DEVELOPMENT OF POLYVINYL ALCOHOL/ MICROCRYSTALLINE CELLULOSE/ ANTHOCYANIN BIOFILM AS pH-SENSITIVE INDICATOR FOR SMART PACKAGING

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2025

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by

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Thesis submitted in fulfilment of the requirements for the degree of Master of Science

September 2025

ACKNOWLEDGEMENT

First and foremost, praise and thank God Almighty for His blessings during the completion of my senior project. With great pleasure, I would like to thank the following individuals who have made generous contributions, both directly and indirectly, to the completion of the laboratory work and this report. Secondly, I would like to thank my supervisor, Dr. Wan Nazwanie Wan Abdullah. I would like to express my deepest and sincere thanks for her guidance, encouragement and enthusiasm in completing this project toward the end of this project, especially for all the comments and support during the research and preparation of this report. I am also grateful to my co-supervisor, Dr. Abdorreza Mohammadi Nafchi from the School of Industrial Technology, and Prof. Madya ChM. Ts. Dr. Nor Hakimin Bin Abdullah, as well as my field supervisor, Soh Kheang Loh from MPOB, for their expert advice, constructive feedback, and continuous support. Their contributions greatly enriched the quality of this work. I would like to acknowledge the contributions of the school administration and staff of the School of Chemical Sciences and the School of Industrial Technology for providing me with the necessary resources, research facilities, and training on handling instruments to undertake this project. Next, I would like to extend my appreciation to my lab mates, Ainnur, Chong Hui Min, and Sarmila, for their collaboration and constructive suggestions, which have significantly contributed to the completion of this project. Finally, I want to express my gratitude to my parents and my friends for their moral support and encouragement in all of the decisions and actions I take. My master's research might not have been accomplished if it were not for all of these people.

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LIST OF ABBREVIATIONS

Al	Aluminium
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared spectroscopy
BPE	Butterfly Pea Extract
BPF	Butterfly pea flower
C	Carbon
CNC	Cellulose nanocrystal
C_{rI}	Crystallinity index
DTG	Derivative thermogravimetric
E	Elongation at break
FESEM-EDX	Field emission scanning microscope with energy dispersive x-ray
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
MCC	Microcrystalline Cellulose
MFC	Microfiber Cellulose
Mg	Magnesium
Na	Sodium
NaOH	Sodium hydroxide
O	Oxygen
OPEFB	Oil palm empty fruit bunches
PVA	Polyvinyl alcohol
TAC	Total anthocyanin content
TGA	Thermogravimetric analysis
TS	Tensile Strength
UV/Vis	Ultraviolet/visible
WVP	Water Vapor Permeability
XRD	X-ray diffraction
YM	Young’s Modulus

LIST OF SYMBOLS & UNITS

cm	centimetre
ºC	degree Celsius
g	gram
g/cm^3	gram per centimetre cube
h	hour
<	less than
MPa	megapascal
μm	micrometre
mg	milligram
mL	millimetre
mm	millimetre
mins	minutes
x	multiplication
nm	nanometre
%	percentage
% v/v	percentage by volume
wt%	percentage by weight
θ	theta

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PEMBANGUNAN BIOFILEM POLIVINIL ALKOHOL/MIKROKRISTAL SELULOSA/ANTOSIANIN SEBAGAI INDIKATOR pH SENSITIF UNTUK PEMBUNGKUSAN PINTAR

ABSTRAK

Kajian terkini telah menekankan kesan negatif terhadap alam sekitar daripada plastik berasaskan petroleum, sekali gus menunjukkan permintaan yang semakin meningkat terhadap bahan pembungkusan makanan yang boleh terbiodegradasi dan pintar. Satu filem pembungkusan makanan yang mampan dan sensitif pH berasaskan polivinil alkohol (PVA, 8%), mikrokristal selulosa (MCC, 2%), dan antosianin (9% w/w) telah dibangunkan menggunakan kaedah tuangan pelarut dalam kajian ini. MCC dihasilkan daripada tandan kosong kelapa sawit (OPEFB) dan ditambah ke dalam filem PVA, manakala antosianin daripada ekstrak bunga telang (BPE) digunakan sebagai penunjuk pH semula jadi untuk memerhatikan kesegaran makanan. Filem tersebut turut dicirikan untuk sifat mekanikal, kebolehtelapan wap air (WVP), keterlarutan, dan tindak balas kolorimetri terhadap perubahan pH. MCC OPEFB yang diekstrak mempunyai saiz zarah yang lebih kecil (259.3 ± 12.44 nm) berbanding selulosa OPEFB mentah (514.4 ± 52.19 nm) dan indeks kristalinitas (C_{rI}) sebanyak 64.1%, jauh lebih tinggi daripada selulosa OPEFB (37.2%), mengesahkan kejayaan penyingkiran kawasan amorfus melalui hidrolisis asid. Ketebalan, WVP dan keterlarutan air bagi filem PVA/MCC/Antosianin yang dihasilkan masing-masing adalah 0.055 mm, 2.76×10^{-7} g·m/hari·kPa·m², dan 82.64%, menunjukkan prestasi penghalang kelembapan yang lebih baik daripada filem PVA tulen. Ia mempunyai kekuatan tegangan sebanyak 1.268 MPa dan modulus Young sebanyak 397.515 MPa,

yang menunjukkan fleksibiliti sederhana yang boleh diterima untuk aplikasi pembungkusan. Filem tersebut menunjukkan perubahan warna yang jelas bergantung kepada pH, beralih daripada merah (pH 1) ke biru (pH 7) dan kuning (pH 13), mengesahkan tindak balas visualnya yang sensitif terhadap pH. Ujian aplikasi pada dada ayam segar yang disimpan pada 5°C dan -2°C menunjukkan bahawa apabila kerosakan berlaku, filem tersebut beralih daripada biru (segar) ke hijau kebiruan (pH 8.03 pada hari ke-7) dan hijau (pH 10 pada hari ke-14), sekali gus mengesan kesegaran makanan melalui perubahan pH. Penemuan ini menekankan potensi filem PVA/MCC/Antosianin sebagai penyelesaian pembungkusan pintar mesra alam, dengan kepentingan yang tinggi untuk pemantauan masa nyata kesegaran dan keselamatan makanan dalam produk mudah rosak.

DEVELOPMENT OF POLYVINYL ALCOHOL/MICROCRYSTALLINE CELLULOSE/ANTHOCYANIN BIOFILM AS pH-SENSITIVE INDICATOR FOR SMART PACKAGING

ABSTRACT

Recent studies have highlighted the negative environmental effects of petroleum-based plastics, emphasizing the increasing demand for biodegradable and smart food packaging materials. A sustainable and pH-sensitive food packaging film based on polyvinyl alcohol (PVA, 8%), microcrystalline cellulose (MCC, 2%), and anthocyanin (9% w/w) was developed using a solvent casting method in this study. The MCC was produced from oil palm empty fruit bunches (OPEFB) and added into PVA films, whereas anthocyanins from butterfly pea flower extract (BPE) were utilized as a natural pH indicator to observe food freshness. The films were also characterized for mechanical properties, water vapor permeability (WVP), solubility, and colorimetric response to pH changes. The extracted OPEFB MCC had a lower particle size (259.3 ± 12.44 nm) than raw OPEFB cellulose (514.4 ± 52.19 nm) and a crystallinity index (C_{rI}) of 64.1%, significantly higher than those of OPEFB cellulose (37.2%), confirming the successful removal of amorphous regions by acid hydrolysis. The thickness, WVP, and water solubility of the prepared PVA/MCC/Anthocyanin films were 0.055 mm, 2.76×10^{-7} g·m/day·kPa·m², and 82.64%, respectively, indicating better moisture barrier performance than pure PVA films. It had a tensile strength of 1.268 MPa, and Young's modulus of 397.515 MPa for its mechanical performance suggests moderate flexibility, which is acceptable for packaging applications. The film exhibited distinct pH-dependent color shifts, transitioning from

reddish (pH 1) to blue (pH 7) and yellow (pH 13), confirming its pH-sensitive visual response. Application testing on fresh chicken breast stored at 5°C and -2°C showed that as spoilage progressed, the film transitioned from blue (fresh) to bluish-green (pH 8.03 on day 7) and green (pH 10 on day 14), effectively detecting food freshness through pH changes. These findings highlight the potential of PVA/MCC/Anthocyanin films as an eco-friendly intelligent packaging solution, with strong relevance for real-time monitoring of food freshness and safety in perishable products.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The global food packaging industry serves as a critical component in modern food systems, fulfilling essential functions that ensure product safety, quality preservation, and consumer convenience. As outlined by Salgado et al. (2021) and shown in Figure 1.1, traditional food packaging systems perform four fundamental roles: (1) containment and protection from physical, chemical, and biological hazards; (2) preservation through barrier properties against moisture, oxygen, and light; (3) communication of product information and branding; and (4) provision of convenience features for handling and consumption. These functions have historically been achieved through petroleum-based plastics like polyethylene (PE) and polypropylene (PP), which offer excellent mechanical strength, processability, and low production costs. However, the environmental consequences of these conventional materials have become increasingly untenable, with food packaging accounting for approximately 40% of the 400 million tons of plastic produced annually (Ferreiro & Monteiro, 2023 and Nayanathara, 2024). The non-biodegradable nature of these materials has led to persistent environmental pollution, particularly in marine ecosystems, where plastic packaging waste is projected to outweigh fish by 2050 if current trends continue (Zeenat et al., 2021). This crisis has prompted both regulatory interventions and market-driven shifts toward sustainable alternatives that can maintain the essential functions of traditional packaging while addressing environmental concerns.

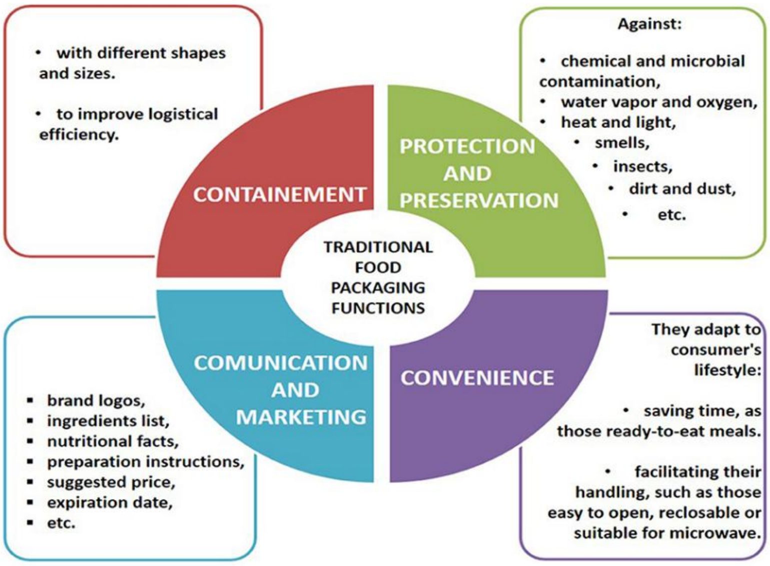

Figure 1.1 Traditional food packaging functions (Salgado et al., 2021)

In this context, biopolymer-based packaging has emerged as a promising solution, with polyvinyl alcohol (PVA) standing out due to its unique combination of biodegradability, film-forming capability, and chemical resistance (Shahid ul et al., 2023). PVA's hydroxyl-rich molecular structure enables excellent compatibility with natural reinforcements like cellulose while remaining water-soluble - a property that facilitates end-of-life degradation but currently limits its practical applications (Van Nguyen & Lee, 2022). The combination of environmental and technological advances, the food packaging industry's shift to sustainable materials aligns with the growing need for intelligent packaging systems that can actively monitor product freshness (Schaefer & Cheung, 2018). This dual imperative has driven innovation in composite materials that combine the structural benefits of biopolymers with functional additives like natural pH indicators.

Transitioning to a green economy requires a more sustainable approach, such as converting agricultural biomass waste into eco-friendly food packaging films with biodegradable, biocompatible, cost-effective, and renewable properties (Varghese et al., 2023). Recent studies indicate that agricultural waste contains valuable components that can be extracted as monomers (such as carbohydrates, proteins, and lipids) or additives (including plastic fillers, antimicrobials, antioxidants, and sensors/indicators) to produce biopolymeric food packaging materials (Cristofoli et al., 2023). Currently, research on the incorporation of fillers like cellulose, chitosan, and lignin into biopolymers is getting popular as the manufactured biopolymers still lack significant functional qualities to challenge conventional plastic concerning barrier, mechanical properties, thermal endurance, and flexibility (Siddiqui et al., 2024; Tyagi et al., 2021).

PVA has emerged as a promising alternative to commonly used plastic packaging materials such as polyethylene terephthalate (PET), polyvinyl chloride (PVC), and PE. However, PVA films exposed to UV radiation experience significant physicochemical changes that compromise their mechanical properties, limiting their applications in polarizing films, automotive components, and packaging membranes. Notably, the addition of cellulose into the PVA matrix has been shown to significantly improve UV-blocking properties. This enhancement is attributed to better UV absorption and dispersion through the cellulose's carbonyl groups (Chowdhury et al., 2019). PVA/microcrystalline cellulose (MCC) membranes or coatings can also exhibit anisotropic properties, leading to substantial improvements in water barrier and transparency.

An important aspect of using MCC for composite production is the potential to utilize agricultural waste materials. These materials, such as rice straw, sugarcane bagasse, sawdust, and cotton straw, are often discarded or burned, contributing to environmental problems (Bakri, Rahman, & Chowdhury, 2022). The utilization of agricultural waste streams, particularly oil palm empty fruit bunches (OPEFB), presents a compelling opportunity to develop sustainable packaging materials while addressing waste management challenges in palm oil-producing regions (Bakri et al., 2022). Malaysia's palm oil industry generates approximately 20 million tons of OPEFB annually, much of which is either burned or left to decompose, releasing greenhouse gases (Mahardika et al., 2024). Recent research has explored extracting cellulose nanomaterials from OPEFB, including MCC. The extraction of MCC from this abundant lignocellulosic waste not only valorizes agricultural byproducts but also produces reinforcement materials that can enhance the mechanical and barrier properties of PVA films (Ng et al., 2021).

Simultaneously, the growing demand for intelligent packaging has driven interest in natural pH-sensitive indicators, with butterfly pea flower (*Clitoria ternatea*) anthocyanins emerging as superior candidates due to their exceptional stability and vivid color transitions across pH ranges (Gamage et al., 2021). These water-soluble pigments change from red in acidic conditions (pH 1-3) to blue/purple at neutral pH (6-7) and green/yellow in alkaline environments (pH 10-13), providing clear visual spoilage detection (Mary et al., 2020). The color of anthocyanins is highly influenced by the surrounding physical and chemical environment, including interactions with other molecules. Unlike other anthocyanin sources, butterfly pea extracts demonstrate remarkable molecular stability in polymer matrices while offering additional antioxidant and antimicrobial benefits (Narayanan et al., 2023). In recent years, food freshness has been promptly monitored through the development of smart packaging films based on pH-sensitive indicators. Given that anthocyanin changes colour across a wide pH range, these organic sensors were used to determine the freshness of food (Zhao et al., 2022).

The integration of OPEFB-derived MCC and butterfly pea anthocyanins into PVA matrices represents an innovative solution that addresses both environmental concerns and functional requirements. This approach aligns with circular economy principles by valorizing agricultural waste while creating intelligent packaging capable of real-time freshness monitoring (Zhao et al., 2022). Studies have demonstrated successful applications in monitoring seafood, poultry, and dairy products, where the anthocyanins' color transitions correlate with microbial spoilage (Akhila et al., 2023). MCC reinforcement and butterfly pea anthocyanins create a biocomposite with enhanced mechanical and intelligent properties, making it a promising, sustainable, and safe alternative to conventional packaging(Handayani et al., 2024).

1.2 Problem statement

The widespread use of conventional petroleum-based plastic packaging has created a critical environmental crisis, with food packaging accounting for approximately 40% of global plastic waste (Nayanathara et al., 2024). These synthetic materials persist in ecosystems for centuries, contributing to marine pollution, wildlife harm, and microplastic contamination of the food chain (Zeenat et al., 2021). While biopolymers like PVA offer biodegradable alternatives, their inherent limitations - including poor mechanical strength (tensile strength typically <2 MPa), high water solubility (>80%), and inadequate barrier properties - restrict their practical application in food packaging (Van Nguyen & Lee, 2022).

The reinforcement of PVA with nanocellulose has shown promise, but current approaches often rely on commercially produced nanocellulose that fails to address agricultural waste management challenges (Ng et al., 2021). In Malaysia alone, the palm oil industry generates over 20 million tons of OPEFB annually, most of which is either burned or left to decompose, releasing significant greenhouse gases (Mahardika et al., 2024). Existing methods for MCC extraction from OPEFB frequently involve harsh chemical treatments that may compromise fiber quality and environmental benefits (Al-Dulaimi & Wanrosli, 2017).

Besides, the development of intelligent packaging faces technological hurdles. Most commercial freshness indicators rely on synthetic dyes that may migrate into food or complicate recycling processes (Schaefer & Cheung, 2018). While anthocyanins from various plant sources have been explored as natural alternatives, many suffer from poor stability, limited pH sensitivity range, or weak color contrast (Zhao et al., 2022). For instance, anthocyanins from common sources like red cabbage often show faded colors at neutral pH and rapid degradation in polymer matrices (Handayani et al., 2024).

The application of micro cellulose in polymer reinforcement is still new, and further research is needed. It is hypothesized that the incorporation of anthocyanin in film can be a smart packaging material to monitor the freshness of food. This study aims to address these challenges by developing a PVA/MCC/anthocyanin bio-composite film as a pH-sensitive indicator for monitoring the freshness of chicken. By leveraging agricultural waste (OPEFB) for MCC extraction and natural anthocyanins from butterfly pea flowers, this research contributes to the development of sustainable, intelligent packaging solutions that align with the principles of a circular economy. The findings of this study have the potential to revolutionize the food packaging industry by reducing plastic waste, enhancing food safety, and improving shelf-life management.

1.3 Research objectives

The objectives of this research are:

1. To isolate and characterize OPEFB microcrystalline cellulose (MCC) with corresponding analyses.
2. To extract anthocyanin from butterfly pea flower (BPF) to apply on PVA/MCC biofilm.
3. To prepare and characterize the PVA/MCC/anthocyanin biofilm
4. To determine the potential application of PVA/MCC/anthocyanin biofilm in smart packaging applications.

1.4 Research scope

This study focused on isolation of cellulose and MCC from OPEFB through the combined alkaline, hydrogen peroxide pretreatment and acid hydrolysis. The functional groups, crystallinity, size, morphology, and thermal properties of both extracted cellulose and MCC was studied by characterizations using ATR-FTIR spectroscopy, XRD analysis, FESEM-EDX analysis, and TGA analysis. Then, the commercial MCC, OPEFB MCC, and anthocyanin as a pH indicator were incorporated into PVA polymer to produce MCC-reinforced PVA bio-composite films for food packaging materials. The properties of the synthesised PVA/MCC and PVA/MCC/Anthocyanin film were compared with pure PVA film as well as the synthesised PVA/MCC Commercial film via characterisations using FTIR spectroscopy, XRD analysis, FESEM-EDX analysis, TGA analysis, and UV/Vis spectroscopy. Then, the potential of PVA/MCC bio-composite film in food packaging was tested through several parameters such as mechanical strength, water solubility, and water vapor permeability. Furthermore, the incorporation of anthocyanin into the

PVA/MCC film was an important aspect of developing its functionality as a pH-indicator smart packaging material. Anthocyanins, natural pigments that were extracted from butterfly pea flowers, were integrated into the composite film due to their ability to exhibit distinct color changes across a wide pH range. Food freshness testing was performed using the PVA/MCC/Anthocyanin film as smart colormetric film for fresh chicken breast over two-week period. The experiment aimed to observe the film's ability to monitor the freshness of the food product over time as a pH indicator smart packaging material.

1.5 Significance of Study

The significance of this research derives from its potential to contribute to the development of sustainable packaging materials that help resolve issues associated with conventional plastics. Considering it is persistent and difficult to dispose of, standard plastic packaging manufactured from non-renewable fossil fuels contributes significantly to pollution and degradation in the environment (Zeenat et al., 2021). This study investigates biofilms developed from MCC and PVA in an attempt to provide a sustainable alternative that combines biodegradability with enhanced performance. Furthermore, this study explores the synergistic effects of integrating PVA/MCC with anthocyanin to develop a biocomposite film, utilizing anthocyanin extract as a natural pH sensor for intelligent packaging applications. (Shao et al., 2021). This approach enhances the unique properties of each component while producing a material that has superior colorimetric film. The study focuses on analyzing its mechanical, barrier, and biodegradation properties to ensure its suitability for practical use in the packaging industry.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodegradable Food Packaging and Its Advancements

The global shift toward sustainable food packaging has been driven by the environmental impact of conventional plastics, which are derived from non-renewable fossil fuels and contribute significantly to pollution and resource depletion (Nayanathara et al., 2024; Zeenat et al., 2021). Biodegradable polymers, such as polyvinyl alcohol (PVA), polylactic acid (PLA), and starch-based materials, have emerged as promising alternatives due to their ability to degrade naturally in the environment (Abdullah et al., 2022; Salgado et al., 2021). These materials are derived from renewable resources, such as agricultural biomass, and offer comparable functionality to conventional plastics while being environmentally friendly.

Recent advancements in biodegradable food packaging have focused on improving the mechanical, thermal, and barrier properties of these materials to meet the demands of food preservation and safety. For instance, PVA has gained attention for its excellent film-forming ability, biocompatibility, and biodegradability (Ferreiro & Monteiro, 2023). However, PVA films have inherent limitations, such as low mechanical strength and poor water resistance, which have been addressed through the incorporation of natural reinforcements like microcrystalline cellulose (MCC) and cellulose nanocrystals (CNC) (Ng et al., 2021; Raza et al., 2022). These reinforcements not only enhance the mechanical properties of PVA films but also improve their barrier properties, making them suitable for food packaging applications (Salgado et al., 2021).

Another significant advancement is the development of active packaging, which incorporates functional additives such as antimicrobial agents, antioxidants, and oxygen scavengers to extend the shelf life of food products (Abdullah et al., 2022). For example, the integration of natural extracts with antimicrobial properties, such as curcumin and essential oils, into biodegradable films has been shown to inhibit microbial growth and preserve food quality (Salgado et al., 2021). Additionally, the use of nanotechnology in biodegradable packaging has enabled the development of nanocomposites with enhanced mechanical and barrier properties, further expanding the applications of these materials (Abdullah et al., 2022).

Despite these advancements, challenges remain in scaling up the production of biodegradable packaging materials and ensuring their cost-effectiveness compared to conventional plastics. Ongoing research is focused on optimizing the extraction and processing of raw materials, improving the performance of biodegradable films, and exploring new sources of renewable polymers (Salgado et al., 2021).

2.1.1 Polyvinyl Alcohol (PVA) for Sustainable Packaging

PVA is a diverse synthetic polymer that is well known for its biocompatibility and ability to produce films. PVA has a low environmental impact due to its solubility and biodegradability, leading to it being a useful industrial and commercial material (Shahid ul et al., 2023). Although PVA is a biodegradable packaging material, research has revealed that it has drawbacks, including low mechanical strength, poor water resistance, weak UV and water vapor barrier qualities, and no antibacterial qualities (Van Nguyen & Lee, 2022). To overcome these drawbacks, researchers have explored reinforcing PVA films with natural nanofillers such as CNC, microfiber cellulose (MFC), and chitosan to enhance mechanical strength, water resistance, and thermal stability (Raza et al., 2022).

Several studies have explored the enhancement of PVA films by incorporating CNC as a natural reinforcement to improve their mechanical strength, water resistance, and durability. For instance, Ng et al. (2021) investigated the effect of CNC derived from oil palm empty fruit bunches (OPEFB) on PVA films and found that the addition of CNC significantly enhanced the mechanical properties, UV resistance, and barrier performance of the films. These improvements are attributed to the strong hydrogen bonding interactions between CNC and the PVA matrix, which contribute to better film integrity and functionality (Ng et al., 2021). Similarly, Tessema et al. (2023) reported that PVA films reinforced with MCC exhibited higher crystallinity and reduced water solubility, making them more resistant to moisture degradation compared to pure PVA films (Tessema et al., 2023).

2.2 Cellulose as a Reinforcement Material

Cellulose is the most prominent sustainable natural biopolymer on the planet and is present in many living things, such as bacteria, plants, and animals. It is the plant's main structural element and reclaims its value as a renewable chemical resource that may be used to replace elements derived from petroleum (Ismail et al., 2021). Agricultural wastes such as OPEFB, rice straw, and sugarcane bagasse are particularly promising sources of MCC, as they are abundant, low-cost, and underutilized (Bakri et al., 2022; Tan et al., 2022). The chemical structure of cellulose is presented in Figure 2.1.

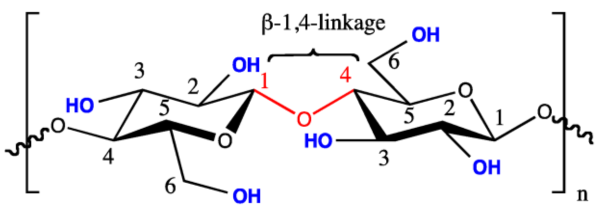

Figure 2.1 Chemical structure of cellulose (Sunasee & Hemraz, 2018).

In Malaysia, OPEFB is among the most abundant lignocellulosic biomasses, offering an inexpensive and environmentally friendly resource for cellulose extraction. The OPEFB are the residual fibrous materials left after the extraction of oil from palm fruits, representing a substantial portion of the waste generated by the palm oil industry (Tahir et al., 2019). The chemical composition of OPEFB on a dry basis reveals its valuable natural source of fibre and its potential as an alternative to conventional reinforcing fibre. Based on Table 2.1, OPEFB fibres contain primarily of cellulose, hemicellulose, and lignin, with smaller amounts of extractives and ash (Mahardika et al., 2024).

Table 2.1 Chemical composition of OPEFB.(Ng et al., 2021; Panugalla & Ramakrishna, 2022)

Composition	**Percentage by weight (wt%)**
Cellulose	23.7-65.0
Hemicellulose	20.58-33.52
Lignin	14.1-30.45
Extractive	3.21-3.70
Volatile matter	70.03–83.86
Fixed carbon	8.97–18.30
Ash	1.30–13.65
Moisture	2.40–14.28

The high cellulose content (37.26–63%) makes OPEFB an excellent raw material for MCC and CNC extraction, as reported by Wanrosli et al. (2007), while the presence of hemicellulose and lignin requires careful removal during the extraction process to achieve high-purity cellulose (Bakri et al., 2022; Tan et al., 2022). The extraction of MCC and CNC typically involves several steps, including alkaline treatment, bleaching, and acid hydrolysis, to remove non-cellulosic components such as lignin and hemicellulose and isolate the cellulose fibers. Alkaline treatment with sodium hydroxide (NaOH) removes lignin and hemicellulose, while bleaching with hydrogen peroxide (H_2O_2) further purifies the cellulose and improves its crystallinity (Ng et al., 2021). Acid hydrolysis, often using sulfuric acid (H_2SO_4), breaks down the cellulose fibers into microfibrils, producing CNC with a high aspect ratio that is ideal for reinforcing polymer matrices (Raza et al., 2022). However, challenges remain in optimizing the extraction process, as over-hydrolysis can degrade cellulose, and achieving uniform dispersion of cellulose in polymer matrices is difficult due to strong hydrogen bonding between fibers, which can lead to agglomeration (Girard et al., 2021). Additionally, acid hydrolysis can reduce the thermal stability of CNC by introducing sulfate groups, lowering its degradation temperature (Al-Dulaimi & Wanrosli, 2017).

When incorporated into PVA films, CNC significantly enhances their mechanical, thermal, and barrier properties. The high aspect ratio of CNC allows it to distribute stress more effectively within the polymer matrix, improving tensile strength and Young's modulus (Tessema et al., 2023). For example, Ng et al. (2021) reported that CNC-reinforced PVA films exhibited a 40% increase in tensile strength compared to pure PVA films. CNC also enhances the water vapor barrier properties of PVA films by creating a tortuous path for water molecules, making them suitable for food packaging applications where moisture control is critical (Raza et al., 2022). Furthermore, CNC improves the thermal stability of PVA films by increasing their crystallinity, although the thermal degradation temperature of CNC itself can be reduced by acid hydrolysis (Chieng et al., 2017). Both PVA and CNC are biodegradable, making their composite films an environmentally friendly alternative to conventional plastics. However, challenges such as achieving uniform dispersion, maintaining thermal stability, and scaling up production for industrial applications remain (Tan et al., 2022).

2.2.1 Structural and functional properties of different types of cellulose.

MCC is characterized by its unique structural and functional properties, which make it an excellent reinforcement material for biodegradable polymers like PVA. MCC is characterized by its short, rod-like particles with diameters typically ranging from 10 to 50 μm and lengths of 50–500 μm, resulting in a low aspect ratio (1–5) compared to nanocellulose (Haldar & Purkait, 2020). This granular morphology arises from controlled acid hydrolysis, which selectively removes amorphous regions of cellulose, leaving behind highly crystalline domains ($C_{rI} \approx 50–70\%$) (Al-Dulaimi & Wanrosli, 2017). This high aspect ratio allows MCC to form a dense, interconnected network within polymer matrices, enhancing mechanical properties such as tensile strength, Young's modulus, and toughness (Sazman et al., 2023). Additionally, MCC's surface is rich in hydroxyl groups, which facilitate strong hydrogen bonding with hydrophilic polymers like PVA, improving the overall integrity and performance of composite films (Girard et al., 2021).

One of the key functional properties of MCC is its ability to improve the barrier properties of polymer films. The dense network of MCC fibrils creates a tortuous path for gas and water molecules, reducing permeability and enhancing the film's ability to act as a barrier against moisture and oxygen (Raza et al., 2022). This makes MCC-reinforced films particularly suitable for food packaging applications, where controlling the internal environment is critical for preserving food quality (Tan et al., 2022). Furthermore, MCC's biodegradability and compatibility with natural polymers align with the growing demand for sustainable packaging materials (Zeenat et al., 2021).

Recent studies have highlighted the thermal stability of MCC, which is influenced by the extraction process. Acid hydrolysis, commonly used to isolate cellulose, can introduce sulfate group that lower the temperature of thermal degradation (Al-Dulaimi & Wanrosli, 2017). However, when properly extracted and incorporated into polymer matrices, MCC can enhance the thermal stability of composites by increasing crystallinity and reducing chain mobility (Chieng et al., 2017). For example, Tessema et al. (2023) reported that MCC-reinforced PVA films exhibited higher thermal degradation temperatures compared to pure PVA films, making them suitable for applications requiring thermal resistance.

MCC also exhibits excellent mechanical properties, such as high tensile strength and stiffness, due to its crystalline structure and strong intermolecular hydrogen bonding. These properties make MCC a superior reinforcement material compared to other cellulose derivatives like cellulose nanofiber (CNF) and microfibrillated cellulose (MFC). While MCCs are highly crystalline and provide excellent mechanical reinforcement, their lower aspect ratio limits their ability to form strong inter-fiber networks (Haldar & Purkait, 2020). MCC, on the other hand, has a larger particle size and lower surface area, making it less effective as a reinforcement material in nanocomposites (Girard et al., 2021). MCC strikes a balance between these two, offering a high aspect ratio, good mechanical properties, and the ability to form strong hydrogen bonds with polymer matrices like PVA (Ng et al., 2021). The comparison between types of cellulose is presented in Table 2.2.

Table 2.2 Comparison between types of cellulose (Haldar & Purkait, 2020; Ng et al., 2021; Isogai et al., 2011)

Property	CNC	MFC	MCC
Diameter	5–20 nm	10–100 nm	10–50 µm
Length	0.1–1 µm	1–100 µm	50–500 µm
Aspect Ratio	5–50	10–100	1–5
Crystallinity (%)	80–90	60–80	50–70
Tensile Strength	300–500 MPa	200–300 MPa	50–100 MPa
Thermal Stability	200–300°C	250–350°C	250–350°C
Barrier Properties	Excellent	Excellent	Moderate
Production Method	Acid hydrolysis	Mechanical treatment	Acid/alkali hydrolysis

Recent studies have further explored the structural and functional properties of MCC. For instance, Sazman et al. (2023) investigated the extraction of MCC from *Gigantochloa scortechinii* and reported that the resulting MCC exhibited high crystallinity (72%) and excellent mechanical properties, making it suitable for reinforcing biodegradable polymers.

2.3 Smart Packaging Technology

Smart packaging represents a significant advancement in food packaging, integrating functional materials, sensors, and indicators to monitor food quality and safety in real-time (Schaefer & Cheung, 2018). Unlike traditional packaging, which serves as a passive barrier, smart packaging interacts with the food and its environment to provide real-time information on freshness, temperature, and spoilage (D'Almeida & de Albuquerque, 2024). This technology is particularly valuable for perishable foods, where maintaining quality and safety is critical. Figure 2.2 summarizes the classification of smart food packaging.

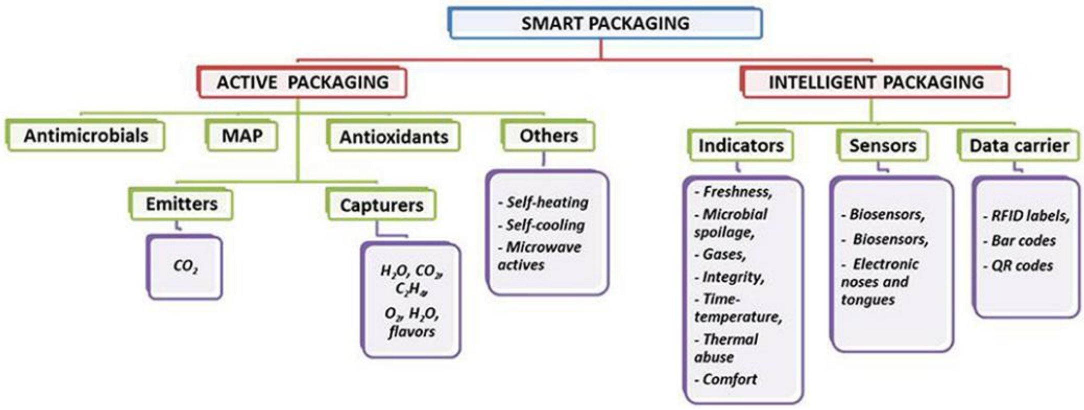

Figure 2.2 Classification of smart food packaging (Salgado et al., 2021)

Smart packaging can be categorized into two main types: active packaging and intelligent packaging. Active packaging is designed to interact with the food to extend its shelf life by controlling factors such as oxygen, moisture, and microbial growth (Salgado et al., 2021). For example, oxygen scavengers and antimicrobial agents can be incorporated into packaging materials to prevent spoilage and maintain food quality. Intelligent packaging, on the other hand, focuses on monitoring and communicating information about the food's condition through indicators, sensors, or data carriers (Schaefer & Cheung, 2018). This includes time-temperature indicators, freshness sensors, and pH-sensitive indicators, which provide visual or digital signals about the food's freshness and safety.

One of the most promising applications of intelligent packaging is the use of pH-sensitive indicators, which change color in response to changes in the pH of the food. This is particularly useful for monitoring the freshness of perishable foods, such as meat, fish, and dairy products, where spoilage is often accompanied by changes in pH due to microbial activity (Zhao et al., 2022). For example, anthocyanins, natural pigments found in plants, have been widely studied as pH-sensitive indicators due to their ability to exhibit distinct color changes across a wide pH range (Mary et al., 2020).

2.3.1 Anthocyanin as a pH-Sensitive Indicator for Intelligent Packaging

According to Schaefer and Cheung (2018), intelligent packaging is an innovative packaging technology that detects changes in the environment, chemicals, or biology to provide real-time food freshness monitoring (Schaefer & Cheung, 2018). Since pH-sensitive indicators may visibly indicate food spoilage they have drawn a lot of attention among intelligent packaging technologies. Figure 2.3 shows the industrial applications of the biopolymer-based intelligent packaging films.

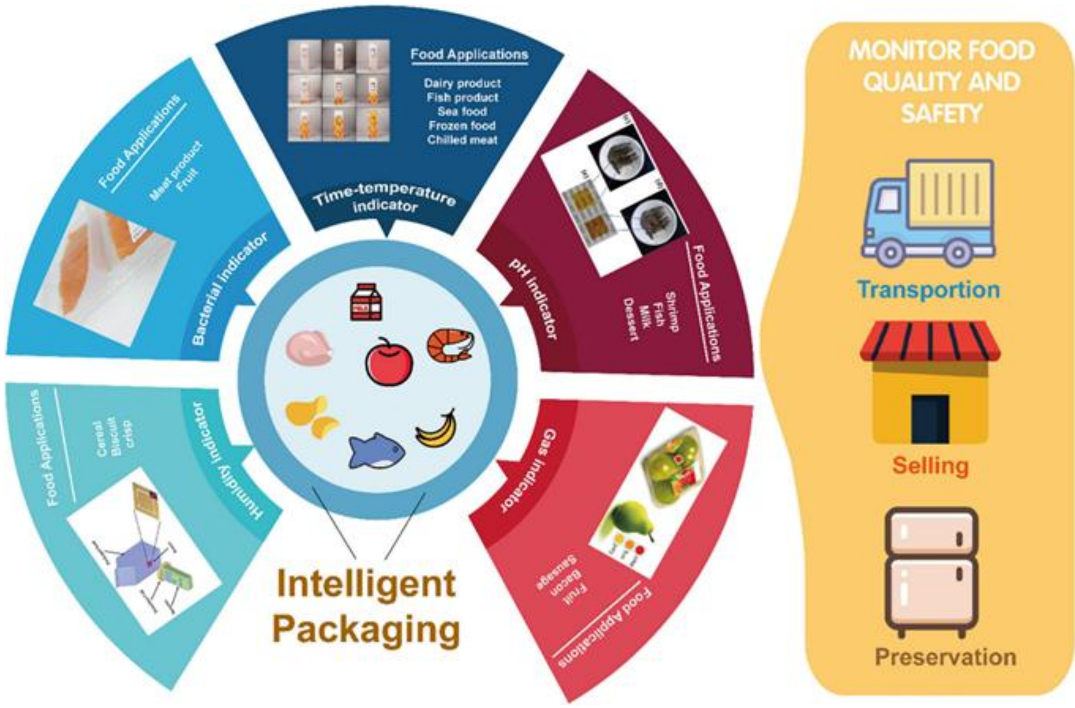

Figure 2.3 Industrial applications of biopolymer-based intelligent packaging films (Abdullah et al., 2022)

Anthocyanins are natural pigments belonging to the flavonoid family, widely found in fruits, vegetables, and flowers such as butterfly pea flowers, red cabbage, and blackberries (Zhao et al., 2022). These pigments exhibit unique pH-dependent color changes, transitioning from red in acidic conditions (pH 1–3) to purple, blue, green, and finally yellow in alkaline conditions (pH 10+). This property makes anthocyanins ideal for use as pH-sensitive indicators in intelligent packaging systems, where they can provide real-time visual cues about food freshness and spoilage (Mary et al., 2020).

The color changes in anthocyanins are caused by structural transformations in the pigment molecules in response to pH variations. In acidic environments, anthocyanins exist primarily as the flavylium cation, which appears red. As the pH increases, the flavylium cation undergoes deprotonation to form the quinoidal base, which appears blue or purple. In highly alkaline conditions, anthocyanins may further transform into chalcone or carbinol pseudo-base structures, resulting in green or yellow colors (Castañeda et al., 2009). This wide range of color changes aligns with the spoilage process of perishable foods, where microbial activity produces alkaline byproducts such as ammonia and amines, raising the pH of the food surface (Hematian et al., 2023).

The use of anthocyanins in intelligent packaging offers several advantages, including their natural origin, biodegradability, and non-toxicity, which align with the growing demand for sustainable and safe packaging materials (Abdullah et al., 2022). However, challenges remain in ensuring the stability of anthocyanins under varying environmental conditions, such as light and temperature, and their compatibility with polymer matrices (Handayani et al., 2024). For instance, Xue Mei et al. (2020) explored the incorporation of anthocyanins into sago starch films and found that the stability of the pigments was influenced by factors such as pH, temperature, and the presence of other compounds in the food matrix. Their study highlighted the importance of optimizing the extraction and stabilization of anthocyanins to ensure their effectiveness in intelligent packaging applications (Xue Mei et al., 2020).

In another study, Saravanan et al. (2024) developed semolina starch/agar-based intelligent films by incorporating butterfly pea flower anthocyanins to monitor the freshness of prawns. The researchers evaluated the colorimetric response of the films to pH changes during prawn storage and found that the films exhibited distinct color transitions from blue (fresh) to green (spoiled), effectively indicating the freshness of the prawns over time. The study also demonstrated that the films maintained good mechanical and barrier properties, making them suitable for practical packaging applications. This work highlights the potential of anthocyanin-based intelligent films for real-time monitoring of seafood freshness, contributing to improved food safety and reduced waste (Saravanan et al., 2024).

The integration of anthocyanins into PVA/MCC films not only enhances the functionality of the packaging material but also contributes to its sustainability. By utilizing natural pigments derived from agricultural by-products, such as butterfly pea flowers (BPF), this approach reduces the reliance on synthetic indicators and aligns with the principles of a circular economy (Varghese et al., 2023). Furthermore, the antioxidant and antimicrobial properties of anthocyanins can help extend the shelf life of packaged foods by inhibiting microbial growth and oxidative spoilage, adding another layer of functionality to the packaging material (Gamage et al., 2021).

Anthocyanins hold great promise as pH-sensitive indicators for intelligent packaging due to their natural origin, biodegradability, and ability to exhibit distinct color changes in response to pH variations. The integration of anthocyanins into PVA/MCC films offers a sustainable and multifunctional packaging solution that enhances food safety, reduces waste, and improves consumer trust. Ongoing research is focused on optimizing the stability and compatibility of anthocyanins in polymer matrices, as well as exploring new sources of natural pigments for intelligent packaging applications.

2.3.2 Butterfly Pea Flower as Source of Anthocyanin

BPFs (*Clitoria ternatea*) is a tropical plant native to Southeast Asia, known for its vibrant blue petals. It has been traditionally used in herbal medicine, food coloring, and beverages due to its rich content of anthocyanins, which are natural pigments responsible for their striking blue color (Handayani et al., 2024; Mary et al., 2020). The flower is also valued for its antioxidant, anti-inflammatory, and antimicrobial properties, making it a popular ingredient in functional foods and beverages (Gamage et al., 2021).

The anthocyanins in BPFs are primarily composed of ternatins, which are unique to this plant and contribute to its intense blue color. These anthocyanins are highly stable compared to those from other sources, making them ideal for applications in food and packaging (Mary et al., 2020). Table 2.3 shows a comparison of anthocyanins from BPFs (*Clitoria ternatea*) with those from other common sources, such as red cabbage, blackberries, and purple sweet potatoes.

Table 2.3 Comparison of Anthocyanin Sources for pH-Sensitive Packaging (Gamage et al., 2021; Zhao et al., 2022)

Property	Butterfly Pea Flower	Red Cabbage	Blackberry	Purple Sweet Potato
Color Range	Blue to purple (pH 6–8)	Red to purple (pH 2–7)	Red to purple (pH 2–7)	Red to purple (pH 2–7)
Stability	High stability in neutral pH	Moderate stability	Low stability	Moderate stability
Antioxidant Activity	High	High	High	High
Antimicrobial Properties	Yes	Yes	Yes	Yes
Extraction Yield	High	Moderate	Low	Moderate
pH Sensitivity	Wide pH range (2–10)	Narrow pH range (2–7)	Narrow pH range (2–7)	Narrow pH range (2–7)
Color Intensity	Intense blue/purple	Intense red/purple	Intense red/purple	Intense red/purple
Cost of Extraction	Low	Moderate	High	Moderate

BPF anthocyanins are highly valued for use in pH-sensitive intelligent packaging due to their unique properties and advantages over anthocyanins from other sources. One of the key reasons for their use is their wide pH range and distinct color changes. BPF anthocyanins exhibit a broad spectrum of color variations, transitioning from red in acidic conditions (pH 1–3) to purple, blue, green, and finally yellow in alkaline conditions (pH 10+) (Zhao et al., 2022). The structural change in the anthocyanin molecules, as well as the shift in the medium's H^+ and OH^-concentration may have contributed for this colour change. The presence of the flavylium ion is responsible for the red colour, the neutral quinoidal base for the blue colour, and the ionic chalcone for the green colour. When the pH of non-acylated anthocyanins increases, the flavylium ion changes into a colourless carbinol pseudo base. However, the presence of acyl groups in BPF anthocyanins inhibits the hydrolysis of flavylium ions to less stable carbinol pseudo base form, forming blue quinoidal compounds that are less sensitive to pH shifts in neutral or mildly acidic conditions (Gamage et al., 2021). Delphinidin-3-glucoside is a type of anthocyanin, which is a class of flavonoid pigments responsible for the red, purple, and blue colors in many fruits, flowers, and vegetables. Figure 2.4 shows the structural alteration of delphinidin-3-glucoside with increasing pH and formation of blue colour in BPF anthocyanin. Path (A, B) shows the transformation of flavylium ion to carbinol or pseudo base. Path (A, C) shows the transformation of flavylium ion to quinoidal base. Path (A, C) shows the structural alteration responsible for the blue colour formation in BPF anthocyanins.