

**BIOLOGICAL TREATMENT OF SPENT COFFEE
GROUND (SCG) AND ITS INFLUENCE ON THE
MECHANICAL PROPERTIES OF BIOPOLYMER
COMPOSITE**

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UNIVERSITI SAINS MALAYSIA

2023

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COMPOSITE**

by

BOEY JET YIN

**Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science**

September 2023

ACKNOWLEDGEMENT

Completing this thesis has been both rewarding and challenging. Apart from my efforts, the success of this project depends largely on the encouragement and guidelines of many others. Therefore, I would like to acknowledge all those who contributed to making this thesis a success.

First and foremost, I would like to express my deepest gratitude and appreciation to my supervisor, Assoc. Prof. Dr. Tay Guan Seng, and my co-supervisor, Assoc. Prof. Dr. Lee Chee Keong, who offered their continuous guidance, priceless advice, and limitless patience throughout the research study and thesis writing. It has been an honour to have them as my supervisors. Their considerable experience and knowledge have shaped me into a better professional person.

My success would have been inconceivable without the financial assistance. Therefore, I would like to thank Kuok Foundation Berhad for the research finance and support through the MSM Fellowship Award that contributed to successful research work.

Besides that, I would like to convey my appreciation to the laboratory technician and staff from the School of Industrial Technology, especially Encik Shamsul and En. Basrul, as they gave permission to use all required equipment and assisted in handling equipment at different stages of the research.

I would not be where I am today without my family and friends. I really appreciate your mental support and being with me throughout my research journey.

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LIST OF SYMBOLS

β	Beta
%	Percentage
$^{\circ}\text{C}$	Degree celsius
&	And
+	Plus
-	Minus
X	Multiply
=	Equal
>	More than
\pm	Plus-minus
wt%	Weight percentage
μl	Microliter
cm	Centimetre
g	Gram
L	Litre
g/L	Gram per litre
kg	Kilogram
min	Minutes
kV	Kilovolt
kN	Kilonewton
MPa	Megapascal
M	Molar
mM	Millimolar

mg	Milligram
mL	Millilitre
mm	Millimetre
nm	Nanometre
mm/min	Millimetre per minute
m/s	Metre per second
g/cm ³	Gram per cubic centimetre
MPa	Megapascal
J	Joule
rpm	Revolution per minute
U/g	Amount of enzyme that produce 1 μmol substrate per minute
v/v	Volume per volume
w/v	Weight per volume
v/w	Volume per weight
T _d	Theoretical density
M _d	Measured density
T _m	Melting temperature
T _g	Glass transition temperature

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
AOAC	Standard Association of Official Analytical Chemists
MS	Malaysia Standard
FE-SEM	Field emission-scanning electron microscopy
SEM	Scanning electron microscopy
KH_2PO_4	Potassium dihydrogen phosphate
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Magnesium sulphate heptahydrate
HCL	Hydrochloric Acid
H_2SO_4	Sulphuric acid
NH_3	Ammonia
NH_4NO_3	Ammonium nitrate
$(\text{NH}_4)_2\text{SO}_4$	Ammonium sulfate
NH_4OH	Ammonium hydroxide
NaOH	Sodium hydroxide
NaCL	Sodium chloride
Na_2CO_3	Sodium carbonate
Na_2SO_4	Anhydrous sodium sulfate
CuSO_4	Copper sulfate
Au	Gold
SeO_2	Selenium dioxide
ABTS	2,2'-azinobis(3-ethylthiazoline-6-sulfonate)
HBT	1-hydroxybenzotriazole
BSA	Bovine serum albumin

MnSO ₄	Manganese sulfate
H ₂ O ₂	Hydrogen peroxide
CMCase	Carboxymethylcellulase
CMC	Carboxymethyl cellulose
FPase	Filter paper activity
FPU	Filter paper units
MnP	Manganese peroxidase
OH	Hydroxyl
PHA	Poly(hydroxyalkanoate)
PLA	Poly(lactic acid)
LA	Lactic acid
PCL	Polycaprolactone
PBS	Polybutylene succinate
PHB	Poly(hydroxybutyrate)
PHV	Poly(hydroxyl-valerate)
PBAT	Poly(butylene adipate-co-terephthalate)
PP	Polypropylene
PVA	Polyvinyl alcohol
PHBV	Poly(hydroxybutyrate-co-hydroxyvalerate)
PE	Polyethylene
Bio-PET	Bio-polyethylene terephthalate
Bio-PA	Bio-polyamide
Bio-PE	Bio-polyethylene
XO	Xylo-oligosaccharides
EFB	Empty fruit bunches

SSK	Coffee silver skin
PSP	Paddy straw powder
AF	Agave fiber
BF	Bamboo fiber
PLF	Pineapple leaf fiber
OSP	Oyster shell powder
DNS	Dinitrosalicylic acid
SCG	Spent coffee ground
USCG	Untreated spent coffee ground
TSCG	Treated spent coffee ground
CH	Coffee husk
PDA	Potato dextrose agar
XRD	X-ray diffraction
MFI	Melt flow index
SEM	Scanning electron microscopy
SMF	Submerged fermentation
SSF	Solid-state fermentation
USM	Universiti Sains Malaysia
UV	Ultraviolet
LiP	Lignin peroxide
MnP	Manganese peroxide
LCF	Lignocellulosic fiber
BC	Bacterial cellulose
ROP	Ring-opening polymerization

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Appendix 1	CMCase standard curve
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Appendix 3	Glucosamine standard curve

**PERAWATAN BIOLOGI TERHADAP SERBUK KOPI TERPAKAI (SCG)
DAN PENGARUHNYA KEPADA SIFAT MEKANIK KOMPOSIT
BIOPOLIMER**

ABSTRAK

Kajian ini dijalankan untuk pembangunan biokomposit diperkukuh dengan bahan biojisim berasaskan serbuk kopi terpakai (SCG), asid polilaktik (PLA), dan polihidroksialkanoat (PHA) sebagai matriks. Pada peringkat pertama kajian ini, kesan kandungan SCG (10–40 wt%) dan nisbah PHA/PLA (100/0, 75/25, 50/50, 25/75, dan 0/100) terhadap sifat biokomposit telah dikaji. Penyemperit skru berkembar telah digunakan untuk proses pencampuran pada suhu 220°C di zon suapan dan 210°C di zon pencampuran, masing-masing dengan kelajuan 75 rpm. Campuran tersebut kemudiannya disejukkan dan dipeletkan sebelum dimampatkan untuk pembuatan komposit dengan menggunakan pengacuan mampatan pada suhu 190°C. Kemudian, biokomposit yang terhasil dipotong mengikut dimensi ujian yang berlainan. Daripada pengukuran sifat mekanik, keputusan menunjukkan bahawa kekuatan komposit dipengaruhi oleh penggumpalan SCG, yang dipercayai ketidakserasian antara SCG dan matriks PHA/PLA. Hal ini dapat dibuktikan daripada kajian morfologi di mana jurang antara SCG dan matriks dapat diperhatikan. SCG menunjukkan kecenderungan untuk menggumpal pada kandungan SCG 40% berat, yang mana dipercayai salah satu factor yang membawa kepada peningkatan pembentukan lompong (8.2–9.1%) berbanding dengan kandungan SCG yang lebih rendah pada 10% berat (7.6–8.1%). Nisbah PHA/PLA (50/50) dengan kandungan SCG (20% berat) telah dipilih untuk membuat biokomposit dengan SCG yang dirawat. Rawatan biologi SCG menggunakan *P.chrysosporium* CK01 dan *A. niger* DWA8 menunjukkan *P.*

chryso sporium CK01 memerlukan kandungan lembapan yang lebih tinggi (55%, b/b) untuk pertumbuhan optimum dan pengeluaran enzim, manakala keadaan optimum untuk pengeluaran enzim adalah berbeza daripada pertumbuhan *A. niger* DWA8. Mikrograf SEM telah menunjukkan sebaran SCG terawat yang lebih seragam dan pembasahan SCG terawat oleh matriks yang lebih berkesan. Biokomposit yang diperkukuh dengan SCG terawat mempamerkan peningkatan masing-masing sebanyak 72% dan 34% dalam kekuatan tegangan dan modulus. Biokomposit PHA50/PLA50/TSCG20_PC45 menunjukkan kekuatan lenturan tertinggi (10.85 MPa) dan modulus (2992.79 MPa). Penemuan ini membuktikan keberkesanan rawatan kulat yang mampan dalam meningkatkan lekatan antara muka antara SCG yang terawat dan matriks PHA/PLA.

**BIOLOGICAL TREATMENT OF SPENT COFFEE GROUND (SCG) AND
ITS INFLUENCE ON THE MECHANICAL PROPERTIES OF
BIOPOLYMER COMPOSITE**

ABSTRACT

This study aimed to develop biomass-reinforced biocomposites by employing spent coffee grounds (SCG) as reinforcement material and poly(lactic acid) (PLA), and poly(hydroxyalkanoate) (PHA) as the matrix. The investigation focused on assessing the effect of SCG content (10–40 wt%) and the PHA/PLA ratio (100/0, 75/25, 50/50, 25/75, and 0/100) on the properties of these biocomposites. The compounding process was conducted using a twin-screw extruder at a temperature of 220°C at the feeding zone and 210°C at the mixing zone at a rotating speed of 75 rpm. The mixture was then cooled and pelletized before it was compressed at a temperature of 190°C using compression moulding for biocomposites making. The biocomposites were then cut according to the different testing dimensions. Incorporating SCG lowered the mechanical properties, primarily due to its incompatibility with the PHA/PLA matrix. This observation was confirmed through morphological analysis, which revealed a gap between the SCG and the matrix. SCG displayed a tendency to aggregate at loading of 40 wt%, leading to increased void formation (8.2–9.1%) compared to lower loading at 10 wt% (7.6–8.1%). A PHA/PLA ratio (50/50) with SCG loading (20 wt%) was chosen to make biocomposites with treated SCG. Biological treatment of SCG using *P. chrysosporium* CK01 and *A. niger* DWA8 indicated *P. chrysosporium* CK01 necessitated a higher moisture content (55%, w/w) for optimum growth and enzyme production, while the optimal condition for enzyme production differed from those promoting *A. niger* DWA8 growth. SEM micrographs highlighted the uniform

distribution and effective wetting of treated SCG within the matrix. Biocomposites with treated SCG exhibited remarkable improvements of 72% and 34% in tensile strength and modulus, respectively. PHA50/PLA50/TSCG20_PC45 biocomposite demonstrated the highest flexural strength (10.85 MPa) and modulus (2992.79 MPa). These findings proved the effectiveness of sustainable fungal treatment in enhancing the interfacial adhesion between treated SCG and the PHA/PLA matrix.

CHAPTER 1

INTRODUCTION

1.1 Research background

Polymers are now one of the most extensively used materials. They play an important role in manufacturing packaging, consumer goods, and automobile parts. The escalating reliance on non-biodegradable plastics is a major issue when sustainable development is in the picture. Sustainability has been the key driver for research and innovation strategies in developing a research study and business plan. In fact, sustainable development is now more than just a catchphrase, as some practices and initiatives have been in the pipeline from various approaches. Material replacement is one of the initiatives aimed at reducing reliance on fossil fuel-based polymer materials by transitioning to biopolymers. Renewable polymers like poly(lactic acid) (PLA), poly(hydroxyalkanoate) (PHA), polycaprolactone (PCL), and thermoplastic starch have piqued the interest of academics and manufacturers. Given this, it is possible to see a reduction in greenhouse gas emissions from fossil fuel usage that are harmful to the environment.

To further improve the material properties, the inclusion of natural or lignocellulosic fillers in the polymer matrix is of great interest (Moustafa et al., 2016; Narancic et al., 2020; Rajak et al., 2019). These fillers contribute unique features to the final composites, particularly those connected to environmental benefits, improved mechanical and physical properties, and reduced density. Natural fillers, as compared to pure polymer materials, greatly lower the cost of the composite product and are renewable with minimal environmental impact (Pickering et al., 2016). Given the scale of coffee waste generated by coffee processing, spent coffee grounds (SCGs) have

been explored as fillers in polymer composites due to their abundance, low cost, and eco-friendliness (Campos-Vega et al., 2015). Several papers describe the application of SCG in reinforcing polymer composites, including PLA (Suaduang et al., 2019), poly(butylene adipate-co-terephthalate) (PBAT) (Moustafa et al., 2016), polypropylene (PP) (Sohn et al., 2019), polyvinyl alcohol (PVA) (Lee et al., 2015), and epoxy (Nguyen & Nguyen, 2021).

The performance of filler-reinforced composites is influenced by several factors, and one of them is the interactions between the filler and polymer matrix (Lule & Kim, 2021b; Vishnu Vardhini et al., 2018). A compatible reinforcement for composites aims to improve adhesion forces and stress transferability between the phases. However, inadequate adhesion across the phase boundary can compromise mechanical performance and overall composite properties. Surface treatment techniques, including chemical treatment (Chihaoui et al., 2020; Fitch-Vargas et al., 2019) and physical treatment (de Farias et al., 2017; Ricciardi et al., 2021), can overcome performance restrictions, paving the way for a new generation of composites that combine sustainability and performance. These techniques have been applied to natural fillers to improve their strength.

Though prior research has been carried out on the enhancement of biocomposites through the introduction of surface-treated filler, a lack of available information in the open literature has been reported on treating SCG biologically and its effect on the biocomposite's mechanical behaviour. This study aimed to analyse the characteristics of PHA/PLA biocomposites by reinforcing SCG at loadings ranging from 10–40 wt% by melt compounding. The principal motivation for blending PHA and PLA was to gain combined performance from two different polymers and study the mechanical property changes of the blends. In the first phase of the study, an

appropriate formulation of PHA, PLA, and SCG was identified. The second phase involves investigating the effect of fungal treatments (*Phanerochaete chrysosporium* CK01 and *Aspergillus niger* DWA8) on SCG's chemical composition and surface structure at different moisture contents. The morphological, mechanical, and physical properties of the resulting biocomposites were assessed. Overall, this work highlights the use of SCG as a reinforcing agent in biocomposites, increasing the mechanical strength of the biocomposites, and promoting an environmentally sustainable waste reduction approach.

1.2 Problem statement

The use of non-biodegradable and fossil fuel-based polymers in the polymer industry contributes to environmental issues such as waste generation, disposal challenges, and sustainability concerns. This dependency on fossil fuel-based polymers is unsustainable due to depleting fossil fuel resources and rising costs. In response, researchers and industries are actively exploring the potential of bio-based polymers as matrix in composite materials, particularly interested in using eco-friendly, abundant, and recyclable natural fillers as reinforcement. This approach aims to produce fully biodegradable biocomposites when combined with a biodegradable matrix. SCG has the potential to be used as a reinforcing material in polymer composites. This application addresses the overproduction issues associated with the coffee industry, which continuously generates significant amount of SCG as a by-product (Murthy & Madhava Naidu, 2012; Obruca et al., 2015). Currently, SCG finds its primary usage in fertiliser production; however, it is considerably underutilised. SCG can be recycled for composite production, avoiding its disposal in landfills or

incineration. It can be transformed into value-added products with biodegradability at the end of its life.

The mechanical properties of biocomposites are dependent on the interfacial bond strength of the matrix and reinforcement materials. Generally, lignocellulosic fillers are hydrophilic as they contain strongly polarised hydroxyl groups in cellulose and hemicellulose. They also have surface barriers like wax, pectin, lignin, and ash, which hinder interactions at the filler-matrix interface (Kabir et al., 2012; Zwawi, 2021). On the other hand, polymer materials, such as PLA and PHA, are non-polar and hydrophobic, creating incompatibility between the polar SCG reinforcement and the non-polar polymer matrix (PHA/PLA) (Essabir et al., 2018). This lack of interaction leads to ineffective stress transfer in the biocomposites, resulting in suboptimal performance (García-García et al., 2015).

Interfacial enhancement can be done through surface treatment techniques, which are commonly conducted using chemical or physical treatments. However, these treatments have environmental implications, requiring specialised equipment, proper disposal of chemical waste, and increased costs. Furthermore, these technologies can negatively impact the green image of the final composites (Ravindran & Jaiswal, 2016). An alternative approach is biological treatment, which is considered safer, milder, and more energy-efficient. This treatment utilises microbes that produce desirable enzymes to degrade non-cellulosic components and impurities on the substrate surface. Enzymatic treatment minimises the need for chemicals and energy while producing no inhibitory substances (Bendourou et al., 2021; De Prez et al., 2018; Sindhu et al., 2016). Previous research has explored biological treatment for fibers like flax, alfa, jute, and date, demonstrating improved surface roughness, better fiber dispersion in the polymer matrix, and enhanced interfacial bonding (Chihaoui et al.,

2020; De Prez et al., 2019; Dong et al., 2016; Geremew et al., 2021; Werchefani et al., 2020). To date, there is a notable gap in the literature regarding the biological treatment of SCG as a reinforcement material and its impact on the mechanical, morphological, and physical properties of resulting biocomposites. Therefore, further investigation is needed to evaluate the potential of treated SCG as a reinforcement material.

1.3 Research scope

This study aimed to develop and characterise biocomposites using SCG as reinforcement in PHA/PLA matrix. It investigated the bioplastic matrix ratio and SCG content in biocomposites production, as well as the impact of biological treatment on SCG for interfacial enhancement. The research was divided into two phases. In the first phase, the effect of PHA/PLA ratio and SCG loading (10–40 wt%) on the properties of biocomposites was investigated. Based on the data from the first phase, an appropriate ratio for creating the biocomposites from biologically treated SCG by *P. chrysosporium* CK01 and *A. niger* DWA8 was chosen in the second phase. After treatment, the composition of untreated and treated SCG was analysed. The study also determined the enzyme activity (CMCase, FPase, and MnP) and fungal growth at various moisture levels. To analyse the change in characteristics of the resultant biocomposites, biocomposites with untreated and treated SCG were compared. The mechanical properties of the biocomposites were characterised by tensile, flexural, and impact tests. Meanwhile, X-ray diffraction (XRD), melt flow index (MFI), void content, and scanning electron microscopy (SEM) were used to analyse the biocomposite's structure and morphology.

1.4 Research objectives

Generally, the objectives of this research study are:

1. To study the effect of SCG loading on the mechanical properties of PHA/PLA biocomposites
2. To determine the effect of biological treatment using *P. chrysosporium* CK01 and *A. niger* DWA8 on SCG composition and enzyme activity
3. To study the effect of biologically treated SCG as a reinforcing agent in PHA/PLA matrix and the comparison between biocomposites with untreated and treated SCG

CHAPTER 2

LITERATURE REVIEW

2.1 Biocomposite

A composite refers to a combination of at least two constituent materials with diverse physical or chemical characteristics that outperform their individual components. These materials are classified based on their composition, which comprises the base material and filler material (Figure 2.1). The base material, known as a matrix, binds or retains the filler material in structures. Filler materials, typically synthetic fibers, blend their traits synergistically to optimise the features of the final product. This improvement elevates composite materials when compared to the properties possessed by individual components (Pommet et al., 2008; Rajak et al., 2019).

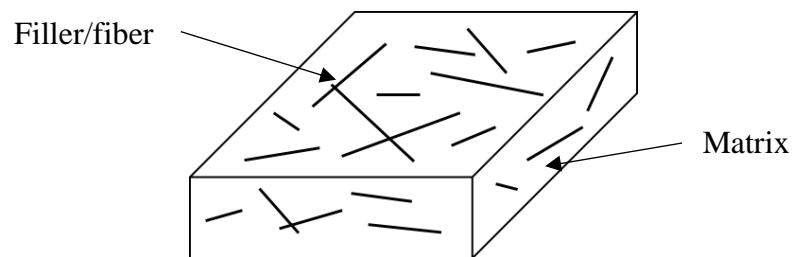


Figure 2.1 Matrix and filler in composite material

Historically, synthetic polymers derived from fossil fuels were used in the production of composite materials, which have high demand in food packaging, textiles, and biomedical fields (Luyt & Malik, 2019). Despite this, they have larger carbon footprints and require more energy for manufacturing. The depletion of fossil fuels and their resistance to degradation jeopardise the long-term sustainability of these synthetic materials (Coppola et al., 2021). Given these constraints, traditional synthetic materials are being phased out of numerous applications in favour of more sustainable

development and a lower environmental impact. Natural polymers, also known as biopolymers, are being researched as potential replacements for synthetic polymers. Plants (cellulose, lignin), animals (collagen, chitin, chitosan), microorganisms (bacterial cellulose, PHA), and biotechnological processes (PLA) produce these polymers. As they are biodegradable and biocompatible, biopolymers serve a diverse role in biomedical applications such as tissue engineering, wound healing, and drug delivery (Aaliya et al., 2021; Sanivada et al., 2020). Table 2.1 lists the properties of natural and synthetic polymers.

Table 2.1 Comparison of natural and synthetic polymers

	Natural polymer	Synthetic polymer
Properties	Produced from natural renewable resources (plant or biomass) Similar chain lengths of molecules Backbone could be of carbon, oxygen, and nitrogen Most polymers are easily degraded by biological processes	Produced from non-renewable resources (fossil fuel or gas) Chain lengths could be varied based on the reaction conditions Backbone is mostly carbon Most polymers are hard to degrade naturally by biological processes
Application	Pharmaceutical, biomedical, cosmetics, automotive, textile, food packaging, agricultural films	Textile, food packaging, consumer goods, electronics, drug delivery, biomedical

Biocomposites were introduced to replace synthetic polymer composites. Ibrahim et al. (2021) describe biocomposites as composites made from bioplastics and plastics impregnated with natural or synthetic fibers, or both. These materials address previously discussed global issues, such as petroleum supply scarcity and waste management. In today's economic situation, these green composites benefit both the environment and the economy. In filler-reinforced composites, the filler acts as reinforcement by providing strength and stiffness to the structure, while the matrix shields the filler surface from mechanical damage and provides dimensional stability (Brodowsky et al., 2020). Depending on the source from which they were produced,

biocomposites can be partially or completely biodegradable (Figure 2.2). Biodegradability involves enzymatic and/or chemical reactions mediated by bacteria or organisms, the effectiveness of which is regulated by environmental factors (Hubbe et al., 2020). They are not inherently biodegradable just because they are bio-based. Non-biodegradable based biopolymers include bio-polyethylene terephthalate (bio-PET), bio-polyamide (bio-PA), bio-polyethylene (bio-PE), and polyester (Garrison et al., 2016). Combining these polymers with natural fiber is not eco-friendly and is labelled as "partial biodegradable".

Completely biodegradable biocomposites are created when the matrix resin is biodegradable. Aliphatic polyesters such as PLA, PHA, starch, and cellulose are examples of bio-based and biodegradable polymers. Biopolymers can be created biologically (by plants, animals, or microorganisms) or chemically (from biological starting ingredients like maize, sugar, starch, and so on). A bio-based and biodegradable matrix is preferred for creating an eco-friendly composite. Biodegradable polymers can be bio- or fossil fuel-based. The combination of fossil fuel-based polymer resins with natural fibers derived from renewable resources creates biodegradable biocomposites. These biodegradable but non-biologically produced polymers are represented by poly(butylene adipate-co-terephthalate) (PBAT), polycaprolactone (PCL), polyvinyl alcohol (PVA), and polybutylene succinate (PBS) (Luyt & Malik, 2019). Although these polymers are partially sourced from fossil fuels, microorganisms may degrade them.

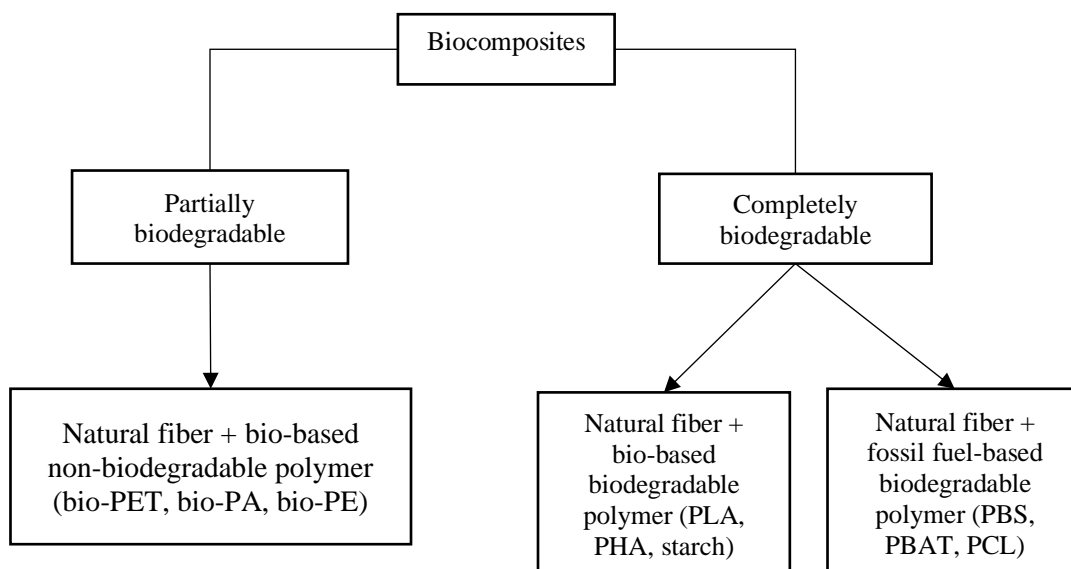


Figure 2.2 Classification of biocomposites

2.2 Biopolymer

Biopolymers can be produced in two ways: directly from biomass (for example, polysaccharides (starch and cellulose) and proteins (gelatin, casein, and collagen)), or by polymerization of bio-derived monomers, such as PLA. Microorganisms or genetically modified bacteria can also produce biopolymers like PHA, poly(hydroxybutyrate) (PHB), and poly(hydroxyl-valerate) (PHV) (Jamshidian et al., 2010; Khosravi-Darani & Bucci, 2015; Reichert et al., 2020). These polymers offer alternatives to non-renewable fossil fuel-based polymers, with PLA and PHA being the main focus.

2.2.1 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA), or polylactide, is a promising substitute for conventional petroleum-based polymers, accounting for 20.7% of the bioplastics market in 2022 (*European Bioplastics*). It is a linear polyester thermoplastic made by direct condensation polymerization of lactic acid (LA) or ring-opening polymerization (ROP) of cyclic lactide. Lactic acid is the key precursor in PLA synthesis and may be

obtained by fermentation of carbon sources such as corn starch, sugar cane, potatoes, beets, and so on (Zwawi, 2021). LA monomers are bonded together in the polycondensation process, resulting in a low molecular weight polymer (around 16,000). In contrast, ROP of lactide can yield PLA with a high molecular weight (20,000–680,000). PLA is available in both crystalline and amorphous forms, with crystallinity influencing tensile strength, melting temperature, hardness, and stiffness (Leluk et al., 2020).

PLA, a biodegradable and renewable polyester, is a popular choice due to its processability, high transparency, and eco-friendly properties (Hamad et al., 2018). It is widely used in industries like packaging, drug delivery systems, and 3D printing (Sanivada et al., 2020; Totaro et al., 2019; Yu et al., 2023). PLA's biocompatibility and thermal plasticity properties make it ideal for biomedical applications such as bone screws, sutures, and tissue engineering scaffolds (Jiang et al., 2021; D. Sharma et al., 2021). As a promising polymer material, PLA is mechanically robust, non-toxic, and cost-effective (Zhao et al., 2020). However, PLA has inherent shortcomings, such as limited flexibility, poor impact toughness, thermal instability, and poor gas and UV ray barrier properties (Fortunati et al., 2017). To overcome these limitations, PLA can be further ameliorated by blending with other polymers, reinforcing natural fillers (Mohammed et al., 2015), and using additives like plasticizers (Georgiopoulou et al., 2016; Qiu et al., 2021; Xie et al., 2014).

2.2.1(a) PLA/fillers composites

Academic research has been centred on PLA blends and composites with natural fibers or fillers to improve specific properties, which are presented in Table 2.2. Filler loading is well recognised as one of the factors determining composite

characteristics, with studies showing that increasing filler content can negatively affect the mechanical properties of PLA composites (Leluk et al., 2020). For example, Totaro et al. (2019) found that increasing coffee silver skin (SSK) content (10–30 wt%) led to decreased tensile strength in PLA/SSK composites. Baek et al. (2013) observed that increasing the filler amount of coffee ground (CG) and bamboo flour affected the mechanical properties of PLA composite. The tensile and flexural strengths of green composites decline as a result of weak interfacial adhesion. These results were confirmed by Field Emission-Scanning Electron Microscopy (FE-SEM), where a gap could be seen in PLA composites with 30 wt% fillers. Leluk et al. (2020) reviewed PLA/cellulose-based composites, finding that Young’s modulus and degree of crystallinity are more pronounced in highly loaded composites (30 wt%), but impact strength values drop as cellulose content increases. According to these studies, filler content governs the structural and mechanical performance of composites by altering the interfacial adhesion between the filler and the matrix.

Table 2.2 Effect of filler loading on the properties of PLA and PHA composites

Matrix	Filler	Filler loading (%)	Observation	References
PLA	Coffee silver skin (SSK)	0–30	- The addition of SSK at its highest concentration (30 wt%) increased the elastic modulus but decreased the tensile strength of PLA/SSK composites.	(Totaro et al., 2019)
	Bamboo flour (BF) and coffee ground (CG)	0–40	- The tensile and flexural strengths were reduced by increasing the filler amount up to 30 wt%.	(Baek et al., 2013)
	Cellulose fiber	5 and 30	- A gap was observed in the composites at 30 wt% filler loading.	(Leluk et al., 2020)
	Coffee ground (SCG)	5 and 15	- Highly loaded composites have higher Young’s modulus values and increased crystallinity.	(Silva et al., 2020)

Table 2.2 (Continued)

Matrix	Filler	Filler loading (%)	Observation	References
PHA	Paddy straw powder (PSP)	0–20	- Increased weight loss of 66% and 78% was achieved by PLA/CG 5 wt% and PLA/CG 15 wt%, respectively.	(Yaacob et al., 2016)
	Agave fiber (AF)	20	- 20 wt% of agave fibers showed improvement in both impact strength and tensile modulus but decreased the tensile and flexural strength of PHB and PHBV composites.	(Gallardo-Cervantes et al., 2021)
	Pineapple leaf fiber (PLF) and oyster shell powder (OSP)	0–20	- A continuous decrease in the tensile strength of PHA/PLF composite from 16.9 to 12.8 MPa with increasing PLF contents ranging from 0 to 20 wt%.	(Wu et al., 2021)
	Pulp fiber	0–40	- The addition of PLF and OSP to PHA was found to increase the biodegradation rate of the composite, with more than 56% of the weight lost by day 30.	(Ren et al., 2015)
	Jute, hemp, and lyocell fibers	10–30	- The impact strength of PHB/pulp fiber composites increases up to 131% relative to their unreinforced PHB.	(Gunning et al., 2013)
	Cellulose fiber	10	- The flexural modulus of PHB/jute and PHB/hemp biocomposites at 30 wt% was improved by 591% and 246%, respectively, when compared with virgin PHB.	(Ruka et al., 2015)

Biodegradability is another advantage of manufacturing biocomposites. da Silva et al. (2020) investigated the biodegradation of PLA with SCG by accelerated degradation (UV radiation) and soil burial. The reinforcement provided by fillers accelerates the biodegradation process of PLA, resulting in an increased weight reduction of 66% and 78%, as indicated by PLA/CG 5 wt% and PLA/CG 15 wt%, respectively. Yaacob et al. (2016) reported on the 6-month biodegradation of PLA/paddy straw powder (PSP) biocomposites in compost. According to their data,

increased PSP concentration resulted in greater weight reduction, with 49% of weight loss occurring after 180 days. PLA/PSP biocomposites degrade faster than PLA because lignocellulosic components are more easily attacked by microorganisms. In addition, the hydrophilic behaviour of PSP exacerbated the water uptake of the biocomposites, causing major degradation. These results demonstrate that the presence of natural fillers in PLA composites accelerates biodegradation due to increased hydrophilicity.

2.2.2 Poly(hydroxyalkanoate) (PHA)

Poly(hydroxyalkanoate) (PHA) is a microbial polyester produced from the fermentation of sugars and lipids by bacteria (Loureiro et al., 2014). It is synthesised as intracellular products by bacteria (e.g., *Pseudomonas putida*, *Alcaligenes latus*, and *Cupriavidus necator*) under stressed conditions with excess carbon sources but limited supplies of other nutrients such as nitrogen, oxygen, and phosphorus (Arrieta et al., 2017; Sisti et al., 2021). It is classified into three types based on the length of its carbon chain: short-chain PHA (three to five carbon atoms), medium-chain PHA (six to fourteen carbon atoms), and long-chain PHA (more than fifteen carbon atoms) (Khosravi-Darani & Bucci, 2015). PHA's melting temperature (T_m), degree of crystallinity, and glass transition temperature (T_g) are all affected by the polymer's monomer composition, which is determined by the organism, growth conditions, and polymer extraction method (Narancic et al., 2020).

Poly(hydroxyl-valerate) (PHV) or poly(hydroxybutyrate) (PHB), along with their copolymer poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) in various molar ratios, belong to the family of PHA. These PHA bioplastics exhibit characteristics similar to those of petroleum-based polymers like PP (Aaliya et al., 2021). Their

biodegradability is an advantage, especially in applications where sustainability and reduced environmental impact are essential. Bacterially synthesised PHA is biocompatible and can be used in diverse fields, including tissue engineering, medical implants, and drug delivery systems (Khosravi-Darani & Bucci, 2015; Reichert et al., 2020; Sisti et al., 2021). PHA polymers offer versatility in terms of mechanical properties. Depending on the specific type of PHA and its processing, PHA materials can be designed to be soft and flexible, making them well-suited for applications like packaging films, disposable utensils, and medical devices. Their physical properties can be tuned by varying their monomeric compositions (Narancic et al., 2020; Nielsen et al., 2017). In 2022, PHA accounts for only 3.9% (almost 0.09 million tonnes) of worldwide bioplastics production capacities (*European Bioplastics*). Large-scale production faces challenges primarily due to the high production costs associated with the use of pure cultures and refined substrates (glucose and sucrose) in industrial production (Zwawi, 2021). Some PHA types, like PHB, can exhibit brittleness, which can limit their suitability in certain applications, including the food packaging industry. In addition, PHB's low resistance to thermal degradation can restrict its use in high-temperature applications (Arrieta et al., 2017; Zhang & Thomas, 2011). A growing body of literature has investigated cost-effective PHA production using mixed microbial cultures and low-cost feedstocks such as coffee, sugar, waste oil, legumes, whey, and starch (Nielsen et al., 2017; Stavroula et al., 2020). Polymer blending with affordable biopolymers and natural fillers holds promise for the production of cost-effective PHA-based composites, further enhancing their applicability.

2.2.2(a) PHA/fillers composites

A significant body of research has been conducted to understand the interactions within PHA/PLA blends. Loureiro et al. (2013) prepared PHA/PLA blends with varying compositions using injection moulding. Their findings revealed that the adhesion between the PHA and PLA phases increased as the PHA content in the blend increased. When PHA was the dispersed phase, the results indicated a decrease in adhesion between the polymer phases, particularly at lower levels of PHA incorporation (up to 30%). Interestingly, the incorporation of 30% PHA led to a remarkable increase in the elongation percentage of the blends, surpassing that of neat PLA and PHA by 119% and 182%, respectively. Their study identified the highest synergetic effect in PHA/PLA blends at a ratio of 30/70, where PLA served as the matrix and PHA as the disperse phase. Similar observations were made by Zhang & Thomas (2011) when investigating PLA/PHB blends with various weight ratios. They noted a substantial improvement in the mechanical properties of the blend in the case of the PLA75/PHB25 blend. This improvement was attributed to the presence of PHB crystals, which acted as both fillers and nucleating agents, promoting the crystallinity of PLA.

Blending with various natural fillers has already been studied as a reinforcement for PHAs, and Table 2.2 shows the characteristics and performance of the resultant composites. Gallardo-Cervantes et al. (2021) examined the incorporation of filler into PHA-based composites. PHB and PHBV with 20 wt% of agave fibers (AF) improved impact strength and tensile modulus while decreasing tensile and flexural strength. Wu et al. (2021) also observed a continuous decrease in the tensile strength of PHA/pineapple leaf fiber (PLF) composites from 16.9 MPa to 12.8 MPa when the PLF content increased from 0 wt% to 20 wt%. The impact strength of

PHB/pulp fiber composites rose by up to 131% relative to their unreinforced PHB (Ren et al., 2015). Gunning et al. (2013) investigated biocomposites based on jute and hemp fibers and PHB, finding significant enhancements in the mechanical properties. When compared to virgin PHB, the flexural modulus of PHB/jute and PHB/hemp biocomposites at 30 wt% was enhanced by 591% and 246%, respectively. However, unlike the case with agave fibers mentioned above, the impact strength showed a decreasing trend with the addition of fibers, possibly due to thermal degradation and excessive shortening of fiber during extrusion. The work reported in this section shows that different filler reinforcements increased some properties while decreasing others or not being evaluated. Given this, appropriate reinforcement should be chosen to improve the composite properties for specific applications.

Other studies were conducted to explore the effect of fillers on the biodegradability of PHA-based materials under different conditions. Gunning et al. (2013) studied the biodegradation of PHB biocomposites with hemp, jute, and lyocell fibers using a rotary aerated composter. Over the 12-week composting test period, the biodegradation rate of all composites was greater than that of virgin PHB and increased with increasing filler content (10–30 wt%). Ruka et al. (2015) found a comparable outcome for PHB composite with bacterial cellulose (BC). PHB/BC composite biodegrades faster and to a higher extent than PHB alone, reaching 80% breakdown after 30 days under aerobic test conditions, whereas PHB did not reach this level of degradation until nearly 50 days of composting. When PHA composites were buried in soil, the addition of pineapple leaf fiber (PLF) and oyster shell powder (OSP) to PHA increased the composite's biodegradation rate, with over 56% of the weight lost by day 30 (Wu et al., 2021). In summary, filler addition has a positive effect on the

biodegradation rate of PHA-based composites, making them suitable for single-use applications with the capacity for biodegradation after disposal.

2.3 Lignocellulosic fiber

Synthetic fibers, such as carbon, aramid, or glass fibers, have been extensively explored in the composite industry for their improved mechanical properties (Chihaoui et al., 2020). However, the depletion of petroleum resources, the volatility of crude oil prices, and the preference to minimise waste disposal have led to the preservation of natural resources. Natural fibers have proven their superiority in replacing costly synthetic fibers throughout the years. They have a lower density (approximately 1.2–1.6 g/cm³) than synthetic fibers (2.4 g/cm³), allowing for the production of lighter composites. They are categorised into three major types based on their source (Figure 2.3) (Latif et al., 2018). Plant fibers, also known as lignocellulosic fibers (LCFs), offer better mechanical properties than animal fibers and are an ecological alternative to synthetic fibers (Pickering et al., 2016; Zini & Scandola, 2011). LCFs have gained interest in filler-reinforced composites, focusing on bast fibers like kenaf, flax, jute, and hemp (Georgiopoulos et al., 2016; Gunning et al., 2013; Mohamad et al., 2020). LCFs are ecologically harmless, cheap, readily accessible, biodegradable, and have a low carbon footprint. They also have excellent specific mechanical properties in terms of strength and stiffness, as well as low acoustic and thermal conductivity. Other studies present more compelling evidence for clear benefits, such as the fact that composite production is less expensive and uses less energy than other materials (Leluk et al., 2020; Loureiro et al., 2014). This represents a new evolution in using natural resources as reinforcing agents for eco-composites.

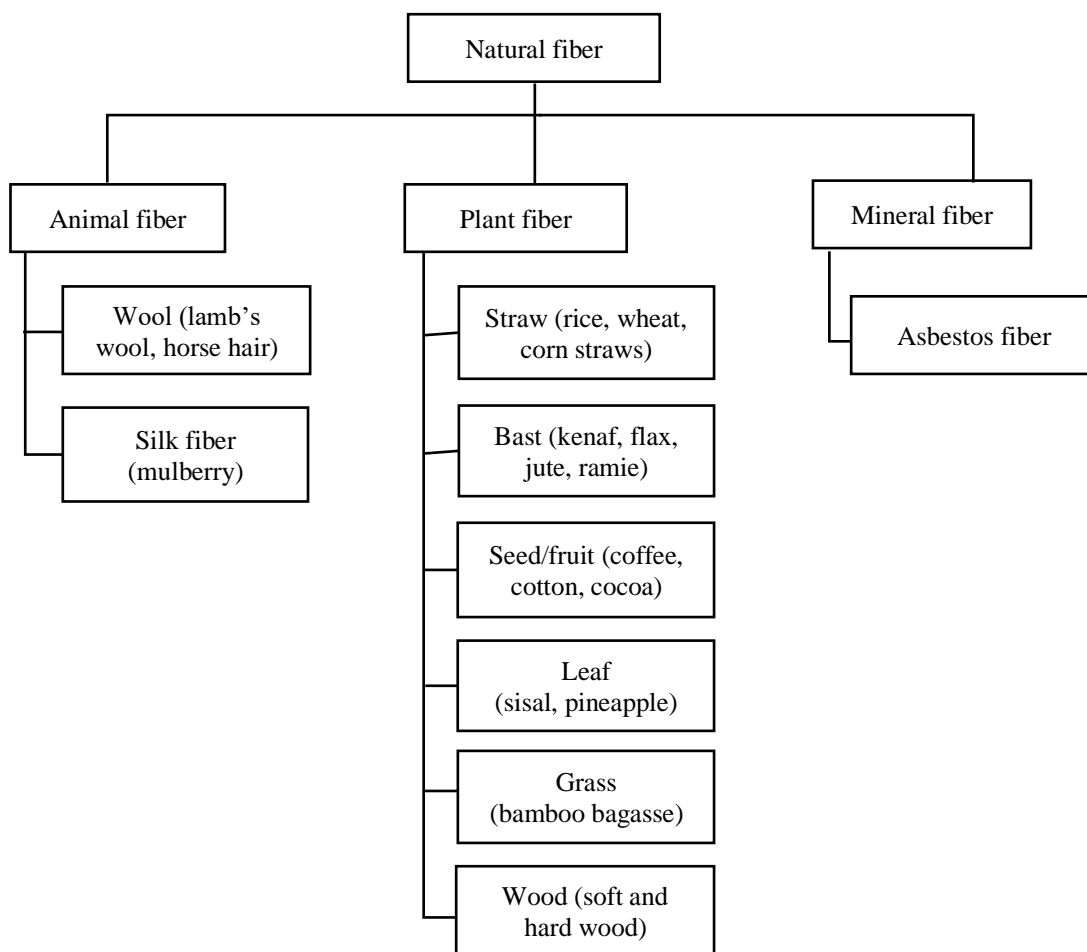


Figure 2.3 Classification of natural fiber

2.3.1 Structure of lignocellulosic fiber

LCFs consist of cellulose, lignin, and hemicelluloses, which are closely linked components in the biomass's cellular complex. These components act as a protective barrier against cell destruction by bacteria and fungus. Cellulose, a major component of plant cell walls, provides strength, stiffness, and structural stability (Aaliya et al., 2021; Ravindran & Jaiswal, 2016). It has crystalline and amorphous regions in various proportions. Hydrogen bonding builds a highly ordered structure in the crystalline region, making it insoluble in most solvents and less degradable. Cellulose is soluble and easily degraded by enzymes in the less-ordered amorphous region (Jayasekara & Ratnayake, 2019). Hemicellulose, on the other hand, is very hydrophilic, has a lower

molecular weight, and is easily degraded by heat and water. It serves as a supporting matrix for cellulose microfibrils (De Prez et al., 2018; Lee et al., 2020). LCFs have an exterior layer composed of lignin, waxes, and oils, with lignin being the most resistant polymer to chemical and enzymatic degradation due to its aromatic network structure (Ravindran & Jaiswal, 2016). The chemical constituents of each LCF vary depending on the type and parts of plants from which fiber is extracted. Therefore, its constituents are crucial in predicting the mechanical and thermal properties of fiber and composites (Aaliya et al., 2021).

2.3.2 Drawbacks of lignocellulosic fiber

Although LCFs are rapidly expanding these days, they have some drawbacks when used in composite materials due to their inherent polarity. The low compatibility of LCF with mostly non-polar matrix restricts their potential as reinforcing fillers, resulting in the formation of unstable interfaces and limited stress transfer. The mechanical properties of filler-reinforced composites are strongly dependent on the dispersion of these fillers and the interfacial adhesion they establish with the polymer matrix (Lule & Kim, 2021b). The interfacial connection is correlated to mechanical interlocking, chemical bonding, and physical bonding (van der Waals force and hydrogen bond) (Shahzad, 2017). Likewise, poor wettability of fillers within the matrix hinders their homogeneous dispersion, which in turn leads to poor composite performance (Gibeop et al., 2013; Kabir et al., 2012; Shahzad, 2017; Zwawi, 2021).

Another barrier to the effective utilisation of natural filler composites is the intrinsic hydrophilicity of fillers, due to the presence of hydroxyl groups (OH) in cellulose, hemicellulose, and lignin (Aaliya et al., 2021). When exposed to high humidity conditions, these OH groups form new hydrogen bonds with water molecules,

causing moisture uptake in the outer layers of composite materials, filler swelling within the matrix, and poor linkage to the matrix. This leads to stress concentration at the interface and micro-cracking between the swollen filler and the matrix, causing dimensional instability and adverse effects on the mechanical performance of the final composite (Mohammed et al., 2015). To develop composite materials with excellent properties, it is crucial to consider these limitations. Fortunately, the intrinsic properties possessed by LCF can be modified through surface treatment techniques before their incorporation into a polymer matrix, as elaborated in Section 2.5.

2.4 Spent Coffee Ground (SCG)

2.4.1 Introduction

Coffee ranks as the world's second-most consumed beverage, following water, with its production primarily concentrated in South America, Asia, and Oceania. Brazil, Colombia, Indonesia, and Vietnam are the foremost producers within these regions (Hejna, 2021). Green coffee is mainly composed of carbohydrates, constituting approximately 60% of its dry weight. These carbohydrates include oligosaccharides, disaccharides, and monosaccharides. The journey from green coffee beans, obtained through the processing of coffee cherries, to aromatic and flavourful roasted coffee beans is a key step in the coffee manufacturing process. These roasted beans are ground and brewed to prepare coffee. The brewing process, which employs hot water under high pressure, extracts soluble materials, including caffeine, from the coffee ground, resulting in the generation of solid residues known as spent coffee grounds (SCG) (Zarrinbakhsh et al., 2016).

SCG is extensively analysed in terms of its composition, as shown in Table 2.3 (Baek et al., 2013; Ballesteros et al., 2015; Jeníček et al., 2022; Martinez-Saez et al., 2017; Mussatto et al., 2011; Yuliyanti et al., 2021; Zainol et al., 2020; Zarrinbakhsh et al., 2016). According to different literature reports, carbohydrates, mainly hemicellulose and cellulose, are the dominant components in SCG (Gaidukova et al., 2021). Apart from carbohydrates, SCG contains a significant amount of crude fiber (19.1–51%) (Baek et al., 2013; Martinez-Saez et al., 2017; Zainol et al., 2020). Protein and fat account for roughly 20% of the total dry mass. Coffee oil, a component of SCG, comprises free fatty acids, monoglycerides, diglycerides, and triglycerides (Campos-Vega et al., 2015; Kovalcik et al., 2018). SCG also contains ash, made up of minerals such as potassium, phosphorus, magnesium, manganese, iron, calcium, and copper, in smaller quantities (Mussatto et al., 2011). It should be noted that the composition obtained varies greatly depending on the plant’s geographical location, age, climate, and soil conditions (Murthy & Madhava Naidu, 2012). The type of coffee beans used, roasting, and processing techniques also bring considerable changes to the composition and biological activity of coffee (Mussatto et al., 2011).

Table 2.3 Summary of composition of SCG according to the literature reports

Carbohydrate	Crude fiber	Fat	Protein	Moisture	Ash	References
74.2	-	10.3	13.3	-	2.2	(Zarrinbakhsh et al., 2016)
-	-	2.3	17.4	-	1.3	(Ballesteros et al., 2015; McNutt & He, 2019)
-	46.6-51	-	10.2-13	-	0.7-0.8	(Baek et al., 2013)
-	-	-	13.6	-	1.6	
-	47.3	24.3	11.2	3.6	0.5	(Martinez-Saez et al., 2017)

Table 2.3 (Continued)

Carbohydrate	Crude fiber	Fat	Protein	Moisture	Ash	References
-	-	-	-	8.2	1.6	(Jeníček et al., 2022)
6.2-8.9	19.1-19.8	1.4-2.8	5.2-7.2	61.8-66.5	0.5-0.6	(Zainol et al., 2020)
81.6	-	4.4	7.6	5.5	1.0	(Yuliyanti et al., 2021)

According to data from the International Coffee Organisation, global economic coffee trading has continually risen over the years, with almost half of the world's coffee production allocated for the preparation of soluble coffee (Murthy & Madhava Naidu, 2012). The Agriculture Department in Malaysia reported a significant surge in coffee production, increasing from 3,559 tonnes in 2019 to 4,241 tonnes in 2020 (*Agriculture Department Ready to Assist Coffee Entrepreneurs*, 2021). In other words, as coffee production and consumption grow, the coffee chain generates an enormous amount of coffee waste and by-products (Hejna, 2021). SCG is one of the biggest by-products of instant coffee manufacture, often dumped in landfills or burned directly after serving its primary function (Mussatto et al., 2011). The disposal of SCG in such a manner can cause environmental issues, as it has the potential to release organic compounds, including caffeine, polyphenols, and tannins, under anaerobic conditions. These materials that leach into water sources cause marine eutrophication and excessive algal blooms (Hudeckova et al., 2018; Tapangnoi et al., 2022). Given these factors, the need for better coffee waste management should be emphasised to address environmental concerns and ensure the sustainability of the coffee industry.

2.4.2 Application of coffee by-products

Coffee by-products have been explored for various applications, contributing to the circular economy concept. Instead of being underutilised, these by-products can be transformed to serve different industries, expanding their potential as co-products. Oil-containing coffee residues have been utilised as feedstock for bioenergy production (biodiesel, bioethanol, and biofuel) following oil extraction. It is more cost-effective, delivers higher quality and stability compared to other waste sources (Atabani et al., 2018; Burniol-Figols et al., 2016). The solid residue remaining after oil extraction is an ideal material for garden fertiliser, compost, ethanol feedstock, or fuel pellets (Cruz et al., 2012; Santos et al., 2017). They have also been proven to be an effective adsorbent for contaminants such as metal ions, dyes, and bioactive compounds (McNutt & He, 2019). Another interesting work is the use of SCG in food-related applications, given its high fiber content. A study by Martinez-Saez et al. (2017) incorporated SCG as a food ingredient in bakery products, formulating biscuits with enhanced nutritional quality and reduced calorific value when combined with low-calorie sweeteners. Furthermore, they have been studied as a recycled building material due to its physical resemblance to sandy soils (Kua et al., 2017).

Apart from these applications, a growing body of research has focused on utilising coffee by-products as filler materials in polymer composites, aiming to create cheap and durable composites. Jaramillo et al. (2021) reinforced polyethylene (PE) matrix composites with 20 and 40 wt% of coffee husk (CH) for value-added consumer goods. Sohn et al. (2019) and Essabir et al. (2018) examined the influence of filler loading (up to 30 wt%) on the mechanical properties of PP/SCG blends. Although the tensile strength declined as SCG concentration rose, Young's modulus of the blends increased, reflecting the stiffening effect of SCG. The material becomes more rigid