

Characterisation of Esparto Grass Fibers Reinforced Biodegradable Polymer Composites

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The natural fiber / polylactic acid (PLLA) composites were prepared with Alfa-Alfa fibers as reinforcement and PLLA as matrix. The composite materials were obtained through the simple mechanical compounding of PLLA matrix with various fibers contents up to 40 wt %, followed by drying, kneading and hot pressing into sheets and were characterized by TGA, DSC, FTIR spectroscopy, SEM and water uptake. Composites prepared from several percentages of PLLA and Alfa-Alfa fibers represent a new category of environmentally safe materials for applications to explore to reduce the raw materials cost of PLLA due to Alfa-Alfa fibers is an abundance local plant in Algeria, the increasing utilization of renewable resources will be one of the strong drivers for sustainable products.

Key words: Polylactic acid (PLLA), Alfa fibres, Composites, Thermal properties.

The biocompatibility of natural fibre-reinforced biopolymers, also known as bio composites, makes them attractive alternative to glass fibre-reinforced petrochemical polymers.

Natural fibers have recently become attractive to researchers, engineers and scientists as an alternative reinforcement for fiber reinforced polymer (FRP) composites. Due to their low cost, fairly good mechanical properties, high specific strength, non-abrasive, eco-friendly and biodegradability characteristics, they are exploited as a replacement for the Conventional fiber such as glass, aramid and carbon.

Petroleum- based polymers are known to cause an environmental problem due to non degradable of disposal daily items such as food utensils, packaging containers and trash bags.

In line with this, researchers are now focusing on environmental friendly plastic, so

called bio plastic for green environment.

In recent years, the use of natural/biofiber reinforced composites has rapidly expanded due to the availability of natural/bio-fibers derived from annually renewable resources, for use as reinforcing fibers in both thermoplastic and thermosetting matrix composites as well as for the positive environmental benefits gained by such materials¹⁻⁶.

In addition, the low cost and high specific properties of these natural fibers provide significant performance with advantages and economic benefits when combined with commodity biodegradable polymers^{2,3}. Recently, poly lactic acid (PLA) has attracted increasing interest because this polymer can be manufactured from renewable resources, e.g. corn starch, to yield articles for use in textiles, industrial packaging or for biocompatible/ bio absorbable medical devices^{2, 7}.

Polylactic acid is linear aliphatic polyester its chemical structure is $-(\text{CH}_2\text{CHO}-\text{CO})_n-$ The monomer used to synthesize PLA is obtained from microbial fermentation of sugars such as glucose and hexose. Usually, the commercial PLA is a poly-L-lactic acid (PLLA) and poly-DL-lactic

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(PDLLA) copolymer^{8,9}. Polylactic acids (PLA) are expensive in comparison to conventional thermoplastics and they are sometimes too weak for some applications. The important thing is that it is considered as “green polymer” being available from renewable agricultural resources by the combination of fermentation and polymerization; thus, its production consumes less fossil resources than comparable petroleum-based plastics. With PLA, carbon dioxide is removed from the atmosphere when growing the feedstock crop, and returned to the earth when the polymer is degraded. To reduce the cost and improve the material properties without interfering its “Green polymer” image, researchers are trying to prepare natural fiber reinforced bio-composites. Short fiber, non woven mat or woven fabrics have been used to prepare bio-composites several papers have reported the preparation of natural fiber reinforced PLA composites but the low compatibility of hydrophobic PLA with hydrophilic natural fibres leads to a composite with poor mechanical

Properties¹⁰. Research is also being conducted on the potential of cellulose-based fibers as reinforcement for polymers, because cellulose materials offer many potential advantages¹¹⁻¹³. Abundant renewable source, inexpensive, low cost, flexibility during processing, desirable fiber aspect ratio, low density, high specific stiffness and strength, biodegradability, reduced wear of the processing machinery, etc. Moreover, considering the extensive intermolecular hydrogen-bonding potential resulting from the surface rich in hydroxyl groups, cellulose has the potential for strong interaction with polar thermoplastics polymers¹⁴.

However, as a result of their low thermal stability during processing, and poor dispersion in the polymer melt, use of cellulose fibers in thermoplastics in general has not been extensive¹⁵. Generally, the utilization of natural fibers as reinforcing materials in thermoplastics requires strong adhesion between the fiber and the polymer matrix. Cellulose has a strong hydrophilic character due to three hydroxyl groups per monomeric unit, but biopolymers like PLA are generally hydrophobic.

Cellulose fibers are attractive reinforcing fillers for thermoplastics, which can reduce material costs and improve certain properties¹⁶⁻¹⁸. Natural fibres are increasingly used as replacements for

glass and other non-renewable fibres in composite materials mainly because they are abundant, cheap and renewable. Their other advantages include low density, high toughness, comparable specific strength properties, reduction in tool wear, low energy consumption in fabrication, and CO₂ neutrality¹⁹. Bio composites (green composites) are a class of composite materials obtained by blending natural fibers with biodegradable polymers, which implies that they should be fully biodegradable. Bio composites are gaining considerable and growing interest to the detriment of petroleum-derived counterparts because of their renewable character, environmental friendly connotation and interesting performances^{20, 21}. Green composites are materials having eco-friendly attributes that are technically and economically feasible while minimizing the generation of pollution.

Plant fibers are long regarded as being promising candidates for replacing conventional reinforcing fibers (e.g. glass fibers) in composites for semi-structural and even structural applications.

The availability of inexpensive plant fibers everywhere in the world has contributed to their use as reinforcement in greener composites. The non-abrasiveness to the processing equipment, the possibility to be incinerated and still keep the CO₂ neutrality are recognized as being the main advantages as well²². Alfa fibres are extracted from the plant *Stipa tenacissima*, or esparto grass (Halfa is the Arab name for esparto), and grows in the dry regions of North Africa. It belongs to the graminaceae family and grows to a height of about 1 m. These fibres are mostly used in the production of paper. Recently, they have been used as reinforcement in the production of biodegradable composites²³.

In this paper, we have used esparto grass fiber to prepare the bio-composites.

In this work, halfa fibre has been added to the bio-composites and the properties of the composites with and without the addition of Alfa-Alfa fibers have been evaluated and discussed.

EXPERIMENTAL

Materials

PLLA samples were dried at 80°C until they completely dried.

Alfa-Alfa fibres are cellulose-based fibres

extracted from the Algerian esparto grass and was subjected to several pretreatments, i.e. washing with water, drying under ambient conditions for 24 h then in a drying oven at 50°C for 24 h.

The cellulose was extracted from Alfa plant with 400 ml toluene/ethanol mixture (2/1, V/V) for 6 hours using Soxhlet apparatus and treated with NaOH (1M) for 8 hours at 25°C²⁴. The extracted fiber of esparto grass are immersed in soda solution (NaOH, 0.25 N), H₂SO₄ (2N) is added as reducing agent to protect the cellulose against oxidation with NaOH at a temperature of 50°C with continuous stirring for 2 h.

The Alfa- Alfa fibers are then picked up and rinsed 4 to 5 times with distilled water in order to eliminate excess of soda. The residue obtained is then bleached using a 40 % diluted sodium hypochlorite solution NaClO during 1 hour in ambient temperature. Finally, the sample is rinsed with water several times and then dried at 80°C until they are completely dry.

Preparation of composites

Preparation of Alfa-Alfa/PLLA composites

PLLA and fibers were dried at 80°C for 24 h before processing and mixed mechanically at 100 rpm with Bra bender (Plastograph EC GmbH & Co.KG) at 183°C for 8 min.

In order to obtain the desired specimen samples for various measurements and analysis, the molten composite samples, was put in liquid nitrogen and transferred to the miller cutter Retsch, a small sample of composite was obtained.

The Alfa-Alfa /PLLA performs were dried at 80 °C for 12 h before hot pressing at 2.45 MPa with laboratory press (Collins) at 180°C for 5 minutes. Finally, the specimens were cooled slowly. In this experiment, 3 different types of specimens were prepared: pure PLLA, PLLA-Alfa/Alfa fibers (60/40) composites, and PLLA-Alfa/Alfa fibers (80/20) composites. The prepared composites were cut into specific-sized specimens for various characterizations.

Characterization

Fourier transform infrared spectroscopy

FTIR has been proven to be an effective technique to investigate interfacial bonding in polymer composites. The fibres and composites was studied by FTIR measurements in attenuated total reflectance mode (ATR) using the Nicolet Avatar 360 FTIR spectrophotometer. Two hundred scans

were collected for each measurement over the spectral range 4000-650 cm⁻¹ with a resolution of 4 cm⁻¹. The IR spectra were presented in absorbance and were assembled in a common scale.

Differential scanning calorimeter:

The melting and crystallization behavior of the composites were studied using a differential scanning calorimeter (DSC Mettler TA 15), under a nitrogen atmosphere. The data were collected by heating the composite specimen from 30°C to 230°C then cooling and heating again at a constant heating rate of 5°C /min.

Thermogravimetric analysis

Thermo gravimetric analysis was carried out by a Perkin- Elmer Thermo gravimetric / Differential thermal analyzer (Pyris Diamond TG/ DTA).

The samples were scanned from 30 to 600 °C at a heating rate of 20°C /min in the presence of nitrogen.

Scanning electron microscopy

In general, SEM is used to observed the topography of a specimen .the function of SEM is as a mapping device which probed by a beam of electron scanned across the surface.

The morphology of impact fracture surfaces of the composites was observed by scanning electron microscope (SEM) at room temperature. A JEOL (Quanta FEI 200 FEG Apparatus) SEM with field emission gun and accelerating voltage of 10 kV was used to collect SEM images for the composite specimen. A gold / palladium coating of a few nanometres in thickness was coated on impact fracture surfaces. The samples were viewed perpendicular to the fractured surface.

Water absorption test

Moisture uptake was determined by measuring the weight periodically by soaking the specimen in water. The specimens were obtained by cutting according ASTM D5229, with 6.3 X 3.5 X 65 mm³ dimensions were used. Prior to absorption experiments, the samples were dried until the weight stabilized at 51°C for 24 hours. The specimens were then immersed in distilled water at room temperature and the weight change monitored as a function of time. The absorption behavior weighed at 24, 48, 72, 96, and 120 up to 250 hour within 5 min of removing from the liquid water, was studied.

RESULTS AND DISCUSSION

Infrared spectroscopy analysis

Alfa fibres were studied by (Fig.1). The bands at 1160 cm^{-1} , the major absorbance peak reflecting the C-C ring of the carbohydrate backbone of cellulose. The C-O-C glycosidic bond of cellulose was detected by the stretching vibration band to 1100 cm^{-1} . The C-OH of the cellulose backbone (C-O secondary and C-O primary alcohols) corresponded to the 1056 cm^{-1} and 1030 cm^{-1} peak, respectively. Peaks due to alcohol groups of cellulose (OH deformation) were located at 1360 cm^{-1} and 1320 cm^{-1} while the peak at 1315 cm^{-1} corresponded to CH_2 wagging of cellulose. The 1426 cm^{-1} band was attributed to the CH_2 bending of cellulose^{25, 26}. The band observed in the 3340 cm^{-1} region was mainly related to the OH groups.

The control of PLLA structure is done using the band at $1748\text{--}1757\text{ cm}^{-1}$, corresponding to C=O Stretching and C-O bands of ester group at $1300\text{--}1000\text{ cm}^{-1}$ region. IR spectra of PLLA revealed characteristic absorption peaks of ester (1759 and 1092 cm^{-1} For COO- and -O- respectively) and CH_2 and CH_3 groups ($2949\text{--}3000\text{ cm}^{-1}$), bands corresponding to bending vibrations of CH_3 (asymmetric and symmetric) were found in 1433 and 1511 cm^{-1} in polymer spectrum.

For the composite PLLA-Alfa fibers the bands are stronger in the regions 1750 cm^{-1} especially in composite PLLA-ALFA (80/20) than composite (60/40), the same thing observed in $1000\text{--}1200\text{ cm}^{-1}$ and this is may be due to increased amount of PLLA, all bands in the region $3100\text{--}3600\text{ cm}^{-1}$ were absent due to processing temperature of composites.

Alfa-Alfa fibers TGA curve

Initial weight loss at 70°C is due to the presence of small amount of moisture in the

Table 1. Compositions of PLA/Alfa Alfa Fibers bio composites prepared

Samples	PLLA matrix (g)	Alfa fiber (g)
PLLA	50	0
PLLA-Alfa fibers (60/40)	30	20
PLLA-Alfa fibers(80/20)	40	10

Thermogravimetry analysis

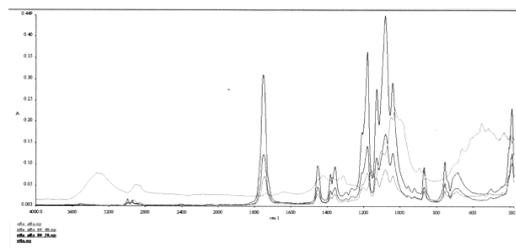


Fig.1. Spectrum of treated, Untreated fibers and PLLA

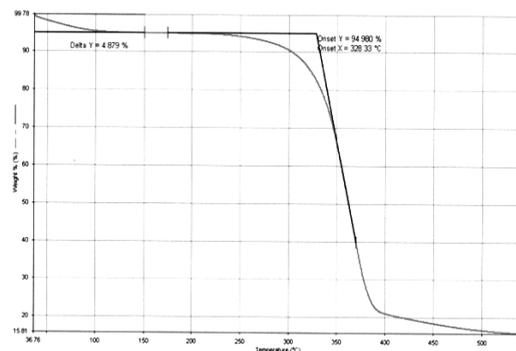


Fig. 2. TGA curve of Alfa-Alfa fibers

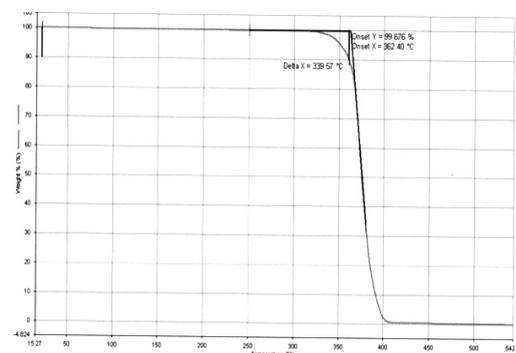


Fig. 3. TGA curve of PLLA

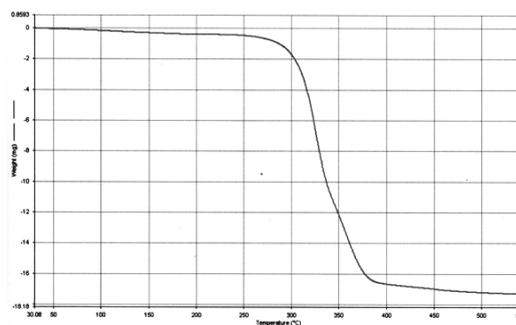


Fig. 4. TGA curve of PLLA/ Alfa-Alfa Fibers (60 /40) composite

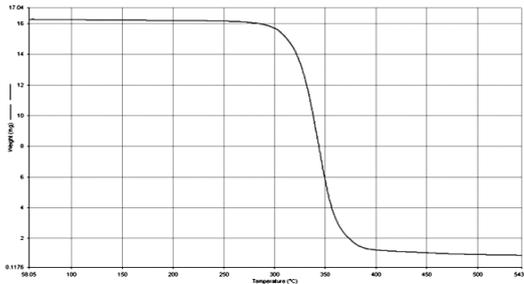


Fig. 5. TGA curve of PLLA- Alfa-Alfa Fibers (80/20) composite

sample, the second loss is due to the loss of CO₂ and the rate of weight loss increased with increase in temperature till degradation at 350°C.

TGA curve of PLLA

PLLA appears single step in the thermal degradation between 350°C and 400°C. It is due to decomposition of the scission of main chain such as the ester linkage.

TGA curve of (60 /40) and (80/20) composite

Figs.4.5. shows that the temperature of the beginning of degradation of (80 /20) composite was Greater than those of (60 /40) composite. The decrease of the stability of (60 /40) composites is probably due to the polarity of the fibers, which increased in the case of (60/40) composite.

Differential Scanning calorimetry DSC

DSC curve of neat PLLA

In first run of PLLA spectre the T_g (glass transition) was at 67.92 °C and the peak of melting point was at 170°C but in 2 run there is three regions: the Tg onset at 58.79°C the mid point at 62.38°C.

The crystallization peak was observed at 119.23°C.

DSC curve of neat Alfa-Alfa fiber

Differential Scanning calorimetry DSC

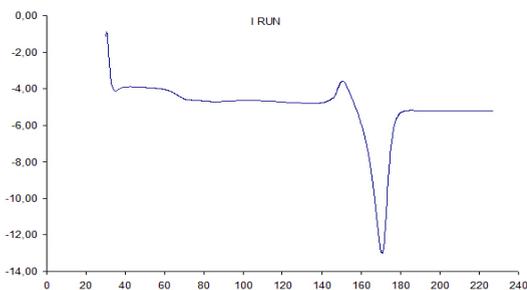


Fig. 1. DSC curve of PLLA (I run)

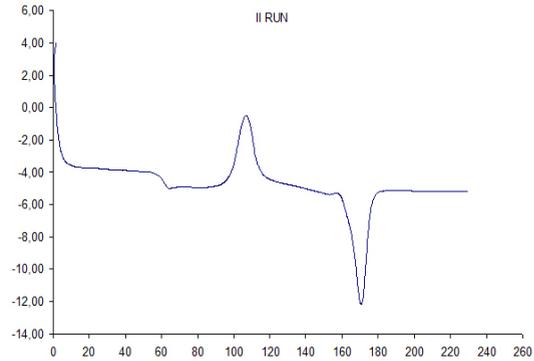


Fig. 2. DSC curve of PLLA (II run)

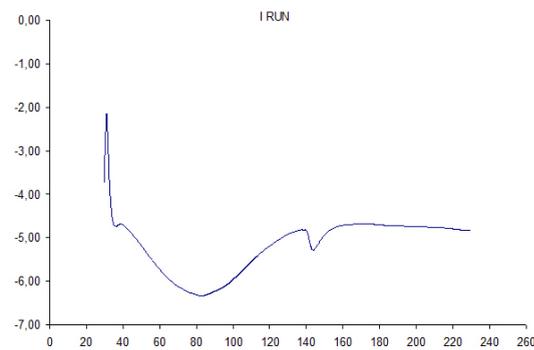


Fig. 3. DSC curve of Alfa fiber (I run)

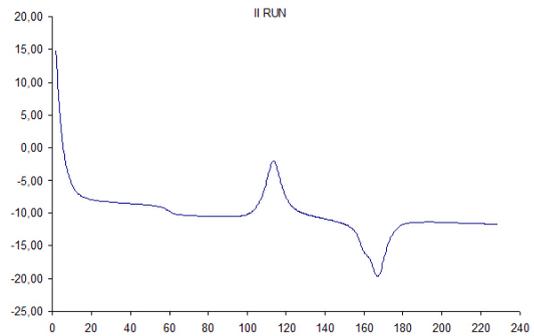


Fig. 4. DSC curve of Alfa fiber (II run)

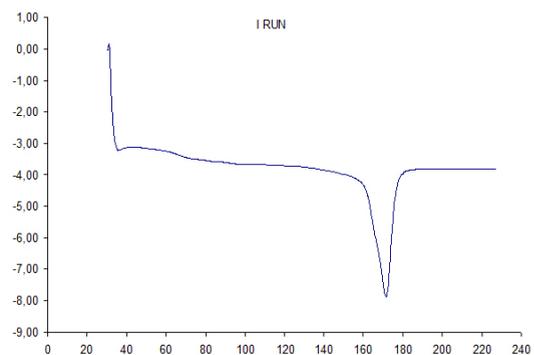


Fig.5. DSC curve of PLLA/Alfa fiber (60/40) composite

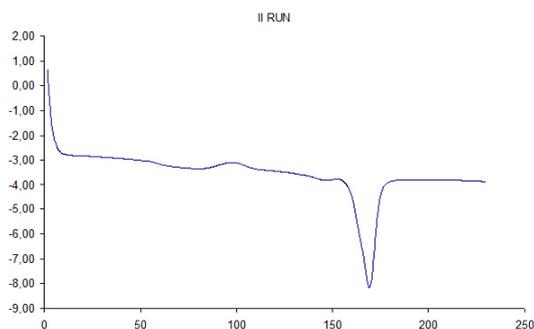


Fig. 6. DSC curve of PLLA/Alfa fiber (60/40) composite

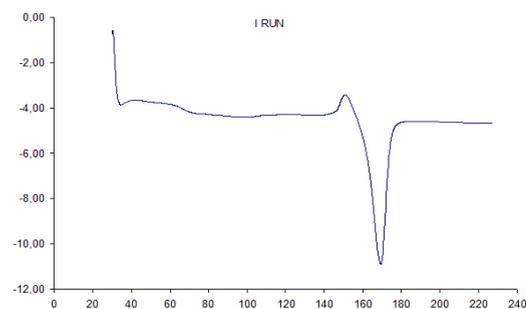


Fig. 7. DSC curve of PLLA/Alfa fiber (I run) (80/20) composite

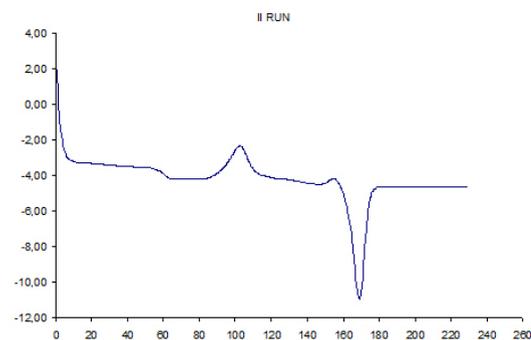


Fig. 8. DSC curve of PLLA/Alfa fiber (II run) (80/20) composite

Cellulose shows one big endothermic curve at 80° C; from the curve the cellulose decomposition higher then 200° C.

DSC curve of PLLA-Alfa-Alfa fibers (60/40)

In first run the Tg observed at 68.31°C but the crystallization was not detectable the peak observed at 171.69°C was the peak of melting point.

In second run the Tg was observed at 58.25 °C the crystallization peak at 98.18°C and the melting point at 169.33°C during the cooling there is crystallization at 102.84°C.

DSC curve of PLLA-Alfa-Alfa fibers (80/20)

The first run the Tg was observed at 67.12 °C and the melting point observed at 168.77 °C, in the second run the Tg was observed at 60.89 °C, the peak at 115.25 was the peak of crystallization

The melting point was found at 167.67°C.

TGA curve of PLLA

The DTG indicating that there is principally one reaction stage during thermal degradation of the Polymer and that is most probably associated with the loss of ester groups²⁷.

Neat PLA exhibited a one-step decomposition profile with a single transition temperature, as demonstrated by TGA. The TGA peak temperature is the temperature at the beginning point of the most weight loss, while the final is the temperature at the end of the degradation. These two points can be determined easily using the derivative graph. The profile for the neat polymer showed that the biodegradable PLLA its peak of degradation was at 362.40°C and it was completely decomposed at 396.28°C.

Scanning Electron Microscopy

The morphology of the alfa-alfa fibers was investigated by SEM as shown in Fig.9. Demonstrate that fibers are totally separated by chemical treatment. From fig.10, it illustrates that the topology of the pure PLLA is relatively smooth and no voids are observed.

The fiber-matrix interface in the composites was also investigated by SEM. SEM micrographs of the impact fracture surfaces of the composites (60/40) in Figs.11, 12 and composite (80/20) are displayed in Figs.13, 14.

The SEM micrograph shows that the addition Alfa-Alfa to PLLA matrix results in a gross phase segregation morphology. In the case of composite samples, the micrograph reveals that no cracks are visible on the surface.

Figs.11, 14, illustrates a better dispersion of the treated Alfa-Alfa in the PLLA matrix resulting from a good compatibility between organophilic treated Alfa-Alfa fibers and organic matrix.

These micrographs illustrate the individual separation and dispersion of the cellulose fibers in the form of single fibers, which indicates that the cellulose fibers have been separated during the extrusion process and well dispersed in the PLLA

matrix. Some fibers are tightly connected with the matrix, and some cellulose fibers are broken and/or torn up.

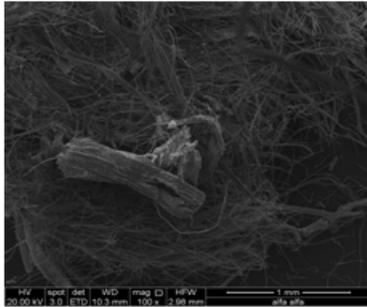


Fig. 9. SEM micrographs of Alfa -Alfa fibers

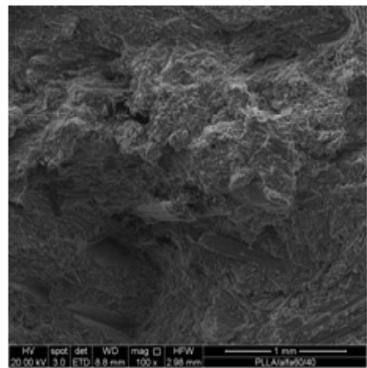


Fig. 11. SEM micrographs of PLLA-Alfa fiber (60/40) composite

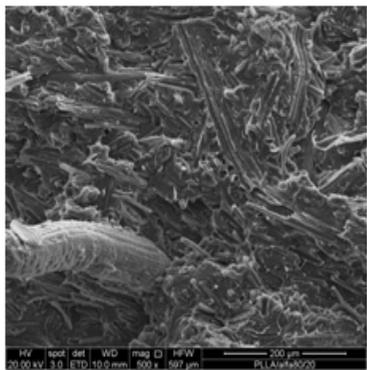


Fig. 13. SEM micrographs of PLLA-Alfa (80/20) composite

Water absorption and physical changes

Water absorption behavior of the composite is a concern in composites structural

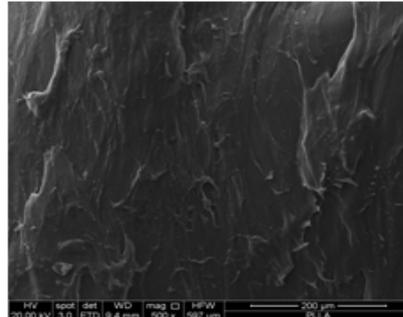


Fig. 10. SEM micrographs of PLLA

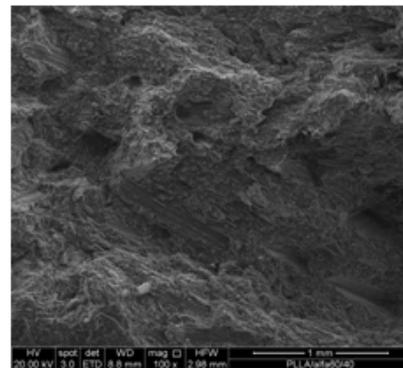


Fig. 12. SEM micrographs of PLLA-Alfa fiber (60/40) composite

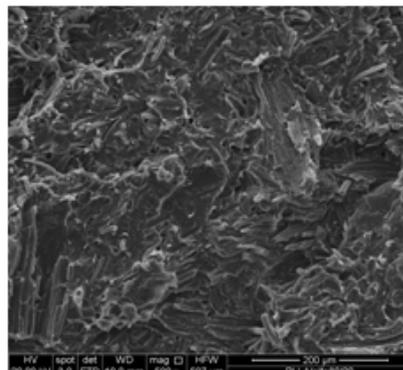


Fig. 14. SEM micrographs of PLLA-Alfa (80/20) composite

applications. The water absorption property depends on the percentage content of the fiber, fiber orientation, temperature, area of the exposed surface, permeability of fibers, void content, hydrophilicity of the individual components etc.²⁸.

Fig.15. Shows the moisture content of composites for composites and flexural specimen in distilled water. Weight gain rate (%) was calculated by:

$$M \% = \frac{M_1 - M_0}{M_0} \cdot 100$$

Where M (%) is the moisture content in

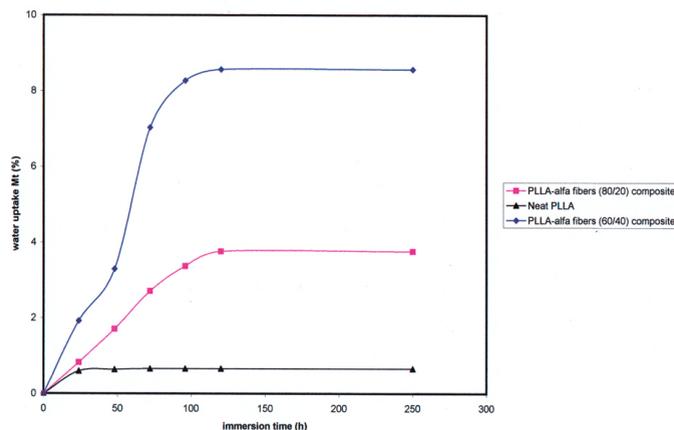


Fig. 15. Moisture absorption in PLA/Alfa composites immersed in water at 25°C

percentage; M_t is the weight of the wet sample at the Time t ; and M_0 is the initial weight of the sample.

From the figure it shows that the moisture content increased with time. When specimens were immersed, the water molecules penetrate and inducing the weight gain. At the beginning of the curve, the weight increased sharply demonstrating the rapid moisture penetration into the composite materials.

The diffusion of water into these products was higher during the first periods and decreased gradually until they were saturated suggesting a classical Fickian diffusion phenomenon.

CONCLUSION

This study examined the physical properties of PLA composites reinforced by different percentage of Alfa fibers which can act as better reinforcement.

Bio based composites were obtained from PLA and esparto grass cellulose fibers that possess superior mechanical and thermal properties as a result of reinforcement.

Indicate that PLA/natural fiber composites have mechanical properties of sufficient magnitude to compete with conventional thermoplastic composites.

In general, the tensile strengths of the natural fiber reinforced polymer composites increase with fiber content.

Hence the use of natural fibers, as reinforcements

in PLA, gives interesting alternatives for production of low cost and ecologically friendly composites and will add value to halfa plant

This study is expected to provide more comprehensive insight into biodegradable green composites.

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