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Exploring the effects of eco-friendly and biodegradable biocomposite with PLA incorporating eggshell and walnut powder as fillers

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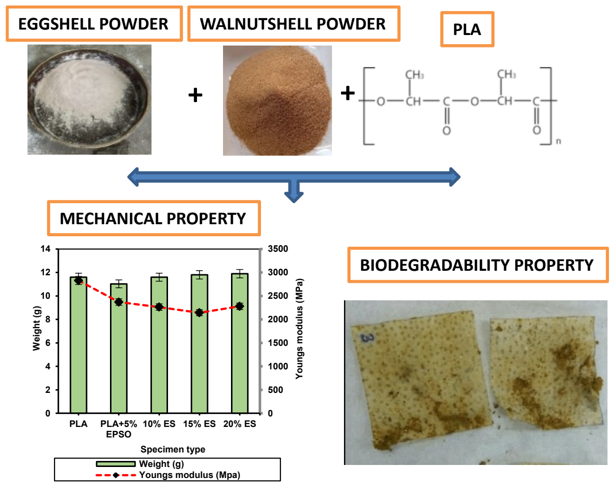
Graphical abstract



Abstract

Composites gain utility when filler materials are incorporated and the quality of the material are changed when filler components are added. In recent years, the use of bio-based components in polymers and polymer composites has significantly increased. Agricultural wastes are employed in this case as filler component to create bioplastic composites since they are inexpensive, plentiful, and easily accessible. By varying the weight ratios of Eggshell(ES) powder and Walnut shell(WS) powder added to the plasticized PLA, bioplastic composite samples are created. Epoxidized soybean oil (5wt%) is used to create the plastic. The obtained bioplastic particles are then subjected to additional processing by being shaped into dog-bone-shaped samples and tested mechanically and thermally. Mechanical testing, including Tensile, Charpy Impact, and Flexural tests, revealed that the PLA possessed inferior properties to those of virgin PLA.The qualities of plasticized PLA-ES composite, however, performed better than those of plasticized PLA-WS composite.

Keywords: Walnut powder, poly lactic acid, egg shell powder, mechanical properties, biodegradability

1. Introduction

The widespread usage of plastics made from petroleum-based resources has a negative impact on the environment, increasing atmospheric CO_2 levels and depleting oil supplies, among other things. Every year, more than a million tons of plastics made from petroleum-based resources are produced, which results in the manufacture of more wasteful plastic. The locally available landfills, rivers, and oceans are used to dispose of the plastic garbage that is produced. By increasing the rate of carbon footprint, this harmful activity has a negative impact on the environment. For the sake of the future and the preservation of fossil resources, this issue requires an alternate strategy (Emadian *et al.* 2017. Green polymer composites, which are compostable and biodegradable, are an alternative to traditional plastic materials (Chieng *et al.* 2014). These are made from biomass and other renewable resources, and they don't give off much carbon dioxide or other greenhouse gases. Even these materials have problems when compared to common polymers, such as high production costs and average mechanical properties (Jainand Tiwari2015). The second barrier on bioplastic manufacturing is food analysts input, as bioplastics are made from plant-based starch, glucoseand other starch foods. Some reports say that if bioplastics kept using plant-based derivatives as raw materials, there would be a big shortage of these food types and a high demand for them in the areas where they are most often used. Taking into account issues like lowering production costs and saving polymer material, a new way of making bioplastics from agricultural residues was developed.

There have been a number of research (Fukushima *et al.* 2009, Donmez *et al.* 2011, El Mechtali *et al.* 2015, Scaffaro *et al.* 2023) that have advocated for the utilization of biomass wastes as natural fillers in polymer-based composites. Utilizing such wastes from renewable sources enhances the financial stability of the agricultural industry while also fostering a safe and responsible environment for coming generations (Chandramohanand Kumar2017).

Crushed walnut shells are used to create walnut shell powder, a hard, fibrous substance. In some areas with a high walnut production, its usage in composite manufacturing may help to ease wood shortages (Zheng *et al.* 2020). They are important crops grown in temperate climates, and the walnut's shell accounts for almost half of its weight. Lignin accounts for 50% of a walnut's composition (Orue *et al.* 2020). A lot of research has been done on nutshell powders mixed with different polymeric composites. PP was used as the matrix material to make the biocompositesand various concentrations and sizes of walnut powder as the filler. The findings showed that the density of the material was enhanced but not its tensile qualities when walnut powder was used as a filler material (Obidiegwu *et al.* 2014). The price of biocomposites can be reduced by adding walnut shell flour to polymer composites. Fences, window frames, door frames, and other buildings might be made from these biocomposites. Using urea-formaldehyde resin, particleboards were built using varying percentages of walnut powder. However, when filler content increased, the internal bond strength declined and the flexural characteristic diminished (Pirayesh *et al.* 2012). Additionally, walnut powder might be used to a mixture of wood particles to create particleboards for exterior uses. Some of the polyphenols, proteins, carbohydrates, and lipids included in pecan nutshells are released during the melt blending process to promote adhesion between the filler and polymer content (Álvarez-Chávez*et al.* 2017, Scaffaro *et al.* 2023) in bio composite containing pecan nutshells in a PLA matrix at concentrations of 0%, 5%, and 7.5% by weight.

According to the results of the inclusion, pecan nutshells also cause a reduction in the mechanical strength properties, however they might be used as disposable products and food trays. The surface of nutshell fillers like argan and walnuts was treated with silane, alkali, and bleaching to improve their mechanical and physical qualities compared to untreated bio composite specimens (Laaziz *et al.* 2017). On the other hand, because so much of the material ends up in landfills, chicken eggshells (ES), a byproduct of aviculture, are seen as the biggest environmental problem in countries with large egg-producing industries. People think that recycling the hundreds of thousands of tons of eggshell waste that the food processing industry alone makes every year costs many millions of euros (Cheung *et al.* 2009).Economically speaking, chicken eggshells are worthless, but they are thought of as a potential calcium source and have a positive impact when used as a product element. The eggshell is composed of 95% calcium carbonate and 5% various organic substances(Ishikawa *et al.* 2002, Yi *et al.* 2004). The mechanical properties of the PP composite were evaluated experimentally by (Toro *et al.* 2007) using conventional talc, calcium carbonate, and chicken eggshells.According to the findings, the PP-ES composite's Young's modulus rises as the filler content does. To optimize matrix reinforcement using fillers and improve composite qualities, the filler's interfacial interaction with the matrix and plasticizer must be considered. There are new methods to reinformce polymeric matrix are available (Acquavia *et al.* 2023). Plasticizers are often contained in polymer matrix materials in amounts ranging from 1% to 10% by weight. Above 10%, the plasticizer tends to leach out of the polymeric material, while below 1%, it may not plasticize the polymeric material as efficiently. Vegetable oils that have undergone epoxidation are thought to be a viable substitute for plasticizing substances based on petroleum. Different levels of triacylglycerols, including glycerol and fatty acid esters, are present in vegetable oils.The main goals of this research are to figure out if it is possible to use biological reinforcement fillings made from waste and to figure out how the amount of filler affects the thermal and mechanical characteristics of polymer composite materials.

2. Methodology

2.1. Materials

The eggshell powder was made at home using a domestic grinder, while the walnut shell powder for this work was given by Sri Jeet Traders, India.The appropriate number of white chicken eggshells were gathered, cleaned, and given a second heat treatment in an oven set at 50°C for 30 minutes. When completely dried, they underwent additional processing in a grinding procedure to produce a fine powder. In order to attain uniform particle size, this powder was sieved. To reduce the moisture content, the powders underwent a second drying procedure for two hours at room temperature. In this work, a biodegradable aliphatic polyester thermosetting polymer called poly(lactic acid) that is generated from renewable feedstock is employed. The company Sri Arun Plastic Industries in Chennai supplied the PLA pellets.The crystallinity, molecular weight, polymer structure, and formulation of the material are some of the factors that affect the mechanical properties of PLA. These factors enable PLA to have qualities ranging from flexible to highly stiff and strong. Epoxidized soybean oil (ESO), graciously provided by SKL. Chemical Industry, India, has an oxirane oxygen content between 6.6% and 8.0% and an iodine value under 3%.

2.2. Sample preparation

To release the absorbed moisture before compounding, PLA granules were dried in an oven at 50°C for 6 hours. First, a consistent weight percentage of 5% of walnut shell powder is applied to plasticize the PLA. In accordance with the desired weight ratio, walnut shell powder was subsequently added to the molten plastic blend. The barrel's temperature profile was kept between 165°C and 180°C, and the screw rotated at a speed of 50 rpm. The filaments that were created as a byproduct of the compounding process were subsequently cooled and pelletized using a cutting machine.The same process was applied to plasticize PLA that had additives at weight percentages of 10%, 15%, and 20%.To remove moisture, the pelletized composite particles were dried in an oven at 50°C for 12 hours. Table 1 shows the percentage of fillers used and density value using the Equation 1. The densities of eggshell powder and walnut shell powder are 0.41 and 0.46 g/cc^3, respectively.

$$ØF = (WF/\rho F) / WF/\rho F + WM / \rho M \quad (1)$$

Where ØF — filler volume fraction, WF — weight fraction of filler, ρF — density of filler, WM — matrix weight fraction, and ρM — matrix density.

2.3. Tests on various properties

2.3.1. Mechanical property test

Various mechanical property testing, including tensile, flexural, impact, and heat deflection tests, were carried out. The TINIUS OLSEN H10KT universal testing machine (Tinius Olsen, Ltd., Noida, India) with a frame capacity of 10 kN was used to measure the specimen's tensile and flexural strength. The tensile behavior of materials is examined using a universal testing device that complies with ASTM D 638. Test samples had the following dimensions: 250 mm long, 25 mm broad, and 2.5 mm thick. The sample was placed between the two grips of a universal testing machine (UTM) that contained a hand-adjustable electronic extensometer with a 60 KN capability. By averaging the results of the three tests, the composites tensile strength was calculated. The three-point bend test is used to determine the flexural strength. Test samples with the following dimensions: 130 mmx25 mmx3.2 mm were used. This process evaluates the flexural properties of composites made of fiber-reinforced polymers. ASTM D 790 is followed in computing the flexural strength. Using an impact machine that adheres to ASTM D256, the composites Charpy impact strength was assessed. For heat deflection testing procedure, the ZwickRoell's HDT/Vicat A was utilized. A confined room was used to conduct this experiment, which used silicon oil as the medium.Following the insertion of the samples into the chamber, loads corresponding to their dimensions were added, and the test began 300 seconds after the specimen had been exposed to the load.

Table 1. Percentage of filler composites

Specimen	Plasticizer [wt.%]	Filler [wt.%]	Filler	Density [g/cm^3]
PLA	0	0	-	1.22
PLA+5% EPSO	5	0	-	1.23
10%WSP	5	10	Walnut shell powder	1.05
15%WSP	5	15	Walnut shell powder	1.08
20%WSP	5	20	Walnut shell powder	1.06
10%ESP	5	10	Egg shell powder	1.26
15%ESP	5	15	Egg shell powder	1.28
20%ESP	5	20	Egg shell powder	1.33

2.3.2. Biodegradability test

A chemical decomposes through a process known as biodegradation as a result of substances or enzymes generated by bacteria or fungi in the soil (Jose *et al.* 2022). Materials biodegradability is evaluated using the soil burial method (ASTM D5988/D5338), and the findings are expressed as weight loss (%) (Sivakumar *et al.* 2022). The weight loss of the buried material can be used to quantify the rate of biodegradation brought on by moisture and microorganisms during the course of the soil burial period (Maran *et al.* 2014). The soil burial test was used to examine the composite specimens' biodegradability. The initial weight (W1) of the samples was determined before they were buried in the soil in order to assess the biodegradation of the samples. Samples from the soil were taken after 2, 4, 6and 9 weeks, and their weights were recorded (W2). The weight loss of the samples was calculated using Equation (1). The amount of sample degradation was determined by calculating the weight loss.

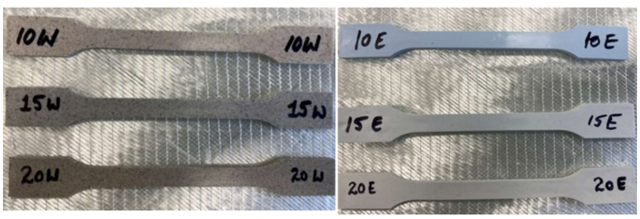
3. Results

3.1. Tensile test

The test was run at a 10 mm/min speed. The 115 mm gap between the two grips was kept constant. Results are shown in Figures 3 and 4 for each type of set from a batch of five test samples, which are shown in Figures 1 and 2. Graphs were drawn based on the average of the sample test findings. Virgin PLA had a higher modulus than other specimen kinds. However, applying the plasticizer increased stiffness compared to virgin PLA. The Tensile strength with respect to Yield strength and yield strain with WS and ES powder is depicted in Figures 5 and 6, respectively.

(a) (b)

Figure 1. (a) Neat PLA (b) PLA plasticized with 5% of EPSO



(a) (b)

Figure 2. (a) PLA–WS composites (b) PLA–ES composites

3.2. Flexural test

Figure 7 shows flexural modulus value of all composite specimen. The inclusion of the plasticizer led to the failure of the other tests at about a 15% strain percentage. The average modulus of the neat PLA samples, which had a failure rate of 5, was 2397.5 MPa. However, the inclusion of the plasticizer led to the failure of the other tests at about a 15% strain percentage. According to the findings in Figure 8 below, PLA-ES had the greatest flexural modulus when it came to eggshell composites (20%).However, in walnut shell composites, PLA-WS (10%) showed the highest flexural modulus. The neat PLA specimen has a higher point of break strength than the other examples given below. The other specimens, as shown in Figure 9, failed at higher strain percentages, whereas PLA failed at extremely low strain percentages and does not withstand bending loads to higher strain percentages because to its brittleness. The material's strength is also very low at the breaking point. According to the study, these biocomposites are ideal for applications that do not require significant weights.

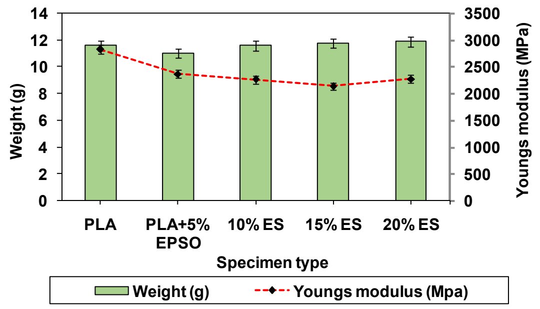


Figure 3. Tensile test with ES powder

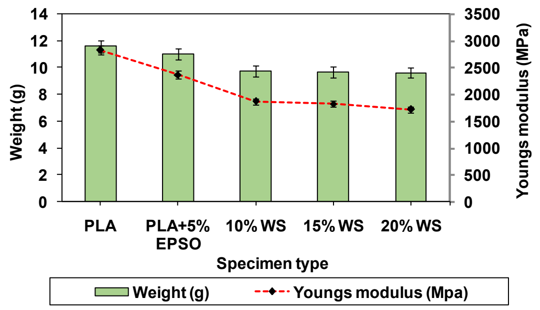


Figure 4. Tensile test with WS powder

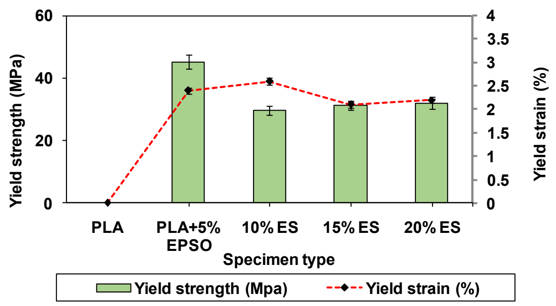


Figure 5. Yield strength and strain with WS powder – Tensile strength

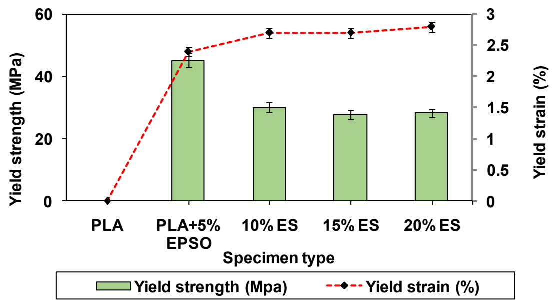


Figure 6. Yield strength and strain of composites with ES powder – Tensile strength

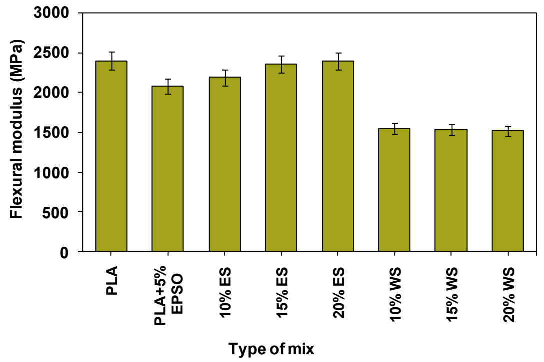


Figure 7. Flexural modulus of all specimen

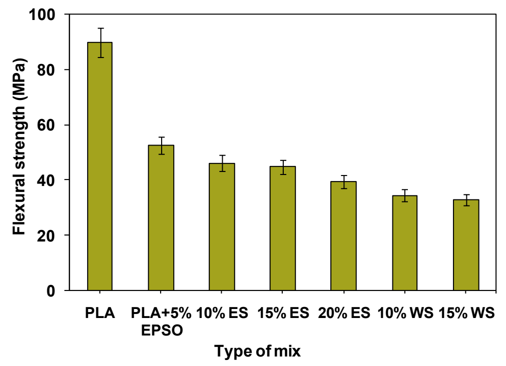


Figure 8. Flexural strength of all specimen

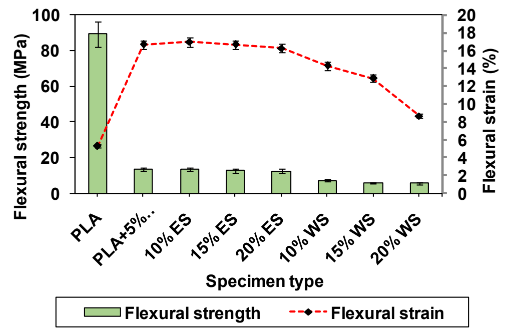


Figure 9. Flexural strength of all specimen at breaking point

3.3. Charpy Impact test

As illustrated in Figure 10, the impact strengths of the filler-based composite materials declined greatly. The impact strength of the material dropped as the filler amount (wt%) increased, indicating that the filler component caused the material to absorb less energy than plain PLA. Among the various filler compositions, the 10% filler-based composites exhibited the highest impact strengths.

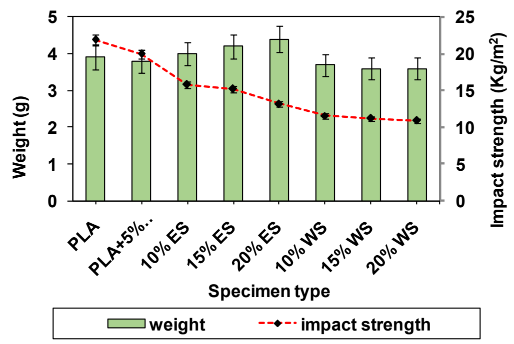


Figure 10. Charpy impact test result

3.4. Heat Deflection Test (HDT)

The materials exhibited nearly identical thermal stability at elevated temperatures and under a specified load, and their temperature values are nearly identical to those of pure PLA. As seen in Figure 11, PLA-WS composite materials have a somewhat higher service temperature than PLA-ES composite materials.

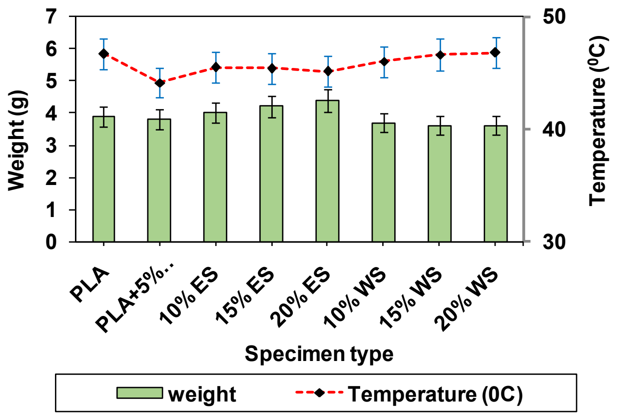


Figure 11. HDT test results for all composite specimens

3.5. Biodegradability test

The rate of biodegradation caused by soil moisture and microorganisms can be assessed by tracking the amount of material lost in weight over time (Jumaidin *et al.* 2017). Figure 12 demonstrates the weight loss at 10,15,20% eggshell and wallnut powder after 2, 4, 6, and 9 weeks of burial. All composites lost more weight after nine weeks of burial compared to two, four, six and nine weeks. This is because the material lost more weight since more microorganisms were active throughout the longer period of time the item was buried (Sivakumar *et al.* 2022). When all of the mixed wallnut composites are compared to egg shell composites, the degradation percentage is always high. This occurrence could be attributed to the higher hydrophilicity of fiber. The largest weight loss of nearly 80% is obtained after 9 weeks of soil burial in comparison to plain PLA composite specimen.

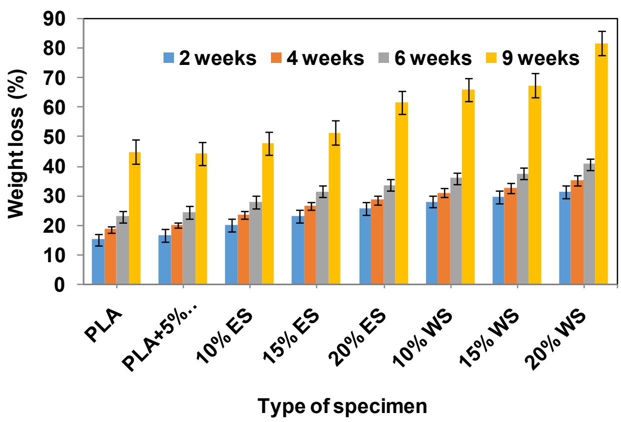


Figure 12. Weight loss after soil burial of all specimen

4. Cost Analysis

Eggshell powder and walnut shell powder can be utilized as filler materials in the bio-composite process to reduce the materials cost. Tables 2 and 3 compare the expenses of using PLA straight versus PLA combined with fillers to create a part that meets the required specifications.According to market surveys, the price of walnut shell flour and eggshell powder was roughly 150 and 200 rupees per kg, respectively.

Table 2. Cost of PLA filled with ES powder

Specimen	Filler (%)	Price per kg(rupees)	Tensile strength (Mpa)
PLA	0	1400	70.2
10%ESP	10	1260	34.9
15%ESP	15	1190	30.8
20%ESP	20	1120	30.4

Table 3. Cost of PLA filled with WS powder

Specimen	Filler (%)	Price per kg(rupees)	Tensile strength (Mpa)
PLA	0	1400	70.2
10%WSP	10	1240	28.5
15%WSP	15	1160	27.5
20%WSP	20	1090	27.1

5. Conclusions

In order to create bio-plastic materials with good mechanical qualities using compounding and injection molding production techniques, ESP and WSP were used as filler materials. The results showed that the mechanical and thermal properties of the pure PLA material were affected by the addition of plasticizer and filler particles. Although the plain PLA had a higher tensile strength than filler-based composite materials, it was brittle and broke easily under small amounts of pressure. On the other hand, a 5% plasticizer improved the material's ductility by accelerating strain rate and elongation at break.

Second, it is probable that the filler's micrometer-scale variations in particle size were the cause of the material's worsening mechanical properties, which led to non-uniform stress changes when a load was applied. When a load was applied, the voids were the main cause of crack formation, which led to early material failure. The fillers and matrix are incompatible with one another because of their dissimilar natures, which reduces the thermal stability. Surface treatments on fillers should be studied in the future to enhance their mechanical, thermal, and moisture penetration capabilities.

The use of walnut shells and eggshells as a sustainable alternative as a filler in bioplastic materials in applications where cost is an issue may help the economic sector while avoiding pollution. These materials are common agro-industrial residues in certain places. Because some of these fillers contain minerals that seep back into the soil and increase its fertility, using them will also aid in the soil degradation.

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