



Research Article

Effect of fiber load and compatibilization on biodegradation of poly(ϵ -caprolactone)/poly(lactic acid) composites

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Novel poly (ϵ -caprolactone)/poly(lactic acid), (PCL/PLA, ratio 90:10) blend composites were prepared with mercerized palm press fibers by melt extrusion and injection molding. The normal soil burial method was used to study the composites biodegradation. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) was employed to study the crystallinity of the blend composites while Dynamic mechanical analysis (DMA) confirmed the glass transition temperature of the composites. Compatibilization using dicumyl peroxide (DCP, 0.01phr) and fiber reinforcement accelerated the rate of biodegradation of the blend composites. The rate of biodegradation increased as fiber load increased from 10 wt% to 25 wt% in the composites. This was confirmed by the residual weights of the composites over the 90 days burial period. The DSC and XRD results showed that compatibilization reduced the melting temperature and crystallinity of the blends respectively. The DMA results confirmed the T_g of the blends composites to be around -62°C . However, incorporating fibers from 10 wt% to 20 wt% enhanced the crystallinity of the compatibilized blend composites.

Keywords: PCL/PLA blends, PCL/PLA composites, biodegradation, crystallinity, palm press fibers

INTRODUCTION

Novel biocomposites have continuously been the focus of many researchers with the aim of meeting up with environmental interest and government legislations in respect of waste disposal. Biodegradable polymers represent polymers that are produced by design to degrade naturally through the activities of microbes in the environment. The commonly available biodegradable polymers in the market are poly(caprolactone), poly(lactic acid), poly(ethylene glycol), polyhydroxyalkanoates, etc. (Mohanty et al, 2005). The relatively high cost of the biodegradable polymers as compared to the conventional non-biodegradable ones is an impediment to use them as substitute to the low cost conventional polymers. These

calls for the need to use low cost fillers to improve the properties and at the same time reduce the cost of the finished products. Natural fibers like sisal, oil palm empty fruit bunch, hemp, palm press fibers, flax, rice husk, jute, abaca e.t.c have been used as reinforcements in biocomposites partly because of their cheap, renewable,

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low mass and good mechanical properties (Campos et al, 2012; Campos *et al*, 2013; Lee and Wang, 2006; Mohanty et al, 2000; Oksman et al, 2003; Ray et al, 2003; Shinoj et al, 2011; Zhao et al, 2008).

Researches carried out on composites of PLA and PCL shows that they are both biodegradable. PLA can be synthesized from corn and sugar feedstock which are renewable. PCL is a linear petroleum based polymer. It is one of the few synthetic polymers that can be fully degraded by microbes. At their pristine states, PCL and PLA have property deficiencies that can be complimented either way to enhance their performances in outdoor applications. This led to blending (Hideto Tsuji., 2007; Salom et al, 2006; Singh et al, 2003; Tait et al, 2011; Takayama et al, 2011; Tuba et al., 2011), reinforcing with mineral fillers (Tsimpliaraki et al, 2011; Wang et al., 2010; Zhu et al, 2011) and natural fibers (Campos et al, 2012; Campos, 2013 et al; Yussuf et al, 2010). Investigations reveal that extensive studies of biodegradation have been carried out using normal garden soils and/or compost. The rate of biodegradation is usually accelerated in compost soil as compared to the normal garden soil due to its high microbial activities (Kumar, 2010; Martucci and Ruseckaite, 2009). Present challenges related to environmental hazards posed by the non-biodegradable conventional composite wastes have necessitated the design and production of the biodegradable composites. This is because the biodegradable composites after they're used and discarded into the environment are degraded naturally by the microbes. The poor human attitude towards waste disposal and also the absence of sufficient waste disposal facilities all over the world have triggered the need to incorporate additives that aid biodegradation of the finished products. In view of the above, this paper focuses on the biodegradation of blend composites prepared from palm press fiber and PCL/PLA blend which was carried out using normal soil to assess the effect of compatibilization and fiber load on the rate of biodegradation of the blend composites. Compatibilization and fiber reinforcement of the PCL/PLA blend enhanced its mechanical properties as earlier discussed in our published article (Akos et al, 2013). This paper focuses on the effect of fiber load and compatibilization on the biodegradation rate of PCL/PLA blend reinforced with palm press fibers.

The biodegradation rate was based on weight loss and burial time of the uncompatibilized and compatibilized blend composites. Fourier transform infrared spectroscopy (FTIR) was used to assess the effectiveness of the alkaline treatment while field emission scanning electron microscopy (FESEM) was used to assess the degradation. DSC, XRD and DMA were employed to study the crystallinity and thermal behavior of the blend composites.

EXPERIMENTAL MATERIALS

PCL (BGH800C) is a commercial product of Shenzhen Esun Industrial Co. Ltd China. It has molecular weight, $M_{wt} = 120,000$ g/mol; melting point, $T_m = 60-62$ °C; glass transition temperature, $T_g = -60$ °C and melt flow index, (MFI) at 190 °C, 2.16 kg, g/10min =7.29. PLA is also a product of the same company with the following properties. $M_{wt} = 80,000$ g/mol; $T_m = 150$ °C; and MFI = 7. Sodium hydroxide (NaOH), Dicumyl peroxide (DCP) and glacial acetic acid (CH_3COOH) are products of Sigma-Aldrich. They were used as received. Unprocessed Dura fibers (DF) were supplied by Amuya palm oil cottage ventures Mayir, Nigeria

Palm Press Fiber Treatment

Hot water was used to wash out left over particles, oil and other debris materials from the unprocessed palm press fibers. The fibers were treated with 5 % NaOH solution which was adjudged to be the best for the fiber treatment. The fibers were treated by soaking in 5% NaOH solution for 24hrs. After the treatment, the fibers were thoroughly washed and rinsed with water containing few drops of acetic acid after which they were dried in hot air oven at 105°C for 24hrs. The dried fibers were pulverized and then sieved to obtain maximum of 400 μ m particle size fillers using Endcotts (EFL 2MK3) sieving machine. These were used to produce the blend composites.

Blend Composites Preparation

To prepare the uncompatibilized blend and blend composites, PCL, PLA and treated palm press fibers were dried to remove moisture. The PCL/PLA (ratio 90:10) was measured and poured into a container that has cover and then mixed by shaking. A Brabender PL 2000 (Germany) twin-screw extruder was used to extrude composites at temperatures between 150 °C feed zone to 180 °C at die head and 40 rpm screw speed to achieve enough shear mixing. The Haitian (China) injection molding machine was used to inject the extruded composites at temperature of 150 °C to 180 °C to obtain standard test specimens. The same procedure was adopted to prepare the compatibilized blend and blend composites, except that in these formulations, DCP was added before the melt extrusion. The fabricated test samples were conditioned at room temperature for 48 h before testing.

Characterization of Blend Composites Morphological Studies

The morphology of fibers, blend and blend composites

were studied using Carl Zeiss Supra 35VP FESEM microscope. The blend and blend composite samples cut from the Izod impact test fractured surfaces were mounted on sample stubs using double sided adhesive tapes and sputter coated with gold. They were evaluated using FESEM at 15keV and 0.65A current.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR of the sodium hydroxide (NaOH) treated fibers, blend and blend composites was carried out using FT-IR spectrometer (Perkin Elmer spectrum one). The dry powdered fibers blend and blend composites obtained by micromechanical chipping of the injection molded samples were dispersed on KBr pellets and compacted into thin films using a hydraulic force press. The infrared spectra was obtained at 500–4000 cm^{-1} range and used to analyze changes in the chemical structure of the fibers, blend and blend composites.

Differential Scanning Calorimetry (DSC)

Melting and crystallization behaviour of the blends and blend composites were studied by using Perkin-Elmer 7 differential scanning calorimetry (Perkin-Elmer 7 DSC) under nitrogen atmosphere. 8-10 mg of each sample was sealed in aluminium pan and used for the DSC scan. The temperature was raised from 30 °C to 250 °C at a heating rate of 10 °C min^{-1} .

X-Ray Diffraction (XRD)

The crystallinity index (I_{cr}) of the fibers, blend and blend composites were determined by X-ray diffraction (XRD) using URD6, VEB CARL ZEISS-JENA diffractometer operating at 40 kV, 20 mA and $\text{CuK}\alpha$ radiation ($\lambda = 1.5406$). The crystallinity index was calculated using the Buschle-Diller and Zeronian equation as shown below

$$I_{cr} = 1 - \frac{I_{min}}{I_{max}} \quad (1)$$

Where I_{cr} is the crystallinity index, I_{min} , intensity at the minimum of the crystalline peak ($18^\circ < 2\theta < 19^\circ$) and I_{max} , intensity at its maximum ($22^\circ < 2\theta < 23^\circ$)

Dynamic mechanical analysis (DMA)

DMA was carried out using Perkin-Elmer DMA 7e instrument. Three-point bending mode measurements were carried out and the corresponding viscoelastic properties (storage and loss modulus as well as dissipation factor) were determined as a function of temperature. Rectangular shape samples of dimension 20×5×3 mm were used for the analysis. The tests were carried out under nitrogen flowing at 30 ml min^{-1} ,

temperature of -110°C to 50°C , heating rate of 3 °C min^{-1} and 1 Hz frequency.

Biodegradation Study

Study of the biodegradation behavior of the blends and blend composites were carried out using the normal soil burial test. Test samples with 40x20 mm dimensions were buried in natural soil without any composting material for a maximum of 90 days with average temperatures of 28°C and relative humidity of 80 % through out the 90 days test period. The samples were evaluated by measuring weight loss using the following equation.

$$\text{Weight loss (\%)} = \frac{W_0 - W_1}{W_0} \times 100 \quad (2)$$

Where W_0 and W_1 are the weight of samples before and after the soil burial test.

The samples were withdrawn from the burial site after 10, 30 and 90 days interval. At the end of each testing time, the withdrawn samples were washed with tap water to remove soil from their surface and then dried in an oven at 50°C until constant weight was obtained. Biodegradability was assess by comparing the weight loss before and after burial. FESEM observation of the samples were carried out to asses the surface morphologies of the samples for visual comparison.

RESULTS AND DISCUSSION

Morphological Studies

The micrographs in Figure 1 show the effect of NaOH treatment on the palm press fibers. The micrographs reveal fibrillated and rougher surfaces for the treated fibers as compared to the untreated fibers. The fibrillation and rough surfaces after treatment is attributed to the removal of natural and artificial dirt. Fibrillation of the fibers after mercerization increases the effective surface area to be wetted by the matrix thereby enhancing fiber/matrix adhesion. Also, the alkali treatment as shown by the FTIR spectrum in Figure 2 removed the hemicellulose component completely. The C=O carbonyl stretch (from hemicellulose) which appears at 1657 cm^{-1} for the untreated fibers disappeared after the alkaline treatment thereby confirming that treatment has taken place (Sgriccia et al, 2008).

The FESEM micrographs of the uncompatibilized blend, compatibilized blend and composites are shown in Figure 3. The micrograph of the uncompatibilized blend shown

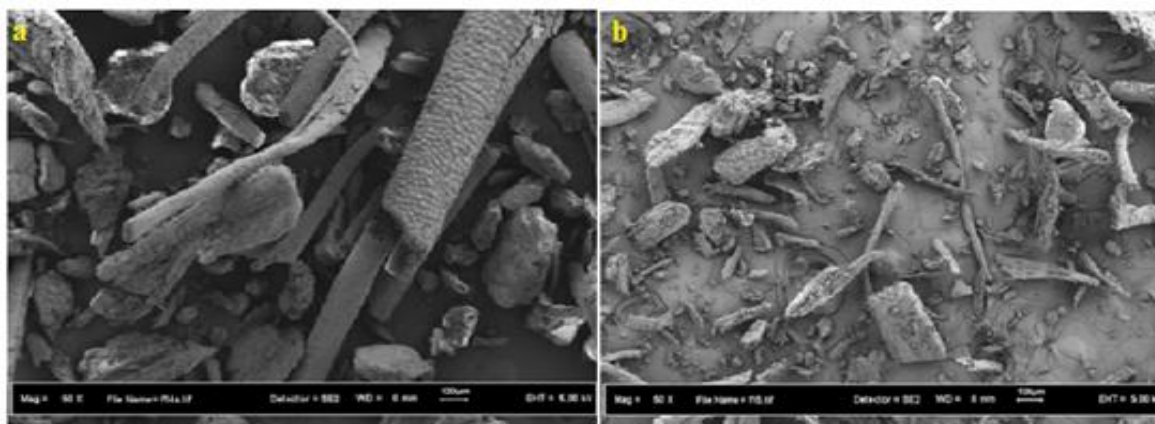


Figure 1. FESEM micrographs of (a) untreated and (b) treated fibers

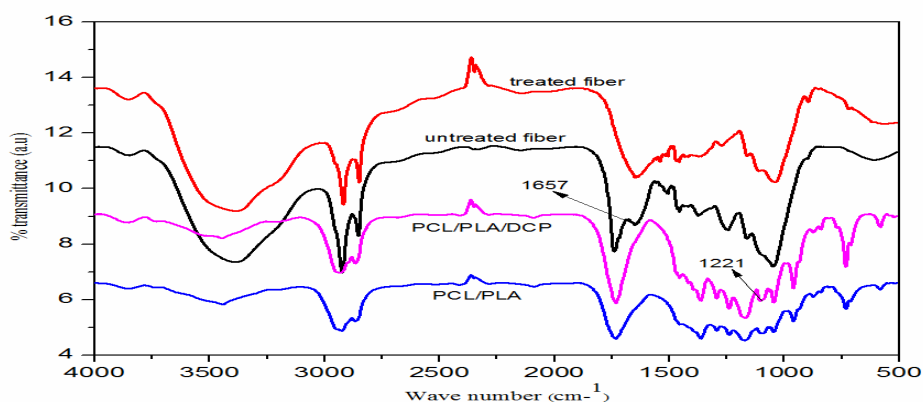


Figure 2. FTIR of treated and untreated palm press fibers

in Figure 3(a) revealed a two-phase structure. This confirms that PCL and PLA are incompatible/immiscible in the blend. PLA which is the minor phase in the blend is seen dispersed as droplets in the major PCL phase. This type of phase separation usually occurs when either of the polymer is in higher concentration. Similar observations have been reported by other researchers (Takeshi Semba., 2006). The compatibilized blend shown in Figure 3(b) reveals a uniform phase as a result of the DCP incorporation. DCP initiates crosslinks between PCL and PLA thereby making the blend compatible (Mishra et al, 2011; Takeshi et al, 2006). The C-C bond which appeared at 1221 as shown in Figure 2 is evidence of the crosslink formation after DCP is incorporated into the blend. The alkaline treatment of the fibers and the elastomeric nature of the blend after DCP addition enhanced the wet ability between fiber/matrix, thus improving the interfacial adhesion between the matrix and fibers. The improved adhesion between matrix and fiber is the cardinal reason behind the mechanical

properties enhancement as reported in our published work (Akos, 2013). The micrograph in Figure 3(c) shows evidence of fiber bundle formation and poor adhesion at high fiber loading as indicated by the circle and arrows. The portion circled in Figure 3(c) shows two fiber surfaces in contact without any polymer matrix between them. The arrows in that same micrograph reveal the gap between the fiber surface and matrix phase which confirms the absence of interfacial adhesion between the fibers and matrix as a result of fiber bundle formation. Figure 3(d) reveals good fiber/matrix adhesion after compatibilization as shown by the arrows. The evidence of good fiber/matrix adhesion and viscous flow is revealed in Figure 3(d) (Alavi et al, 2013). The arrows in Figure 3(d) show adhesion and interaction between the fiber and the blend matrix.

Differential Scanning Calorimetry

Table 1 presents the glass transition temperature (T_g),

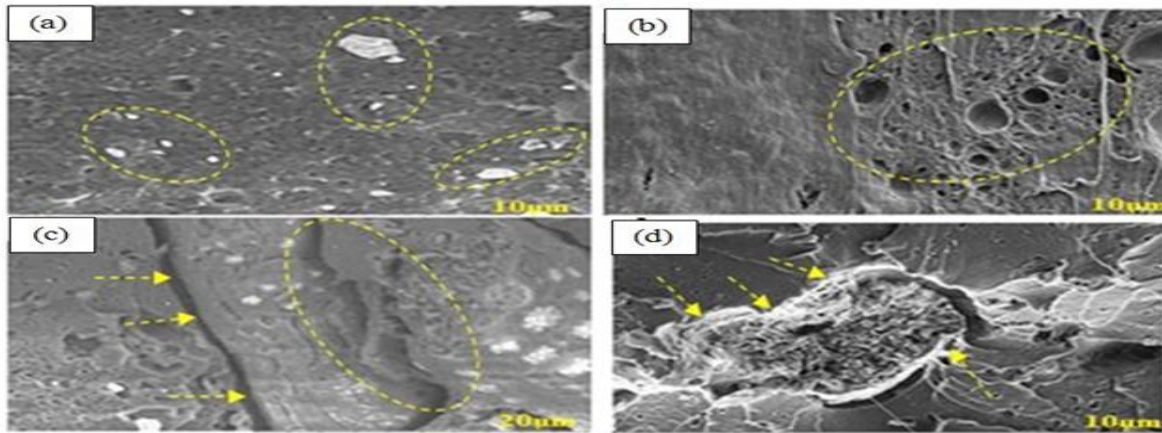


Figure 3. FESEM micrographs of (a) PCL/PLA (90/10), (b) PCL/PLA/DCP (90/10/0.01phr) (c) PCL/PLA/DF (90/10/25), (d) PCL/PLA/DF/DCP (90/10/10/0.01phr)

Table 1. DSC scans of virgin polymers, blends and blend composites

Composition	Glass transition temperature, T_g (°C),	Crystallization temperature, T_c (°C)	Melting point, T_m (°C)	Crystallinity, X_c (%)
Neat PCL	Not observed	Not observed	54.3	46
Neat PLA	75.6	101.3	143.8	12
PCL/PLA	Not observed	104.0	48.3/127.6	37/12
PCL/PLA/DCP	Not observed	Not observed	42.5/127.3	32/11
PCL/PLA/DCP/10	Not observed	108.0	41.4/128.7	23/9
PCL/PLA/DCP/15	Not observed	107.4	41.8/128.6	26/11
PCL/PLA/DCP/20	Not observed	89.9	41.8/127.1	36/12
PCL/PLA/DCP/25	Not observed	88.4	41.8/127.3	35/9

crystallization temperature (T_c), melting temperature (T_m) and percentage crystallinity (X_c) obtained from DSC scans of the neat polymers, blends and blend composites. T_g is not observed for PCL, PCL/PLA and PCL/PLA/DCP because PCL, the major phase in the blends has negative T_g (-60°C). In the blends, the T_g of PLA is not observed because PCL being the major phase with a negative T_g masked the T_g of PLA as such it was not observed. A drop in T_m and X_c which was more pronounced in the compatibilized blend was observed. Compatibilization with DCP results in cross linking thereby hindering orderly polymer chain arrangement. As a result of the hindered chain arrangement, the crystallinity of the blend is reduced (Inoue and Suzuki, 1995). The percentage crystallinity for the blend composites was observed to be lower as compared to that of the pristine blends at low fiber loading. However,

an initial rise in crystallinity was recorded as fiber load increased from 10 wt% to 20 wt% after which it dropped at 25 wt% fiber loads. The initial increase in X_c as fiber load increases was attributed to the possibility that the fibers acted as nucleating sites during the composites preparation (Ahmad and Luyt, 2012). The drop in X_c at 25 wt% was attributed to the possible inhibition of the crystallization process as more fibers were incorporated into the blend (Campos et al, 2012). The T_c of the composites was observed to drop as fiber load increased from 10 wt% to 25 wt%. This was also attributed to the inhibition of the recrystallization process at high fiber loading. Fiber loading was observed to generally reduce the thermal stability of the composites as compared to their virgin counterparts.

Figure 4 is a graphical presentation of the dynamic storage modulus (G') for the blends and composites. G'

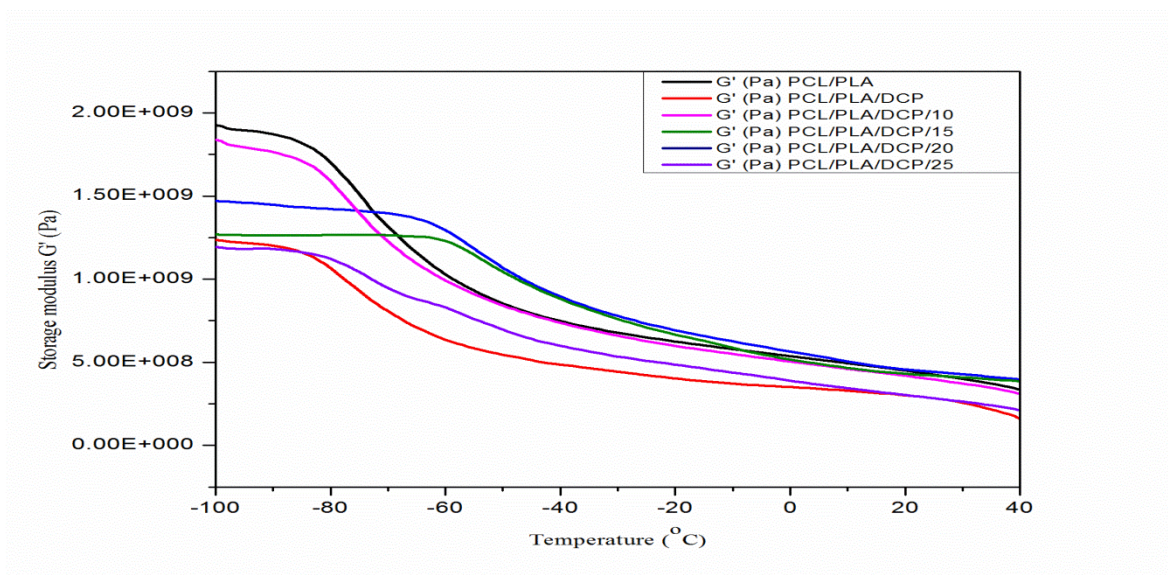


Figure 4. Dynamic storage modulus of blends and blend composites

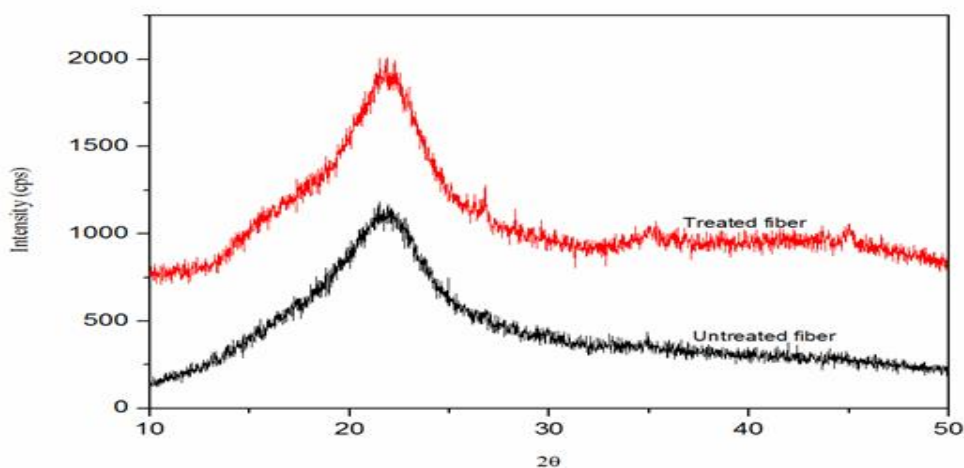


Figure 5 XRD of palm press fibers

for the blend composites slightly dropped as temperature rises from -100°C to -62°C after which a rapid drop was observed. The rapid decrease in G' beyond -62°C is attributed to the glass transition temperature, T_g of PCL. Poly(ϵ -caprolactone) reaches its minimum T_g value around -62°C .

X-Ray Diffraction

The XRD traces of untreated and treated fibers are as shown in Figure 5. Considering the peak areas obtained by integration in relation to crystallinity; the larger the area of the peaks, the more crystalline the material is.

The peak area for the untreated fiber was 3814 as compared to 5148 for the treated fiber. This implies increase in crystallinity after treatment. The percentage crystallinity of the fibers increased from 41 % for the untreated fiber to 53 % for the treated fibers. The crystallinity increase after alkaline treatment was attributed to the removal of materials that cement the cellulose chains together. As a result of this, better rearrangement and packing of the cellulose chains takes place. Also, NaOH treatment decreases the spiral angle and increases molecular orientation (Mohanty et al, 2001). In the mercerized cellulose, the orientation of parallel chains in cellulose I is transformed to anti-parallel

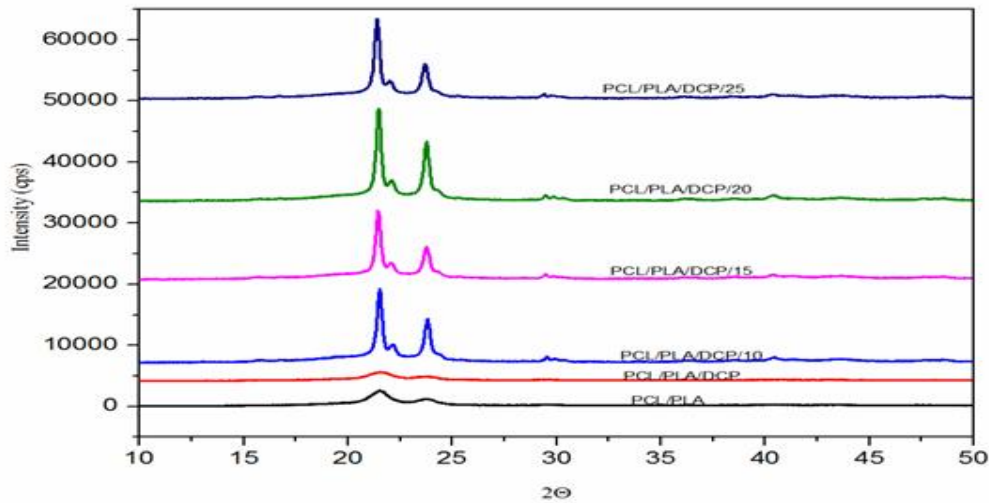


Figure 6. XRD of blends and blend composites

orientation in cellulose II without dispersion of the intermediate molecules of cellulose (Klemm et al, 2005; Zugenmaier, 2001).

The XRD patterns of the blends and blend composites are as shown in Figure 6. The crystallinity of the composites is discussed in respect of the peak areas obtained by integration and the crystallinity index. For the blends and blend composites, an increase in the peak area indicates increase in crystallinity. The uncompatibilized blend was observed to have higher crystallinity than the compatibilized blends. This was attributed to the incorporation of DCP. As earlier observed, compatibilization results in restricted polymer chain rearrangement because of the cross links. This reduces the crystallinity of the composites. The peak areas of the composites increased from 9506 to 11593 at 15 wt% fiber load after which it dropped to 8095 at 25 wt% loading. A similar trend was observed for the crystallinity index as fiber load increased from 10 wt% to 25 wt%. The incorporation of fibers into the compatibilized blend was observed to increase the composites crystallinity. Also, the blend composites still showed clear crystalline PCL phase peaks. Similar observation have been reported for PCL/Starch nanoclay composites by other workers (Vertuccio et al, 2009). The typical PCL peaks appeared at $2\theta = 21.3^\circ$ and 23.7° . Ramesh *et al* reported similar findings (Neppalli et al, 2010). The characteristic peaks of PLA which were expected to appear at $2\theta = 16.4^\circ$ and 18.6° (Hsin-Tzu, 2009) were absent. This was attributed to the low crystallinity and possibly the quantity of the PLA in the blends and blend composites. The PCL which makes up 90% of the blend might have suppressed the expected

PLA peaks from appearing. Similar observation of low quantity and crystallinity for electrospun nylon fibers used as fillers in PCL matrix has been reported (Neppalli et al, 2010). The crystallinity of the composites was observed to increase with fiber loading upto 15 wt% after which it dropped. The initial increase up to 15 wt% fiber loading was attributed to the good interaction between the fibers and the blend matrix. Also, the fibers at this stage were acting as nucleating centers (Campos et al, 2012; Campos et al, 2013). The fibers behavior as nucleation centers allowed recrystallization of the polymer matrix to occur. The drop in crystallinity above 15 wt. % fiber load is attributed to inhibition of nucleation which only allows crystal growth to continue (Campos et al, 2012).

Biodegradation

One important factor that determines the fate of materials is their performance in outdoor applications. The durability of products is of major concern no matter the application area, partly due to maintenance, usefulness during life time and replacement. The degree of interaction between the materials and the environment determines how they deteriorate (Alexandre and Dubois, 2000; Mohanty et al, 2001).

In this work, the blend composites were withdrawn from the burial site after 10, 30 and 90 days interval. However, only the FESEM micrographs for the 90 days biodegradation are presented in this discussion. The weight loss recorded after 10, 30 and 90 days burial are presented graphically in Figure 7. After 10 days soil burial, the neat polymers and unfilled blends retained their weight. The weight retention by the pristine polymers and blends after the 10 days burial period was

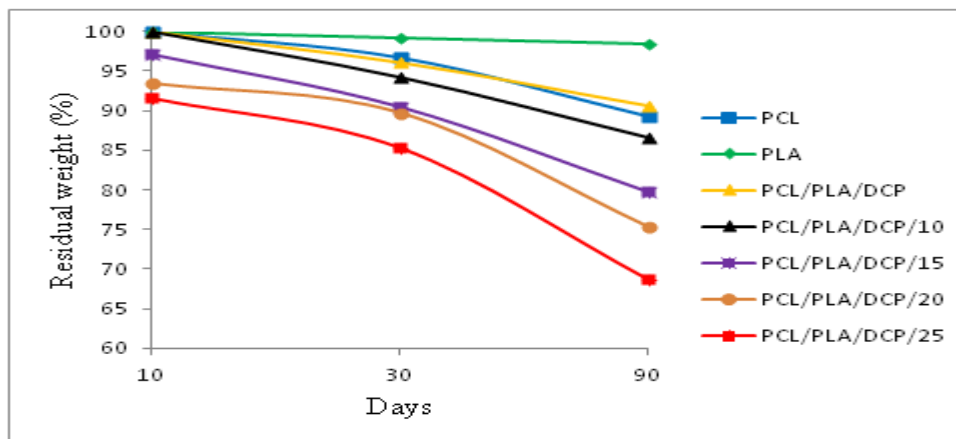


Figure 7 Residual weights of neat polymers, compatibilized blend and blend composites

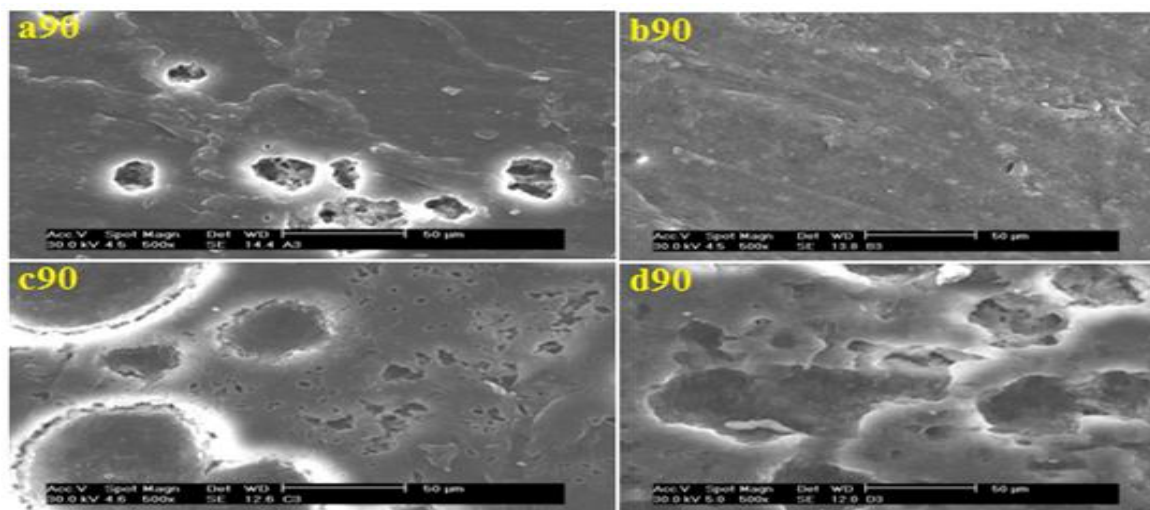


Figure 8 FESEM micrographs after 90 days soil burial (a90) PCL (b90) PLA (c90) PCL/PLA/DCP (d90) PCL/PLA Mag

attributed to their hydrophobic nature. The hydrophobic behavior of the pristine polymers and blends delayed their interaction with moisture, an essential component in degradation and surface erosion process (Hakkarainem, 2002). There was noticeable reduction in weight for both the compatibilized and uncompatibilized blend composites after the 10 days burial period. The weight loss for the blend composites slightly increased as fiber load increases from 10 wt% to 25 wt% as shown in Figure 7. The weight loss was attributed to the activity of microbes on the incorporated fibers and probably surface erosion of the PCL by hydrolysis. Similar observations have been reported by other workers (Hakkarainem, 2002; Tsuji et al, 1998).

The small holes which appear on the composite surfaces after 10 days (micrographs not shown) are evidences of

activities of microbes on the fibers which contributed to the weight loss. As hydrolysis of the major phase and microbial activity progressed over the 90 days burial period, the surface erosion and fragmentation of the composites became more pronounced as shown by the FESEM micrographs in Figure 8 and Figure 9 and also evidenced in the weight loss (Figure 7). The FESEM micrographs reveal more microbial activity on the neat PCL and the PCL/PLA/DCP blend than in neat PLA and the PCL/PLA blend. This was attributed to the surface erosion of PCL through hydrolysis and also the compatibilization effect on the blend.

Biodegradation of the blend composites was observed to increase in the compatibilized composites as revealed in the micrographs (Figure 9). This was attributed to the effect of the DCP compatibilizer and fiber incorporation. Compatibilization with DCP results in crosslinking which

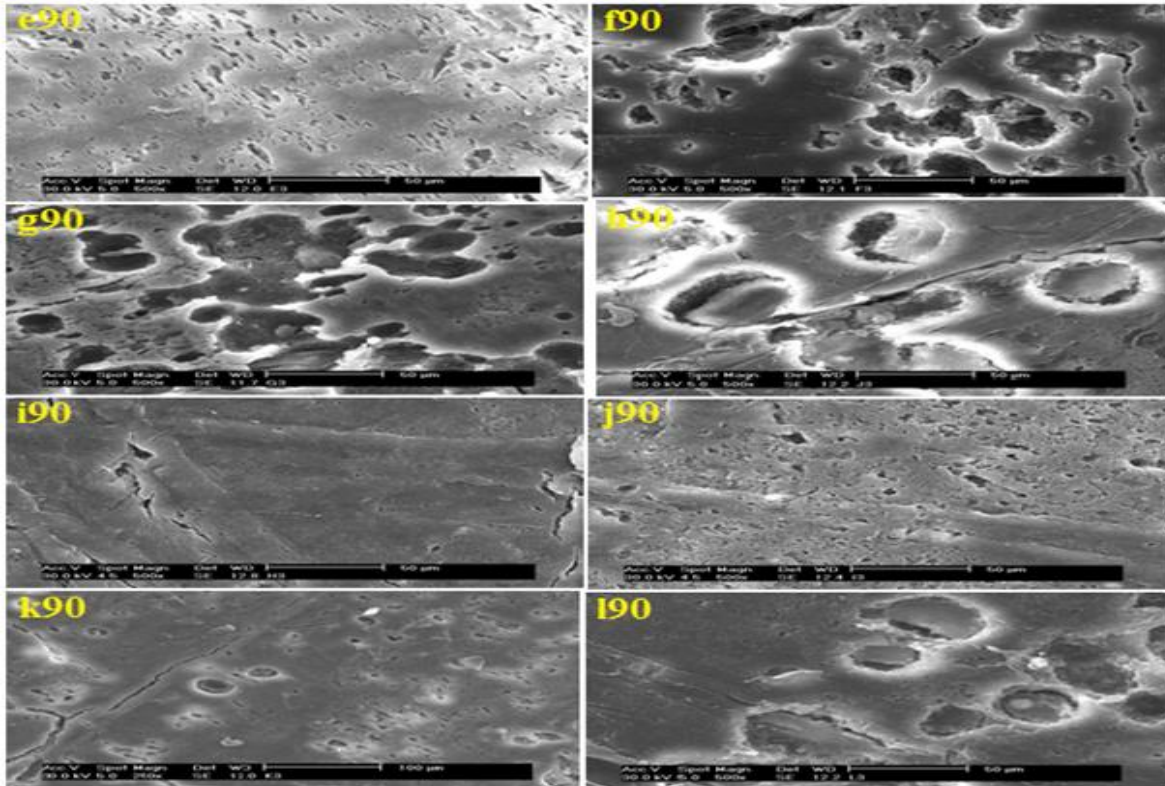


Figure 9 FESEM micrographs after 90 days soil burial (e90) PCL/PLA/DCP/10 (f90) PCL/PLA/DCP/15 (g90) PCL/PLA/DCP/20 (h90) PCL/PLA/DCP/25 (i90) PCL/PLA/10 (j90) PCL/PLA/15 (k90) PCL/PLA/20 (l90) PCL/PLA/25 Mag. x500

hinders orderly polymer chain arrangement. The hindered polymer chain arrangement reduces the crystallinity of the composites (Inoue and Suzuki, 1995). The reduction in crystallinity implies increase in the amorphous regions of the composites thereby creating voids for microbes to have more access to the composites. Fiber incorporation which results in depression of crystallinity of the PCL phase accelerate the degradation effect (Zhao et al, 2008). Another reason attributed to the increase in degradation with fiber load is the effect of fiber bundle formation due to poor distribution of the fibers in the matrix. The formation of fiber bundles implies poor adhesion in the system. Poor adhesion allows easy access by moisture and microbes into the composites thereby accelerating degradation. The reduction in weight by the PLA phase was very slow. This was attributed to the much higher temperatures (between 55-70°C) and compost soil required by PLA to initiate the first step hydrolysis of its ester linkages before microorganisms can act on the low molecular weight products (Manuela et al, 2004). These conditions were absent during the test period. The average temperature during the entire test period was 28°C. This was also a likely contributing factor for the slow biodegradation rate of the entire composites over the 90 days period.

CONCLUSION

PCL/PLA blend composites were successfully prepared using mercerized palm press fibers obtained from the Dura oil palm species. Alkali treatment increased the crystallinity of the fibers and DCP improved the blend compatibility but reduced its crystallinity. Studies of the biodegradation and crystallinity of the blend and composites showed that compatibilization and fiber reinforcement accelerated the rate of biodegradation of the blend composites. Incorporating the treated fibers up to 15 wt% fiber load into the blend enhanced the composites crystallinity, and the rate of biodegradation increased as fiber load increased from 10 wt% to 25 wt% in the blend composites.

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