MODIFIED KENAF BAST FIBRE MAT REINFORCED BIOPOLYMER COMPOSITE ENHANCED WITH SPENT COFFEE GROUND MICROFILLER

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MODIFIED KENAF BAST FIBRE MAT REINFORCED BIOPOLYMER COMPOSITE ENHANCED WITH SPENT COFFEE GROUND MICROFILLER

by

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LIST OF SYMBOLS

°	Degree
%	Percentage
±	Plus minus
$<$	Less than
$>$	Greater than
ρ	Density
ρ_m	Matrix density
ρ_f	Filler Density
ρ_{fb}	Fiber Density
µm	Micrometer
°C	Degree Celsius
ΔW	Change in Weight
ΔH_m	Specific melting enthalpy
ΔH_o	Theoretical melting enthalpy
b	Breadth
cm	Centimeter
g/cm^3	Gram per cubic centimeter
GPa	Giga Pascal
J	Joule
l	Length
m	Mass
m^2	Meter square
mJ	Millijoule
MPa	Mega Pascal
t	Thickness

T_m	Melting temperature
T_g	Glass transition value
T_{max}	Maximum Degradation Temperature
T_{onset}	Initial Degradation Temperature
v	Volume
v/v	Volume per volume
w/w	Weight per weight
W_f	Filler Weight Fraction
W_{fb}	Fiber Weight fraction
W_i	Initial Weight
W_f	Final Weight
X_c	Crystallinity Index

LIST OF ABBREVIATIONS

Al_2O_3	Aluminum oxide
ASTM	American Society for Testing and Materials
ATBC	Acetyl tributyl citrate
APTES	(3-aminopropyl) triethoxysilane
BCNW	Bacterial cellulose nanowhiskers
BN	Boron nitride
CO_2	Carbon dioxide
$C_6H_{10}O_3$	Propionic anhydride
$CaCO_3$	Calcium carbonate
CH	Coffee husk
CHF	Corn husk fiber
CMC	Carboxymethyl cellulose
CNC_S	Cellulose nanocrystals
CNT_S	Carbon nanotubes
CS	Corn straw
DDGS	Distillers' dried grains with solubles
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTG	Derivative thermogravimetric
FT-IR	Fourier transform infrared
H_2O	Water
HB	Hydroxybutyrate
HNTs	Halloysite nanotubes
HV	Hydroxyvalerate
KBr	Potassium bromide
MA	Maleic anhydride
MBF	Modified bast fiber
MFI	Melt flow index
MLO	Maleinized linseed oil
MW	Molecular weight

NFC	Nanofibrillated cellulose
OHF	Olive husk flour
OWF	Oak wood flour
pMDI	Polymethylene-diphenyl-diisocyanate
PBAT	Poly (butylene adipate-co-terephthalate)
PBF	Propionylated bast fiber
PBS	Poly(butylene succinate)
PCL	Poly(ε-caprolactone)
PEG	Poly (ethylene glycol)
PHA	Polyhydroxyalkanoates
PHB	Poly(hydroxybutyrate)
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly (lactic acid)
PP	Polypropylene
PPp	Peach palm particle
pMDI	Polymethylene-diphenyl-diisocyanate
PSA	Particle size analysis
PSR1	Particle size range 1
PSR2	Particle size range 2
PTAcEt	Poly(3-thiophene ethyl acetate)
RCF	Recycled cellulose fiber
SCG	Spent coffee grounds
SCBP	Spent coffee bean powder
SEM	Scanning electron microscope
SS	Soy stalk
TGA	Thermal Gravimetric Analysis
TMOS	Trimethoxyoctadecylsilane
TPF	Tea plant fibers
TPS	Thermoplastic starch
UD	Unidirectional
ViSH	Vine shoots
WCA	Water contact analysis
WF	Wood fiber
WPG	Weight percent gain

WS	Wheat straw
WSF	Wheat straw fibers
XRD	X-ray diffraction
ZnO	Zinc oxide
ZP	Zeta potential

KOMPOSIT BIOPOLIMER DIPERKUAT TIKAR KULIT GENTIAN KENAF TERMODIFIKASI DENGAN PENAMBAHBAIKAN OLEH PENGISI MIKRO KISAR SERBUK KOPI TERPAKAI

ABSTRAK

Kebimbangan yang semakin meningkat mengenai kesan buruk plastik yang dibuang ke atas alam sekitar telah mendorong pembangunan polimer mesra alam 'hijau'. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) adalah sejenis polimer mesra alam yang terkenal dengan kebolehbiodegradasi dan boleh diperbaharui. Walau bagaimanapun, prestasi mekanikalnya agak terhad. Penambahbaikan boleh dicapai dengan menggabungkannya dengan gentian semula jadi untuk menghasilkan komposit hijau. Komposit ini tidak hanya memberikan sifat mekanikal yang lebih baik tetapi juga mengekalkan kebolehbiodegradasian. Dalam kajian ini, biokomposit mesra alam dibangunkan menggunakan PHBV dan gentian kenaf bast bukan tenun yang telah diubah suai secara kimia dengan Propionic anhydride (untuk memperbaiki antara muka gentian/matriks dan ketahanan kelembapan). Kajian awal dijalankan ke atas pengisian gentian bast yang diubah suai secara optimum yang diperkukuhkan dengan PHBV. Komposit disediakan melalui acuan mampatan serbuk matriks, dengan tikar gentian bast yang telah diubah suai diselitkan di dalamnya. Penambahan 30% tikar gentian bast ke dalam PHBV menghasilkan peningkatan yang ketara dalam sifat keseluruhan. Selanjutnya, kajian ini juga meneroka penggunaan Sisa Kopi Tanah (SCG), produk sisa industri kopi sebagai zarah mikropengisi. Zarah-zarah ini sebagai mikropengisi diperkenalkan ke dalam PHBV pada pelbagai saiz zarah dan kepekatan (1%, 3%, 5%, dan 7%) untuk mencipta variasi PHBV yang mengandungi SCG. Variasi ini disediakan menggunakan mesin acuan panas. Variasi yang terhasil kemudiannya dikarakterisasi dan dibandingkan. Akhirnya, biokomposit PHBV yang diperkukuhkan dengan tikar gentian bast yang diubah suai dan mengandungi mikropengisi SCG telah disediakan. Biokomposit ini pada setiap peringkat dinilai dari segi sifat fizikal, morfologi, terma, fungsi, penyerapan air, bengkak ketebalan, sudut sentuhan air, sifat mekanikal, dan sifat biodegradabel. Biokomposit berasaskan gentian bast propionylated menunjukkan peningkatan dalam sifat fungsian, kestabilan terma yang lebih baik, dan prestasi mekanikal yang unggul. Kebolehbiodegradasian PHBV tulen adalah minima, tetapi ia meningkat dengan ketara dengan penambahan kedua-dua gentian bast dan SCG. Kepekatan sisa kopi tanah yang lebih rendah menghasilkan peningkatan dalam sifat biokomposit. Walau bagaimanapun, sifat-sifatnya menurun pada kepekatan pengisi tertinggi (7%) disebabkan oleh pengagregatan sisa kopi, yang masih menjadikannya sesuai untuk aplikasi pembungkusan yang mampan. Kajian ini menunjukkan potensi biokomposit ini untuk penyelesaian pembungkusan mesra alam.

MODIFIED KENAF BAST FIBRE MAT REINFORCED BIOPOLYMER COMPOSITE ENHANCED WITH SPENT COFFEE GROUND MICROFILLER

ABSTRACT

The escalating concern over the harmful effects of discarded plastics on the environment has prompted the development of eco-friendly 'green' polymers. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a type of environmentally friendly polymer known for its biodegradability and renewability. However, its mechanical performance is somewhat restricted. Enhancing it can be achieved by combining it with natural fibers to produce green composites. These composites not only provide improved mechanical properties but also maintain biodegradability. In this study, an eco-friendly biocomposite is developed using PHBV and chemically modified non-woven kenaf bast fibers with Propionic anhydride (to improve the fiber/matrix interface and moisture resistance). The initial investigation was conducted on the optimum modified bast fiber loading reinforced PHBV composite. Composites were prepared through the compression molding of a matrix powder, with modified bast fiber mats interleaved within. The incorporation of 30% bast fiber mats into PHBV resulted in significant overall enhancement of properties. Subsequently, this study also explores the utilization of Spent Coffee Grounds (SCG), a residual product of the coffee industry as microfiller particles. These particles as microfillers are introduced into PHBV at varying particle sizes and concentrations (1%, 3%, 5%, and 7%) to create different PHBV-incorporated SCG particle variations. These variations were prepared using hot compression molding machine. The resulting variations were then characterized and compared. Finally, PHBV-reinforced modified bast fiber mats incorporated SCG microfillers were prepared. These biocomposites at every stage were evaluated for physical, morphological, thermal, water absorption, thickness swelling, water contact angle, mechanical properties and biodegradable properties. Propionylated bast fiber-based biocomposites showed improved functional properties, enhanced thermal stability, and superior mechanical performance. The inherent biodegradability of pure PHBV was minimal, but it was significantly enhanced by the addition of both bast fibers and SCGs. Lower concentrations of SCG filler led to improved biocomposite properties. However, the properties declined at the highest filler content (7%) due to the agglomeration of coffee grounds, which still renders them suitable for sustainable packaging applications. This study demonstrates the potential of these biocomposites for eco-friendly packaging solutions.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

The increasing concern over the environmental impact of discarded plastics has spurred the development of environmentally friendly "green" polymers (Abdur Rahman, Haque, Athikesavan, & Kamaludeen, 2023). These materials are sourced from renewable resources and possess the ability to biodegrade in the natural environment with the help of soil microbes. While biodegradability offers a commercial advantage, the mechanical performance of biopolymers still remains crucial for meeting the load-bearing requirements in engineering applications. Consequently, biopolymers have yet to compete with synthetic polymers in this aspect. However, the mechanical properties of "green" plastics can be enhanced by incorporating natural plant fibers as reinforcement. This approach is appealing due to the renewability and biodegradability of the fibers. By integrating these fibers into biopolymers, it becomes possible to create a fully "green composite" (Weyhrich, Petrova, Edgar, & Long, 2023).

Packaging remains a prominent application for plastics derived from petroleum products, with a substantial daily production of thousands of plastic materials specifically designed for this purpose (Ahmed & Varshney, 2011). Global statistics indicate that approximately 8.5 tons of plastic products are manufactured each day. The demand for plastics is steadily rising due to population growth, leading to a projected exponential increase in the utilization of plastic packaging in the foreseeable future (Borrelle *et al.*, 2020).

Plastic waste has emerged as the leading contributor to global land and marine pollution, with alarming statistics to support this claim. The production of plastic-based goods has experienced a substantial increase, reaching an annual output of 300 billion tons, with roughly 50% of it being single-use items (Embrandiri, Kassaw, Geto, Wogayehu, & Embrandiri, 2022). Disturbing reports on marine pollution indicate that over 8 million tons of plastic waste find their way into the oceans (Napper & Thompson, 2020). Delving deeper into the analysis of plastic waste reports, it becomes apparent that countries with large populations, such as China, the USA, and Germany, are at the forefront of plastic production. Statistical projections have even predicted that by 2050, the volume of plastic waste in the oceans will surpass that of fish (Zong).

Plastic waste pollution is a global challenge that has prompted the development of various policies and solutions. One prominent solution is plastic recycling, which is widely encouraged by government policies. Plastic waste disposal has also been categorized using color codes, and manufacturing companies have introduced disposal symbols on plastic packaging (Maraveas, 2020). Among the countries with effective waste disposal practices, Germany stands out as a leader. In this process, disposed plastics are recycled to be used in future production. However, it is important to note that approximately 50% of the synthetic plastic produced cannot be recycled (Borrelle *et al.*, 2020). This limitation is exacerbated by population growth, as the demand for plastics continues to rise. Consequently, the most effective solution to plastic waste pollution currently lies in the production of alternative biodegradable materials to replace synthetic polymers (Kabir, Kaur, Lee, Kim, & Kwon, 2020).

Biopolymers, such as cellulose, chitosan, and starch, are naturally occurring polymers known for their unique biodegradable characteristics. They are derived from plant or animal sources and exhibit compatibility with the human body (B. Das, Paul, & Sharma, 2021). Researchers have shown great interest in the biodegradability of biopolymers and have proposed them as potential substitutes for synthetic polymers (Gowthaman, Lim, Sreeraj, Amalraj, & Gopi, 2021). Their natural abundance makes (Muthuraj, Hajee, Horrocks, & Kandola, 2019). Moreover, biopolymers are generally non-toxic and possess properties that make them well-suited for packaging applications.

In addition, a diverse range of biodegradable polymers is currently available, sourced from both renewable and non-renewable origins. Among the renewable options are polyhydroxyalkanoates (PHA), poly (lactic acids) (PLA), and thermoplastic starches (TPS). On the other hand, non-renewable sources contribute to biodegradable polymers like poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS), and poly(butylene adipate-co-terephthalate) (PBAT) (Naser, Deiab, & Darras, 2021; Satti & Shah, 2020).

While polylactic acid (PLA) is commonly recognized as the most well-known biopolymer, there are other biopolymers that offer no advantages over PLA. One such polymer is poly(hydroxybutyrate-co-valerate) (PHBV), a naturally occurring bacterial polyester (S. Zaidi, 2019). In the production of biocomposites, the processing temperature plays a crucial role as the natural fibers used for reinforcement start to degrade thermally above approximately 200°C. However, the processing temperature is determined by the melting temperature of the specific polymer used (Thakkar, Thakkar, Pillai, Ashour, & Repka, 2020). In the case of PHBV, it is possible to achieve a lower processing temperature compared to PLA by adjusting the hydroxyvalerate (HV) copolymer content during the polymerization process. Some literature reports indicate a melting temperature as low as 92°C for PHBV grades with 25 mol.% HV content (Antunes *et al.*, 2020). In contrast, the melting temperature of PLA typically falls within the range of 150–170°C. Additionally, PHBV possesses biodegradability in various environments, while PLA is primarily considered "compostable," meaning it can only degrade in specific composting conditions, limiting its disposal options (Gioia *et al.*, 2021). PHBV, an aliphatic polymer with a hydrolysable carbon backbone, can undergo degradation by bacteria and enzymes, mitigating landfill accumulation (Alhanish & Ali, 2022). Although the reinforcement of PLA with natural fibers has been extensively researched and reviewed (Rajeshkumar *et al.*, 2021), the investigation of natural fiber reinforcement in PHBV has received less attention. Nonetheless, the utilization of PHBV as a matrix material is experiencing significant growth.

Natural fiber has a distinct advantage over synthetic fiber and is commonly used as a functional reinforcement material in composites. This is primarily because of its biodegradability, non-toxic nature, and recyclability. Additionally, natural fibers possess low density while exhibiting relatively high strength and stiffness (Kamarudin *et al.*, 2022). Consequently, researchers have shifted their focus from traditional fiber-reinforced composites to biofiber-reinforced composites, owing to the functional properties of natural fibers. (Sreenivas, Krishnamurthy, & Arpitha, 2020). Kenaf fiber, in particular, has gained significant attention in scientific literature due to its abundant availability and inherent properties such as high aspect ratio, exceptional toughness, non-abrasiveness, and biodegradability (Y. Wu *et al.*, 2020). When compared to other natural fibers like cotton, sisal, jute, flax, sun hemp, and pineapple, kenaf bast fibers have shown superior tensile strength and elastic modulus (Abbas, Aziz, Abdan, Mohd Nasir, & Norizan, 2022). As a result of these unique characteristics, Kenaf fiber has found wide-ranging applications in reinforcing composites.

Kenaf fiber, a natural biofiber, or biofiber has found significant use in the production of nonwoven fiber mats as a viable alternative to synthetic fibers. It possesses unique and inherent advantages such as low density, good thermal stability, and high strength, making it an ideal choice for reinforcement materials in biocomposites (Sapiai, Jumahat, Jawaid, Midani, & Khan, 2020). Its renewable nature, biodegradability, and non-toxic properties have attracted attention in composite applications. Numerous studies have focused on establishing kenaf fiber as a reinforcement agent in composite materials (Yusuff, Sarifuddin, & Ali, 2021). In a particular study by kenaf fiber was utilized as a reinforcement agent, resulting in enhanced thermal stability and improved mechanical properties compared to composites without reinforcement (Prakash & Viswanthan, 2019).

Kenaf bast has great potential as a reinforcing agent for natural fiber composites due to its long fibers, excellent mechanical properties, and high strength, which enable the production of high-performance composites (Juliana, Aisyah, Paridah, Adrian, & Lee, 2018). Compared to softwood fibers, bast fibers are slightly shorter, ranging from 2.48 to 3.6mm, but they are thinner, resulting in enhanced bonding and strength development (Khalil, Yusra, Bhat, & Jawaid, 2010). Additionally, bast fibers have a low lignin content of 14.7%, which is advantageous for their quality. Over the past few years, kenaf fibers have been successfully utilized in fiber-reinforced composites, demonstrating their suitability and potential in this application (Aisyah *et al.*, 2019).

However, a significant drawback in utilizing biofiber as a reinforcing agent lies in its inherent tendency to absorb moisture (Venkatasudhahar, Ravichandran, & Dilipraja, 2022). Overcoming the challenge of weak biocomposite functionality arising from the interaction between a hydrophobic matrix and hydrophilic biofiber remains a key concern. To address this issue, researchers have explored surface modification techniques for biofiber to enhance the chemistry and structure of cell walls, thereby improving the functional properties of biocomposites (Birnin-Yauri *et al.*, 2017). In one study, the impact of chemical modification using propionic anhydride on aspen wood flour in the composite structure showed substantial increase in the mechanical characteristics of the resulting composites following surface modification with the anhydride. Another recent study employed propionic anhydride to chemically modify agave biofiber, resulted in enhanced compatibility of biocomposites (Gallardo-Cervantes *et al.*, 2021). Therefore, the strategic use of propionic anhydride modification on bast fiber is crucial for enhancing compatibility and hydrophobicity in the interaction with the vinyl ester matrix, ultimately improving the functional properties of biocomposites.

1.2 Problem statement

In recent years, there has been a growing concern about the environmental impact of waste disposal, particularly in the packaging industry. The improper management of waste systems worldwide has led to a significant accumulation of plastic packaging in natural environments, with approximately 8 million tons of plastic entering the oceans annually. This plastic pollution not only endangers wildlife and disrupts ecosystems but also poses risks to human health. The challenge is further compounded by the labor-intensive nature of waste management, often carried out in resource-limited regions. Given that packaging products typically have short lifespans and are made from materials that either do not degrade or degrade slowly, there is an urgent need for more sustainable alternatives.

One promising solution is the adoption of green materials, such as biopolymers, which offer a more environmentally friendly option compared to traditional synthetic polymers. However, biopolymers often suffer from inadequate mechanical properties, necessitating reinforcement to match the performance of synthetic materials used in packaging. While non-woven kenaf bast fibers have been explored as reinforcement for various biopolymers, their integration into a PHBV matrix remains largely un-investigated. This gap in research highlights the need to address compatibility challenges between hydrophilic natural fibers and hydrophobic polymers to improve bonding and enhance the mechanical properties of these composites.

Furthermore, the potential of microfillers derived from bio-waste materials, such as spent coffee grounds (SCG), presents an opportunity to improve the properties of biocomposites. SCG, being an abundant waste product, contains cellulose and lignin, which can reinforce the composite matrix. SCG, with their inherent lipids and oils, can serve as natural adhesives significantly enhancing the bonding between hydrophobic polymer and natural fibers in composite materials. This increased adhesion helps mitigate the typical incompatibility between the fiber and polymer matrix, leading to a stronger interfacial bond. Furthermore, the physical presence of SCG particles can create a complex interlocking structure between the fibers and the matrix, facilitating better load transfer and overall mechanical performance. Although previous research has investigated coffee grounds as a reinforcement in PHBV, their use as a filler has not been extensively studied. This study aims to explore the feasibility of utilizing SCG as a novel filler in a PHBV matrix and to assess its impact on the composite's mechanical and thermal properties.

1.3 Objectives of the study

This study aimed to overcome the existing limitations of PHBV natural fibre composites in achieving desirable mechanical, thermal, and functional properties. In addition to reinforcing the matrix with natural fibres, the researchers also explored the potential of enhancing the composites with SCG, which is the residue generated during coffee brewing and the byproduct obtained after coffee preparation. This research was conducted as part of a larger initiative focused on developing environmentally friendly materials suitable for packaging applications, in response to the growing concern surrounding plastic waste. The specific objectives of the study were as follows:

1.3.1 Objective 1

To study the effect of propionic anhydride modification on the properties of non-woven bast fibre/PHBV composites.

1.3.2 Objective 2

To study the effect of different particle sizes and concentrations of spent coffee grounds in PHBV/ SCG composites for the enhancement of properties.

1.3.3 Objective 3

To evaluate the PHBV/Propionylated non-woven bast fibre composite enhanced with SCG optimum size microfiller.

1.4 Thesis structure

Chapter 1: This chapter serves as an introduction to the work, providing an overview of the project aims and outlining the structure of the thesis.

Chapter 2: This chapter explores previous studies conducted on PHBV green composites used in packaging applications and investigates the biodegradation of these composites.

Chapter 3: In this chapter, the focus is on the development of composites made from PHBV, nonwoven bast fiber, and SCG. The chapter also details the methodology employed in the preparation of these biocomposites.

Chapter 4: This chapter outlines the techniques utilized to analyze the morphological, mechanical, thermal, water contact angle, and biodegradation properties of the biocomposites studied. Additionally, it presents the results and discusses the properties of these biocomposites.

Chapter 6: The final chapter of the thesis provides conclusions drawn from the research and offers insights into future prospects and directions for further study.

CHAPTER 2

LITERATURE REVIEW

This chapter examines the current level of knowledge regarding PHBV-based green composites. The chapter is divided into four sections: (1) an introduction to biopolymers, (2) an introduction to PHBV and its processing and properties, 3) an overview of plant based natural fibers, highlighting kenaf bast fiber, (4) PHBV based natural fiber composites and their properties, (5) Effect of microfiller enhancement in PHBV based natural fiber composites, (6) Coffee and SCG based biocomposites, and finally (7) a summary of this chapter.

2.1 Biopolymers

2.1.1 Introduction

Biopolymers are made up of biodegradable polymers derived from renewable sources, biodegradable polymers derived from petroleum sources, and non-biodegradable polymers derived from renewable sources. Biodegradable polymers are made from renewable resources and decompose in specific environmental circumstances (Yin & Yang, 2020). Several mechanisms occur during biopolymer breakdown, including hydrolysis, UV degradation, and oxidation. Depending on environmental circumstances, there are conditions for each to occur at different phases.

Biopolymers undergo a degradation process involving photo-degradation, oxidation, and hydrolysis. This property makes biodegradable polymers increasingly attractive to researchers as a viable alternative to oil-based plastics. Biodegradable polymers can be enzymatically decomposed by microorganisms, leading to the production of carbon dioxide and methane over time (Folino, Karageorgiou, Calabrò, & Komilis, 2020). The Biodegradable Plastic Society Japan (BPS, Japan) has reported that these polymers can naturally degrade in soil under normal climate conditions. During degradation, the molecular structure of biopolymers is reduced, and this process can be expedited by specific factors such as pH, humidity, oxygen levels, and sometimes a degradation catalyst.

Biopolymers' biodegradable qualities are a possible remedy to pollution caused by synthetic polymers. Because of their low environmental impact, biopolymers are categorized as green materials. Because of this feature, biopolymers have been used in packaging and agricultural composites. In addition, some biopolymers are biocompatible with the human body and are employed in biomedical and tissue engineering applications such as scaffolding and interim organ replacement (Biswas *et al.*, 2022). According to past research, biopolymers are classified into distinct categories based on their origins and qualities (Balart, Garcia-Garcia, Fombuena, Quiles-Carrillo, & Arrieta, 2021).

2.1.2 Classification of biopolymers

Biodegradable polymers, also known as biopolymers, are derived from renewable and biomass sources. These biopolymers, like cellulose, can be extracted from agro-biomass through fractionation, which involves breaking down larger molecules into smaller ones using either chemical processes or microorganisms. One example of obtaining biopolymers is through the fermentation of biomass or plants to yield monomers. Hence, biopolymers can be categorized into two main groups: agropolymers and biodegradable polyesters (Dilshad, Waheed, Ali, Amin, & Ahmed, 2021). Biodegradable polymers produced from nature using microorganisms come from renewable sources. Figure 2.1 illustrates a schematic diagram that showcases the classification of biopolymers based on their polymer backbone, types of monomer, and biodegradability.

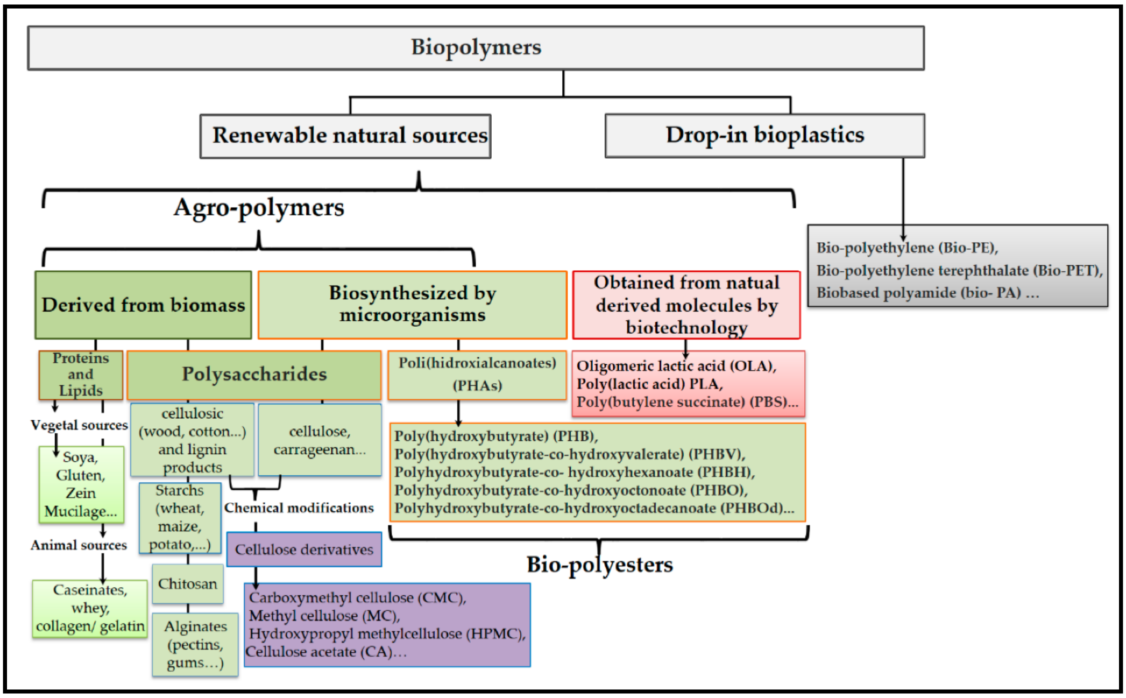

Figure 2. 1 Classification of Biopolymers (Balart *et al.*, 2021)

Biopolymers derived from renewable sources are gaining popularity due to their biodegradability, composability, and environmentally-friendly nature. Researchers are increasingly using these polymers to close the carbon process cycle, enabling plant-based carbon to return to the soil through biodegradation or composting, thereby reducing environmental pollution. Additionally, biopolymers help decrease fossil fuel usage and carbon dioxide emissions during production and product life cycles, making them valuable materials in the 21st century that contribute significantly to the material world (Gowthaman *et al.*, 2021). Biopolymers offer a solution to address environmental concerns and the uncertainty of continuous petroleum supply. Their annual commercial valorization growth rate exceeds 30%, and they are now competing with conventional plastics (Mohanty, Vivekanandhan, Pin, & Misra, 2018). This shift towards using biopolymers in manufacturing has enabled zero-emission and green production, aiming to combat global warming and climate change caused by the greenhouse effect (Ita-Nagy, Vázquez-Rowe, Kahhat, Chinga-Carrasco, & Quispe, 2020; Peydayesh, Bagnani, Soon, & Mezzenga, 2023).

2.2 Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)

2.2.1 Introduction

PHBV is a random copolymer consisting of the monomers hydroxybutyrate (HB) and hydroxyvalerate (HV) from the polyhydroxyalkanoates (PHA) family of polyesters (Ibrahim, Alsafadi, Alamry, & Hussein, 2021). (Furutate *et al.*, 2021). Many microorganisms manufacture these polymers as a carbon and energy store, with PHB accumulating inside the microorganisms that thrive in an environment lacking specific nutrients.

PHB possesses certain drawbacks such as limited processability, brittleness, and high cost. Its tensile elongation to break is measured at 3.8%, and the average impact resistance is around 24 J/m. The material has a narrow processing temperature range, with a melting point of approximately 178°C and a rapid thermal degradation tendency above 180°C. At temperatures beyond 200°C, it undergoes decomposition, forming a product known as crotonic acid (Ariffin, Nishida, Shirai, & Hassan, 2010; Mamat, Ariffin, Hassan, & Zahari, 2014). Due to this restricted processing range, precise temperature control during production becomes essential, which can contribute to increased expenses.

PHBV is a copolymer that is derived from polyhydroxybutyrate (PHB) by incorporating hydroxyvalerate (HV) units into its structure. The addition of HV helps to overcome the brittleness limitation of pure PHB. PHV, which is produced through a bacterial process, serves as the source of hydroxyvalerate units. The suiTable substrate materials for the production of PHV have odd-carbon numbers and include propionic acid, propanol, sodium propionate, valeric acid, pentanol, valerate, levulinic acid, heptanoic acid, and olive and sunflower oils (S. Zaidi, 2019). Commercially available PHBV grades come in a variety of formulations with different HV contents, allowing for customized material properties. By varying the HV content, the mechanical properties of PHBV can be adjusted to meet specific requirements for different applications. In the current research, we utilized ENMAT Y1000 grade in powder from, which incorporates 3 mol.% HV. This specific material is available in two forms: powder (Y1000) and pellets (Y1000P).

2.2.2 Properties of PHBV

PHBV is a highly promising and competitive biopolymer. It exhibits comparable mechanical and physical properties to other materials while standing out due to its biocompatibility and complete biodegradability, making it an environmentally sustainable choice. PHBV surpasses other PHAs in terms of flexibility, mechanical strength, and ease of processing. Additionally, it claims non-toxicity, resistance to corrosion, ultraviolet radiation, and oils (Fernandez-Bunster & Pavez, 2022). One of its key advantages is its versatility in production, as it can be synthesized from various microorganisms and utilizes cost-effective and waste resources from different industries and wastewater. Furthermore, PHBV serves as a renewable energy and raw material source.

2.2.2(a) Biodegradability

Biodegradability refers to the process through which substances undergo fragmentation, breaking down gradually due to the action of microorganisms under specific metabolic conditions. During this degradation process, the chemical structure and properties of polymers also undergo changes, ultimately converting into carbon dioxide or methane. The biodegradability of biopolymers is a crucial aspect, ensuring they can completely decompose in diverse environments and fulfill their intended purposes for which they were created (Meereboer, Pal, Cisneros-López, Misra, & Mohanty, 2021). Various factors, such as temperature, humidity, pH, light, oxygen availability, polymer composition, surface area, porosity, crystallinity, and molecular weight, all play roles in influencing the rate at which biodegradation occurs (La Fuente, Maniglia, & Tadini, 2023).

PHBV has been extensively studied for its biodegradability in various environments, such as soil, compost, water, and marine settings. Notably, it degrades rapidly in soil compared to other biopolymers. In a 120-day period, PHBV film lost fully fragmented, while PLA observed 30 % and 45 % in dry and wet environment conditions, respectively (D. Wang *et al.*, 2024). The biodegradation of PHBV in soil is facilitated by micro-organisms present in the environment. During degradation, PHBV undergoes color fading, cracking, and the formation of microscopic cavities when buried for up to 4 months (A. M. B. da Silva, Martins, & Santana, 2021). Compost conditions enhance the biodegradation of PHBV, with enzymatic environments showing better degradation compared to hydrolytic conditions (Brdlík, Borůvka, Běhálek, & Lenfeld, 2022). Surface degradation is more prominent in compost settings (Pantaloni, Shah, Baley, & Bourmaud, 2020).

The rate of PHBV biodegradation is greatly influenced by the 3HV content in the copolymer. An increase in the 3HV fraction results in a higher degradation rate, and conversely, a decrease in 3HV mol% leads to a reduction in the degradation rate, as illustrated in Figure 2.2. Incorporating lignocellulosic fillers, such as wood flour, in PHBV composite materials accelerates the biodegradation rate. Composite samples with wood content showed a fivefold higher degradation rate compared to neat PHBV, indicating the potential for improving biodegradation while maintaining other material properties (Chan *et al.*, 2019). Furthermore, research demonstrates that the addition of reinforcements, such as CNC and ZnO, can provide additional benefits to PHBV composites, such as antibacterial activity. In such cases, the degradation rate remains moderate at 9-15% within one week (Abdalkarim *et al.*, 2017). This suggests that incorporating reinforcements in PHBV composites can offer a scope for enhancing specific properties while maintaining biodegradability.

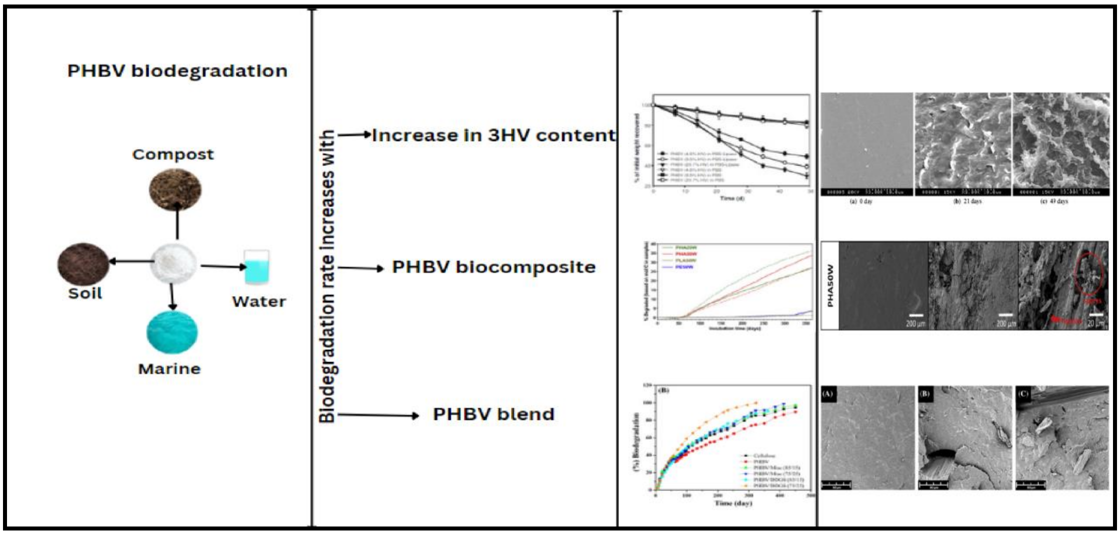

Figure 2. 2 The biodegradation rate of PHBV is influenced by various factors, and it varies accordingly.

In a recent study, researchers explored the potential of enhancing the biodegradability of PHBV in marine environments by incorporating natural fibers and proteinaceous fillers into the material. Two types of biocomposites were prepared: PHBV biocomposite with Miscanthus fibers and PHBV biocomposite with proteinaceous DDGC (Distillers' dried grains with solubles). These biocomposites were then subjected to degradation in the marine environment for 412 and 295 days, respectively. The results showed that the addition of these fillers significantly improved the biodegradation of PHBV compared to the neat PHBV. Specifically, the PHBV biocomposite with Miscanthus fibers enhanced biodegradation by 15-25% more than the neat PHBV (Meereboer *et al.*, 2021). This research highlights the potential of incorporating natural fibers and proteinaceous fillers to enhance the biodegradability of PHBV in marine environments, presenting a promising step forward in the development of more environmentally-friendly materials.

2.2.2(b) Physical properties

PHBV is a thermoplastic known for its hardness, crystalline nature, low flexibility, and brittleness, as indicated in Table 2.1. However, these characteristics limit its use in various applications (J. Wang *et al.*, 2012). To overcome these drawbacks, several modification techniques have been proposed, with blending PHBV with other polymers being the most popular approach. This blending process is advantageous due to its ease of processing, cost-effectiveness, speed, and ability to control PHBV's properties effectively (Kennouche *et al.*, 2016; Kuntanoo, Promkotra, & Kaewkannetra, 2015).

PHBV blend with polybutylene adipate terephthalate (PBAT) showed improved properties (Yolacan & Deniz, 2024). PHBV was melt compounded with poly (butylene succinate) (PBS) at various weight ratios. The thermal stability of the blends was improved, which showed a higher degradation temperature for PHBV in all blend compositions (Kennouche *et al.*, 2016). In conclusion, blending PHBV with other polymers, offers a promising strategy to enhance its properties, making it more suitable for a wider range of applications.

Table 2. 1 Physical properties of PHBV

Properties	**PHBV**
Density (g/cm^3)	1.25
Elasticity modulus (GPa)	2.38
Traction Resistance (MPa)	25.9
Elongation (%)	1.4
Fusion temperature (^0C)	153
Glass Transition Temperature (^0C)	-1

The molecular weight (MW) of PHBV, a copolymer, plays a crucial role in determining its mechanical properties. Changes in molecular weight can have significant effects on the overall performance of the polymer. The molecular weight of PHBV is highly dependent on the micro-organism used in its production process. For instance, PHBV produced by the bacterium *Pseudomonas pulida* exhibited molecular weights lower than 1×10^6 kDa, whereas the methanotrophic bacteria *Methylocystis sp.* yielded PHBV with molecular weights ranging from 1.5 to 1.8×10^6 kDa. Moreover, the extraction process also had a noticeable impact on the molecular weight of the produced PHBV. Aqueous extraction with thermal and enzymatic treatment resulted in PHBV with a molecular weight of 6×10^5 kDa, while using solvents during extraction led to a higher molecular weight of 1×10^6 kDa. It was also observed that certain chemicals or compounds involved in the extraction processes caused a reduction in molecular weight by approximately 30–50% (Rivera-Briso & Serrano-Aroca, 2018). In summary, the molecular weight of PHBV is influenced by various factors, such as the micro-organism used in production and the extraction method employed. Understanding and controlling these factors are essential to tailor the mechanical properties of PHBV for specific applications.

The morphology of a polymer is its most crucial aspect, encompassing factors such as crystallinity, molecular weight, and structural properties, all of which play a key role in determining its physical characteristics. PHBV is a thermoplastic with properties heavily influenced by its morphology. By employing chemical treatments that break ester bonds and introduce functional groups, the polymer's morphology can be modified or maintained. These treatments enhance its hydrophobic properties. Additionally, incorporating maleic anhydride into the PHBV matrix improves its oxygen barrier and water vapor barrier properties (Remila *et al.*). On the other hand, treating PHBV with ethylenediamine reduces its hydrophobicity while simultaneously altering its mechanical properties (Hsu *et al.*, 2024).

2.2.2(c) Mechanical properties

Polymers exhibit various mechanical properties, including toughness, stiffness, impact resistance, percent elongation to break, modulus of elasticity, and viscoelasticity. These properties are heavily influenced by factors such as molecular weight, cross-linking, and crystallinity. When considering PHBV, its mechanical properties are currently inferior to those of petroleum-based polymers, leading to limitations in numerous applications. PHBV is known for its brittleness, low impact resistance, and limited break elongation due to its crystalline nature (Feijoo *et al.*, 2023). However, there is a viable solution to enhance these drawbacks. By blending PHBV with materials of a different chemical nature as reinforcements, PHBV biocomposites or nanocomposites can be created. This technique not only improves PHBV's mechanical properties but also expands its potential applications by making it more versatile and adaptable.

Another technique to improve mechanical qualities (low impact strength and brittleness) is to reinforce PHBV with natural fibers derived from renewable sources. Furthermore, natural fibers have the benefit of being produced from inexpensive and plentiful sources, cutting the production costs of PHBV biocomposites, and 100% biodegradability leads to an environmentally favorable environment. Several publications have been published in the recent few decades in support of PHBV biocomposites with increased mechanical properties, such as rice straw, flax fiber, bamboo fibers, kenaf, wood fiber (WF), and so on. Injection molding and melt blending were used to create biocomposites with improved properties from PHBV reinforced bamboo fibers (Zhuo *et al.*, 2020). If there is no interfacial connection between the polymer matrix and the bamboo fiber, the tensile strength of the PHBV will be reduced. Compatibilizers were discovered to be the most effective method of improving biocomposites' interfacial adhesion performance. To improve the mechanical qualities of PHBV, an extruded biodegradable biocomposite of PHBV and pine wood flour (WF) is created. The influence of three compatibilizing procedures on the mechanical characteristics of biocomposite was investigated: silanization of wood flour using Sigmacote, maleic anhydride grafting of PHBV matrix (MA-PHBV), and addition of polymethylene-diphenyl-diisocyanate (pMDI). Sigmacote reduced tensile strength by 205%, MA grating in PHBV matrix improved tensile strength of composites by 53% and impact strength by 104%, and pMDI improved tensile strength until its 2wt% addition, further increase in pMDI loading to 4 wt% resulted in a decrease in tensile strength. These negative effects on mechanical properties were caused by processing conditions and forceful extrusion (Chan *et al.*, 2018b).

Organic wastes from agriculture sectors used as reinforcement materials give a sustainable economic method for generating low-cost biocomposite material. The thermal and mechanical properties of biocomposites composed of PHBV reinforced potato pulp powder (a byproduct of starch extraction) were studied. The findings revealed that potato pulp powder works as a filler in the PHBV matrix, resulting in a little decrease in mechanical characteristics. However, using surface-treated potato pulp powder in a polymeric matrix increased the mechanical characteristics of the manufactured biocomposites (Righetti, Cinelli, Mallegni, Stäbler, & Lazzeri, 2019). Extrusion was utilized to incorporate three types of plant fibers (flax, hemp, and wood) as fillers in PHBV biocomposites. Mechanical qualities of hemp and flax biocomposites improved, with hemp fiber performing best. Only the wood fiber/PHBV biocomposites degraded rather than improved mechanical characteristics (Frącz, Janowski, Smusz, & Szumski, 2021). Recently, agricultural wastes have been employed as reinforcements in PHBV to improve mechanical qualities. Reinforcing three different types of fibers, nettle fibers (leaves and stalks), pine cone flour, and walnut shell flour, biodegradable composites were created. Mechanical properties were investigated at three distinct temperatures (-24, 23, and 800^{0}C). Figure 2.3 depicts the results, which demonstrate a 20% increase in Modulus of Elasticity for all biocomposites. However, tensile strength was somewhat reduced, but the degree of crystallinity improved (save for nettle stalk fibers) and great stiffness stability was seen at high temperatures. Recent studies have shown that agricultural wastes can be used to make entirely biodegradable polymer composites. Fiber integration not only reduces production costs but also increases polymer stiffness. Furthermore, by utilizing this technology, waste materials will be able to efficiently fill gaps, facilitating their handling (Mazur, Jakubowska, Gaweł, & Kuciel, 2022).

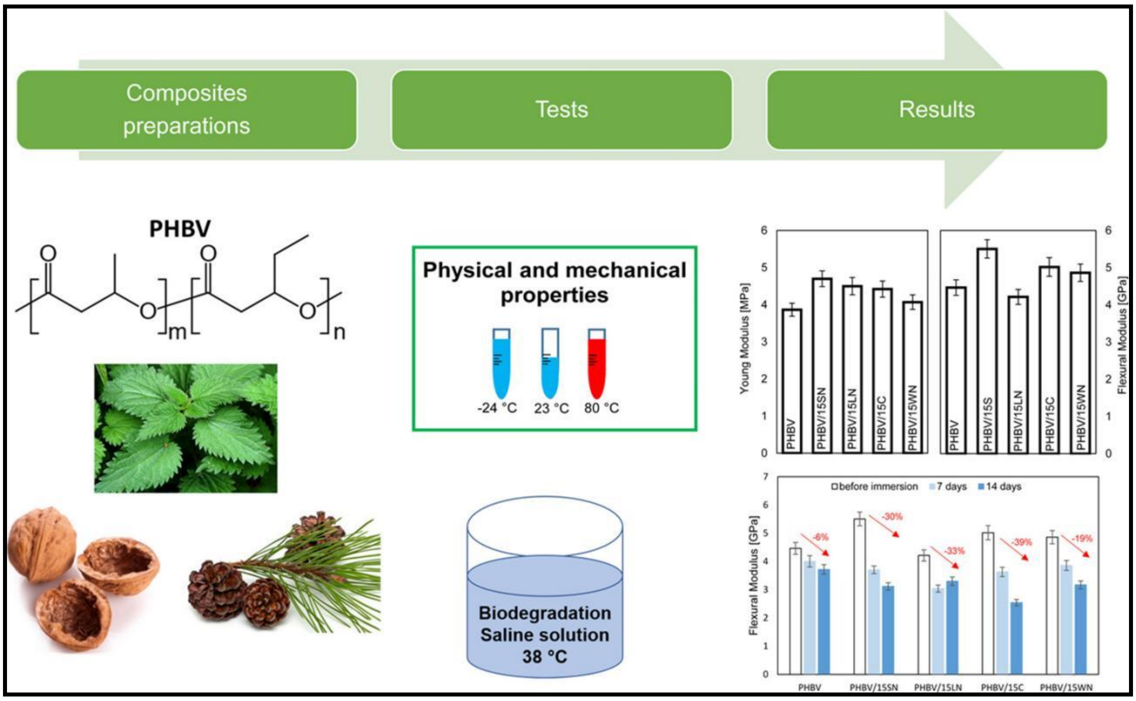

Figure 2. 3 PHBV biocomposites with improved mechanical properties (Mazur *et al.*, 2022).

2.2.2(d) Thermal properties

The thermal properties of materials, especially polymers like PHBV (a microbial biopolymer), play a crucial role in their processing and applications. Before using PHBV in practical scenarios, it is advisable to conduct preliminary experiments to understand its behavior under various thermal conditions. PHBV has specific melting and glass transition temperatures, which are essential to know for proper processing. PHBV's melting temperature is 175°C, and its glass transition temperature is 90°C. During melt processing, it becomes unstable around its melting temperature and exhibits rubber-like behavior at room temperature. It is important to note that PHBV already has a relatively small processing window, and its thermal properties are significantly influenced by the 3HV (3-hydroxyvalerate) fraction. To enhance mechanical properties and processing functionalities, 3HV is often added to PHBV. However, increasing the 3HV content in PHBV results in a decrease in its crystallization and melting temperature. This, in turn, leads to improved flexibility, ductility, and workability of the PHBV polymer. Therefore, careful consideration is necessary when selecting PHBV with the appropriate 3HV content to achieve the desired properties. Moreover, changes in PHBV's crystallinity and the addition of plasticizers or exposure to radiation also affect its thermal properties (Rivera-Briso & Serrano-Aroca, 2018). Adding plasticizers lowers the melting temperature of PHBV, allowing processing to occur at lower temperatures and reducing the likelihood of thermal degradation at elevated temperatures. Thermal and mechanical parameters of PHBV copolymers at 25^0C are presented in Table 2.2. In summary, understanding and controlling the thermal properties of PHBV, considering factors like 3HV content, crystallinity, plasticizers, and radiation, are vital for successful processing and application of this biopolymer (Ramli, Othman, Bakar, & Hassan, 2021).

Table 2. 2 Thermal and mechanical parameters of PHBV copolymers at 25 ^{0}C.

Composition **Mol% HV**	**Melting Temp. (^{0}C)**	**Glass Transition Temp. (^{0}C)**	**Tensile strength (MPa)**	**Elongation at break (%)**	**Elastic Modulus (GPa)**
0	175	9	45	4	3.8
11	157	2	38	5	3.7
20	114	-5	26	27	1.9
28	102	-8	21	700	1.5
34	97	-9	18	970	1.2

One notable approach is blending PHBV with compatible polymers, which has proven to be successful in improving thermal stability compared to pure PHBV. For instance, blending PHBV with poly(butylene succinate -co-butylene adipate) (PBSA) led to improved thermal stability (Feijoo *et al.*, 2023). Another blend, namely poly(ε-caprolactone) (PCL)/PHBV, demonstrated enhanced thermal stability (Kalva *et al.*, 2023). Moreover, a blend of Polylactic Acid with PHBV (PLA/PHBV) also showed improved thermal stability (Brütting, Dreier, Bonten, Altstädt, & Ruckdäschel, 2023). Similarly, another study involved blending PHBV with cellulose acetate and incorporating triethyl citrate as a plasticizer and chain extender to create sustainable packaging materials. The blending process, which involved high temperatures, caused a reduction in the melt temperature of PHBV and increased porosity in the blend. However, the impact strength of PHBV was significantly improved, showing a 110% increase (Meereboer, Pal, Misra, & Mohanty, 2020).

The enhancement of PHBV properties can be achieved through the addition of nanoparticles derived from various biopolymers. These nanoparticles impart superior