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Poly lactide-Based Polymer Composites with Rice Husk Filler

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Abstract: In this work, composites made of polylactide (PLA) and filled with alkali-pretreated rice husk (RH) were investigated. Composites containing 20, 30, and 40 wt.% of RH were synthesized. It was shown that alkaline treatment, along with the change in crystal lattice, led to an increase in the content of non-crystalline parts and the volume of intercrystalline spaces, and the internal surface of the cellulose fiber increased, which resulted in improved adhesion of the fiber with the matrix. The addition of rice husk to the PLA matrix led to an increase in the flexural modulus, which increased to 2881 MPa for the PLA/RH (80/20 wt.%) and 3034 MPa for the PLA/RH (70/30 wt.%) composites and lowered the peak load stress by approximately 43% for the composite with 20 wt.% RH and 56% for the composite with 30 wt.% RH. The reduction in the degree of PLA crystallinity allows macromolecules to move more freely in amorphous regions, which has a positive effect on increasing the flexibility of materials in general. The optimal formulation is a composite consisting of 30% RH and 70% PLA matrix.

Keywords: polylactide; rice husk; composites; X-ray phase analysis; FTIR spectra; thermal properties



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1. Introduction

Fillers are introduced into polymers in order to create new polymeric materials with a range of valuable operational properties, such as the recyclability of filled polymers, lower cost, waste utilization, and solutions to environmental problems, as well as to obtain decorative properties. The main types of fillers can be grouped into two main categories, organic and inorganic, which can be dispersed (chalk, asbestos, aluminum hydroxide, talc, etc.), fibrous (metal, glass, carbon, boron, organic, ceramic, thread crystals, and whiskers), or sheets (fabrics, paper, wood veneer, tapes, canvases, nets, and nonwoven materials). However, in recent years, there has been a growing interest in the use of natural fibers. Natural fibers and polymer composites reinforced with natural fibers are attracting more and more attention from researchers due to the lack of toxicity to living organisms and harmlessness to the environment. In addition to the environmental advantages of incorporating natural fibers into polymer composites, these composites are also known for their light weight, low cost, low density, durability, and mechanical properties, which have led to further research. Applications of natural plant fibers have become popular in the automotive, construction, and furniture sectors [1–3]. Wood flour and fibers are the most commonly used natural fibers in the creation of fillers. Environmental concerns such as global warming and biodiversity conservation due to deforestation have prompted researchers to explore the possibility of finding affordable alternatives to wood [4–6]. There is an increasing number of publications on the use of various agricultural by-products that can be used either as a supplement or as a direct replacement for wood in the development of polymer composites. Progress in the use of agricultural residues as alternatives to wood derivatives has begun to take hold, reducing the high demand for wood-based materials. Potential wood substitutes include hemp hibiscus (kenaf), wheat straw, flax, and rice

husk (RH) [1–3,7]. It has been shown [8] that when RH is used to substitute wood in the development of particle boards, the physical characteristics of RH-reinforced composites are similar to those of wood-based composites. Some of these natural fibers have been effectively used as reinforcement in particle board production [8], which highlights their reinforcing potential.

An example is rice (*Oryza sativa* L.), one of the monocotyledonous cereal plants, which covers about 1% of the Earth's surface and is among the most cultivated; it is also the primary source of nutrition for billions of people in South Asia and Africa as their staple food crop. Unmilled rice consists of edible and inedible components and is mechanically processed before being eaten. The milling process separates the grain of rice from the other edible (bran and germ) and inedible (husk) components of rice. Peeling is the mechanical removal and separation of the outer loose husk of the rice, called the hull, which results in brown rice. The production of annually renewable rice produces a large amount of milling by-products each year. Most of the semilled by-products have little or no commercial value. For this reason, attempts have been made to add value to the RH waste by utilizing the characteristics and composition of its constituents, primarily in the manufacture of composites. Silica, the main component of rice husk, has been shown to improve the mechanical properties of various polymeric materials. In addition, it has been reported to improve the fire resistance when husk is added to polyethylene-based composites [9]. Also, it has been proposed to use this type of waste material as a reinforcing filler for composite panels [8–10]. Additional advantages are the better dimensional stability of RH-reinforced composites when exposed to moisture, as well as their higher resistance to termites and biological impacts compared to wood-fiber-reinforced composites. The use of RH as a reinforcing filler for polymeric materials also allows researchers to study the combined reinforcing effect of organic (lignocellulose) and inorganic (silica) components.

Effective compatibility and strong interfacial adhesion between RH and the matrix are essential for enhancing the mechanical properties of the resultant materials. However, the presence of waxy components on the surface of the husk and the hydrophilic nature of the husk contribute significantly to the inefficient interaction between the vegetable filler and the polymer matrix. In order to solve this problem, different strategies, alkaline treatments, and acetylation and silane treatments have been proposed. Compatibilizers with polar and non-polar functional groups that can interact with both the filler and matrix material are used to enhance the interaction.

Conventional polymeric materials derived from crude oil have been widely used for many decades. However, this trend has caused enormous environmental problems. The disposal of such wastes is a global problem, because it is impossible to achieve complete degradation with existing technologies without polluting the air, water, and soil. Poly lactic acid (PLA) is one of the most promising biodegradable polymers and has attracted considerable attention as an environmentally friendly substitute for conventional plastics [11]. This is due to three main reasons. Firstly, since lactic acid is obtained in the process of lactic acid fermentation of polysaccharides contained in raw plant materials, the synthesis of polylactides (PLAs) does not require raw petrochemical materials. Secondly, unlike the majority of currently used large-tonnage polymers derived from petrochemical feedstock, PLAs are easily degraded under the influence of environmental factors. Thirdly, depending on the stereoregularity of the initial monomers, PLAs can be obtained in different phase states, in completely amorphous or in amorphous–crystalline ones, due to which they have fundamentally different mechanical properties. Nevertheless, the cost of pure PLA is relatively high compared to the cost of conventional bulk plastics [12]. In order to reduce the cost of PLA composites, PLA is usually blended with cheaper fillers/fibers that do not necessarily affect its thermal and mechanical properties [13–15]. The mechanism of thermal degradation of PLA is complex and includes random chain breakage, hydrolysis, intra/intermolecular transesterification, depolymerization, cis-elimination, and radical degradation.

This work presents the possibility of creating PLA composites filled with RH that has been pretreated with an alkaline treatment. Alkaline treatment removes lignin, hemicellulose, fats, and waxes from the RH shell, which gives the RH a rougher surface. The use of alkaline treatment helps to improve the interfacial adhesion with the polymer matrix, which leads to improved physical and mechanical properties of the composite.

2. Materials and Methods

The L-PLA Ingeo™ Biopolymer 4043D PLA in pellet form (Nature Works LLC, Plymouth, MN, USA) was chosen as the base for the polymer matrix with a density of 1.24 g/cm^3 and a melt flow index (MFI) of about 7 g/10 min ($210^\circ\text{C}/2.16 \text{ kg}$). The RH is from the Krasnodar region in Russia.

Sodium hydroxide (NaOH) (CAS number 1310-73-2) with a molecular weight of 40 g/mol was supplied by Uralpolychim Ltd. (Chelyabinsk, Russia).

A WM3 vibrating mill (Consit Holding Ltd., Moscow, Russia) was used for RH grinding.

Scanning electron microscopy was carried out using TESCAN MIRA 3 LMU equipment (Tescan, Brno, Czech Republic).

The PLA and RH were mixed under shear strain in a Brabender mixer (Plastograph EC, Dury, France) at 160°C for 10 min. The composites with different RH contents were obtained by extrusion using a Wellzoom B extruder (Shenzhen Mistar Technology, Shenzhen, China) at $T = 165^\circ\text{C}$ using a specific combination of mixing time and screw speed (3 min with 8 rpm, 4 min with 16 rpm, and 3 min with 32 rpm). Prior to extrusion, the ingredients were mixed and then fed into the extruder, which was heated to a predetermined temperature. The milled RH was vacuum-dried for 24 h prior to extrusion. Wafers with thicknesses of 1 mm and 3 mm were prepared for testing by compression molding using a REM-100-A-1-1 testing machine (METROTEST LLC, Republic of Bashkortostan, Neftekamsk, Russia) at $T = 170^\circ\text{C}$ and $p = 150 \text{ bar}$ for 10 min, followed by pressure cooling at a rate of $\sim 15^\circ\text{C/min}$.

The density (ρ) of the samples was determined using electronic analytical scales CAUW 220D (CAS Corporation, Seoul, Republic of Korea) by the immersion method according to the PN-EN 1936 standard. Five measurements were taken for each composite to obtain the average value and calculate the relative standard deviation.

The structure of the fillers was studied by X-ray diffraction on a DRON-3 diffractometer (SPE Burevestnik, St. Petersburg, Russia) using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Monochromatization was carried out using a Ni filter.

The effects of chemical modifications on the filler surface were observed by Fourier infrared spectroscopy (FTIR). FTIR measurements were performed on a VERTEX 70 FTIR spectrometer (Bruker, Ettlingen, Germany) with a scan frequency of 40 and a wave number range of $400\text{--}4000 \text{ cm}^{-1}$. KBr powder was used to prepare the tablets for spectroscopic analysis.

Vick's softening temperature (VST) was determined using a MT 206 instrument (Metrotex LLC, Moscow, Russia). The samples were placed in an oil bath in accordance with the ASTM-D1525 standard. VST was measured with a load of 5 N at a heating rate of 50°C per hour.

The thermal properties of the composite material were studied using an STA 449F1 Jupiter® (NETZSCH-Gerätebau GmbH, Selb, Germany). The thermal properties were studied in an argon atmosphere (Ar) in the temperature range from 20 to 800°C at a rate of 10°C/min .

Measurements of water absorption during hydrolytic degradation were carried out as follows. The samples were immersed in distilled water mixed with salt (2%) as a physiological saline solution and incubated at 40°C for 1, 7, and 28 days. Then, they were dried and weighed to the nearest 0.0001 g using a CAUW 220D electronic analytical scale (CAS Corporation, Seoul, South Korea). The measurements were performed three times for each sample. Finally, the water uptake was calculated as a percentage, using the following formula: $M_t = \left[\frac{W_t - W_0}{W_t} \right] \times 100$. Here, M_t means the percentage of water content, W_t means the weight of the sample after being kept in the solution, and W_0 indicates the original

weight of the sample. The purpose was to determine the effect of water absorption on the basic mechanical properties of the samples after being kept in water for 28 days.

The prepared composites were subjected to tensile and bending tests. The tensile tests were carried out in accordance with ASTM D 638-99 on a testing machine, REM-100-A-1-1 (METROTEST LLC, Neftekamsk, Republic of Bashkortostan, Russia), at a traverse speed of 2 mm/min and room temperature. To conduct the fracture tests at room temperature and a low strain rate, the samples with sharp three-point bends and notches were used. The same testing machine, REM-100-A-1-1, (METROTEST LLC, Republic of Bashkortostan, Neftekamsk, Russia) (48 mm test range), was used for measurements at a low strain rate on $60 \times 6 \times 3$ mm samples. The bending modulus of the elasticity measurements was performed using the same equipment and under the same conditions as above, using unnotched samples.

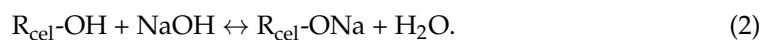
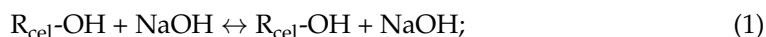
3. Results

3.1. Alkaline Treatment of Rice Husk

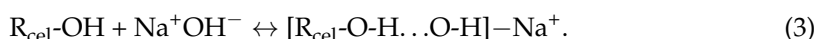
Natural fibers are widely used to reinforce polymers. It is known that the hydrophilic nature of natural fibers leads to the accumulation of moisture at the fiber–matrix interface and causes composite swelling, a decrease in interfacial strength, fiber delamination from the matrix, a decrease in the glass transition temperature, and a change in viscoelastic properties [16].

Chemical treatment is considered a good method to reduce the hydroxyl group in natural fibers, improve the effect of cellulose on the fiber, improve the fiber surface roughness, etc. In nature, cellulose is obtained as a result of biosynthesis, when glucose units passing through the plasma membrane are formed into macromolecular chains linked by β -glucoside and hydrogen bonds. The most important role in this process is played by structures that allow us “to stamp” elementary fibrils, in which intra- and intermolecular bonds are provided with the help of hydrogen bonds [17]. Currently, there are data on six polymorphic modifications of cellulose in the literature: I, II, III, IIII, IVI, and IVII [18,19]. Cellulose I, or native cellulose, is the form found in natural materials, which, according to recent data, has two polymorphic modifications: $I\alpha$ and $I\beta$. Cellulose II, the second most intensively studied form, can be obtained from cellulose I by one of two methods: (a) regeneration, which is the process of dissolving cellulose I in a solvent and then re-depositing it when diluted with water; and (b) mercerization, which is the process of native fibers swelling in concentrated sodium hydroxide.

The interaction of cellulose with alkali can occur to form additive, or molecular, compounds in which the bonding between cellulose and alkali is caused by intermolecular forces, mainly hydrogen bonds (1), or to form alcoholates (cellulosates), which have the same properties as sodium alcoholates derived from ethanol and sodium hydroxide:



The formation of cellulosates in aqueous alkali solutions is explained by the increased acidity of the hydroxyl group at C^2 . In aqueous alkaline solutions, the interaction occurs between cellulose hydroxyls and alkali hydroxide ions with the formation of hydrogen bonds.



A model of a hydration complex is also proposed, in which one water molecule is displaced by the hydroxyl group of cellulose in the hydrate shell of the Na^+OH ion pair. In the mixed structure model, the alkali cellulose is considered both an additive and an alcoholate compound. Recently, a theory of inclusion compound formation has been developed, according to which alkali cellulose belongs to layered lattice inclusion compounds. Inclusion compounds are systems in which guest molecules are embedded in

existing or emerging cavities in the structure of another host substance. These systems are formed spontaneously, i.e., with a decrease in free energy, as a result of the formation of H-bonds, dipoles, and even partially ionic interactions and interactions between the “host” and the “guest”.

To carry out the alkali treatment, RH was soaked in 5% NaOH solution at room temperature in a 15:1 ratio. The soaked RH was washed with normal water to remove foreign particles. After the alkaline treatment, the RH was air-dried. After complete drying, the RH was immersed in an alkali solution for 4 h. After that, it was washed with distilled water and neutralized with diluted acetic acid to pH = 7. The RH was dried in air for 2 days, then in a drying oven for 6 h ($T = 100\text{ }^{\circ}\text{C}$). The obtained modified RH fibers were ground in a vibration mill for 240 min. Physicochemical processes lead to intensive swelling of fibers with partial destruction of the intermolecular hydrogen bonds, as well as partial dissolution of the low-molecular-weight cellulose fractions and hemicellulose impurities. Chemical reactions lead to the formation of a new chemical compound, alkaline cellulose. Partial degradation of the cellulose occurs, which is promoted by oxidation due to air oxygen, i.e., the oxidative–hydrolytic degradation of cellulose.

Before milling the rice husk, the particles have a variety of shapes, from needle-like to rounded, and their sizes range from 1 to 50 μm . In addition, there are particles with a spiral structure, which is characteristic of natural fibers. After milling, the particles acquire an irregular shape (Figure 1a) with an average diameter of 11 μm (Figure 1b).

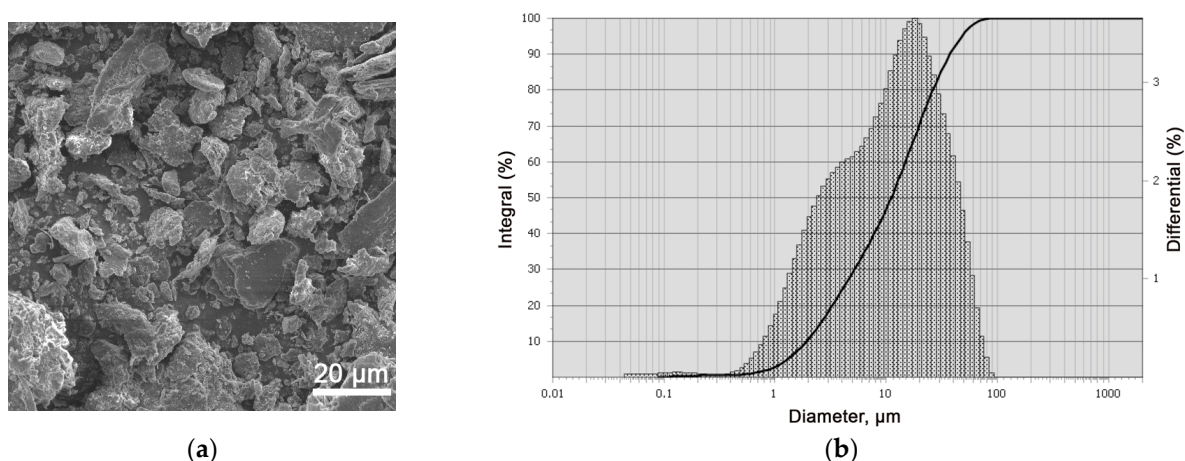


Figure 1. Morphology (a) and size distribution (b) of alkali-treated RH particles after milling.

The density and particle size of the filler have a significant effect on the strength of the polymer composites. The increase in the size of filler particles leads to a decrease in the contact area, which cannot but affect the intensity of the intermolecular interaction between the filler and matrix.

3.2. FTIR Analysis

The effect of chemical modifications on the fiber surface was studied by FTIR. A comparison of the representative FTIR spectra of RH before and after chemical treatment is shown in Figure 2. Compared to unmodified rice husk, the alkali-treated RH showed a decrease in the intensity of absorption spectra due to the dissolution of non-polar covalent compounds such as wax, fat, etc. The broad absorption peak of ordinary RH around 3404 cm^{-1} indicates the existence of free hydroxyl groups. The stretching C–H vibration around 2925 cm^{-1} indicates the presence of an alkane functional group. The peaks between 1641 and 1737 cm^{-1} correspond to C=O stretching, which can be attributed to the carbonyl groups of hemicelluloses and lignin. The C=C stretching vibrations between 1546 and 1652 cm^{-1} indicate double bonds and aromatic functional groups. Peaks around 1461 cm^{-1} indicate the presence of CH_2 and CH_3 groups, while peaks at 1380 cm^{-1} indicate CH_3 . The

peak in the region of 1379 cm^{-1} can be attributed to aromatic CH and carboxyl carbonate structures. The peaks in the region of $1153\text{--}1300\text{ cm}^{-1}$ correspond to vibrations of the CO group in lactones. The peaks around 1076 , 813 , and 470 cm^{-1} indicate the presence of silica in the form of Si-O-Si and Si-H.

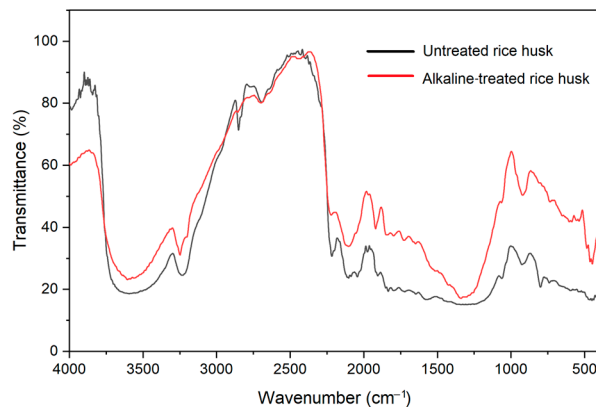


Figure 2. FTIR spectra of untreated and alkaline-treated RHs.

The major functional groups in RH generally remain unchanged even after chemical treatment. However, a decrease in peak intensity and peak shifts are observed in many cases. The chemically treated fiber shows a decrease in the O-H stretching intensity and peak shift from 3425 cm^{-1} to 3382 cm^{-1} , which indicates the participation of some free hydroxyl groups in these chemical reactions. The reaction point was probably located at the -OH of the lignin and $\text{C}^2\text{-OH}$ of the glucopyranose unit in the cellulose component. A strong and sharp band at 1730 cm^{-1} is observed due to the C=O stretching of carbonyl groups ($>\text{C}=\text{O}$) in the hemicellulose components in the untreated fiber, which disappeared in the alkali-treated fiber.

The treatment of RH with alkali degrades the C=O residue of uronic acid in hemicellulose, probably as a result of the intermolecular attachment of alcoholate ($-\text{CH}_2\text{-O-Na}^+$) from cellulose and lignin components to the C=O group.

The average intensity band at 935 cm^{-1} , which is due to β -glycosidic linkage in the unmodified rice husk, underwent a shift towards a lower wave number. This was due to the rotation of glucose residues around the glycosidic bond and indicated a slow transition from unmodified to chemically modified rice husk.

3.3. X-ray Diffraction Analysis

X-ray diffraction was carried out to evaluate the crystallographic structure of semi-crystalline materials such as RH and to determine the change in the crystalline character of the material after chemical treatment. The X-ray diffractograms of the untreated and alkali-treated RH are shown in Figure 3. It can be observed that the main crystalline peak of each profile occurred when the 2θ value was between 22.0 and 22.50° , which represented the crystallographic plane of cellulose (002), while the amorphous peak occurred when the 2θ value was between 15.50 and 16.50° .

It can be seen that the degree of crystallinity decreased with chemical treatment. It is possible that structural changes lead to a change in the crystalline structure of cellulose. Under the action of a NaOH solution at room temperature, natural cellulose with cellulose I crystal lattice transforms into alkaline cellulose with a new Na-cellulose crystal lattice. After washing with alkali water, the latter transforms into hydrated cellulose (mercerized cellulose) with a cellulose II crystal lattice. Along with the change in crystal lattice, the content of the non-crystalline part and the volume of the intercrystalline spaces increase and the inner surface of the cellulose fiber increases, which leads to an improvement in the adhesion of the fiber with the matrix.

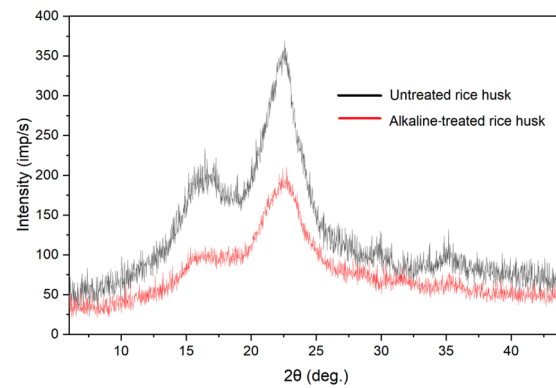


Figure 3. XRD patterns of untreated and alkaline-treated rice husks.

3.4. Thermogravimetric Analysis

A thermogravimetric analysis of the PLA, alkaline-treated RH, and composite based on them is shown in Figure 4. Lignocellulosic materials have poor thermal stability. Natural fiber consists of three main components, i.e., cellulose, hemicellulose, and lignin. Thermal degradation of lignin, hemicellulose, and cellulose occurs in the temperature ranges of 160–900 °C, 220–315 °C, and 315–400 °C, respectively. The process is irreversible. Lignin degrades more slowly than the other components of lignocellulose.

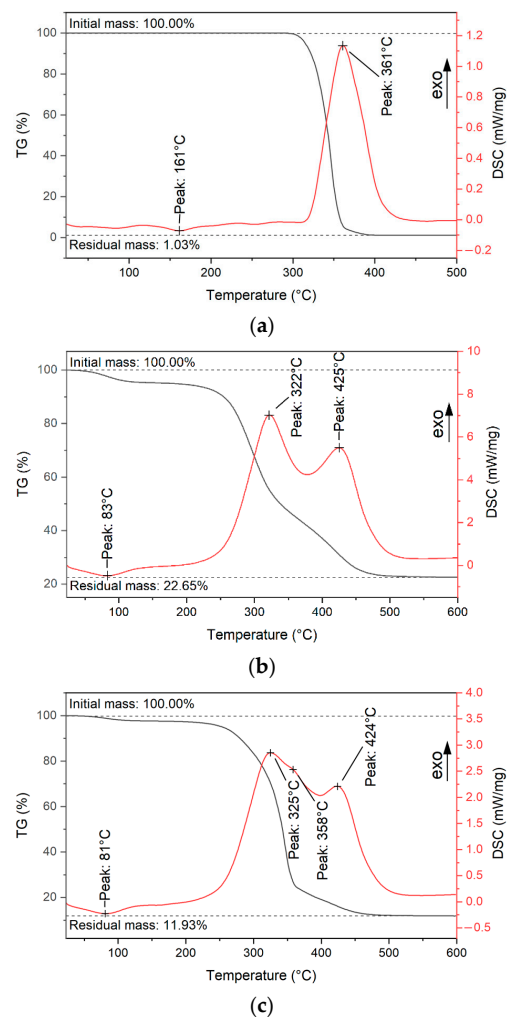


Figure 4. Thermal stability of PLA (a), alkaline-treated RH (b), and the composite based on them (c) (PLA 60%-RH40%).

As can be seen, RH undergoes a two-step weight loss process: at temperatures below 110 °C, the weight loss occurs due to the evaporation of absorbed moisture, and in the temperature range from 170 to 500 °C, the weight loss occurs due to the degradation of the three main components of rice husk. Lignocellulosic materials are chemically active and decompose thermochemically at temperatures between 150 and 500 °C: hemicellulose degrades mainly at temperatures between 150 and 350 °C, cellulose degrades at temperatures between 275 and 350 °C, and lignin degrades at temperatures between 250 and 500 °C. The ash in RH (12%) is mainly composed of silica (~96%), and the amount and distribution of silica in RH is probably an important factor in determining the properties of composite products. PLA gradually loses 10% of its weight up to 350 °C, and after that, there is almost complete weight loss in the temperature range from 350 °C to 400 °C. It should be noted that in an argon atmosphere at 600 °C, RH shows a high residual weight of 22.65%. The thermal stability of PLA/plant fiber composites is lower than the thermal stability of a pure PLA matrix.

3.5. Mechanical Properties

In order to evaluate the effect of the filler content on the mechanical properties of the obtained composites, pure PLA and composites based on it were analyzed. The density and Vicat softening temperature (VST—Vicat softening temperature) data and tensile test results for the PLA and PLA/RH-based composites obtained during the tests at room temperature are presented in Table 1. The introduction of filler resulted in a 34% increase in Young's modulus when 30 wt.% RH was added to the PLA matrix. In fact, RH acts as a rigid filler that is responsible for increasing the stiffness of the polymer matrix. As expected, the peak value stress decreases with the increase in the amount of RH added, reaching 65% for the PLA/RH composite (80/20 wt.%) compared to the 49.3 MPa achieved by pure PLA. Taking the hydrophilic character of RH and hydrophobic character of PLA into account, it can be noted that the strength of composites decreases due to the lack of adequate interfacial interaction, i.e., the formation of a continuous matrix that is capable of absorbing external loads and preventing the growth of cracks due to high plasticity or local delamination from the dispersed particle.

Table 1. Mechanical properties of PLA/RH composites.

Sample	ρ (g/cm ³)	VST, °C	Young's Modulus, MPa	Tensile Strain Stress, MPa	Flexural Peak Stress, %	Flexural Modulus, MPa	Peak Stress, MPa
PLA	1.25	60.8	2071	3.17	49.3	2416	31.9
PLA/RH 80/20	1.27	68.4	2602	1.36	17.5	2881	18.1
PLA/RH 70/30	1.29	70.5	2730	1.06	10.3	3034	14.0
PLA/RH 60/40	1.30	72.8	2185	0.89	8.59	2401	11.89

In addition, when irregularly shaped reinforcing elements are used, the strength of the composites is reduced due to the inability of the reinforcing element to support the transfer of stress from the polymer matrix.

The inclusion of RH in the PLA matrix resulted in an increase in flexural modulus, reaching 2881 MPa and 3034 MPa, respectively, for the PLA/RH (80/20 wt.%) and PLA/RH (70/30 wt.%) composites, and a reduction in peak load stress by about 43% for the composite with 20 wt.% RH and 56% for the composite with 30 wt.% rice husk. The reduction in the degree of crystallinity of the PLA allows macromolecules to move more freely in the amorphous regions, which has a positive effect on increasing the flexibility of the materials in general.

In order to determine the water absorption, the samples were made in the form of a square with a side of 50 ± 1 mm and a thickness that was equal to the thickness of the material. The surface of the slices was smooth. Before testing, the samples were dried at 50 ± 2 °C for 4 ± 1 h and then cooled in a desiccator over a desiccant at 23 ± 2 °C. After cooling, the samples were removed from the desiccator and weighed, and the length, width, and thickness were measured. Then, the samples were immersed in a saline solution at 40 ± 3 °C, and then, they were weighed at intervals. Figure 5 shows the percentage change in mass observed in pure PLA and its composites. It was noted that the addition of lignocellulose significantly increased the ability of the composites to absorb water (Figure 5). This effect is well known and is related to the composition of the husk, which consists of hydrophilic compounds such as carbohydrates and lignin that cause water absorption.

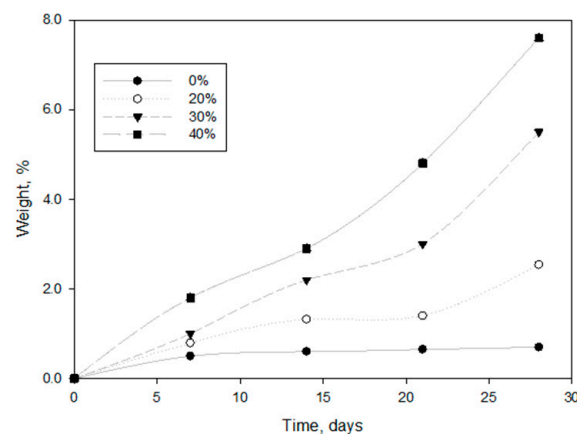


Figure 5. Weight increase in pure PLA and its composites (20%, 30%, and 40% RH immersed in saline solution at 40 °C).

The higher the husk content is, the higher the water adsorption is, which is associated with the swelling of lignocellulosic fibers, which causes matrix cracking and the formation of microchannels through which water can penetrate into the sample.

The data in Table 2 show that PLA and agro-industry wastes are widely used to produce environmentally friendly polymer composites.

Table 2. A comparative analysis of recent advances in PLA-based polymer composites and agricultural waste.

Material	Filler Content, wt.%	Properties of Composites
Composites studied in this work (PLA + RH)	30	At the ratio of PLA 70 wt.%/RH 30 wt.%, the composite material has the following properties: density—1.29 g/sm ³ , VST—70.5 °C, Young's Modulus—2730 MPa, tensile strain—1.06%, bending strength—21.31 MPa, peak stress—10.3%, flexural modulus—3034 MPa, peak stress—14.0 MPa.
PLA + BHS [20]	20	Increased the flexural modulus by approximately 12% compared to pure PLA.
PLA + egg shells [20]	20	Increase in flexural modulus of approximately 30% compared to pure PLA.
PLA + RH + clay [21]	75 20 5	Young's modulus 1.90 GPa, tensile strength 3244 MPa.
PLA + RH [22]	30	Tensile strength 11.3 MPa, tensile modulus 322.12 MPa, elongation at break at 3.508%.
PLA + RH [23]	7.5	Tensile strength 59.65 MPa, modulus in flexure 90.6 MPa, hardness Shore D 53.4.

Using natural fibers as reinforcing material can significantly reduce the price of composites based on them, and since they are obtained from renewable resources, they can replace traditional fillers. In addition, natural fibers reduce tool wear and increase energy recovery and can improve the mechanical properties of polymer matrices. It is generally reported that the tensile and flexural moduli of the PLA matrix are improved by the addition of natural fibers. A PLA/natural fiber composite has some limitations that prevent its successful application in various fields, such as poor flame resistance and high moisture absorption. The higher commercial price of biodegradable polymers compared to commercially available petroleum-based polymers may be offset by lower disposal costs, which should be considered in the future. The prices of biodegradable polymers, especially those produced from natural sources, are expected to decrease in the coming years, and biodegradable polymers could replace traditional polymers, which could help solve the huge waste management problem in relation to traditional polymeric materials.

Further studies will be aimed at assessing the life cycle of the developed composites (assessments of the biodegradation of composites).

4. Conclusions

The results showed that the stiffness of the composites increased with increasing RH content, while the strength decreased. In terms of strength, the inclusion of RH in PLA increased the stiffness of the material. The thermal stability of the PLA/RH composites was lower than that of pure PLA, which was determined by TG analysis. The optimal formulation is a composite with a 30% RH and 70% PLA composition. The composite PLA/RH (70/30 wt.%) has the following properties: density—1.29 g/cm³, VST—70.5 °C, Young's modulus—2730 MPa, tensile strain—1.06%, peak stress—10.3 MPa, and flexural modulus—3034 MPa.

Agricultural waste such as RH can be used and be promising as fillers for biodegradable polymer composites, which is especially important for preserving the ecology of the Earth. Further research on physicochemical treatments is needed to improve the inter-facial adhesion with the polymer matrix, as the fiber–polymer interaction plays an important role in determining the final properties of the composite.

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