



Original Research Article

Assessment of the Degradation of PLA/PCL Biocomposites in a Landfill Environment

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ABSTRACT

In this study, a biodegradable blend of Poly(lactic acid) (PLA) with Poly(ϵ -caprolactone) (PCL) compounded with boehmite (BAI) and natural fiber were prepared and their biodegradation rate under real savannah environmental conditions was assessed for 13 weeks burial time. The effect of temperature and moisture content on the biodegradation rate were studied by weight loss monitoring with respect to the percentage loading of PCL, BAI, and natural fiber. The result indicated that the degradation rate of the pristine PCL was approximately 9%, while pristine PLA showed no changes during the study period. However, the degradation of PLA/PCL blends started after the first six weeks of soil burial, with the sample reaching a 19% weight loss for 70/30 (w/w) blend of PLA/PCL. The addition of 4% nanoparticles (BAI) retarded the degradation rate to 3.5% for the 70/30/4 sample due to improved compatibility. While the nanocomposite blend containing natural fiber (PLA/PCL/BAI/Fiber) showed a higher degradation rate above 19%. The results showed that natural fiber composites of PLA/PCL blend remained very sustainable material regardless of the immediate environment and can be considered a friendlier alternative to its pure blend or nanocomposites.

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1. INTRODUCTION

Over the past five decades, polymers have been primarily utilised as alternatives to materials such as paper, wood and metals for various usage, due to their exceptional properties in terms of durability, buoyancy, steadiness, and low cost (Lucas *et al.*, 2008). As a result, these polymeric materials are used extensively in many areas, such as packaging, agricultural films, clothing, biomedical and engineering products (Scaffaro *et al.*, 2019). The global consumption of polymeric materials has thus increased exponentially since the

nineteen fifties. The rapid rise in technology and infrastructure, which has led to increased polymer utilization globally, has tagged this era "the age of polymers" (Nowak *et al.*, 2011).

Due to recent ecological and environmental problems such as depletion of fossil fuel, emission of greenhouse gases and waste management issues arising from increased exploitation of synthetic polymers, the need for developing materials that are renewable, degradable and recyclable, also known as "green materials" as a substitute to the petro-derived polymers has been gaining significant attention (Jbilou *et al.*, 2011). In this respect, attempts have been made to improve the biodegradability of these petro-derived synthetic polymers by incorporating biodegradable polymers into their matrix. Rodriguez-Gonzalez *et al.*, (2003), in their study to produce a sustainable substitute to pure polyethylene (PE), the authors synthesised a blend of high-performance low-density polyethylene/thermoplastic starch (LDPE/TPS). They concluded that the physical properties of the polymer were significantly improved and predicted the blend to be biodegradable due to the presence of starch in the polymer matrix. Numerous studies regarding the production of partially degradable biocomposites to replace pure synthetic polymers have also been reported (Simmons and Thomas 1995; Chandra and Rustgi 1997; Thakore *et al.*, 2001). Although, these partially degradable polymers present a more sustainable alternative to pure synthetic polymers due to their partial degradation they, however, contain an appreciable portion of the persistent non-biodegradable residues after degradation and can further give rise to secondary pollution (Nakamura *et al.*, 2005; Wojtowicz *et al.*, 2009). Several researches reported that a feasible resolution to the polymer waste problem is the utilisation of fully biodegradable polymers since biodegradable polymers can decompose completely into biomaterials without any harmful effects to the environment (Aranguren *et al.*, 2012; Agwuncha, 2015; Agwuncha *et al.*, 2018; Salomez *et al.*, 2019). Many biodegradable polymers (biopolymers) possess good physical, mechanical, and thermal properties that compare to most synthetic polymers (Borkotoky *et al.*, 2020). Therefore, they are gradually replacing conventional polymers in applications such as medicine, packaging, clothing etc. (Rydz *et al.*, 2018; Khalil *et al.*, 2019). Biopolymers that have attracted an increased amount of attention are aliphatic polyesters such as poly(lactic acid) (PLA), poly(ϵ -caprolactone) (PCL), polyethylene oxide (PEO), poly(3-hydroxybutyrate) (PHB) and polyglycolic acid (Liao and Wu, 2009).

PLA has drawn much interest due to its high strength and biocompatibility (Agwuncha *et al.*, 2017). PLA is synthesised by the fermentation of lactic acid from renewable agricultural sources. It can be processed like conventional plastics using standard processing techniques, such as extrusion, injection, compression, and blow moulding (Pivsa-Art *et al.*, 2016). Notwithstanding, biopolymers often experience performance limitations in certain areas when compared to synthetic based polymers (Khalil *et al.*, 2019). The disadvantages of PLA include its slow crystallisation rate, slow biodegradation, brittleness, poor elongation as well as limited gas barrier properties (Agwuncha *et al.*, 2015). Recently various researches have reported that the limiting physical properties of PLA can be ameliorated by using suitable composite and blending approaches (Pires *et al.*, 2020). The biodegradability of the modified PLA biocomposite has also been reported. Kumar *et al.*, (2010) evaluated the biodegradation of flax fiber-reinforced PLA and concluded that the presence of the natural fibers accelerated biodegradation of flax fiber/PLA composites. In a similar study by Stloukal *et al.*, (2015), blends of PLA with organically modified montmorillonites (OMMT) was prepared and evaluated for their biodegradability. The study showed that the addition of nanoclay enhanced the biodegradation of PLA nanocomposites under composting conditions. A series of literature investigated PLA based biocomposites under different microorganism rich environments such as soil for composting and industrial composting conditions (Musioł *et al.*, 2016; Nieddu *et al.*, 2009).

Typically, the most effective methodology in improving the physical performance of a brittle polymer such as PLA is its blending with a soft, biocompatible, ductile polymer such as PCL (Fortelny *et al.*, 2019). Studies on blending PLA and PCL have reported that the blends complemented various shortcomings of each individual material (Navarro-Baena *et al.*, 2016; Luyt and Gasmi, 2016). Although PLA/PCL blends should display improved biodegradability and physical performance than neat PLA (Rydz *et al.*, 2018), they are, however, thermodynamically incompatible and thus, blending with a suitable ternary bio-product have been reported to improve its compatibility (Agwuncha *et al.*, 2015). Liao and Wu (2009) reported on the

biodegradability of ternary blends composed of PLA, PCL and starch. The biodegradability studies of these biopolymers via soil burial indicated that the biodegradation of ternary blends was faster due to the presence of starch in the polymer matrix. Hence blending with a third biocompatible suitable (organic or inorganic) material is believed to improve the biodegradability of the blends. In another study by Wang (2018), various ternary blends of PLA, PCL and TPS biocomposite were prepared and their biodegradability studies were carried out using soil burial test procedures. It was reported that the blend with the highest proportion of TPS presented the best biodegradability result, reaching 48% after 6 weeks and a total degradation after 16 weeks. The author concluded that the biodegradability of biopolymers is linear, and degradability increases with an increasing amount of TPS in its blend.

Literature about the biodegradation behaviour of pure PLA and its blends in a real soil environment is scarce. To the best of our knowledge, very little study about the degradation behaviour of PLA/PCL biopolymer blend in real environmental conditions has been reported in West Africa, where indiscriminate disposal of solid waste materials (waste polymer) is on the rise. Therefore, this work seeks to fill the knowledge gap. In previous reports the authors reported on the preparation, characterisation and properties of biodegradable PLA/PCL blends and nanocomposites (Agwuncha, 2015; Agwuncha *et al.*, 2015). The neat PLA, PCL, their blends, biocomposites (with BAI) and their bionanocomposites (BAI/natural fiber) were prepared and characterised for their physical and morphological properties, and their biodegradation under simulated laboratory conditions was studied. Complementing on our previous studies on biodegradation of biopolymers and aiming to further understand the biodegradation mechanism of PLA/PCL biopolymers in real environmental conditions, the biodegradation behavior and effect of soil burial on degradation of PLA/PCL blends and composites was studied.

2. MATERIALS AND METHODS

2.1. Materials Collection and Processing

Commercial grade PLA (20002D) was obtained from NatureWorks LLC, USA with the following specifications. A D-isomer content of 4 wt%, molecular weight of 235 kg mol⁻¹, a density of 1.24 g cm⁻³, a glass transition temperature (T_g) of 60 °C, and a peak melting temperature (T_m) of 153 °C. The PCL was supplied by Sigma Aldrich (South Africa) with CAS no: 24980-41-4; Pcode: 1001304963; Molecular weight between 70000 and 90000 gmol⁻¹, as determined by gel permeation chromatography. The boehmite (BAI) powder was a commercial product manufactured and supplied by SASOL (Germany) under the trade name Dispersal 40, containing 80 wt% Al₂O₃. SASOL developed this product to yield high dispersion and have low levels of common impurities such as iron, sodium, and silica. Natural fiber (sisal) was obtained from New Delhi, India

The samples were prepared and characterized as reported by Agwuncha, (2015) and Agwuncha *et al.*, (2015). The samples were labelled with respect to the percentage PLA, PCL, BAI and natural fiber added. Therefore, the pristine PLA and PCL were labelled 100/0/0/0 and 0/100/0/0, respectively, and a blend of 80 wt% of PLA, 20 wt% of PCL and 4 wt% of nanoparticle and 0 wt% of treated natural fiber was labelled as 80/20/4/0T. In addition, triplicate samples of the pristine polymers of PLA and PCL; the blends of 90/10, 80/20, 70/30 and 60/40; PLA/PCL/BAI bionanocomposites of 70/30/2, 70/30/4 and 70/30/6; and PLA/PCL/BAI/natural fiber bionanocomposites of 70/30/0/10T, 70/30/4/10T, 70/30/4/15T, 70/30/4/20T were used.

2.2. Soil Burial Analysis

Two sites were selected for biodegradation study. The first site was close to the student accommodation and the other behind the Faculty of Natural Sciences building, both located within the campus of Ibrahim Badamasi Babangida University Lapai, Niger State, Nigeria. Compressed films of melt blend polymers samples were prepared and cut into 5 × 5 cm² sizes in triplicates. The samples were labelled before burial in soil at depth of about 5 cm for a duration of 13 weeks.

2.3. Biodegradation Monitoring

Samples were weighed before burial. Burial sites were watered morning and evening throughout the duration of the experiment. Samples were dogged out weekly, washed thoroughly to remove slits, dried of ambient temperature overnight, weighed to constant weight and then reburied immediately. This procedure was repeated for the entire experimental duration. The percentage weight loss by samples was calculated using Equation (1).

$$\% w = \frac{w_i - w_f}{w_i} \times 100 \quad (1)$$

Where w_i was the initial dry weight before burial and w_f was the final weight after samples were exhumed at stipulated times from the soil. Samples were weighed repeatedly using an analytical weighing balance (Citizen CX-220) until constant weight was obtained.

The temperature and moisture content of the selected sites were recorded regularly at 5 cm below the soil surface (interval of 4 hours daily). For temperature measurement, a pilot hole was used to make a depth of 5 cm deep, and the temperature probe inserted and read after temperature readings stabilizes. For moisture content, soil sample was then collected at a depth of 5 cm and was used in moisture content analysis. The moisture content was determined by drying approximately 10 g of soil sample at 105 °C in an oven for 6 h. The dried sample was allowed to cool in a desiccator before weighing using analytic balance. The samples were analyzed in duplicate, and the average result reported. The percentage moisture content was calculated using Equation (2).

$$\% M = \frac{A_i - A_n}{A_i} \times 100 \quad (2)$$

Where A_i is the weight of the moist sample, A_n is the weight of the dried sample, and $\% M$ is the percentage moisture weight.

3. RESULTS AND DISCUSSION

3.1. Ambient Temperature and Moisture Content

The soil temperature and moisture at a depth of 5 cm were recorded daily throughout the study period. Figure 1 shows the average temperature data for soil at 8 am, 12 pm, 4 pm and 8 pm, as well as the moisture content.

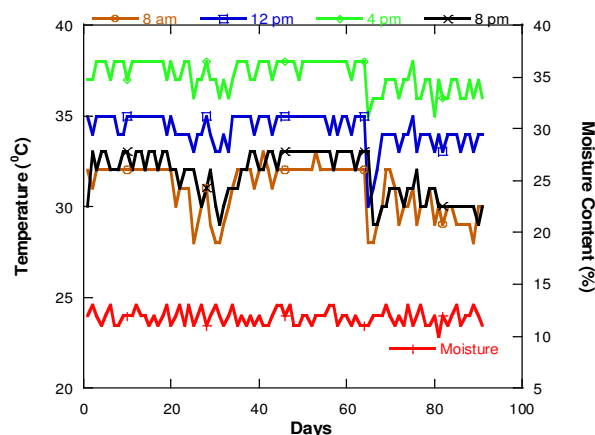


Figure 1: Average Ambient temperature and moisture content around burial sites for the period of experiment

The results obtained from the two sites used were identical. Average temperature values for the soil environment for both sites were observed to be the same and it varied from around 28 °C to 38 °C daily throughout the experiment. Also, the average moisture level was observed to be maintained at approximately

12% for both sites. The moisture content is synonymous with soil moisture level reported in literature for northern Nigeria (Sani and Alhassan, 2019). From the result, temperature and moisture were maintained at a favourable range, which supports microbial growth of the active degrading species.

3.2. Biodegradability Studies

3.2.1. Biodegradability of pristine PLA, PCL and their blends

The degradation of the samples was monitored via weight loss measurement. Figure 2 presents the trend of weight loss of the pristine PLA, PCL and their blends after 13 weeks of monitoring on two different sites.

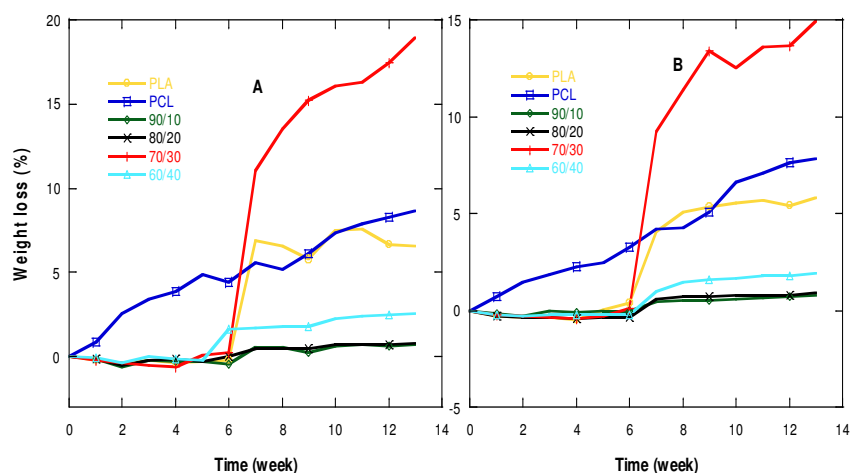


Figure 2: Trend of weight loss of pristine PLA, PCL and their blends from the two sites used (A and B)

From the result, the pristine PCL showed a steady increase in degradation, with a total weight loss of about 9 % for both sites after 13 weeks. The steady increase in the degradation rate of the pristine PCL has been attributed to the degradation induced by the microorganism in the soil (Neppalli *et al.*, 2011). Furthermore, moderate temperature and moisture content of about 35 °C and 12 %, respectively, favour this steady degradation observed (Lotto *et al.*, 2004). Also, there are possibilities of enzymatic activities, as reported by Calil *et al.*, (2006). A similar degradation behaviour for PCL has been reported by Nevoralova *et al.*, (2020). The authors reported a 12% weight loss for PCL after 90 days. However, the results obtained was observed to be higher than that reported by Lyu *et al.*, (2019), who reported only about 2.5 % weight loss at 30 °C for PCL after 60 days in the natural environment. This difference in degradation rates may be attributed to environmental variations, including soil composition, type of microorganisms, temperature, and moisture content (Emadian *et al.*, 2017).

In contrast, a slow degradation was observed for the PLA sample and its blends. The weight loss was observed to have only begun after week 6. All PLA containing samples showed an initial weight gain for about the first 4 weeks of the experiment which could be attributed to the fact that PLA poses little resistance to moisture due to the presence of carbonyl group in its backbone, absorbing moisture from the soil (Lv *et al.*, 2017). According to Karamanlioglu *et al.* (2017), hydrolysis can occur in the presence of a small amount of moisture in the soil environment. Therefore, for the pristine PLA, a sharp increase was observed in week 6 of soil burial, which was relatively constant with an approximated weight loss of about 6% for both sites after 13 weeks. Wu (2012) reported a similar degradation of neat PLA with about 10% weight loss after 14 weeks. Although there are authors that have reported little or no degradation of pristine PLA samples after soil burial in a natural environment for a long time (Karamanlioglu and Robson, 2013), and some others have reported quick degradation in the same natural environment over a short time (Adhikari *et al.*, 2016). This inconsistency in the degradation of pristine PLA has been attributed to variations in surface area,

molecular mass and ecological factors (La Mantia *et al.*, 2017; Anderson and Shive, 2012). Moreover, it is known that biodegradation of biopolymers differs depending on the soil environment and that PLA degrading microorganisms are not widely distributed in the natural environment (Emadian *et al.*, 2017).

The degradation of PLA blends followed trends similar to that of the pristine PLA due to the high percentage content of PLA in their matrix. However, they differ in the rate of degradation with respect to the amount of PCL in the blends. For the blends, it was observed that as the PCL wt % loading increased, biodegradation also increases and was optimum at 30 % PCL wt loading (70/30 blend), with about 19 % for site A and 15 % for site B. Further addition of PCL decreased the biodegradation rate as observed in the blends 60/40, which showed a weight loss of about 2.5 % and 1.9 % for sites A and B, respectively. Interestingly, biodegradation of the blends of 90/10, 80/20 and 60/40 was observed to be slower than the neat PLA. So many factors could have hindered the degradation of these blends, which includes characteristics of blends such as chain flexibility, optical purity, glass transition temperature, crystallinity, regularity and heterogeneity, and also biotic factors such as pH, bio-surfactant and enzymes (Lucas *et al.*, 2008; Karamanlioglu *et al.*, 2017).

3.2.2. Effect of BAI loading on PCL/PLA blend

Figure 3 presents the trend of weight loss of PLA/PCL BAI nanocomposites. This was done to understand the effect of BAI 4 % wt loading effect on blends. Here, a similar trend in biodegradation behaviour as observed for the neat blends were also observed for the nanocomposites. This degradation showed that as the PCL wt % loading was increased, the biodegradation of nanocomposite also increased and was optimal at 30 % PCL wt % loading. Furthermore, the degradation rates were similar to those of the neat blends except the 70/30/4 blend, which gave a degradation rate of about 3.4 % of site A and about 4 % for site B. When comparing these rates to those of the neat blends (Figure 2), it is observed that the biodegradation rate for the blend 70/30/4 decreased on the addition of the 4 %wt BAI. Therefore, it can be concluded that the compatibilizing effect of the nanoparticles, as reported by Agwuncha *et al.*, (2015), increased the compactness and adhesion of the neat blends, hence reducing the accessibility of degrading microorganisms and water molecules into the polymer matrix, with this effect being optimal for the blend 70/30/4 (Agwuncha *et al.*, 2015).

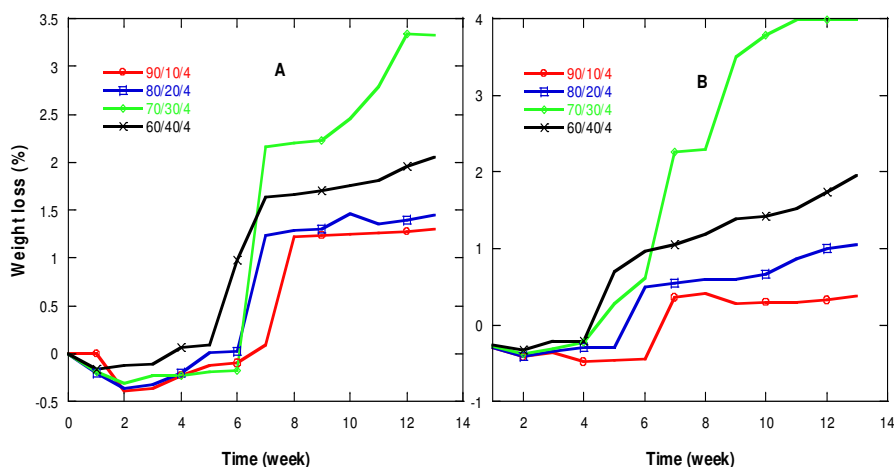


Figure 3: Effect of BAI %wt loading on the biodegradation PLA/PCL blends from the two sites used (A and B)

3.2.3. Effect of natural fiber loading on PLA/PCL/BAI nanocomposite

Figure 4 present the weight loss trend of PLA/PCL/BAI samples compounded with treated natural fiber. From the results, it can be observed that the biodegradation rate increased with increasing wt% of fiber loading. The biodegradation rate was observed to be higher than that of the neat blends and their

nanocomposites. The degradation of sample with 10 % fiber loading did not show much difference in degradation behaviours when compared with samples without natural fiber, indicating that the 10 % fiber loading addition did not influence the biodegradation rates of the neat nanocomposite. However, by week 10 and week 11 in sites A and B, the degradation of samples with 10 % fiber showed high degradation rates. The addition of 15 % fiber or more lead to rapid degradation of the composites with higher degradation rates. Dungani *et al.*, (2019) concluded in their work that fiber-reinforced biocomposites are susceptible to environmental factors such as temperature, moisture, especially those factors controlled by the fiber/polymer matrix interphase. These results also add to existing literature that confirmed that the presence of natural fiber increases the degradability and the degradation rates of biopolymers. Thereby making them more environmentally friendly or green composites (Wu, 2012; Surip and Jaafar, 2018). Akos *et al.*, (2014) reported a similar observation in their work on the biodegradation studies of PCL/PLA blends with the various proportion of fiber loading ranging from 10 wt% to 25 wt% in a natural environment. They also reported an increasing linear relationship in weight loss of composites as fiber loading increases. These studies conform to reports by Wang (2018), who concluded that the biodegradability of biopolymers is linear, and the degradation rate increases with an increasing amount of biomaterial loading.

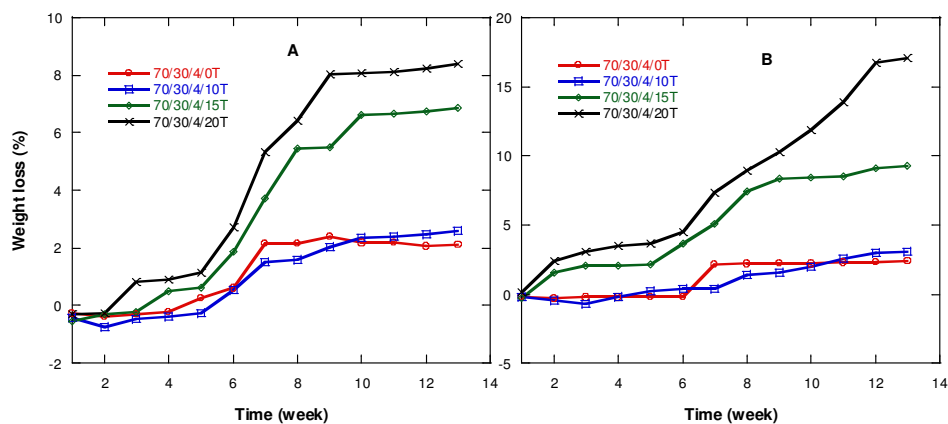


Figure 4: Effect of treated natural fiber loading on the biodegradation of PLA/PCL/BAI nanocomposites from the two sites used (A and B)

3.2.4. Morphological analysis

The observations discussed earlier, may be explained with the morphological structures observed in the SEM images as presented in Figure 5. The SEM of cryo-fractured samples before burial for sample 70/30/0/10 with 10 wt% treated natural fibers (TNF) (A') with no nanoparticle showed some protruding fibers that were not firmly held by the matrix, indicating the existence of unbonded space for water molecules and micro-organism to diffuse through (Fukushima *et al.*, 2010 & 2013). However, for sample 70/30/4/10 (B), the number of protruding fibers were significantly lower. In fact, the fibers appeared to be more firmly held, as most fibers are observed to be better embedded in the matrix. An indication of improved bonding between the matrix and fiber, leading to a delay in degradation of the sample (see Figure 4). On the other hand, samples 70/30/4/15 (C) and 70/30/4/20 (D) showed increased numbers of protruding fibers, which increased with increasing wt % of TNF, an indication of poor matrix-fiber bonding. Hence, the increased rate of degradation observed. The SEM images clearly showed these in A'', C'' and D'' (Figure 5).

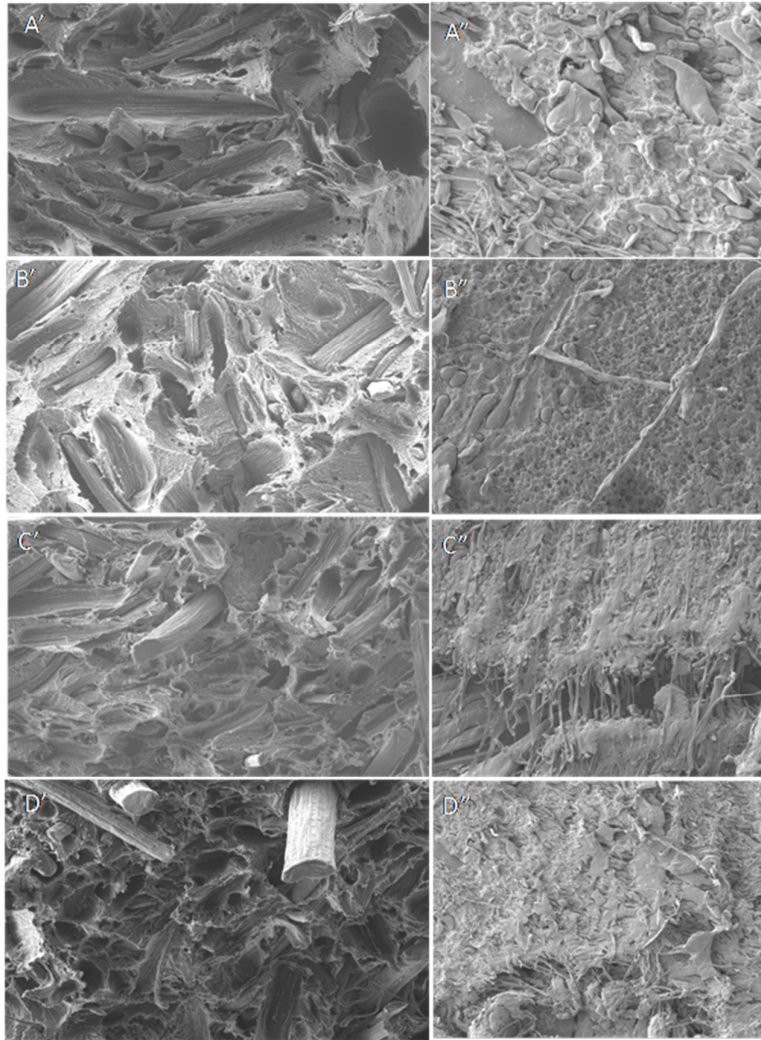


Figure 5: SEM images of the internal morphology of cryo-fractured sample before degradation (') and surface morphology after degradation (") for samples A – 70/30 blend with 10 % TNF, B – 70/30/4 nanocomposite with 10 % TNF, C – 70/30/4 nanocomposite with 15 % & D – 70/30/4 nanocomposites with 20 % TNF respectively.

4. CONCLUSION

In general, the eco-friendliness of polymer materials requires innovations that will not alter the materials application properties. The compounding of PLA/PCL nanocomposite with treated fibers has shown to be effective in this regard. The biodegradation study of PLA/PCL blend, nanocomposites and bionanocomposites carried out and been report here has confirmed that the materials are biodegradable in a natural environment with no special preparation for eventual disposal in landfills. The rate of degradation of the natural fiber nanocomposites is encouraging and, therefore, may be considered for composting to fully recover the materials energy.

5. ACKNOWLEDGEMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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