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MECHANICAL AND BIODEGRADABILITY STUDIES OF TOLUENE - 2,4 - DIISOCYANATE (TDI) MODIFIED OKRA FIBER REINFORCED POLYESTER COMPOSITE

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ABSTRACT
The compatibility of natural fiber in a synthetic matrix is an important factor affecting bio-composite properties. Several methods have been used to enhance the fiber matrix interface, however, the use of toluene-2,4-diisocyanate (TDI) though recommended in literature, has gained little attention. This study, therefore, presents the mechanical and biodegradability properties of TDI modified Okrafiber as reinforcement in unsaturated polyester resin. Short okrafiber of average length 5 mm was modified with the TDI concentration varied from 0 to 4 wt% at1 wt% intervals. The modified fiber was then used to reinforce the unsaturated polyestermix using the casting method and compressed under 350 N. Mechanical tests (such tensile impact, hardness and water absorption) were conducted on the fabricated composites using ASTM standards. Weight loss coupled with Surface Morphological studies was used to estimate the biodegradability of the fabricated composites. Increase concentration resulted in improvement intensile strength, percentage elongation and water resistance of the composites (The maximum average tensile strength of 149.23 Mpa and a percentage elongation of 9.6% was recorded at 3% TDI concentration) while hardness and modulus of elasticity reduced. The water absorption capacity of 1.09% was recorded at 4% TDI concentration.0 wt%, 1wt% and 2 wt% TDI modifications was buried and significant biodegradation was observed after 90 days sample burial with 2% treatment recording the highest weight loss of 0.15%. These properties will find application in indoor furniture panels, footboards and platforms.
Keywords: *Biodegradability, mechanical, surface morphology, composites, okra, toluene-2,4-diisocyanate.*

INTRODUCTION
The study of natural fibers as a viable substitute to synthetic fibers is growing interests among polymer engineers (Devi *et al*., 1997; Mohanty *et al*., 2005; Guo *et al*., 2013, Chauhan and Chauhan, 2013; Ramachandran *et al*., 2016; Iqbal *et al*., 2018). Natural fibers derived from plants have attractive properties which include lightweight, low cost, abundance and environmental friendliness as compared to metals, ceramics, and plastics (Agaral and Broutman, 1990; Hull and Clyne, 1996; Prasanna *et al*., 2017). Other Fillers and fibers used to reinforce polymers are calcium carbonate, glass fibers, talc and high-performance fibers such as carbon and aramidic (Facca *et al*., 2007; La Mantia and Morreale, 2011). The major advantages of composites lie in their ease of tailorability towards specific applications (Callister, 2007; Asasutjarit *et al*., 2007). Reinforced natural fibers in composites have proven efficient and economical in engineering applications such as in automobiles, aerospace, oil and gas and other process industries (Yu *et al*., 2006). Although natural fibers and their composites promise several advantages such as environmental friendliness and renewability, they have some setbacks (Bismarc *et al*., 2005; Najafi, 2013). These setbacks include their poor wettability, incompatibility with some polymeric matrices and high moisture absorption. Low compatibility of fiber and matrix is responsible for the low reliability of composites, hence the need for fiber modification (Yuhazri and Dan, 2007; Sawpan *et al*., 2012; Azwa *et al*., 2013). Some of the modification processes that has been used includes physical treatments: (cold plasma treatment, corona treatment) and/or chemical treatments: (such as maleic anhydride, organosilanes, isocyanates, sodium hydroxide, permanganate, and peroxides) help to improve material stiffness comparable to glass fibers (Luo and Netravali, 1999). Chemical treatment remains the most widely used form of modification on natural fibers because of its ease and low cost.

Several studies have reported the use of alkaline treatment on fibers for reinforcement with positive results, however, scanty works are available on the use of toluene-2,4-diisocyanate (TDI) treatments for fiber modification. Therefore, this study focuses on the mechanical and biodegradability properties of composites formed from TDI modified okra fiber reinforced polyester composite.

MATERIALS AND METHODS
Materials
Okra fiber was sourced from Juneng Nigeria Limited, Nsukka Enugu State, while General purpose polyester resin and toluene-2,4-diisocyanate (TDI) manufactured by Sigma-Aldrich Inc, USA used in this work was purchased from Haddis Chemicals, Zaria Nigeria.

Methods
Modification of Okra Fibre with Toluene-2,4-diisocyanate (TDI)
The Okro fiber was chopped to fiber length of about 6 mm after which it was immersed in chloroform. Drops of dibutyltindilaurate catalyst were added and stirred for 2 hours (The TDI - chloroform ratio was 1:2). The fibers were then rinsed in acetone then dried in an oven for 10 minutes (La Mantia and Moreale, 2011). The procedure was repeated for 1, 2, 3 and 4% TDI by weight.

Preparation of the Polyester Resin Matrix
1.0 wt.% each of Methy Ethyl Ketone Peroxide catalyst (MEKP)was added to the prepared sample and stirred for 3 minutes. This was followed by the addition of 1.0% by

weight of cobalt naphthenate accelerator, and then stirred for 2 minutes. The mixture was then poured into the mold coated with a release agent and thereafter allowed to cure at room temperature for 1 hour. It was finally post cured in an oven at 60^{o}C for 24 hours.

Composite Preparation by Casting Method

Untreated okra fiber (0% TDI) was prepared by transferring 18 g of the untreated fiber into the mold. A 200 ml of polyester resin matrix was prepared using the method previously described and poured over the entire face of the okra fiber laid in the mold. It was compacted under the mold lid at 350 N for 50 minutes and allowed to cure. The composite was then carefully removed and post cured. The same procedures were carefully followed for the remaining samples: 1%, 2%, 3%, and 4% by weight TDI treated okra fibers respectively.

Mechanical and Biodegradability Properties Determination

The samples for the tensile strength test were prepared and tested according to ASTM standard D638M (ASTM, 1996) using Hounsfield tensometer W3179, Impact Strength test according to ASTM standard D256M using Impact Testing Machine Cat.Nr.412, Shore A Hardness test was carried out using Durometer hardness tester, model no. 5019, 2007, Water Absorption Test according to ASTM D570 and biodegradability test by soil burial using weight loss as criterion, was carried out on the samples for a period of 90 days (Bello *et al*., 2017).

RESULTS AND DISCUSSION

Mechanical properties results of the fabricated composites are presented in Figures 1 – 6 while the results for biodegradation are shown in Figure 7. Figure 1 shows the tensile strengths behavior of the fabricated composites.

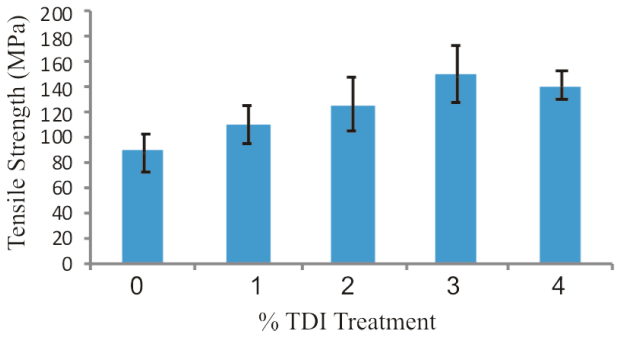

Figure 1: Tensile strength of TDI modified okra fiber reinforced polyester composite

An increasing trend was observed in the tensile strength of the composites as the concentration of TDI increased. The increase was from 88.77 MPa at 0 wt% TDI treatments to 149.23 MPa at 3 wt% TDI which is an increase of 68.10%. TDI was expected to improved compatibility between matrix and the fiber by increasing roughness on the fiber leading to improved interfacial adhesion between the fiber and matrix (Ku *et al*., 2011). A maximum value in tensile strength was reached at 3 wt.% TDI after which a downward trend was observed. This downward trend may be due to fiber breakages due to chemical attack on the fiber at high concentration of TDI. Tensile strength up to 150 MPa find application in footboards and platforms applications (Netravali and Chabba, 2003).

Figure 2 shows the elongation properties of the fabricated composites. It was observed that the TDI treatment enhanced the ductility of the composite material up to 9.6% at 3% TDI modification from 5.4 % unmodified fiber composite.

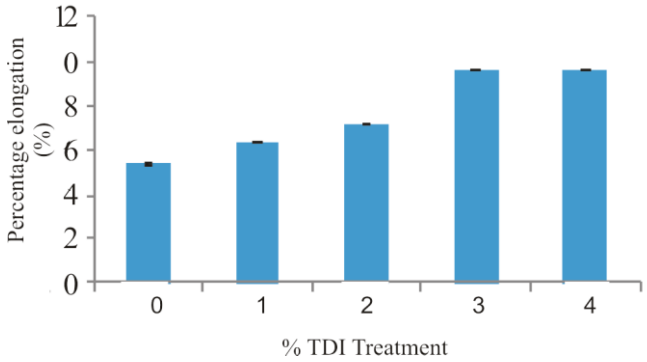

Figure 2: Percentage elongation of TDI modified okra fiber polyester composite

Increase in fillers in composites are generally known to reduce percentage elongation of the composite, however treatments and modifications of fibers before being fabricated into composited causes stretching effect of cross linked bonds in fibers thereby improving elongation at break (Netravali and Chabba, 2003; Paul and Robeson, 2008).

Figure 3 shows the modulus of elasticity (degree of stiffness) of the composite material. It was noted that there was no significant change in the stiffness of material for the unmodified fiber up to 2% TDI treatment. However, a significant decrease in stiffness was observed at higher TDI modification concentration of 1.59 GPaat 3% and 1.46 GPaat 4% modification concentration. This decline is known to occur when treatment concentration increases continuously.

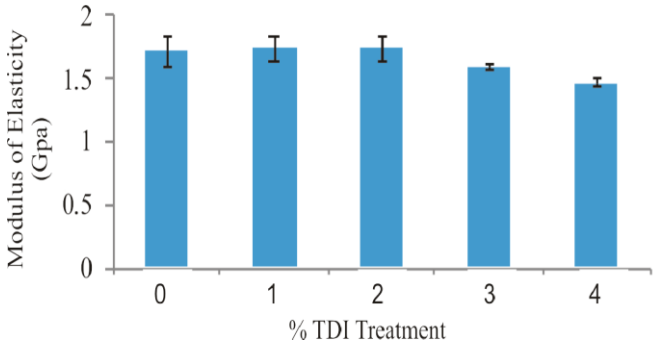

Figure 3: Modulus of elasticity of TDI modified okra fiber reinforced polyester composite.

A similar trend which gave a decline in stiffness with increase in treatment concentration was reported in the use of NaOH in an alkaline treatment method on sisal fiber (Mishra *et al*., 2003).The Impact strength of the composite which is a measure of the total energy absorbed by the material is shown in Figure 4.

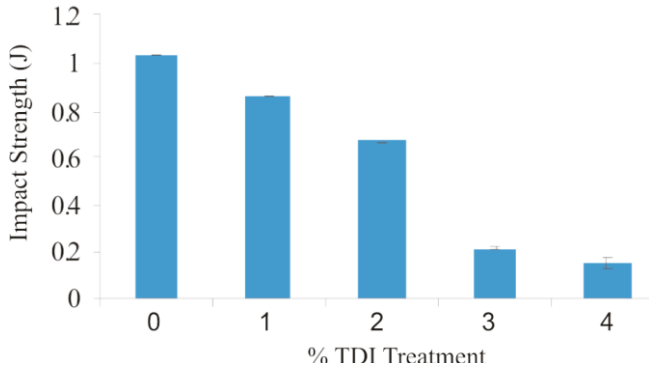

Figure 4: Impact strength of TDI modified okra fiber reinforced polyester composite

It was noted that using TDI to modify the okra fiber reduced the impact strength of the composite hence reduced energy absorbed by okra fiber reinforced polyester composite. The untreated sample had the highest strength of 1.033J which dropped by 15.29% at 1% TDI treatment (0.857J) and by 85.45% at 4% TDI treatment (0.150J). This implies that the use of TDI as a fiber modifier (okra) in a composite (random fiber load) has a negative effect on the energy absorbing capacity of the material. This behavior may be due to the success of fiber treatment which improved fiber matrix compatibility (Yuzari and Dan, 2008). When a composite with good adhesion property is subjected to shock, fiber breakage occurs instead of pull out implying good fiber and matrix compatibility (Li *et al*., 2011; Rajesh *et al*., 2016).

Figure 5 shows no effect on the hardness of the material between untreated and 1% (85.67 Shore A) treated sample. A slight decrease was noted as the modification concentration increased to 2% and was constant up to 4%.

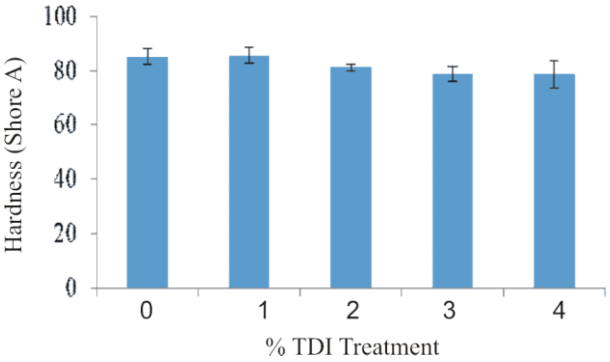

Figure 5: Hardness characteristics of TDI modified okra fiber reinforced polyester composite

The observed decrease in hardness after 1% TDI treatment can be attributed to the reduction in molecular weight of the oligomers as they react with more concentrated TDI, that is, more lignin component was increasingly removed with higher concentration of TDI (Novak, 1993; Sule *et al*., 2014). In terms of water absorption capacity as shown in Figure 6, a decreasing trend was observed.

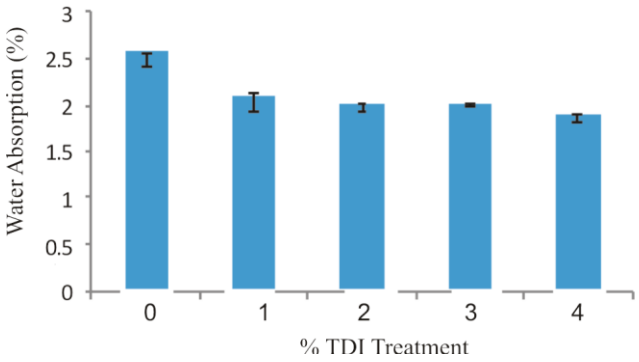

Figure 6: Water absorption of TDI modified okra fiber reinforced polyester composite

This implies that TDI modification improved interfacial adhesion (reducing water accumulation in interfacial voids) of the fiber and matrix thereby leading to an improved hydrophobicity of the fiber. The low moisture in the void structure of the composite reduces the swelling ratio/thickness swelling of the material, hence an increased water resistance of the material, a prospect property suitable for packaging (food, pharmaceuticals and electronics), upholstery and indoor furniture panels (Majeed *et al*., 2013; Ou *et al*., 2014). Figure 7 shows the weight loss of the fabricated composited buried for 90 days. Significant increasing weight loss was observed from 60 days with highest TDI treatment concentration recording highest average degradation at 90 days of 0.025%, 0.078% and 0.152% for untreated, 1 wt% TDI and 2 wt% TDI treatment respectively. This implies high TDI concentration treatment increases removal of lignin during treatment thereby exposing more cellulose for bacterial degradation. This observation can further be seen in Plate 1 showing the morphology of degradation before burial and after 90 days of burial.

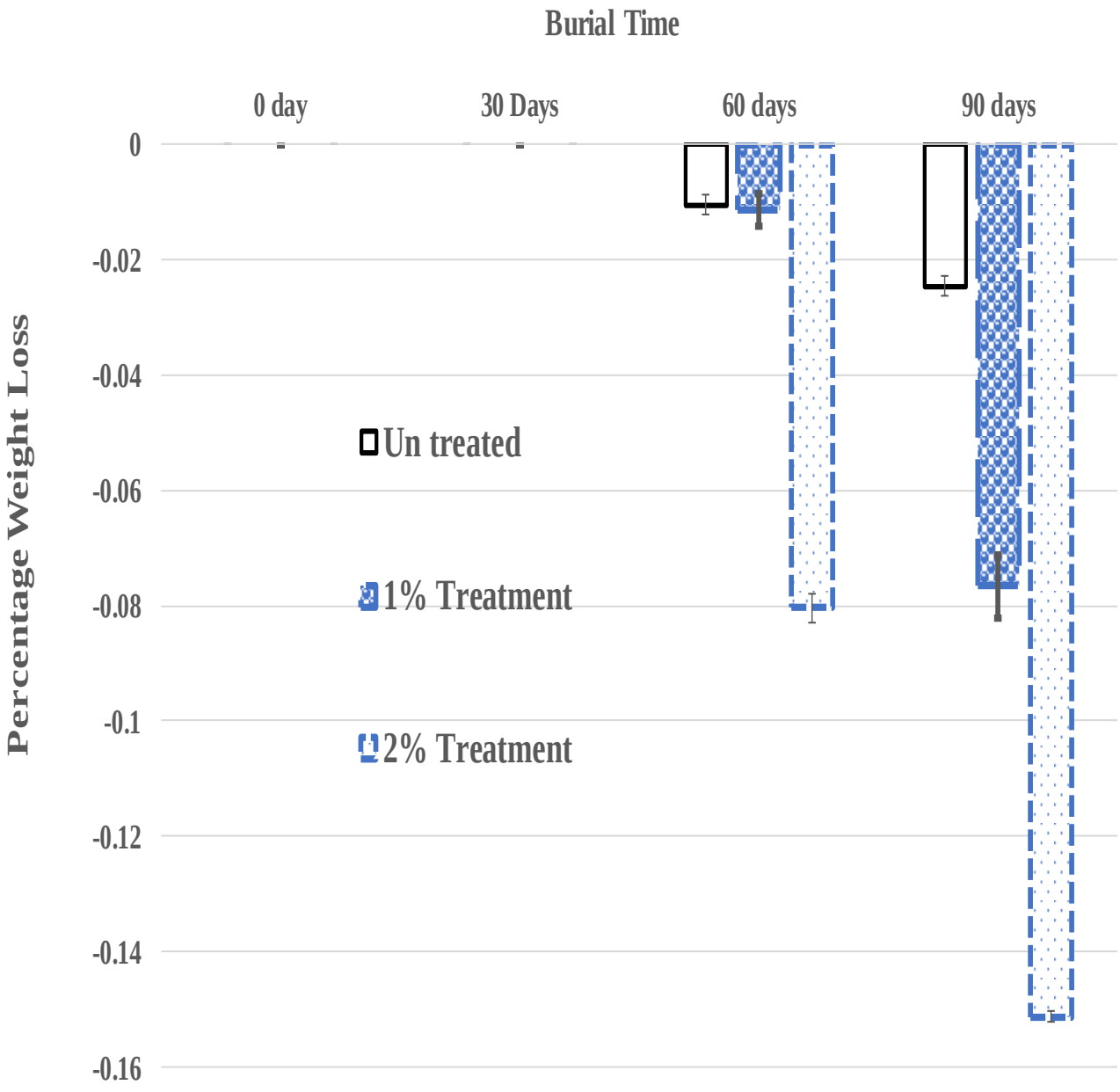

Figure 7: Percentage weight loss of untreated and treated fiber reinforced composite

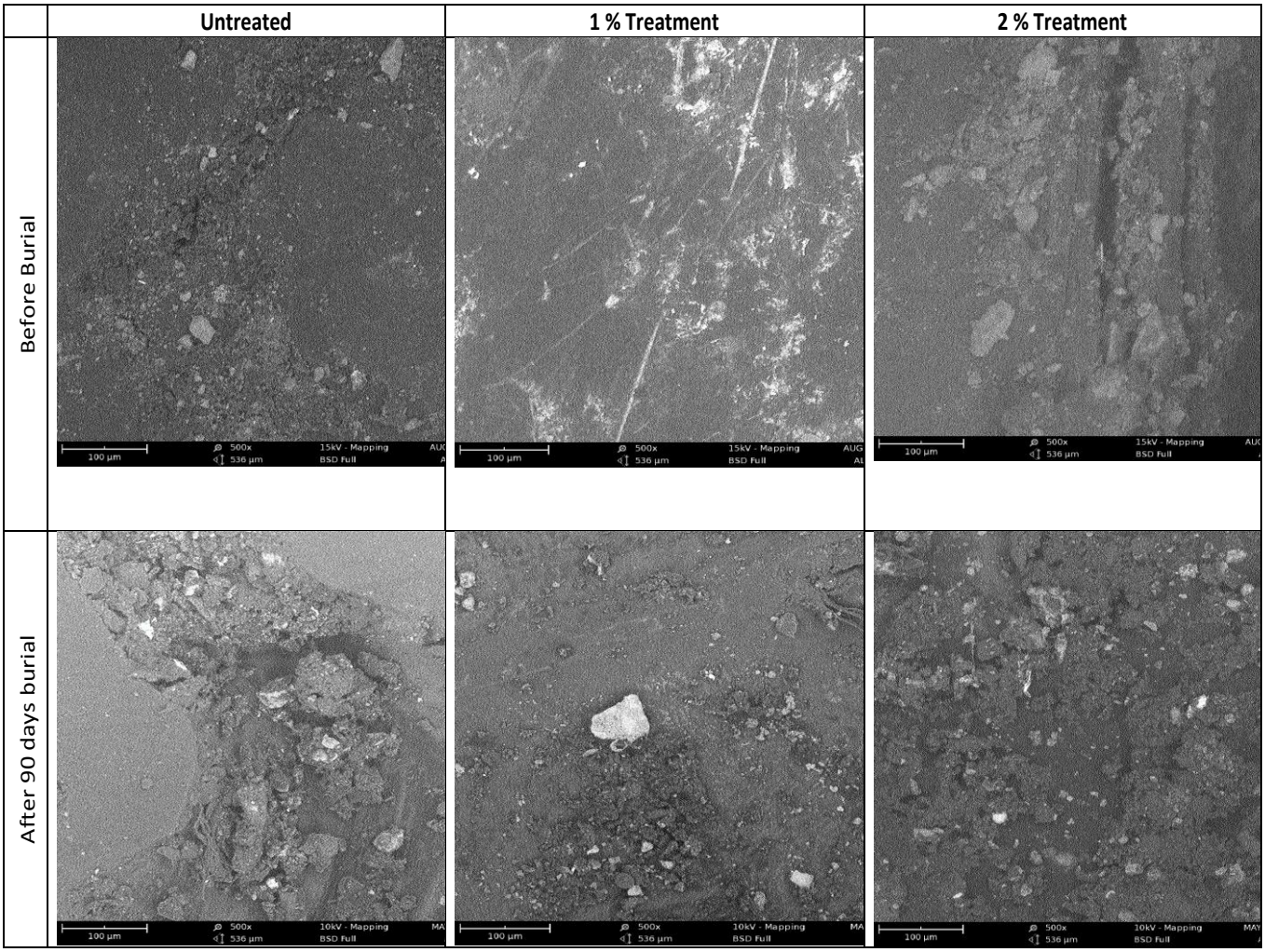

Plate 1: Scanning electron micrograph showing degradation of fabricated composite

Although cracks are evident in the composite before burial, this may be due to imperfection during fabrication but greater cracks due to microbial activity can be seen after 90 days burial. The cracks are avenues for soil bacterial penetration for degradation thereby resulting in loss of material (Rajesh *et al*., 2016; Liu *et al*., 2017; Haghighatnia *et al*., 2017).

CONCLUSIONS

The following conclusions can be drawn from this study:

The tensile property of Okra Modified Polyester composite was improved by 68% from 88.77 MPaun modified to 149 MPaat 3% TDI treatment, Elongation was improved by 78%.

No effect was observed on the hardness and modulus of elasticity of the material at low TDI concentration of 1%. However, a significant drop was recorded for hardness and Modulus of elasticity at 2 wt% and 3wt% TDI modification respectively.

The impact strength showed a decreasing trend with increasing TDI concentration. The highest strength was observed with the untreated okra fiber composite followed by 1 wt%, 2 wt%, 3 wt% and 4 wt% TDI respectively.

TDI treatment lowered the water absorption capacity of the composite with the least value of 1.9% recorded at 4 wt% TDI.

Increased fiber treatment enhanced the biodegradability of the composites due to the removal of protective layers of lignin and hemicellulose.

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