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Development of Eco-Friendly Composite Material for Pinewood Replacement Using Agricultural Waste

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Abstract

The demand for wood products contributes greatly to deforestation, resulting in severe environmental effects. Each year, almost 18 million acres of forest are destroyed, which is equivalent to 27 soccer fields vanishing every minute. This rapid deforestation exacerbates climate change, habitat loss, and natural resource depletion. As a result, finding alternatives to traditional wood for building applications such as doors, windows, roofing, beams, furniture, and packaging is essential. This study looked at replacing pinewood with a composite manufactured from agricultural waste, such as rice husks, wheat husks, and safflower husks, together with polylactic acid and zeolite. Alkaline and silane treatment improved the composite's mechanical and thermal characteristics. This study found that composite 1 from multi-husk and composite 4 from single husk had the highest mechanical properties, such as tensile strength (38.46 MPa & 42.4 MPa), flexural strength (62.9 MPa & 69.2 MPa), and compression strength (49.48 MPa & 46.06 MPa). Similarly, multi-husk Composite 1 has shown the highest thermal properties, such as heat deflection temperature (52.9˚C) and differential scanning calorimetry (172.7˚C), among other composites. The addition of zeolite powder in small quantities (5, 7.5, 10 w%) has proved minimal or no effect on the overall thermal stability of the composite.

Subject Areas

Agricultural Science

Keywords

Polylactic Acid, Husks, Zeolite, Injection Molding Process, 3-aminopropyltriethoxysilane ($C_9H_{23}NO_3Si$), Potassium Hydroxide (KOH)

1. Introduction

Due to heightened awareness of the misuse of natural resources, global social concern has intensified in the last two decades. This has prompted numerous researchers and industries to explore methods for minimizing waste as they strive to combat this issue. The use of agricultural byproducts as reinforcements in composite materials raises additional issues. FAO's latest forecast raises global cereal production to 2853 million tons in 2024. The forecast places the wheat production at 792.9 million tons. Each ton of wheat grain generates 1/5 tons of the husk; according to statistics, the world will generate 158.58 million tons of wheat husk [1] in 2024. Likewise, the safflower seed production rate was 6.5 lakh tons worldwide in 2020. Every safflower seed generates 1/3 of the husk; according to statistics, the world generated 2.16 lakh tons of safflower husk in 2020. According to the corporate statistics of the Food and Agriculture Organization, Kazakhstan accounted for 35% of the global safflower production [2]. Every year, rice grain production is increasing rapidly. Each year, the world generates 150 million tons of husk for every 750 million tons of rice grains. The research has primarily categorized rice husks based on their rice genotype, soil chemistry, and the climate conditions under which they have grown. This research has demonstrated that burning rice husk at various temperatures and atmospheric conditions can produce different rice husk derivatives. Burning the rice husks at less than 700˚C under limited oxygen will result in rice husk biochar (RHB). Burning the rice husk at 780˚C will result in rice husk ash (RHA). Burning the rice husk in an aqueous environment will result in rice husk hydrochar (RHH) [3].

The research on biofiber has focused on matrices and their classification based on their degradability and demerits of plant fibers, such as shape retention and hygroscopic nature [4]. PLA is extensively used as a completely biobased and fully biodegradable aliphatic polyester due to its excellent properties. The study has extended the steadiness, decomposability, and methodology of PLA affected by its mechanical properties [5]. Plastic generation has become common these days. However, proper degradation or recycling of plastic after its usage is crucial. Otherwise, it affects the environment severely. Despite being a fully biodegradable material, the degradation process of polylactic acid in a landfill takes a significant amount of time and effort. The research has conducted a study on recycling polylactide to enhance its properties through physical and chemical upgrading strategies and techniques [6].

Husk surfaces are initially rough and irregular due to waxes, lignin, impurities, and hemicellulose present in its topmost layer. The study on geopolymer, which initially treated the hemp shiv fiber with aluminum chloride and potassium hydroxide, found that the hemp shiv fiber's surface functioned as a moisture-absorbent barrier [7]. Similarly, alkaline (NaOH) and silane treatment (γ-aminopropyltriethoxysilane (APS) and γ-glycidoxypropyltrimethoxysilane (GPS)) were used to make the husk surface better so that the matrix and fibers stick to each other effectively. The study conducted husk treatment between 6 h and 48 h at normal room temperature. Then the silane-treated husks were dried in an oven at 60˚C for 24 hours. The results indicated that the husk weight decreased when using the alkaline treatment, while the humidity sensitivity decreased when using the silane treatment [8]. Some chemicals, like γ-aminopropyltriethoxysilane, are added to the poly (L-lactide)/pinewood filler composite to help the matrix and filler stick together better. However, pine wood is very sensitive to temperatures. The study found that the composite of PLA/pine wood biocomposites has lower thermal properties than pure PLLA [9]. On the other hand, the study on composites made from PLA and pine wood flour has shown that the percentage of pinewood filler in a composite has a positive impact. Tensile strength increases as the filler content increases [10].

Polylactic acid, rice husk, and eucalyptus globulus wood form the basis of biocomposites. An early study from 2007 revealed that the injection molding process produced samples with minimal variation in their tensile strength. The composite made of polylactic acid, rice husk, and eucalyptus globulus wood has shown similar results in comparison to pure PLA [11]. Zeolite can increase the temperature-dependent elastic and viscous modulus of a composite material. In 2009, a study stated that the composite made of PLA and four different proportions (0, 1, 3, 5) w% of zeolite has minimal variations in heat deflection temperature. In addition, composites with 3% zeolite have the highest tensile strength [12]. In 2010, researchers carried out additional research to improve the mechanical properties of a composite material that included hemp and polylactic acid. The study found that the strongest composites were those made from 30% hemp fiber treated with alkali and silane and 70% polylactic acid. These composites had the best tensile strength (75.5 MPa) and impact strength (2.64 kJ/m^2). The results have shown that when the amount of hemp fiber increases from 10% to 30%, the mechanical properties also gradually increase [13].

In 2012, researchers focused on creating a composite material by blending fully biodegradable and biobased matrices like thermoplastic pehuen starch (TPS), polylactic acid (PLA), and polyvinyl alcohol (PVA) with natural husk fiber like pehuen cellulosic husk. the test results demonstrated the superior thermal stability of the composite incorporating pehuen cellulosic husk. Conversely, the blend of thermoplastic pehuen starch with PLA and PVA has shown superior mechanical properties such as tensile strength [14]. These days, research has expanded to encompass every field and aspect of life. Particularly, material science, technology, health, and infrastructure fields have seen significant growth. The addition of additives in polymer science has widened the research area. In 2013, researchers used solid waste, such as olive pit powder, a residue from an olive oil mill, as an additive in the production of composites. The research focused on creating a composite by blending polylactic acid and olive oil pits in various proportions through a melt blending process, using these materials as additives. The test results have shown that adding more additives without treating them properly makes the olive pit powder and PLA not interact well. As a result, poor flexural strength [15].

The study of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a composite of ZSM 5 zeolite/poly (L-lactide) under a nitrogenic atmosphere in 2015 revealed tremendous variations in its thermal properties [16]. In 2019, a study analysis revealed that the use of a single-type fiber in a composite did not significantly alter its physical, thermal, and mechanical properties. The research results recommended that adding more than one type of fiber leads to improved properties [17]. Innovation and research in developing a lightweight, cost-effective, durable material for building construction applications is growing rapidly. Materials like rice husk, wheat husk, wood fiber, and textile waste fiber are reinforced using matrices like poly (butylene adipate-co-terephthalate) and poly (lactic acid). The outcomes of this study have shown high thermal stability and mechanical properties [18].

In 2021, advanced technologies like 3D printing in composite manufacturing increased the prospects of the production process with high accuracy and precision. Research has concentrated on printing dog bone and rectangle samples using 1.75 mm-diameter filaments made of PLA and wood sawdust extracted from extrusion. The results confirm that 3D printing can print filaments containing up to 20% wood sawdust [19]. Additionally, research on fused deposition modeling 3D printing uses PLA and biomass filaments to print 3D samples [20].

In 2022, blending rice husk, sawdust, and bagasse as reinforcing materials with polylactic acid in hot compression molding created a new type of material with high stiffness and strength. Overall, the composite made with rice husk and PLA has demonstrated the highest mechanical characteristics compared to the other two materials [21]. In the hot press, research on composites made of PLA reinforced with enset fiber has revealed improved mechanical and thermal properties [22].

Building upon the findings of previous studies, this research aims to develop a composite material using agricultural waste products, specifically rice, wheat, and safflower husks, as potential reinforcements, because there is a possibility of converting these waste products into useful material, especially in the construction sector. This study will focus on improving the mechanical and thermal properties of composite materials. The goal is to demonstrate the feasibility of utilizing agricultural byproducts in composite materials for various applications, thereby contributing to the advancement of sustainable materials and practices.

2. Materials and Methods

2.1. Materials

2.1.1. Rice Husk

Rice husk, the outer shell of rice grains, is a byproduct of rice milling. The rice husk required for this research was purchased from a Thai Tantee online store from Indonesia, and shipped to Germany, where this research was carried out. The rice husk is composed primarily of cellulose (32% - 47%), hemicellulose (19% - 27%), lignin (21% - 26%) [3], and silica (15% - 22%). Its high silica content provides excellent thermal stability [18], making it suitable for high-temperature applications. The lightweight nature of rice husk contributes to reduced overall material weight [11], beneficial in the construction, automotive, and aerospace industries. Additionally, as a natural and renewable resource, it enhances the biodegradability of composites, promoting environmental sustainability [17] [21]. Utilizing rice husk is cost-effective, adding value to an agricultural byproduct. The monographic and microscopic view with a range of 100 µm of a single rice husk fiber is shown in **Figure 1** and **Figure 2**.

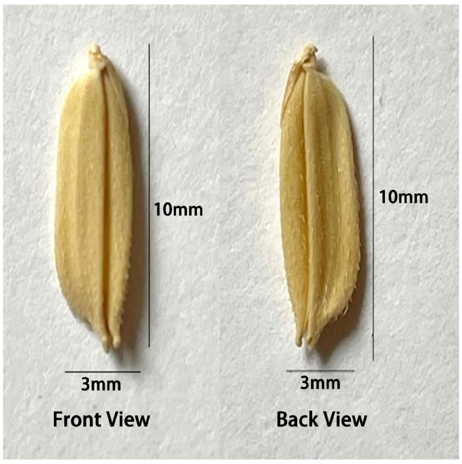

Figure 1. Rice husk (original image).

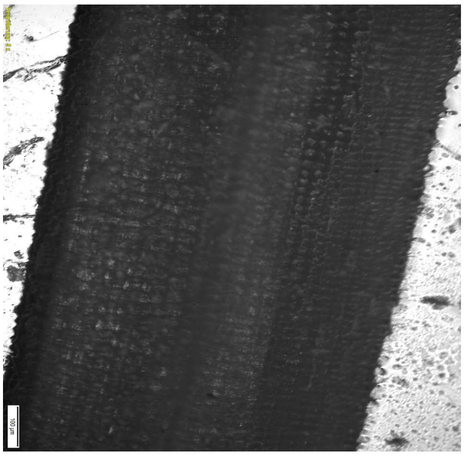

Figure 2. Microscopy of treated rice husk.

2.1.2. Wheat Husk

Wheat husk, the outer layer of wheat grains, is primarily composed of cellulose (35% - 40%), hemicellulose (20% - 30%), lignin (15% - 20%), and ash (10% - 15%) [1]. The wheat husk required for this research was purchased from a local vendor from Hyderabad, India, and shipped to Germany. Wheat husk is utilized in composite materials to enhance mechanical properties such as tensile strength, impact resistance, and thermal stability [18]. Its natural composition makes it biodegradable and eco-friendly, contributing to sustainable development. It finds applications in producing biodegradable plastics, construction materials, and packaging. The monographic and microscopic view with a range of 100 μm of a single wheat husk fiber is shown in **Figure 3** and **Figure 4**.

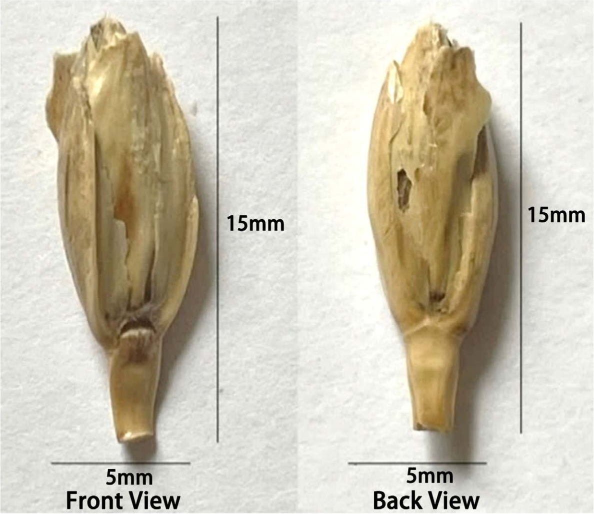

Figure 3. Wheat husk (original image).

Figure 4. Microscopy of treated wheat husk.

2.1.3. Safflower Husk

The outer shells of safflower seeds, known as safflower husks, consist of approximately 40% - 45% cellulose, 20% - 25% hemicellulose, 15% - 20% lignin, and 5% - 10% ash. We purchased the safflower husk required for this research from a local vendor in Hyderabad, India, and shipped it to Germany. The high cellulose and hemicellulose content make safflower husk an excellent source for producing bio-based materials [2], such as biodegradable plastics and bio-composites, which are gaining traction in sustainable product development. Its significant lignin content provides structural integrity and enhances the ductility of materials. However, this study revealed a dearth of research on composites that use safflower husks as reinforcing agents. The monographic and microscopic view with a range of 100 μm of a single safflower husk fiber is shown in **Figure 5** and **Figure 6**.

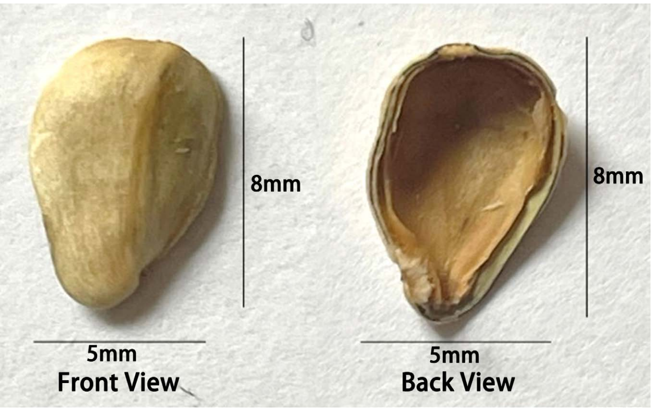

Figure 5. Safflower husk (original image).

Figure 6. Microscopy of treated safflower husk.

2.1.4. Potassium Hydroxide (KOH)

Potassium hydroxide KOH UN 1813 in solid pellet form was purchased from an online vendor, Algin Chemie, from Germany. The potassium hydroxide (KOH) in the chemical treatment of rice, wheat, and safflower husks greatly improved their efficiency in composite material production. The treatment increases the moisture absorbent capacity [7] and surface roughness from which improved mechanical interlocking planes originate; the hemicellulose and lignin are taken away, making the cellulose content to be higher while the fiber hydrophilicity is reduced. Therefore, these transformations increase compatibility with hydrophobic polymer matrices and yield higher levels of durability and better mechanical characteristics [8]. Moreover, the KOH treatment enhanced the thermal stability of the fibers and created open porosity, which enhanced matrix penetration and uniform distribution across the fibers, which handled impact and energy absorption. Furthermore, KOH as an alkali Group 1 element is more environmentally friendly and relatively cheaper to use, especially when it comes to the massive production of green composite material. Moreover, using KOH as a chemical treatment can affect the environment in both positive and negative ways.

Positive effects:	**Negative effects**
Waste minimization by reusing the solution.	Chemical waste and residue
Biodegradable Composites	Neutralization Requirements

Reduction of synthetic materials

Lightweight materials

Improved material properties

2.1.5. Ethanol

Ethanol effectively removes waxes, oils, and other contaminants from the husk fiber surface, thereby improving the cleanliness of the fiber surface in the matrix [7]. We purchased an ethanol 80% V/V liquid solution from B. Braun Melsungen AG, a German manufacturer, via third-party delivery services. This treatment has increased the hydrophobic nature of the fibers, assisting in their compatibility with hydrophobic polymer matrices, leading to the improvement of the mechanical properties of the composite [8]. It also played a crucial role in the maintenance of the mechanical properties of the fibers, as it does not substantially modify their physiochemical properties, hence preserving the inherent strength and elasticity of the fibers. Also, ethanol is another more or less environmentally friendly and less toxic solvent that lessens harm to the environment and human beings that may occur once they apply chemical solutions.

2.1.6. 3-aminopropyltriethoxysilane ($H_2N(CH_2)Si(OC_2H_5)_3$)

3-aminopropyltriethoxysilane (APTES or APTS) product no. 440140 liquid solutions required for the research were purchased from Sigma-Aldrich Lab and production materials from Germany. 3-APTES reacts with the terminal hydroxyl groups on the fiber surfaces and the silane functional groups [8] of the molecular species to create a high degree of cross-linking and better fiber-to-matrix adhesion, resulting in the improvement of the mechanical properties of the composites [9]. This treatment has enhanced the compatibility between the fibers and the polymer, preventing aggregation and promoting better dispersion of the fibers throughout the polymer matrix.

2.1.7. Zeolite

Natural mineral zeolite powder, a grain size of 10 - 15 μm, in a very micronized and soluble product, was purchased from a NaturaForte zeolite powder vendor in Germany. Zeolite powder is a crystalline aluminosilicate mineral that has a variety of uses and applications in agriculture, industry, and chemical products. Specifically, in composite systems, the addition of zeolite powder to the composites brought about an improvement in the mechanical properties, thermal stability [16], and adsorption capability of the systems [12]. Many of its advantages include its ability to perform ion exchange and act as a tool for environmental conservation. Zeolite powder is low toxic and has a large surface area, rendering it suitable for various uses in composites.

2.1.8. Polylactic Acid

PLA's biodegradability [4] ensures that the resulting composites are environmentally friendly, reducing long-term waste accumulation [5] [6]. This research has used 123-3D PLA pellets, purchased from an online store 123inkt.nl in Germany. Its high tensile strength and rigidity [14] contribute to the mechanical robustness of PLA-based composites, making them suitable for demanding applications [10] [19] [20] [22]. PLA's compatibility with natural fibers, such as those derived from rice [11] [21], wheat, and safflower husks, facilitates strong husk-matrix bonding [9], resulting in improved structural integrity and durability of the composites [13]. Additionally, PLA can be easily processed using conventional plastic manufacturing methods, which simplifies the production of PLA composites [15] [16] [18].

2.1.9. Pinewood

Pine wood is a versatile and widely used softwood known for its pale color and distinctive grain patterns. Pinewood was purchased from the local supplier in India with 150 × 20 × 4 mm dimensions for easy testing operations. Pinewood is primarily composed of cellulose, hemicellulose, and lignin. Pine wood is lightweight, easy to work with, and has a good strength-to-weight ratio, making it ideal for construction, furniture, and cabinetry [9] [10].

2.2. Methods

2.2.1. Injection Molding

Injection molding is a widely used manufacturing process for producing filled and unfilled plastic materials in large quantities with high precision and efficiency [5]. It is particularly valued in industries requiring high-volume production, such as construction, automotive, consumer goods, and medical devices. The technique allows for the creation of intricate shapes with excellent surface finish and dimensional accuracy. Injection molding is also versatile, accommodating a range of materials from thermoplastics to thermosetting polymers and composites, enabling the development of innovative, sustainable materials. This method supports rapid production cycles, making it ideal for large-scale manufacturing while maintaining consistency and quality in the final products [11].

2.2.2. Hot Press Molding

Collin SCD mini hydraulic hot press molding, also known as hot compression molding or thermoforming, is especially used for preparing samples for compression tests with 80 mm × 10 mm × 10 mm dimensions. Hot press molding is a manufacturing technique used to shape and form materials under heat and pressure. It is particularly effective for producing high-strength and high-performance composite materials [5]. This method is widely utilized in industries such as construction, aerospace, automotive, and sports equipment, where the strength-to-weight ratio is critical [15]. Hot press molding allows for precise control over the material's properties, resulting in components with excellent mechanical strength [21], durability, thermal stability [22], and dimensional stability. It is also favored for its ability to create complex shapes and detailed surface finishes, making it a versatile choice for various high-performance applications.

3. Manufacturing Process

3.1. Chemical Treatment

The chemical treatment of husk materials like rice, wheat, and safflower husks involves a step-by-step quenching and drying process. Initially, these husk materials were dried at 100˚C for 24 hours to remove any moisture content. Next, a solution of potassium hydroxide (KOH) was prepared by combining it with 92 weights% (distilled water), 3 weights% (ethanol), and a concentration of 5 weights% (KOH) per every 500 g of each husk material. The husk materials were then immersed and left in this KOH solution for 24 hours for thorough chemical treatment. Subsequently, they were rinsed with tap water to remove any residual solution. Following rinsing, the wet husk materials underwent a two-step drying process: firstly, the husks were dried under atmospheric air at ambient conditions for 3 days until they were completely dry. Followed by, they were placed in an oven at 100˚C for 48 hours to expedite the drying process.

3.2. Silane Treatment

Silane solution preparation: For every 500 g of husk material, 1000 mL of silane solution was taken [Scale 1:2]. The solution was prepared by adding three different liquids with different volume percentage ratios as mentioned in Table 1 as follows:

Table 1. Silane solution.

Distilled water	Ethanol	3-aminopropyltriethoxysilane	Husks
90%	7%	3%	500 g

After the KOH chemical treatment process, the dried husk materials were immersed in the silane solution. The solution was stirred for 30 minutes immediately after immersion. Subsequently, the husk materials were left in the silane solution again for 24 hours before being washed with tap water and subjected to a drying process. After 24 hours, firstly, these husks were kept in normal atmospheric conditions (open air) for 3 days, followed by drying in an oven at 100˚C for 48 hours. The following Figures 7-12 illustrate rice, wheat, and safflower husk before and after alkaline and silane treatment.

Figure 7. Rice husk before treatment.

Figure 8. Rice husk after treatment.

Figure 9. Wheat husk before treatment.

Figure 10. Wheat husk after treatment.

Figure 11. Safflower husk before treatment.

Figure 12. Safflower husk after treatment.

3.3. Design of Experiments (DOE)

Based on the statistical approach method using design expert software, the DOE of materials was designed in six different weight proportions under two different categories (1 & 2) to find the lower and upper limits of husk allowed to extract the dog bone composite from the injection molding die, which are mentioned in Table 2 and Table 3 below in terms of weight percentages (w%).

Table 2. Design of experiments of multi-husk composite material, Category 1.

Materials	Composite 1 (w%)	Composite 2 (w%)	Composite 3 (w%)
Rice husk	10	7.5	5
Wheat husk	10	7.5	5
Safflower husk	10	7.5	5
Zeolite	10	7.5	5
Polylactic acid	60	70	80
Total	100	100	100

Table 3. Design of experiments of single-husk composite material, Category 2.

Materials	Composite 4 (w%)	Composite 5 (w%)	Composite 6 (w%)
Rice husk	0	15	0
Wheat husk	15	0	0
Safflower husk	0	0	15
Zeolite	5	5	5
Polylactic acid	80	80	80
Total	100	100	100

In simple terms, DOE under ***multi-husk, Category*** 1 *indicates as follows*:

Composite **1:** 10% *rice husk* + 10% *wheat husk* + 10% *safflower husk* + 10% *zeolite* + 60% *PLA*.

Composite **2:** 7.5% *rice husk* + 7.5% *wheat husk* + 7.5% *safflower husk* + 7.5% *zeolite* + 70% *PLA*.

***Composite* 3:** 5% *rice husk* + 5% *wheat husk* + 5% *safflower husk* + 5% *zeolite* + 80% *PLA*.

*Similarly, DOE under **single husk, category** 2 indicates as follows*:

***Composite* 4:** 15% *wheat husk* + 5% *zeolite* + 80% *PLA*.

***Composite* 5:** 15% *rice husk* + 5% *zeolite* + 80% *PLA*.

***Composite* 6:** 15% *safflower husk* + 5% *zeolite* + 80% *PLA*.

Note: *All proportions were considered in terms of weight percentages*.

3.4. Kneader and Granulator

Thermo Scientific's twin screw device (Kneader) from Haake Polylabs Germany was used for blending husks and zeolite powder with PLA. The kneader (blending) process started with preparing rice husks, wheat husks, safflower husks, zeolite, and PLA according to the design of experiments and fed into the mixing chamber. The materials were thoroughly mixed and kneaded to achieve a consistent mixture at 190˚C and 30 rpm. Figure 13 illustrates the working of a twin-screw machine (Kneader). After blending, the composite was cooled and removed from the machine manually. Figure 14 illustrates blended composite material. Subsequently, a granulator is a cutter machine used to granulate or cut the blended composite into pellets. These pellets, approximately 3 to 5 mm in diameter, were collected and used as raw material for further processing in injection molding and hot press molding.

Figure 13. Husks pouring in kneader device.

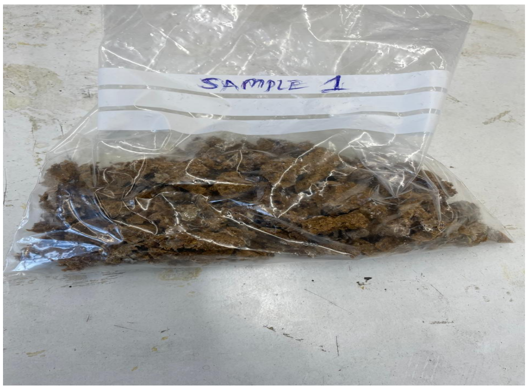

Figure 14. Blended composite from kneader.

3.5. Injection Molding

This research was especially focused on injection molding techniques used for producing composite materials in the shape of a dog bone. It is especially important in those industries where large volumes of production are demanded, including the construction, automotive industry, industries producing various types of consumer goods, and medical device industries. Indeed, using the technique, very elaborate patterns and shapes with a fine surface finish and good dimensional control were produced. **Figure 15** illustrates a dog bone sample extracted from an injection molding die.

Figure 15. Dog bone composite.

3.6. Hot Press Molding

The press begins with the preparation of composite material, where the pellets composed of reinforcing particles (rice husks, wheat husks, and safflower husks) and a polymer matrix (polylactic acid, PLA) were placed manually into the mold with the dimensions of 10 cm × 10 cm × 0.5 cm. **Figure 16**. illustrates the die with the composite in it. Subsequently, the filled mold cavity was placed into a hydraulic press. The press process was performed under 190˚C and 60 bars with a compression cycle time of 20 minutes. Finally, the part was trimmed off according to the compression test specimen size of 45 mm × 14 mm× 13 mm.

Figure 16. Die with composite.

4. Test Equipment and Test Parameters

4.1. Moisture Content

The moisture removal test was conducted on both chemical and silane-treated husk and untreated husk materials to determine the amount of moisture absorption. Equal quantities of rice husk, wheat husk, and safflower husk, both treated and untreated, were placed in an oven for 24-hour intervals. **Figure 17** illustrates equal quantities of KOH treated, followed by silane-treated husks and untreated husks. After every 24 hours, the husk materials were removed from the oven and weighed to measure any weight difference, which indicated the amount of moisture removed. This process was repeated for a total of 72 hours or until the weight difference became zero, signifying that the husk materials were completely dry (moisture content = 0). This test allowed us to accurately determine the duration of oven treatment required for each type of husk material to achieve complete dryness. **Figure 18** illustrates the process of oven treatment of KOH-treated, followed by silane-treated husks and untreated husks.

Figure 17. Equal quantities of Husks.

Figure 18. Husks oven treatment.

4.2. Tensile Tests

Tensile testing was carried out by the Zwick universal testing machine using the DIN EN ISO 527 test standard on samples produced from injection molding. Tensile tests were conducted for six types of composites, which are mentioned in the

Design of Experiments. For each type of composite, an average set of five specimens was taken. Mechanical tests were also conducted for pinewood, to compare the results with six types of composites. The test was run with the following parameters: 0.1 N preload, 1 mm/min tensile modulus, and 115 mm span length. Throughout the test, the specimen's force and displacement were meticulously monitored, facilitating the plotting of a comprehensive stress-strain curve. Using the TestXpert II testing software, tensile strength, and Young's modulus were measured between 0.05% and 0.25% yield strain. This test was carried out on composites measuring 120 mm × 10 mm × 5 mm.

4.3. Flexural Tests

Flexural tests were conducted by the Zwick universal testing machine using the DIN EN ISO 178 test standard on composites produced from injection molding. Flexural tests were conducted for six types of composites, which are mentioned in the Design of Experiments; for each composite, an average set of five specimens was taken. Similarly, flexural tests were also conducted for pinewood and compared the flexural test results of pinewood with the flexural test results of six types of composites. The test was performed with the following parameters: 0.1 N preload and a velocity of 1 mm/min. Using the TestXpert II testing software, flexural strength and modulus were measured. For each composition, an average set of five specimens was taken.

4.4. Compression Tests

Compression tests were conducted by the Zwick/Roell universal testing machine using the DIN EN ISO 604 test standard on composites produced from hot press molding. Compression tests were conducted for six types of composites, which are mentioned in the Design of Experiments. For each type of composite, an average set of five specimens was taken. Compression tests were also conducted for pinewood to compare the results with six types of composites. The test was performed with the following parameters: 0.1 MPa preload and a velocity of 1 mm/min. Using the TestXpert II testing software, compression strength, and compression modulus were measured.

4.5. Heat Deflection Temperature Measurements

Heat deflection temperature (HDT) measurements were conducted on composites produced by injection molding with the Vicat A (ISO 306/ASTM D 1525) test method, using an HDT/Vicat A machine. Heat deflection temperature tests were conducted for six types of composites, which are mentioned in the design of experiments, for each type of composite, an average set of three specimens was taken. The test was run with the following parameters: 35˚C Start Temperature and a 50 K/h temperature gradient. Using the TestXpert II testing software, the average values of the group's softening temperature and softening temperature (VST/HDT) were measured.

4.6. Differential Scanning Calorimetry Measurements

Differential Scanning Calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC 7 with six composite types, as mentioned in the design of the experiments. For each composite type, an average set of three specimens was taken. The test was run with a 10 K/min heat flow rate. Using the Pyris series testing software, the average melting temperatures were measured. The examination was conducted on sample weights between 8 mg to 12 mg.

5. Results

5.1. Moisture Content for Husk Materials

A moisture test was conducted on treated husk materials. Three chemically and silane-treated husk materials (rice, wheat, and safflower) were taken in equal amounts (25 grams considered as 100%). During the moisture test, the amount of moisture removed from the husks was calibrated under a regular interval of 24 hours at a constant temperature of 100˚C. After the first 24 hours of oven treatment, there was a noticeable decrease (90.88%, 97.94%, and 93.7%, respectively) in the husk's overall weight. However, additional oven treatment at 48 (90.84%, 97.26%, and 93.20%) and 72-hour (90.69%, 96.79%, and 93.19%) intervals showed minimal weight changes. Overall, wheat husk has a low moisture-absorbing capacity, followed by safflower husk and rice husk. Figure 19 compares the moisture content removed from the husks at these intervals.

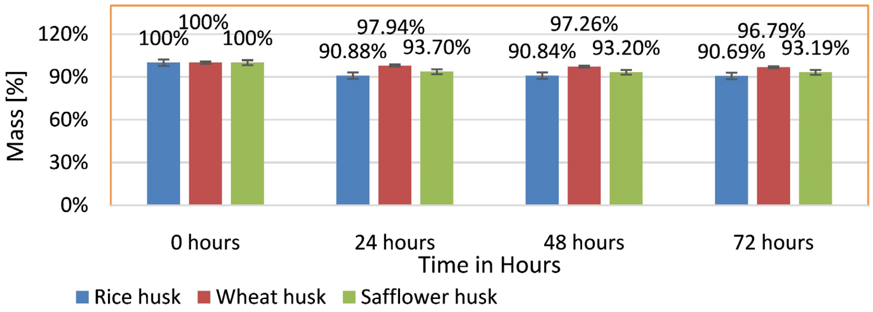

Figure 19. Comparison of moisture % in treated husk materials every 24 hours at 100˚C.

5.2. Tensile Tests

Tensile testing was conducted on composites using the DIN EN ISO 527 standard. According to the DOE, in multi-husk category 1, the composite with the highest husk weight ratio (30%) exhibited the maximum tensile strength (38.46 MPa), while samples with lower husk weight ratios (22.5%, 15%) showed reduced strength (37.68 MPa and 37.54 MPa). In single-husk Category 2, the composite with wheat husk at a 15% weight ratio had the highest tensile strength (42.4 MPa), compared to composites with rice and safflower husks at the same ratio (38.26 MPa and 3.7 MPa). Additionally, tensile testing was performed on pinewood, and the results were compared with those from the DOE composites. Overall, compared with other composites, the composite with wheat husk at 15% has a similar tensile strength

(42.4 MPa) to pinewood tensile strength (43.46 MPa). **Figure 20** shows the tensile test results for each DOE composite compared to pinewood.

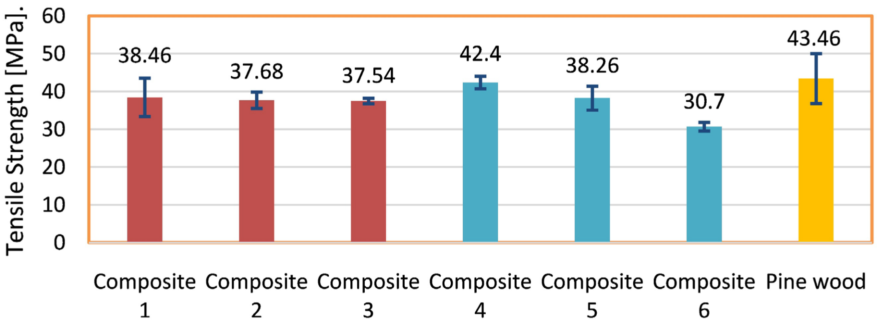

Figure 20. Comparison of tensile strength of composite materials with pinewood.

5.3. Flexural Tests

Flexural testing was conducted on composites using the DIN EN ISO 178 standard. In multi-husk category 1, the composite with the highest husk weight ratio (30%) exhibited the maximum bending strength (62.9 MPa), while the composite with lower husk weight ratios (22.5%, 15%) showed reduced strength (62.34 MPa and 57.38 MPa). In single husk category 2, the composite with wheat husk at a 15% weight percentage had the highest bending strength (69.2 MPa), compared to composites with rice and safflower husks at the same ratio (63.56 MPa and 52.76 MPa). Additionally, the bending testing was performed on pinewood, and the results were compared with those from the DOE composites. Compared with other composites, the composite with wheat husk at 15% has flexural strength (69.2 MPa) like pinewood flexural strength (78 MPa). **Figure 21** shows the three-point bending test results for each DOE composite compared to pinewood.

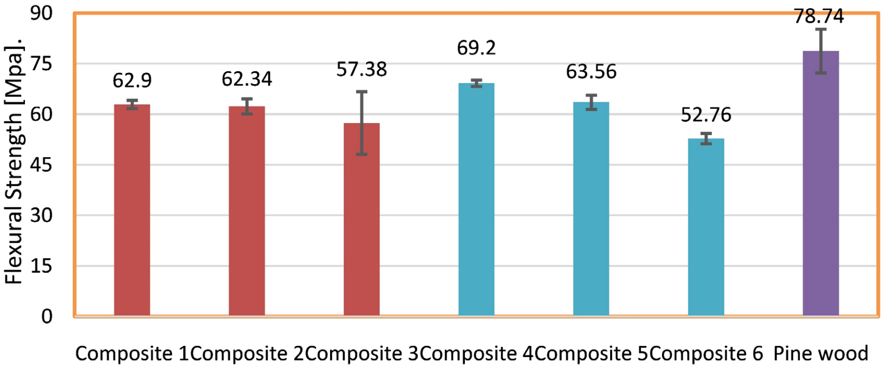

Figure 21. Comparison of flexural strength of composites with pinewood.

5.4. Compression Tests

Compression testing was conducted on composites using the DIN EN ISO 604 standard. According to the DOE, composites with rectangular shapes (45 mm × 14 mm × 13 mm in dimensions) were designed with varying weight percentages under two types of categories. In multi-husk category 1, the composite with the highest husk weight percentage (30%) exhibited the maximum compression strength (49.48 MPa), while composites with lower husk weight percentage (22.5%, 15%) showed reduced strength (38.52 MPa and 30.08 MPa, respectively). In single husk category 2, the composite with wheat husk at a 15% weight ratio had the highest compression strength (46.06 MPa), compared to composites with rice and safflower husks at the same ratio (25.42 MPa and 18.02 MPa, respectively). Additionally, bending testing was performed on pinewood, and the results were compared with those from the DOE composites. Overall, the composite with the highest husk weight percentage (30%) under multi-husk category 1 has more compression strength (49.48 MPa) than the pinewood (29.74 MPa). Figure 22 shows the three-point bending test results for each DOE composite compared to pinewood.

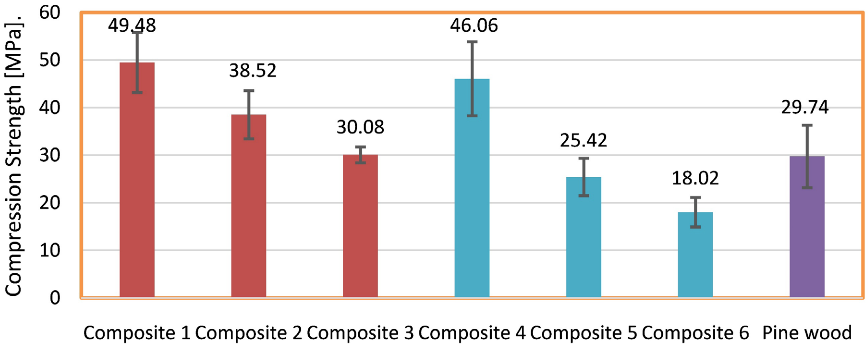

Figure 22. Comparison of compression strength of composites with pinewood.

5.5. Heat Deflection Temperature Tests

The VICAT 306/ASTM D 1525 standard conducted the heat deflection temperature test on composites. Based on DOE, composites with rectangular shapes (80 mm × 10 mm × 4 mm) were designed with varying weight percentages under two types of categories: multi-husk category 1 (combinations of rice, wheat, and safflower husks) and single-husk category 2 (individual husk types with equal amounts). Composites were created and tested for deflection under heat using a heat deflection testing machine. During the HDT test, the maximum deflection (0.34 mm) under a softening temperature (VICAT) was calibrated. Figure 23. shows the comparison of VICAT temperatures of each sample with other samples.

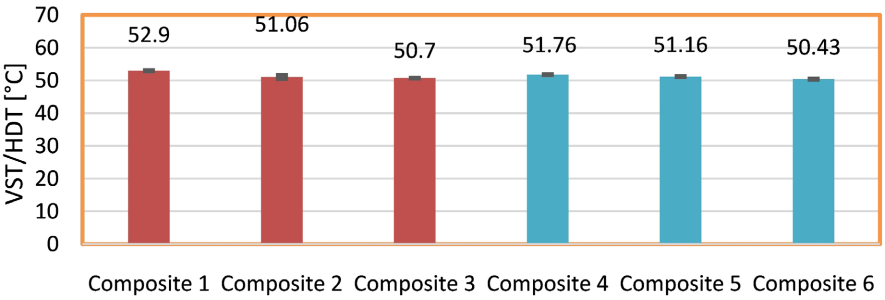

Figure 23. Comparison of heat deflection temperature of each composite with other composites.

5.6. Differential Scanning Calorimetry Tests

Differential scanning calorimetry (DSC) tests were conducted on composites using the Perkin-Elmer DSC 7 standard. Composites created through injection molding and hot pressing weighed between 8 mg and 12 mg and were tested for melting temperatures. Adding zeolite powder to the composites increased their melting temperatures. Composites with 10% zeolite powder had higher melting temperatures (172.7˚C), while those with 5% zeolite had lower melting temperatures (171.033˚C). **Figure 24** compares the melting temperatures of each composite with pure polylactic acid (167.77˚C).

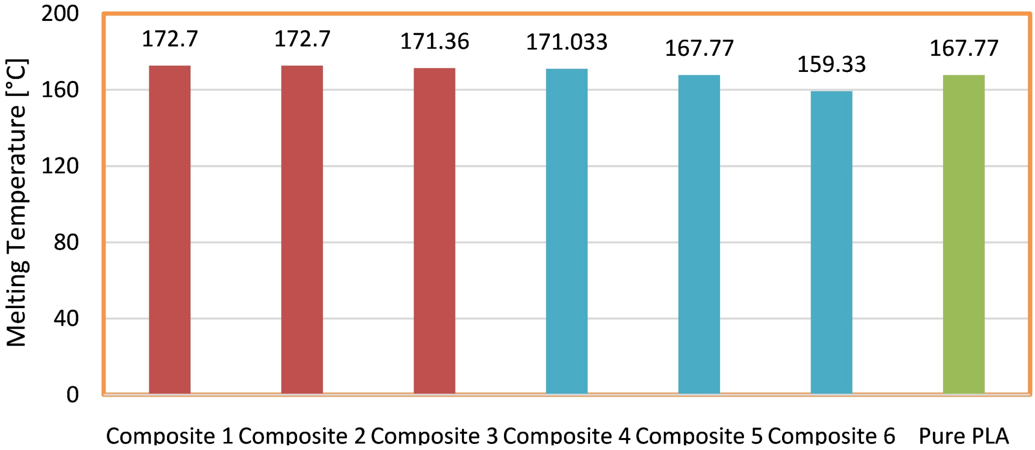

Figure 24. Melting point temperatures of each composite and peat PLA.

6. Discussion of the Results

This research confirmed that using equal amounts of husks (50%) and polylactic acid (50%) in a dog bone composite resulted in extreme brittleness. Consequently, the composites were not properly ejected from the injection molding die, even with providing an increased cooling time from twenty seconds to one minute for proper crystallization of the composite from molten to solid state. Therefore, the experiments were designed to blend husks and zeolites at a maximum content of 30% and 10%, with a minimum weight percentage of 60% polylactic acid. Similarly, the minimum content of husks and zeolite was 15% and 5% blended with a maximum content of 80% polylactic acid. The mechanical tests conducted on both categories, including pinewood, revealed that composite 4 with 15% wheat husk showed properties a little lesser, however nearly equal to pinewood samples compared with the other five types of composites. On the other hand, only six types of composites and peat polylactic acid were put through thermal tests like differential scanning calorimetry and heat deflection temperature. The test results showed that adding zeolite powder in slight variations, such as 5%, 7.5%, and 10%, significantly increased the thermal stability of the composite materials compared to peat polylactic acid. **Figures 25-27** illustrate the composites and pinewood samples before and after failure.

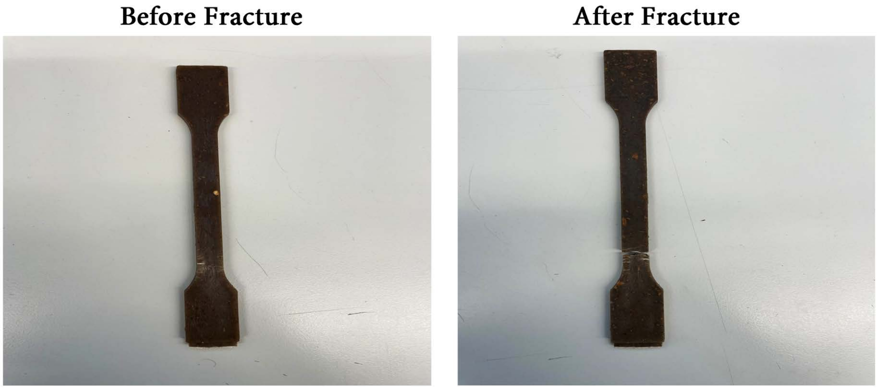

Figure 25. Dog bone composite before and after tensile testing.

Figure 26. Rectangle composite before and after Flexural testing.

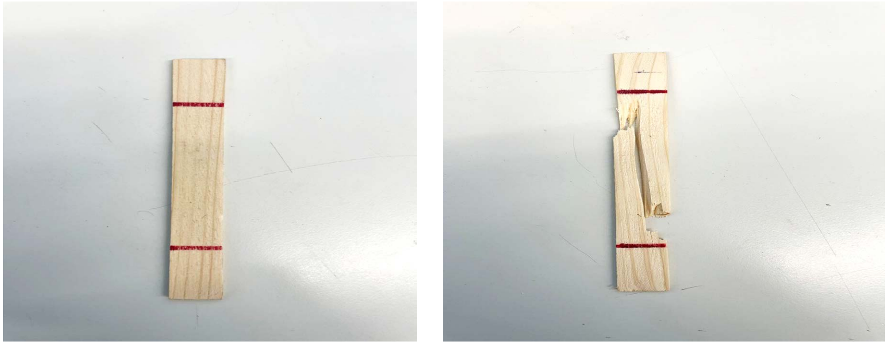

Figure 27. Pinewood images before and after failure.

7. Conclusions

Every year more than a thousand million tons of husk are produced worldwide. These husks were used as animal feed, soil amendments, landfills, and bioenergy feedstock. These husks are seasonal and not available year-round. This research has been conducted to make the best utilization of this husk to make a better alternative for pinewood. Using rice, wheat, and safflower husks in sustainable applications comes with several limitations. One significant challenge is the variability in their chemical and physical properties, which depend on factors such as regional differences, farming methods, and post-harvest processing. This inconsistency can affect the performance of these materials in industrial applications and hinder the reproducibility of experimental results. However, these husks represent a renewable and sustainable source of raw materials that can reduce reliance on non-renewable resources such as petroleum-based plastics, synthetic materials, and wood, contributing to the development of a circular economy. Economically, valorizing these husks can provide additional income streams for farmers and create rural job opportunities through the establishment of local processing facilities. Environmentally, utilizing these residues can lower carbon footprints.

Firstly, the study was based on the Design of Experimentation (DOE), which uses Design Expert Software. The analysis has proven effective in determining the functional relationship between the composition of husks in composite structures and their mechanical responses. The current study focused on comparing the performance of composite materials made of rice husk, wheat husk, safflower husk, zeolite powder, and polylactic acid (PLA) with the performance of pinewood. In conclusion, the evidence obtained from this research showed that husk content has an impact on the mode of failure. The dense composites that incorporated higher husk content exhibit a brittle nature, while the ones with less husk incorporate ductility as evidenced by plastic deformation before failure. Most of these composites have comparatively lesser tensile strength and modulus of elasticity compared with pinewood caused mainly by the lower husk weight percentage, since the PLA matrix content plays the primary role in determining the mechanical properties, including higher ductility but lower strength.

Secondly, Among the various types of husks used, it was found that the safflower husk could be considered ductile because the husk tends to yield slightly before it fractures. On the other hand, wheat husk behaved in a brittle manner–it could not withstand the force of impact, failing without any sign of deformation. Starch (rice husk), on the other hand, is somewhere in between, further determined by the concentration of the material and the specific mixture of the substances. The brittle nature of wheat husks likely stems from their high lignin and cellulose content, which makes them less flexible and prone to cracking under stress. However, these same components contribute to their stiffness and rigidity, leading to enhanced mechanical performance, such as higher tensile and flexural strength.

Finally, PLA-husk composites exhibited good mechanical properties due to the reinforcing nature of the husks and the structural integrity provided by PLA. Wheat husks, with their silica content, contribute to higher stiffness and tensile strength compared to rice and safflower husks, which are more fibrous but less stiff. However, both PLA and natural husks are hydrophilic, making the composite susceptible to water absorption, swelling, and loss of mechanical integrity in humid conditions. Moreover, wheat husks provide slight advantages due to their silica layer, which imparts some water repellence. Additionally, the thermal stability of the composites was moderate. Testing with heat deflection temperature and differential scanning calorimetry revealed that incorporating zeolite into the composite enhanced its melting point to 170˚C. This improvement makes it thermally more resilient compared to pinewood, which shows a high sensitivity to elevated temperatures.

8. Future Scopes

1) Future research can explore the creation of samples using untreated husks and compare the results with those obtained from treated husk samples and pinewood.

2) Additionally, replacing short-length husk with husk powder in the samples could provide valuable insights when these results are compared to those of treated short-length husk samples.

3) Based on the findings of this study, it is determined that using a range of 0% to 30% husk, 0% to 10% zeolite, and 50% to 60% PLA produces optimal results. Considering these minimum and maximum values, a total of 23 different samples with varying proportions can be produced using Design Expert Software as mentioned in Table 4, offering a comprehensive understanding of the material properties and potential applications.

Table 4. DOE using design expert software.

Run	Polylactic acid (weight%)	Rice husk (weight%)	Wheat husk (weight%)	Safflower husk (weight%)	Zeolite (weight%)	Total (weight%)
1	54.9	14.6	18.7	1.8	10.0	100%
2	50.0	00	0.0	40.0	10.0	100%
3	50.3	11.2	2.9	35.6	0.0	100%
4	50.0	23.4	19.5	2.3	4.8	100%
5	60.0	13.3	13.1	13.6	0.0	100%
6	50.0	2.9	28.4	8.8	10.0	100%
7	60.0	20.4	1.0	8.6	10.0	100%
8	54.1	5.9	40.0	0.0	0.0	100%
9	60.0	5.4	0.0	24.6	10.0	100%
10	58.8	0.0	1.3	40.0	0.0	100%
11	50.0	37.2	0.0	2.8	10.0	100%
12	50.0	0.0	40.0	0.0	10.0	100%
13	53.5	18.7	0.0	24.0	3.8	100%
14	50.0	30.9	2.9	16.2	0.0	100%
15	54.3	0.0	21.0	19.3	5.3	100%
16	54.3	0.0	21.0	19.3	5.3	100%
17	60.0	6.3	25.2	8.5	0.0	100%
18	50.0	23.4	19.5	2.3	4.8	100%

Continued

19	50.0	2.5	16.1	31.4	0.0	100%
20	60.0	0.0	33.8	0.0	6.3	100%
21	53.5	18.7	0.0	24.0	3.8	100%
22	59.6	35.1	0.0	0.0	5.3	100%
23	52.6	40.0	3.7	3.6	0.0	100%

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Conflicts of Interest

The authors declare no conflicts of interest.

References

[1] FAO (2024) FAO Cereal Supply and Demand Brief. https://www.fao.org/worldfoodsituation/csdb/en

[2] Wikipedia Contributors (2024, August 12) Safflower. https://en.wikipedia.org/w/index.php?title=Safflower&oldid=1239858762

[3] Kordi, M., Farrokhi, N., Pech-Canul, M.I. and Ahmadikhah, A. (2024) Rice Husk at a Glance: From Agro-Industrial to Modern Applications. *Rice Science*, **31**, 14-32. https://doi.org/10.1016/j.rsci.2023.08.005

[4] Faruk, O. and Ain, M.S. (2013) Biofiber Reinforced Polymer Composites for Structural Applications. In: Uddin, N., Ed., *Developments in Fiber-Reinforced Polymer* (*FRP*) *Composites for Civil Engineering*, Elsevier, 18-53. https://doi.org/10.1533/9780857098955.1.18

[5] Farah, S., Anderson, D.G. and Langer, R. (2016) Physical and Mechanical Properties of PLA, and Their Functions in Widespread Applications—A Comprehensive Review. *Advanced Drug Delivery Reviews*, **107**, 367-392. https://doi.org/10.1016/j.addr.2016.06.012

[6] Badia, J.D. and Ribes-Greus, A. (2016) Mechanical Recycling of Polylactide, Upgrading Trends and Combination of Valorization Techniques. *European Polymer Journal*, **84**, 22-39. https://doi.org/10.1016/j.eurpolymj.2016.09.005

[7] Narattha, C., Wattanasiriwech, S. and Wattanasiriwech, D. (2022) Thermal and Mechanical Characterization of Fly Ash Geopolymer with Aluminium Chloride and Potassium Hydroxide Treated Hemp Shiv Lightweight Aggregate. *Construction and Building Materials*, **331**, Article ID: 127206. https://doi.org/10.1016/j.conbuildmat.2022.127206

[8] Tran, T.P.T., Bénézet, J. and Bergeret, A. (2014) Rice and Einkorn Wheat Husks Reinforced Poly(Lactic Acid) (PLA) Biocomposites: Effects of Alkaline and Silane Surface Treatments of Husks. *Industrial Crops and Products*, **58**, 111-124. https://doi.org/10.1016/j.indcrop.2014.04.012

[9] Dobrzyńska-Mizera, M., Knitter, M., Woźniak-Braszak, A., Baranowski, M., Sterzyński, T. and Di Lorenzo, M.L. (2020) Poly(*L*-Lactic Acid)/Pine Wood Bio-Based Composites. *Materials*, **13**, Article No. 3776. https://doi.org/10.3390/ma13173776

[10] Yue, Z., Wang, H., Zhang, M. and Wang, M. (2022) Mechanical, Thermal and

Rheological Properties of Polylactic Acid (PLA)/Epichlorohydrin Modified Pine Wood Flour (EWF) Composites. *European Journal of Wood and Wood Products*, **80**, 1111-1120. https://doi.org/10.1007/s00107-022-01810-w

[11] Vila, C., Campos, A.R., Cristovão, C., Cunha, A.M., Santos, V. and Parajó, J.C. (2008) Sustainable Biocomposites Based on Autohydrolysis of Lignocellulosic Substrates. *Composites Science and Technology*, **68**, 944-952. https://doi.org/10.1016/j.compscitech.2007.08.006

[12] Yuzay, I.E., Auras, R. and Selke, S. (2009) Poly(Lactic Acid) and Zeolite Composites Prepared by Melt Processing: Morphological and Physical-Mechanical Properties. *Journal of Applied Polymer Science*, **115**, 2262-2270. https://doi.org/10.1002/app.31322

[13] Sawpan, M.A., Pickering, K.L. and Fernyhough, A. (2011) Improvement of Mechanical Performance of Industrial Hemp Fibre Reinforced Polylactide Biocomposites. *Composites Part A*: *Applied Science and Manufacturing*, **42**, 310-319. https://doi.org/10.1016/j.compositesa.2010.12.004

[14] Castaño, J., Rodríguez-Llamazares, S., Carrasco, C. and Bouza, R. (2012) Physical, Chemical and Mechanical Properties of Pehuen Cellulosic Husk and Its Pehuen Starch Based Composites. *Carbohydrate Polymers*, **90**, 1550-1556. https://doi.org/10.1016/j.carbpol.2012.07.029

[15] Koutsomitopoulou, A.F., Bénézet, J.C., Bergeret, A. and Papanicolaou, G.C. (2014) Preparation and Characterization of Olive Pit Powder as a Filler to Pla-Matrix Biocomposites. *Powder Technology*, **255**, 10-16. https://doi.org/10.1016/j.powtec.2013.10.047

[16] Hao, Y., Huang, Z., Wang, J., Yang, X., Fan, X., Li, Y., *et al.* (2016) Improved Thermal Stability of Poly(l-Lactide) with the Incorporation of Zeolite ZSM-5. *Polymer Testing*, **49**, 46-56. https://doi.org/10.1016/j.polymertesting.2015.11.010

[17] Krishnasamy, S., Thiagamani, S.M.K., Muthu Kumar, C., Nagarajan, R., R.M., S., Siengchin, S., *et al.* (2019) Recent Advances in Thermal Properties of Hybrid Cellulosic Fiber Reinforced Polymer Composites. *International Journal of Biological Macromolecules*, **141**, 1-13. https://doi.org/10.1016/j.ijbiomac.2019.08.231

[18] Muthuraj, R., Lacoste, C., Lacroix, P. and Bergeret, A. (2019) Sustainable Thermal Insulation Biocomposites from Rice Husk, Wheat Husk, Wood Fibers and Textile Waste Fibers: Elaboration and Performances Evaluation. *Industrial Crops and Products*, **135**, 238-245. https://doi.org/10.1016/j.indcrop.2019.04.053

[19] Narlıoğlu, N., Salan, T. and Alma, M.H. (2021) Properties of 3D-Printed Wood Sawdust-Reinforced PLA Composites. *BioResources*, **16**, 5467-5480. https://doi.org/10.15376/biores.16.3.5467-5480

[20] Bhagia, S., Bornani, K., Agrawal, R., Satlewal, A., Ďurkovič, J., Lagaňa, R., *et al.* (2021) Critical Review of FDM 3D Printing of PLA Biocomposites Filled with Biomass Resources, Characterization, Biodegradability, Upcycling and Opportunities for Biorefineries. *Applied Materials Today*, **24**, Article ID: 101078. https://doi.org/10.1016/j.apmt.2021.101078

[21] Kumar, A.M., Jayakumar, K. and Shalini, M. (2023) Enhancing the Performance of Polylactic Acid (PLA) Reinforcing with Sawdust, Rice Husk, and Bagasse Particles. *Journal of Polymer Materials*, **39**, 269-281. https://doi.org/10.32381/jpm.2022.39.3-4.7

[22] Abraha, K.G., Debeli, D.K., Ghani, M.U., Tesfahunegn, A.A. and Guo, J. (2024) Exploring the Potential of Agricultural Waste Enset Fibers Reinforced Poly Lactic Acid Biocomposites. *Industrial Crops and Products*, **221**, Article ID: 119322. https://doi.org/10.1016/j.indcrop.2024.119322