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MECHANICAL, DEGRADATION AND MORPHOLOGICAL INVESTIGATIONS ON TAMARINDUS INDICA REINFROCED POLY LACTIC ACID BIO-COMPOSITE FOR BIOMEDICAL APPLICATIONS

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This research investigates the degradation and mechanical potential of Tamarindus Indiaca Fiber (TIF) reinforced into Poly Lactic Acid (PLA) resulting in a Wood Plastic Composite (WPC) that could be a potential alternative for prosthetic limbs. Fiber weight ratios at 10, 15, 20 and 25 wt%, were processed in micro and nano sizes individually through extrusion. Mechanical investigations were studied to analyze tensile, flexural, impact and hardness properties. Water Absorption Test (WAT) and Thermo Gravimetric Analysis (TGA) were performed for degradation studies. Field Emission Scanning Electron Microscope (FESEM) was used to study morphology. Nano TIF filled WPCs had superior properties than the micro TIF filled WPCs.

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Keywords: Poly lactic acid, Tamarindus indica, Micro fillers, Nano fillers, Wood plastic composite, Green composite

1. Introduction

Wood Plastic Composites are widely used in foreign countries in all kinds of constructional applications like fencing, interior decoration and furniture. On the other hand, countries like India stay with costly wood furniture which leads to both deforestation and lower durability of the wood materials. Termite attack and other wood rot fungal diseases also are disadvantages over using wood based furniture even in the cases of hardwoods like teak, mahogany and rosewood. Inorder to over-come these drawbacks, and replace the wood based constructional materials with Wood Plastic composites in a developing country like India, Tamarindus Indica (TI) wood was selected as a reinforcement to fabricate WPCs. Natural fiber reinforcements into polymers are known to provide enhanced mechanical strength to the base matrix material [1]. TI has a very high wood density (850 kg/m^3) [2] and possesses special chemical characteristics, which allows it to prevent itself from termite and fungal attacks when compared with other wood fibers. TI is a tropical tree found widely in all parts of Asia and abundantly available in India [3],[4]. Its fruit pulp is used in the food industry and extensively in Asian cuisines [5]. Poly Lactic Acid which is the most widely used biopolymer around the globe is a starch derivative obtained from the polymerization of starchy plants like cassava and corn [6]. It is widely being used in aerospace, automobile, biomedical and food packaging industries [7]. Detailed reviews on PLA reinforced with various natural fibers with different fiber sizes like long, short and powdered filler forms and states that smaller sized reinforcements provide better mechanical properties [8],[9].

Wang et al. [10] had experimented with PLA reinforced bamboo flour composites using compression moulding technique. Bamboo was reinforced into PLA in weight ratios ranging from 5 to 25% with variations of 5% between each reinforcement level. The 15 wt% reinforced composite had shown the best tensile strength. Bamboo flour addition had improved the tensile properties of PLA and had proven to be in good adhesion with the matrix. Petchwattana and Covavisaruch [11] blended PLA with rubber wood flour to obtain composites in the ratios of 5, 10,

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20 and 30 wt% reinforcement level. Tensile strength and tensile modulus of the rubber PLA composite was found to increase with increasing fiber content level upto 30 wt%. PLA had a tensile strength of 61 MPa while the best composite produced a tensile strength of 150 MPa. Flexural strength of PLA was also found to increase with reinforcement of rubber wood flour but the impact strength had a drastic reduction with increasing fiber content into PLA matrix. PLA had impact strength of 120 J/m and the least impact strength of the 30 wt% reinforced composite had 25 J/m. Huda et al. [12] used maple wood flour as the reinforcement with PLA in weight ratios of 20, 30 and 40%. All the reinforced composites showed higher flexural strengths than neat PLA but higher reinforcement levels had led to a reducing pattern of mechanical properties. The flexural modulus had increased with increasing fiber content with plain PLA having a modulus of 3.3 GPa and the 40 wt% reinforced composite had a flexural modulus of 10.2 GPa. The tensile and impact properties had a reducing pattern with increasing maple flour content with all the values lower than plain PLA. Yaacob et al. [13] had reinforced paddy husk flour in PLA in weight ratios of 5, 10, 15 and 20 wt%. The addition of paddy flour showed drastic reduction on the mechanical properties of PLA but the tensile modulus increased with increasing fiber content. The tensile strength of the 20 wt% reinforced composite had a reduction of around 300% in its values when compared with plain PLA. Wan and Zhang [14] studied the tensile effect of poplar wood flour reinforced PLA composites. The composite with 20 wt% fiber reinforcement had resulted in a marginal increase in tensile strength. The tensile strength of the composite was 64 MPa while plain PLA had a tensile strength of 63.5 MPa. Tisserat et al. [15] had researched with paulownia wood flour-PLA composite. The size of wood flour particles were varied using different mesh sizes from 30 upto 200 which had resulted in particulate sizes of 599 and 75 µm respectively. Tensile strengths of the composites were lower than PLA and on comparing the composites alone, the smallest size wood flour reinforced composite had produced superior tensile strength when comparing with the larger sized wood flour reinforced composites. PLA had had a tensile strength of 52.2 MPa, the 599 µm sized composite had 38.4 MPa and the 75 µm sized wood flour composite had 44.2 MPa. There is very scarce literature under the usage of TI fiber as reinforcements for polymers. Indira Devi et al. [16] had reinforced TI nut powder into Polypropylene carbonate to obtain a bio-composite material. The TI nut powder was reinforced in a ratio of 10 wt% and the powder had a size of 20 µm. Mechanical analysis had not been performed and the composites had been tested only under thermal investigations which had shown positive results.

2. Materials and methodology

2.1. Materials

Poly Lactic Acid in the form of pellets was sourced form Nature tek industries, Chennai, Tamilnadu. The 3052 D injection mould grade polymer had a density of 1240 kg/m^3 and a melting temperature of 170 °C to 180 °C (specifications given by the dealer). The TI wood was obtained from the waste lands of Namakkal district in Tamilnadu, India.

2.2. Fiber extraction

The complete fiber extraction process is in illustrated in Fig. 1 (a, b, c and d). A wood piece was cut from the TI tree and placed in a furnace at 80 °C for 24 hours [12], [13] to remove the moisture. It was then machined using a lathe machine to obtain continuous fiber lengths. The fiber lengths were soaked for 12 hours in a solution containing NaOH-5% and Water-95% mixture [17]. This alkali treatment was done to improve the adhesion between the matrix and fiber during the processing. The soaked fibers were then placed in an oven at 80 °C for 48 hours to dry, after which they were then gathered and pulverized. The pulverized fiber was then sieved using a fine mesh of size greater than #200 [15], to obtain the Micro sized Tamarindus Indica (MTI) wood flour reinforcement. The size of the micro particles was between 5 and 15 µm (measured using FESEM). A portion of the MTI was again ground into finer powder using a food blender at 10000 rpm [18] for 2 minutes. This finely powdered wood flour, was considered as the Nano sized

Tamarindus Indica (NTI) wood flour reinforcement. The size of the nano particulates was between 10 and 15 nm (measured using nano particle size analyzer, model: Nanophox 0143 P).

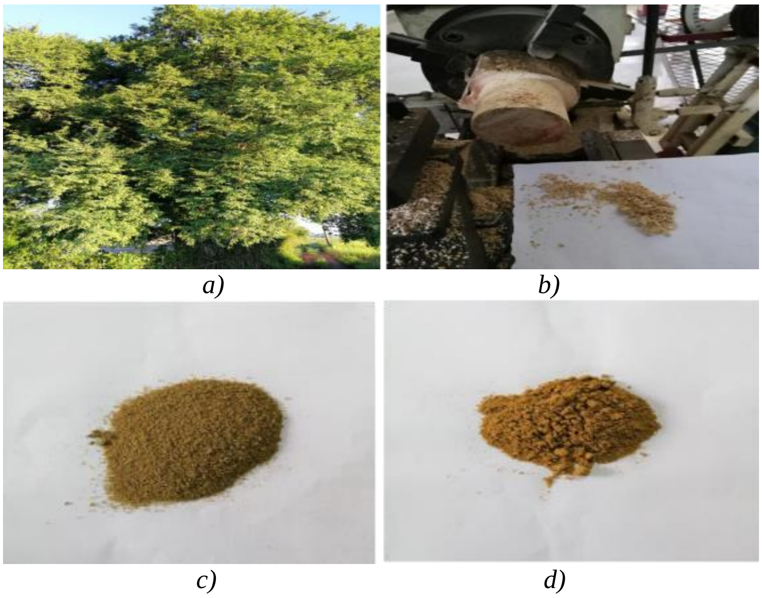


Fig. 1. (a) Tamarindus Indica tree, (b) Extraction of fiber using lathe machine, (c) Micro Sized TIF reinforcement and (d) Nano sized TIF reinforcement.

2.3. Fabrication of the WPCs

The PLA granules and the TI wood flours were measured in weight ratio as denoted in Table 1 and processed using a mini extruder machine at Kongu Engineering College, Erode, Tamilnadu.

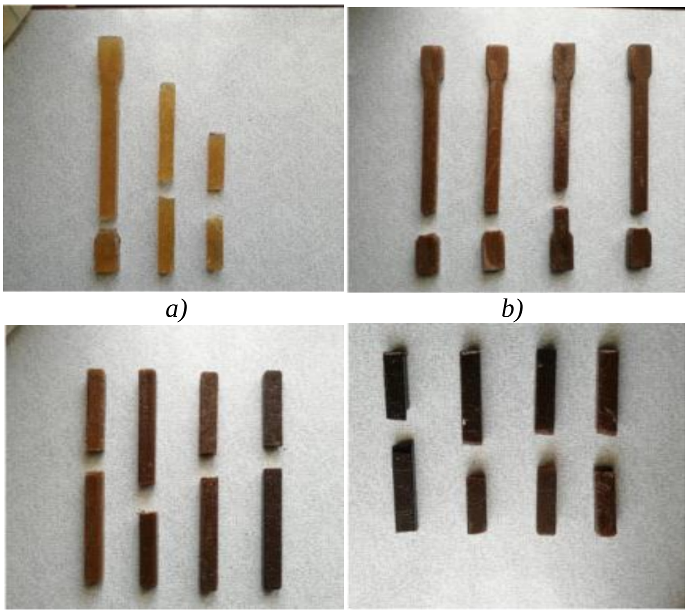
Table 1. Name of the WPC and the composition of PLA to Tamarindus Indica wood flour in wt%.

Size of the Fiber	**Name of the sample**	**wt% of PLA**	**wt% of TI fiber**
-	PLA	100	0
Micro sized TI reinforcement	MTI1	90	10
	MTI2	85	15
	MTI3	80	20
	MTI4	75	25
Nano sized TI reinforcement	NTI1	90	10
	NTI2	85	15
	NTI3	80	20
	NTI4	75	25

The maximum fiber reinforcement was restricted to 25 wt%, since this is article is part of a comparative research work. The equipment had four stages of processing, Material feeding stage, Reinforcement addition and mixing stage, Blending into molten composite stage and the final stage was ejection of the WPC through the exit nozzle. The molten composite was extruded into dies to obtain WPC test specimens of ASTM standard dimensions suitable for polymer composite testing [19]. Stage 1-2-3-4 of the extruder machine, were set to processing temperatures of 170-180-190-170 °C respectively [20].

2.4. Mechanical characterization

Tensile and Flexural tests were performed on a Universal Testing Machine (Brand: Kalpauk, model KIC-2-1000-C). ASTM D638 and ASTM D790 were followed for the tensile and flexural test respectively [11]. A cross head speed of 5 mm/min and a load of 10 kN were set as standard testing parameters for the tests [14], [19]. Izod impact test was performed on unnotched samples to ASTM D256 standard [12], [19]. Vickers micro hardness test was carried out to determine the hardness of the composites. Similar mechanical testing parameters were also followed by many other researchers [21], [22], [23] who had worked with various other polymers in their research work. The specimens mechanically tested are displayed in Fig. 2 (a, b, c and d).



a) *b)* *c)* *d)*

Fig. 2. (a) PLA specimens, (b) WPC tensile test specimens, (c) WPC flexural test specimens and (d) WPC impact test specimens.

2.5. Degradation studies

The fabricated WPC, being a bio-composite material has an inherent tendency to undergo degradation. Hence degradation studies were carried out to substantiate the durability. Water absorption test was carried out to determine the water intake ability of the specimens. The specimen with larger water intake proves greater degradation nature when exposed to a water based environment. The specimens for the water absorption test were considered from the fractured specimens of the flexural test. This was to ensure that the fibers were exposed to the water during the test to achieve maximum water surrounding. Each specimen was submerged in a beaker containing normal water for 24 hours. The specimens for the test were initially weighed in their dry state using a micro digital weighing scale. After 24 hours of exposure in water, the specimens were again weighed. Both the initial and final weights of the specimens were used to calculate the percentage of water uptake using the formula in Equation 1 [11].

[(Wet weight – Dry weight) x 100] / Dry weight - Equation 1

Thermo Gravimetric Analysis was performed at Avinashilingam College, Coimbatore, Tamilnadu, India. The temperature was varied between 30 °C and 500 °C [24] with variation of 20 °C/min. The TGA curves were derived for PLA, TI fiber and NT4 specimen.

3. Results and discussions

3.1. Mechanical investigations

The tensile strength of the MTI WPCs showed lower values than plain PLA as shown in Fig. 3. This may be due to the poor adhesion property of the TI fibers to bond with PLA. The increase in fiber content upto 25 wt% further reduced the tensile strength of the composites. Tensile modulus values (Fig. 4) increased marginally at higher fiber reinforcement levels and did not show much change at lower fiber content. The tensile properties showed that the NTI WPCs had greater properties than the MTI WPCs. The elongation at break (Fig. 5) showed reduced patter with increasing fiber content. This may be due to the nature of the TI fibers to be loosely bound with the polymer hence resulting in lower necking of the specimens during the tensile test. The MTI fiber reinforced WPCs showed reduced variation in elongation with addition of more fiber fillers, while the NTI fiber reinforced WPCs had not much variation change in the elongation with increasing fiber content.

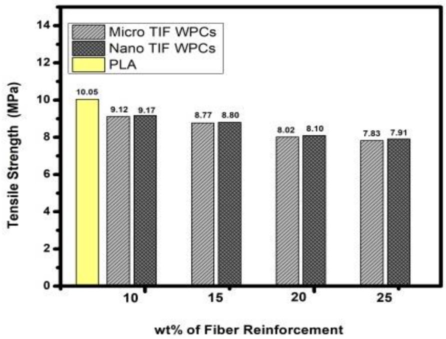


Fig. 3. Tensile strength.

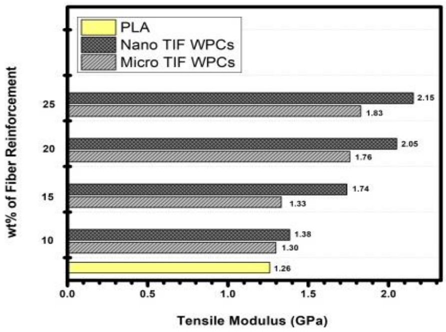


Fig. 4. Tensile modulus.

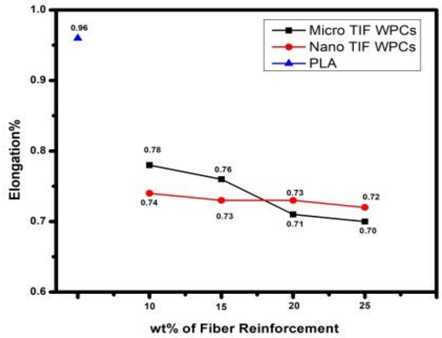


Fig 5. Elongation.

The initial addition of TI fibers in both the micro and nano sizes showed reduced flexural strength (Fig. 6). This may be due to the very low quantity of fiber added into the polymer which had formed agglomeration of the fiber into the matrix material and had made the WPC susceptible to fracture during the testing. The increase in fiber content upto 25 wt% showed an improving pattern in the flexural strength of the WPCs. Increase in fiber content had improves the flexural strength of the WPCs. Higher fiber reinforcement levels also showed greater flexural modulus vales (Fig. 7). This shows that the TI fiber reinforced WPCs have better stiffness compared with plain PLA. The NTI WPCs reacted in had superior flexural characters over the MTI WPCs.

The Izod impact test conducted on the WPCs showed no significant change when compared with the impact strength of PLA as shown in Fig. 8. For both the MTI and the NTI reinforced WPCs the impact strengths had no change at lower fiber loading levels. WPCs with higher fiber content showed reduced the impact strength than that of PLA. This may be due to the reason that the toughness of PLA had reduced with addition of TI fibers. On comparing the MTI and NTI fiber reinforced WPCs, the nano reinforced composites showed slightly enhanced impact strengths at higher fiber levels.

Vickers micro hardness test proved that hardness of PLA reduced by adding TI fibers irrespective of the size of reinforcement. For each consecutive WPC sample, an increase in wood flour content showed further reduction in hardness values as shown in Fig. 9. Hardness of the NTI reinforced WPCs had marginally greater values than the MTI reinforced WPCs in all cases of relative fiber loading in this research. This may be due to the greater mechanical inheritance of nano particles over the micro particles that had been reinforced into the PLA polymer. Alternatively the addition of TI fibers at higher levels further reduced the toughness of the PLA polymer thereby forming a reduced fashion of impact strengths with increasing fiber ratio. Table 2 shows the mechanical characterization of past literature where PLA had been reinforced with various wood flours.

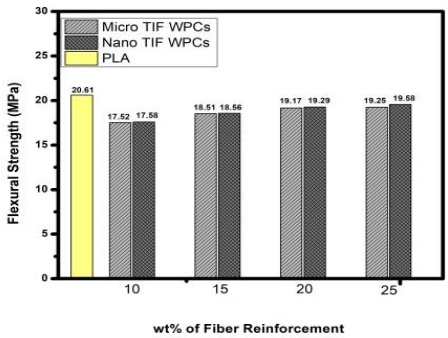


Fig. 6. Flexural strength.

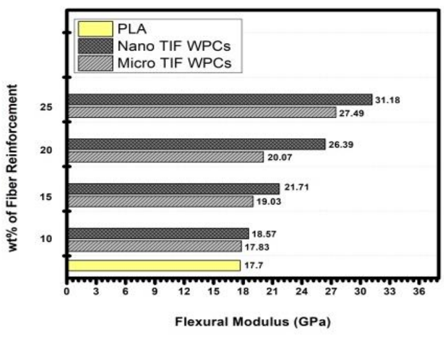


Fig. 7. Flexural modulus.

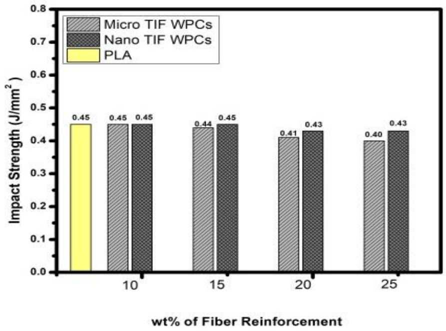


Fig. 8. Impact strength.

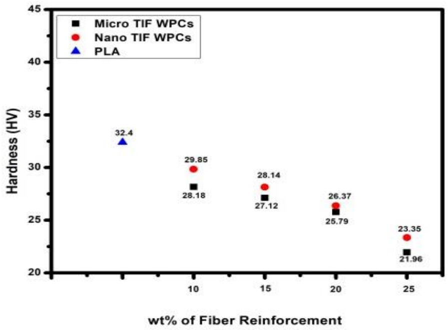


Fig. 9. Hardness.

Table 2. Comparison table depicting the mechanical properties of PLA reinforced with various flour reinforcements.

Matrix	Filler	% of filler that provided the best results	Maximum % variation in the mechanical properties of PLA due to different wood flour reinforcements			Reference
			Tensile Strength	Flexural Strength	Impact Strength	
PLA	Tamarindus Indica wood	25	32% lower than PLA	5% lower than PLA	4% lower than PLA	This study
PLA	Rubber wood	30	138	122	300% Lower than PLA	[11]
PLA	Maple wood	20	5	20	8% lower than PLA	[12]
PLA	Poplar wood	20	15	34	-	[14]
PLA	Paulwonia wood	25	18% lower than PLA	-	-	[15]
PLA	Almond Shell	30	313% lower than PLA	-	128% lower than PLA	[25]
PLA	Pine wood	20	No change	-	130% lower than PLA	[26]
PLA	Bamboo wood	10	43% lower than PLA	20% lower than PLA	-	[27]
PLA	Prosopis Juliflora wood	20	146	228	142	[28]
PLA	Azadirachta Indica wood	20	148	164	73	[29]

3.2. Degradation analysis

Water absorption test revealed that in both the MTI and NTI fiber reinforced cases the increase in fiber content showed increased water uptake. This may be due to the nature of the TI fibers to absorb water while plain PLA had nil water absorbing tendency. On comparing the micro and nano TI fiber reinforced WPCs the NTI specimens had lower water absorption at the end of the test when compared to the MTI fiber reinforced specimens at respective fiber content levels as tabulated in Table 3. The greater water absorption shown by the MTI specimens may be due to the larger surface area of the TI fibers which give it a tendency to absorb more moisture when compared with the nano wood particulates.

Table 3. Water absorption test results for PLA, MTI WPCs and NTI WPCs.

Sample	Initial weight of the sample (grams)	Final weight of the sample (grams)	% of water absorbed
PLA	3.488	3.488	0
MTI1	2.738	2.924	0.068
MTI2	2.722	3.089	0.135
MTI3	2.692	3.262	0.212
MTI4	2.675	3.464	0.295
NTI1	3.194	3.241	0.015
NTI2	3.168	3.352	0.058
NTI3	3.118	3.445	0.105
NTI4	3.080	3.726	0.210

Fig. 10 shows the TGA curves of the thermal degradation of the tested specimens. PLA had the lower stability comparing to the plain TI fiber and the WPC, TN4. The polymer had good initial stability upto around 230 °C beyond which there was a drastic reduction in its mass when the temperature reached 400 °C left with just 2% of mass. At 500 °C there were no remains of any residue. This may be because PLA would have turned volatile at very high temperatures. The TI fibers had a gradual reducing pattern with good thermal stability upto 300 °C. At 400 °C the residue remained at 25% and at 500 °C the ash content was 14%. The WPC had mean values of both the raw materials and had improved thermal stability when compared with PLA. The material had 78% mass content at 300 °C and was thermally degraded to 6% mass. At the maximum temperature, the residue remained at 1% mass.

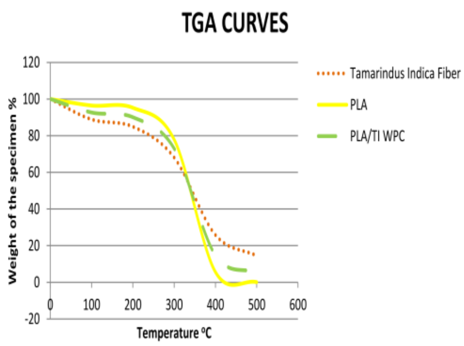
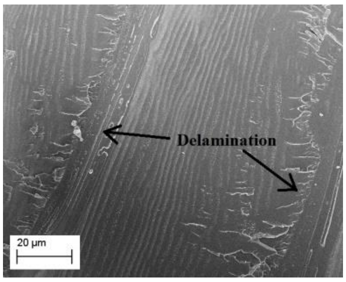


Fig. 10. TGA curves.

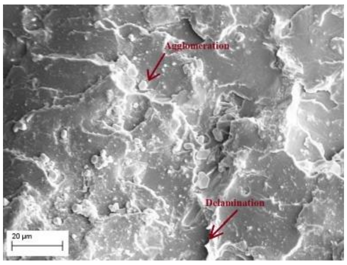
3.3. Morphological analysis

All the fractured surfaces of the flexural tested specimens were scanned under Field Emission Scanning Electron Microscope at a magnification varying between 1000 X and 2000 X to obtain clear images that gave conclusive comparisons. The scale was fixed at a constant 20 µm and the morphological images were scanned. The FESEM image of the plain PLA specimen is shown in Fig. 11 a.

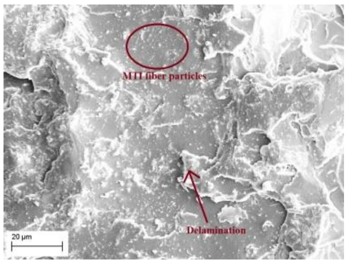
The delamination in the MTI samples shows the amount of resistance produced by the WPC towards the testing load. The FESEM image of the MTI1 (Fig. 11 b) shows agglomerated defects of the TI fibers which had led to the lower flexural strength. FESEM images of MTI2, MTI3 and MTI4 (Fig. 11 c, d and e respectively) shows increasing amount of delamination respectively. The MTI4 also shows good and equal dispersion of the fiber into the matrix material hence proving the increasing flexural strength. At the same time the larger size delamination with increasing fiber content may be the reason behind the lowering of the impact and tensile strength depicting large pieces of material being easily detached due to the lower bonding between the matrix and fiber materials. The NTI1 (Fig. 11 f) in similar fashion shows areas having nil resistance to force without any delamination found while the FESEM images of NTI2, NTI3 and NTI4 (Fig. g, h and i respectively) shows increasing and completely filled delamination on the fractured surface thereby justifying the fact of the increasing flexural strength at higher fiber reinforcement levels.



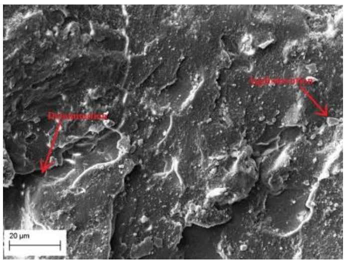
a – FESEM image of PLA



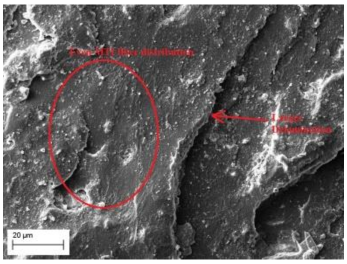
b – FESEM image of TM1



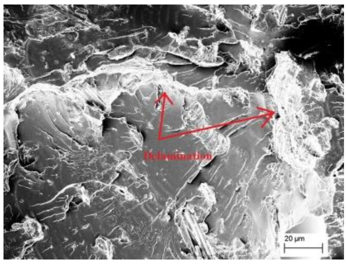
c – FESEM image of TM2



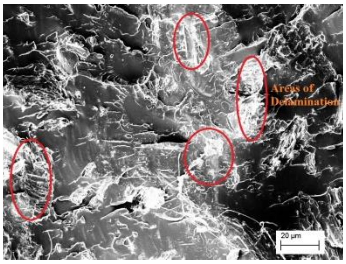
d – FESEM image of TM3



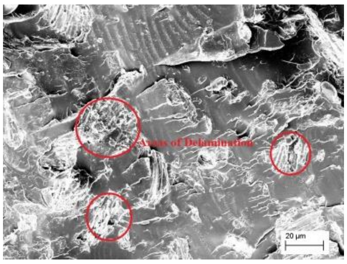
e – FESEM image of TM4



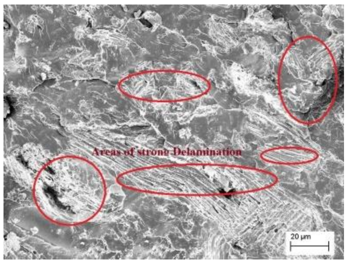
f – FESEM image of TN1



g – FESEM image of TN2



h – FESEM image of TN3



i – FESEM image of TN4

Fig. 11. FESEM images.

4. Conclusion

The Bio-Wood Plastic Composite was successfully fabricated using Tamarindus Indica wood flour/ PLA combinations. Mechanical properties were not as desirable and expected due to the lowering of tensile and impact strength properties with increasing TI content in the PLA matrix. Hardness was also observed to reduce, during the research with addition of TI into the PLA matrix irrespective of the fiber size. Flexural strength though initially found a decrease at lower fiber reinforcement levels, improved with increasing fiber content. Further fiber increment beyond 25 wt% may lead to further betterment of the flexural properties which will be carried out in future studies. The modulus value of PLA though was found to improve with addition and increment of TI reinforcement thereby proving that TI fibers provide good stiffness to PLA with reduced plasticity character. TI/PLA WPC having positive modulus and flexural properties along with low water absorption ability and good thermal stability cannot be therefore recommended as an optimal prosthetic material in its current form. Further research is hereby encouraged from researchers to focus on advancements to enhance the properties of this novel WPC. It is also noted in this study that the nano TI wood flour reinforced WPCs showed superior properties throughout all investigations research work in comparison to the micro TI fiber reinforced WPCs.

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