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Reference

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ABSTRACT

Natural fillers have been used as reinforcing material for many years in the research field of biobased polymers. It is widely known for being low cost, eco-friendly, and easily available. The biobased polymer composites have strong future prospects in the application for transportation and packaging industries. In this study, the biobased composite is fabricated at 40 % hazelnut shell flour (HSF) content with 2.5, 7.5, and 10 % of inorganics-based additives like mica, glass ball, talc by extrusion, and press molding method. The mechanical and thermal properties and water absorption of those composites are investigated. The result reveals that inorganic powder-filled composites shows clearly higher impact energy than pure polylactic acid (PLA). However, there was a general decrease in tensile and flexural properties with the addition of mica and glass ball powders, and an increase in properties between 10 % and 30 % was determined with the addition of talc powder (7.5 % and 10 %). The highest flexural strength of the 7.5 % talc-filled PLA/HSF composites is obtained as 51 MPa and the highest tensile strength of 22 MPa was observed for both 7.5 % and 10 % talc. The scanning electron microscopic image reveals the uniformly distributed organic and inorganic fillers and microstructural deformation of the fractured composite surfaces.

Keywords

hazelnut, property, polylactic acid, inorganic powder, polymer composites

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Introduction

Eco-efficient materials are gaining more attention because of increasing concerns about environmental protection, sustainability, petroleum depletion, and the use of renewable resources. The environmentally friendly materials contribute to sustainable development by minimizing wastes at the end of the life cycle with potential recycling, upgrading, and biodegradation. It leads to a low environmental impact. In this field, researchers have given attention to new polymeric materials from renewable resources or potentially biodegradable materials, or both.

Natural fibers such as sisal, jute, flax, and hemp fibers are used instead of man-made synthetic fibers, especially glass fibers in many industrial and research studies because of easy availability, renewability, low weight, and specific mechanical properties. They were generally used in the filler or powder form with synthetic thermoplastic polymers such as polypropylene, polyethylene, polyvinyl chloride, and acrylonitrile butadiene styrene for automotive and customer applications because of economic reasons, easy processing features, and good mechanical and thermal properties of synthetic polymers. However, natural fillers used in plastic and composite applications show a minimal effect on the environment because of the slow biodegradable process of synthetic polymers. For this reason, natural polymers like polylactic acid, polyglycolic acid, polyhydroxy butyrate, and polycaprolactone have been extensively investigated for plastic and composite applications to decrease the environmental pollution risk of synthetic plastic wastes. Polylactic acid (PLA) is one of the widely used natural biodegradable polymers at the industrial level. It is produced by fermenting biobased starch sources from sugar-rich compounds, cellulose, and starches, such as potato, corn, wheat, and sugarcane.[1–4] Conventional PLA is characterized by a crystallinity degree (X_c) of about 37 %, a glass transition temperature (T_g) between 60.8°C and 65.8°C, a melt temperature (Tm) in the range of 173°C–175°C, and an elastic modulus between 2.7 and 16 GPa.

Researchers have investigated PLA plastic and PLA composites with different types of organic and inorganic fillers and most of them are currently commercially available.[5,6] Büyükkaya[7] investigated the mechanical behavior of hazelnut and short nettle fiber reinforced poly methyl methacrylate (PMMA) hybrid composites and reported a partial decrease in flexural, tensile, and impact properties compared to nonhybrid composites. According to the PMMA matrix, the properties of flexural, fracture, and impact strength of nettle fiber-PMMA composites were significantly increased. Balart et al.[8] indicated hazelnut shell flower (HSF), a byproduct of the food industry, can optimally be used as reinforcing filler in fully biodegradable composites with PLA matrix. Characterization of HSF-filled PLA composites shows that the addition of HSF leads to stiffer materials (as much stiffer as the hazelnut flour content increases). Lignocellulosic HSF provides a slight nucleating effect on polylactic acid chains, thus increasing crystallinity, which has a positive effect on the dimensional stability of PLA/HSF composites together with highly dispersed HSF that act as interlock points.

Inorganic powders as a nucleating agent for synthetic polymers also find common applications in the literature.[9–12] Liu et al.[13] investigated the effects of talc and hydroxyapatite (HA) on the thermal and mechanical properties of two types of PLA (one amorphous and one semicrystalline). They stated that the melting mixing made the inorganic filler distribute homogeneously in the PLA matrix and that was confirmed by TGA and scanning electron microscopy (SEM). Nevertheless, gel permeation chromatography (GPC) analysis indicated that the melting mixing could decrease the molecular weight of PLA, possibly because of shear, thus decreasing the mechanical strength. Differential scanning calorimetry (DSC) analysis showed that talc increased the crystallinity, but HA decreased the crystallinity of PLA. Mechanical tests indicated that both talc and HA increased the toughness of PLA; tensile strength depended on the crystallinity and the interfacial properties. Balart et al.[14] studied the effect of varying epoxidized linseed oil (ELO) content on the overall properties of polylactic acid and PLA composites with a constant 20 wt.% HSF. The results revealed a dual effect provided by ELO: on the one hand, it contributes to plasticizing PLA with a noticeable decrease in the T_g. ELO acts as a coupling agent through potential interactions with hydroxyl groups from both lingo cellulosic filler and terminal groups in PLA macromolecular chains. A synergistic effect is provided by ELO, which enhances the overall properties of PLA-HSF composites. Kumar and Das[15] studied the effect of nettle fiber content in PLA and reported that the fiber dosages

enhance its mechanical properties. They suggested that the tensile, flexural, and impact properties of the nettle-reinforced PLA composites had increased initially with the increase of fiber dosages up to 50 wt.%. After that, such properties started to decrease.

Jonoobi et al.[16] researched the preparation of the cellulose nanofiber–reinforced polylactic acid composite by twin-screw extrusion. In this work, composites were prepared with different concentrations, viz., 1, 3, 5 wt.%. It was reported that tensile strength and modulus had been increased for the 5 wt.% concentrated composites. Ozyhar et al.[17] experimented on the effect of alkenyl succinic anhydride (ASA) surface-treated calcium carbonate in the wood dust–filled PLA composites. ASA surface-treated calcium carbonate at 10 wt.% with 40 % optimum of wood dust PLA composites exhibited an improvement in their properties as compared to the untreated one. The addition of such additives also improves the fiber adhesive and leads to an improvement in the properties. There is greater interest in the use of PLA-based composite because, at present, the current cost of PLA is not competitive with the petroleum-based solutions.[18] The various inorganic minerals that have been investigated for application in PLA composites include talc and kaolinite[19,20] barium sulphate, mica,[21] and calcium carbonate[22,23] in the various fibers as reinforcement. The use of the minerals in composites exhibits additional advantages such as improvements in thermal stability[24] and fire retardance and impact strength.[25]

In this context, some researchers have investigated the effects of organic and inorganic fillers (sand, wood dust, fine wire, household wastes, etc.) on mechanical and refractive behavior. In this study, PLA matrix hybrid composites were produced using different volume ratios as HSF and inorganic filler (glass ball [GB], mica, and talk powder) material. The obtained composite is characterized by a tensile test, three-point flexural and fracture test, and DSC methods in terms of mechanical and thermal properties.

Material and Methods

MATERIALS

PLA commercial-grade Ingeo 6201D obtained from Nature Works LLC was used as a matrix for making the composites in this work. This PLA possesses a density of 1.18 g/cm^3 and a melt flow index of 15–30 g/10 min at 210°C. Hazelnut shell (Corylusavellana variety) was obtained as a hazelnut from the food industry and used as lingo cellulosic filler for composites. **Table 1** shows themechanicalproperties of PLA. The GB sphere was supplied by Carbonate OMYA in Turkey. The talc and mica were procured from Acar Kimya in Turkey.

Hazelnut shell *(Corylusavellana L.)* as an organic powder source is composed of two main layers. The mesh size of the ground hazelnut wafers was taken as 425 μm, and it was used by separating the soft part to use the powder obtained from the hard vomit of the shell.

Talc is an aqueous magnesium silicate with a density ranging from 2.58 to 2.83 g/cm^3. Although it is weak to heat and electrically conductive, it is resistant to fire. When heated at high temperatures, it hardens and solidifies. They are not affected by acids. The particle size is distributed around 2 μm.

The use of other fillers (talc, calcite, etc.) instead of or in combination reduces the weight of the product, resulting in a bulkier and lighter product. The air-filled GB beads increase the mechanical properties of the material. These insulators, which are insulated for heat, electricity, and sound, increase the insulation property of the material. The particle size is distributed in the range of 30 to 50 μm.

TABLE 1
Mechanical properties of PLA

Mechanical Properties	PLA
Tensile strength, MPa	65
Elastic modulus, MPa	6,500
Elongation at break, %	7.5
Flexural strength, MPa	97

Mica is one of the transparent minerals having elasticity. The hardness centerline of Mohs stiffness is 2–3 GPa, and the density is between 2.5–3.5 g/cm^3. The particle size is distributed in the range of 25 to 107 μm.

PREPARATION OF PLA-BASED COMPOSITES

First, all powders and PLA raw materials were dried before being used in the extrusion process. The composites were prepared by a single-screw extruder (RONDOL 3212). In the first step, PLA resin was mixed with HSF and other inorganic powders with heat and screw speed parameters. The extruder had three heating zones, and the temperature profiles of the barrel were 190°C, 220°C, and 240°C from the hopper to the die at the constant screw velocity set at 75 rpm. The extruded HSF with PLA granules was subsequently cooled down in a water cabin and then long composite strands were pelletized to smaller sizes with a scrap granulator. From the machine, the plastic products were extruded as a physical mixture of talc, GB, and mica by using this method, and the high-strength materials with low cost can also be produced easily. In this study, PLA composites were fabricated with HSF of 40 wt.% loading and inorganic additives in a different range of inclusion (2.5 %, 7.5 %, and 10 %) for talc, GB, and mica powders. After the samples were manufactured, the samples were kept in the oven for 24 h at 60°C and cut based on ASTM-specific test standards. The compound pellets were then molded in a hot press under a temperature range of 175°C to 195°C and pressure of 10 bars.

PHYSICAL PROPERTIES

The properties such as density and water absorption of the samples were studied. The Archimedes principle was used to find the density of the produced specimen. To determine density by the Archimedes method, samples were cut to the size of 2 by 2 cm and kept at 60°C for 24 h at room temperature until the moisture in the sample was completely dried. Then, the samples were taken from the oven and weighed for 15–20 min in the desiccator. The liquid was coated with paraffin to prevent samples from collecting moisture before measuring the weights in water. The density calculation of the coated samples was performed.

The water absorption test was held to measure the effects of inorganic filler content on the compatibility of HSFs and PLA polymer used in the composite material by measuring the weight and dimensional changes after the samples were kept in water for 2 h and 24 h.

MECHANICAL PROPERTIES

Tensile and flexural tests were conducted using the universal testing machine (MTS Criterion Model 45) with 20-kN loading capacity based on ASTM D638, *Standard Test Method for Tensile Properties of Plastics*, and ASTM D790, *Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*. The samples were cut to the size of 90 by 13 by 4 mm and the tests were performed at a speed of 5 and 2.7 mm/min, respectively. The elastic modulus, strength, and elongation amount of the samples were determined. The average values of the five tests were reported.

The Charpy impact test was carried out according to ASTM D256, *Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics*. Five test samples were used for each ratio and absorbed average energy values were obtained. To evaluate the fracture energy, the nondotted rectangular rod samples were tested with a Charpy impact device (Instron Ceast 9050) with a span of 40 mm and a 50 J pendulum attractive and impact strength (kJ/m^2) calculated.

THERMAL PROPERTIES

Thermal characterization of the composite samples was performed by DSC in a Hitachi 7020. The test was carried out with the 3–6-mg specimens and the cooling rate was applied from 30°C to 230°C at 15°C/min under a nitrogen atmosphere. The cooling and reheating cycle steps were also applied to the samples to determine all thermal parameters. The T_g, melting temperature (T_m), melting enthalpy (ΔHm), and crystallinity (X_c) were determined from the first heating scan, whereas the crystallization temperature (T_c) and crystallization enthalpy (ΔHc) were obtained from the first cooling scan. T_m is defined as the maximum of the endothermic melting peak and T_g as

the deflection of the baseline temperature from the first heating scan. The X_c was obtained by the following expression:

$$X_c(\%) = \left[\frac{\Delta Hm}{\Delta H_{m(crys)}}\right] \times 100 \quad (1)$$

where ΔHm is the enthalpy of the sample and $\Delta H_{m(crys)}$ is the enthalpy of 100 % crystalline PLA taken as 93.7 J/g. The ΔHm, ΔHc, and X_c were converted by the mass fraction of the pure PLA in the composites.

MICROSTRUCTURAL OBSERVATION

The fracture surfaces of the failed tension test samples were observed with a scanning electron microscope (ZEISS EVO LS10, Germany) with a field emission gun and an accelerating voltage of 5 Kv. A nano level of gold layer in thickness was coated onto the fracture surfaces.

Results and Discussion

EFFECT OF FILLERS ON THE PHYSICAL PROPERTIES

Figure 1 shows the density of different composites produced. A higher density of 7.5 % mica-added specimen is observed and a significantly lower density of 10 % GB-added specimen is noted. The maximum density of 0.849 g/cm^3 was observed for 7.55 % mica-added composite and the lowest density of 0.835 g/cm^3 was observed for 7.55 % GB-added composite. There was no significant difference in the densities of all the composites.

The water absorption effect of additive filler content on the hazelnut powder/PLA composite is shown in figure 2. The experiments were performed on those composites in two categories, 2 h and 24 h. It is observed that the 10 % mica-added composites hold the high water absorption among the other addition of mica composites for the two categories for 2 h and the same results were observed for 10 % GB-added composite for the 24 h. The higher values for water absorption were noted for 10 % talc-added composites among talc-based composites. More water abortion was found for the 10 % GB and 10 % mica-added composite for 24 h and 2 h, respectively. It is observed that the addition of the inorganic additive increases the water absorption properties. PLA matrix composites containing GB powders achieved the highest water intake compared to other inorganic powders with an increase of approximately four times when the 2-h and 24-h water intake was examined. Similar results were obtained with Abdulhosseini Sarsari, Pourmousa, and Tajdini[5] and Zahedi et al.,[26] which showed increasing water

FIG. 1

Density of composites.

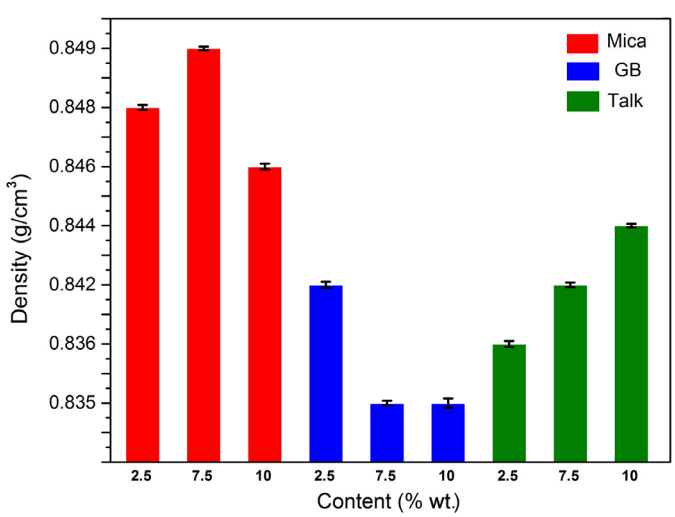
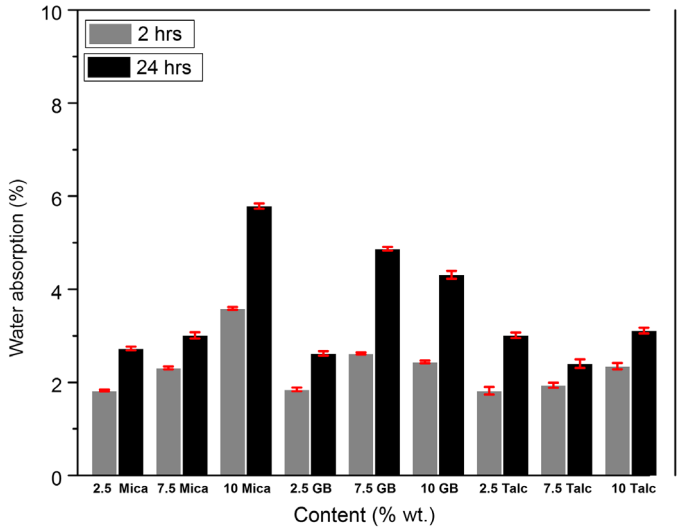


FIG. 2

Water absorption of prepared composites.

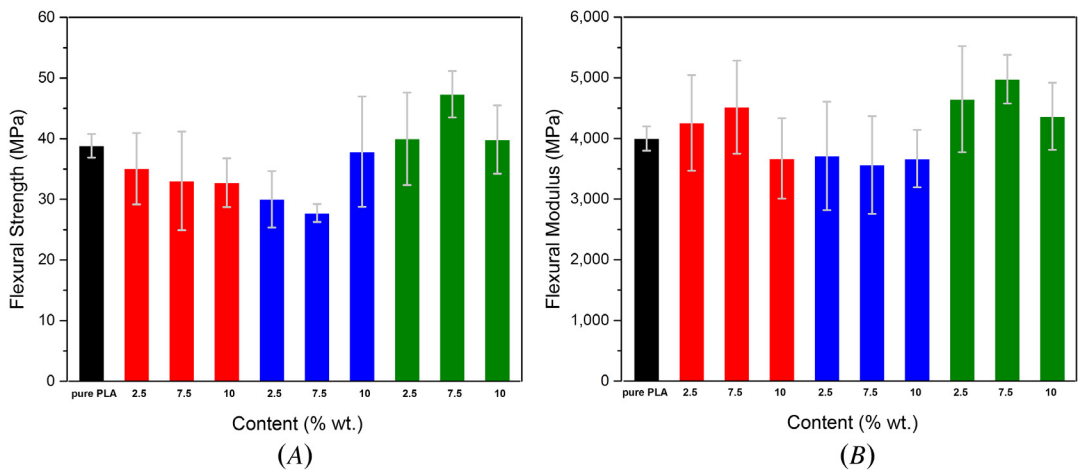


absorption in a composite structure via porosities in the matrix and interface because of the possible weak interaction of inorganic powders with strongly hydrophobic PLA structure.

EFFECT OF FILLERS ON MECHANICAL PROPERTIES

The flexural strength and the flexural modulus of the various inorganic additives added in hazelnut/PLA composite are shown in figure 3*A* and 3*B*. The flexural strength of the HSF-filled PLA composites with no inorganic additives is shown as 39 MPa. From figure 3*A*, it is observed that the increase in mica content leads to enhanced flexural strength. Among the GB-based composites, the 5 % GB shows the highest value of flexural composites. It is also noted that the greater flexural strength was noted for the 7.5 % talc-based composite compared to all other composites. It is also noted that 2.5 % talc-added composites show less factual strength than the other composites. This could be caused by the lack of interfacial adhesion between the PLA and talc.

FIG. 3 Flexural properties: (*A*) PLA and (*B*) PLA composites reinforced with hazelnut flour.



The flexural modulus of the produced composites is shown in figure 3*B*. The greatest modulus was observed for the composite having 10 % and 7.5 % mica additives. It is important that the abovesaid samples lead to having a high standard deviation. It is very hard to interpret the results because it does not show the proper trending according to the various types of composite samples. The flexural modulus increases for mica-added composite when the percentage of addition of mica increases. But the same trend was not observed in the GB and talc-added composites because of a lack of bonding between the fiber and filler. Similarly, Balart et al.[8] found that addition of organic powder made significant decrease in flexural strength results because of poor particle-polymer interactions, which cause embrittlement. However, addition of inorganic powders, especially with talc, minimized that negative effect and increased flexural properties at certain rates could be achieved.

The elasticity modulus and tensile strength of the samples were calculated from the tensile test. As represented in figure 4*A* and 4*B*, the strength and elasticity drop of the pure HSF PLA sample, excluding 7.5 % talc and 10 % talc HSF-PLA composites. The tensile strength of the neat PLA samples was 1.9 MPa and the elastic modulus was 6,500 MPa. Addition of talk powder in composites, elastic modulus values of 7.5 % and 10 % talc HSF-PLA composites were calculated as 6,300 MPa and 8,200 MPa, respectively. However, the lowest tensile strength was determined as 7 MPa for 7.5 % GB and 10 % mica HSF-PLA composites. Table 2 shows the

FIG. 4 Tensile strength and elastic modulus: (*A*) PLA and (*B*) PLA composites reinforced with hazelnut flour.

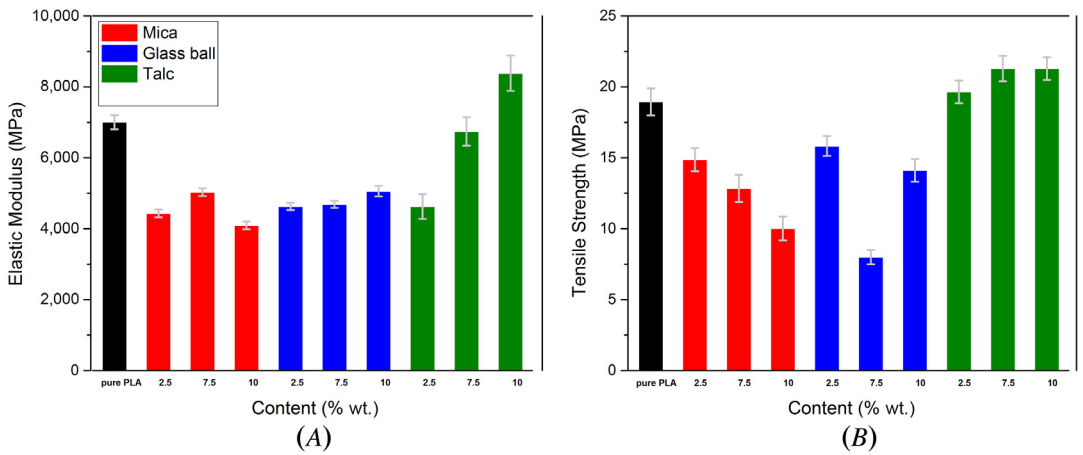


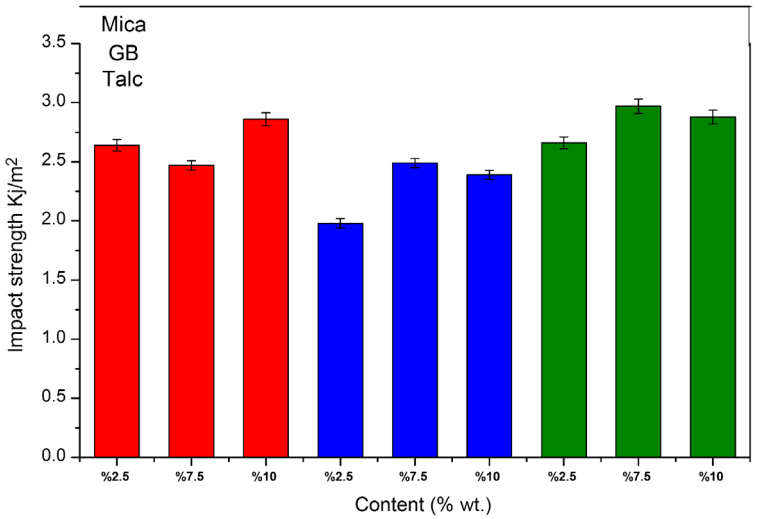
TABLE 2

Mechanical and physical properties of inorganic and pure PLA composites

Specimens	Density, g/cm^3	Tensile Strength, MPa	Elastic Modulus, MPa	Strain to Failure	Flexural Strength, MPa	Flexural Modulus, MPa	Flexural Strain	Impact Strength, KJ/m^2
Neat PLA	1.300	18.9 ± 0.95	7,003 ± 200	0.4577 ± 0.07	38.82 ± 1.95	4,000 ± 200	1.12 ± 0.29	1.87 ± 0.071
%2.5 mica	0.848	14.8 ± 0.85	4,433 ± 112	0.366 ± 0.08	35.58 ± 1.64	4,257 ± 789	0.53 ± 0.29	2.64 ± 0.05
%7.5 mica	0.849	12.8 ± 0.95	5,031 ± 111	0.418 ± 0.03	29.68 ± 1.62	4,516 ± 769	0.30 ± 0.17	2.47 ± 0.04
%10 mica	0.846	10 ± 0.83	4,094 ± 110	0.289 ± 0.04	26.81 ± 1.09	3,670 ± 663	0.70 ± 0.35	2.86 ± 0.055
%2.5 GB	0.842	15.8 ± 0.71	4,628 ± 100	0.395 ± 0.01	30.65 ± 1.17	3,712 ± 893	0.58 ± 0.27	1.98 ± 0.038
%7.5 GB	0.835	14.9 ± 0.53	4,686 ± 100	0.224 ± 0.09	28.65 ± 1.07	3,563 ± 806	0.64 ± 0.13	2.49 ± 0.041
%10 GB	0.835	14.1 ± 0.85	5,059 ± 149	0.301 ± 0.09	36.98 ± 1.03	3,666 ± 474	0.62 ± 0.17	2.39 ± 0.038
%2.5 talc	0.836	19.6 ± 0.87	4,628 ± 351	0.441 ± 0.05	27.33 ± 1.71	4,648 ± 875	0.67 ± 0.31	2.66 ± 0.05
%7.5 talc	0.842	21.2 ± 0.92	6,742 ± 390	0.496 ± 0.08	50.98 ± 1.43	4,978 ± 403	0.40 ± 0.21	2.97 ± 0.06
%10 talc	0.844	21.3 ± 0.87	8,385 ± 498	0.487 ± 0.09	41.43 ± 1.35	4,364 ± 552	0.43 ± 0.27	2.88 ± 0.057

FIG. 5

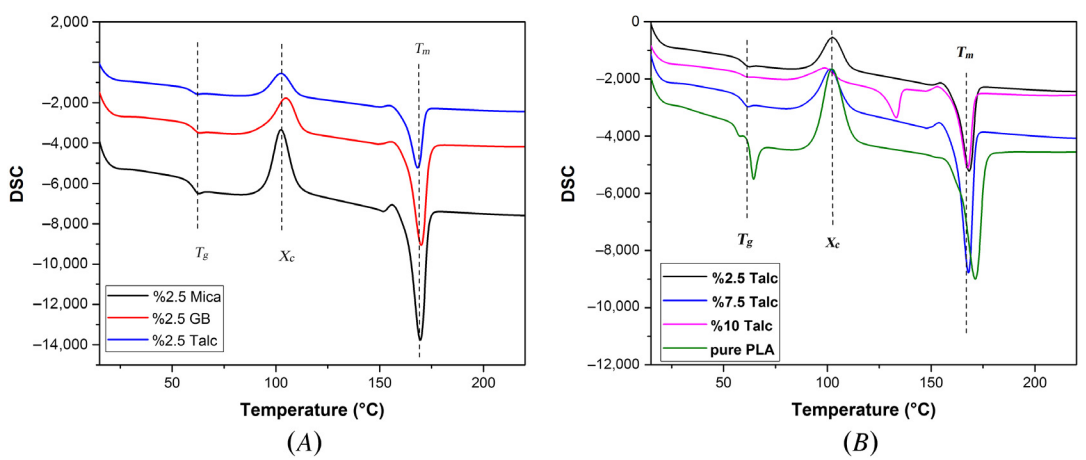
The impact strength of PLA/inorganic composites reinforced with hazelnut flour.



mechanical properties of composites. However, Lee et al.[27] discovered that adding talk powder to the neat PLA resulted in no improvement in tensile strength because of the fact that brittle fillers act as stress concentrator and initial cracks, therefore resulting in easier breakage. They also show that PLA/talc composites became more brittle with increasing talc content.

The presence of HSF has significantly improved the durability of the PLA matrix impact. According to pure-PLA, impact toughness increased by approximately 40 % in 2.5–7.5–10 % inorganic powder-filled HSF-PLA composites. From **figure 5**, it is observed the amount of filler below the critical ratio caused a decrease in impact strength and an increase in the impact strength of the fiber values above the critical value. As expected, talc, a significant increase in the resistance of the crack growth was observed, resulting in a significant increase in impact strength. Although the mechanisms mentioned above are effective, the mechanism of fracture mechanism is the most effective in impact tests. Other mechanisms do not have sufficient time to perform the system because of the relatively high speed. **Figure 5** shows that 7.5 and 10 % talc and 10 % mica HSF-PLA composites had the greater impact strength, whereas 2.5 % GB had the lowest value of 1.98 kJ/m^2. As can be seen from the results, the

FIG. 6 (*A*) DSC analysis of PLA-2.5 % additive sample; (*B*) DSC analyses of PLA-PLA/talc sample.



addition of GB to composites caused a decrease in impact strength values compared to talc-reinforced composites. Rafał et al.[28] also discovered that PLA treated with GB had improved longitudinal modulus of elasticity, flexural modulus, and mass flow rate. However, they stated that the impact and flexural strengths were unchanged while tensile strength and tensile strain at break were both reduced.

EFFECT OF FILLERS ON THERMAL BEHAVIOR OF HSF/PLA COMPOSITE

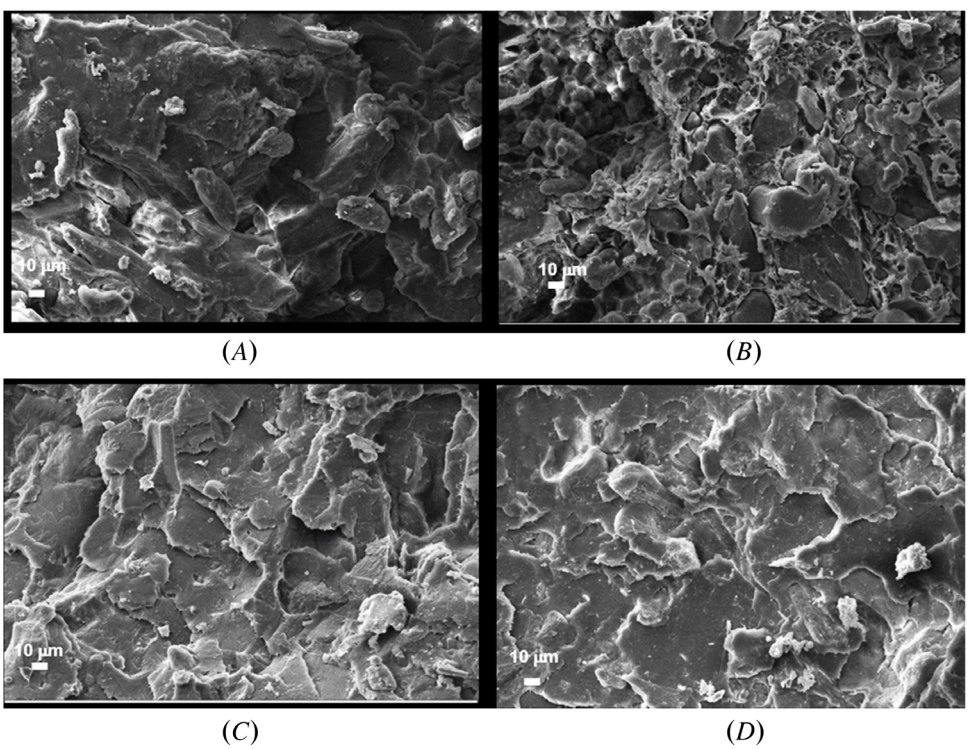
The DSC thermograms recorded with PLA-2.5 % additive, and PLA/talc composites are reported, respectively, in figure 6*A* and 6*B*. The initial temperature was 15°C, heating up to 230°C and then cooling and heating were continued by repeating the same cycle twice. PLA alone does not crystallize during cooling. Talc induces PLA crystallization on cooling, as already reported, the crystallization percentage increases with the filler concentration. The T_m and T_C of PLA have practically the same absolute value and this confirms that crystallization of neat PLA occurs only during heating.

TABLE 3

Thermal behaviors of hazelnut flour-filled PLA composites with different inorganic powders

Samples	T_g, °C	X_c, %	T_m, °C	ΔHm, J/g
Pure PLA	67.5	15.9	174.3	17.4
%2.5 mica	62.5	5.73	169.2	5.65
%2.5 GB	58.8	6.33	171.1	6.16
%2.5 talc	57.7	9.21	169.9	8.69
%7.5 talc	58.1	7.79	169.9	7.3
%10 talc	61.2	6.18	167.6	5.8

FIG. 7 SEM of composite with PLA specimen with (*A*) hazelnut, (*B*) hazelnut and 10 % mica, (*C*) hazelnut and 7.5 % talc, and (*D*) hazelnut and 10 % talc.



The addition of 2.5 wt.% of talc leads to a considerable decrease of T_C (~23°C), as well as to an increase of total crystallinity with respect to neat PLA. The T_C remains similar for all the samples containing talc. The PLA crystals in PLA/talc composites are formed partially during cooling and partially during cold crystallization. The percentage of crystallization during heating (T_C) is evaluated by the heat released by cold crystallization. It decreases with the increase of talc concentration. Similarly, the overall crystallinity (T_m) decreases with the increasing concentration of talc. This is probably because of the presence of a higher percentage of crystals formed during cooling, thereby reducing the chain mobility. This reduction negatively affects the cold crystallization process.[7] **Table 3** shows the thermal behaviors of various composites produced. Kim, Song, and Youn[29] also found that crystallization of the PLA improved the interfacial adhesion between the PLA and mica particles through the annealing process.

MORPHOLOGY

Fracture surface analysis of the composite samples applied did not clearly show any specific difference in terms of fiber breaking and displacement at the fiber-matrix interface. The composite samples were damaged in a ductile manner with a slow and steady crack growth even though the damage in the PLA samples was brittle. This behavior confirms that the composites reinforced by the mica, GB, and talc absorb more energy while breaking. SEM micro photos of the pure HSF and the necrosis of the HSF-PLA composite sample are given in **figure 7*A***. The greatest reading was recorded in the 7.5 % and 10 % talc samples, which are shown in **figure 7*B*** and **7*C***, respectively, whereas the lowest results were recorded for 7.5 % GB and 10 % mica (**fig. 7*D***). In addition, SEM images of pure filament shell and PLA sample showing higher results are compared to other filled samples.

Conclusions

The hazelnut flour/PLA composites were fabricated with different addition of inorganic additive. The following observations are reported:

- 7.5 % mica filled composites are reported for higher density when compared with all other composites.
- The more water abortion was found for the 10 % GB and 10 % mica-added composite for 2 and 24 h, respectively.
- The flexural strength was decreased with the addition of mica to the samples. The best flexural test results were 7.5 % talc-filled samples. The flexural modulus values are reported high for the 7.5 % talc-added sample and low for 7.5 % GB-added samples.
- In the tensile testing, the highest results were obtained for 7.5 % and 10 % talc, whereas the lowest results were reported for 7.5 % GB and 10 % mica-added composites.
- The higher overall crystallinity was noted for 2.5 % talc-added composites among the inorganic-added composites. However, as pure PLA with HSF holds higher crystallinity than all other composites.

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