PREPARATION AND CHARACTERIZATION OF OIL PALM FIBER REINFORCED POLY(ε-CAPROLACTONE)/POLY(LACTIC ACID) COMPOSITES

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Dedicated to my parents late Mr. Ibrahim Akos and late Mrs. Asibi I. Akos

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ABSTRACT

Palm press fibers of Tenera and Dura palm oil species of Malaysia and Nigeria respectively were used to prepare poly(ε-caprolactone)/poly(lactic acid) blend composites. All the blends and composites were produced using the twin screw extruder and the test specimens were fabricated using the injection molding machine. The morphology, mechanical, thermal, water absorption and biodegradation properties of the composites were studied. Fourier Transforms Infrared (FTIR) revealed that the hemicelluloses were completely removed after alkali fiber treatment. Field Emission Scanning Electron Microscope (FESEM) showed the improvement of fiber/matrix adhesion and the confirmation of compatibilization in the blend and composites. X-ray Diffraction (XRD) confirmed the increase in crystallinity of the fibers after alkali treatment. Compatibilization and fiber reinforcement significantly enhanced the mechanical and thermal properties, biodegradation and char yield of the composites. The Tenera composites exhibited higher mechanical properties than the Dura composites, while the Dura composites were thermally more stable than the Tenera composites. The Dura fibers also increased the percentage crystallinity of the composites more than the Tenera fibers. Compatibilization and fiber reinforcement increased the rate of biodegradation of the blend and composites. There was no significant difference in the biodegradation rate between the Tenera and Dura composites. The optimum properties were obtained for Tenera and Dura composites at 15 wt. % fiber loading. In view of the above, the composite was adjudged as the best formulation for both fiber reinforcements.

ABSTRAK

Gentian kelapa sawit termampat Tenera dan Dura daripada spesis kelapa sawit dari Malaysia dan Nigeria masing-masing digunakan untuk menyediakan komposit dari adunan poli(ε-kaprolakton)/poli(laktik asid). Kesemua adunan dan komposit dihasilkan dengan menggunakan penyemperit skru berkembar dan spesimen ujikaji di hasilkan menggunakan pengacuan suntikan. Ciri-ciri morfologi dan sifat-sifat mekanikal, termal, kadar penyerapan air, dan biodegradasi bagi bahan komposit telah dikaji. Fourier Infra-merah (FTIR) membuktikan penyingkiran lengkap hemiselulosa selepas rawatan alkali dilakukan terhadap gentian. Mikroskop Imbasan Elektron (FESEM) menunjukkan peningkatan lekatan gentian/matriks, dan mengesahkan keserasian dalam adunan dan komposit. Pembelauan Sinar-X (XRD) mengesahkan peningkatan penghabluran dalam gentian selepas rawatan alkali. Penserasi dan gentian penguat meningkatkan sifat-sifat mekanikal dan termal, biodegradasi dan kandungan arang komposit tersebut. Komposit Tenera memaparkan sifat-sifat mekanikal yang lebih tinggi berbanding komposit Dura, manakala komposit Dura mempunyai kestabilan terma yang lebih baik berbanding komposit Tenera. Gentian Dura juga meningkatkan peratusan penghabluran komposit melebihi gentian Tenera. Penserasi dan gentian tetulang meningkatkan kadar biodegradasi adunan dan komposit. Tiada perbezaan yang ketara dalam kadar biodegradasi antara adunan komposit Tenera dan Dura. Sifat-sifat optimum untuk campuran komposit Tenera dan Dura diperolehi pada 15 % kandungan gentian. Berdasarkan keputusan di atas, adunan komposit tersebut telah dikenalpasti sebagai formulasi terbaik untuk kedua-dua gentian tetulang.

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LIST OF ABBREVIATIONS

PCL	-	Poly(ε-caprolactone)
PLA	-	Poly(lactic acid)
DCP	-	Dicumyl peroxide
NaOH	-	Sodium hydroxide
H_2SO_4	-	Sulphuric acid
$NaClO_2$	-	Sodium chlorite
CH_3COOH	-	Acetic acid
CH_3OH	-	Methanol
TF	-	Tenera fibers
DF	-	Dura fibers
TAPPI	-	Technical Association of the Pulp and Paper Industry
ASTM	-	American Society for Testing and Materials
DSC	-	Differential Scanning Calorimetry
TGA	-	Thermogravimetric Analysis
DMA	-	Dynamic Mechanical Analysis
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared Spectroscopy
UTF	-	Uncompatibilized Tenera fiber blend composites
CTF	-	Compatibilized Tenera fiber blend composites
UDF	-	Uncompatibilized Dura fiber blend composites
CDF	-	Compatibilized Dura fiber blend composites
wt. %	-	Weight percent

LIST OF SYMBOLS

Pa	-	Pascal
MPa	-	Mega pascal
kJ/m^2	-	Kilo joules per meter square
J/g	-	Joules per gram
ΔH_m	-	Melting enthalpy
ΔH_m^o	-	Melting enthalpy for 100 % crystalline material
T_g	-	Glass transition temperature
T_m	-	Melting temperature
T_c	-	Crystallization temperature
I_{cr}	-	Crystallinity index
G'	-	Dynamic storage modulus
X_c	-	Degree of crystallinity
θ	-	Theta
μm	-	Micrometer
mg	-	Milligram
h	-	Hour
^oC	-	Degree Celsius
g	-	Gram
A	-	Amperes
Hz	-	Hertz
nm	-	Nanometer
l	-	Liter
sec	-	Second
min	-	Minutes
ml	-	Milliliter
rpm	-	Revolution per minute
mm	-	Millimeter

$mol.l^{-1}$	-	Mole per liter
g/l	-	Gram per liter
cm^{-1}	-	Per centimeter

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The utilization and over exploitation of resources that cannot be replaced or re-introduced into the environment prompted research interest in the development, production and application of natural polymers. The last decade of the 20th century has experience a geometric growth of plastic demand due to their extensive use in the packaging industries. The reasons adduced to the high demand are safety, low cost and aesthetics [1].

Sinha and Bousmina [2] reported that 41% of plastics worldwide are used for packaging out of which 47% of these are used for foodstuff packaging. These materials produced from non-renewable sources are used and discarded into the environment that cannot degrade them as such 40% ends up as refuse which constitute global environmental problem. For the environment to be free from wastes disposal methods like land filling, incineration and recycling have been used. However, land filling and incineration of wastes eventually leads to generation of CO_2 which causes temperature rise globally. Another alternative in use in waste disposal is recycling which unfortunately is costly and labor intensive because of the processes involved. In view of the above, the development of green polymeric materials has become necessary. The fact is that these polymeric materials can be prepared without using toxic or noxious components and also, they can be easily broken down naturally in the environment. Materials scientist and engineers all over the world have been challenged to develop biodegradable materials with properties that can be manipulated to solve the above mentioned problems. As a result of this, manufacturing of various products using composites produced from natural fibers and other friendly materials is being developed [2-5].

There are overwhelming reports from scientists and other researchers in the field in respect of the friendly nature and numerous advantages that natural fibers have over conventional reinforcing fibers. These advantages have attracted industries like the automobile industries to embrace the use of natural fibers in place of the regular conventional fibers used in most products [3, 4]. Report have shown that the hydrophilic nature of natural fibers is one major disadvantage in terms of their compatibility with the hydrophobic polymers [4]. It has also been reported that this deficiency can be enhanced by modifying the fibers or polymer properties [5-9].

Several methods have been adopted by scientists to modify the fibers or polymers to enhance their performance. Alkali and acids were used by Alawar and co-workers [10] to modify the surface of date palm fibers to enhance the fibers performance. They recorded improvement in tensile strength and surface morphology for the fibers treated with alkali. However, the performance of the fibers dropped remarkably with acid treatment.

Valadez-Gonzalez and co-workers [11] reported improvement in interfacial shear strength between matrix and fibers after morphological modification of the fiber surface with alkali. The alkali treatment increased the roughness of fiber surface thereby leading to better mechanical interlocking. Also, better exposure of cellulose on the fiber surface was achieved after alkali treatment thereby resulting in increased number of reaction sites. Their work with silane coupling treatment further enhanced the fiber-matrix adhesion and improved the interfacial load transfer of the composites.

In a review of chemical treatments of natural fibers, Kabir and co-workers [12] concurred that treatment is an important factor that has to be considered when processing natural fibers. They observed that fibers loose hydroxyl groups due to different chemical treatments thereby reducing the hydrophilic behavior of the fibers. Their general conclusion was that chemical treatment of natural fibers results in remarkable improvement of the natural fiber composites.

Matrix modification is another option used to improve the performance of polymers and their composites. Avella and co-workers [13] prepared compatibilzed polycaprolactone/starch composites using pyromellitic anhydride as compatibilizer and studied the performance of the composites. The result showed improved properties performance of the composites. They also observed that the composite properties can be modified by altering the quantity of compatibilizer and starch.

The effect of dicumyl peroxide (DCP) as a cross linking agent in blends of poly(lactic acid)/poly(ε-caprolactone), (PLA/PCL) has been investigated [14]. Improved mechanical properties due to the incorporation of DCP were reported for the blends. The researchers concluded based on the DMA, melting interfacial tension and tensile test results that the blends were compatible when small quantity of DCP is added. Also, they submitted that DCP was a good compatibilizer for the PLA/PCL blend.

In another work, PCL-g-MA coupling agent composites were prepared and their mechanical properties investigated [15]. It was reported that increasing the quantity of coupling agent resulted in composites with better mechanical properties. Evidences from these literatures establish the fact that polymer composites prepared with modified natural fibers and blends exhibit improved properties and performance over their neat counterparts.

This research has formulated and prepared environmentally friendly and enhanced blend composites of poly(ε-caprolactone)/poly(lactic acid) using palm press fibers obtained from the Tenera and Dura palm oil species from Malaysia and Nigeria respectively. X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR) and proximate analysis were employed to characterize the fibers, blends and blend composites. The mechanical and thermal properties, water absorption and biodegradability of the fibers, blends and blend composites were also studied.

1.2 Problem Statement

PCL is petroleum derived synthetic biodegradable polymer. At ambient temperature it is tough and fairly rigid with an average modulus like that of polyethylene. Its low melting point (58-60^{o}C) and biocompatibility makes it suitable in the production of composites and biomedical use respectively. However, the very low glass transition temperature, T_g and low melting point, T_m of PCL are major setback of this biodegradable polyester thereby reducing its chances of being used in some applications, especially outdoor.

PLA is a biodegradable thermoplastic produced from sources like tapioca products, corn starch and sugarcane which are considered renewable. It has high melting point (173-178°C), high strength and modulus but is brittle. The intrinsic brittleness of PLA greatly reduces its application areas. For PLA to be used in various applications, modifications like plasticization, copolymerization, addition of rigid fillers and blending with varieties of flexible polymers or rubbers has to be carried out.

These individual weaknesses exhibited by PCL and PLA have prompted researchers to improve on them through blending with other polymers [16-18], blending and reinforcing with fibers [19, 20], reinforcing the single polymers with fibers [11, 15, 21-23] and other treatment methods [12]. It is therefore imperative to improve the properties of these polymers to make them fully competitive with the conventional polymers in use. These polymers with their unique properties even though not compatible but biodegradable have in this research been successfully blended and reinforced with palm press fibers to produce biodegradable composites with enhanced properties.

The use of natural fibers as reinforcements in single polymers has been extensively reported [5, 7, 8, 24-27]. Major drawbacks observed with natural fibers and their composites is their hydrophilic nature and incompatibility with polymers yet researches show that they can be improved upon through chemical and other treatments [6, 26, 28-31]. Composites formation using natural fibers as fillers and biodegradable polymers as matrix will help to solve the environmental and waste management problems associated with conventional polymers. Most researches carried out using natural fibers as reinforcement have been with conventional polymers which are still not friendly to the environment and also difficult to manage [3, 6-9].

To the best of the researcher's findings with respect to literature review for this research, no work has been carried out using palm press fibers of any palm tree species as reinforcement in PCL/PLA blend. In view of the above, palm press fibers which are highly generated by the palm industry (but seldom used) were used as reinforcement in PCL/PLA blend to improve the blend properties and expand their outdoor application fields. The aim of this research is to formulate, prepare and investigate PCL/PLA blends reinforced with palm press fibers obtained from the Tenera and Dura palm oil species of Malaysia and Nigeria respectively.

1.3 Objectives of the Study

This research aims at developing environmentally friendly composites using PCL/PLA blend as matrix and palm press fibers obtained from the Tenera and Dura palm oil tree species of Malaysia and Nigeria respectively. The objectives of this study are as follows:

(i) To formulate, prepare and characterize PCL/PLA blends and composites of palm press fibers obtained from the Tenera and Dura palm oil tree species of Malaysia and Nigeria.

(ii) To study the effect of compatibilization and fiber content on the morphology, mechanical, thermal, water absorption and biodegradation properties of the blends and composites.

(iii) To characterize the fibers and determine the proximate chemical composition of the fibers and its effect on properties of the composites.

1.4 Scope of the Study

In order to achieve the objectives of this research, the following activities were carried out:

(i) Collection, processing and treatment of palm press fibers based on existing methods.

(ii) Proximate determinations of the fibers composition using the Technical Association for the Pulp, Paper and Converting Industry (TAPPI T13M-54) methods.

(iii) Formulation of PCL/PLA blends and composites of palm press fibers.

(iv) Preparation of PCL/PLA blends and composites of palm press fibers using melt blending technique.

(v) Fabrication of PCL/PLA blends and composites of palm press fibers using injection molding technique.

(vi) Evaluating physical and mechanical properties of the fabricated PCL/PLA blends and composites by determining water absorption, tensile, flexural and impact properties.

(vii) Characterizing the thermal properties and structural composition of the fibers, PCL/PLA blends and composites using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Fourier Transform Infrared Spectroscopy (FTIR).

(viii) Evaluating the biodegradation behavior of PCL, PLA, PCL/PLA blends and composites by normal outdoor soil burial test.

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