaline treatment, wherein soaking is for 15 minutes, has several positive effects: it can effectively remove residual lignin, hemicellulose, and other surface impurities, induces partial depolymerization on the fiber surface, improves pore volume and surface roughness, hence providing better interfacial bonding with the polymer matrix. Upon soaking, pH testing with litmus paper revealed a pH of around 12, as expected for the alkaline character of the solution around the rice husk fibers.

To neutralize the alkaline state and enhance the chemical surface properties of the rice husk to the best, 60 milliliters of chromic acid was added subsequently. This was following established procedures such as those outlined by Akil et al. (2011) and was meant to control the pH level of the mixture from strongly alkaline to neutral, which is crucial in preventing degradation of the fibers and enabling proper interaction with the polymer when producing the biocomposite.

Subsequent to pH neutralization, the treated rice husk fibers were placed in distilled water and washed twice to remove excess NaOH, chromic acid, and dissolved impurities. The fibers were filtered to remove solids from the wash water prior to sun drying for another one hour to reduce moisture content. To proceed with complete drying and prepare the husk for milling, the material was oven-dried under controlled temperature for 1 hour and 15 minutes. The weight of the rice husk after combined chemical treatment, washing, and drying was taken at 146.2 grams, which accounted for the removal of soluble content and moisture content.

The final stage was comminution of the processed rice husk fibers into fine powder form of quality for composite filler purposes. For this, a pulverizing machine was used with different settings to be operated for one-minute duration at 120 seconds runtime, resulting in powder particles that were approximately 63 microns in size. This homogenous particle size was selected to offer uniform distribution within the polymer matrix and maximize surface area for interaction with SPLA polymer. The particle size and morphological characteristics of the resultant rice husk powder were subsequently analyzed to validate its capacity to be utilized as a reinforcing material.

2.3 Synthesis of TiO₂ Filler

TiO₂ was synthesized by a sol-gel route using titanium tetraisopropoxide (TTIP) and Terminalia catappa leaf extract. This route integrates chemical synthesis with a plant-assisted component. However, the archived dataset did not report direct measurements of TiO₂ particle size, particle-

size distribution, specific surface area, crystalline phase, or surface chemistry. For this reason, the present manuscript does not make any claims that depend on those unreported measurements.

The preparation of the *Terminalia catappa* leaf extract, which serves as the reducing and stabilizing agent for the titanium dioxide nanoparticle synthesis, began with the careful processing of dried *Terminalia catappa* leaves. Initially, the dried leaves were chopped into smaller pieces. Prior to extraction, the chopped leaves were thoroughly washed with clean water to remove any adhering dust or impurities. They were then placed under direct sunlight for approximately 20 minutes to enhance moisture removal and prepare them for subsequent extraction.

For the extraction process, a specific quantity of 160 grams of the prepared chopped leaves was transferred into a hammer bottle containing 1000 milliliters of distilled water. This mixture was then placed in a controlled water bath system equipped with dual stirring mechanisms a mechanical stirrer set to rotate at 1.8 revolutions per minute (rpm) and the water bath itself rotated at 60 rpm. The purpose of these controlled stirring actions was to ensure uniform heat distribution and adequate agitation to facilitate effective extraction of the bioactive compounds from the leaves. The extraction was conducted at a sustained temperature of 65°C over a prolonged period of 150 minutes. This temperature and time frame were carefully optimized to maximize the dissolution of phytochemicals such as alkaloids and phenolic acids, which play critical roles in the subsequent reduction of the titanium precursor.

Following the completion of the extraction period, the heated leaf mixture was subjected to filtration using suitable filter mesh to separate the solid leaf residues from the aqueous extract. Approximately 300 cubic centimeters of the resulting clear leaf extract was collected, to be used in the nanoparticle synthesis.

The synthesis of titanium dioxide nanoparticles followed the sol-gel approach as outlined by Dubey et al. (2019). In this step, 300 cm³ of the *Terminalia catappa* leaf extract was mixed with 40 cm³ of titanium tetrakisopropoxide (TTIP), the titanium precursor salt. Upon combining these reactants, an immediate off-white precipitate formed, indicating the initiation of the chemical reduction of TTIP by the bioactive compounds present in the leaf extract. To promote thorough mixing and reaction progression, the mixture was manually stirred by hand over a period of 10 minutes. Subsequently, the mixture was subjected to continuous, controlled agitation on a magnetic stirrer operating for 150 minutes to ensure complete homogeneity and advancement of the reduction reaction.

After the stirring phase, the pH of the reaction mixture was measured using indicator paper, revealing an acidic environment with a pH value of approximately 5. Given that the nanoparticle synthesis requires a neutral pH to facilitate optimal particle formation and stability, the pH was adjusted by the dropwise addition of 20 milliliters of sodium hydroxide solution. This neutralization step aligns with the controlled methodology described by Nisha et al. (2022) to prevent the formation of undesired by-products and ensure thorough precipitation of nanoparticles.

Following pH adjustment, the precipitate was separated from the mixture via filtration using Whatman filter paper or an equivalent medium to recover the titania nanoparticles. The filtered nanoparticles initially appeared as a reddish-brown powder, reflecting the presence of organic

residues and incomplete crystallinity at this stage. To purify and crystallize the nanoparticles, the powder was sun-dried for approximately three hours to remove residual moisture and volatile organic compounds. Thereafter, the dried nanoparticles underwent thermal treatment via calcination in a furnace at a prescribed temperature for 1 hour and 30 minutes. This calcination process serves to decompose the organic constituents from the leaf extract, enhance crystallinity, and improve particle purity. Upon completion, a clean, white powder consisting of well-formed titanium dioxide nanoparticles was obtained. This final product exhibits the desired physical and chemical characteristics suitable for reinforcement in polymer composite applications.

This detailed synthesis protocol highlights the integration of green chemistry principles with carefully controlled process parameters, thereby producing high-quality TiO₂ nanoparticles with potential for enhancing the mechanical and functional properties of sustainable biocomposites.

2.4 Composite Formulations and Fabrication

The SPLA biocomposites were prepared in three formulation groups together with a virgin SPLA control:

- R1, R2, and R3: RH/SPLA biocomposites containing 10, 20, and 30 wt% RH, respectively
- T1, T2, and T3: TiO₂/SPLA biocomposites containing 1, 3, and 5 wt% TiO₂, respectively
- H1, H2, and H3: RH/TiO₂/SPLA hybrid biocomposites containing 11, 23, and 35 wt% combined RH/TiO₂ filler, respectively

The soft polylactic acid SPLA biocomposite samples were fabricated using compression molding with varying filler content: RH at 10, 20, and 30 wt%, TiO₂ nanoparticles at 1, 3, and 5 wt%, and hybrid composites with combinations of both rice husk and titanium nanoparticles in 11, 23, and 35 wt% respectively and the virgin SPLA as the control sample. The two-roll mill machine was used in blending the fillers with soft polylactic acid at a temperature of 165°C and speed of 25rpm in 12 minutes. During the blending process, the biocomposite was treated with 5% of polyethylene glycol PEG (4000 g/mol), which serves as a plasticizer. This PEG content was selected as a moderate plasticizer loading intended to improve flexibility and processability of SPLA while avoiding excessive softening that could compromise the structural support expected of orthopedic insole materials. According to (A.P. Johari et al., 2016), the plasticizers lower the storage modulus E' of the RH/SPLA biocomposite and thereby increase the loss modulus E'', which is a measure

of viscous liquid behavior. Increase polymer chain mobility and improve filler dispersion of TiO₂ nanoparticles.

After blending, each formulation was wrapped with baking paper and compression moulded at 160 °C under 3.5 MPa for 5 min. The moulded sheets were then cooled at room temperature for 90 min before demoulding. The cooling method is void of the risk of debonding, cracking, and delamination of the matrix, as is commonly found in other forms of fast cooling processes. The virgin SPLA, R1, R2 and R3 T1, T2, and T3, and H1, H2, and H3 were used to differentiate individual fabricated samples that represent rice husk composite RH/SPLA (R1-R3), titanium nanoparticles composite TiO₂/SPLA (T1-T3) and hybrid rice husk with titanium nanoparticles RH/TiO₂/SPLA (H1-H3) and finally the sample of the virgin SPLA.

2.5 Characterization

2.5.1 Apparent density

Apparent density was determined from specimen varying mass and geometric volume of 5.280cm³ and reported in g/cm³ for ten (10) specimen tested.

2.5.2 Water absorption

Water absorption was measured gravimetrically from the increase in specimen mass after immersion. Distilled water was used as immersion medium to eliminate ionic interference, using a standard temperature of 38°C. Before immersion the specimen was dried in an oven at 60°C for 24 hours to remove absorbed moisture and cooled in a desiccator for 30 minutes, the initial dry weight was taken as W_i using a precision balance, then followed by full immersion of the specimen in water bath for 7days at 24 hours' intervals. After each interval, the specimen is removed, surface cleaned and weighed immediately as the final weight W_f.

The percentage water absorption was calculated as
$$= \frac{W_i - W_f}{W_f} \times 100$$

where W_i is the initial dry weight and W_f is the weight after immersion at the specified time point.

2.5.3 Micro Vickers hardness

Surface hardness was measured using the Micro Vickers method and reported as the Vickers hardness number (HV). The hardness measurements on polymeric and

plasticized biocomposites are sensitive to viscoelastic recovery, the indentation load of 0.98N to produce clear indentation geometry and dwell time of 20 seconds for full plastic deformation with 5 indentations (HV_{1-5}) per specimen to improve statistical reliability and as well capture microstructural variability. The average varying procedure was calculated per specimen as:

$$HV = \frac{HV1+HV2+HV3+HV4+HV5}{5}$$

2.5.4 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to compare fracture-surface morphology and visible microstructural features of virgin SPLA and the different biocomposite formulations. The specimen was cut into manageable size of 15mm, and then immersed in nitrogen for 5min, it was also mounted in epoxy resin for polishing and ensure scratch free surface. Sputter coating using gold of 5nm thickness to prevent charging effect and image distortion. 10kv voltage was applied for deep penetration and good resolution with a magnification range of 500x for rice husk distribution and titanium nanoparticles dispersion and scale bar of 50 μ m for clear contrast.

3. Results and Discussion

3.1 Apparent Density of Virgin SPLA and Filled SPLA Biocomposites

Table 1: Biocomposite formulations and apparent density of virgin SPLA and filled SPLA biocomposites.

S/N	Samples	Biocomposite Composition (%)	Apparent Density (g/cm ³)
1	SPLA	Virgin soft PLA	1.026
2	R1	10%wt RH/SPLA	0.988
3	R2	20%wt RH/SPLA	0.845
4	R3	30%wt RH/SPLA	0.851
5	T1	1 wt% TiO ₂ /SPLA	0.893
6	T2	3 wt% TiO ₂ /SPLA	1.076
7	T3	5 wt% TiO ₂ /SPLA	1.057
8	H1	11wt% RH/TiO ₂ /SPLA	0.974
9	H2	23 wt% RH/TiO ₂ /SPLA	0.950
10	H3	35 wt% RH/TiO ₂ /SPLA	0.950

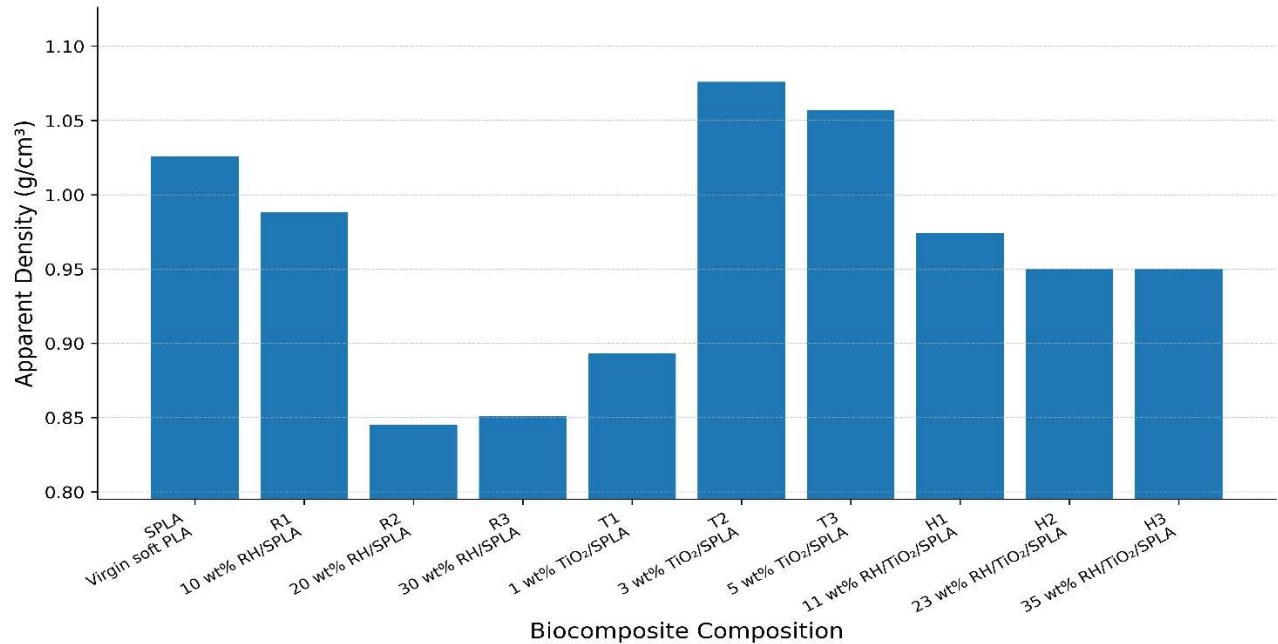


Figure 1. Effect of filler composition on the apparent density of virgin SPLA and filled SPLA biocomposites.

3.1 The Effect of Filler Percentage Composition on the Biocomposite Apparent Density

The figure 1 indicates that incorporating rice husk (RH) into polylactic acid (PLA) biocomposites typically results in a decrease in the apparent density of the composite material produced and the amounts of added rice husk equally influence the overall apparent density of the biocomposite.

The apparent density results showed a clear dependence on filler type. T2 exhibited the highest apparent density (1.076 g/cm^3), whereas R2 exhibited the lowest apparent density (0.845 g/cm^3). These values are physically consistent with solid compression moulded PLA-based biocomposites and confirm that the materials are non-foamed biocomposites.

The lower apparent density observed in the RH-filled series is consistent with the lower effective density of lignocellulosic RH relative to TiO_2 and many mineral fillers. In applications such as orthopedic insoles, reduced material mass may be advantageous for comfort and wearability. By contrast, the TiO_2 -filled biocomposites showed higher apparent density, which is expected because TiO_2 is a denser rigid inorganic phase. However, the increase in density might be limited depending on the quantity of TiO_2 used and its distribution within the SPLA matrix. Titanium dioxide (TiO_2) nanoparticles possess a density of approximately $3.8 \text{ g}\cdot\text{cm}^{-3}$, which is about 3.5 times higher than that of polylactic acid PLA ($1.2 \text{ g}\cdot\text{cm}^{-3}$), as reported by (Kaseem et al., 2019) on PLA/ TiO_2 nanocomposites. Thus, the incorporation of TiO_2 into the SPLA matrix typically leads to an overall increase in the biocomposite's apparent density. This inherent high density of titanium nanoparticles influenced the increase in apparent density as the filler content increases from T1 to T3 as shown in figure 1 above.

Additionally, the H-series of the prepared SPLA biocomposites exhibited trends similar to those seen in the R-series. It was observed that the use of the RH/TiO₂ hybrid filler leads to a reduction in density due to the presence of RH in the SPLA biocomposites. The combined impact of TiO₂ and RH on SPLA apparent density is twofold. While titanium oxide typically raises density, the RH is acting in opposite direction by reducing the density, and the higher percentage of the RH in the hybrid biocomposite lead more displacement of some SPLA particles, potentially resulting in the linear decrease in apparent density of the H-series, a similar behavior was noted by (Ana et al., 2020).

Table 2: Water absorption of virgin SPLA and filled SPLA biocomposites at 7 days

Sample	Initial Weight (g)	Obtained weight at 24 hours Interval							Final – Initial	% Water Absorption
		1	2	3	4	5	6	7		
SPLA (100)	5.130	6.110	7.01	7.910	7.99	8.790	9.490	10.240	0.602	62.230
T1	5.132	5.132	5.132	5.133	5.133	5.135	5.135	5.135	0.002	0.031
T2	5.116	5.117	5.119	5.120	5.122	5.122	5.122	5.122	0.005	0.089
T3	5.120	5.124	5.128	5.133	5.139	5.140	5.142	5.142	0.015	0.293
R1	5.186	5.192	5.193	5.252	5.286	5.299	5.299	5.299	0.074	1.430
R2	5.162	5.173	5.182	5.190	5.204	5.204	5.204	5.204	0.032	0.630
R3	5.186	5.196	5.236	5.250	5.250	5.250	5.250	5.250	0.054	1.047
H1	5.110	5.112	5.113	5.232	5.266	5.269	5.269	5.269	0.087	1.720
H2	5.104	5.111	5.117	5.120	5.272	5.280	5.284	5.284	0.105	2.071
H3	5.098	5.106	5.136	5.255	5.260	5.300	5.302	5.303	0.139	2.735

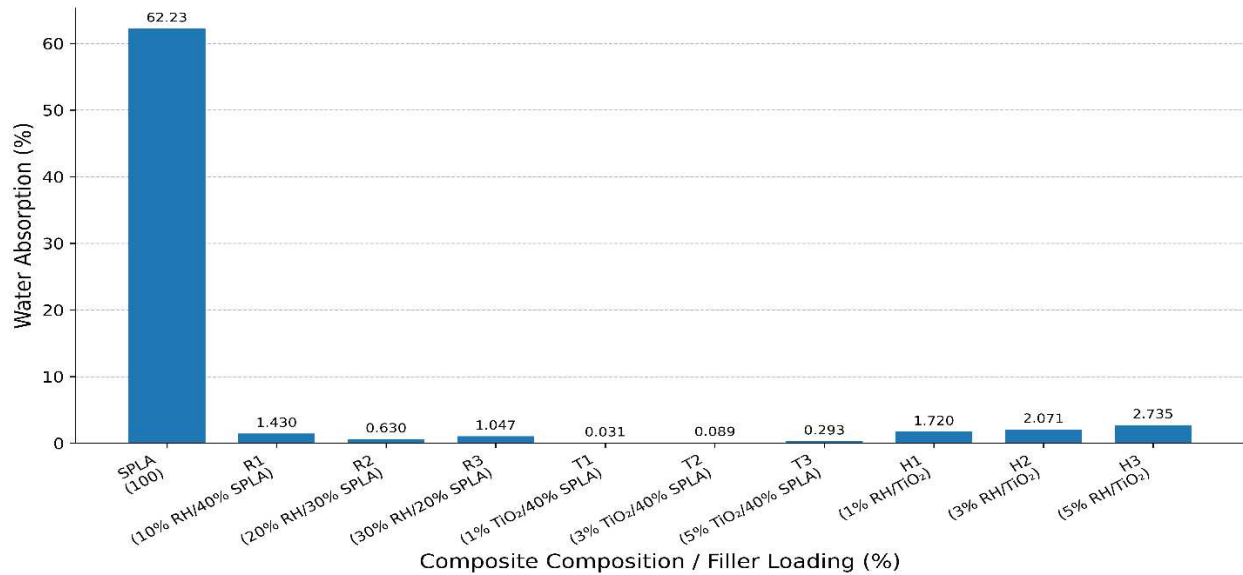


Figure 2: Effect of water absorption on the virgin and filled SPLA biocomposite for 7 days monitoring period

3.2 Water Absorption Behaviour of Virgin SPLA and Filled SPLA Biocomposites

The water absorption behaviour of the virgin SPLA and filled biocomposites after seven days of immersion is presented in Figure 2. The results indicate that all formulations exhibited relatively low moisture uptake, suggesting that the developed biocomposites possess acceptable resistance to water penetration for potential orthopedic insole applications where exposure to perspiration and humid environments is expected.

Among the investigated formulations, T1 exhibited the lowest water absorption value (0.031%), whereas the highest value was observed for H3 (0.056%). Although differences between formulations were relatively small, the results demonstrate that filler type and filler loading influenced moisture uptake behaviour. Since replicate-level measurements were not available from the archived experimental dataset, statistical significance could not be established; therefore, the observed trends is interpreted cautiously.

The moisture absorption behaviour of the RH-filled Biocomposites (R1–R3) can be partially attributed to the lignocellulosic nature of rice husk. Natural fibres contain cellulose, hemicellulose, and residual hydroxyl containing constituents that may interact with water molecules and promote moisture uptake. Although alkali treatment reduces some hydrophilic constituents and improves fibre-matrix compatibility, complete elimination of moisture sensitive sites is generally not achieved. Consequently, RH containing formulations may retain a certain tendency to absorb water when exposed to humid environments.

For the TiO₂-filled composites (T1–T3), the relatively low water absorption observed may be associated with improved filler dispersion and reduced void formation within the SPLA matrix. SEM observations revealed comparatively smooth fracture surfaces and fewer visible defects in the TiO₂-filled systems, indicating enhanced filler matrix interaction. However, it should be noted that no surface chemistry characterization techniques such as FTIR, XPS, or contact angle measurements were performed in the present study. Therefore, direct attribution of moisture behaviour to hydroxyl groups on TiO₂ surfaces cannot be confirmed and remains speculative.

The hybrid RH/TiO₂ composites (H1–H3) exhibited slightly higher water absorption values than the TiO₂ only systems. This behaviour may result from a combination of factors, including the hydrophilic nature of the RH component, filler-induced porosity, interfacial defects, and variations in filler dispersion. SEM micrographs of the hybrid systems revealed the presence of pull-out cavities, localized agglomeration, voids, and heterogeneous fracture features, particularly at higher filler loadings. These microstructural defects may provide pathways for moisture ingress and retention within the composite structure.

Furthermore, the SEM image of H3 revealed evidence of filler agglomeration and fibre pull-out, suggesting less efficient filler-matrix bonding at the highest hybrid filler loading. Such morphological features have been reported to facilitate water penetration by creating microvoids and interfacial gaps within composite materials. Therefore, the slightly higher moisture uptake observed in H3 may be associated with these microstructural characteristics rather than solely with the intrinsic hydrophilicity of the fillers.

Overall, the results suggest that water absorption in the developed SPLA biocomposites is governed by a combination of filler chemistry, interfacial adhesion, filler dispersion quality, and microstructural integrity. While the TiO₂-filled systems demonstrated the greatest resistance to moisture uptake, the hybrid systems still maintained relatively low water absorption values, indicating their potential suitability for orthopedic insole applications. Nevertheless, future studies incorporating statistical analysis, porosity measurements, water contact-angle testing, and advanced interfacial characterization are recommended to establish the precise mechanisms governing moisture absorption in these biocomposites.

Hardness Test

Table 3: The vicker hardness test result of virgin SPLA and filled SPLA biocomposites

S/N	Composite composition (%)	Average Vickers Hardness (HV)
1	SPLA (100)	46.3
2	R1(10 %RH/40 % SPLA)	56.1
3	R2(20 %RH/30 % SPLA)	57.0
4	R3(30 %RH/20 % SPLA)	58.1

5	T1(1 % TiO ₂ /49 % SPLA)	63.4
6	T2(3 % TiO ₂ /47 % SPLA)	64.1
7	T3(5 %TiO ₂ /45 % SPLA)	65.4
8	H1 (10 %RH/ 1%TiO ₂ /39 %SPLA)	60.6
9	H2 (20 %RH/3%TiO ₂ /27 %SPLA)	62.5
10	H3 (30%RH/5%TiO ₂ /15 %SPLA)	62.7

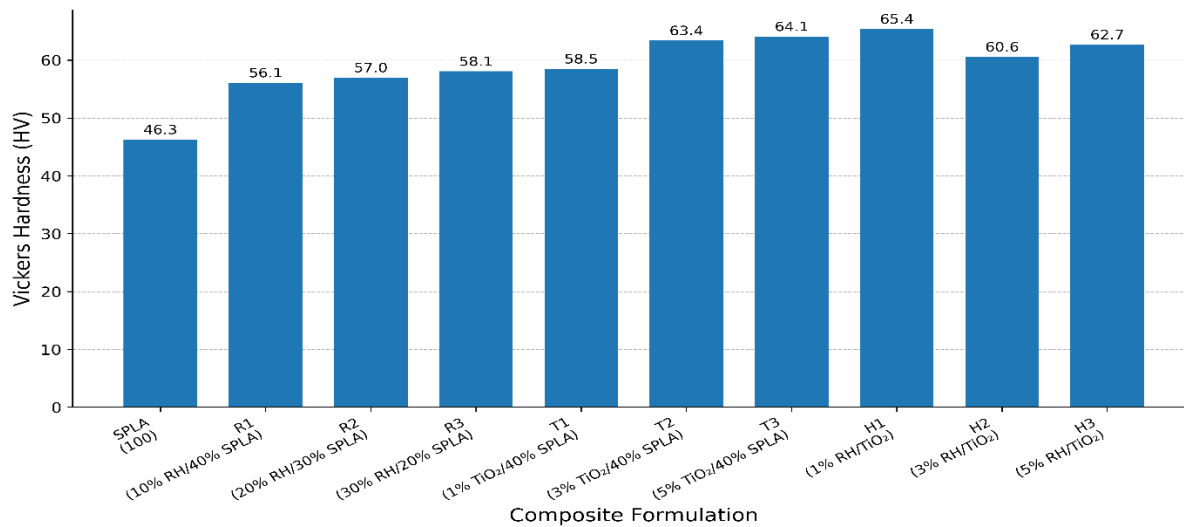


Figure 3: Effect of filler loading on Vickers hardness of virgin SPLA and filled SPLA biocomposites

3.4 Effect of Filler loading on Vickers hardness of virgin SPLA and filled SPLA biocomposites

Micro Vickers hardness reflects resistance to localized surface deformation and is relevant to orthopedic insole materials because it relates to support, wear resistance, and underfoot response. In the present study, all filled systems showed higher hardness than virgin SPLA. Virgin SPLA exhibited the lowest hardness (46.3 HV), whereas T3 exhibited the highest hardness (65.4 HV). The increase in hardness observed in the RH-filled biocomposites is consistent with the reinforcing effect of a rigid lignocellulosic filler and with the surface modification expected from alkali treatment. The TiO₂-filled biocomposites exhibited an even stronger increase in hardness, which

is consistent with the rigid ceramic nature of TiO_2 . The hybrid systems showed intermediate hardness, suggesting a compromise between the lighter-weight RH-filled systems and the harder TiO_2 -rich formulations.

The Vickers Hardness (HV) is an important parameter reflecting the surface mechanical strength and wear resistance of polymers and their composites. This study systematically investigates how different filler compositions influence the Vickers Hardness of SPLA-based biocomposites incorporating rice husk (RH), titanium dioxide (TiO_2), and their hybrid combinations. Figure 3 illustrates the influence of filler loading in the biocomposition on Vickers hardness values of virgin SPLA, single filler biocomposites (RH/SPLA as R1, R2, and R3; TiO_2 /SPLA as T1, T2, and T3), and hybrid filler biocomposites (RH/ TiO_2 /SPLA as H1, H2, and H3) of various filler loadings. The results evidence clearly a trend of hardening as fillers are added, from virgin SPLA to single-filler biocomposites and up to hybrid-filler biocomposites. This order reflects the reinforcing action of the fillers as well as the complex interaction between their types and loadings.

The virgin SPLA recorded a relatively low baseline hardness value of 46.3 HV. This reading conforms to the natural property of polylactic acid (PLA) as a biodegradable thermoplastic polymer with naturally relatively low crystallinity and no reinforcement. Thus, its mechanical response to indentation testing indicates low resistance to deformation, which is important in noting the need for filler addition towards enhancing surface hardness.

Upon incorporation of rice husk (RH) into the SPLA matrix, there was a considerable improvement in Vickers hardness, ranging between about 21% and 25% from that of the pure SPLA. The hardness improved progressively from 56.1 HV in R1 to 58.1 HV in R3, indicating that the rice husk particles were functioning as rigid particulate reinforcements. The midsoft hardness of 15 to 30 shore A is required for compliance of plantar soft tissues and helps reduce peak plantar pressure during gait as noted by (Maimaitirexiati et al, 2024) while a high materials hardness as seen in sample R1 and R3 biocomposite would lead to an increase in peak pressures at localized contact points which can cause discomfort and risk of injury (Peng et al., 2023; Peduzzi et al., 2014; Melia et al., 2020).noted the effect of varying hardness of prefabricated orthopedic insoles on plantar pressure and muscle fatigue during uphill walking with a heavy backpacks.

These natural fillers contribute hardness enhancement primarily due to their native rigidity, which they acquire through the cellulose content and structural rigidity of the lignocellulosic skeleton.

Secondly, the rice husk fillers were alkali-treated with 20% NaOH, which is known to modify the filler surface through removal of impurities and enhancing interfacial adhesion between the filler and polymer matrix. This chemical alteration therefore permits more effective load transfer and improves filler-matrix interaction, supporting the observed increase in hardness.

The generally modest incremental gains after a 10% filler content suggest filler content increments introduce difficulties such as particle agglomeration, capping additional improvement. This effect has been commonly observed in polymer composites, wherein excess content of the filler can undermine the homogeneity and mechanical behavior of the biocomposite. These findings are in good agreement with earlier work done by (Neeraj et al., 2018), who also observed similar improvements in hardness on adding alkaline-treated rice husk into polymer matrices.

Coming to TiO₂-filled biocomposites, the results of the study show even greater hardness value increases for T1, T2, and T3 in relation to virgin SPLA and rice husk biocomposites. The improved hardness improvement with the addition of TiO₂ is attributed to numerous reasons. Titanium dioxide with a nanoscale particle size is expected to disperse uniformly into the polymer matrix and exhibit greater reinforcement efficiency compared to larger filler particle sizes. Chemical treatment of TiO₂ particles' surfaces and plasticization of the matrix enhanced the nanoparticles to spread evenly through soft polylactic acid leading to stronger bonding and improved stress transfer instead of forming clumps. The nanoparticles behave like a tiny stone inside the polymer which restricts polymer chain movement around the biocomposite and thus increases hardness. This is consistent with previous research such as that of (Dua et al., 2023; El Fawal et al., 2021), which pointed towards the enhancement of mechanical properties in polymer composites by TiO₂ nanoparticles as a result of their nanoscale nature and high surface area for enabling stress transfer to be improved.

For the hybrid biocomposites with a combination of rice husk and TiO₂ (H1, H2, and H3), there was an overall trend towards increased hardness with increasing content of filler. The increase flattened out between H2 (62.5 HV) and H3 (62.7 HV), indicating that there is an optimum after which there is no longer any notable increment in hardness with an increase in filler. This act means that while an organic-inorganic hybrid filler system may be able to leverage the strengths of its constituents that is lignocellulosic RH's stiffness and Nano TiO₂ high surface activity there is a complication in realizing the optimum interaction wherein these fillers are present together.

Possible filler-filler interactions, such as agglomeration or incompatibility between the two fillers, could be limiting uniform distribution and stress transfer efficiency in the matrix. This leads to a level of saturation in hardness improvement beyond which additional filler loadings give diminishing returns. Inorganic and organic filler synergy is beneficial but also comes with challenges of dispersion and interfacial adhesion that must be carefully managed in the formation of biocomposites. The findings indicate that filler addition enhances the Vickers hardness of SPLA biocomposites with a clear ranking in efficiency of reinforcement: virgin SPLA < RH/SPLA < TiO₂/SPLA > RH/TiO₂/SPLA (hybrid) in other words, the vicker hardness of the T-series that is T1, T2, and T3 biocomposite (TiO₂/SPLA) is higher than the virgin SPLA, R-series (R1-R3) and H-series (hybrid) biocomposite.

3.5 The Morphological Characterization of virgin SPLA and filled SPLA biocomposites

Using SEM

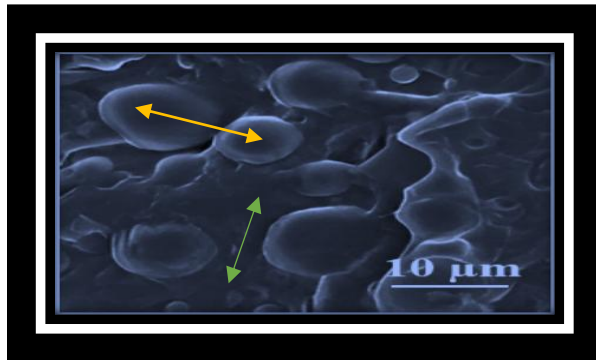


Figure 4: SEM image of Virgin SPLA

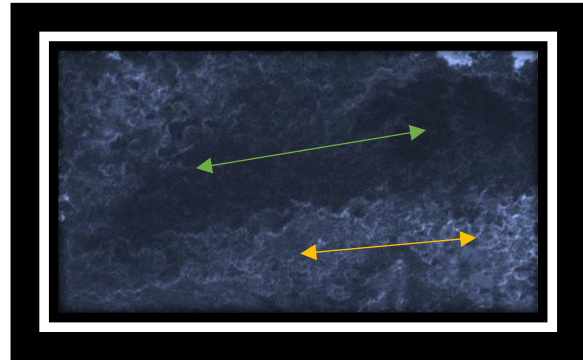


Figure 5: R1 SEM Image at 500x and (50 µm)

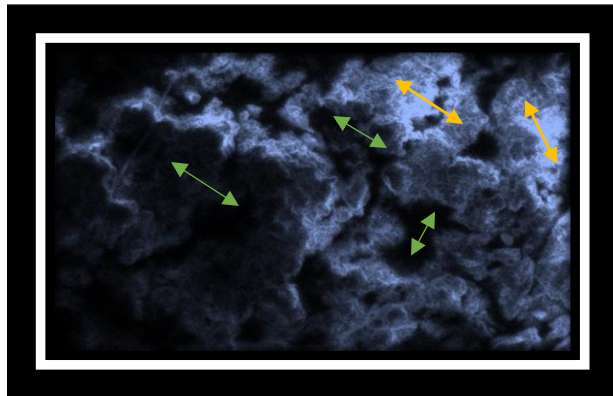


Figure 6: R2: SEM Image at 500x and (50 µm)

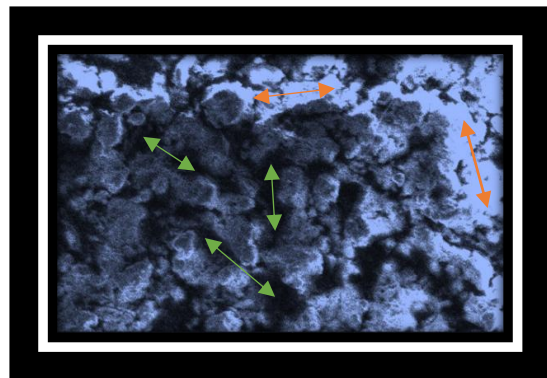


Figure 7: R3 SEM Image at 500x and (50 µm)

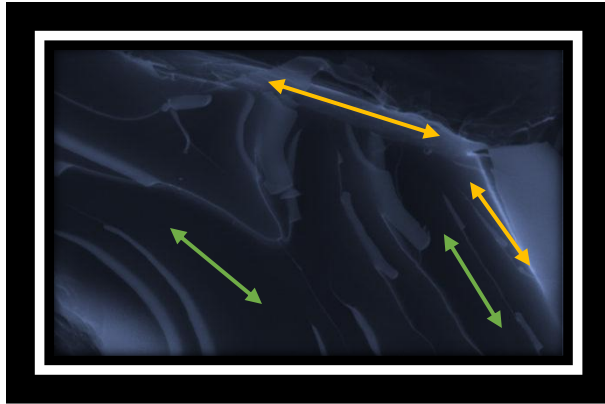


Figure 8: T1 SEM Image at 500x and (50 μm)

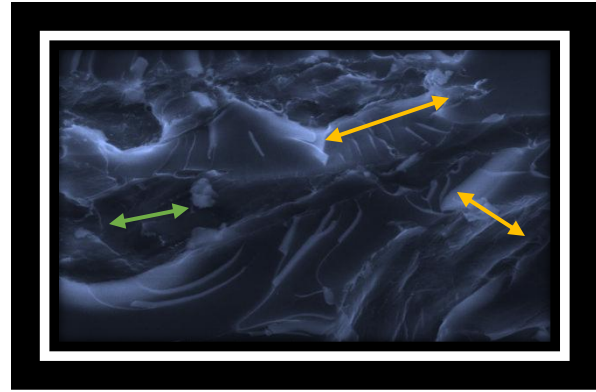


Figure 9: T2 SEM Image at 500x and (50 μm)

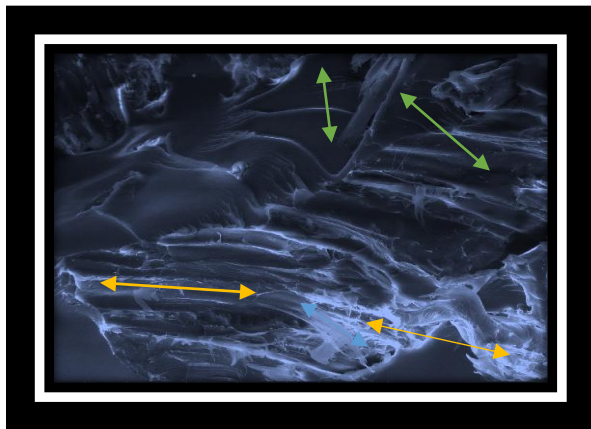


Figure 10: T3 SEM Image at 500x and (50 μm)

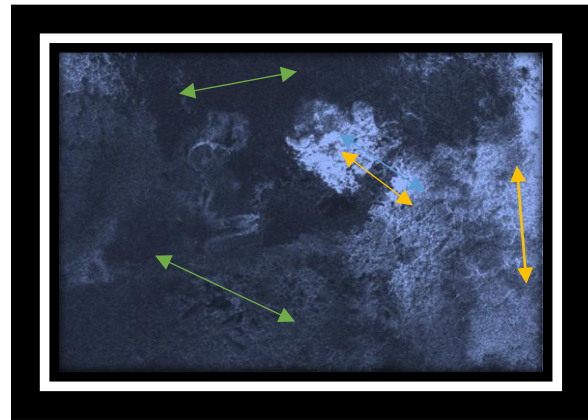


Figure 11: H1 SEM Image at 500x and (50 μm)

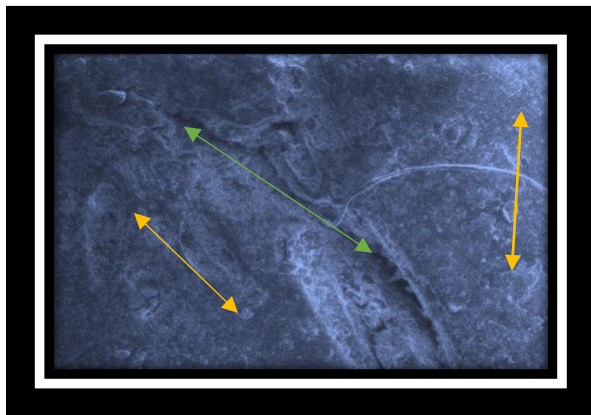


Figure 12: H2 SEM Image at 500x and (50 μm)

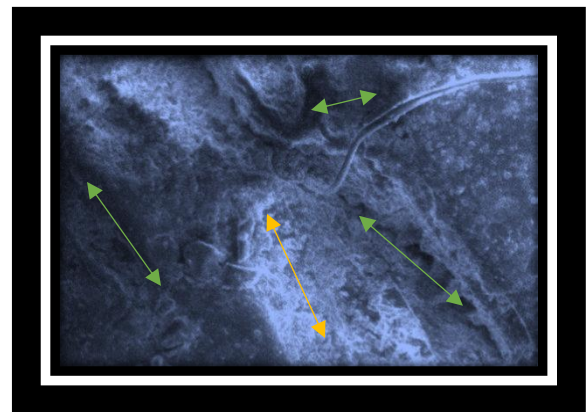


Figure 13: H3 SEM Image at 500x and (50 μm)

3.6 The Morphological Characterization of the Rice Husk, Titanium Nanoparticles and their hybrid Biocomposite Using SEM

The surface characteristics of virgin SPLA in figure 4, biocomposites containing 20% NaOH treated rice husk fiber at varying loadings (10–30%) designated as R1, R2, and R3 biocomposites in figure 5 to 7 with plasticized titanium oxide nanoparticles at loadings of 1–5% designated figure 8 to 10 (T1-T3) as well as hybrid of rice husk and titanium nanofiller biocomposites with loadings ranging from 11–35% as shown in figure 11 to 13 (H1-H3), were systematically examined through scanning electron microscopy (SEM). Figure 4 to 13 represent the longitudinal cross-sectional micrographs of these fabricated materials. SEM analysis was employed to elucidate the morphological evolution and interfacial adhesion characteristics of the single filler biocomposites relative to the hybrid filler biocomposites across the various loading levels.

The SEM micrograph of the virgin SPLA reveals a relatively smooth fractured surface punctuated by the presence of voids and cracks as seen by the green arrow, indicative of an absence of filler matrix interactions. This morphological feature correlates well with the observed lower hardness of virgin SPLA, as inefficient stress transfer occurs across the matrix interface (John & Thomas, 2008; Kabir et al., 2012). Furthermore, the bubble like, smooth regions in the microstructure as shown by the yellow arrow in the virgin SPLA suggest a brittle fracture mechanism accompanied by significant plastic deformation.

In the biocomposites containing NaOH treated rice husk fiber (R1–R3) in figure 5 to 7, the SEM images show filler particles dispersed and embedded within the SPLA matrix as shown by yellow arrows. An increase in filler content, from R1 through R3, is visually manifested by a denser filler distribution and corresponds with incremental enhancements in hardness as clearly seen in the microstructure of R2 and R3 yellow arrows, adhesion between filler and matrix appears moderate. The green arrows on the SEM showing dark gaps, micro voids around filler particles and fiber pull out indicate poor bonding leading to low strength and higher water uptake.

The surface morphology transitions from relatively smoother in R1 (brittle) to rougher in R2 and R3 (harder) shows the overall fiber arrangement which plays a crucial role in determining the physical, mechanical and chemical properties exhibited by the fibers concomitant with higher filler loadings (R.K Mishra et al., 2018). This SEM structural evolution elucidates the increased stiffness relative to virgin SPLA. However, the poor bonding noted in R1 contributes to a reduction in hardness. Despite chemical treatment of the rice husk fillers, the presence of smooth and waxy surface in R1 and large void with RH pull out cavities with green arrow in R3 are characteristic of

untreated natural fillers specifically hydrogen bonding interactions suggests suboptimal compatibility with the hydrophobic SPLA matrix as noted by (Faruk et al., 2012), attributed chiefly to insufficient filler-matrix interfacial interaction.

SEM micrographs of the titanium oxide (TiO_2) reinforced biocomposites in figure 8 to 10 display marked morphological differences, characterized by smoother surfaces and uniform bright dot with no large clusters are attributed to the nanoscale size of the fillers that is mostly pronounce in T1 with green arrows. The filler nanoparticles exhibit dense packing with minimal void formation as shown with yellow arrows in figure 8 to 10, indicative of substantially improved filler matrix adhesion. The SEM polymer matrix appears continuous and well embedded with the fillers, this uniform dispersion of the titanium Nano particles in TiO_2 /SPLA biocomposite can also be attributed to the effect of plasticizer treatment that increases polymer chain mobility which reduces brittleness, improve nanoparticles spread more evenly through the matrix thereby preventing TiO_2 from clumping by coating the biocomposite surface, facilitating more efficient stress transfer and thereby enhancing hardness.

This morphology aligns with literature on inorganic nanoparticle reinforced composites, where nanoparticles enhance interfacial strength and restrict polymer chain mobility (Zhou et al., 2011). The high surface area to volume ratio of the titanium dioxide nanoparticles significantly suppresses void formation. Notably, issues such as filler agglomeration and fiber pull out prominent in virgin SPLA and R-Series biocomposites are greatly mitigated in the T-Series and this is also attributed to the chemical treatment effect of plasticizer. Correspondingly, Vickers hardness testing corroborates these findings, with the T-Series exhibiting superior hardness during mechanical loading where clearly observed on the SEM images of the biocomposite microstructures.

The hybrid filler biocomposites in figure 11 to 13 display improved filler dispersion relative to the R-Series, the SEM image of the hybrid fillers biocomposite shows a reduced fiber pull outs and fewer surface cracks shown with green arrows. The rough, irregular and uneven of the matrix surface with yellow arrows on the SEM image in figure 11 to 13 where caused by the presence of the rice husk filler present in the hybrid fillers and also suggests ductile fracture behavior while the tiny uniform bright dots shows good TiO_2 nanofiller dispersion, indicating enhanced filler matrix compatibility and thus potentially higher stiffness and increase in crystallinity.

Effective interfacial adhesion promotes efficient stress transfer from the matrix to the reinforcing fillers, which is consistent with mechanical property improvements noted at optimized hybrid filler loadings (Bajpai et al., 2018). However, the micrograph of figure 13 (H3) reveals a complex fracture surface characterized by both ductile tearing and brittle regions with green arrows, this was caused by TiO₂ agglomeration around rice husk particles showing a visible fiber pull out on the contrary increased the hardness of the biocomposite.

Fiber ends appear partially embedded with visible pull-outs, indicating incomplete bonding. This mixed fracture morphology is emblematic of hybrid composites where inorganic and natural fillers coexist; this regions of strong bonding promote rigidity, whereas poorly bonded zones reduce toughness, resulting in intermediate physical and mechanical performance (Luzi et al., 2019). Noteworthy, the SEM showing agglomeration and poor dispersion detected in figure 13 (H3) leading to fiber pullout justify the observed increase in water absorption through the gap created by the pullout and increase in hardness effects predominantly attributed to excessive filler loading, similar observation was made by (Saba et al., 2015). Such agglomerates act as crack initiation sites, undermining the biocomposite integrity and increasing susceptibility to moisture ingress and environmental degradation (Kabir et al., 2012). The elevated porosity observed in these biocomposites also explains the reduction in hardness and heightened environmental vulnerability.

The SEM analyses validate that the morphological characteristics and degree of filler dispersion critically influence the interfacial adhesion and consequently the mechanical performance of SPLA based biocomposites. While the incorporation of Nano sized TiO₂ fillers enhances filler matrix adhesion and reduces defect sites, natural fiber fillers require optimized surface treatment and loading to mitigate debonding. Hybrid fillers offer balanced mechanical properties but are sensitive to filler content and distribution, necessitating careful control to avoid agglomeration and porosity that detrimentally affect composite performance.

4. Practical Relevance to Orthopedic Insole Design

The present results suggest that SPLA-based biocomposites can be tailored for different orthopedic insole roles by changing filler type and loading. Lower-density formulations may improve comfort by reducing insole mass, whereas higher-hardness formulations may provide greater support and wear resistance.

On this basis, TiO₂-rich formulations such as T2 and T3 appear promising for relatively rigid insole applications where structural correction and motion control are priorities. RH/TiO₂ hybrid formulations appear more suitable for semi-rigid applications where moderate stiffness, lower weight, and improved sustainability are desirable. RH-rich formulations may be useful where a softer and more compliant response is preferred. From a clinical perspective, reducing the weight of orthopedic insoles may improve user comfort and long-term compliance, particularly among individuals requiring prolonged orthotic use. The RH-filled SPLA biocomposites demonstrated lower apparent density than the TiO₂-rich systems while maintaining improved hardness relative to virgin SPLA. These characteristics suggest that RH-containing formulations may be suitable for semi-rigid orthopedic insoles designed to provide moderate support and pressure redistribution without excessive material mass.

These application-related implications remain preliminary. For stronger translational relevance, future work should include complete statistical analysis, fuller process reporting, nanoparticle characterization, BET analysis, quantitative image analysis, Shore hardness testing, biocompatibility evaluation, and biomechanical validation under realistic use conditions and plantar-pressure evaluation during gait.

Conclusion

This study evaluated the physicochemical properties of soft polylactic acid biocomposites reinforced with rice husk, titanium dioxide, and RH/TiO₂ hybrid fillers for orthopedic insole applications. Based on the available experimental evidence, the following conclusions can be drawn:

1. RH reduced the apparent density of SPLA composites, whereas TiO₂ increased apparent density because of its higher intrinsic density. T2 exhibited the highest apparent density (1.076 g/cm³), while R2 exhibited the lowest (0.845 g/cm³).
2. All filled systems showed lower water absorption than virgin SPLA, with the lowest water uptake observed for T1 (0.031%). The reported final absorption values correspond to the 7-day measurements unless equilibrium saturation is independently verified.
3. Hardness increased in all filled composites relative to virgin SPLA, and the highest Micro Vickers hardness was obtained for T3 (65.4 HV).

4. SEM revealed formulation-dependent differences in fracture morphology, visible voids, pull-out features, and micron-scale heterogeneity, but did not confirm nanoscale dispersion or interfacial bonding.

5. TiO₂-rich formulations appear more suitable for relatively rigid orthopedic insole applications, whereas RH/TiO₂ hybrid systems may offer a balance between moderate stiffness, lower effective mass, and sustainability.

The study further demonstrates that rice husk functions not only as a sustainable reinforcement but also as a lightweight engineering filler capable of modifying the density and support characteristics of SPLA-based materials. The RH/TiO₂ hybrid systems exhibited a balance of reduced density, enhanced hardness, and acceptable moisture resistance, suggesting potential for the development of semi-rigid orthopedic insole materials where comfort, support, and sustainability are simultaneously required.

Overall, the results support the potential of RH and TiO₂ as useful fillers for tailoring the physical response of SPLA-based materials for orthopedic insole development.

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Ethics Approval: This study did not involve human participants or animals. Therefore, ethical approval was not required.

Data Availability Statement: All data generated or analyzed during this study are available from the corresponding author upon reasonable request.

Consent to Participate: Not applicable, as this study did not involve human participants.

Consent to Publish: All authors have read and approved the final manuscript and consent to its publication.

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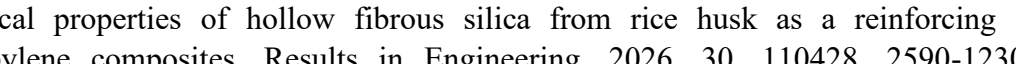
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