INVESTIGATION OF CHEMICOMECHANICAL PROPERTIES OF POLYAMIDE 12 COMPOSITE REINFORCED WITH FILLERS FROM AGRICULTURE BIOWASTE AS A POTENTIAL DENTAL POST

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by

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TABLE OF CONTENTS

APPENDICES

LIST OF PUBLICATION

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF ABBREVIATIONS

OPF	Oil Palm Fibre
ETT	Endodontically Treated Tooth
EFB	Empty Fruit Bunch
EFBF	Empty Fruit Bunch Fibre
OPEFB	Oil Palm Empty Fruit Bunch
EFBOPF	Empty Fruit Bunch Oil Palm Fibre
CNC	Crystallized Nanocellulose
CO_2	Carbon Dioxide
APTES	(3-Aminopropyl) Triethoxysilane
FTIR	Fourier Transform Infrared
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
SiO_2	Silica Dioxide
NMR	Nuclear Magnetic Resonance
FRC	Fibre Reinforced Composite
PVA	Polyvinyl Alcohol
PLC	Polylactic Acid
PA12	Polyamide 12
PA6	Polyamide 6
PA66	Polyamide 66
PA11	Polyamide 11
RH	Rice Husk

LIST OF APPENDICES

PENYIASATAN SIFAT KIMIA MEKANIKAL KOMPOSIT POLIAMIDA 12 DIPERKUKUH DENGAN PENGISI DARIPADA SISA BIO PERTANIAN YANG BERPOTENSI SEBAGAI POS PERGIGIAN

ABSTRAK

Pengisi nano dan gentian pendek telah ditambah kepada komposit polimer sebagai tetulang untuk memperbaiki sifat mekanikalnya. Gentian kaca E sintetik yang digunakan dalam komposit bertetulang gentian bagi pos pergigian komersial dilaporkan berbahaya. Gentian asli daripada gentian kelapa sawit (GKS) dan silika daripada sekam padi (SP) adalah lebih murah daripada gentian kaca dalam banyak keadaan. Selain murah, gentian asli dan silika juga dilaporkan/dibuktikan kurang mendatangkan masalah kesihatan kepada penghasil komposit berbanding pembuatan komposit menggunakan gentian kaca. Matlamat penyelidikan ini adalah untuk menghasilkan tiang dan teras pergigian yang menggabungkan Gentian asli daripada kelapa sawit dan silika sekam padi daripada sisa pertanian ke dalam matriks dan juga untuk menyiasat sifat-sifat kimia mekanikal tiang yang dihasilkan berbanding tiang komersial. Penyediaan tiang nanokomposit bertetulang GKS/SP Silika/Poliamida 12 (PA12) dilakukan dengan memasukkan silika terawat daripada sekam padi dan nanoselulosa terhablur gentian kelapa sawit (NST GKS) ke dalam matriks PA12. Enam sampel bersaiz 1.5mm x 2.0mm x 25.0 mm telah disediakan untuk 7 kumpulan (n=6, N=42); dan enam sampel bersaiz 4mm diameter x 6mm tinggi turut disediakan untuk 7 kumpulan (n=6, N=42); Kumpulan 1 100% PA12, Kumpulan 2 PA12 (99%) + NST GKS (1%), Kumpulan 3 PA12 (98%) + NST GKS(2%), Kumpulan 4 PA12 (80%) + (20%) silika SP, Kumpulan 5 PA12 (80%) +(19%) silika SP+ (1%) NST GKS, Kumpulan 6 PA12 (80%) +(18%) silika SP+ (2%) NST GKS, Kumpulan 7 everStick post (ujian lentur)/ everX Flow^{TM} (ujian mampatan). Ujian lentur dan mampatan telah dijalankan menggunakan Mesin Pengujian Sejagat Instron (Shimadzu, Jepun). Spektroskopi inframerah transformasi Fourier (SITF), pengimbasan mikroskop elektron (PME) dan analisis Termogravimetrik (ATG) digunakan untuk memeriksa sampel kekuatan lenturan yang retak. Ujian lentur menunjukkan terdapat perbezaan yang signifikan secara statistik dalam kekuatan lentur antara kumpulan yang berbeza ($\chi 2$ (df) = 38.65 (6), di mana PA12 dengan pengisi NST GKS menunjukkan peningkatan nilai kekuatan lentur berbanding PA12 yang tidak terisi dan tidak mempunyai perbezaan signifikan dengan tiang komersial. Penggabungan NST GKS ke dalam komposit PA12 bagaimanapun tidak meningkatkan nilai mampatan berbanding PA12 yang tidak terisi dan menunjukkan pengurangan ketara dalam kekuatan mampatan berbanding komposit komersial. Analisis PME mengesahkan terdapat kedua-dua pengisi dalam komposit dan menunjukkan permukaan yang lebih licin dengan kehadiran lompang yang lebih kecil dan jurang dengan penambahan berat% pengisi yang mencadangkan ikatan antara muka yang dipertingkatkan. Analisis ATG menunjukkan bahawa NST GKS menurunkan kestabilan termostabiliti komposit manakala silika dari SP memperbaiki/mengekalkan kestabilan termostabil komposit. Penggabungan NST ke dalam matriks PA12 meningkatkan sifat lentur komposit. Penambahan silica dari SP pula dilihat mengurangkan sifat lentur PA12. Walau bagaimanapun, penambahan NST GKS ataupun silica dari SP dilihat tidak memberi kesan kepada sifat mampatan PA12.

Kata kunci: **OPF**, **gentian asli**, **sifat kimiamekanik**, **Poliamida 12**, **pengisi nano**, **kekuatan lentur**

INVESTIGATION OF CHEMICOMECHANICAL PROPERTIES OF POLYAMIDE 12 COMPOSITE REINFORCED WITH FILLERS FROM AGRICULTURE BIOWASTE AS A POTENTIAL DENTAL POST

ABSTRACT

Nanofillers and short fibres were added to polymer composites as the reinforcements to improve their mechanical properties. The synthetic E-glass fibres used in fibre-reinforced composite of commercial dental post was reported to be hazardous. Oil palm fibres and rice husk silica are cheaper and generally safer for workers than glass fibres in composite production. The aim of this research is to produce dental post and core which incorporated natural oil palm fibre (OPF) and rice husk (RH) silica from agricultural waste into the matrix and also to investigate the chemicomechanical properties of the produced post compared to the commercial post. Preparation of OPF/RH Silica/PA12 reinforced nanocomposite post was done by incorporating treated silica from rice husk and oil palm fibre crystallized nanocellulose (OPF CNC) into Polyamide 12 (PA12) matrix. Six samples with a size of 1.5mm x 2.0mm x 25.0mm were prepared for 7 groups (n=6, N=42) and six samples with the size 4mm diameter x 6mm height, were also prepared for 7 groups (n=6, N=42); Group 1 100% PA12, Group 2 PA12 (99%) + OPF CNC (1%), Group 3 PA12 (98%) + OPF CNC (2%), Group 4 PA12 (80%) + (20%) RH silica, Group 5 PA12 (80%) +(19%) RH silica + (1%) OPF CNC, Group 6 PA12 (80%) +(18%) RH silica + (2%) OPF CNC, Group 7 everStick post (flexure test)/ everX Flow^{TM} (compressive test). The flexure and compressive tests were carried out using Instron Universal Testing Machine (Shimadzu, Japan) and the data were analysed using IBM SPSS version 26.0 (SPSS Inc, Chicago, IL, USA). Fourier- transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and Thermogravimetric analysis (TGA) were used to examine the fractured flexural strength samples. Flexural test showed that there was a statistically significant difference in flexural strength between different groups (χ^2 (df) = 38.65 (6), whereby the PA12 with CNC fillers showed an increased in flexure strength value compared to unfilled PA12 and has no significant difference with commercial post. The incorporation of OPF CNC in the PA12 composite however did not increase the compressive value compared to unfilled PA12 and showed a significantly reduction in compressive strength compared to commercial composite. SEM analysis confirmed the presence of both fillers in the composite and showed smoother surface with presence of lesser voids and gaps with increment of filler wt% which suggested enhanced interfacial bonding. TGA analysis showed that OPF CNC lowered the thermostability of the composite while RH silica improved the thermostability of the composite. Incorporation of OPF CNC into PA12 matrix increased flexure strength of the composite. Incorporation of silica on the other hand reduced the flexure strength of PA12. However, the incorporation of OPF CNC or RH silica did not give any impact to the compressive strength of PA12.

Keywords: **OPF, natural fibre, chemicomechanical properties, Polyamide 12, nanofiller, flexural strength**

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Restoration of endodontically treated tooth (ETT) provides a challenge for the practitioner. The primary cause of failure for endodontically treated tooth is poor repair (Zarow, Devoto and Saracinelli, 2009). According to Randow and Glantz, (1986), when the pulp is removed, the protective feedback system from the pulp will be lost, contributing to tooth breakage. When a considerable amount of the coronal tooth structures was removed, adequate anchoring of a restoration in the remaining dentine is sometimes impossible. In such cases, it is suggested that a root canal-retained repair to be used (Zarow, Devoto and Saracinelli, 2009).

Post is defined as a small rod that is employed for upholding teeth structure with short clinical crown in holding the definitive restoration (Krishnakumar and Senthilvelan, 2019). Prefabricated posts were originally built of gold-plated brass and stainless steel but were later upgraded by employing titanium alloys as the primary material. Unfortunately, metallic posts had been reported to cause stress concentration into the tooth structure. As when two materials with different mechanical characteristics are joined together, stress will be localised at the weaker material. This is especially true for metal post, which is mechanically stronger than dentine. To counter this issue, fibre post was introduced (Zarow, Devoto and Saracinelli, 2009). Despite of having less superior mechanical properties in comparison to metals post, the fibre posts are still considered as the ultimate replacement to metals solely for their remarkable properties such as they are lighter than metal (Krishnakumar and Senthilvelan, 2019) as well as possessing advanced aesthetic and mechanical properties (Abdelkader and Salman, 2021).

Over the decade, there has been an increased in the utilization of diverse polymer-based composite materials in biomedical fields, including dentistry and orthopaedics fields. Nanofillers and short fibres were added to the polymer composites as the reinforcements to improve their mechanical properties (Krishnakumar and Senthilvelan, 2019). Because of their wide spectrum of physicochemical and mechanical characteristics, polymer materials have been widely embraced for research and commercial purposes. Polyamide 12 (PA12) is a semi-crystalline polymer that is one of the most often utilised. The melting temperature is much greater than the crystallisation temperature. PA12 is said to have the best impact resistance and the lowest moisture absorbance of any polyamide. It also has lower thermal stability and mechanical strength than metal. The melting point for PA12 is reported to be 178 °C – 180 °C (Touris *et al.*, 2020). A substantial research on polyamide 12 has been conducted and continues to be conducted in order to create functional components with specific mechanical characteristics (O’ Connor and Dowling, 2020).

Oil Palm Fibre (OPF) is obtained from parts of the oil palm tree including leaf, empty fruit bunch, fond and trunk. Its’ essential qualities are determined by the post-processing procedure used and the location of the obtained fibre (Mohammad Padzil *et al.*, 2020; Asyraf *et al.*, 2022; Bangar *et al.*, 2022; Lim *et al.*, 2022). The most common fibre used in the development of composite is from the empty fruit bunch fibre (EFBF) due to its abundance and low price. The second area of choice is the mesocarp fibres which usually are palm-pressed fibre obtained from biomass residue during oil extraction of palm fruit (Asyraf *et al.*, 2022). OPF fibre structures are made of cellulose and hemicellulose, which strengthen the lignin matrix, allowing OPF to be classified as a lignocellulosic fibre (Mohammad Padzil *et al.*, 2020; Asyraf *et al.*, 2022).

Oil palm fond has higher hemicellulose and cellulose percentage but lower lignin percentage compared to oil palm empty fruit bunch (OPEFB). The alignment of cellulose fibrils is the influencing factor for OPF's properties including tensile, flexural and rigidity. The higher percentage of cellulose content in OPF compared to other natural fibres suggested that it has higher tensile properties (Asyraf *et al.*, 2022). Because of its superior mechanical qualities, large specific surface area, availability for diverse surface functionalization, non-toxicity, and biocompatibility, OPF in the form of nanocellulose is widely employed in biomedical applications (Mohammad Padzil *et al.*, 2020; Asyraf *et al.*, 2022; Lim *et al.*, 2022). The OPF in the form of nanocellulose has remarkable properties which includes lighter weight, large ratio of surface area to volume, as well as possessing higher stiffness and strength in comparable to when OPF is in the form of cellulose (Mohammad Padzil *et al.*, 2020; Lim *et al.*, 2022). The number of crystallinity degree areas and cellulose stiffness are inter-related, as with an increase in the number of crystallinity regions, the stiffness of the fibres increase (Asyraf *et al.*, 2022; Bangar *et al.*, 2022). Higher crystallinity in the chemically-treated fibres is associated with a higher tensile strength. Crystallized nanocellulose (CNC) has a high bio-renewability, low manufacturing energy consumption, and a large aspect ratio (Bangar *et al.*, 2022; Lim *et al.*, 2022). Mechanical properties of natural fibres itself are determined by certain factors such as the extraction methods, aspect ratio, harvest time, matrix selection, interfacial strength, fibre dispersion, fibre orientation, composite manufacturing process, and porosity (Jariwala and Jain, 2019; Bangar *et al.*, 2022; Lim *et al.*, 2022).

OPEFB fibre, on the other hand have some unwanted qualities which include hygroscopicity due to their chemical contents. OPEFB fibre have a high moisture content, usually above 60% on a wet EFB basis, making them a poor fuel when not dried. The hemicellulose component in OPFEFB contains huge amount of hydroxyl groups and are responsible for poor adhesion with hydrophobic polymer matrices (Jariwala and Jain, 2019; Asyraf *et al.*, 2022; Li *et al.*, 2022). The qualities of natural fibre composites vary depending on the type of fibre, the source, and the moisture conditions.

Mechanical composition, microfibrillar angle, structure, defects, cell dimensions, physical and chemical properties and fibre interaction with the matrix influence the performance of natural fibre polymer composites (Jariwala and Jain, 2019; Asyraf *et al.*, 2022; Lim *et al.*, 2022). The OPF reinforced polymer composite has been reported to have many unfavourable outcomes such as poor compatibility with polymers, low thermal degradation, and high water-absorption, with the key issue being the compatibility between the matrix and the filler (Asyraf *et al.*, 2022; Bangar *et al.*, 2022; Lim *et al.*, 2022). Poor OPF-matrix compatibility results in reduced mechanical properties due to the inability of the polymers to interact with polar moieties like OPF. The non-polar nature of OPFs causes inadequate adhesion, insufficient dispersion, and decreased fibre properties, leading to agglomeration of natural fibres within the matrix and poor interaction. Additionally, the hydrophilic nature of polar fibres exacerbates the problem when combined with the hydrophobic polymer matrix. The solution for this problem is by modification of the surface of the fibres (Asyraf *et al.*, 2022).

Rice husk is mostly composed of organic elements such as hemicellulose, cellulose, and lignin, with 17 - 20% of ash concentration of remaining (Bakar, Yahya and Gan, 2016). The ash consists of mostly silica with minor metallic particles. Under regulated settings, rice husk combustion produces rice husk ash containing practically pure silica. Silica (SiO_2) is a fundamental raw element widely utilised in the electronics, ceramic, and polymer material industries. Because of their small particle size, ultrafine silica powders have a wide range of technological applications, including thixotropic agents, thermal insulators, composite fillers, and others (Sun and Gong, 2001; Liou, 2004). At the moment, nanoscale silica materials are created using a variety of techniques, including vapor-phase reaction, sol-gel, and thermal degradation. However, their high preparation cost has hindered their widespread adoption. Under controlled conditions, it is possible to make extremely fine particle size with high purity and high surface area of silica powder due to the natural consistent distribution by molecular units of the silicon atoms in the rice husk (Liou, 2004).

There is no report on the use of fillers derived from agriculture biowaste for the fabrication of dental post polymer composite. However, there was a study conducted by Wang et. al (2017) which they fabricated a novel anatomical post using PA12 reinforced with short glass fibre as a filler material which has shown good flexure property compared to commercial fibre reinforced post. Thus, PA12 is assumed to become a potential alternative as a tooth-coloured fibre reinforced post material. However, the use of synthetic fibre as a filler material was reported to have hazardous effect to the handlers during fabrication process (Zhang and Matinlinna, 2012; Asyraf *et al.*, 2022). There is no study conducted at the moment to investigate the physical and chemical properties of PA12 composite reinforced with natural fibre, thus this study is hoped to provide and alternative material in restoring endodontically treated teeth (ETT) and at the same time utilising the agriculture biowaste as the source of filler material.

1.2 Problem statement and study rationale

Not all prefabricated post can fit the root canal due to its shape. Originally, the material for custom post is made of metal. As reported by many studies, the use of cast metal post may lead to unfavourable fracture if it fails and leads to the loss of teeth itself. This was due to the rigidity of the metal itself and the different in modulus of elasticity between dentine and cast metal post. The other factor which makes metal post less popular was due to aesthetic value itself where the metallic appearance gives less satisfactory outcome (Zarow, Devoto and Saracinelli, 2009; Sarkis-Onofre *et al.*, 2014).

Nowadays, FRC post are used in restoring ETT which utilised E glass fibre while most of dental composite used in restorative material used silica as part of their filler content. The synthetic E-glass fibres used in fibre-reinforced composite was reported to be hazardous (carcinogenic) to the handlers during fabrication process (Asyraf *et al.*, 2022; Zhang and Matinlinna, 2012). According to Theng *et al.,* (2019), natural fibres are cheaper than that of glass fibres in many occasions. Besides being cheap, natural fibres are also expected to cause less health problems to the people producing the composite compared to when making composite using glass fibres. This is due to natural fibres not causing skin irritations and are non-carcinogenic. However, there is yet any report of the use of natural fibres to fabricate a post or the use of bio silica as a filler material for dental post.

PA12 has been widely used in dentistry to fabricate flexible denture to cater the need of patients with prominent undercut in teeth replacement. It was known to have high moulding property (Katsumata *et al.,* 2009; Fueki *et al.,* 2013). This probably make it suitable as a material to restore the canal space as it will take the shape of the canal without any void formation. The material is however having lower modulus of elasticity when compared to dentine. The addition of fillers into the polymer was hoped to overcome this problem. Thus, the fabrication of a new post from non-metal materials with flexure strength that is almost similar to the dentine might be a new hope to save the root canal treated tooth.

There was a single study reported on the use of PA12 post reinforced with short glass fibre by Wang et al., (2017) which resulted in good clinical outcome when compared to commercial FRC post. However, as reported before, the use of synthetic fibres possesses harmful effect and cost more, thus, the use of filler materials from natural sources might be the alternative to synthetic one. This will also help to preserve the environment. Hence the aim of this study is to produce and characterize dental post PA12 nanocomposite incorporated with nanocellulose and nano silica.

1.3 Research Question

1. Do the mechanical properties (flexural and compressive strength) of the fibre reinforced PA12 composite, silica reinforced PA12 composite and fibre and silica reinforced PA12 composite comparable to the Everstick fibre post and everX flow composite?
2. How is the morphology of PA12 nanocomposite dental post under Field Emission Scanning Electron Microscopy (FESEM)?
3. Have new functional groups detected in the newly formulated PA12 nanocomposite dental posts using Fourier Transform Infrared spectroscopy (FTIR)?
4. Has good thermal degradation achieved in the newly formulated PA12 nanocomposite dental posts when examined using Thermogravimetric analysis (TGA)?

1.4 Research Hypothesis

1. If the flexural and compressive strength of fibre reinforced PA12 composite, silica reinforced PA12 composite, and fibre and silica reinforced PA12 composite are comparable to the everStick fibre post and everX flow composite, then these composite materials could exhibit similar mechanical properties.
2. If the flexural samples of PA12 nanocomposite dental posts are examined using Scanning Electron Microscopy (SEM), it is hypothesized that the morphology will be effectively observed and analyzed.
3. If Fourier Transform Infrared spectroscopy (FTIR) is utilized, successful isolation and characterization of the PA12 nanocomposite dental posts can be achieved.
4. Utilizing Thermogravimetric analysis (TGA) will enable successful examination of the thermal degradation of PA12 nanocomposite dental posts.

1.5 Research Aim and Objectives

1.5.1 General Objective

To produce and characterize dental post PA12 nanocomposite incorporated with nanocellulose and nano silica.

1.5.2 Specific Objective

1. To produce silica reinforced PA12 nanocomposite and fibre and silica reinforced PA12 composite.
2. To isolate and characterize PA12 nanocomposite dental posts using Fourier Transform Infrared spectroscopy (FTIR).

3. To compare the flexural and compressive strength of fibre reinforced PA12 composite, silica reinforced PA12 nanocomposite and fibre and silica reinforced PA12 composite with everStick fibre commercial post and everX flow composite.
4. To analyse the morphology of flexure sample of PA12 nanocomposite dental posts using Scanning Electron Microscopy (SEM).
5. To examine the thermal degradation of PA12 nanocomposite dental posts via Thermogravimetric analysis (TGA).

CHAPTER 2

LITERATURE REVIEW

2.1 Dental Post

2.1.1 Types of Dental Post

Advanced tooth decay often requires endodontic treatment to repair the affected tooth. Whether the damage is caused by dental caries or due to trauma, the restoration of teeth through endodontic procedures is a routine aspect in dental practice. This form of treatment becomes necessary when a significant amount of the tooth's coronal structure is lost. In cases of severe damage, the use of endodontic posts is often necessary. These posts are primarily utilized to support the reconstruction of the tooth's structure before placing a crown (Henry, 1977; Machado et al., 2017; Zarone *et al.*, 2006; Zarow, Devoto and Saracinelli, 2009).

Endodontically treated teeth (ETT) are expected to be structurally distinct from natural teeth. ETT may be more brittle and fracture more easily than healthy teeth because the strength of a tooth is directly correlated with the amount of remaining dentin (Machado et al., 2017; Zarow, Devoto and Saracinelli, 2009). Consequently, ETT may carry a higher risk of biomechanical failure compared to vital teeth (Akkayan & Gulmez, 2002; Machado et al., 2017). Studies have indicated that both post preparation and the presence of a post could compromise the structural integrity of the tooth, potentially increasing susceptibility to fracture (Akkayan & Gulmez., 2002; Alharbi et al., 2014; Machado et al., 2017). This structural alteration is attributed to changes in dentin, including the loss of water and collagen post-treatment, which diminishes its natural strength (Alharbi et al., 2014; Machado et al., 2017). Despite ongoing debate in current literature regarding the efficacy of posts in tooth restorations (Alharbi et al., 2014; Machado et al., 2017), some authors advocate for their use only when the remaining coronal tooth structure cannot adequately support the restorative material (core), and when no alternative options exist to retain this core (Machado et al., 2017; Zarow, Devoto and Saracinelli, 2009).

Various materials have been utilized in the fabrication of dental posts. The ideal post should ensure effective core retention while minimizing stress on the remaining tooth structure (Alharbi et al., 2014; Machado et al., 2017). Key requirements for dental posts include high tensile strength, resistance to fatigue from occlusal and shear forces, and even distribution of forces on the tooth root (Machado et al., 2017). Additionally, precision, biocompatibility, and absence of harmful electrochemical activity are crucial factors. Historically, metal alloys have been the preferred material for dental posts. Prefabricated posts were originally manufactured of gold-plated brass stainless steel, but were later upgraded by employing titanium alloys as the fundamental components. However, a notable drawback of these structures is the concentration of stresses in areas critical to the integrity of the tooth root (Akkayan & Gulmez, 2002; Machado et al., 2017; Henry, 1977; Zarow, Devoto and Saracinelli, 2009). The use of metallic posts results in a root fracture index of 2 to 4%, which has been linked to stress concentration (Zarow, Devoto and Saracinelli, 2009).

Numerous authors have different views when discussing about employing a dental post with a Young's modulus that is higher than that of dentin which could generate stresses at cement interfaces, potentially leading to post separation or root fractures. Furthermore, the utilization of posts with high elastic moduli carries inherent risks, as stress concentration in the dental root area may result in root rupture, necessitating tooth extraction (Alharbi et al., 2014; Machado et al., 2017). Some authors emphasize the importance of utilizing posts with biomechanical properties similar to dentin. In recent years, fibre-reinforced resin posts (such as glass and carbon fibres) have been introduced. Compared to metallic posts, fibre posts exhibit lower stiffness, leading to more favorable stress distribution in the root, potentially reducing post-restoration fractures (Akkayan & Gulmez, 2002; Machado et al., 2017). Additionally, the white translucent color of these materials (except for carbon fibre) enhances the aesthetics of the restoration. In contrast, metallic posts can darken the tooth, which is less desirable for anterior tooth restorations. However, metallic posts offer superior retention of the post-and-core system, while fibre-reinforced composites pose a higher risk of debonding (Machado et al., 2017).

2.2 Fibre Reinforced Composite Post

Fibre reinforced composite (FRC) post is widely used nowadays in contemporary dental practice due to its advantages including its aesthetic features, less clinical time, and can be easily retrieved from root canals in cases of retreatment. Additional advantage of FRC post that gives rise to its popularity and preference is its compatible modulus of elasticity with dentin compared to metallic posts that enables even distribution of the occlusal stresses resulting in favourable root fractures that can be easily repaired hence reduced the chance of extraction (Haralur *et al.*, 2018; Özlek *et al.*, 2019).

The reason for the development of FRC posts is to replace metallic posts due to its disadvantages such as high rigidity and low aesthetic values. Some available FRC posts that are developed are Spirapost (DMG in, USA), Everstick post (GC inc, USA) and Ribbond (Ribbon inc, USA). Spirapost is made of polyfibre strands and surgical steel wire and are used in resin cement forming homogenous unit. This post had adapted to irregularities and curvature of the canal because of its special and flexible design allowing ultra-conservative post space restoration and able to preserve more of tooth structure for a stronger tooth. The everStick post is an individually formed glass FRC post. It can be customized to form customized FRC post and core due to its ability to adapt to the shape of root canal that also prevented the risk of dentin perforation. The everStick post is an adaptable unpolymerized glass fibre post impregnated with resin that is flexible and soft. Another example of commercial FRC post is Ribbon fibres post which was reported to be able to efficiently absorb water as the treatment reduces the superficial tension and ensure good chemical bonding to composite matrix. Properties of Ribbond post includes biocompatible, aesthetic and translucent, transparent and it disappears within the composite or acrylic without any show-through (Nayak et al., 2020).

2.3 Oil Palm Fibre (OPF)

Malaysia is the largest producer of palm oil (51% of global output) and greatest provider of biomass producing massive amounts of wastes each year with only a small portion of which is transformed into value-added goods besides has also become an essential economic resource for the country (Ferrer *et al.*, 2012; Asyraf *et al.*, 2022; Lim *et al.*, 2022), thus deemed the oil-palm (*Elaeis guineensis*) as a valuable economic crop in Malaysia (Lamaming *et al.*, 2015; Palamae *et al.*, 2017). The extraction of crude oil from fresh palm fruit bunches produces a large amount of lignocellulosic waste, primarily fibrous empty fruit bunch (EFB). EFB is composed of two primary components: stalk and spikelet (Xiang, Mohammed and Samsu Baharuddin, 2016). Fruit bunches are typically 15-25 kg in weight and include 1000-4000 oval-shaped, 3-5 cm length fruits. Fruit production peaks between 20 and 30 years, after which it begins to decrease and becomes unprofitable (especially because their fruits are too high to collect). Each hectare of oil palm yields around 10 tonnes of fruits each year, yielding approximately 3000 kg of palm oil as the major product. If separated by pulping operations, a large quantity of residual empty fruit bunch fibre (EFBF) can be exploited as a source of cellulosic fibres (Ferrer *et al.*, 2012). EFBF is made up of cellulose (24-65%), hemicellulose (21-34%), and lignin (14%-31%) (Chang, 2014; Palamae *et al.*, 2017).

For every tonne of oil produced, over 1.1 metric tonnes of EFBF must be disposed. Every year, around 37.7 million tonnes of EFBF are produced worldwide (Cui *et al.*, 2014) while in Malaysia, around 15 million tonnes of EFBF biomass were produced (Mohamed *et al.*, 2016). This EFBF biomass has limited applications. It is usually mulched to make organic fertiliser or burned to provide power (Chang, 2014; Palamae *et al.*, 2017). The remaining oil palm waste is burnt or left to decompose which leads to emission of hazardous gases that often causes acute air pollution (Lim *et al.*, 2022). Both methods of disposal processes cause substantial environmental damage, such as methane and carbon dioxide (CO_2) gas emissions and can also provide breeding grounds for pests like rats and snakes. This causes a huge effort by researchers for sustainable palm oil circular economy (Ooi *et al.*, 2017).

2.3.1 Chemical Composition of Oil Palm Fibre (OPF)

OPF fibre structures are made of cellulose and hemicellulose, which strengthen the lignin matrix, allowing OPF to be classified as a lignocellulosic fibre. The structure and composition of each cell wall of the OPF differ depending on the species and portion of the plant collected. The three primary components (hemicellulose, cellulose, lignin) of OPF might vary, and are influenced by growth, soil conditions, plant age, and environment (Mohammad Padzil *et al.*, 2020; Asyraf *et al.*, 2022).

Lignocellulosic fibres are made up of 30% - 60% cellulose, 20% - 40% hemicellulose, and 15% - 25% lignin. When compared to other natural fibres, OPFs have a high cellulose concentration and hence possibly strong tensile qualities. The chemistry of lignocellulosic fibres alters throughout growth because it is affected by plant environment. The alignment of cellulose fibrils, which are normally oriented along the fibre length, influences the tensile, flexural, and stiffness characteristics of OPFs. Cellulosic fibrils develop in parallel with each other in crystalline structures and some amorphous areas, according to chemical theory. In some cases, an OPF's cell wall is composed of two primary walls. This layer has multiple orientations of cellulose fibrils (Asyraf *et al.*, 2022).

These amorphous and crystalline types of OPF cell structure play an important role in determining the mechanical performance of final composite products. The crystalline area has the highest stiffness value in a composite. OPFs derived from oil palm biomass as a thread-like bundles. OPF are roughly 10~30 or 50~60 mm length in the post-processing stage with the average length of a fibre is reported to be 200 mm (Asyraf *et al.*, 2022). Mohamed Yusoff et al. (2009) investigated the effect of OPF length on mechanical parameters and they find out that the range of diameter for single OPEFB fibre was from 250 to 550 µm while the moisture content was between 2.2 to 9.5%. The diameter of the fibre can affect the tensile properties where the tensile strength will decreased when the diameter was increased (Mohamed Yusoff et al., 2009).

2.3.2 Chemical Composition of Empty Fruit Bunch Fibre

According to Shinoj *et al.*, (2011), the cellulose percentage of EFBF varies between 42.7% and 65%. This was in accordance to the reports from previous studies where Zianor Azrina *et al.*, (2017) reported that raw EFBF consists of 25.33% lignin, 71.21% holocellulose, 12.07% hemicellulose, 59.14% cellulose and 1.16% ash.

Palamae *et al.*, (2017) on the other hand, reported that prior to any treatment, the chemical makeup of the EFBF consists of 36.6% hemicellulose, 28.3% cellulose, and 35.1% lignin (w/w, dry basis). This is due to the fact that EFBF is a natural product, its composition can vary based on a variety of circumstances, including the maturity of the fresh fruit bunches used to recover EFBF, the geographic location of the source plant, and the season of fruit gathering (Palamae *et al.*, 2017).

2.3.3 Cellulose

Cellulose, a fundamental element found in natural fibres, is frequently used as an organic filling material in composite production because of its superior strength and stiffness relative to its weight. Additionally, it serves as the foundational substance for extended fibrous cells. Natural cellulose is becoming increasingly important because of its abundance, low cost, low density, low abrasiveness, nontoxicity, strong mechanical properties, biocompatibility, and biodegradability (Kalia *et al.*, 2011; dos Santos *et al.*, 2016).

Wood is the most often utilised commercially available cellulose-containing natural resource. Other non-wood plant fibres utilised as cellulose sources include hemp, flax, jute, ramie, and cotton. Furthermore, bio-residue from industries, agricultural waste, and cellulose-rich municipal solid waste such as OPEFB fibre, corrugated cardboard, and waste papers represent another cellulose source with high potential for cellulose derivatives (Iyer, Flores and Torkelson, 2015). Furthermore, the integration of nanofillers such as cellulose nanocrystals (CNC) in manufacturing nanocomposites is thought to be an efficient technique for tailoring the characteristics of the polymeric material. The nanofillers are distinguished by their high aspect ratio, which serves as structural reinforcement to improve the mechanical and barrier characteristics of the matrix (Othman, 2014).

OPF waste is composed of lignocellulosic components that are rich in cellulose. The holocellulose content of oil palm trunks range from 72% to 78% (Hashim *et al.*, 2011; Lamaming *et al.*, 2015). As a result, the trunks are a useful source of cellulose nanofibres for the industry. Cellulose is a poly-1,4,d anhydroglucopyranose with a regular network of inter and intramolecular hydrogen bonding structured into flawless stereoregular microfibrils (Janardhnan and Sain, 2006; Lamaming *et al.*, 2015). Naturally, cellulose is divided into two major regions: amorphous and crystalline. Strong acid hydrolysis was used to remove the amorphous portions, allowing access to the crystalline regions. It is water insoluble but can be destroyed by microbial and fungal enzymes (Li *et al.*, 2009; Lamaming *et al.*, 2015).

The ability to synthesise cellulose from lignocellulosic materials is particularly beneficial in a variety of applications, including the potential use as a reinforcing component in high-performance composite materials (Faria *et al.*, 2006; Lamaming *et al.*, 2015). This past year, there has been a lot of interest in cellulose nanofibre research, with various separation methods and raw materials. Mechanical, chemical, chemo-mechanical, and enzymatic separation procedures have all been described as ways for isolating cellulose microfibres (Jonoobi *et al.*, 2015; Lamaming *et al.*, 2015).

The usage of oil palm waste as a source of natural cellulose fibres is belief to have a substantial impact on agricultural use, fibre resource, food, and energy demands. It will also benefit the environment because the items are made of environmentally friendly components. This will help to address the issue of oil palm trash being left in the field or burnt, while also contributing to the economy by converting it into useful items (Tang *et al.*, 2008; Lamaming *et al.*, 2015).

2.3.4 Nanocellulose

Nanocellulose is a novel class of biopolymer with nanoscale dimensions that is causing a bio-based materials revolution in the twenty-first century for a wide range of interdisciplinary applications such as packaging, biomedical, pharmaceuticals, membrane, 3D printing, energy devices, and flexible electronics (Tang *et al.*, 2008; Yahya, Lee and Hamid, 2015; Lim *et al.*, 2022). This is due to the unique qualities of nanocellulose, which include high reinforcing strength and stiffness that is typically similar to Kevlar and steel, has large surface area, exhibit amazing optical properties, customised crystallinity, and facile surface functionalization (Lim *et al.*, 2022).

Nanocellulose is rendered as an attractive environmentally-friendly choice for future exploration due to its biodegradable and renewable qualities in both industry and academic fields. According to its form and sources, nanocellulose may be divided into three categories: cellulose nanocrystals (CNCs), cellulose nanofibres (CNFs), and bacterial nanocellulose (BNC). Both CNCs and CNFs are produced top-down by decomposing plant materials through chemical or mechanical treatment. CNC is a needle or rod-shaped crystalline made from a variety of raw materials, including plants (coniferous and deciduous), non-woody materials (bagasse, bamboo, raphia palm), agricultural wastes such as OPF, and small-like creatures known as tunicates as well as bacteria and fungi (Zianor Azrina *et al.*, 2017; Bangar *et al.*, 2022). CNC is typically extracted using strong acid hydrolysis (Martínez-Sanz *et al.*, 2014; Kumar *et al.*, 2020). Other ways of producing CNC include ultrasound (Li, Yue and Liu, 2012), homogenisation (Kaushik and Singh, 2011), and enzyme aided acid hydrolysis (Satyamurthy and Vigneshwaran, 2013). However, the acid hydrolysis process has significant limitations, such as time consumption and cellulose degradation, which reduces CNC output (Zianor Azrina *et al.*, 2017).

Acid hydrolysis is one of the most used chemical synthesis methods for producing CNCs' extremely crystalline or needle-like pieces. Mechanical shearing procedures, on the other hand (e.g., high pressure homogenization, grinding, and cryocrushing) will dissolve cellulose fibres into their sub-structural nanoscale components, yielding longer CNCs with micrometric lengths. A few researchers have reported on their studies on CNC extraction utilising empty fruit bunches (Fahma *et al.*, 2010; Mohamad Haafiz *et al.*, 2013; Jonoobi *et al.*, 2015). Fahma *et al.*, (2010) used acid hydrolysis to extract the CNC from EFBF whereas Lamaming *et al.,* (2015) had also utilized the same technique to obtain CNC from oil palm trunks. Jonoobi *et al.*, (2015) had also isolated CNC from microcrystalline cellulose (MCC) using sulphuric acid hydrolysis. Hydrolysis of cotton fabric waste to produce microcrystalline cellulose (MCC) using hydrochloric acid was reported by Chuayjuljit, Su-uthai and Charuchinda, (2010). The amorphous regions of native cellulose can be readily hydrolyzed, with almost no weight loss when subjected to strong acid hydrolysis (Mohamad Haafiz *et al.*, 2013). These acids are used to eliminate the relatively disordered amorphous domain, which is more vulnerable to reagents, water, and heat from the crystalline regions and enhance the crystallinity of CNCs (Bangar *et al.*, 2022). According to Lim *et al.*, (2022), the diameter of obtained CNC range from 5–70 nm while the length range from 100–250 nm. Sulfuric acid (H2SO4) stands as the most commonly employed hydrolyzing agent, interacting with the surface hydroxyl groups of cellulose through an esterification process. This interaction enables the grafting of anionic sulfate ester groups. The addition of these negatively charged sulfate groups facilitates improved dispersion of CNCs in water by creating electrostatic repulsion. Typically, CNCs produced from sulfuric acid hydrolysis exhibit high crystallinity and suspension stability due to the esterification reaction between sulfuric acid and cellulose's hydroxyl groups, forming anionic sulfate ester groups. The presence of these negatively charged sulfate ester functional groups induces electrostatic repulsion, enhancing the dispersion of nanocellulose in water (Lim *et al.*, 2022).

Because of its availability, renewability, biodegradability, and outstanding mechanical qualities, CNC synthesis from cellulosic material has grown in popularity in recent years (Li, Wang and Liu, 2011). Furthermore, CNC has been recognised for its uses in pharmaceutical and drug delivery additives, bone replacement and tooth repair, better paper and packaging goods, polymer composite reinforcement, food and cosmetics additives, and also aerogels (Zianor Azrina *et al.*, 2017). Mohammad Padzil *et al.*, (2020) exemplified some of the most current synthesis methods for EFBF-derived nanocellulose hydrogels and their potential uses in food and biomedicine. The methods used to extract nanocellulose from oil palm biomass have a significant impact on the shape and characteristics of the resulting materials. Mechanical treatment, chemical treatment, enzymatic treatment, or any combination of these three tactics are the most common isolation methods utilised for nanocellulose extraction. However, pre-treatment of lignocellulosic feedstocks is required to disturb the refractory structure of oil palm biomass prior to nanocellulose separation (Lim *et al.*, 2022)

The use of nanocellulose in polymer reinforcement is still relatively new, and more study is required. Incorporating nanocellulose with polyvinyl alcohol (PVA), polylactic acid (PLA), starch, and polycaprolactone, as well as polyethylene or polypropylene, are among the uses (Bangar *et al.*, 2022). Tang *et al.*, (2008) created PVA biocomposite film which is water soluble and biodegradable, and it may be utilised to make pharmaceutical cachets, surgical yarn, and controlled drug delivery systems since it has no negative effect on the human body.

There has been a lot of interest in creating nanocomposite materials in recent years. This interest stems from the exceptional capabilities demonstrated by nanoscale reinforcement, which provides qualities such as large surface area for bonding with resins, optical transparency, and additional/multifunctional properties, such as electrical conductivity. Both the polymer matrix and the nano reinforcement must be produced from renewable resources in order to develop fully renewable and biodegradable nanocomposites (Petersson, Kvien and Oksman, 2007). Researchers are interested in using CNC as a viable starting material for cellulose reinforced nanocomposites (Mathew, Oksman and Sain, 2005).

CNC can also be employed as a universal filler in the extrusion/spheronization process, according to the literatures. As cellulose nanofibers have outstanding mechanical qualities, such as a high modulus (Šturcová, Davies and Eichhorn, 2005), they are an excellent materials as the reinforcer in a transparent polymeric matrix since they do not scatter light. This is because their lateral dimensions, for example, bacterial cellulose fibrils, are smaller than the wavelength of visible light (Yano et al., 2005). Although the separation and classification of CNC from OPEFB fibre has previously been described, no studies have provided a detailed characterization of isolated CNC from OPEFB, or its comparison with OPEFB-pulp and commercial CNC, until now (Mohamad Haafiz *et al.*, 2013).

2.3.5 Advantages and application of OPF

Natural fibres provide the advantages of low density and cheap cost, as well as being non-toxic and ecologically benign. Furthermore, they are widely available and renewable and they produce less equipment wear besides being straightforward to process. Because of their high cellulose content, good mechanical properties and crystallinity, OPFs are well suited for composite applications. Oil palm bio-composites produced with thermoset and thermoplastic polymers have excellent mechanical, physical, electrical, thermal, and biodegradation properties. Many studies focused on the characteristics of bio-composites under diverse loading circumstances, such as tensile, compression, impact, flexural, and static, to assess the composites' structural and load-bearing applications. The potential of OPF as a composite reinforcement and filler material has been highlighted. Besides that, researchers are also interested in the use of natural fibre as a reinforcing filler in polymer composites because natural fibres offer several benefits over synthetic fibres. They are environmentally beneficial, entirely biodegradable, plentiful, renewable, and inexpensive, with a low density (Asyraf *et al.*, 2022).

Indeed, in composite cross arms for transmission tower applications, OPF can substitute calcium carbonate as a filler and glass fibre as fibre reinforcement (Johari *et al.*, 2020; Asyraf *et al.*, 2022). Other possible applications for oil palm biocomposites include packaging, the construction industry, and waste water treatment. In general, the qualities of the OPF can impact the final composite products with desirable attributes for certain applications. This knowledge is critical for selecting appropriate industrial procedures that produce high-quality goods (Asyraf *et al.*, 2022).

OPF from EFB has been turned into prospective value-added goods such as fertiliser, mattress filler, medium density fibreboard, moulded wares, composite material, pulp and paper, cooking oil, mulching material for palm oil plantations and boiler fuel in palm oil mills, bedding material, particleboard, and medium density fibreboard are examples of non-traditional use (and other potential products by this new industry which generates large amounts of biomass waste, which is a pollutant if discharged directly into the environment (Razuan *et al.*, 2010; Farma *et al.*, 2013; Lamaming *et al.*, 2015). OPF in the form of nanocellulose membrane has piqued the interest of many researchers due to its unique 3D network, excessive porosity, and low cytotoxicity, for cell attachment and proliferation, plasma treatment method and many more. The biodegradability and lower harmful chemical release associated with the usage of natural fibre composites are very desirable since they would aid in environmental protection. There is less report on the application of oil palm fibres in medical field thus demanding more research to be made in order to fulfil discover the potential of OPF in said field (Norrrahim *et al.*, 2021; Asyraf *et al.*, 2022).

2.3.6 Disadvantages of OPF and solution

The growing demand for natural fibre composites is mostly due to the benefits that may be gained from natural fibre features. However, the intrinsic incompatibility between hydrophilic fibres and their hydrophobic polymer matrix equivalents is one of the key difficulties to the manufacturing of natural fibre reinforced polymer composites. Because hydroxyl groups are present, the fibres become hydrophilic, resulting in poor interfacial adhesion with hydrophobic polymer matrix (Shinoj *et al.*, 2011; Kabir, 2012; Asyraf *et al.*, 2022) and poor physical and mechanical performances of the final composites (Asyraf *et al.*, 2022; Bangar *et al.*, 2022).

Mechanical characteristic of final composites will reduce due to polymers fail to interact with the reinforcement that contains polar moieties such as OPF. The non-polar structure of OPFs causes poor filler dispersion, inadequate adhesion, and a loss in fibre characteristics. Because of the hydrogen bonds of the hydroxyl groups, natural fibre such as OPF tend to cluster in the polymer matrix, resulting in poor fibre dispersion within the matrix and poor matrix and fibre interaction. The polymer matrix's non-polar hydrophobic characteristic exasperates the dispersity of the polar fibre, which is hydrophilic by nature. Furthermore, OPFs for composite manufacture have low thermal degradability, and high water-absorption capabilities. As a result, fibre surface modification is required (Asyraf *et al.*, 2022).

Coupling agents or compatibilizers, as well as surface modification techniques, are consequently required since they enhance chemical interaction across the matrix-filler interface and diminish the hydrophilicity of OPFs. The uniformity of dispersion of the fibres in the matrix is essential to increase its' range of applications. Hemicellulose removal can reduce the hydrophilicity of fibres to improve interfacial adhesion between fibres and polymer matrices. Because of its efficacy, chemical treatment is commonly utilised in the production of composites. To increase fibre matrix adherence, chemical changes such as alkali treatment, acetylation treatment, iso cyanate treatment, maleated coupling agents, silane coupling agents, and grafting are among the methods reported by previous studies(Eng *et al.*, 2014; Asyraf *et al.*, 2022).

Among all available chemical treatments for natural fibres, alkalisation is considered as among the most cost-effective and is frequently utilised to improve the efficacy of other therapies. It eliminates non-cellulosic compounds that coat cellulose fibres and bind fibrils together such as impurities, waxes, pectin, and hemicellulose. The elimination of these compounds results in a roughened fibre surface, which encourages surface contact. This encourages mechanical interlocking between polymers and fibres, resulting in improved mechanical characteristics. Natural fibre chemical alteration exposes more reactive groups on the fibre surface, promoting more effective interaction with polymer matrix (Eng *et al.*, 2014).

2.4 Silica from Rice Husk

Rice husk (RH) is the outer coating of the rice grain. It is a by-product of rice milling process. It is considered as an agricultural waste in all rice-producing countries.