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EFFECT OF WALNUT SHELL POWDER AND NANO-TIO2 ON THE MECHANICAL, THERMAL, AND WATER ABSORPTION PROPERTIES OF POLYESTER COMPOSITES

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ABSTRACT

This study investigates the potential of using ground walnut shell powder as a natural reinforcement for unsaturated polyester resin for sustainability and recycling, as an alternative to synthetic reinforcements. The main objective is to assess the effect of various filler contents 5%, 15%, and 25% wt. on the thermal and mechanical performance of the prepared composites. Hand lay-up technique was used to fabricate the casts, and the designated test specimens were cut according to the dimensions in the standard specification of each test (Impact strength, flexural strength, water uptake, and thermal conductivity). The results showed a significant improvement in the impact and flexural strengths at 15% wt. reinforcement, while thermal conductivity dropped with increasing filler weight fraction, suggesting enhanced thermal insulation. Water uptake increased at the first few weeks until a steady state is reached, after which the 25%wt. specimens showed the highest rate of water absorption, followed by the 15% and 5%wt. specimens, respectively. These findings show the suitability of using locally-available and inexpensive agricultural waste as an eco-friendly reinforcement for polymeric composites.

KEYWORDS

Polymers; Composites; Walnut shell; Reinforcement; Mechanical properties; SEM; Recycling; Unsaturated polyester.

1. INTRODUCTION

In the current scientific literature, there has been a great interest in substituting industrial and costly materials with natural and recyclable ones, while maintaining lightweight and good properties. Among those natural materials, walnut shell powder (WSP) appeared as an eco-friendly and lightweight material, combined with availability and low cost, as a replacement for traditional wood and industrial reinforcements. The WSP is noticed to have superior properties even when compared with other wood-derived reinforcements (Pradhan et al., 2020).

Walnut shell, a well-known lignocellulosic filler, was added to the urea-formaldehyde-based composite particle board through the conventional pressing method. The filler content, curing time, temperature, particle size, and mechanical properties were studied, and the results proved that flexural strength dropped when the filler content increased due to decreased continuity of the resin, hence weaker adhesion between the two phases. Fly ash was incorporated, and it showed a positive role in improving flame retardancy, a main concern for construction parts, while the addition of phenol formaldehyde reduced water absorption and thickness swelling. Sem investigation also confirmed uniformity on a microscopic scale. The researchers concluded that walnut shell powder can be an advantageous addition to produce cost-effective, eco-friendly, and robust composite (**Gürü** et al, 2006).

When this material is included within polymeric matrices, it can yield a material with good properties, while maintaining the environment and keeping costs low. However, the accompanying challenges include moisture retention, bonding between the two phases, and uniform distribution remain as obstacles in the development of a fully environmentally-friendly material that may reach its full potential if used as an alternative to the already existing industrial materials. A composite needs to be efficient via efficient bonding between the matrix and the reinforcement, so that the stress can be transferred effectively between the two phases, which ensures consistent distribution of loads across the whole material, and prevents stress concentration zones. On the other hand, weak bonding results in discontinuity and premature failure, in addition to the creation of pathways for moisture and chemicals to easily penetrate the matrix, and act as stress concentration zones, thereby reducing durability. To address these issues, nano additives may be included to minimise them and refine their performance. Nano titanium dioxide (TiO_2) is known for being chemically stable, having a high surface area, and possessing barrier properties, making it an ideal option to reinforce polymeric composites even at low weight fractions. This study discusses the combined reinforcing effects of walnut shell powder and nano TiO_2 on some mechanical and physical properties of polyester composites, proposing insights into the fabrication of bio-based composites for structural and mechanical applications (Rathnam et al, 2022). A collection of literature surveys focused on the use of WSP in the manufacture of polymeric composite materials. Polypropylene was chosen by Ayrilmis et.al. to be reinforced with WSP with different weight fractions of 40, 50, and 60%. The specimens were fabricated using the injection molding technique, and selected mechanical properties (bending and tensile modulus) were significantly improved with the addition, while bending and tensile strength decreased. The water absorption also showed a direct relationship with the filler content. The researchers also investigated the effect of a maleic anhydride polypropylene (MAPP) as a compatibilizer on the properties of the prepared material, and it showed an improvement in adhesion at the interface area between the two phases. The researchers concluded that a formulation of the three phases (Polypropylene, WSP, and compatibilizer) can be manufactured into a composite material that can be useful for outdoor applications and withstand the weather elements (Ayrilmis et al., 2013).

In 2018, Salasinska et.al. studied the potential use of WSP as a reinforcement to epoxy. The mechanical properties (impact and tensile strengths, and hardness) of the resulting material were studied, and a scanning electron microscope was used to investigate the microscopic structure. Various weight fractions were investigated (20, 30, 40, and 50%), and the resulting composite showed an improvement in stiffness and hardness, although it unexpectedly exhibited reduced tensile strength and impact resistance (Salasinka et al., 2018).

The dynamic mechanical thermal analysis showed an enhancement in the stiffness at high temperatures, which may have been caused by WSP In 2020, research published by Pradhan et.al. discussed the fabrication and thermal properties of polyester reinforced with WSP, with a focus on the thermal conductivity, thermal expansion coefficient, and glass transition temperature (Tg), with the use of a proposed mathematical model to compare the theoretical and experimental findings, which were found to be consistent with each other, and the researchers concluded that WSP offers good thermal insulation properties, when added in moderate percentages (Pradhan et al., 2020).

Pradhan and Satapathy also performed another study on the WSP in 2021, in which they elaborated on the dry sliding wear resistance of polyester reinforced with WSP as a reinforcement. They used the pin-on-disc method to assess the wear resistance of the composite, and also compared the experimentally obtained results with those obtained through ANSYS 19.2 model, and found that they were closely related in values (Pradhan and Satapathy, 2021).

Przemysław Pączkowski employed walnut shell powder as a reinforcement to unsaturated polyester resin derived from recycled polyethylene terephthalate (PET), manufacture sustainable composite materials. The study assessed the mechanical and chemical durability of the prepared materials, and the results showed a deterioration of flexural strength and modulus, in addition to the decrease in chemical resistance, especially after immersion in 1% NaOH solution, which resulted in a high absorption and fragmentation of the immersed specimen, compared to specimens immersed in water, acetone, and toluene. The researcher found that despite the decrease in mechanical and chemical properties, the polymeric composites reinforced with walnut shell powder are still a viable alternative to polymer composites reinforced with synthetic fillers (Pączkowski, 2023).

As the world is heading to more sustainable resources and more eco-friendly options, reviews have been elaborated to show the importance of recycling agricultural wastes and by-products into useful materials. The nutshell wastes (including walnut, peanut, or coconut, for example) constitute a considerable share, up to 80% of the total production process, which is unused. Substantial efforts are being made to make use of this large portion on a global scale, in industries like the automotive and marine industries, furniture, or the biomass fuel industry. The biodegradable polymer industry alone can contribute to the reduction of greenhouse gas emissions by 35-80%, and reduce energy consumption by about 65%. In this context, not only can the walnut shell powder be used, but also almond, pistachio, hazelnut, cashew, coconut, or peanut shells, all of which are main ingredients in the global food industries and thousands of tonnes are produced annually (McNeil et al. 2024).

Walnut shell powder was used in combination with delignified bamboo fibers as a hybrid reinforcement to melamine-hexamethylenediamine-urea (MHU) resin. The composite was manufactured using the hot-pressing technique, and the mechanical, thermal, and flame-retardant properties were investigated for the prepared material. The bamboo fibers enhanced tensile and flexural behavior, while the walnut shell powder raised hardness and improved the appearance, although a higher content of filler may lower these properties due to a reduction in load-bearing characteristics. Flame retardancy improved as the MHU resin is intrinsically flame resistant. SEM observations showed good interfacial bonding and evenly-distributed microstructure. The study concluded that the hybrid reinforcement of the delignified bamboo fibers and walnut shell powder can be employed to improve the properties of polymeric composites (Li et al, 2024).

Walnut shell powder can also be used to reinforce thermoplastics, like polypropylene (PP), and create sustainable characteristics of polymer composites in automotive applications. In a study by Alsarraf (M. Alsarraf, 2024), PP was reinforced with various weight fractions of walnut shell powder (10, 20, 30, and 40%)wt. and alkaline treatment and microwave irradiation were applied to improve compatibility between the two phases. Mechanical properties (tensile, impact, and flexural strengths) were studied, in addition to Fourier transform infrared radiation (FTIR), scanning electron microscope (SEM), and X-ray diffraction, as characterization techniques. The researcher found that the optimum addition ratio was 20% wt., which increased the tensile strength by 1.2 times over the unreinforced PP. The NaOH treatment further enhanced the final product for all specimens. The NaOH-treated specimens revealed properties consistent with those of materials used in commercial airbag covers.

The present study is an attempt to develop and characterize a polymeric composite material made of unsaturated polyester as a matrix, and reinforced with walnut shell powder and nano TiO_2. The study analyses how the different weight fractions of reinforcement (5, 15, and 25% wt.) can affect different mechanical and physical properties, together with the presence of nano TiO_2. The aim is to pinpoint the optimum addition ratio that creates a balance between strength, moisture resistance, and thermal performance, for the material to be useful in applications as a sustainable material.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Polyester resin

Unsaturated polyester in the current work is manufactured by Saudi Industrial Resins Limited™, under the trade name Siropol™, purchased from the local distributor. The resin is composed of two components: The transparent, amber-colored polyester resin and the hardener (methyl ethyl ketone peroxide), and they solidify when mixed in a weight ratio of 99:1 by weight, respectively. The resin was chosen for its good performance and durability when exposed to mechanical stresses and weathering effects. Polyester is also known for its high adhesion, hence high performance in various environments (Salih et al, 2025). The main characteristics of the resin are summarized in Table 1 below.

Table 1. The general characteristics of the unsaturated polyester resin (Siropol™) used in this research.

Colour	Clear to amber
Specific gravity	1.04±0.2
Viscosity, cps	450-500
Percent solid	60-63%
Gel time, 25°C	20-25 minutes.
Tensile strength (ASTM D-638).	94 N/mm^2
Tensile modulus (ASTM D-638).	9.8 N/mm^2

2.1.2. Walnut shell powder

This powder was prepared by collecting empty walnut shells from the local food markets, as it is used in confectionery and other food industries. The hard shells were dried to remove all the moisture before grinding by a ball mill for 2 hours. Fig. 1 (a) and (b) below show the dry walnut shells before and after grinding, respectively. The powder was added to the three composite casts in a weight ratio of 5%, 15%, and 25% by weight as a reinforcement. Lignocellulose is the primary constituent of walnut shell powder, which is responsible for the desired properties that contribute to the composite's performance, such as the presence of active functional groups, compatibility with numerous resins, high carbon content, and chemical stability. The walnut shell powder may contain cellulose, lignin, ash, and hemicellulose in 23.9, 50.3, 3.4, and 22.4 %weight, respectively, in addition to other minor constituents such as wax, essential oils, and volatile materials. These constituents make walnut shell powder an ideal choice as a reinforcement for polymeric composite (Pączkowski, 2023). A traditional particle size analysis was carried out on the ground shell by sieving, and the results are shown in Table 2 below.

Table 2. Average particle size distribution of the ground walnut shells.

Particle size range (mm)	Sieve mesh equivalent (US standard)	Approximate percentage by mass (%)
> 2.4	< 8 Mesh	~10%
1.2 – 2.4	8 – 16 Mesh	~15%
0.6 – 1.2	16 – 30 Mesh	~18%
0.42 – 0.6	30 – 40 Mesh	~17%
0.125 – 0.42	40 – 120 Mesh	~28%
0.032 – 0.125	120 – 400 Mesh	~10%
< 0.032	> 400 Mesh	~2%

(a) (b)

Fig. 1. (a) The dried walnut shells before grinding, and (b) the ground walnut shell.

2.1.3. Nano titanium (TiO_2)

Nano TiO_2 was also added in a weight ratio of 1% to all casts to achieve maximum dispersion, as the walnut powder may float to the surface of the casts. The nano TiO_2 was purchased from U.S. Research Nano Materials Inc.™. The addition of nano TiO_2 has transformed the casts from transparent to a white colour. The addition also serves as an additional reinforcement to the composites. The addition of nano TiO_2 contributes to the achievement of a higher dispersion of the reinforcement, better mechanical properties, and better weather resistance (Al-Zubaydi et al., 2021). The general properties of the nano TiO_2 used in this study are given in Table 3 below.

Table 3. The general characteristics of the unsaturated polyester resin (Siropol™) used in this research.

Colour	White
Density (g/cm3)	4- 4.5
Melting point °C	1870
Moh's hardness	5.5- 7
Purity	99.9%
Average particle size	20-50 nm.
Refractive index	2.55- 2.75

2.2. METHODS

2.2.1. Preparation of ground walnut powder

Ground walnut shells were collected from local markets in raw, non-uniform shape shells, which were then dried at 120°C for 3 hours to ensure that the remaining humidity is evaporated, which eventually improves adhesion within the polymer matrix, and facilitates the grinding into fine powder, since the presence of humidity hinders grinding. The grinding was done using a ball mill for 2 hours, after which the ground powder was collected in a sealed jar to keep it dry to be used later in the casting of the polymer composite.

2.2.2. Casting

Hand lay-up was used to cast the polymeric composites, using three weight fractions of 5, 15, and 25% of ground walnut shells. The nano TiO_2 was added, and the mixture was ultrasonicated for an hour before the walnut shell powder, which was then added in the designated fractions mentioned above. The mixture was also ultrasonicated for another hour before the hardener was added and mixed to start the casting process. The mixture was poured into a previously made mould with dimensions of 100×150 mm, and left for 24 hours for primary solidification. The casts were removed and put in a drying oven to achieve full cross-linking and remove the residual stresses that originate during manufacturing and solidification. The casts were eventually cut according to the standard specifications of each test.

2.3. The tests.

2.3.1. Impact test

This test was performed using a Charpy impact tester by Amityville, USA, as per the ISO-179 specification, with a 5 Joule hammer. The test is implemented by raising the hammer to a certain height and allowing it to drop freely onto the horizontally mounted specimen of standard dimensions. The energy required to break the specimen is taken from the gauge and is divided by the cross-sectional area, according to the following formula:

$$I.S. = \frac{U}{A} \quad (1)$$

Where I.S. is the impact strength (J/m^2), A is the cross-sectional area of the specimen (m^2), and U is the breaking energy (Joules). Fig. 2 and Fig. 3 below show the dimensions and shape of the prepared specimens, and Fig. 4 shows the Charpy impact test apparatus used in this work.

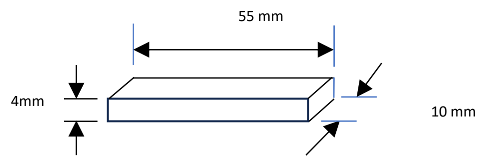

Fig. 2. The dimensions of the impact specimens.

Fig. 3. The shape of the impact specimens.

Fig. 4. The Charpy impact test apparatus used in this work.

2.3.2. Flexural strength

This test was carried out according to the standard specification ASTM- 790 using the Jianqiao™ testing machine, and the values were calculated according to the following formula:

$$\text{Flexural strength (F.S.)} = \frac{3PL}{2bd^2} \quad (2)$$

Where P is the load (Kg), L is the length of the specimen between the two horizontal supports (m), b is the width, and d is the thickness of the specimen (both in m). The test involves horizontally mounting the rectangular specimen on two supports and exposing it to a gradual loading at the center until failure (breakage) occurs. The flexural strength is taken in formula no.2 above, and the flexural strength is calculated accordingly. Fig. 5 and Fig. 6 illustrate the details of the flexural specimens, while Fig. 7 shows the hydraulic testing machine used to carry out flexural test.

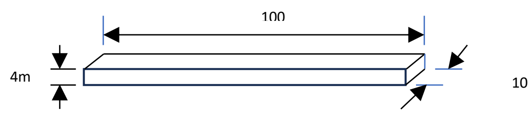

Fig. 5. The dimensions of the flexural strength specimens

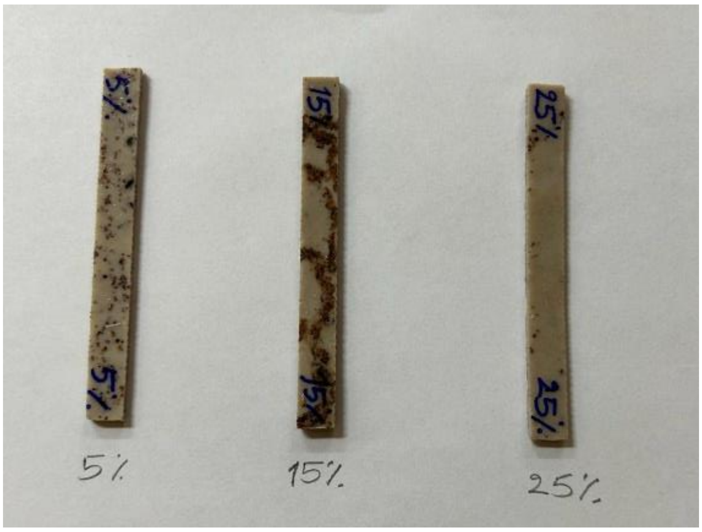

Fig. 6. The flexural strength specimens.

Fig. 7. The Flexural test apparatus.

2.3.3. Thermal conductivity

This test is designed to assess the material's ability to conduct heat, and is used for insulating materials. The thermal conductivity test was performed by Lee's disc apparatus, manufactured by George and Griffin Ltd., 1970s model, a classical steady-state method used to measure low thermal conductivity materials, which consists of an arrangement of three brass discs (A, B, and C) in which the disc-shaped specimen is placed between the A and B discs, while an electric heater is placed between the B and C discs (Hilal RH, 2023).

As the heater is turned on, the temperature rises with adjacent discs B and C. Since disc B is in turn in contact with the specimen, its temperature also eventually increases, which in turn heats disc A adjacent to the specimen from the other side. The temperature of disc A indicates the amount of heat passing through the specimen and its insulation ability. The temperatures of the discs are taken from thermometers positioned inside the discs. After a period of time, the temperature reaches a steady state in which disc A records a lower temperature than the other discs. Thermal conductivity can be calculated by the following formula:

$$K=\frac{t_2-t_1}{d_1}=e\left[t_1+\frac{2}{r}\left(d_1+\frac{1}{4}\,d_s\right)+\frac{1}{2r}d_s t_2\right] \quad (3)$$

Where e can be found through the formula below:

$$H=IV=\pi r^2 e\,(t_1+t_2)+2\mu re\left[d_1\,t_1+\frac{1}{2}d_s\,(t_1+t_2)+\,d_2 t_2+d_1 t_1\right] \quad (4)$$

Where *e* is the amount of heat passing through the unit area of the composite material per second ($W/m^2.k$), *I* is the electric current used in measurement (0.6 Amp.), and *V* is the voltage (220V), *IV* is the heat that passes through the heating coil per second. *r* and *d* are the radius and thickness of the disc, respectively. *t* is the temperature in each respective disc (^oC) (Salih RM., 2021). Fig. 8 and Fig. 9 show the shape and dimensions of the prepared specimens, while Fig. 10 shows the Lee's disc apparatus used in this test.

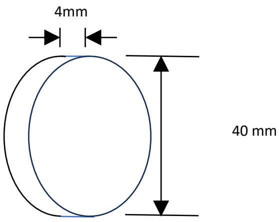

Fig. 8. The dimensions of the specimens of thermal conductivity.

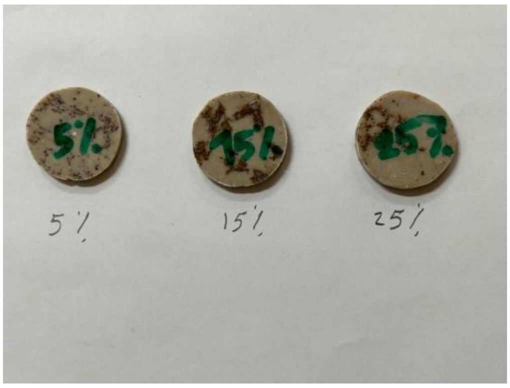

Fig. 9. The dimensions of the specimens of thermal conductivity.

Fig. 10. The Lee's disc apparatus for thermal conductivity measurement.

2.3.4. Water uptake

Diffusion of water into the specimens was studied as per the standard specification ASTM D570. The specimens were immersed in distilled water at room temperature (approximately 23-26 °C) for 10 weeks. Each week, they were removed from the water to be dried and weighed on a 4-digit scale. They were then returned to the water until the same procedure was repeated the following week. The weight change of the specimens indicates the material's ability to absorb water and suggests the mechanisms of liquid penetration into the composite material. The weight change can be given by the following formula:

$$\text{Weight gain\%} = \frac{M_1 - M_0}{M_0} \tag{4}$$

Where M_0 and M_1 are the weights of the specimens before and after water immersion (g), respectively. Fig. 11 and Fig. 12 below illustrate the details of the water uptake specimens.

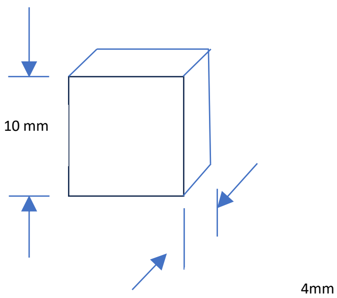

Fig. 11. The dimensions of the water uptake specimens.

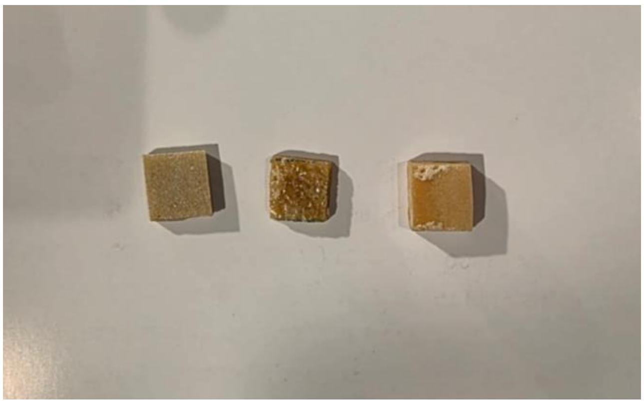

Fig. 12. The water uptake specimens.

2.3.5. Scanning electron microscopy (SEM)

This technique is essential to characterize the surface morphology and defects of the material and evaluate the general microscopic features. SEM was taken of the fracture surfaces of the specimens to assess their internal structure (Salih RM, 2019).

All specimens were coated with a gold layer, as polymers are non-conductive materials, and a voltage of 10 kV was used for imaging. The magnification for all specimens was the same, i.e., 500, 1000, 10000, 50000, and 200000 x. A flow chart of the current work is illustrated below in Fig. 13.

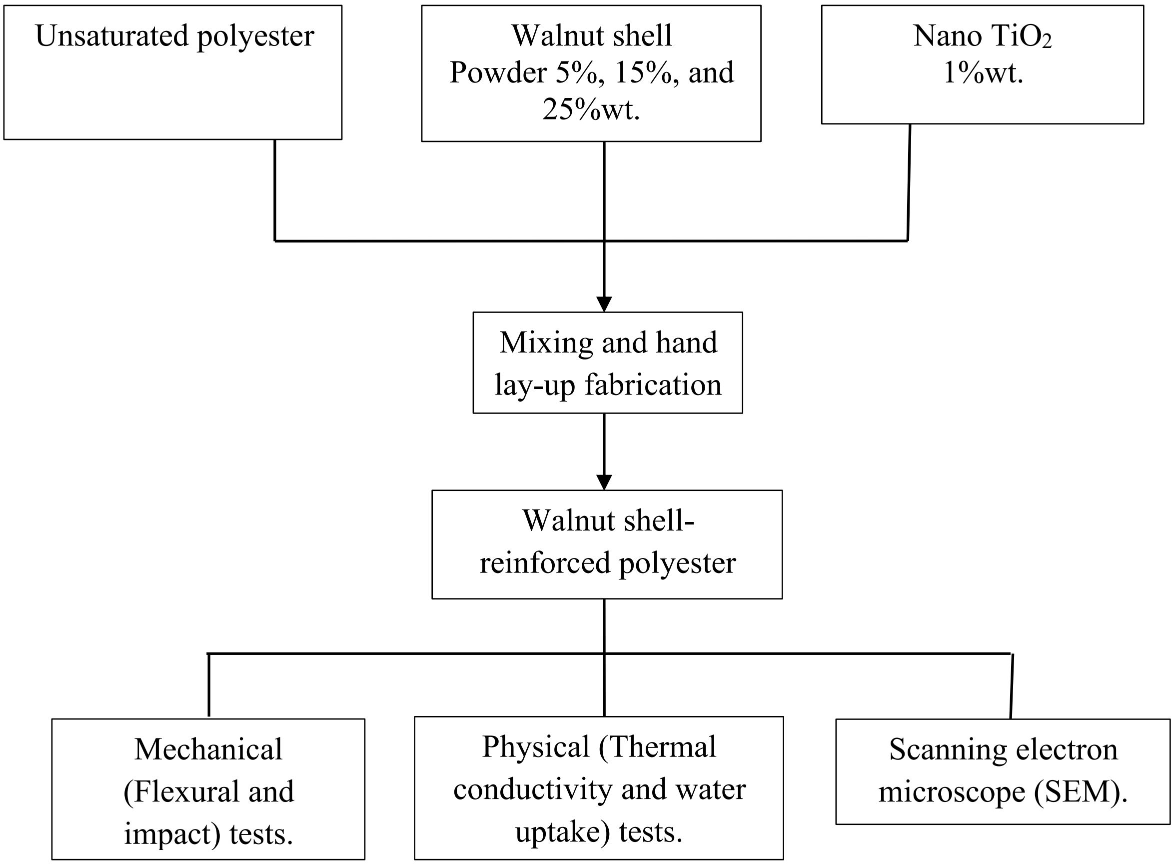

Fig. 13. A flow chart of the current work.

3. RESULTS AND DISCUSSION

3.1. Impact strength

The impact resistance of composite materials is greatly affected by several interrelated facets, such as the filler's form, interfacial bonding, dispersion, and the material's ability to dissipate impact energy. Walnut shell, particularly, is a lignocellulosic filler with an irregular shape that can enhance energy absorption due to mechanical interlocking with the matrix. In addition, the TiO_2 particles acts even better to restrict the crack propagation, thus contributing collectively to the improved behavior of the composite.

Fig. 14 (a) shows the values of the impact strength for the specimens. Although the difference in the impact strength values is small and the values are almost the same, the impact strength increases slightly with the addition of walnut shell powder. This indicates that moderate reinforcement is essential to enhance the impact strength, and the presence of walnut shell powder improves energy absorption of the material. The 15% wt. specimen shows a medium value between the other two weight fractions. It can represent the optimum reinforcement, and this can be attributed to the relatively uniform dispersion of the filler, combined with the powder's natural irregular shape of particles, contributing to mechanical interlocking between the two phases, which assists in the efficient stress transfer between the matrix and the powder, and eventually maximum energy dissipation under impact (Al-Arkawazi et al., 2025).

However, the difference between the 15% and 25% wt. Specimens are negligible regarding the impact strength, as this could be caused by the onset of agglomeration of the filler, leading to poor wettability between the latter and the resin. The situation became more complicated with the presence of the nanophase, which helps in this adverse effect. Such a situation may introduce voids and weakness within the material, which act as stress concentrators, encouraging crack formation and propagation when the material is under sudden loading (Pączkowski, 2023). The incorporation of nano TiO_2 with the walnut shell powder has affected the impact strength positively; nevertheless, the addition of nano powders must be optimized to prevent agglomerations and eventually get the desired properties. The suggested mechanism for improvement may be the interaction between the nanoparticles and the resin, as the nanopowders have a high specific surface area, which enables high interaction with the resin, thereby boosting mechanical properties. Another suggested mechanism is the hindrance of crack growth by the nanoparticles, which act as barriers that add to the strength of the material (Iyer T. et al., 2023).

3.2. Flexural strength

The values of flexural strength are displayed in Fig. 14 (b). What stands out in the Figure. above is the steady drop in flexural strength with the addition of walnut shell powder. The results here show a contrast to what is expected when reinforcement is added, since many studies suggest that the increase in weight fraction is directly related to an increase in flexural strength, but the situation is somewhat different. The specimen with 5% weight fraction exhibited the highest value at 12.8 MPa, followed by the 15% (11.7 MPa), and finally the 25% wt. fraction, which showed a flexural strength of 10.8 MPa. This trend suggests that the weight fraction of reinforcement does not always need to be high to get the highest values of properties studied, and sometimes even a small fraction can add the optimum value. Also, sometimes even the high filler content leads to adverse effects and deficiencies.

At the 5% wt. specimen, the high flexural strength may be associated with the effective distribution of the filler, leading to good adhesion between it and the resin. The filler content at this moderate level is potentially responsible for the inhibition of polymer chain movement and encourages load transfer under bending.

The specimens with the 15% and 25% wt. fractions showed lower values of flexural strengths, compared to the 5% wt. specimen. This may have stemmed from the agglomeration, which takes place at higher weight fractions, higher porosity, and eventually lower wetting between the resin and the powder. All these factors contribute to the reduction of interfacial bonding and eventually flexural strength.

These findings agree with previous studies by Pradhan and Satapathy (Pradhan and Satapathy, 2022), and Ahlawat et.al. (Ahlawat et al., 2019). Both found that excessive addition of walnut shell powder has led to a decrease in flexural strength in polyester composites, for the same reasons explained above.

The inclusion of nanoTiO_2 powder within the polymeric composite has positively influenced the flexural strength, which is due to the nano-reinforcement. This effect is caused by the presence of the rigid nano filler, which acts as a deformation restriction due to its fine size and high surface area, which assists in filling microvoids and elevates strength by efficient stress transfer between the two phases of the composite. Also, the TiO_2 nano particles are known for their contribution to enhancing the bonding at the interface region between the lignocellulosic powder and the polymer, and this promotes better continuity and stress transfer throughout the whole composite. However, this mechanism can not be fully effective unless good dispersion is achieved, such that agglomeration is prevented and the whole material has a uniform density. Since the amount of TiO_2 was within the normal addition range, its addition was optimum. These results align with previous studies by Zhi Xu et. al. (2021) and Bangera and Kotian (2020), who concluded that the nano additives improved mechanical strengths due to the mechanical interlocking of the reinforcement and the matrix.

An important point should be mentioned here: The impact test results indicated that the composite with 15%wt. walnut shell powder showed the highest value, which is likely the result of an optimum balance between the filler content and impact energy absorption, together with good dispersion that reduces stress concentration. On the other hand, with the higher concentration like 25%wt., the weight fraction induces agglomeration leading to localized stress concentration, and lower bonding between the matrix and the reinforcement. Consistent behavior is also noticed with the flexural test, as the mechanical integrity and material's continuity were affected by filler overloading. These results are similar to previous findings reported earlier, which stated that mechanical performance begins to diminish when higher weight fractions of fillers are added (Onwubu et al, 2025), (Lee et al, 2025).

As a summary, the flexural strength decreases with increasing walnut shell powder percentage; therefore, the highest flexural strength (12.8MPa) was observed with 5% walnut shell powder, while the lowest (10.8MPa) was noticed with the 25%wt. content.

This behavior may be caused by the effect of interfacial bonding and filler distribution, such that the lower filler loading is more evenly-distributed, hence higher adhesion within the two phases of the composite, and eventually better resistance to bending. Another reason might be agglomeration associated with a higher weight fraction of reinforcement, which is directly proportional to porosity; therefore, lower flexural strength. The presence of nano TiO_2 plays a positive role through nanoparticle interlocking, or filling of micro spaces, which leads to better interfacial bonding. The large specific surface area of the nano TiO_2 also facilitates stress transfer, since the nano phase is uniformly dispersed.

3.3. Thermal conductivity

Fig. 14(c) shows the thermal conductivity specimens and results, respectively. The results show that there has been a gradual increase in thermal conductivity with the increase in reinforcement weight fraction.

Thermal conductivity values were observed to directly relate to the walnut shell powder content, and this pattern suggests that the reinforcement plays a role in the heat transfer process. This result is somewhat counterintuitive to the well-known fact that lignocellulosic additives lower thermal conductivity; however, this can be driven by a reduction in the overall volume of the polymer as the reinforcement increases, which results in a higher density of the prepared composite.

First, when the filler content is 5% wt., thermal conductivity was moderate, which is likely due to the smaller weight fraction of the shell powder and higher continuity of polyester resin. As the weight fraction increases to 15% and 25% wt., the density of the composite rises, and it becomes filled with solids. As a result, heat is bridged across the material more efficiently, encouraged by the low void content, and is further enhanced by the reduced number of air pockets associated with denser material, which further enhances thermal conductivity. Another justification is that the fine particle size of the walnut shell powder may be responsible for the increased thermal conductivity of the composite, since it increases the contact surface area between the resin and the filler, and hence better heat transfer.

Furthermore, the fine particle size of walnut shell powder may help increase the contact surface between the filler and the matrix, enabling better transfer of thermal energy. However, it should be noted that too much filler can cause agglomeration, which could ultimately impede thermal transport if not properly dispersed. The current results show a steady increase in conductivity, indicating adequate dispersion within the matrix. While walnut shell powder has a naturally low thermal conductivity, its inclusion in a polyester matrix leads to increased thermal conductivity, likely due to higher packing density within the composite. Similar findings have been reported in other studies (Hejna et al, 2020) and (Barczewski et al., 2024). The intrinsic thermal conductivity of nano TiO_2 also contributes to the composite's heat conduction. When uniformly dispersed, it enhances the thermal conductivity by creating pathways that facilitate heat flow within the material. An additional factor promoting thermal conductivity is the high surface area of the nanoadditive, which allows effective interaction with both phases (the reinforcement and the polymer), bridging microgaps and improving contact. This reduces voids that would otherwise act as insulators, ultimately resulting in a higher total thermal conductivity (Kumar et al., 2016). Although lignocellulosic fillers, like walnut shells, have low thermal conductivity, in the case of the current work, the thermal conductivity increased by increasing the filler content due to enhanced filler-matrix bonding and creating heat conduction paths. Generally, improved filler networking and structural changes at higher filler content proved to significantly affect thermal conductivity in polymer composites, even though the intrinsic conductivity of the filler is small (Czel G. et al, 2023), (Xu, N et al, 2025).

In general, the use of a higher weight fraction of walnut shell powder increased thermal conductivity, a result that can be attributed to several related mechanisms. First, the dominant matrix behavior with the 5%wt. reinforcement means that lower conductivity is prevalent since polyester has lower thermal conductivity. On the other hand, when a higher weight fraction of reinforcement is added, leading to a higher density of the composite, the porosity is reduced, and better flow of heat through the solid matrix. Additionally, the irregular and small-sized particles of walnut shell powder improve the interfacial bonding and eventually enhance heat transfer efficiency, despite the low intrinsic thermal conductivity of walnut shell powder. However, the compact structure of the matrix lowers the percentage of air gaps (which are naturally poor heat conductors) and hence increases thermal conductivity. The presence of the nano TiO_2 further enhances thermal conductivity by creating thermal conductive paths and improving bonding at the interface due to its high surface area. All these effects collectively contribute to boosting thermal conductivity with increasing reinforcement.

3.4. Water uptake

Fig. 14(d) shows the water uptake specimens and behaviour in the current study, respectively. The composite consists of 25% wt. walnut powder showed the highest weight gain after immersion in water, followed by 15% wt. walnut powder, and finally the 5% wt. The specimen had the lowest moisture uptake of all specimens. In general, the specimens show a pattern of increase in weight gain when the reinforcement increases, i.e., the weight gain is directly proportional to the weight fraction of reinforcement. The pattern seems coherent for all the specimens in the first two weeks. The amount of water appears to stabilize over time in this period, after which the specimen reinforced with 25% begins to retain water more than the other specimens. Moisture uptake seems to increase in an accelerated manner when compared with 15% and 5% wt.

Around the 7^{th}. Week of immersion, the 25% wt. specimens suffered a higher increment, followed by a gradual loss of weight that took place over the following weeks until the 10^{th}. Week. The same behaviour was also observed for the specimen reinforced with 15% wt.

Key observations include that the water uptake increases with reinforcement content, since the walnut shell powder is naturally water absorbent, and the filler percentage is directly proportional to water absorption. The 5% wt. composite reveals lower water uptake, which means better adhesion and fewer microgaps. It is also noticed that all specimens reached stable water content; nevertheless, the specimen with higher filler content showed delayed stabilization when compared to the other specimens (McNeil et al., 2024; Khantwal et al., 2016). The addition of nano TiO_2 is believed to have reduced the water uptake due to the enhanced bonding at the interface region, and reduced the continuity and size of microgaps. The presence of the nano TiO_2 also creates a barrier towards water diffusion, thus lessening its penetration inside the material, especially when lignocellulosic filler exists (Fei et al., 2013).

Water absorption is usually strongly dependent on the filler weight fraction, so the addition of walnut shell powder to the composite increased water uptake due to the hydrophilic nature of the lignocellulosic fibers, accompanied by the capillary action via microchannels within the material's body (Gbenebor et al., 2020).

It is important to point out that polymer-based composites have shown that water uptake is directly proportional to time, and the incorporation of various fillers significantly affects weight gain, as it stabilizes after immersion intervals, depending on the type of both the matrix and the filler. The density and interfacial bonding also play a major role in this behavior (Hilal and Nassif, 2025)

Generally, the water uptake is directly proportional with the weight fraction of walnut shell powder, and it is clearly related to the hydrophilic nature of the lignocellulosic fibers that naturally absorb moisture. At lower reinforcement (5%wt.), the polyester phase is dominant, hence better adhesion and lower water uptake. When the reinforcement increases to 15% and 25%wt., porosity and micro voids associated with it increase, hence higher water uptake since it becomes easier for water to fill in the gaps and reach the highly hydrophilic fibers. Additionally, the loose packing and irregular shape of particles encourage capillary action. However, the nano TiO_2 present in the material reduced the moisture uptake across the three specimens via enhanced interfacial bonding and filling the diffusion paths within the matrix. These effects combined to contribute to the distinct water uptake behavior of the composites, which eventually reached equilibrium at longer intervals of immersion.

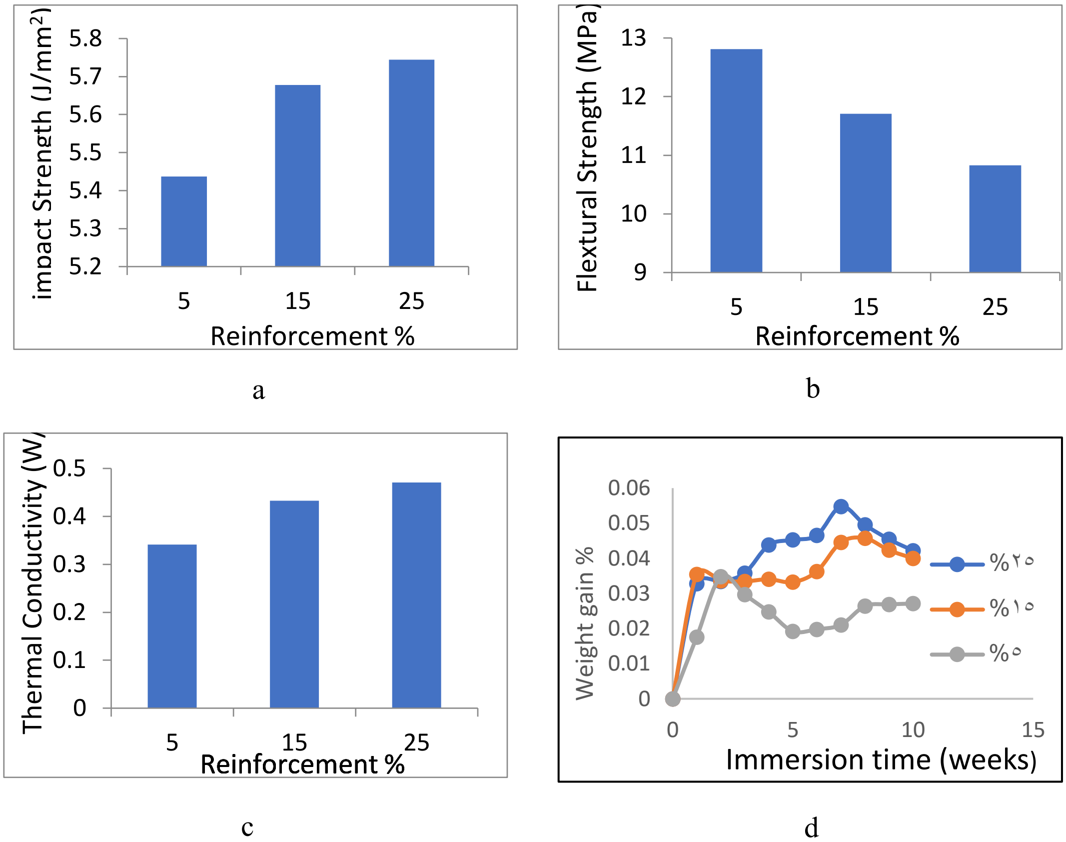

Fig. 14 (a, b, c, and d) shows the behaviors of the prepared composites in the impact test, flexural strength test, thermal conductivity, and water uptake, respectively.

3.5. Scanning Electron Microscopy

3.5.1. Specimen with 25% weight of walnut shell powder.

A set of microscopic images is shown in Fig. 15 (a-e) below, with magnifications of 500, 1000, 10000, 50000, and 200000 x. First, in terms of dispersion of the particles, the filler appears to be evenly distributed throughout the polyester matrix, although at this scale, some small clusters or agglomerations can be seen. However, the fillers are mostly dispersed in an even manner. It is also important to mention that the nano TiO_2 played a role in the dispersion and bonding between the two phases of the composites, as it acted as a coupling agent or a compatibilizer to link the filler and the matrix (Burhan et al, 2018).

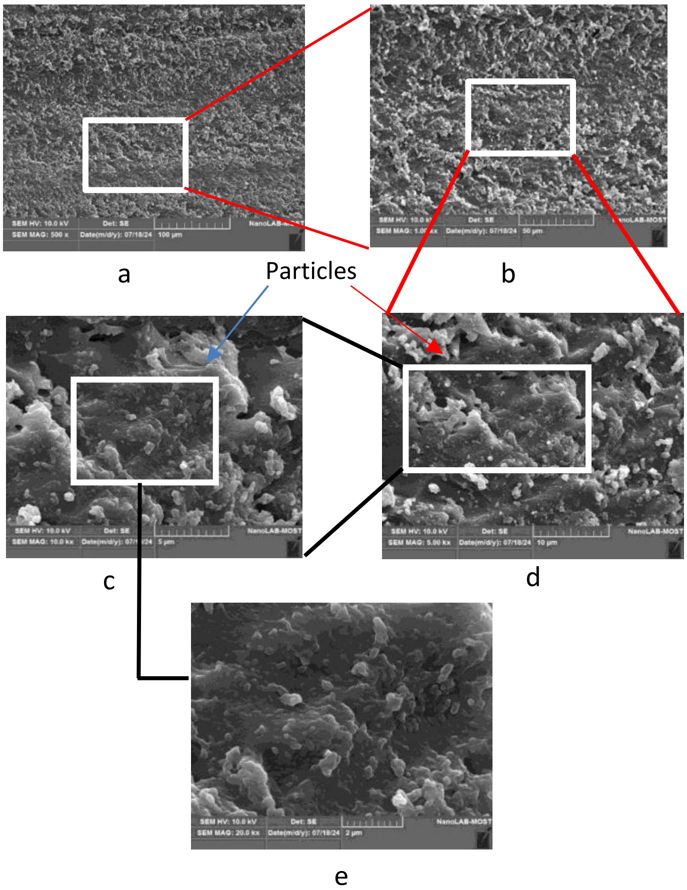

Fig. 15 (a-e) The microscopic details of the specimen reinforced with 25% walnut shell powder.

Observation of micro-images in other magnifications also shows that the Porosity and microcavities in some regions, and these could be attributed to the incomplete wetting of the powder with the resin, or entrapment of small air bubbles within the matrix during the mixing of both phases. The porosity contributes directly to the material's ability to uptake water and other liquids, and eventually to the weight change of the composite. The adhesion between the two phases looks good, and both of them seem well-bonded. Some gaps appear at the interface area. Regarding the fracture mode: the materials exhibit both brittle and ductile fracture modes with some visible tearing, which suggests that the material absorbed an amount of energy before breakage. Other areas display a clean-cut fracture, which is a characteristic of brittle fracture, which might have resulted from poor adhesion or the presence of porosity.

3.5.2. Specimen with 15% weight of walnut shell powder

Fig. 16 (a-e) shows multiple magnifications of the specimen reinforced with 15%wt. of walnut shell powder. As a general overview, the specimen shows better distribution of particles compared to the specimen reinforced with 25%wt. Large agglomerations are also present, but in lower amounts than the 25% specimen, which might indicate that the lower weight fraction presents better homogeneity of the specimen. As was noticed with the 25% specimen, voids and gaps exist, and these might have originated due to the pullout of the filler, while others may have resulted from entrapped air bubbles. However, the porosity appears to be high, which might affect the mechanical performance of the material. The presence of gaps may also indicate weaker bonding between the two phases, especially at the interfacial area. The fractured surface reveals a dominant brittle fracture mode, possibly due to lower adhesion and porosity.

In general, the 15%wt. the specimen shows better dispersion than that observed with the 25%wt. specimen, probably as a result of lower filler content. Weaker points of adhesion might be due to the presence of voids, and a more brittle fracture, although there are small signs of clean-cut surfaces that suggest smaller ductile fractured areas.

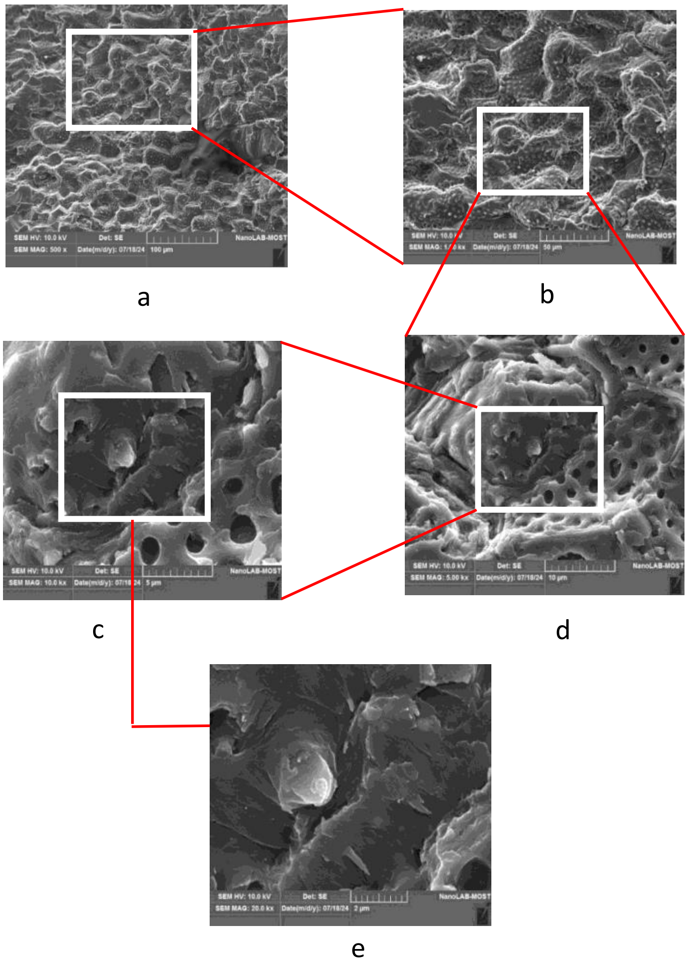

Fig. 16 (a-e) The microscopic details of the specimen reinforced with 25% walnut shell powder.

3.5.3. Specimen with 5% weight of walnut shell powder.

Fig. 17 (a-e) shows multiple magnifications of the specimen reinforced with 5%wt. of walnut shell powder. From a general perspective, the fractured surfaces appear to be very smooth compared to the previous specimens. A smaller weight fraction of sawdust was used, as small pieces are scattered throughout the specimen. Surface irregularities indicate higher matrix continuity and a flaw-free matrix. The dominant fracture mode here seems to be a ductile fracture, showing a layered and smooth structure, with some small and scattered voids. The localised brittle regions are also visible in the micrographs, which might indicate small, brittle fractures in the matrix, as a result of stress concentrations or minor detachment sites.

In terms of adhesion, the materials appear to be well-bonded, with insignificant or very small filler pullout. The lower filler content might have also positively affected compatibility with the polyester, although it might reflect lower mechanical interlocking between the two phases, and eventually lower mechanical properties.

When compared with the other two specimens reinforced with 25% and 15%wt., the current specimen demonstrates higher dispersion, stronger bonding at the interface, and a more ductile fracture. On the other hand, it might not be as mechanically efficient as the previous two specimens, as a result of lower filler content.

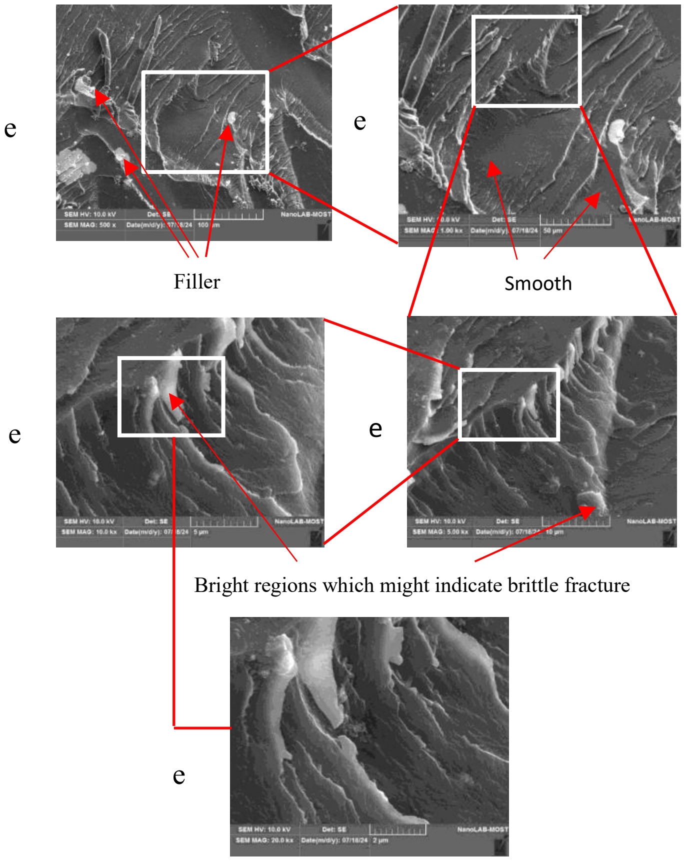

Fig. 17 (a-e) The microscopic details of the specimen reinforced with 5% walnut shell powder.

4. CONCLUSIONS

This study investigated the effects gained by the reinforcement of unsaturated polyester resin by ground walnut shell powder and nano TiO_2. The study examined mechanical, thermal, and morphological properties of the composites, which were reinforced with three weight fractions of filler (5, 15, and 25) %wt., and nano TiO_2 by 1%wt. The outcomes of this study can be summarized in the points below:

Moderate weight fractions (especially 5-15) %wt. offered a balance between stability and strength, hence the highest flexural strength was demonstrated at 5%wt. filler content due to the enhanced dispersion and interfacial bonding.

On the other hand, higher filler loadings led to agglomerations.

Impacts strength increased with increasing weight fraction, reaching a maximum value at 15%wt., suggesting that moderate filler content leads to enhanced properties and better energy dissipation.

Thermal conductivity also showed a correlation with reinforcement, as a result of decreased porosity, higher packing density, and intrinsic conductivity of the nano TiO_2.

SEM analysis showed higher homogeneity at lower filler content, while the higher weight fractions prompted brittleness and voids.

Water uptake is directly proportional to the weight fraction of walnut shell powder, as the micro gaps that originated during manufacturing and processing facilitated penetration into the material, besides the hydrophilic nature of the reinforcement, although the incorporation of nano TiO_2 contributed to the improved bonding at the interface region.

Overall, the results emphasize the importance of balance between the weight fraction used as a reinforcement and the results obtained in each test.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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