

**INVESTIGATION OF THE IMPACT OF
MULTI-WALLED CARBON NANOTUBES ON
THE PROPERTIES OF PVOH-CORN
STARCH COMPOSITES SYSTEM**

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**INVESTIGATION OF THE IMPACT OF MULTI-WALLED CARBON
NANOTUBES ON THE PROPERTIES OF PVOH-CORN STARCH
COMPOSITES SYSTEM**

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Mechanical
Engineering with Honours**

**Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman**

May 2026

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ABSTRACT

This study investigates the effects of multi-walled carbon nanotubes (MWCNTs) on the mechanical, structural, and antioxidant properties of polyvinyl alcohol (PVOH)–corn starch composite films for sustainable food packaging applications. Using a solution casting method, 9 formulations with a 75:25 PVOH-to-starch base ratio were produced by varying the MWCNT loading (0.1g to 0.3g) and Tween 20 surfactant ratios (1.0:1 to 2.0:1). A wide range of characterization tests, such as mechanical testing (tensile strength, Young's modulus, and elongation at break), scanning electron microscopy (SEM) for morphological analysis, Fourier transform infrared spectroscopy (FTIR) for chemical interaction tracking, X-ray diffraction (XRD) for crystallinity assessment, and the DPPH Scavenging Activity Assay for antioxidant potential, were used to assess the effect of nanofiller dispersion on the matrix. Mechanical tests showed a major trade-off. At higher concentrations, MWCNT loading simultaneously caused brittleness and reduced tensile strength even though it greatly increased stiffness, peaking at a Young's modulus of 527.78 MPa. Formulation 9 (0.3g MWCNT, 2.0:1 surfactant ratio) achieved the best crystalline perfection with a maximum lateral crystal size of 0.82 Å and a uniform, defect-free surface according to structural analysis using XRD and SEM. The 2.0:1 surfactant-to-nanotube ratio was crucial for enhancing molecular integration through improved hydrogen bonding according to FTIR measurements. Furthermore, this ideal ratio produced a high antioxidant activity of 6.073% by maximizing the nanotubes' ability to scavenge radicals. Although MWCNTs significantly reinforce the composite while offering sufficient functionality, the 2.0:1 surfactant ratio is essential to prevent agglomeration and structural defects. Future research should look into higher surfactant ratios and useful shelf-life testing to further enhance material performance for active packaging.

Keywords: Polyvinyl alcohol (PVOH), Corn Starch, Multi-walled carbon nanotubes (MWCNTs), Solution Casting, Tween 20, Mechanical Properties, SEM, FTIR, XRD, DPPH Antioxidant Assay.

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LIST OF SYMBOLS / ABBREVIATIONS

σ	Tensile Strength, MPa
ϵ	Elongation at Break, %
E	Young's Modulus, MPa
F_{max}	Maximum Force, N
A	Cross-sectional Area, mm^2
L_0	Original Gauge Length, mm
ΔL	Change in Length, mm
λ	X-ray Wavelength, Å
d	d-spacing, Å
θ	Bragg Angle, °
β	Full Width at Half Maximum (FWHM), rad
K	Scherrer Constant
L	Lateral Crystal Size, Å
$A_{control}$	Absorbance of the DPPH Control
A_{sample}	Absorbance of the Film Sample

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

During the COVID-19 pandemic, the usage of single-use plastic food packaging has increased dramatically, adding to the issue of plastic waste. Plastic packaging materials that have not been adequately managed might end up in the ocean, where they decompose into microplastics that can be harmful to human health if consumed through the food chain. Human blood and tissues have been found to contain microplastic particles, which may be connected to the development of several kinds of diseases (Hao Deng *et al.*, 2024). Biopolymer materials for food packaging and preservation have been the subject of a lot of study, and there is an increasing demand for biodegradable materials as an alternative to synthetic packaging. Since they can decrease water absorption in food, control solute movement, and reduce moisture and smell loss, edible and biodegradable films are being explored as possible replacements for synthetic packaging materials.

The development of polymer materials for biodegradable food packaging films has advanced significantly, mostly using abundant natural and renewable resources. Materials that are inexpensive and frequently considered waste or by-products, such proteins and polysaccharides have been used. The potential of biodegradable biopolyester materials, such as polyvinyl alcohol (PVOH) in food packaging has been thoroughly investigated. The production of biodegradable matrices has made significant use of starch which comes from a variety of plant sources.

In industrial settings, polyvinyl alcohol (PVOH) is a synthetic thermoplastic polymer that is popular for its semi-crystalline structure, hydrophilicity, non-toxicity, and biodegradability (Bushra H. Musa *et al.*, 2019). It is chemically resistant, sticky, and thermally stable, and it has a great ability to create films through solution casting. Due to these characteristics, PVOH can be used as a thickening in polyvinyl acetate emulsions, a textile sizing agent, a membrane material, a support material for 3D printing, and to create vinylon fiber.

PVOH has a lot of benefits but its usage in applications that need durability and stress tolerance is limited by its relatively low mechanical strength (British Plastics Federation, 2025). PVOH is frequently combined with other polymers to improve its performance to fix this weakness.

Starch is an attractive additive among natural polymers because of its low price, biodegradability, renewability, and availability (Peng Zhou *et al.*, 2021). One of the main sources of carbohydrates in plants including corn, rice, wheat, and potatoes is starch. PVOH and starch can be blended to fulfill environmental goals while lowering total material costs (Peng Zhou *et al.*, 2021). PVOH and starch films are frequently prepared using the solution casting approach because it offers consistent thickness, excellent clarity, and low haze. Starch and PVOH (polyvinyl alcohol) are relatively easy to mix in water-based systems. This is because Polyvinyl alcohol and starch are both polar substances with hydroxyl groups in their chemical structures. Due to their polarity, the hydroxyl groups in PVOH and starch can form intramolecular and intermolecular hydrogen bonds and thus improving their miscibility.

PVOH and starch blends still have lower mechanical and physical qualities compared to conventional petroleum-based polymer. Researchers have investigated using reinforcing agents or additions to enhance these qualities. For instance, Otey *et al.* examined blends using potato starch (Bushra H. Musa *et al.*, 2019), while Hameed *et al.* examined the mechanical performance of PVOH-corn starch composites containing SiO₂ nanoparticles. A highly promising reinforcing material is multi-walled carbon nanotubes (MWCNTs). Multi-walled carbon nanotubes (MWNTs) are multiple layers of graphite sheets wrapped into concentric tubes form the cylindrical nanostructures. These layers are usually separated by about 3.4 Å. The Russian Doll model, in which each graphene layer creates a nested cylinder inside another, and the Parchment model, in which a single graphene sheet spirals around itself like a rolled-up newspaper, are the two primary models that allow for the structural representation of MWNTs. MWNTs are excellent candidates for reinforcing polymer composites because of their distinctive architectures, which provide them with remarkable mechanical, electrical, and thermal capabilities.

MWCNTs have significance as reinforcing fillers in composite materials because of their outstanding mechanical, electrical, and thermal capabilities. Since the delocalization of π -electrons throughout their tubular structure, MWCNTs can transport charge efficiently in terms of electrical conductivity. In MWCNTs, the fourth electron is in a π -bond and each carbon atom makes strong covalent connections with three adjacent carbon atoms. These π -electrons are free to move along the length of the nanotube and create a huge π -conjugated system since they are not bound to any one atom or bond (Dr. Amelia Wood, n.d). MWCNTs are extremely conductive and can pass on this characteristic to composites they are added to because of this arrangement, which enables effective charge transport throughout the structure.

Furthermore, MWCNTs have strong thermal conductivity, which is mainly due to phonon conduction. Heat transfer is made possible by the nanotube's strong carbon-carbon bonding and reduced phonon dispersion. Due to their strong carbon lattice structure, MWCNTs have a very rigid and strong mechanical structure. Although MWCNTs have a slightly lower tensile strength per tube than SWCNTs, but they are more robust and reliable especially when subjected to cyclic loading. MWCNTs have benefits but adding them to polymer matrices poses difficulties. Strong van der Waals forces cause them to clump together which makes uniform dispersion challenging (Dr. Amelia Wood, n.d). Without chemical modification, interfacial bonding with PVOH is frequently poor. Furthermore, the high cost of high-quality MWCNTs restricts their use on an extensive basis, and traditional processing methods might not be appropriate.

Chemical groups such as hydroxyl, carboxyl, or amide groups can also be used to functionalize the surface of MWCNTs (Dr. Amelia Wood, n.d). By improving their dispersibility in hydrophilic polymer matrices such as starch and PVOH, this change increases compatibility and bonding between surfaces. MWCNTs' dispersibility and processibility are frequently enhanced following functionalization. It is possible to connect other molecules to new functional groups by creating binding sites. In biological applications, this is particularly beneficial since biomolecules may be added to the surface of MWCNTs to regulate biological uptake

1.2 Importance of the Study

By using MWCNTs and corn starch to reinforce PVOH, this study overcomes its drawbacks, including its low mechanical strength. Although PVOH is commonly used in packaging, biomedical, and 3D printing applications and is biodegradable and non-toxic, but it is limited to mechanical performance which prevent it to wider adoption. The goal of the resulting composite is to improve structural integrity and use by combining PVOH with starch, a plentiful and biodegradable natural polymer, and adding MWCNTs. Additionally, this research advances the creation of environmentally friendly materials that may find use in healthcare shipment, biodegradable electronics, and sustainable food packaging. Additionally, it examines the difficulties in dispersing MWCNTs in hydrophilic polymer matrices and looks for practical solutions to enhance compatibility and performance, like casting techniques and starch incorporation.

1.3 Problem Statement

Since polyvinyl alcohol (PVOH) is water soluble, biodegradable, and typically less harmful to the environment than many other kinds of plastic, it is considered a sustainable packaging material. Its water solubility allows for innovative dissolvable packaging designs, and its biodegradability contributes to a decrease in waste. PVOH is a desirable choice for environmentally friendly packaging applications because of these characteristics.

However, PVOH's wider application is restricted by its comparatively high cost. One frequent method to save material costs and remain its biodegradability is to blend PVOH with cheap corn starch. However, because corn starch is hydrophilic, it can degrade the blend's mechanical tensile strength.

Due to the poor mechanical strength and ability to enhance composite performance, reinforcing fillers like multi-walled carbon nanotubes (MWCNTs) are being investigated as a solution to this problem. However, in the hydrophilic PVOH-starch matrix, MWCNTs are hydrophobic and challenging to evenly distribute. Agglomeration brought on by this inadequate dispersion could decrease their reinforcing effect and jeopardize the strength of the composite.

Consequently, there is a critical need to utilize a non-ionic surfactant, specifically Tween 20 to facilitate stable dispersion through steric stabilization . It remains unclear how different ratios of Tween 20 to MWCNT loading influence the molecular integration, crystallinity, and functional properties of the final composite films. Therefore, this study systematically evaluates the impact of Tween 20 concentration on the mechanical, chemical, and antioxidant performance of PVOH–corn starch–MWCNT composites. A high-performance biodegradable composite for packaging applications must be developed by choosing the right PVOH–starch ratio and refining processing techniques, such as the use of dispersion agents.

1.4 Objectives

1. To evaluate the effect of the MWCNTs in PVOH/ Corn Starch composites in terms of mechanical, chemical, physical and antioxidant properties.
2. To evaluate the effect of the Tween 20 in MWCNTs-PVOH/Corn Starch composites in terms of mechanical, chemical, physical and antioxidant properties.
3. To obtain the optimum formulation of Tween 20 and MWCNTs in the PVOH/Corn Starch composites in terms of mechanical, chemical, physical and antioxidant properties.

1.5 Aims of the study

To create a high-performance, biodegradable active packaging film, the main goal of this work is to examine the synergistic effects of adding multi-walled carbon nanotubes (MWCNTs) into a polyvinyl alcohol (PVOH)–corn starch biopolymer matrix. The concept behind this research is that MWCNTs' high aspect ratio and better mechanical strength will serve as a structural reinforcement, effectively bridging the polymer chains to improve the composite's overall stiffness and Young's modulus. It is also predicted that the nanotubes' intrinsic characteristics will add useful antioxidant characteristics, turning a typical biodegradable film into a functional packaging material that can scavenge free radicals. Tween 20's function as a non-ionic surfactant is

crucial to this study. Before starting the experiment, it was expected that the surfactant ratio would play a crucial role in the composite's performance. It was hypothesized that a higher ratio, specifically approaching 2.0:1 would be a mechanical necessity to overcome the strong van der Waals forces that typically cause nanotubes to agglomerate. A highly ordered crystalline network and a consistent surface morphology were expected as a result of successful dispersion which would be verified by XRD and SEM investigation.

1.6 Scope and Limitation of the Study

This study focuses on fabricating and evaluating polyvinyl alcohol (PVOH)–corn starch composite films reinforced with multi-walled carbon nanotubes (MWCNTs). The research is divided into two phases: sample preparation using the solution casting method and comprehensive sample characterization.

1.6.1 Material Formulation and Fabrication

1. Base Matrix: A fixed 75:25 ratio of PVOH to corn starch was used, totaling 27g of polymer per batch.
2. Reinforcement Loading: MWCNTs were added at concentrations of 0.1g, 0.2g, and 0.3g.
3. Dispersion Agent: Tween 20 was employed as a non-ionic surfactant to facilitate uniform nanotube dispersion.
4. Processing: The mixture underwent controlled heating and stirring before being cast onto metal plates and dried in an oven at 40°C to achieve uniform thickness.
5. Drying: The wet films are peeled and cut for analysis after being dried at 40°C in an oven until a uniform weight is reached.

1.6.2 Characterization and Analysis

The following methods were used to evaluate the films' functional and structural characteristics:

6. Mechanical Testing: Using ASTM D882 guidelines, tensile strength, Young's modulus, and elongation at break are evaluated.

7. Morphological Analysis (SEM): Examining possible nanotube aggregation, interfacial adhesion, and surface topography.
8. Chemical Spectroscopy (FTIR): Hydrogen bonds and molecular interactions between the matrix and fillers are detected.
9. Crystallinity Analysis (XRD): Examining the polymer network's transition from crystalline to amorphous.
10. Antioxidant Assay: The DPPH method is used to measure the activity of free radical scavenging.

1.6.3 Limitations

The fact that production and testing were limited to a laboratory scale which might not accurately mirror industry manufacturing conditions is one of the study's many drawbacks. Additionally, the investigation did not include assessments of long-term stability or durability. Instead, it concentrated on the materials' immediate performance. Finally, only the DPPH method was used for antioxidant assessment; other popular assays like FRAP or ABTS were left out.

1.7 Contribution of the study

This study makes a contribution by carefully examining the dual function of MWCNTs and corn starch in PVOH composites. It contributes to examine the ways that every component influences the composites' mechanical, physical, chemical, and antioxidant properties. The study determines the interactions that control film performance by comparing the impacts of starch input and nanotube reinforcement. Additionally, the study determines the ideal PVOH–starch–CNT formulation that is supported by Tween 20 dispersion, ensuring both structural integrity and functional activity. These results offer an outline for creating bio-nanocomposite films that are suitable for active and sustainable packaging uses.

1.8 Outline of report

There are five major chapters in this report. In Chapter 1, the problem description, aim, objectives, and scope of the research are discussed, followed by an explanation of the study's background and importance. This provides the foundation for understanding the purpose of the project and the reasons for it.

The study's relevant research is reviewed in Chapter 2. An introduction to PVOH and starch as biodegradable polymers is provided first, followed by reinforcing techniques utilizing nanofillers such carbon nanotubes, cellulose nanocrystals, and montmorillonite. There is additional discussion of the function of surfactants such as Tween 20, SDS, CTAB, and SC in dispersing CNTs. The antioxidant potential of CNTs is further highlighted and it also provides an overview of important characterization methods such as SEM, FTIR, XRD, and antioxidant tests. The evaluation is concluded with a brief summary relating previous findings to the current field of research.

The methods used in this project is explained in Chapter 3. It describes the chemicals and materials that are employed, as well as the steps involved in solution casting the PVOH–starch/MWCNT films. This covers procedures including blending, casting, creating polymer solutions, and dispersing CNTs using Tween 20. The characterisation techniques used to evaluate the films are also covered in length in this chapter, including SEM, FTIR, XRD, mechanical testing, and the DPPH radical scavenging experiment for antioxidant activity. The technique guarantees a methodical approach that directly tackles the goals of the study.

The experiments' outcomes and a discussion of the results are presented in Chapter 4. SEM structural observations are examined together with the films' mechanical characteristics, including tensile strength, elongation, and Young's modulus. Crystallinity variations and molecular interactions are explained by FTIR and XRD data. Additionally, the antioxidant capacity as determined by DPPH is shown. After finishing the testing, the best formulation for achieving balanced mechanical and functional performance will be addressed.

Chapter 5 wraps up the report by providing a summary of the study's main conclusions and contributions. It considers the difficulties faced throughout the study while offering recommendations for improvement.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Polymer-based plastic packaging materials, which are lightweight, stable, and resource-rich, have found widespread use in a variety of industries. Petroleum-based plastics are used extensively in many industries, including packaging. Since they are not biodegradable, they have caused significant environmental issues. Researchers and developers have focused a lot of focus on creating biodegradable materials from renewable resources like starch, chitosan, protein, fibre, and others because of the growing awareness of sustainable development and environmental protection. Starch serves as the matrix for the study and manufacturing of packaging materials among all biopolymer studies. One type of green biodegradable polymer that comes from a variety of renewable resources is starch. It is a cheap and easily accessible polysaccharide polymer. Because of these benefits, starch has several uses in the food, pharmaceutical, and chemical sectors. To improve the physical mechanics of the starch membrane, reinforcing materials such as polypropylene, PVOH, and others can be used. PVOH is a petroleum-based polymer that is either biocompatible and thermoplastic. It is also one of the few completely biodegradable polymers with a C-C single bond backbone. Making biodegradable starch–PVOH composites could be one method to overcome some of the starch's drawbacks.

However, the PVOH/starch composite has poor mechanical performance and water barrier qualities because both PVOH and starch include a lot of hydroxyl groups, which introduce a strong hydrophilic tendency. Nano clay and carbon nanotubes are used to create nano polymeric composites, which enhance the mechanical, flame-redundant, moisture-resistant, and water-blocking qualities of polymers. Researchers have looked into adding nanofillers to PVOH–starch matrices to solve these problems. By encouraging interfacial contacts and crystallinity, montmorillonite (MMT) nanoclay has been demonstrated to dramatically increase tensile strength, modulus, and thermal stability. MMT was shown to diffuse more efficiently in PVOH–starch blends

than in pure PVOH, which improved stress transfer throughout the matrix and provided greater reinforcement (PVOH starch 2.pdf). These results demonstrate how important nanofiller dispersion is in influencing composite performance.

This problem can be addressed with the help of recent research on CNT dispersion methods. As an example, research on CNT nanofluids showed that when it is used at the right concentrations, PVOH itself can function as a dispersion through hydrogen bonding and steric repulsion. Stable dispersions with improved thermal conductivity and regulated viscosity were produced at the proper ratios of CNT to PVOH, while instability was brought on by either too much or too little dispersant (STABILITY AND CHARACTERIZATION OF CNT NANOFLUIDS.pdf). To enhance CNT dispersion in starch-based films, Alves et al. (2021) looked into the use of ionic surfactants, specifically sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and sodium cholate (SC). They stated that CTAB provided the highest electrical conductivity (~ 14.75 S/m) and antioxidant activity, SC produced the most homogeneous dispersion, resulting in a 75% increase in tensile strength and a 60% rise in Young's modulus. These findings demonstrate how the choice of surfactant directly affects the functional results of CNT–starch composites, emphasizing dispersion control as an essential performance factor.

The best formulation that balances starch content, CNT loading, and dispersion agent concentration is still up for discussion, although earlier research showing the potential of nanofillers including clays and CNTs to reinforce PVOH–starch composites. The majority of studies have either looked at the function of CNTs or starch separately or concentrated on dispersion techniques in aqueous settings without applying these findings to solid composite films. As a result, it is still unknown what exact CNT ratios should be used in PVOH–starch matrices as well as the type and amount of dispersing agent needed to provide stable dispersion and efficient reinforcing. The current study aims to determine the best formulation and dispersion conditions for PVOH–corn starch–CNT composites to maximize their mechanical, chemical, physical, and antioxidant qualities. It also aims to systematically evaluate the impact of starch and CNT incorporation.

2.2 PVOH and Corn Starch

Most people agree that polyvinyl alcohol (PVOH) is a synthetic polymer that is naturally biodegradable. This characteristic is largely due to its water solubility, which makes dissolved PVOH accessible to a broad range of microorganisms found in soil, compost, and wastewater environments. The OECD 301B guidelines classify PVOH films used in unit-dose packaging and detergent pods as readily or intrinsically biodegradable, as they decompose into carbon dioxide and water upon microbial community metabolism. More than 50 species of adapted organisms have been shown to effectively decompose PVOH in activated sludge and municipal wastewater treatment systems, demonstrating its sustainability. In particular, the degree of hydrolysis and molecular weight of PVOH have a significant impact on the rate and extent of its biodegradation. Since fully hydrolyzed PVOH is often more crystalline, degradation is slowed down and microbial accessibility is decreased. On the other hand, because of water penetrates them more easily, so the partially hydrolyzed grades are less crystalline and break down more quickly. Environmental factors are also important. In aerobic surroundings, microorganisms break down dissolved PVOH into carbon dioxide and water, while in anaerobic environments, the breakdown is slower and less thorough.

Furthermore, studies have demonstrated that combining PVOH with natural polymers like starch can greatly increase its biodegradability. N A Azahari, Nadras Othman and Hanafi Ismail (2011) found that films made from a blend of PVOH and corn starch degraded at significantly faster rates than films made entirely of PVOH. For instance, in an enzymatic solution, a 30/70 PVOH/corn starch blend lost nearly 90% of its weight in 60 hours, indicating the catalytic role of starch in speeding film breakdown.

Additionally, corn starch is quite biodegradable. According to a recent study, bioplastics made from corn starch and formulated with fructose and glycerol as plasticizers "display remarkable biodegradability, breaking down naturally without harming the environment," while maintaining important mechanical properties like higher durability and tensile strength (Lakshmiganthan S.M *et al.*, 2025). Similarly, studies on bioplastics made from corn starch showed that over 80% of the material breaks down in soil in 28 days with the help of moisture and soil microbes (Novia Putri Safira *et al.*, 2024).

PVOH exhibits a useful mix between biodegradability and functional strength overall. The breakdown is accelerated and enhanced when starch is added, although usually at the price of mechanical strength. This trade-off has encouraged ongoing studies to generate PVOH–starch composites that maintain biodegradability while enhancing mechanical and barrier performance, including the use of multi-walled carbon nanotubes (MWCNTs).

2.3 PVA and CNC Composites

The development of biodegradable food packaging films has recently focused a lot of study on cellulose nanocrystals (CNC) because of its availability, non-toxicity, and reinforcing properties. However, direct application in packaging systems is limited by their intrinsic constraints, which include low thermostability and sensitivity to humidity. To overcome these drawbacks, Ulaganathan, R.K. *et al.* (2022) investigated the incorporation of CNC to polyvinyl alcohol (PVA) matrices. PVA is a film-forming, biodegradable polymer with excellent hydrophilicity and transparency, but its limited large-scale use is due to its weak barrier qualities and relatively high cost. Thus, the PVA/CNC blend increases the biodegradability of PVA. Since these PVA/CNC blends contain many hydroxyl groups and are naturally hydrophilic, one of their biggest disadvantages is that they have poor water barrier characteristics.

In this work, the solvent casting process was used to generate bio-nanocomposite films using various CNC loadings (2–6 wt%). According to optical microscopy, the PVA/CNC film at 2 wt% CNC had an even surface with evenly distributed particles, indicating suitable compatibility. CNC agglomeration developed at higher concentrations (4–6wt%), creating cavities and degrading the polymer matrix.

These findings were confirmed by FESEM results. A uniform fracture surface was seen in the 2 wt% sample, while agglomerates and dry areas were seen in the 4 wt% sample. Due to CNC clustering, which provided stress concentration places and reduced structural integrity, blister and dimple marks started to form at 6 wt%.

Despite of these modifications, all films maintained high transparency with around 90% light transmission in the visible range. This suggests that

incorporating CNC did not affect film clarity and thus it is a crucial factor for the food packaging application.

According to mechanical testing, 2 wt% CNC produced the best results, with tensile strength of 43.34 MPa, modulus of 31.15 MPa, and elongation of 4.08%. Higher CNC content decreased tensile strength and elongation, making films more brittle, while the modulus varies because of stiff agglomerates. The study showed that the ideal balance of mechanical performance, transparency, and structural uniformity was achieved by introducing CNC at 2 wt%. Agglomeration, brittleness, and weak characteristics were caused by excessive CNC loading. According to these findings, PVA/CNC nanocomposites have a great deal of interest as sustainable alternatives for food packaging applications when optimized at low CNC levels.

2.3.1 PVA/Starch Films with Cellulose Reinforcement

Since hydrodegradable materials dissolve in water, they may be a better option than biodegradable ones for replacing plastic and extending the life of landfills. However, biodegradable materials need specific facilities for breakdown and strictly regulated waste disposal. To address this problem, Chan, M.-K. and Tang, T.-H. (2022) looks into the creation of hydrodegradable films using polyvinyl alcohol (PVA), cellulose (extracted from rice husk), and starch. The goal was to reinforce starch-based films with cellulose and PVA to increase their low strength while preserving their water solubility for breakdown.

Clean fibrous structures were seen in the FESEM images, and crystalline Type-1 cellulose with a crystallinity index of 78.98% was shown by XRD analysis. These findings show that rice husk can produce high-quality cellulose, which directly supports the hydrodegradable films' improved structural qualities and reinforcement. In addition, the starch–cellulose film without PVA (PVA-0) showed a rough, uneven surface with nodules in the cross-section. It indicated the poor compatibility. However, the surface and cross-section became smooth and uniform with the addition of PVA (PVA-3), indicating strong interactions between PVA, cellulose, and starch.

The films' strength and flexibility were greatly increased by the addition of PVA. Elongation increased from 7.5% to 17%, and tensile strength increased from 2 MPa (PVA-0) to 4.2 MPa (PVA-3). These enhancements demonstrate

how PVA is essential for strengthening starch-cellulose films and preserving their hydrodegradable properties while increasing their mechanical strength. Even though the strength is still lower than that of some biopolymer films, it is sufficient for single-use plates or disposable wraps.

Water uptake tests demonstrated the films' hydrodegradability. After a day, all of the film samples absorbed between 88% and 89% water. PVA-0 films swelled and broke apart, but PVA-2 and PVA-3 films remained together while they swelled, showing that PVA slightly but not significantly reduced water uptake. The fact that these films dissolve or decompose in humid environments is confirmed by their significant water absorption. Their ability to degrade quickly after disposal makes them ideal for short-term, single-use applications.

The Chan, M.-K. and Tang, T.-H. (2022) study offers helpful information for the current study. Using cellulose obtained from rice husk to reinforce cassava starch–PVOH films, the researchers showed that fillers may greatly enhance the uniformity and tensile properties of the films, raising their strength from 2 MPa to 4.2 MPa and their elongation from 7.5% to 17%. However, although with these advancements, the films' significant water absorption (about 89%) limited their applicability for conventional packing. This finding is important for the current study because it indicates that natural fillers, although helpful would not be enough to solve the intrinsic flaws in PVOH–starch composites.

2.3.2 PVOH–Starch Blends with Nanofiller

To create biodegradable polymer films for packaging and other related uses, blending polyvinyl alcohol (PVOH) with starch has generated a lot more research. Starch is a desirable sustainable raw resource since it is inexpensive, plentiful, and renewable. However, its direct application is severely limited by its intrinsic brittleness, low mechanical strength, and sensitivity to moisture. PVOH, a water-soluble polymer with superior mechanical stability, flexibility, and film-forming capacity, is combined with it to create composites that function better and are still biodegradable. Although large starch amounts (such as 70%) are tend to lead for lower expenses and enhance biodegradability, but mechanical integrity is forfeited in the process.

According to Tee, T.-T. *et al.* (2013), reinforced the PVOH–starch system with nanofillers can get over these limitations. Exfoliation and intercalation methods for nanoclays, including montmorillonite (MMT) have been extensively researched. They enhance strength and thermal stability through enhancing stress transmission and improving crystallinity. Due to their higher tensile strength, electrical/thermal conductivity, and extremely high aspect ratio, carbon nanotubes (CNTs) have been studied as alternative nanofillers. Strong interfacial contacts between CNTs and PVOH and starch are achieved by hydrogen bonding and van der Waals forces when they are suitably distributed. By serving as bridging agents within the polymer network, CNTs are able to restore flexibility and tensile characteristics while counteracting the brittleness that comes with different starch-rich formulations.

The structural and functional performance of PVOH–starch blends can be considerably enhanced by adding nano-sized MMT clay through solution casting. For clean PVOH, agglomeration, stress concentration, and reduced mechanical performance were produced by larger loadings, whereas tensile strength was improved by low quantities of MMT (<5 phr). Conversely, blends of PVOH and starch (50:50) demonstrated consistent increases in tensile strength, modulus, and elongation with the addition of MMT. It highlights the beneficial connection between the biopolymer matrix and the MMT nanofiller. When the MMT's maximum appropriate phr value is exceeded, the PVOH's elongation tends to decrease significantly. As seen in the Figure 2-1, this can be explained by the simultaneous agglomeration of MMT which results in an irregularity in the chain rearrangement and makes it difficult to recrystallize during deformation.

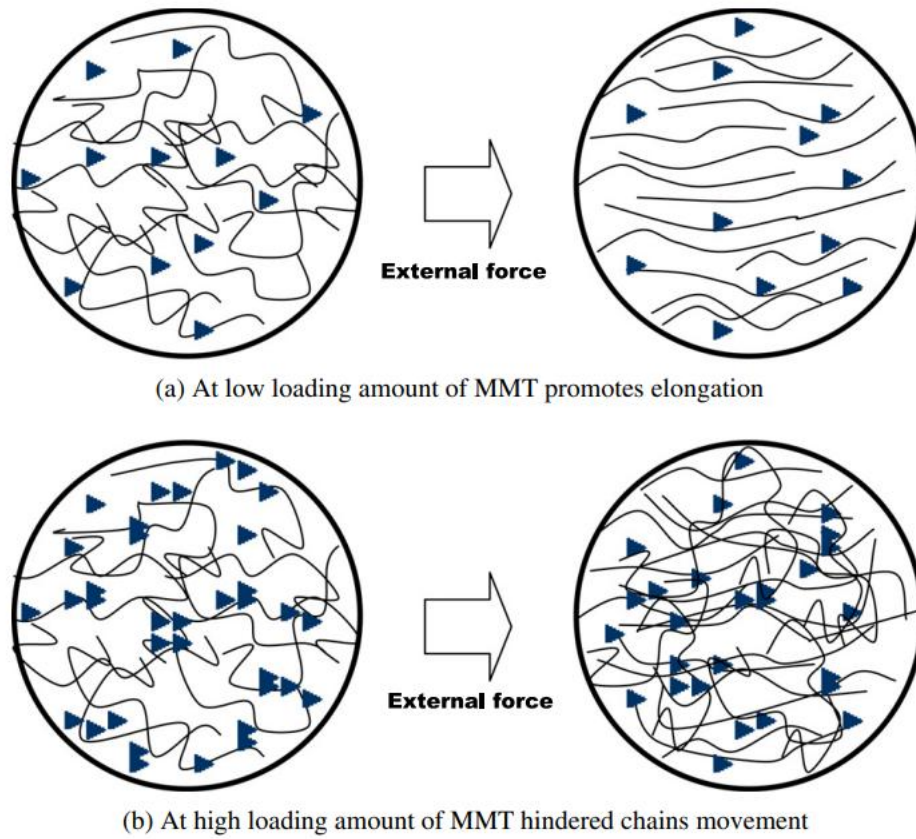


Figure 2-1: MMT acts similarly in PVOH at low and high levels. (Tee, T.-T. *et al.*, 2013),

2.4 PVOH–Starch Ratios

PVOH and starch contribute differently to strength, stiffness, and flexibility, so the blending ratio has a significant impact on the mechanical performance of PVOH–starch blends. Bushra H. Musa *et al.* (2019) used solution casting to create PVOH–starch films in a range of ratios (100:0, 75:25, 70:30, 65:35, 60:40, and 50:50) and then carefully examined their tensile characteristics. According to their research, tensile strength and elongation were continuously decreased by increasing starch concentration, but Young's modulus increased because of the flexibility of the starch particles.

The blend with the best tensile strength (60.08 MPa) among the 75:25 PVOH–starch ratio outperformed those with higher starch amounts, because it resulted in mechanical degradation. Optical microscopy verified that up to about 30% of the PVOH matrix was made up of consistently distributed starch, just like the Figure 2-2. It allowed for efficient stress transfer between the phases. Beyond this point, agglomeration and voids formed at especially at 35–50%

starch, leading to decreased strength and poor interfacial adhesion. For instance, elongation drastically dropped to 1.14% at 50:50, while tensile strength decreased to 42.64 MPa at 60:40 and then to 35.97 MPa at 50:50.

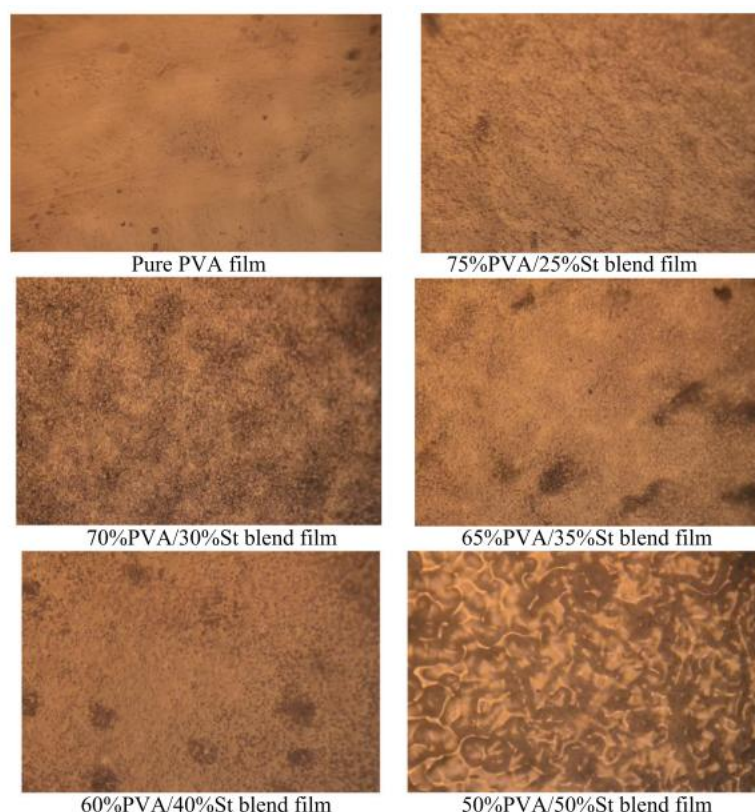


Figure 2-2: The PVA/Starch blend films are optically seen in micrographs.

(Bushra H. Musa *et al.*,2019)

According to these findings, the ideal ratio for structural integrity is 75:25, indicating that moderate starch incorporation offers the best balance between mechanical performance and biodegradability. Therefore, I can determine the ideal ratio for my research and then find out the ideal MWCNT/Tween 20 ratio for the PVOH/Starch composites.

2.5 MWCNT–starch with surfactants

MWCNTs are extremely strong, and their many layers provide them durability and stiffness. They improve durability and reliability when added to a material composite. Additionally, MWCNTs save costs in the synthesis and purification of these materials and are helpful for applications that benefit from their enhanced dispersibility (Ossila, 2025). Since multi-walled carbon nanotubes

(MWCNTs) can add electrical conductivity, mechanical reinforcement, and antioxidant activity, their incorporation into starch-based matrices has generated a lot of interest. Nevertheless, MWCNTs' inherent hydrophobicity and propensity to gather in aqueous solutions offer significant challenges to achieving even dispersion and strong interfacial adhesion. Alves et al. (2021) investigated the purpose of ionic surfactants in dispersing MWCNTs in starch-based films and evaluated the effect of dispersion quality on the general features of the film to address this problem. Sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB), and sodium cholate (SC) were the three surfactants that were evaluated. Their different molecular structures influence how they interact with MWCNTs and starch.

According to structural analysis, MWCNT dispersions stabilized with SC showed the best homogeneity, which was verified by SEM. This was because SC's amphiphilic steroid structure encouraged hydrogen bonds with starch chains while maintaining a strong connection with the nanotube surface. In contrast, at higher MWCNT loadings, SDS and CTAB tend to agglomerate, resulting in stratified morphologies inside the starch films. The mechanical properties were directly impacted by these morphological differences. Films containing SC maintained modulus and tensile strength values that were comparable to those of plain starch (1.2 GPa and 27.7 MPa, respectively), while SDS and CTAB significantly reduced strength, emphasizing the significance of surfactant type in reinforcing activity.

The addition of MWCNTs added new functions in addition to their mechanical qualities. Using the ABTS radical test, antioxidant activity was very low in normal starch films but significantly increased when MWCNTs were added. The maximum radical scavenging activity (~30%) was supplied by CTAB-dispersed MWCNTs among the systems under study, while SDS and SC had moderate and lower activities respectively. At 5% MWCNT loading, electrical conductivity increased significantly as well, especially in CTAB-based composites, achieving around 14.75 S/m compared to about 11.56 S/m for SC and 6.21 S/m for SDS. These results show that CTAB provides the best electrical and antioxidant performance, although at the cost of some mechanical reinforcement, while SC is most successful at stabilizing MWCNT dispersions.

Since the study by Alves et al. (2021) also focuses on the incorporation of multi-walled carbon nanotubes (MWCNTs) into starch-based polymer films, it is quite relevant. Their main difficulty, which directly relates to your PVOH–corn starch composites, was obtaining MWCNTs to disperse uniformly within a hydrophilic starch matrix. They showed that the resulting film qualities are significantly influenced by the quality of the dispersion. The better dispersion (with sodium cholate) preserved the film's strength and homogeneity, poor dispersion (with SDS and CTAB) caused aggregation and reduced mechanical performance. Since achieving a uniform distribution of MWCNTs in PVOH–corn starch will be essential to achieving their reinforcing potential, this finding highlights the importance of dispersion procedures such as surfactants, sonication, or functionalization.

2.5.1 Tween 20

Polyoxyethylene (20) sorbitan monolaurate (Tween 20) are found in many culinary, pharmaceutical, and nanotechnology applications because of their strong stabilizing and dispersing abilities. Tween 20, also referred to as polysorbate 20, is a nonionic detergent and emulsifier that is frequently used in biochemistry and life science research to stabilize solutions, solubilize membrane proteins, and prevent non-specific binding in testing such as ELISAs and Western blotting (Merck, 2025). It is a surfactant that has both hydrophilic and hydrophobic components, which makes it appropriate for use in cell culture, DNA/RNA extraction, and as a component in formulations for medications and cosmetics. This characteristic enables it to be used as a dispersion agent for carbon-based nanofillers, such as multi-walled carbon nanotubes (MWCNTs), which often have poor dispersibility because of hydrophobic surfaces and van der Waals interactions.

Tween 20 is thought to be safe, but Eskandani, M., Hamishehkar, H. and Ezzati Nazhad Dolatabadi, J. (2013) evaluated its effects on normal and cancer cell lines in detailed cyto/genotoxicity research. Tween 20 was found to limit cell proliferation in a dose- and time-dependent manner, with IC_{50} values of 0.4 mL/mL in A549 lung cancer cells and 0.3 mL/mL in HUVECs. Chromatin fragmentation was detected by nuclear staining, and significant DNA cleavage and strand breaks were verified by DNA laddering and comet assays.

Additionally, Tween 20 treatment caused early and late phases of apoptosis in the majority of treated cells based on the flow cytometry. These results demonstrate that although Tween 20 works effectively as a stabilizer, at higher levels it can cause DNA damage and apoptosis.

These results are significant for two reasons in the present study, which investigates the incorporation of MWCNTs to PVOH–corn starch composites. First, Tween 20 offers a useful dispersion method to produce stable MWCNT suspensions before polymer blending, ensuring uniform nanofiller distribution throughout the composite matrix. It is expected that better dispersion will optimize the reinforcing action of MWCNTs, improving the PVOH–starch films' mechanical and thermal properties. Second, Tween 20's reported cytotoxicity emphasizes how crucial it is to optimize its concentration to stabilize nanocarbons, but not so much that it poses a safety risk, especially if the composites are being used for packaging or biomedical purposes.

2.5.2 Tween 20 for Dispersion of Multiwalled Carbon Nanotubes

Multiwalled carbon nanotubes (MWCNTs) have a high aspect ratio, a hydrophobic surface, and strong van der Waals interactions that cause agglomeration, making their dispersion in aqueous fluids an important problem. Both ionic and non-ionic surfactants are frequently used to stabilize CNT suspensions. Among these, the ability of the non-ionic surfactant Tween 20 to produce stable dispersions through steric stabilization has been studied. Van der Waals interactions allow Tween 20's hydrophobic tail to attach to the nanotube surface, while the hydrophilic head groups of polyoxyethylene radiate out into the water-based environment. Since it provides steric repulsion between individual nanotubes, this dual attraction stops CNTs from aggregating.

According to the UV-vis tests, Tween 20 generated dispersions that were clearer than SDS, and greater absorbance values indicated that the nanotubes were better suspended. However, its absorbance peak intensity was still less than the Triton X-100, indicating a lower dispersion power. Transmission electron microscopy (TEM) study confirmed that Tween 20 dispersions showed larger bundles than Triton X-100 but fewer aggregates than SDS. The ideal ratio of CNT to surfactant is also an essential aspect of Tween 20 performance. Poor suspension stability is due to a lack of surfactant molecules to cover CNT surfaces at concentrations lower than this ratio. On the other hand, flocculation is caused by excess Tween 20 beyond the ideal level because more surfactant molecules encourage particle formation and depletion attraction between CNTs, which results in re-aggregation. (Eskandani, M., Hamishehkar, H. and Ezzati Nazhad Dolatabadi, J., 2013). Table 2-1 summarises the type of the surfactant and its quality of dispersion.

Table 2-1: Types of Surfactant

Surfactant	Type	Dispersion Quality	Stability (Thermal / Long-term)
Triton X-100	Non-ionic (aromatic polyoxyethylene)	Best dispersion– highest UV–vis absorbance and	High thermal stability

		smallest bundles in TEM	
Tween 20	Non-ionic (polyoxyethylene sorbitan monolaurate)	Moderate dispersion – better than SDS, but weaker than Triton X-100	Lower thermal stability
Tween 80	Non-ionic (polyoxyethylene sorbitan monooleate)	Moderate dispersion	Moderate stability
SDS (Sodium dodecyl sulfate)	Ionic	Poor dispersion – lowest absorbance, large bundles in TEM	Lower stability

Tween 20 is essential to your PVOH/starch–MWCNT composite because it improves polymer–filler interactions and ensures uniform nanotube dispersion. While the hydrophilic polyoxyethylene groups extend into the aqueous PVOH/starch solution, offering steric stability and preventing agglomeration, the hydrophobic lauryl tail firmly adsorbs onto the CNT surface. In addition to uniformly dispersing MWCNTs throughout the matrix, this promotes hydrogen bonding between the hydrophilic chains of Tween 20 and the hydroxyl groups of PVOH and starch, so bridging the space between the nanotubes and the polymer.

2.5.3 Usage of the surfactant (SDS) to disperse CNTs

The strong van der Waals interactions and propensity to form bundles of carbon nanotubes (CNTs) make their dispersion in aqueous environments a significant issue. Since they adsorb onto CNT surfaces and stabilize them against re-aggregation, surfactants have been used extensively to overcome this problem. In sodium dodecyl sulfate (SDS), Yu, J., Grossiord, N., Koning, C. E., & Loos,

J., 2007 showed that the ideal surfactant-to-MWCNT ratio was roughly 1.5:1 by weight, which offered enough coverage for exfoliation and stable colloidal suspensions over a couple of months. They used transmission electron microscopy (TEM) together with UV-visible spectroscopy to monitor the exfoliation of multi-wall carbon nanotubes (MWCNTs) during sonication. The nanotubes were big, entangled bundles with low UV-vis absorbance at the beginning of sonication. Van der Waals bonds were broken as energy traveled via a probe sonicator, causing the bundles to gradually exfoliate. This was shown in the Figure 2-3 below as an increase in UV absorbance around 260 nm.

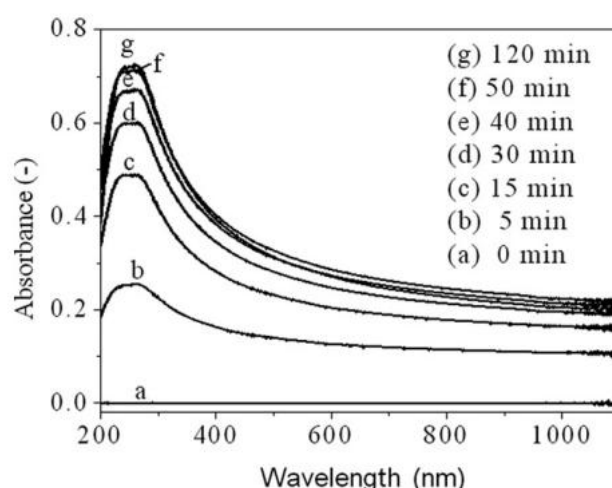


Figure 2-3: UV absorbance (Yu, J., Grossiord, N., Koning, C. E., & Loos, J., 2007)

The weight ratio of SDS to MWCNT was the main experimental variable. By making several solutions with varying ratios, they discovered that the absorbance plateau never reached the maximum dispersion that might have been achieved below 1.5:1, indicating that the nanotubes were not completely coated. The persistence of big aggregates was verified by TEM pictures taken at these inadequate ratios. On the other hand, TEM micrographs revealed primarily individualized nanotubes coated by a thin SDS layer (~5–10 nm thick) at 1.5:1 and higher, and the UV-vis absorbance curves achieved a stable plateau faster. Crucially, raising the surfactant ratio above 1.5:1 raised the possibility of depletion-induced aggregation because of excessive micelle production rather than improving dispersion quality (Yu, J., Grossiord, N., Koning, C. E., & Loos, J., 2007).

TEM pictures provided more proof of this finding. Large bundles of MWCNTs were still visible after only five minutes of sonication (Figure 2-4), which is consistent with low UV-vis absorption. However, the TEM pictures (Figure 2-5) showed individualized nanotubes with little aggregation after 90 minutes at the ideal ratio, indicating that exfoliation had been accomplished. At higher magnification, TEM verified that a thin layer of SDS, measuring roughly 5–10 nm (Figure 2-6), had been applied to the nanotubes. It gave both electrostatic and steric stability. According to their subsequent stability studies, this surfactant coating was essential in preserving colloidal stability for more than three months by preventing re-bundling.

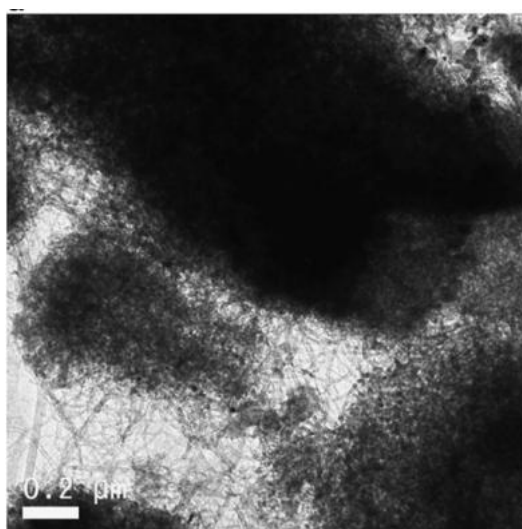


Figure 2-4: TEM pictures after only five minutes of sonication (Yu, J., Grossiord, N., Koning, C. E., & Loos, J., 2007)

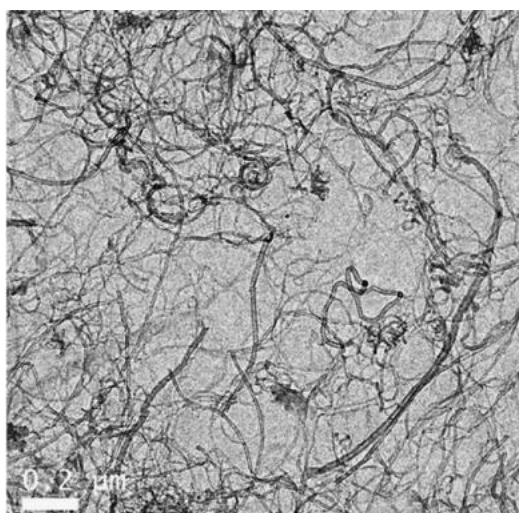


Figure 2-5: TEM pictures of little aggregation formed after 90 minutes (Yu, J., Grossiord, N., Koning, C. E., & Loos, J., 2007)

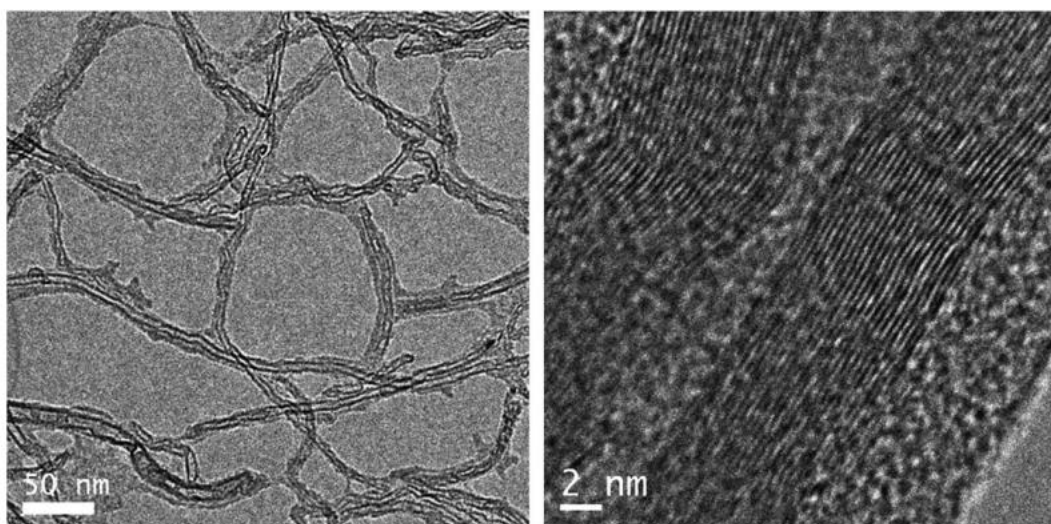


Figure 2-6: TEM pictures at higher magnification (Yu, J., Grossiord, N., Koning, C. E., & Loos, J., 2007)

Although Tween 20 differs structurally from SDS since it is a non-ionic polysorbate and not an anionic surfactant, the idea is the same. The stability requires a sufficient equilibrium between hydrophilic head–hydrophobic tail interactions with CNT surfaces. According to research on non-ionic surfactants, Tween 20 molecules can surround carbon nanotubes (CNTs) and provide steric stability instead of electrostatic repulsion. This suggests that ratios that are around the SDS recommendation (1.5:1 to 2.0:1) may also work well. To maximize dispersion and prevent excess surfactant from affecting film characteristics in polymer composites, a dispersant-to-MWCNT weight ratio in this range may be chosen.

2.6 Antioxidant Potential of Carbon Nanotubes

With growing interest in creating multifunctional composites that can combine mechanical, barrier, and biochemical functions, the antioxidant potential of tiny particles has come to be as an important research topic. Materials having intrinsic antioxidant activity are greatly desired because oxidative stress carried on by free radicals is a major contributor to food spoilage, polymer degradation, and biological harm. Due to its high electron mobility, uncommon π -conjugated structure, and ability to interact with radical species, multi-walled carbon

nanotubes (MWCNTs) have attracted interest in this sector. The antioxidant activity of pristine MWCNTs, carboxyl-functionalized MWCNTs, and hybrid MWCNTs when combined with inorganic nanoparticles like SiC and Fe₃O₄ was examined in this context by Periklis Vardakas *et al.*, 2023. The researchers used a variety of cell-free tests that assess different processes, including free radical scavenging activity, reducing power, and antigenotoxic activity to capture the wide range of antioxidant behaviour of these materials.

The Free Radical Scavenging Assay evaluated the nanomaterials' ability to neutralize free radicals. According to the results, the CNTs@ Fe₃O₄ hybrids outperformed both pristine and functionalized CNTs in terms of radical scavenging activity. This showed that hybridization with Fe₃O₄ nanoparticles improved the surface reactivity and enhanced the ability to neutralize electrons in a synergistic manner.

In the Reducing Power Assay, reducing power measurements were employed to evaluate the nanomaterials' ability to donate electrons. The extended delocalized π -electron system of pure CNTs (CNTs-Ref) allowed for efficient electron transfer, which is why they had the maximum reducing capacity in this case. This finding emphasized CNTs' intrinsic antioxidant properties, which are not impacted by surface modifications.

Finally, the materials' ability to prevent DNA oxidative damage was evaluated using the antigenotoxic assay. The strongest antigenotoxic activity was shown by CNTs@SiC hybrids, which successfully reduced DNA strand splitting and prevented the formation of peroxy radicals (Periklis Vardakas *et al.*, 2023). This demonstrated their potential use in biomedical applications by showing that some hybridizations can impart additional protective properties beyond simple radical scavenging.

Although the study by Periklis Vardakas *et al.*, 2023, evaluated the antioxidant properties of multi-walled carbon nanotubes using cell-free tests like antigenotoxicity, reducing power, and free radical scavenging, these techniques were mainly used to bring focus to the wide range of biological and impact on the environment. The findings showed the possible use of MWCNTs as synthetic antioxidants by showing that both pristine and functionalized MWCNTs had intrinsic electron-donating and radical-scavenging properties. However, standardized and commonly used assays like the DPPH radical

scavenging method and the ABTS assay are more suited for food packaging applications because they offer a simple, repeatable, and quantitative method of evaluating the polymer films' ability to scavenge free radicals.

2.7 Scanning electron microscopy (SEM)

Sample preparation for scanning electron microscopy (SEM) has evolved as imaging technology has advanced. The ability modern SEMs to function at ultralow voltages and low vacuum allows for the investigation of non-conductive and outgassing samples with no prior treatment. By reducing electron beam penetration, low-voltage imaging reduces charging artifacts and reveals fine characteristics of the surface. Similar to this, low-vacuum modes enable higher voltage analyses that are necessary for additional techniques like electron backscatter diffraction (EBSD), cathodoluminescence (CL), wavelength-dispersive spectroscopy (WDS), and energy-dispersive X-ray spectroscopy (EDS) without requiring a lot of sample preparation (Jeol, 2020).

For many SEM applications, conductive coating techniques are still essential despite these improvements in technology. Traditionally, small layers of conductive materials like carbon, gold, platinum, or gold-palladium are sputter coated or evaporated onto non-conductive surfaces. These coatings, which are often 5–50 nm thick, offer a conductive pathway that minimizes beam damage, dissipates heat buildup, and lowers charging while maintaining surface shape (Jeol, 2020). Coating improves accuracy for analytical investigations such as EDS or WDS by lowering beam scatter in high-vacuum mode.

Every coating technique has its own set of benefits and limitations. Since they produce a very thin grain structure that improves high-resolution imaging, gold coatings are frequently used. However, with very high magnifications, the grain size of platinum is much finer, resulting in clearer images. Platinum is the favored choice for nano-scale imaging because it performs exceptionally well when edge definition and ultra-fine detail are required, while gold typically offers a stronger secondary electron yield. Platinum generates less interferences than gold, which is a disadvantage for EDS studies because gold's strong X-ray peaks may overlap with elements of interest.

Uncoated samples show obvious charging artifacts at 10 kV and 0.1 Pa. Although charging can be reduced by lowering the accelerating voltage (5 kV) or increasing the chamber pressure (60 Pa), this results in images that have lower contrast and noise. These limitations become clearer as magnification rises because the electron beam adds more charge in a smaller region. The sample becomes conductive when a small layer of gold is applied, enabling steady imaging at higher voltages and vacuums without the effects of charging. For high-magnification examination, this produces clearer and more contrast images.

Every coating technique has its own set of benefits and limitations. Since they produce a very thin grain structure that improves high-resolution imaging, gold coatings are frequently used. However, with very high magnifications, the grain size of platinum is much finer, resulting in clearer images. Platinum is the favoured choice for nano-scale imaging because it performs exceptionally well when edge definition and ultra-fine detail are required, while gold typically offers a stronger secondary electron yield. However, gold's powerful X-ray peaks might overlap with elements of interest, making it a disadvantage for EDS research (Nanoscience, 2025). Platinum, on the other hand, produces fewer interferences. However, platinum is prone to stress cracking when exposed to oxygen, thus sputter coating should be done in a high-purity gas such as argon. Although platinum targets are often more costly than gold, they perform significantly better when the features of interest are smaller than 100 nm.

In general, metal sputter coating (Au, Pt, and Ir) allows for greater working voltages, which enhances image resolution by enabling lower effective beam diameters. Additionally, these coatings improve signal-to-noise ratios by increasing secondary electron yield. However, they have the ability to interfere with X-ray signals and absorb low-energy electrons, which reduces the sensitivity of backscatter electron (BSE) imaging for specimens with low atomic numbers.

Conversely, conductivity is generated through carbon evaporation without the introduction of X-ray radiation that interfere. It is appropriate for analytical characterisation techniques like EDS because of its low absorption,

which improves the detection of BSE signals. Therefore, metal coatings (especially gold or platinum) are more suitable for high-resolution imaging, especially with low atomic number specimens, while carbon coatings are frequently selected when chemical analysis is prioritised. Carbon is the preferred coating for precise EDS and BSE analysis, platinum is better for extremely high resolution and edge detail, and gold provides excellent general-purpose imaging performance. Therefore, I would suggest Gold or Carbon for my research because it is cheaper while yet having the potential to give me the clear image for my specimens.

2.8 Fourier Transform Infrared (FTIR)

The distinctive structural, electrical, and thermal characteristics of carbon nanotubes (CNTs) have drawn a lot attention and make them desirable for use in enhanced composites, energy storage, and sensors. They stand out from other carbon-based nanomaterials due to their excellent mechanical strength, high aspect ratio, and high electron and thermal conductivity.

CNTs can be produced using a variety of methods, including as chemical vapor deposition (CVD), arc discharge, and laser treatment. High-quality CNTs are created through arc discharge and laser treatment, but because of the high temperatures needed, both processes are expensive. However, there are still issues such as impurities and structural defects with CVD, which provides a more practical method of growing CNTs on substrates at relatively lower costs (Caccamo, M.T., Mavilia, G. and Magazù, S., 2020).

In terms of physical performance, carbon nanotubes (CNTs) have a tensile strength of roughly 150 GPa, which is five times lighter and 20 times greater than steel. Additionally, they show great thermal stability, withstanding temperatures beyond 400 °C in air, and demonstrate excellent thermal conductivity at room temperature (up to 3500 W/mK). Due to these characteristics, CNTs show great potential for thermal energy conversion and storage systems.

Spectroscopic methods like Fourier Transform Infrared (FTIR) and Raman spectroscopy are often used to describe the thermal behaviour of CNTs. The typical D, G, and 2D bands of Raman spectroscopy offer information

related to defects, while FTIR offers insights into vibrational shifts and nanoscale structural modifications. It measures how much infrared light is absorbed at particular frequencies and they are all associated with the vibrational modes of the material's chemical bonds. The presence or shift of new peaks indicates chemical changes like oxidation or bond rearrangements, while stable peaks related to C–C bonding validate the integrity of the tubular framework for CNTs. FTIR enables researchers to identify the temperature at which key structural transformations take place by capturing spectra over a broad temperature range (25–450 °C).

Every material generates a distinct "molecular fingerprint," which enables FTIR to detect interactions or modifications in chemical structure as well as to identify polymers, additives, and nanomaterials. Since overlapping chemical characteristics can show how different components interact, FTIR is very useful for investigating complicated combinations and composites. FTIR has been used to monitor the thermal behaviour of carbon nanotubes (CNTs) while they are heated. For example, the Figure 2-7 shows that heating CNTs from 25 °C to 450 °C dramatically alters their FTIR spectrum, especially in the fingerprint region (1450–500 cm^{-1}). The emergence of new peaks at approximately 1143 cm^{-1} (C–O stretching) and 868 cm^{-1} (C–C stretching) indicates the beginning of structural relaxation and oxidation (Caccamo, M.T., Mavilia, G. and Magazù, S., 2020). The Figure 2-7 below also shows the example of the FTIR result looks like and how a graph would be shown in the spectrum after the testing.

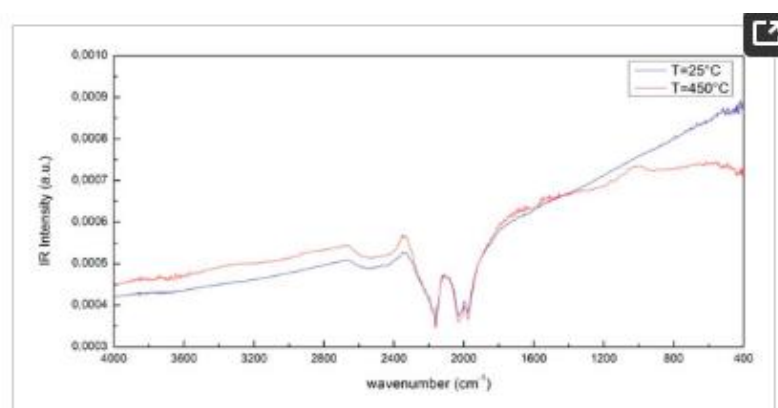


Figure 2-7: Example of IR Spectrum oxidation (Caccamo, M.T., Mavilia, G. and Magazù, S., 2020)

A popular method in FTIR spectroscopy that improves spectral analysis and simplifies sample preparation is Attenuated Total Reflectance (ATR). This technique involves directing an infrared beam at a specific angle of incidence into a high-refractive-index crystal, like zinc selenide or diamond. The beam goes through several internal reflections within the crystal instead of going straight through the sample like the Figure 2-8. An invisible wave is produced at each reflection point, and it enters the sample in contact with the crystal surface a few micrometers deeper. Unlike conventional transmission techniques, this shallow penetration depth enables the infrared energy to interact with the sample's molecular bonds without the need for the sample to be translucent or specifically prepared (RTI Laboratory, 2015). The contact between the energy and the sample increases with the amount of reflection spots and it will improve the spectral quality. After that, the beam leaves the crystal with a spectrum, which is a set of data on the molecular vibrations of the sample. ATR is particularly useful for examining solids, powders, and thin films. Since it requires little preparation and still gives strong, clear spectra, it is a great choice for composite systems like PVOH/starch with MWCNTs and Tween 20.

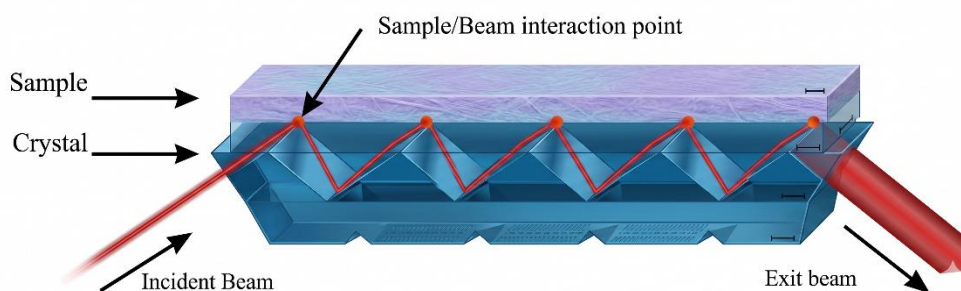


Figure 2-8: Schematic Representation of ATR-FTIR Working Principle

From the case that FTIR, which analyses the ratio of PVOH/starch combined with MWCNTs and Tween 20, can offer equally important insights for this FYP. FTIR can confirm whether proper interactions and bonding take place inside the composite by tracking the distinctive peaks of each component, such as O–H stretching in PVOH and starch, C=C bonds in MWCNTs, and functional groups from Tween 20. Peak intensity shifts or variations would indicate the level of MWCNT dispersion, Tween 20's effectiveness as a surfactant, and the strength of the hydrogen relationship between PVOH and

starch. Additionally, FTIR can detect early oxidation or degradation indicators like CNT thermal tests, ensuring that the chosen ratios result in chemically stable films.

2.9 X-ray diffraction (XRD)

X-ray diffraction (XRD) is commonly used to analyze the crystalline structure and quality of carbon nanotubes (CNTs). Reflections from the hexagonal carbon lattice and graphitic crystalline planes are represented by the two primary distinctive diffraction peaks that are commonly seen in both single-walled (SWCNTs) and multi-walled CNTs (MWCNTs) at $2\theta = 25^\circ$ and 43° , respectively. However, in contrast with conventional crystalline materials, there is frequently a lot of noise in CNT XRD patterns. The inherent tubular structure of CNTs and the van der Waals (VDW) interactions between and within nanotubes are closely related to this noise. CNT peaks are usually broader and asymmetric than graphite because of curvature, turbostratic disorder, and various tube diameters (Rasel Das, Sharifah Bee Abd Hamid and Md. Eaqub Ali, 2015). A two-dimensional hexagonal lattice layout of tubes is confirmed by the observation of an additional Bragg peak in SWCNT bundles at $q = 0.43 \text{ \AA}^{-1}$. XRD is especially useful since it offers information at the bulk level compared to just focusing on individual CNTs. This enables researchers to evaluate crystallinity, tube orientation, and domain size in many different kinds of large samples. A simple yet efficient method of figuring out the degree of vertical alignment is provided by Figure 2-13 in the same review, which illustrates how the strength of the (002) peak drops as CNT alignment increases (Eman J. Theyab *et al.*, 2023). Additionally, XRD can differentiate crystalline CNTs from catalyst residues or a variety of impurities, which frequently make purity tests more difficult. To reduce mistakes, meticulous sample preparation is necessary since peak broadening or shifting might be caused by inhomogeneity, specimen displacement, or grinding. A vital technique for assessing global structures, XRD still supports local probes like TEM and SEM.

Figure 2-9 shows that Eman J. Theyab *et al.*, 2023 expanded on this basis by examining the XRD patterns of SWCNTs and MWCNTs and highlighting the importance of noise in diffraction spectra. The distinctive peaks

at about 26° and 44° were present in both varieties of CNTs, however SWCNTs had smaller peaks and a significantly larger baseline noise than MWCNTs. According to the Eman J. Theyab *et al.*, this is caused by intra- and inter-van der Waals (VDW) pressures. While intra-VDW forces occur between the concentric walls of MWCNTs, inter-VDW forces occur between adjacent tubes in CNT bundles (Eman J. Theyab *et al.*, 2023). Additional secondary reflections are produced by these interactions and appear as "noise" on top of the original peaks. According to the results, SWCNTs display weaker peaks with wider noise bands, whereas MWCNTs display sharper, higher-intensity peaks with lower background noise. A schematic of van der Waals forces is shown in Figure 2-10, which shows how interactions within and across tubes produce both primary reflections and secondary noise signals.

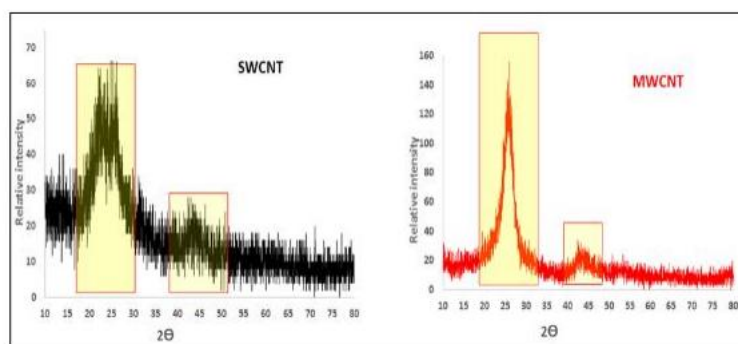


Figure 2-9: XRD patterns for SWCNTs and MWCNTs (Eman J. Theyab *et al.*, 2023)

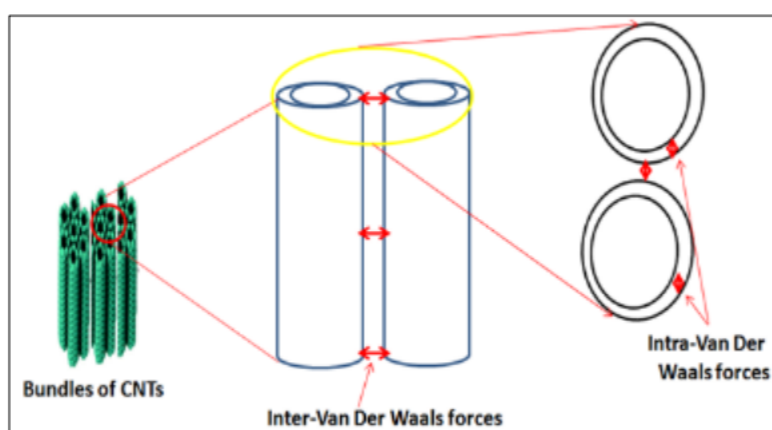


Figure 2-10: Inter and intra VDWs forces in CNTs (Eman J. Theyab *et al.*, 2023)

The 2023 study shows the so-called "noise" in diffraction patterns contains important structural information, whereas the 2015 review validates XRD as a technique that can identify lattice structures, interlayer distances, bundle sizes, and contaminants. One important finding from both is that SWCNTs are more prone to background scattering, while MWCNTs because of their many graphene layers so they are shown in sharper and more defined XRD peaks with less noise.

2.10 Antioxidant Activity Assay

To understand how foods can help to prevent chronic disease and reduce oxidative stress, it is essential to assess their antioxidant capacity. The most widely used in vitro tests for radical scavenging are DPPH (1,1-diphenyl-2-picrylhydrazyl) and ABTS (2,2'-azino-bis-3-ethylbenzothiazoline-6-sulphonic acid) because of their simplicity of use and reliability. To evaluate variations in measurement results, Floegel et al. (2011) compared these two tests using 50 common antioxidant-rich foods in the United States, such as fruits, vegetables, and beverages.

The study discovered that DPPH and ABTS had a significant positive correlation ($p = 0.949$, $p < 0.001$), indicating that both assays usually agree when it comes to evaluating foods that contain antioxidants. However, as Figure 2-11 shows, ABTS consistently produced greater antioxidant capacity values than DPPH across all food classes (fruits: 151 vs. 138 mg VCE/100 g, vegetables: 96 vs. 72 mg VCE/100 g, beverages: 80 vs. 66 mg VCE/100 g). These changes were found to be significant by statistical analysis ($p < 0.05$ for fruits and beverages, $p < 0.01$ for vegetables).

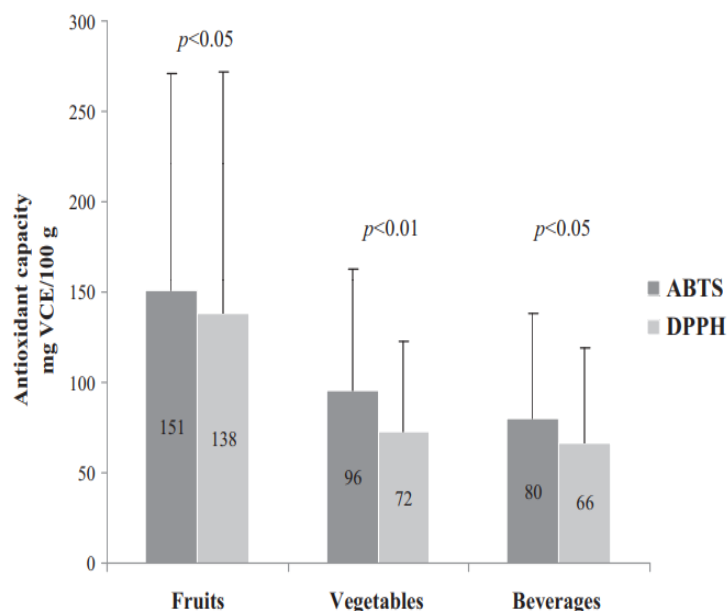


Figure 2-11: Comparison of antioxidant capacities measured by ABTS and DPPH assays (Floegel et al., 2011)

The chemical composition of the radicals explains this difference: DPPH mostly reacts with lipophilic molecules, while ABTS can react with both hydrophilic and lipophilic antioxidants. Therefore, complex food matrices, particularly those high in hydrophilic antioxidants like berries and some beverages, have a higher antioxidant activity that is better reflected by ABTS. Furthermore, ABTS's broader sensitivity was reinforced by a greater correlation with USDA's total phenolic content, flavonoid levels, and oxygen radical absorbance capacity (ORAC) ($\rho = 0.593\text{--}0.946$) than DPPH ($\rho = 0.539\text{--}0.897$). Although ABTS offers a more comprehensive evaluation of antioxidant activity, DPPH is still often used due to its simplicity, low price, and little reagent requirements. To evaluate the radical scavenging ability of the PVOH/starch/MWCNT films, the DPPH test will be used with restrictions mentioned in the discussion.

2.11 Summary

Starch-based polymers are growing as an important option because of their abundance, renewability, affordability, and full biodegradability. This is in line with the global effort to reduce the reliance on petroleum-based plastics. However, starch's practical applications are limited due to its low mechanical

strength, high water sensitivity, and restricted thermoplasticity. Starch is frequently combined with polyvinyl alcohol (PVOH). They are a synthetic but biodegradable polymer known for its superior film-forming properties, flexibility, tensile strength, and transparency, to overcome these disadvantages. These blends combine the structural advantages of PVOH with the biodegradability of starch, making them for uses like biomedical films, and packaging.

PVOH–starch mixtures have significant drawbacks despite their potential. Since both polymers are hydrophilic, they absorb a lot of water, swell, and lack stability in humid environments. Due to weak interfacial adhesion and aggregation, starch incorporation mechanically decreases tensile strength and elongation, particularly at higher concentrations. With the starch evenly distributed throughout the PVOH matrix, Bushra H. Musa *et al.* (2019) showed that the 75:25 PVOH–starch blend had the highest tensile strength (60.08 MPa) among the different compositions. Brittleness and void formation became obvious at starch loadings more than 30%, significantly decreasing elongation and tensile strength. This result emphasizes that the optimal balance between mechanical performance and biodegradability is achieved through moderate starch addition.

Researchers have looked into modification techniques and strengthening tactics with nanofillers to further improve these blends. Through exfoliation and intercalation effects, montmorillonite (MMT) nanoclay has been demonstrated to enhance crystallinity, tensile modulus, and stress transfer in PVOH–starch blends. However, excessive loading may result in agglomeration. To improve uniformity and strength in starch–PVOH systems, cellulose nanocrystals (CNCs) produced from agricultural leftovers like rice husk have also been utilized but their high water absorption (~89%) limits their use in conventional packaging. Due to their outstanding aspect ratio, electrical conductivity, and capacity to scavenge free radicals, carbon nanotubes (CNTs) provide an even more strong reinforcement method. Dispersion is still a significant problem because CNTs aggregate in aqueous solutions by nature. CNT dispersions have been stabilised using surfactants such as SDS, CTAB, SC, and Tween 20, and effective dispersion immediately enhances the films' mechanical and antioxidant properties.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Introduction

Establishing an organized method which allows the reliable production of biodegradable films, formulation optimization, and evaluation of their mechanical and functional characteristics is the primary objective of the method.

A 75:25 PVOH–starch ratio was selected as the foundation for formulation based on results from the literature as it showed the best tensile strength and good starch dispersion inside the PVOH matrix while also maintaining biodegradability. To address the inherent disadvantages of PVOH–starch blends, such as their hydrophilicity and brittleness, multi-walled carbon nanotubes (MWCNTs) were used as reinforcing nanofillers. To increase the stability of nanotubes in aqueous solutions, Tween 20 was used as a dispersion agent. This prevented agglomeration and ensured uniform integration into the polymer matrix.

The process consists of the following steps: making raw solutions and dispersions, casting PVOH–starch/MWCNT films, and carefully drying the finished product to create test specimens. After that, the produced films undergo functional, structural, and mechanical characterization. The DPPH radical scavenging assay was employed to assess antioxidant activity as a simple but accurate way to measure the films' potential to remove free radicals, whereas mechanical testing focused on tensile strength, elongation at break, and Young's modulus.

In overall, the methodological framework was developed to closely match the objectives of the study. This method offers a simple way to evaluate the suitability of the films created by optimizing the PVOH–starch blend ratio, adding MWCNTs using effective dispersion techniques, and carrying out mechanical and antioxidant testing. The methodology not only ensures systematic preparation and characterisation, but it also provides the foundations to assess their potential as green substitutes for conventional plastic packaging.

3.2 Materials

The main polymer base was fully hydrolyzed polyvinyl alcohol (PVOH) of Sekisui Selvol™ 325 grade. The manufacturer of the PVOH employed in the present study was Sekisui Specialty Chemicals America, LLC. The Selvol™ 325 graded PVOH had a hydrolysis and viscosity of 98.4 mol% and 4.00 cP (4% solution viscosity at 20 °C), respectively. Ant Spirits Sdn. Bhd. of Malaysia supplied the multiwalled carbon nanotubes (MWCNTs) with an average particle diameter of 50 nm. The food-grade native maize starch employed as the secondary polymer foundation was purchased under the CAP Bintang brand, which is sold commercially in Malaysian supermarkets. The non-ionic surfactant Tween 20 (Polysorbate 20), which is often used as an emulsifier and solubilizer and has a typical purity of $\geq 99\%$, was utilized to help with the dispersion of MWCNTs in the aqueous PVOH/corn starch matrix. The commercial liquid-grade Tween 20 used in the study was bought on Lazada Malaysia.

3.3 Sample Preparation

There were two stages in sample preparation which included the incorporation of MWCNT Dispersion into the PVOH – Corn Starch Matrix and film casting.

3.3.1 Incorporation of MWCNTs and Tween 20 into the PVOH – Corn Starch Matrix

To prepare the nanocomposite films, the experimental apparatus must be assembled meticulously. A 500mL beaker is used as a water bath to guarantee even heating, while a 250 mL beaker is the main reaction device. This configuration is set on an electric heater with a continuous stirring motor and secured with a stand clamp. A 500 mL measuring cylinder is used to properly measure 250 mL of distilled water, which is then added to the reaction beaker to start the process. To provide the thermal energy required for polymer dissolution, the beaker is subsequently partially submerged in the water bath and heated until the internal temperature reaches a boiling point.

After the water is boiling, 20 g of polyvinyl alcohol (PVOH) is added to the beaker gradually while being stirred continuously. The combination is kept at this temperature until all of the PVOH has been dissolved, producing a

crystal-clear solution. 7g of Corn starch is then added to the mixture. To ensure that the starch granules are completely included and gelatinized within the PVOH matrix, stirring continues for around half an hour. When the mixture turns into an uniform, cloudy solution, this phase is completed and the base polymer blend is prepared for reinforcing.

Multi-walled carbon nanotubes (MWCNTs) and the surfactant Tween 20 are added during the last stage. These materials are added in line with the surfactant ratio listed in Table 3-1 to facilitate the production of a variety of sample sets. This allows for the creation of various film ratios in batches. The solution is heated and continuously stirred until the total volume drops to 200 mL to ensure that the final films have the required structural integrity and thickness. By increasing the viscosity of the solution by evaporation, excessive dilution is avoided and films with uniform mechanical qualities are produced throughout the casting process.

Table 3-1: Different ratio of the MWCNTs/Tween 20 mix with PVOH/Corn Starch

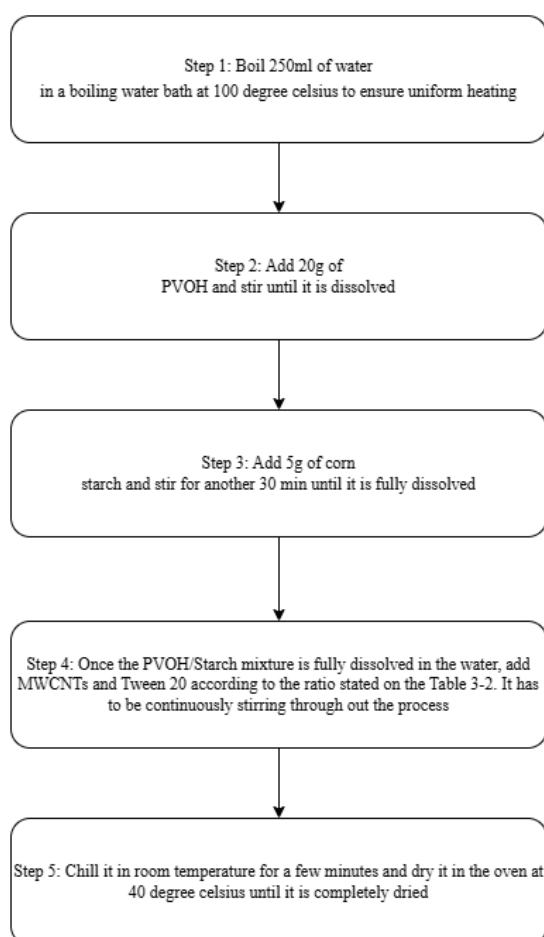
Formulation	PVOH (g)	Starch (g)	Tween 20 (g)	Tween 20: MWCNTs	MWCNT (g)
1	20	7	0.1	1.0:1	0.1
2	20	7	0.15	1.5:1	0.1
3	20	7	0.2	2.0:1	0.1
4	20	7	0.2	1.0:1	0.2
5	20	7	0.3	1.5:1	0.2
6	20	7	0.4	2.0:1	0.2
7	20	7	0.3	1.0:1	0.3
8	20	7	0.45	1.5:1	0.3
9	20	7	0.6	2.0:1	0.3

3.3.2 Film Casting

The carefully mixed PVOH–starch–MWCNT solutions (made using the formulas in Table 3-1) were poured onto clean, flat metal plates (18 × 9 cm) and

evenly distributed until the half of the height of the metal plate to provide uniform thickness to create homogenous films. In some cases, drying and peeling were made easier using aluminium casting dishes. To ensure that all remaining water was gone, the wet films were dried in an oven at 40 °C until they reached a consistent weight. After that, the films were carefully removed from the plate and cut into the proper sizes for further analysis.

Summary of the Sample Preparation:



3.4 Characterization Method

3.4.1 Mechanical testing (Tensile test)

Before testing, the samples were cut into standard rectangular strips that were at least 8 cm long and roughly 5 cm wide. Every measurement was made with a crosshead speed of 50 mm/min and at room temperature. Young's modulus (MPa), elongation at break (%), and tensile strength (MPa) were all the parameters evaluated. Three to five specimens were tested for each formulation, and the mean were calculated by averaging the data.

3.4.2 Morphological Analysis (Scanning Electron Microscopy – SEM)

The samples were cut into $1 \times 1 \text{ cm}^2$ pieces and placed on copper stubs with the fractured surface facing up before imaging. To increase conductivity, a small layer of gold was sputter-coated onto the surfaces. It is typically 5–50 nm thick for the coating. The identification of MWCNT dispersion, potential agglomerates, and interfacial adhesion between the nanotubes and the polymer matrix was made achievable by SEM imaging. The representative micrographs were captured at magnifications of 1000 $\times$, 5000 $\times$ and 10000 $\times$.

3.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

To get the accurate result, the FTIR recording spectra is in the 4000–500 cm^{-1} range. The PVOH–starch composite films with varying MWCNT–Tween 20 dispersion phr values were cut into small pieces and put directly onto the sample holder for scanning. By tracking distinctive peaks like O–H stretching peak, O–H bending peak, C–H bonds, and so on, the study aimed to detect chemical interactions between PVOH, starch, MWCNTs and Tween 20.

3.4.4 X-ray diffraction (XRD)

The MWCNT–Tween 20 dispersion was modified in various phr levels to examine its impact on crystallinity, while the PVOH–starch ratio remained constant throughout all formulations. The samples were scanned at a rate of 2.0°/min throughout a 2θ range of 5° to 40°. The Scherrer equation was used to figure out the crystallite size (L), Bragg's equation was used to determine the d-

spacing (d), and the Klug and Alexander relation was used to determine the inter-chain separation (R).

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (3.4)$$

$$d = \frac{\lambda}{2 \sin \theta} \quad (3.5)$$

$$R = \frac{5\lambda}{8 \sin \theta} \quad (3.6)$$

Where

K is Scherrer constant (usually is 0.9)

β is the full width at half maximum (FWHM) of the deflection peak

λ is constant, 1.542 Å

θ is the Bragg angle in radians

3.4.5 Antioxidant Activity Assay

s

DPPH Scavenging Activity (%) can be calculated as the equation below;

$$S = \left(\frac{A_0 - A_1}{A_0} \right) \times 100 \quad (3.1)$$

where

A_0 is the absorbance of the DPPH control

A_1 is the absorbance in the presence of the film extract

3.5 Summary

In this study, a 75/25 PVOH–starch blend reinforced with multi-walled carbon nanotubes (MWCNTs) was used to create biodegradable films. Stable dispersion of nanotubes was accomplished by using Tween 20 as a dispersing agent. Solution casting was used to create the films, and they were then carefully dried. A variety of tests were used to characterize the prepared samples: X-ray diffraction (XRD) to assess crystallinity; Fourier Transform Infrared Spectroscopy (FTIR) to identify functional groups and molecular interactions; Scanning Electron Microscopy (SEM) to observe surface morphology and

dispersion of starch/MWCNTs; and mechanical testing (tensile strength, elongation, and Young's modulus). Furthermore, the DPPH radical scavenging assay was used to measure the ability of antioxidants and verify free-radical scavenging activity. These approaches work together to offer an extensive evaluation of the films' structural, mechanical, and functional performance, showing their potential as environmentally friendly packaging material.

CHAPTER 4

RESULTS AND DISCUSSION

Characterization Test

This chapter goes into the findings from the lab tests on the nine different PVOH/corn starch/MWCNT film samples. The main goal was to see how changing the amount of nanotubes and the Tween 20 surfactant ratios actually changed the properties of the final composite. To get a full picture of how the films performed, several different characterization tests were carried out in a specific order.

The evaluation started with Mechanical Testing to measure the physical strength and flexibility of the strips, focusing on their tensile strength, Young's modulus, and how much they could stretch before snapping. After that, Fourier Transform Infrared Spectroscopy (FTIR) was used to look at the chemistry of the films and confirm if the nanotubes and the polymer matrix were actually bonding together through hydrogen groups. To actually see what the surfaces looked like, Scanning Electron Microscopy (SEM) imaging was used to check for a smooth mix or if there were problems like air bubbles and clumps of nanotubes. X-ray Diffraction (XRD) was then used to study the crystals inside the films and calculate things like the d-spacing and crystal size. Finally, a DPPH Scavenging Assay was done to test if the films had the antioxidant power needed for active food packaging. By looking at all these results together, the best formulation for a strong and functional biodegradable film can be identified.

4.1 Tensile Test

Following the preparation of the nine formulations, the study first examined the effects of the surfactant ratios and multi-walled carbon nanotubes (MWCNTs) on the mechanical durability of the films. The results of the tensile testing, which is a crucial method of assessing how the composite material handles physical stress and stretching, are discussed in this section. By examining the tensile strength, elongation at break, and Young's modulus, the data clearly illustrates the trade-off between making the film stiffness for practical packaging. The results for each specimens are examined in the following subsections.

4.1.1 Tensile Strength

The highest stress a material can handle when stretched before breaking is determined by its tensile strength. The data shows a complicated relationship between MWCNT loading and surfactant concentration across all nine formulations, suggesting that the amount of nanotubes is not the only factor influencing reinforcing.

From the Figure 4-1 and Table 4-1, the data shows that for the 2.0:1 ratio group, tensile strength drops as more filler is added. The best average strength of 15.63 MPa happened at the lowest loading of 0.1g in Formulation 3. This suggests that having a lot of surfactant with a small amount of nanotubes creates a strong and well-spread reinforcing network. However, the strength fell to 9.26 MPa and 9.09 MPa when the nanotube mass increased to 0.2g and 0.3g. This decrease shows there is a physical limit to how much nanotubes that the PVOH/Starch mix can actually hold. When the loads are too high, the nanotubes take up more space than the Tween 20 can coat. Instead of reinforcing the film, the nanotubes form brittle clumps that act as weak spots where the material snaps. This behavior is supported by Young et al. (2026), who emphasize that clumping reduces the effective aspect ratio of the nanotubes below the critical length required for effective stress transfer, ultimately leading to interfacial pull-out rather than material reinforcement.

The most reliable performance middle ground was offered by the 1.5:1 ratio. As the nanotube volume rose from 0.1g to 0.2g, Formulations 2 and 5 maintained comparatively steady strengths at 14.07 MPa and 14.60 MPa. However, Formulation 8's strength decreased to 10.92 MPa when subjected to the maximum loading of 0.3g. This means that although the 1.5:1 ratio offers a better chemical buffer compared to lower ratios, it eventually yields to the oversaturation effect that can be observed in the 2.0:1 group. The high density of nanotubes breaks the polymer matrix's movement.

The 1.0:1 ratio was very unpredictable because the surfactant level was barely enough to separate the nanotubes. Formulation 4 dropped to 12.83 MPa, while Formulation 7 actually hit 15.50 MPa. This is because the surfactant level is so low, the nanotubes are prone to clumping together instantly regardless of the loading mass. This makes it an unstable choice for making standard films

because the final quality depends too much on tiny changes during the mixing process.

Table 4-1: All 9 specimens' Tensile Strength data according to the lowest loading of the MWCNTs to the highest loading of the MWCNTs.

Ratio	Formulation		Tensile Strength/ MPa	Average of Tensile Strength/ MPa
2.0: 1	3 (0.1g MWCNTs)	Test 1	15.39	15.63
		Test 2	15.84	
		Test 3	15.66	
	6 (0.2g MWCNTs)	Test 1	6.37	9.26
		Test 2	9.54	
		Test 3	11.88	
	9 (0.3g MWCNTs)	Test 1	4.03	9.09
		Test 2	12.77	
		Test 3	10.45	
1.5: 1	2 (0.1g MWCNTs)	Test 1	14.02	14.07
		Test 2	13.99	
		Test 3	14.19	
	5 (0.2g MWCNTs)	Test 1	10.71	14.60
		Test 2	17.08	
		Test 3	16.02	
	8 (0.3g MWCNTs)	Test 1	6.40	10.92
		Test 2	13.08	
		Test 3	13.27	
1.0: 1	1 (0.1g MWCNTs)	Test 1	16.45	15.08
		Test 2	15.90	
		Test 3	12.89	
	4 (0.2g MWCNTs)	Test 1	14.15	12.83
		Test 2	15.30	
		Test 3	9.03	
		Test 1	4.71	15.50

7 (0.3g MWCNTs)	Test 2	20.18
	Test 3	21.62

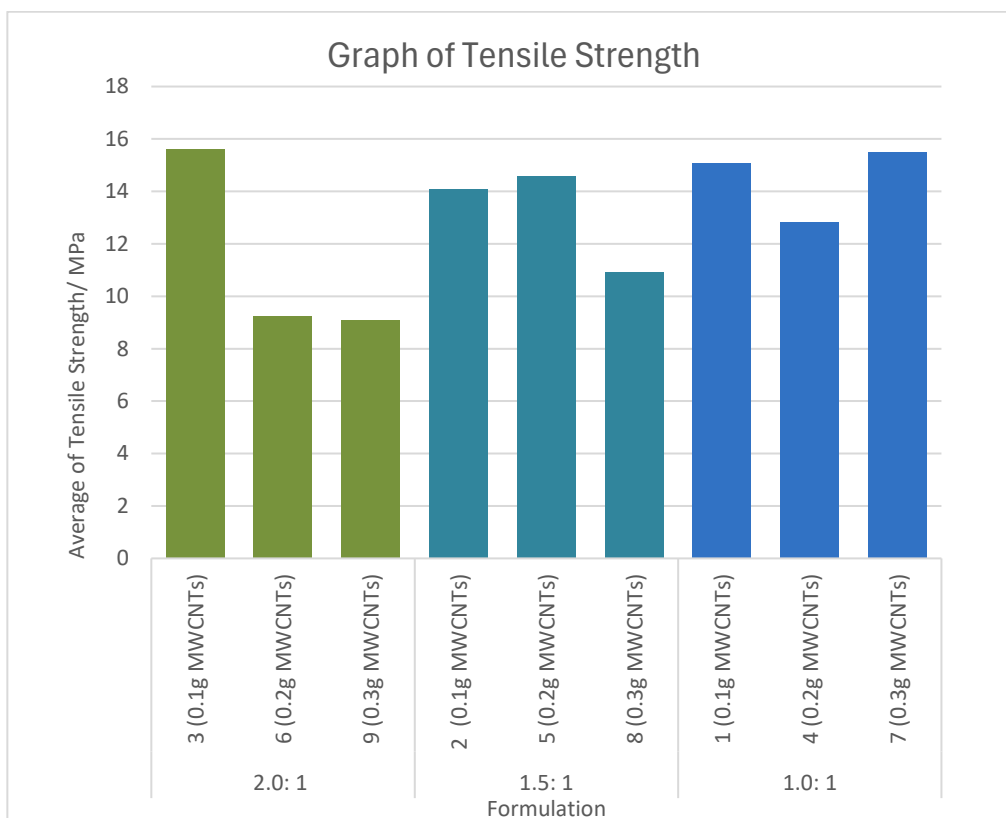


Figure 4-1: Graph of Tensile Strength

4.1.2 Elongation at break

The highest percentage of stretch a material can withstand before breaking is measured by elongation at break, which indicates the material's overall ductility. The data shows a fast ductile-to-brittle shift across all nine formulations as MWCNT loading rises, indicating that the creation of an internal nanotube network is very sensitive to the material's ability to expand.

From the Figure 4-2 and the Table 4-2, the 2.0:1 ratio shows how high surfactant ratios can support ductility at first but become ineffective as more filler is added. Although individual tests revealed significant instability, ranging from 8.64% to 70.53%, the film stays relatively flexible with a low loading of 0.1g at Formulation 3. It has an average elongation of 41.67%. However, the average elongation decreased to 5.17% and 5.02% respectively when the MWCNT loading was increased to 0.2g at Formulation 6 and 0.3g at

Formulation 9. This suggests that high nanotube concentrations create a stiff internal framework that traps the polymer chains in place, making the material extremely brittle no matter how much surfactant is used.

In comparison to the other groups, the 1.5:1 ratio group displayed a much more consistent range of ductility. The average elongation was only 12.23% even at the lowest loading of 0.1g at Formulation 2, which is a big drop from the flexibility seen in other sets. The ductility further decreased to 7.75% and 5.20% as the loading increased to 0.2g at Formulation 5 and 0.3g at Formulation 8. Although the 1.5:1 ratio offers stability but it doesn't provide enough of a buffer to stop the nanotubes from stiffening the entire structure.

The 1.0:1 ratio really highlights how unstable things get when there isn't enough surfactant. Formulation 1 performed like a very flexible plastic, achieving the maximum average elongation of the entire sample at 57.75% using just 0.1g of MWCNTs. However, the elongation dropped to 9.66% in Formulation 4 and 8.81% in Formulation 7 as soon as the loading reached 0.2g. This huge 83% decrease in stretching ability indicates that in a 1.0:1 ratio, the surfactant very instantly hits its limit as filler load increases, causing the polymer chains to bond poorly and snap early.

Table 4-2: All 9 specimens' Tensile Strength data according to the lowest loading of the MWCNTs to the highest loading of the MWCNTs.

Ratio	Formulation		Elongation at Break %	Average of Elongation at Break %
2.0: 1	3 (0.1g MWCNTs)	Test 1	45.82	41.67
		Test 2	70.53	
		Test 3	8.64	
	6 (0.12g MWCNTs)	Test 1	5.78	5.17
		Test 2	4.13	
		Test 3	5.59	
	9 (0.3g MWCNTs)	Test 1	5.33	5.02
		Test 2	3.63	
		Test 3	6.09	

1.5: 1	2 (0.1g MWCNTs)	Test 1	13.77	12.23
		Test 2	11.48	
		Test 3	11.45	
	5 (0.2g MWCNTs)	Test 1	8.00	7.75
		Test 2	8.14	
		Test 3	7.10	
	8 (0.3g MWCNTs)	Test 1	7.45	5.20
		Test 2	3.88	
		Test 3	4.29	
1.0: 1	1 (0.1g MWCNTs)	Test 1	56.84	57.75
		Test 2	55.27	
		Test 3	61.14	
	4 (0.2g MWCNTs)	Test 1	10.38	9.66
		Test 2	9.95	
		Test 3	8.66	
	7 (0.3g MWCNTs)	Test 1	8.67	8.81
		Test 2	8.68	
		Test 3	9.08	

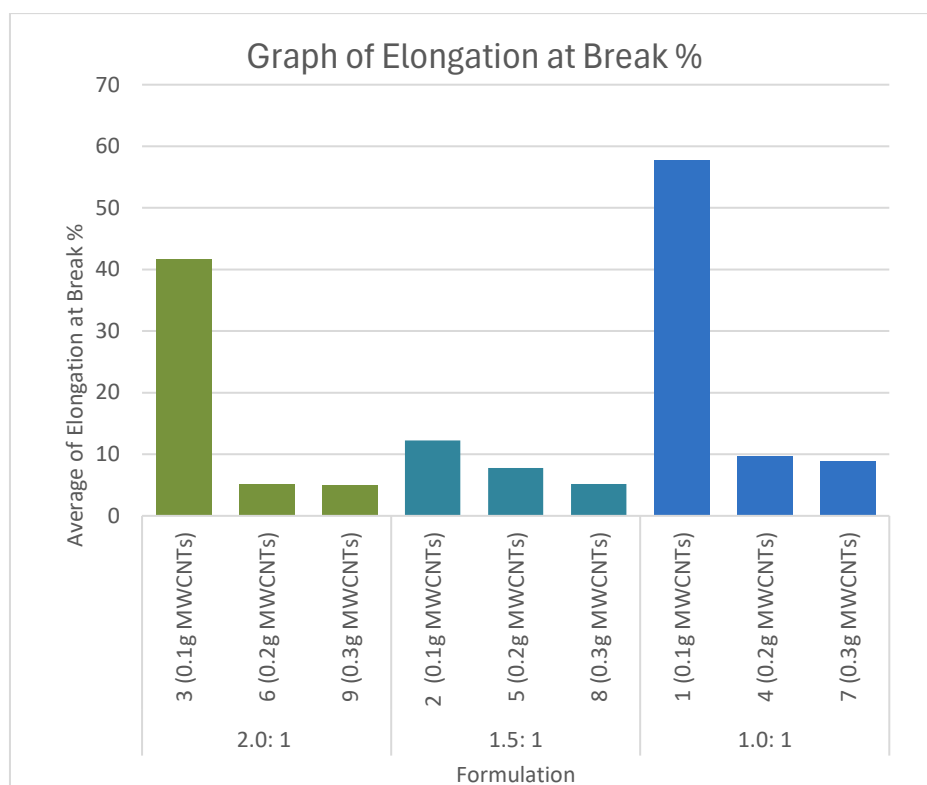


Figure 4-2: Graph of Elongation at Break %

4.1.3 Young Modulus

Young's modulus, which is the stress to strain ratio in the elastic loading range, measures a material's stiffness. The data shows a steady rise in material rigidity as MWCNT loading increases throughout all nine formulations, indicating that the nanotubes successfully function as a stiff reinforcing structure within the polymer matrix.

Based on the Table 4-3 and the Figure 4-3, the 2.0:1 group showed the highest stiffness. The average Young's modulus increased gradually from 413.33 MPa to 516.67 MPa as the MWCNT concentration was increased from 0.1g to 0.3g. This suggests that the increased volume of surfactant effectively coats the nanotubes at a 2.0:1 ratio, enabling them to form a stiff network that is securely bonded and extremely resistant to elastic deformation. It's crucial to recall that these films are the most brittle although being the most rigid.

As more MWCNTs was added, the 1.5:1 ratio group showed a steady increase in stiffness. Formulation 2 began at 348.33 MPa, increased to 408.33 MPa in Formulation 5, and peaked at 527.78 MPa in Formulation 8. Surprisingly throughout the entire test, Formulation 8 showed the highest

individual average stiffness. This means that the 1.5:1 ratio may actually offer a denser packing of nanotubes than the 2.0:1 ratio at maximum loading of 0.3g, resulting in an incredibly rigid composite structure. The review article by Rashko et al. (2022) helps to prove that this is correct as it confirms that the Young's modulus of carbon nanotubes is associated with strong sp^2 bond strengths and that their inclusion in a composite typically results in the strongest and hardest structures ever created in terms of elastic modulus.

Despite having the lowest overall stiffness, the 1.0:1 ratio maintained to exhibit the pattern of increasing young modulus with larger filler loading. From 303.33 MPa at Formulation 1 to 455.56 MPa at Formulation 7, the average Young's modulus increased. Nevertheless, the lower findings in comparison to the other groups suggest that the stiffness of the nanotubes is unable to be fully utilized at a 1.0:1 surfactant ratio. The nanotubes cannot transfer stress as effectively without a sufficient surfactant coating, which makes the finished product less stiff.

A typical material science trade-off is confirmed by the findings. When MWCNTs are added, the formulation's stiffness increases, but its tensile strength and ductility are significantly reduced. The high aspect ratio of the nanotubes makes it possible to create a continuous inner structure that is resistant to stretching, and so increasing the Young's modulus. However, the stiffest formulations like 8 and 9 also show the lowest elongation and toughness because the same internal network prevents polymer chain movement.

Table 4-3: All 9 specimens' Tensile Strength data according to the lowest loading of the MWCNTs to the highest loading of the MWCNTs.

Ratio	Formulation		Young Modulus/MPa	Average of Young Modulus/ MPa
2.0: 1	3 (0.1g MWCNTs)	Test 1	190.00	413.33
		Test 2	500.00	
		Test 3	550.00	
		Test 1	200.00	500

1.5: 1	6 (0.2g	Test 2	600.00	516.67
	MWCNTs)	Test 3	700.00	
	9 (0.3g	Test 1	450.00	
	MWCNTs)	Test 2	500.00	
		Test 3	600.00	
	2 (0.1g	Test 1	120.00	348.33
	MWCNTs)	Test 2	450.00	
		Test 3	475.00	
	5 (0.2g	Test 1	275.00	408.33
	MWCNTs)	Test 2	550.00	
		Test 3	400.00	
8 (0.3g	Test 1	533.33	527.78	
MWCNTs)	Test 2	600.00		
	Test 3	450.00		
1.0: 1	1 (0.1g	Test 1	160.00	303.33
	MWCNTs)	Test 2	350.00	
		Test 3	400.00	
	4 (0.2g	Test 1	225.00	352.78
	MWCNTs)	Test 2	333.33	
		Test 3	500.00	
	7 (0.3g	Test 1	300.00	455.56
	MWCNTs)	Test 2	600.00	
		Test 3	466.67	

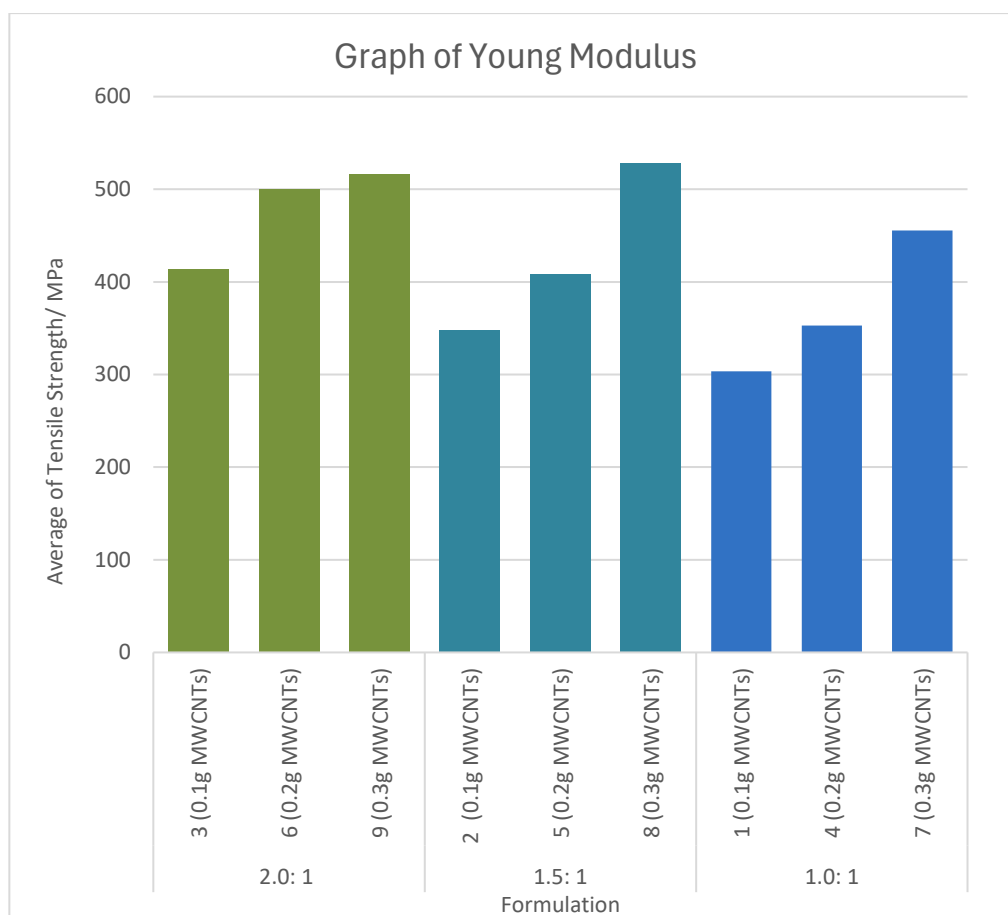


Figure 4-3: Graph of Young Modulus

4.1.4 Summary of the Tensile Test

From the Figure 4-4, the mechanical performance of the composite films follows a conventional material science trade-off in which an increase in one characteristic often results in a significant reduction in another. When the loading of multi-walled carbon nanotubes (MWCNTs) goes from 0.1g to 0.3g, the most obvious pattern is the constant increase in material stiffness as determined by the Average Young's Modulus. The long, thin nanotubes provide a stiff internal structure that successfully strengthens the PVOH-starch matrix, increasing the final films' resistance to elastic deformation and producing an upward trend.

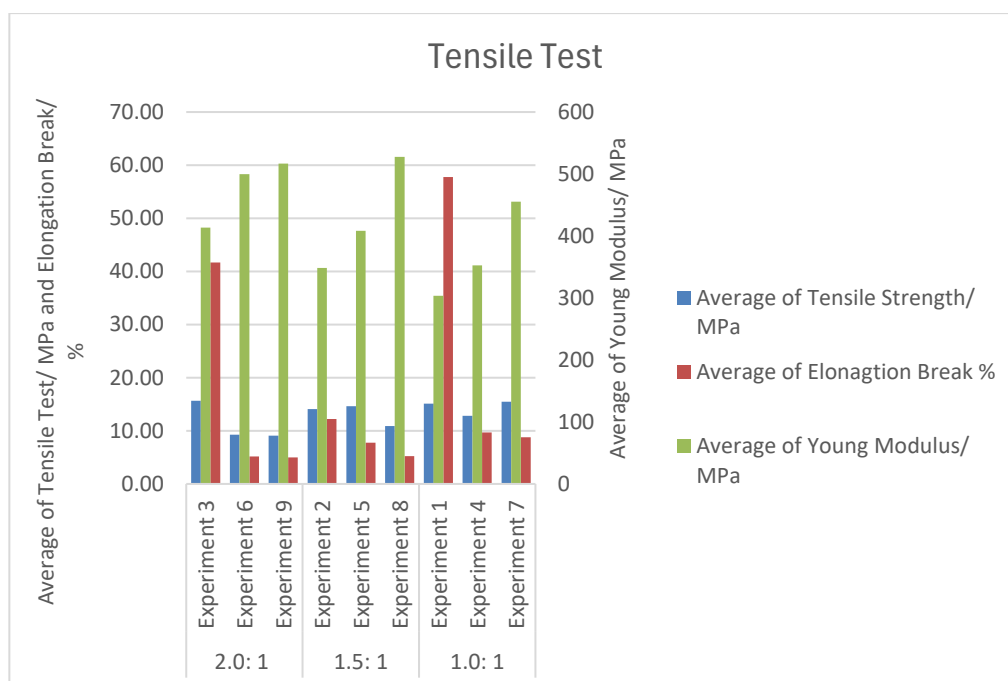


Figure 4-4: Tensile Test for the 9 Samples

However, as the significant decrease in Elongation at Break shows this improved rigidity comes at the high cost of material ductility. The internal network that gives stiffness is also acts as a physical barrier that holds the polymer chains in place and stops them from stretching or sliding as more MWCNTs are added. As a result, when the concentration of reinforcement is increased, the material transitions from a plastic-like state to a very brittle one. The elongation decreasing significantly in almost all formulations.

Lastly, as the filler loading approaches the higher 0.3g range, the tensile strength generally shows a downward trend. Higher concentrations of nanotubes promote agglomeration due to insufficient Tween 20 to cover them although a small amount of nanotubes already can effectively reinforce a structure. Compared to the better-dispersed and low-load formulations, these clumps fracture the film under a lower total force because they function as internal structural defects or stress concentrators. In conclusion, the films become lot stiffer when the MWCNT content is increased but they also become weaker and much less flexible.

4.2 FTIR Result

All the FTIR data that is recorded in the table forms are referred from the Appendix 1, 2 and 3. This is because it is more easy to do the analysis by comparing all the values in table forms. Hence, the compilation data of FTIR are located in the Appendices section.

4.2.1 Set 1: Formulation 1, 2 and 3 (0.1g MWCNTs)

Based on the Table 4-4 of Set 1 which low loading of the MWCNTs are involved, there is a distinct shift of the O-H stretching peak from 3262.44 cm^{-1} in Formulation 1 at the 1.0:1 ratio down to 3258.37 cm^{-1} in Formulation 3 at the 2.0:1 ratio. This downward trend observed is significant because it indicates that the O-H bond is being or weakened. This happens when adjacent polar atoms pull the hydrogen atoms from their primary covalent bonds through a process called hydrogen bonding. As a result, Formulation 1's higher wavenumber of O-H stretching peak indicates that it has the weakest hydrogen bonding. Basically, it means the O-H groups remained comparatively isolated. Formulation 3's lower value confirms that the hydrogen atoms are more actively engaged in a tighter and more stable bonding network. This shift is fundamentally driven by the synergy between the Tween 20 surfactant and the MWCNTs. The synergy between the MWCNTs and the Tween 20 surfactant is what basically drives this change. A 2.0:1 ratio provides enough surfactant to cover the nanotubes in a protective layer. Since it stops the nanotubes from clumping together, it means this encapsulation is essential. The polyoxyethylene chains from Tween 20 serve as molecular bridges after the nanotubes have been effectively separated and dispersed. The PVOH and starch polymer chains are connected to the nanotubes by these chains, creating a more solid composite structure.

Table 4-4: FTIR Data Value for Formulation 1,2 and 3

Feature	Formulation 1 (1.0:1 Ratio)	Formulation 2 (1.5:1 Ratio)	Formulation 3 (2.0:1 Ratio)
O-H Stretching	3262.44 cm^{-1}	3260.79 cm^{-1}	3258.37 cm^{-1}
O-H Bonding	1326.00 cm^{-1}	1327.61 cm^{-1}	1327.98 cm^{-1}
C-H Stretching	2917.27 cm^{-1}	2934.27 cm^{-1}	2920.12 cm^{-1}
C-O-C Stretching	1084.48 cm^{-1}	1082.48 cm^{-1}	1085.64 cm^{-1}

The inverse relationship of the O-H stretching peak and the O-H bonding peak actually can double justify the stronger tensile strength of the Formulation 3 compared to Formulation 1. The individual O-H bond within a single molecule gets slightly weaker is because it is busy forming a Hydrogen Bond with a neighbour. As a result, it signifies the formation of a strong physical connection between the filler and the composites. The filler is now creating bridges to connect to the polymer chains rather than just sitting loosely inside the polymer. This makes it possible for the filler to support the load. The polymer passes the stress to the filler, which is usually much stiffer and stronger, resulting in a higher overall tensile strength for the composite.

4.2.2 Set 2: Formulation 4, 5 and 6 (0.2g MWCNTs)

From the Table 4-5, The FTIR analysis for Set 2 that involves the moderate loading of 0.2g MWCNTs shows a unexpected result about the characterisation peak. The O-H stretching frequency in this group increases from 3256.33 cm^{-1} in Formulation 4 to 3261.13 cm^{-1} in Formulation 5, then slightly decreases to 3260.37 cm^{-1} in Formulation 6, instead of decreasing linearly with the surfactant ratio. The difference suggests that the increased mass of nanotubes and particular Tween 20 concentrations are significantly altering the molecular interactions. The peak found in Formulation 5 at 1.5:1 ratio indicates that the hydrogen bonding system inside the polymer matrix is becoming weaker. In chemical terms, this could be explained by the surfactant's physical interference. The volume of Tween 20 may be enough to coat the nanotubes at this specific ratio, but the excess surfactant may result in a "oily" interface. Formulation 5 has the lowest O-H bonding value of 1327.31 cm^{-1} in the set. This layer can

cause the O-H groups of the PVOH and starch to "slip away" from their neighbors rather than forming strong and stable bonds.

Table 4-5: FTIR Data Value for Formulation 4,5 and 6

Feature	Formulation 4 (1.0:1 Ratio)	Formulation 5 (1.5:1 Ratio)	Formulation 6 (2.0:1 Ratio)
OH Stretching	3256.33 cm^{-1}	3261.13 cm^{-1}	3260.37 cm^{-1}
OH Bonding	1327.74 cm^{-1}	1327.31 cm^{-1}	1327.97 cm^{-1}
CH Stretching	2938.60 cm^{-1}	2938.60 cm^{-1}	2913.74 cm^{-1}
C-O-C Stretching	1085.36 cm^{-1}	1085.67 cm^{-1}	1081.98 cm^{-1}

A different event happens in Formulation 6 when the surfactant ratio rises to 2.0:1. While the O-H bonding achieves its maximum value of 1327.97 cm^{-1} , the O-H stretching frequency decreases again. This change indicates an overbonding state. The composites will be highly constrained and is forced by the high density of Tween 20 molecules. This can be double confirmed by the tensile test as the Formulation 6 has the lower tensile strength and very low elongation. The material can become so rigid that it loses its ability to deform, making it brittle.

4.2.3 Set 3: Formulation 7, 8 and 9 (0.3g MWCNTs)

From the Table 4-6, The FTIR analysis for Set 3 that contain the highest loading of 0.3g MWCNTs shows how the high density of nanotubes interacts with increasing surfactant levels. The O-H stretching peak in this group shifts from 3263.86 cm^{-1} in Formulation 7 to 3257.25 cm^{-1} in Formulation 9. A steady downward trend as the surfactant ratio rises is shown. Interestingly, the O-H bonding values show an anomaly. Increase in the O-H bonding peak is normally correlated with a decrease in O-H stretching but before increasing to 1327.84 cm^{-1} in Formulation 9, the bonding value initially decreases from 1328.04 cm^{-1} in Formulation 7 to 1327.28 cm^{-1} in Formulation 8. The decline observed in Formulation 8 at 1.5:1 ratio highlights a molecular condition similar to that identified in Formulation 5. Although the volume of Tween 20 is enough to encapsulate the nanotubes at this particular ratio, the additional surfactant will create a greasy surface. This layer effectively causes the polymer matrix's O-H

groups to separate from nearby molecules, preventing the development of a stable bonding network and producing the lowest O-H bonding value. This explains the reduction in tensile strength.

Table 4-6: FTIR Data Value for Formulation 4,5 and 6

Feature	Formulation 7 (1.0:1 Ratio)	Formulation 8 (1.5:1 Ratio)	Formulation 9 (2.0:1 Ratio)
OH Stretching	3263.86 cm^{-1}	3262.25 cm^{-1}	3257.25 cm^{-1}
OH Bonding	1328.04 cm^{-1}	1327.28 cm^{-1}	1327.84 cm^{-1}
CH Stretching	2912.88 cm^{-1}	2935.46 cm^{-1}	2938.23 cm^{-1}
C-O-C Stretching	1081.42 cm^{-1}	1084.94 cm^{-1}	1085.40 cm^{-1}

In Formulation 9, when the ratio approaches 2.0:1, the bonding value increases and the O-H stretching decreases. This shows an overbonding state. The dense population of Tween 20 molecules in this condition severely restricts the polymer matrix, forcing the chains into a restricted and stiff configuration. Formulation 9 has very little elongation and a lower tensile strength. This demonstrates that the material can no longer undergo plastic deformation, resulting in the end result that is brittle.

4.3 SEM Result

After the mechanical and chemical tests were finished, Scanning Electron Microscopy (SEM) was used to actually look at the surface and the fractured parts of the composite films. This imaging was important because it allowed for a close-up look at how well the nanotubes were spread out and if they were sticking properly to the PVOH and starch matrix. By zooming in at magnifications of 1000 $\times$, 5000 $\times$, and 10000 $\times$, the study could identify visible defects like air bubbles, cracks, or white clusters where the nanotubes might have clumped together. These pictures help to explain the results from the tensile tests, as they show exactly how the internal structure and surface flaws changed when the MWCNT loading and surfactant ratios were adjusted. The following sections discuss the specific observations for each set of formulations to see which mix produced the smoothest and most uniform film.

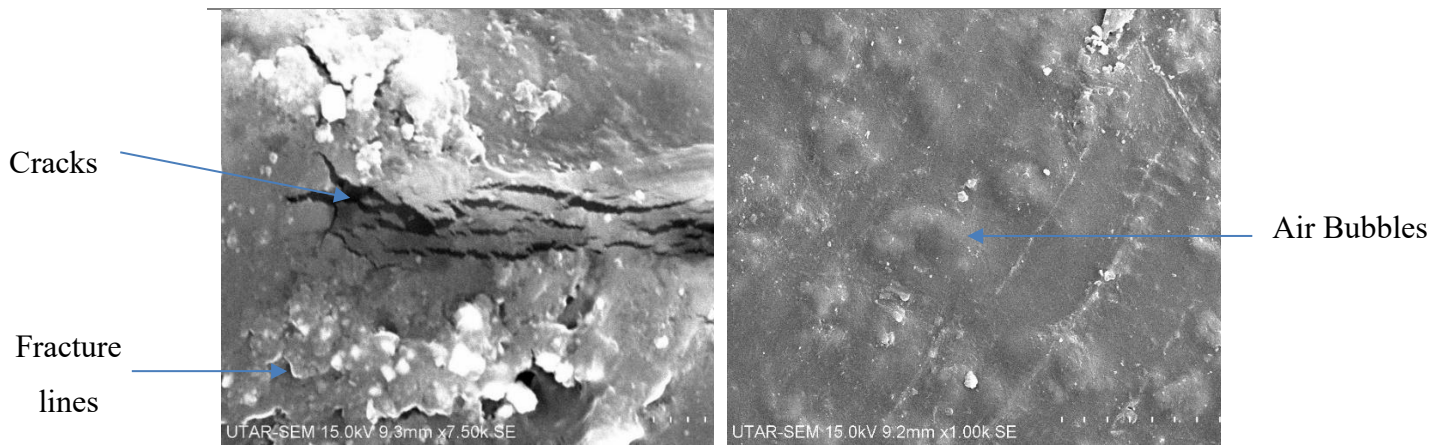
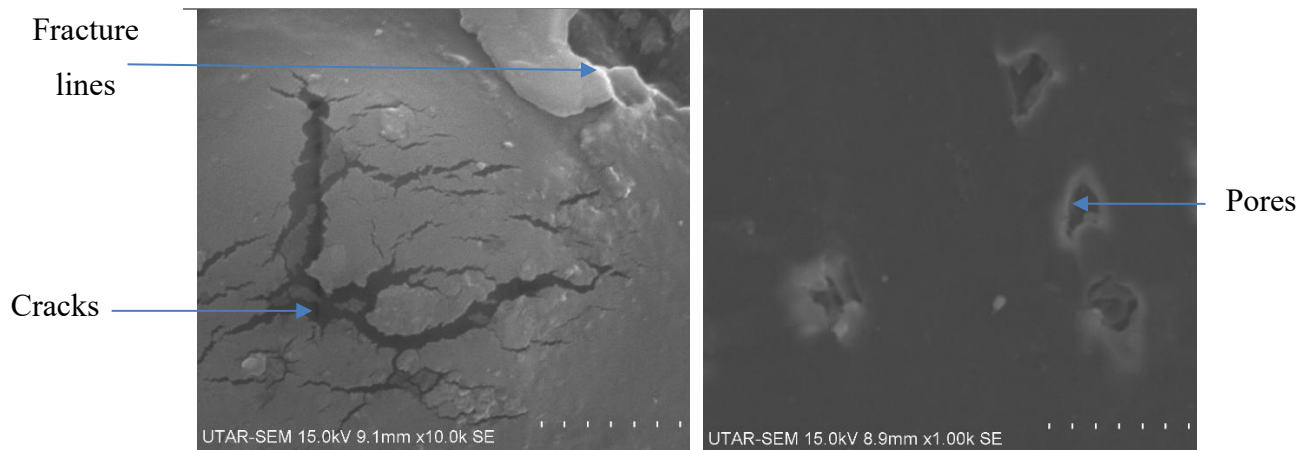
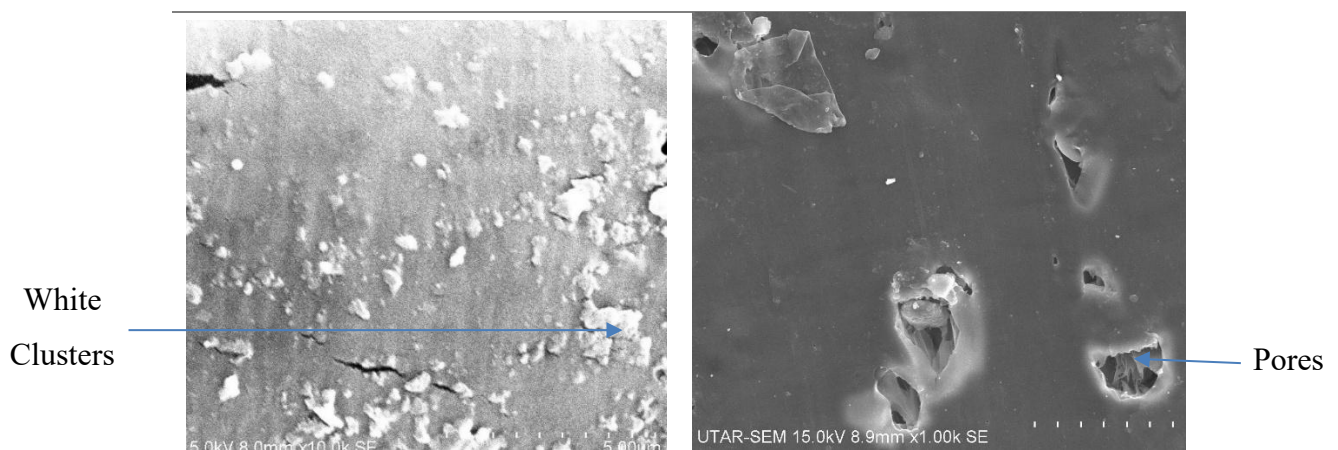
4.3.1 Set 1: Formulation 1, 2 and 3 (0.1g MWCNTs)

A series of 5k and 1k magnified images of the samples under SEM imaging are shown in Table 4-7 to analyze their characteristics. The 10k magnification is not used since the structure deteriorates and cracks even before a photo is taken. The high-energy electron beam beneath the SEM equipment is what causes the cracks rather than the dispersion issue. In Formulation 1, the surface has many visible flaws like rounded bumps and scattered shapes. These come from air bubbles trapped in the PVOH/Starch mix during the casting process. There are also sharp cracks and fracture lines that become worse when the SEM's electron beam hits them. This is because of these air pockets and cracks, the film is quite uneven. Mechanically, these flaws act as weak spots. So while the film can stretch quite a bit which is 57.75%, it has a lower Young's Modulus of 303.33 MPa.

Formulation 2 looks much smoother and more uniform, which suggests the materials are mixed together better. However, the sample still has small pores and internal defects like white clusters and hollow spots. Even though it looks smoother, these internal holes make the film less stretchy, causing the elongation to drop to 12.23%. On the better side, the better integration makes the film stiffer, resulting in a higher Young's Modulus of 348.33 MPa.

On the other hand, the surface of Formulation 3 is much more complex and harder to predict. It is covered in white clusters, which are likely nanotubes clumping together and deep sunken holes that break up the smooth texture. These craters give the surface a rough texture that isn't found in Formulation 2. Due to the higher surfactant ratio, the film reaches its highest stiffness at 413.33 MPa, but it also becomes very brittle with an unpredictable average elongation of 41.67%.

Table 4-7: SEM Pictures of Formulation 1,2 and 3 (5k and 1k Maginification)

Formulation 1 (1.0:1 Ratio)**Formulation 2 (1.5:1 Ratio)****Formulation 3 (2.0:1 Ratio)**

4.3.2 Set 2: Formulation 4, 5 and 6 (0.2g MWCNTs)

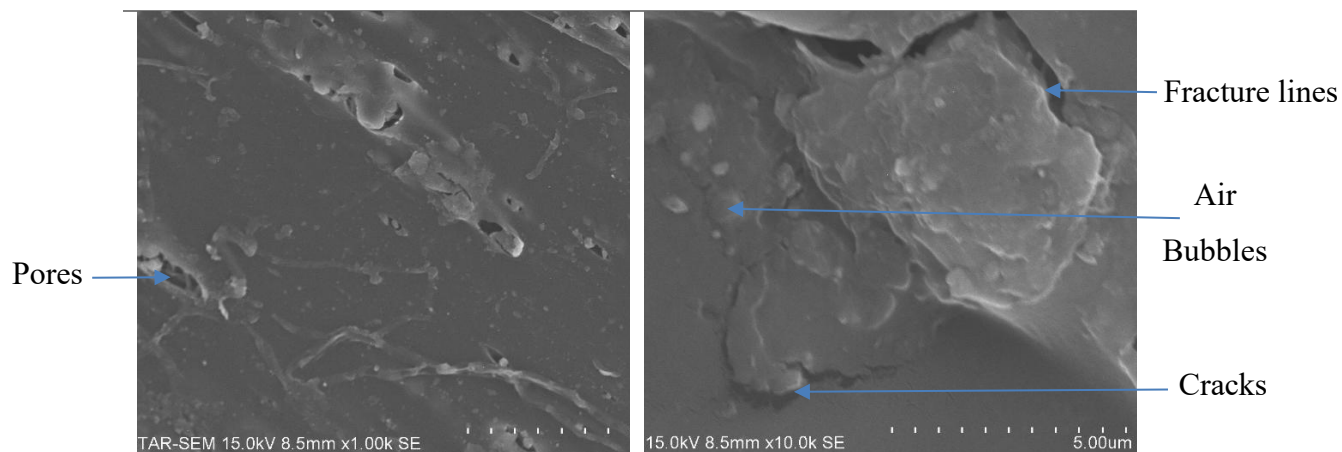
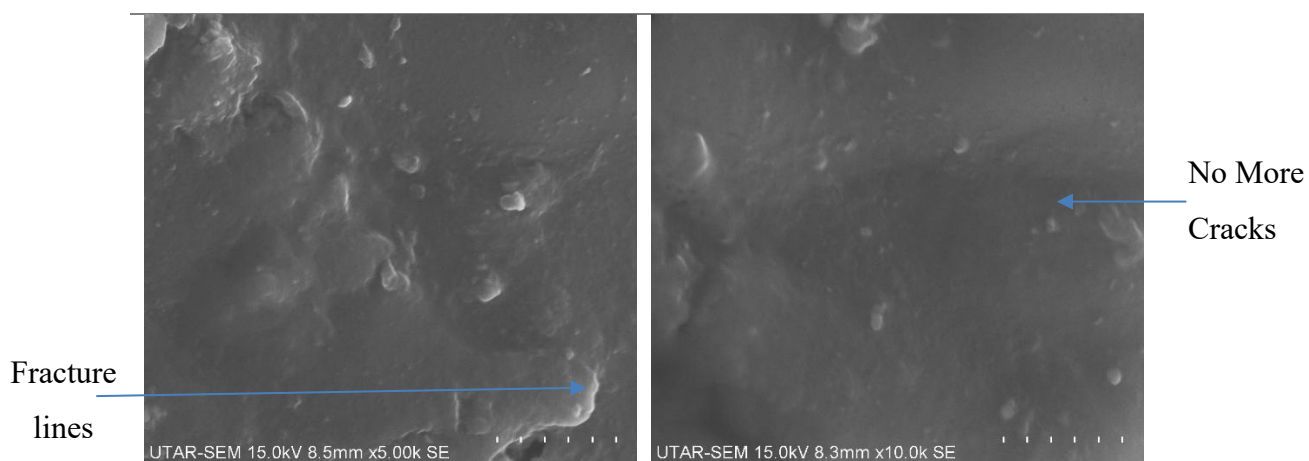
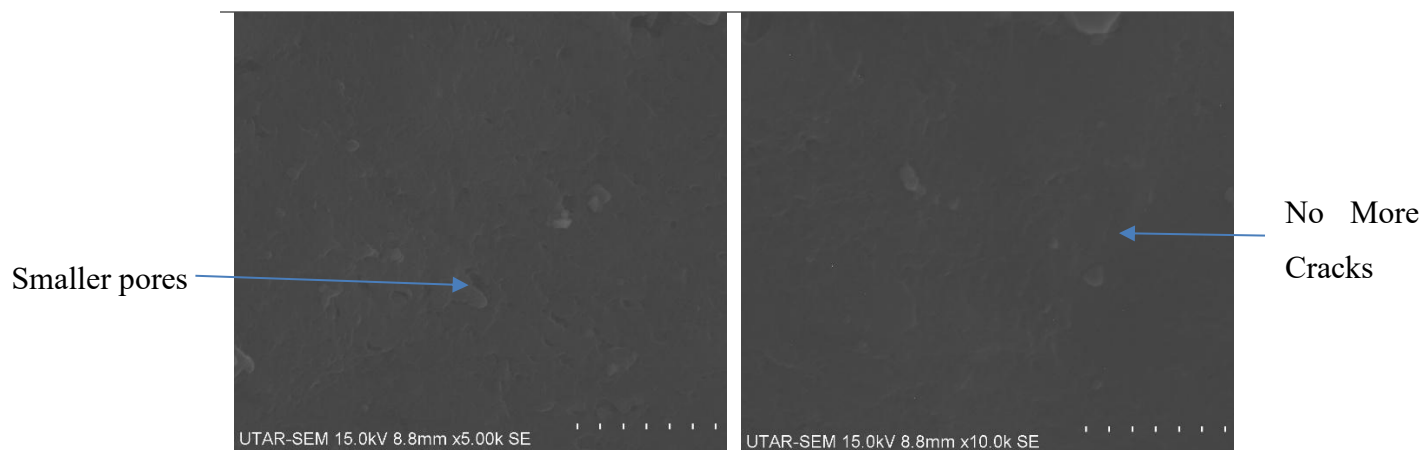
In Formulation 4, the surface still has quite a few defects, like visible pores, cracks and air bubbles. These holes are similar to what was seen in the first set and act as weak spots where the film can easily break. This explains why this sample has the lowest tensile strength at 12.83 MPa and a very low elongation of 9.66%. Basically, at a 1.0:1 ratio, there isn't enough surfactant to spread out the 0.2g of nanotubes, leaving the material brittle and full of holes.

In Formulation 5, as the surfactant ratio goes up to 1.5:1, the surface becomes much denser, and the number of holes drops significantly. When looking closely under the Table 4-8, the surface damage and cracks almost disappear, making the film feel more solid. Since there are fewer pores, the tensile strength rises to 14.60 MPa, but the extra nanotubes make the film even stiffer, causing the elongation to drop further to 7.75%.

In Formulation 6, the surface gets even better, appearing smoother and having even smaller pores compared to Formulation 5. Even at high magnification, there are no obvious cracks or large holes but there is still a few of small white clusters might due to the inadequate mixing. This shows that the 2.0:1 ratio is perfect for dispersing the 0.2g of nanotubes. This dense and flawless structure gives the film its highest stiffness at 500 MPa, but the trade-off is a major loss in flexibility.

There is also another new observation obtained. As the MWCNT loading and the surfactant ratio increase across this set, the film no longer shows cracks even at high magnification. In the Set 1 samples, cracks often formed because the composites were weaker due to lower MWCNTs amount and would break down under the high-energy electron beam. However, the improved integration in these formulations makes the surface strong enough to withstand that intensity.

Table 4-8: SEM Pictures of Formulation 4,5 and 6 (5k and 10k Magnification)

Formulation 4 (1.0:1 Ratio)**Formulation 5 (1.5:1 Ratio)****Formulation 6 (2.0:1 Ratio)**

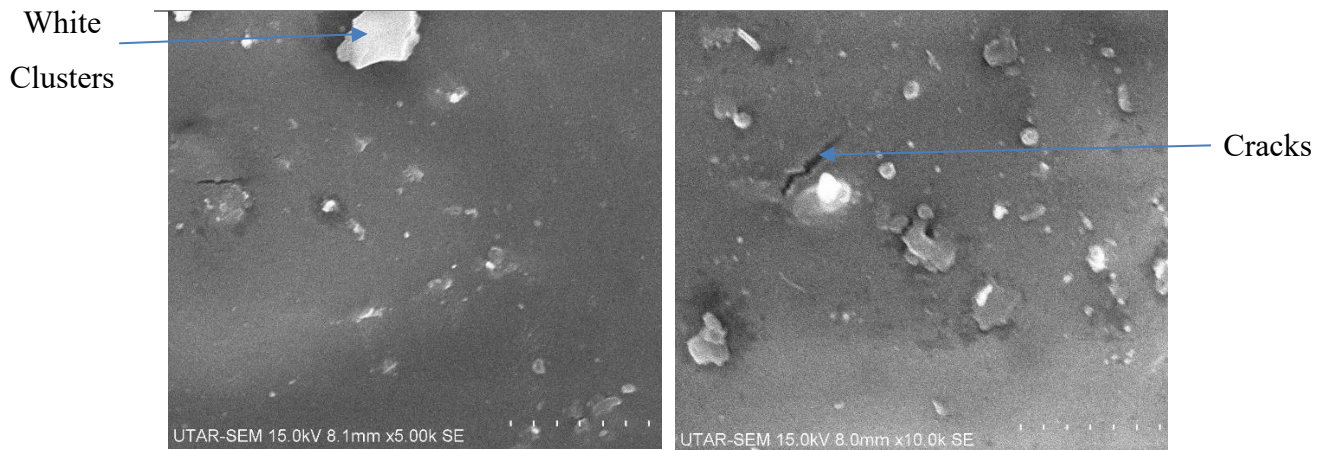
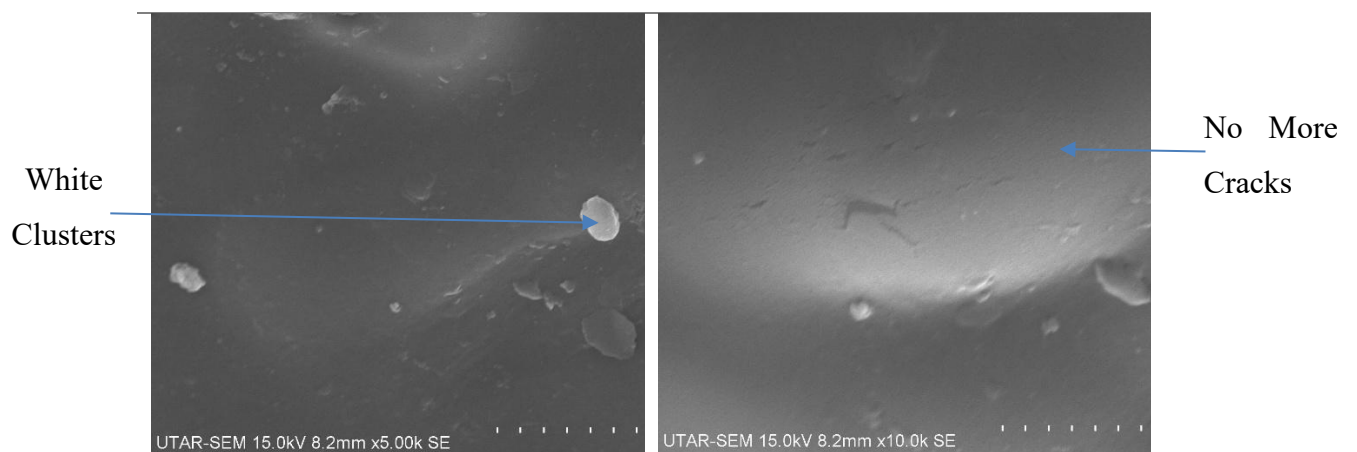
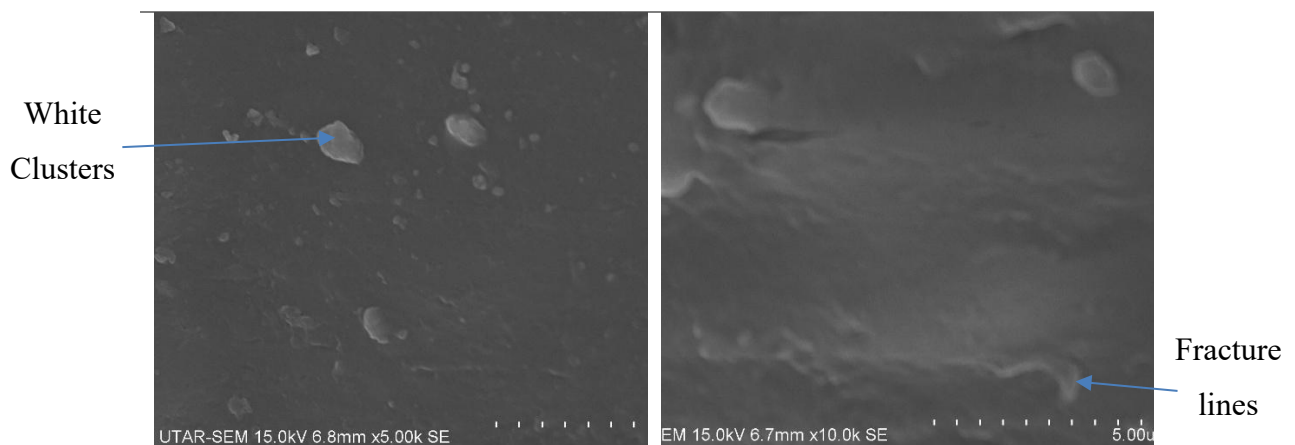
4.3.3 Set 3: Formulation 7, 8 and 9 (0.3g MWCNTs)

From the Table 4-9, the SEM results for the third set indicate that the maximum loading of 0.3g nanotubes requires a high surfactant ratio to prevent clumping and maintain structural integrity. In Formulation 7, the surface appears extremely crowded and dense, but it still have some visible cracks and large white clusters. These clusters are essentially large areas where the nanotubes failed to spread out because the surfactant ratio was too low. Due to these clumps and cracks, the film is very unstable. Even though the average tensile strength is 15.50 MPa, but at the elongation test, it dropped as low as 4.71 MPa because the poorly integrated material snaps suddenly.

When moving to Formulation 8, the surface becomes considerably smoother and shows fewer white clumps. This suggest that the extra surfactant is starting to get the high nanotube amount under control. There are no visible holes, creating a very solid layer. As the components are packed so tightly, this sample reaches a Young's Modulus of 527.78 MPa, which is the highest stiffness recorded in the previous test. However, the trade-off is that the film becomes incredibly rigid but at the same time it loses almost all flexibility with the elongation dropping to just 5.20%.

Finally, Formulation 9 shows the most refined surface in this group. Even when zooming in at 10.0k magnification, the texture is continuous and uniform with no significant cracks or pores. This proves that a 2.0:1 ratio is necessary to sustain such a large volume of reinforcement.

Table 4-9: SEM Pictures of Formulation 7,8 and 9 (5k and 10k Magnification)

Formulation 7 (1.0:1 Ratio)**Formulation 8 (1.5:1 Ratio)****Formulation 9 (2.0:1 Ratio)**

4.4 XRD Result

From the Figure 4-5, all the peak position values are noticed. Clearly, the Formulation 4's graph shifts left and it shows the lowest peak position values of 19.41° and so it has the highest value of d-spacing which is $4.57 \text{ \AA}$ among the 9 samples. Meanwhile, the graph of Formulation 4 has shifted to the right, indicating that it has the highest peak position among all samples. Hence, it shows its d-spacing value is the lowest.

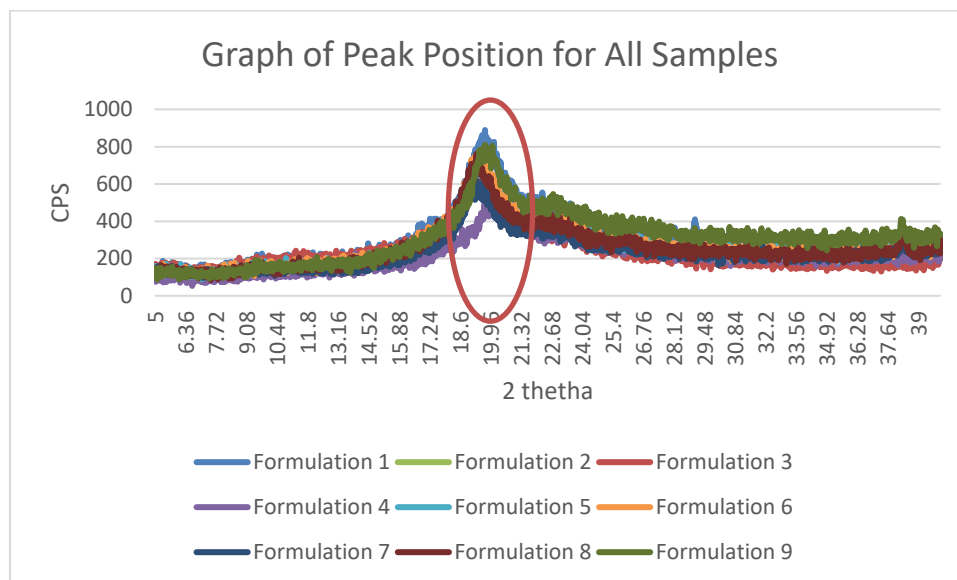


Figure 4-5: XRD Result for All Samples

4.4.1 Set 1: Formulation 1, 2 and 3 (0.1g MWCNTs)

From the Table 4-10, the XRD findings show that the interplanar spacing of the PVOH matrix which is controlled by Bragg's Law ($n\lambda = 2d\sin\theta$), is directly affected by increasing the Tween 20 to MWCNT ratio. In Formulation 1 (1.0:1 ratio), the main crystalline peak is located at 19.78° with a d-spacing of $4.48 \text{ \AA}$. As the surfactant concentration increases in Formulation 2 which is 1.5:1 ratio, the peak shifts to 19.64° , increasing the d-spacing to $4.52 \text{ \AA}$. When the peak reaches the lowest angle of 19.45° , Formulation 3 at 2.0:1 ratio provides a maximum d-spacing of $4.56 \text{ \AA}$. However, the lateral crystal size drops to $0.69 \text{ \AA}$ at this higher ratio. This is because the additional surfactant molecules are intercalating between the PVOH polymer chains, physically pushing them apart and increasing the crystal lattice.

Through the Scherrer Equation ($L = \frac{K\lambda}{\beta \cos\theta}$), the peaks provide data on the size and perfection of the crystalline domains. Formulation 1 exhibits a lateral crystal size (L) of 0.66 Å when its FWHM reaches the highest value of 2.178°. However, at the higher ratio, Formulation 3's lateral crystal size decreases to 0.69 Å due to the higher FWHM value, and higher peak position angle. Therefore, the denominator increases and so lead to the decreasing in the lateral crystal size. Formulation 2 shows the lowest FWHM of 1.943°. As the Scherrer's principle states that larger or more ordered crystallite sizes are indicated by a smaller peak (β), which means lower FWHM. The calculated L value of 0.74 Å confirms that the crystals in Formulation 2 are significantly larger and more ordered than the other two ratios. This suggests that Tween 20 produces the best dispersion of MWCNTs in a 1.5:1 ratio, enabling them to function as effective nucleating agents for PVOH crystallization. On the other hand, the peaks in Formulation 1 which is 2.178° and Formulation 3 that is 2.075° are wider. This may because of the excessive surfactant interference in Formulation 3 or insufficient dispersion in Formulation 1 leads their smaller lateral crystal sizes.

The interchain spacing is lowest at 5.60 Å in Formulation 1, 1.0:1 ratio. As there are fewer surfactant molecules to occupy the space between them, the polymer chains are packed very closely together at this lower surfactant concentration. It can be said the composite is dense now. However, in Formulation 2, the separation distance increases to 5.64 Å as the ratio increases to 1.5:1. The Tween 20 molecules could be successfully intercalating between the polymer chains. The peak position shifts toward a lower angle because of the physical buffer effect which pushes the chains slightly further apart. The inter-chain separation reaches its highest value of 5.70 Å in Formulation 3. Since the chains have more room to move around but weaker connections to hold them together, this additional space between the chains is often a sign that the material is becoming more amorphous or plasticized.

Hence, after considering all the factors, Formulation 2 actually is the optimal choice when low loadings of MWCNTs is used. This is because it has higher crystal size, lower FWHM and average d-spacing although it has higher inter-chain separation than Formulation 1.

Summary of Set 1

The green highlighted column in the Table 4-11 means the formulation has the best result for Set 1 while the red highlighted columns means the formulation is not suitable for the low loading, 0.1g of MWCNTs.

Table 4-10: Overall Performance of Formulation 1,2 and 3

Formulation	Peak Position (2θ)/ $^{\circ}$	d- spacing / $\text{\AA}$	FWHM / $^{\circ}$	Inter- chain separation (R)/ $\text{\AA}$	Lateral crystal size (L) / $\text{\AA}$
1 (1.0:1 Ratio)	19.78	4.48	2.178	5.6031	0.6603
2 (1.5:1 Ratio)	19.64	4.52	1.943	5.6427	0.7400
3 (2.0:1 Ratio)	19.45	4.56	2.075	5.6973	0.6928

4.4.2 Set 2: Formulation 4, 5 and 6 (0.2g MWCNTs)

From the Table 4-10, When Bragg's Law ($n\lambda = 2d\sin\theta$) is applied, the d-spacing clearly changes as the surfactant ratio increases. The principal peak in Formulation 4 (1.0:1 ratio) is situated at 20.32° , resulting in the smallest d-spacing of $4.37 \text{ \AA}$. The peaks in Formulation 5 (1.5:1) and Formulation 6 (2.0:1) move to lower angles of 19.51° and 19.55° , respectively which means that the d-spacing expands to about $4.54 \text{ \AA}$. This is due to the reason of the lower peak position. The increased distance between the molecular planes is because of the higher concentration of Tween 20 intercalating between the polymer chains.

Using the Scherrer Equation, $L = \left(\frac{K\lambda}{\beta \cos\theta} \right)$ to analyze these peaks shows how the surfactant ratio affects crystal ordered pattern. Formulation 6 (2.0:1 ratio) has the lowest FWHM value of 1.94° in this group. The corresponding lateral crystal size of $0.74 \text{ \AA}$ in Formulation 6 confirms this high level of crystal perfection compared to Formulation 5, which has the L value of $0.69 \text{ \AA}$. In contrast to Formulation 4 which has a much wider FWHM of 2.32° , Formulation 6's narrower peak suggests larger structured crystallite sizes.

Clearly, Formulation 4 having the smallest lateral crystal size in this set at 0.62 Å. This indicates that a larger surfactant ratio, 2.0:1 is needed to obtain the dispersion required for high-quality PVOH crystal formation at higher MWCNT loadings that is 0.2g.

From the Table 4-10, as the Klug and Alexander approach is used, the interchain separation in Formulation 4, with a 1.0:1 ratio is at its lowest for this set at 5.46 Å. At this stage, the polymer chains are still relatively close to each other. However, as the surfactant concentration increases in Formulation 5 (1.5:1 ratio), the distance between the chains jumps significantly to 5.68 Å. This indicates the Tween 20 molecules are successfully sliding between the PVOH and starch chains, physically pushing them apart and creating more space in the molecular network. in Formulation 6 (2.0:1 ratio), the interchain separation actually slightly drops to 5.67 Å. The difference between Formulation 5 and 6 is actually very small, and it can be negligible so it can be assumed to have same interchain separation.

Hence, in this case, the bigger crystal size which is Formulation 6 is chosen for Set 2. This is because at the same time, the d-spacing and inter-chain separation is almost the same as the Formulation 5. Therefore, it means Formulation 6 has the highest ordered crystal structure and so it has high and narrow peak and low defect density.

Summary of Set 2

The green highlighted column in the Table 4-12 means the formulation has the best result for Set 2. Meanwhile, the red highlighted columns means the formulation is not suitable for the 0.2g of MWCNTs.

Table 4-11: Overall Performance of Formulation 4,5 and 6

Formulation	Peak Position (2θ)/ $^{\circ}$	d- spacing /Å	FWHM / $^{\circ}$	Inter-chain separation (R)/ Å	Lateral crystal size (L) / Å
4 (1.0:1 Ratio)	20.32	4.37	2.320	5.4557	0.6204

5 (1.5:1 Ratio)	19.51	4.55	2.093	5.6799	0.6869
6 (2.0:1 Ratio)	19.55	4.54	1.940	5.6684	0.7411

4.4.3 Set 3: Formulation 7, 8 and 9 (0.3g MWCNTs)

From Table 4-10, the final set shows a constant trend of lattice expansion as the Tween 20 ratio increases when Bragg's Law ($n\lambda = 2d\sin\theta$) is applied. The main peak in Formulation 7 (1.0:1 ratio) is located at 19.52° with a d-spacing of $4.55 \text{ \AA}$. In Formulation 8 (1.5:1 ratio), the peak drops to a lower angle of 19.41° as the surfactant concentration increases, raising the d-spacing to $4.57 \text{ \AA}$. However, in Formulation 9 (2.0:1 ratio), the d-spacing drops to $4.48 \text{ \AA}$ as the peak returns to a greater angle of 19.78° . This means that the highest surfactant ratio might lead the polymer chains to pack more tightly again at higher filler loadings. This is because of a saturation effect where the surfactant starts to aggregate rather than intercalate.

While the Scherrer equation is a standard tool in material science, its suitability in this study is specifically aimed at determining the lateral crystal size and the perfection of the crystalline regions rather than the absolute degree of crystallinity. In a composite system like PVOH/Starch/MWCNT, the addition of nanotubes can act as a nucleating agent, which changes how the polymer chains organize themselves. The use of this equation is justified because the FWHM is highly sensitive to the internal order of the polymer. The Scherrer Equation, $L = \left(\frac{K\lambda}{\beta \cos\theta} \right)$ evaluation of the peaks shows that Formulation 9 produced the most developed crystal structure in this group. In contrast to the wider peaks in Formulation 7 and 8 which is 1.95° and 1.94° respectively, it displays the lowest FWHM of 1.76° . According to Scherrer's principle, it suggests larger and perfected crystalline structure. While Formulation 8's lateral crystal size has only $0.74 \text{ \AA}$, the Formulation 9 has a better value which is $0.82 \text{ \AA}$ for L value. As seen in Formulation 9, a decrease in FWHM suggests that the Tween 20 assisted the MWCNTs in integrating into the matrix without disturbing the crystal lattice, resulting in bigger, more stable crystalline domains.

Scherrer is therefore the most effective method to measure how the nanofillers and surfactant ratios enhanced the structural quality and order of the composite, even though it does not offer a total crystallinity percentage.

Comparing the three samples, Formulation 9 (2.0:1 Ratio) shows the most efficient packing with the lowest inter-chain separation of 5.60 Å. In contrast, Formulation 8 shows the widest separation at 5.71 Å, suggesting that at that specific ratio, the arrangement of chains is slightly more loose. When the inter-chain separation decreases, as seen in Formulation 9, it typically indicates that the polymer chains are close enough to form stronger intermolecular bonds, reinforcing the overall structure. Formulation 7 has a higher inter-chain separation of 5.68 Å compared to the 5.60 Å found in Formulation 9. This indicates that the polymer chains in the 1.0:1 ratio are physically further apart, leading to the hydrogen bonding between the PVOH and starch molecules are weaker.

Since the Formulation 7 and 8 have higher value of inter-chain separation and lower lateral crystal size, so Formulation 9 is the optimal choice when encountering high loading of MWCNTs. This is because it has highest lateral crystal size, reflecting the high and narrow peak and the lowest defect density. At the same time, it has the lowest inter-chain separation.

Summary of Set 3

The green highlighted column in the Table 4-13 means the formulation has the best result for Set 3. Meanwhile, the red highlighted columns means the formulation is not suitable for the high loading, 0.3g of MWCNTs.

Table 4-12: Overall Performance of Formulation 7,8 and 9

Formulation	Peak Position (2θ)/°	d-spacing /Å	FWH M / °	Inter- chain separati on (R)/ Å	Lateral crystal size (L) / Å
7 (1.0:1 Ratio)	19.52°	4.55	1.950	5.6770	0.7372

8 (1.5:1 Ratio)	19.41°	4.57	1.935	5.7089	0.7428
9 (2.0:1 Ratio)	19.78°	4.48	1.760	5.6031	0.8171

Table 4-13: XRD Data Value of All Formulation

Sets	Formula tion	Peak Position (2θ)/°	d- spaci ng /Å	FWHM M /°	Inter-chain separation (R)/ Å	Lateral crystal size (L) / Å
1 (0.1g MWC NTs)	1 (1.0:1 Ratio)	19.78	4.48	2.178	5.6031	0.6603
	2 (1.5:1 Ratio)	19.64	4.52	1.943	5.6427	0.7400
	3 (2.0:1 Ratio)	19.45	4.56	2.075	5.6973	0.6928
2 (0.2g MWC NTs)	4 (1.0:1 Ratio)	20.32	4.37	2.320	5.4557	0.6204
	5 (1.5:1 Ratio)	19.51	4.55	2.093	5.6799	0.6869
	6 (2.0:1 Ratio)	19.55	4.54	1.940	5.6684	0.7411
3 (0.3g MWC NTs)	7 (1.0:1 Ratio)	19.52	4.55	1.950	5.6770	0.7372
	8 (1.5:1 Ratio)	19.41	4.57	1.935	5.7089	0.7428
	9 (2.0:1 Ratio)	19.78	4.48	1.760	5.6031	0.8171

4.5 Antioxidant Test

The Table 4-14 provided summarizes the antioxidant data for all nine sample formulations, along with the DPPH baseline used for the formulation. To get these values, the baseline was first determined using distilled water as a reference before measuring the actual samples. This baseline provides the starting point to calculate how much of the DPPH radicals were actually scavenged by the different film mixtures.

4.5.1 Set 1: Formulation 1, 2 and 3 (0.1g MWCNTs)

Based on the Table 4-14, the antioxidant results indicate that scavenging activity is highly dependent on the lowest level of 0.1g. The Figure 4-6 demonstrate the graph's rising trend indicates that when the surfactant ratio rises, the film's antioxidant activity increases. At a 1.0:1 ratio in Formulation 1, the activity is slightly negative at -0.645%, and it remains nearly negligible at 0.080% for the 1.5:1 ratio in Formulation 2. A significant increase to 3.215% is only observed at the 2.0:1 ratio in Formulation 3. This trend suggests that for low concentrations of MWCNTs, a minimum surfactant ratio of 2.0:1 is required to effectively activate the material's antioxidant properties. Essentially, the increased volume of Tween 20 ensures that the nanotubes are sufficiently dispersed to interact with the DPPH radicals.

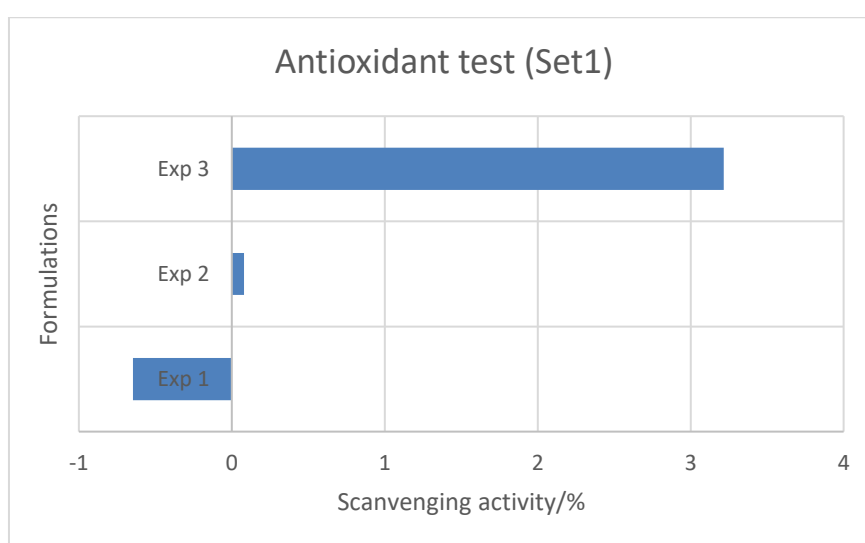


Figure 4-6: Antioxidant Test for Formulation 1, 2 and 3

4.5.2 Set 2: Formulation 4, 5 and 6 (0.2g MWCNTs)

Based on the Table 4-14 and Figure 4-7, it shows similar upward trend like Set 1 which has lower MWCNTs amount, indicating that when the surfactant ratio rises, the film's antioxidant capacity increases. In comparison to the first set, the baseline scavenging activity improves across the lower ratios in the second set, where the MWCNT load is doubled to 0.2g. Positive activity is observed in both the 1.0:1 ratio in Formulation 4 and the 1.5:1 ratio in Formulation 5, with values of 0.717% and 0.842% respectively. Similar to the first set, the 2.0:1 ratio in Formulation 6 remains the most effective, reaching 2.428%. Interestingly, even though the results for the lower ratios were improved by the increased loading of nanotubes, the 2.0:1 ratio in this set did slightly worse than the 2.0:1 ratio in Formulation 3. This indicates that at this particular loading, the balance between the nanotubes and the surfactant begins to change. Formulation 6's larger actual surfactant amount than Formulation 3 could start to have a slight shielding effect that slightly restricts the antioxidant reaction.

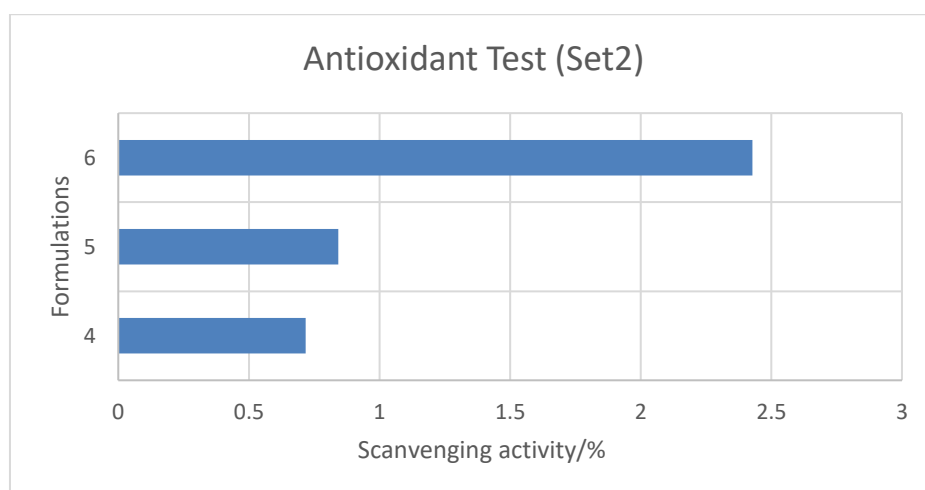


Figure 4-7: Antioxidant Test for Formulation 4,5 and 6

4.5.3 Set 3: Formulation 7, 8 and 9 (0.3g MWCNTs)

The Table 4-14 and Figure 4-8 shows the third set which contains the highest loading of nanotubes at 0.3g provides the most significant results of the study and shows a different pattern compared to the first set. Unlike the first set, this group does not follow a simple upward trend as the surfactant ratio rises. While there is an unexpected drop to 1.291% in Formulation 8 but the overall activity levels in this set are much higher than in previous trials. This might because the

excess surfactant layer may physically shield the nanotubes, making it harder for the DPPH radicals to come into direct contact with the carbon surface. They may essentially slip past the surfactant-coated surface and so they didn't react to the DPPH radicals. The 1.0:1 ratio in Formulation 7 scores 2.703%, which is already higher than any results seen in the first two sets except for the Formulation 6. The most important finding is in Formulation 9, where the 2.0:1 ratio produces a scavenging activity of 6.073%. This is the highest total activity recorded in the entire test, confirming that combining the maximum nanotube load with the highest surfactant ratio creates the most effective antioxidant performance.

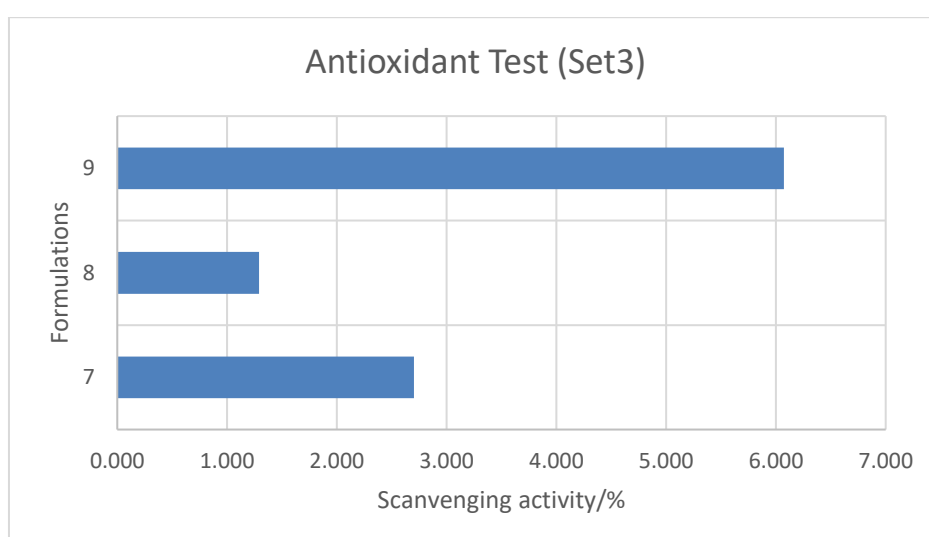


Figure 4-8: Antioxidant Test for Formulation 7,8 and 9

Table 4-14: Effect of MWCNT Loading and Surfactant Ration on DPPH Scavenging Activity

Sets	Formulations	Ratio (Tween 20: MWCNTs)	WL4/ nm (517.0)	Scavenging activity/%
1 (0.1g)	1	1.0:1	-0.023	-0.645
	2	1.5:1	0.003	0.080
	3	2.0:1	0.116	3.215
2 (0.2g)	4	1.0:1	0.026	0.717
	5	1.5:1	0.030	0.842
	6	2.0:1	0.088	2.428

3 (0.3g)	7	1.0:1	0.098	2.703
	8	1.5:1	0.047	1.291
	9	2.0:1	0.219	6.073

4.5.4 Summary of the Antioxidant Performance

As the ratio of Tween 20 to MWCNT increases from 1.0:1 to 2.0:1, an obvious upward trend in the surfactant ratio is seen within each set. For that specific loading level, the 2.0:1 ratio (Formulation 3, 6, and 9) consistently performed better than the 1.0:1 and 1.5:1 ratio. This means that the optimal threshold needed to successfully activate the surface of the nanotubes is the 2.0:1 ratio. The 2.0:1 ratio ensures that the nanotubes are sufficiently available to interact with the DPPH solution, while lower ratios give the impression that the nanotubes are chemically shielded or poorly integrated, leading to negligible or even negative scavenging values.

The absolute scavenging leads to all nine formulation are still below 10% despite these obvious increases in the surfactant ratio. These results would be categorized as having low antioxidant properties in the context of active food packaging. Although the 2.0:1 ratio and greater MWCNT loading are shown to be the best option parameters in the formulation but the total efficiency is restricted. This is probably because the PVOH/Starch matrix is dense and the nanotubes' low relative weight makes it more difficult for radicals to reach the antioxidant sites.

4.6 Comparative Performance and Industrial Suitability

Low-Density Polyethylene (LDPE), the industry standard for flexible food packaging was used as a benchmark to assess the developed PVOH/Starch/MWCNT films' practical potential. Commercial LDPE is distinguished by its remarkable flexibility and toughness, usually displaying a tensile strength of 8–25 MPa and an extraordinary elongation at break of 400–800% based on the technical requirements supplied by Laird Plastics (2022). There is a noticeable mechanical trade-off between these requirements and the study's findings.

When compared to the industrial 8–25 MPa range of LDPE, Formulation 9 showed much less elongation and a lower tensile strength. This

demonstrates that although the PVOH-starch matrix is effectively strengthened by nanotubes, it is still not as stretchable as polymers produced by petroleum. The Young's Modulus of LDPE is only 150–250 MPa (Laird Plastics, 2022), while Formulation 9 achieved a higher value of 516.67 MPa, indicating a significant improvement in structural stiffness. This suggests that the produced film is much stiffer than regular LDPE, which means that it is more appropriate for rigid or semi-rigid packaging applications than flexible wraps like food trays or structural liners.

Moreover, conventional LDPE provides no active defense against food degradation and is chemically inert. On the other hand, Formulation 9's 6.073% DPPH scavenging activity offers a functional benefit. This implies that the film offers a dual-functional advantage which are high structural stiffness and low antioxidant protection which conventional commercial plastics do not offer, although its mechanical versatility is still being improved. The 2.0:1 Tween 20 to MWCNT ratio effectively improves biopolymer performance closer to industrial requirements, especially for particular type of packaging that needs both strength and shelf-life extension.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The investigation into PVOH/corn starch/MWCNT composites shows that the interactions between the polymer matrix, nanotube loading, and surfactant ratio are critical in determining the final film properties. While various formulations were tested, the 2.0:1 Tween 20 to MWCNT ratio consistently emerged as the most effective for achieving structural and functional stability across all nanotube concentrations.

The XRD data is the main source of evidence from a structural perspective. Only the 2.0:1 ratio produced the biggest lateral crystal sizes and the lowest Full Width at Half Maximum (FWHM) values at higher loadings (0.2g and 0.3g). This suggests that this particular ratio helps the polymer chains arrange into a more perfected crystalline network with fewer flaws rather than simply blending the components. This is a crucial point. When the surfactant ratio is 2.0:1, the nanotubes function as a structured template. Otherwise, they operate as impurities that interfere with the crystal formation.

The SEM observations clearly show this structural perfection. The 2.0:1 formulation, particularly Formulation 9 displayed a smooth, uniform, and integrated surface even at 10,000x magnification, whereas other ratios displayed surface roughness or microscopic aggregates. This demonstrates that the 2.0:1 ratio offers sufficient "coverage" to mitigate the nanotubes' natural tendency to stick to themselves (van der Waals forces), allowing them to disperse and form bonds with the starch and PVOH instead.

Apart from that, the FTIR measurements offer more proof of this integration, showing that the O-H bonding typically gets stronger as the surfactant ratio approaches 2.0:1. This increase in bonding shows that the Tween 20 molecules are effectively serving as molecular bridges, linking the nanotubes to the starch and PVOH chains and forming a more solid and stable composite network. This chemical bridging is what allowed the Young's

Modulus to peak at 516.67 MPa. Although the film became more brittle, this is a standard trade-off in high-performance composites; the gain in stiffness and structural integrity is more valuable for a packaging material than the loss in stretchability.

Finally, the DPPH scavenging results provide the functional justification. In terms of antioxidant effectiveness, the DPPH scavenging experiments demonstrate that the characteristics of the nanotubes must be activated with a minimum surfactant ratio of 2.0:1. At 6.073%, Formulation 9 had the highest overall scavenging activity of the entire investigation, proving that the nanotubes' functional properties are only fully "unlocked" when they are properly dispersed.. In conclusion, the 2.0:1 ratio is justified as optimal because it is the only ratio that successfully balances high-filler loading with crystal perfection, surface integration, and maximum antioxidant power.

5.2 Recommendation

Firstly, observations from the casting process show that using metal plates instead of silicon molds helps eliminate trapped air bubbles and provides a more uniform surface. The Figure 5-1 is just only for the references and they are not involved in the testing process. The Figure 5-1 show that silicon molds can result in failed films because they have heavy bubble formation and a very crinkled appearance. By switching to metal plates, these structural weak spots are reduced, which creates more stable results for mechanical testing.



Figure 5-1: Right Handside is the One Used Silicon Mold and Left Handside is the One Used Metal Plate

Another important refinement for the methodology is keeping the oven temperature at around 35°C for nearly a week. This slower drying process is necessary to prevent the film from curving or warping as it solidifies. A more gradual evaporation of water ensures that the PVOH and starch matrix settles evenly. The Figure 5-2 is the example of putting too high oven temperature and cause it to be crinkle and curved. This is essential for maintaining the uniform thickness required for accurate analysis.



Figure 5-2: The Wrinkle Appearance of the Failed Example

Other than that, it is suggested to increase the range of surfactant-to-filler ratios beyond the existing limits to obtain even clearer results. Testing ratios such as 3.0:1 or 4.0:1 would reveal whether the material reaches a saturation threshold or whether the inter-chain gap continues to increase. Changing the amount of Tween 20 while maintaining a very low nanotube load might also show how the surfactant alone influences the composites' crystallinity.

Finally, the antioxidant analysis could be improved to offer more helpful evidence of the film's effectiveness. Despite being an usual test, the DPPH assay often produces very low values in dense films and might not accurately indicate the material's potential. Students can therefore take the second test to confirm the result. Casting the film into a container-shaped mold might be a better personal choice. An excellent qualitative test of the film's oxygen barrier and antioxidant qualities would thus be to store an item, such as an apple, inside and see if it oxidizes or browns over time. A more

comprehensive quantitative picture would also be obtained by combining the DPPH test with the ABTS assay. This is because it is generally more sensitive to different types of antioxidants.

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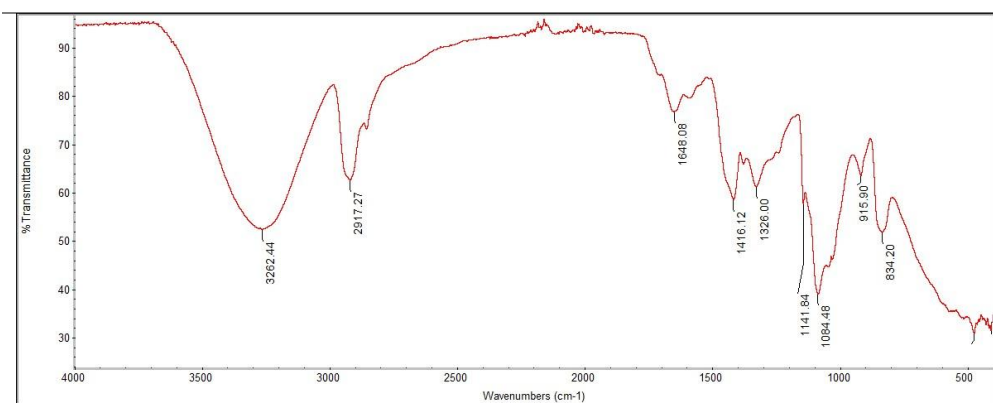
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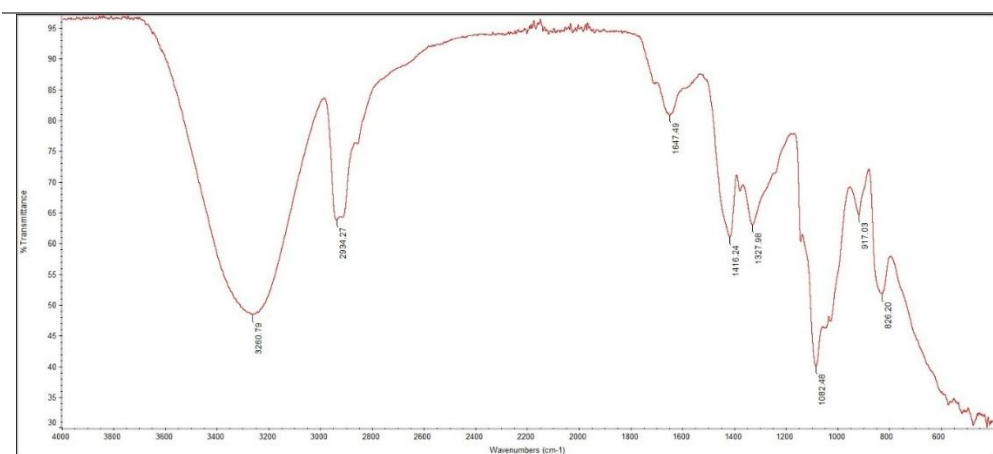
APPENDICES

Compilation of FTIR Result

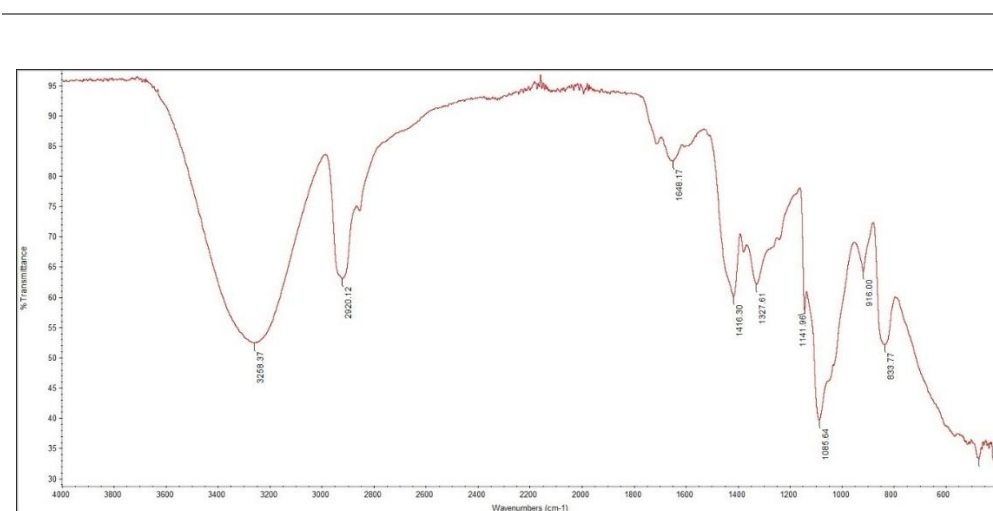
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Formulation 2 (1.5:1)

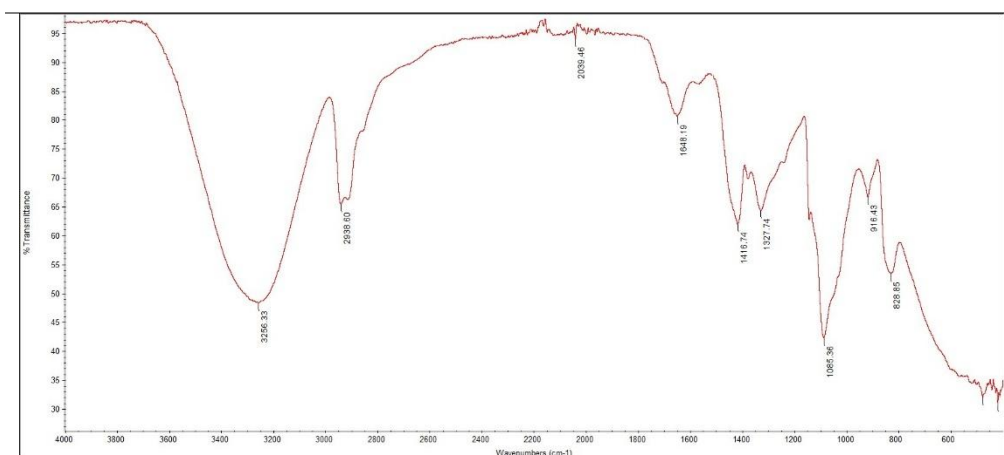


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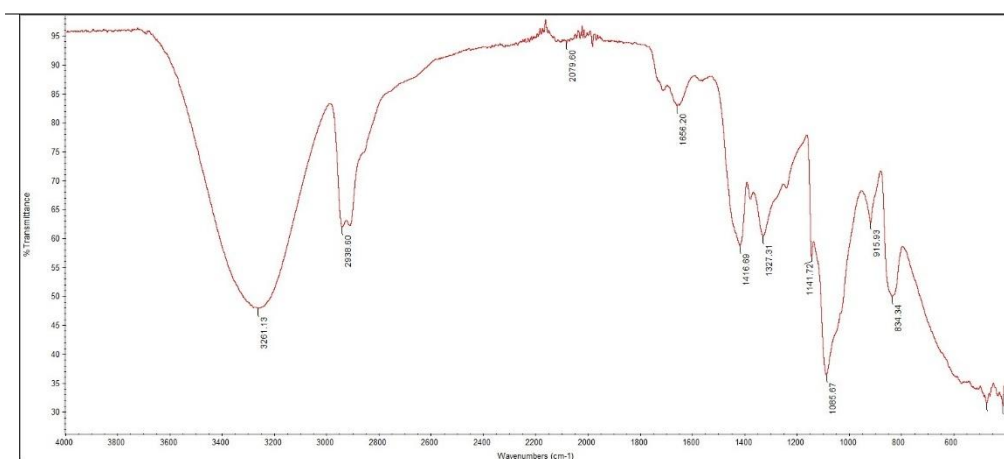


Appendix 1: SET 1: Experiment 1, 2 and 3 (0.1g MWCNTs)

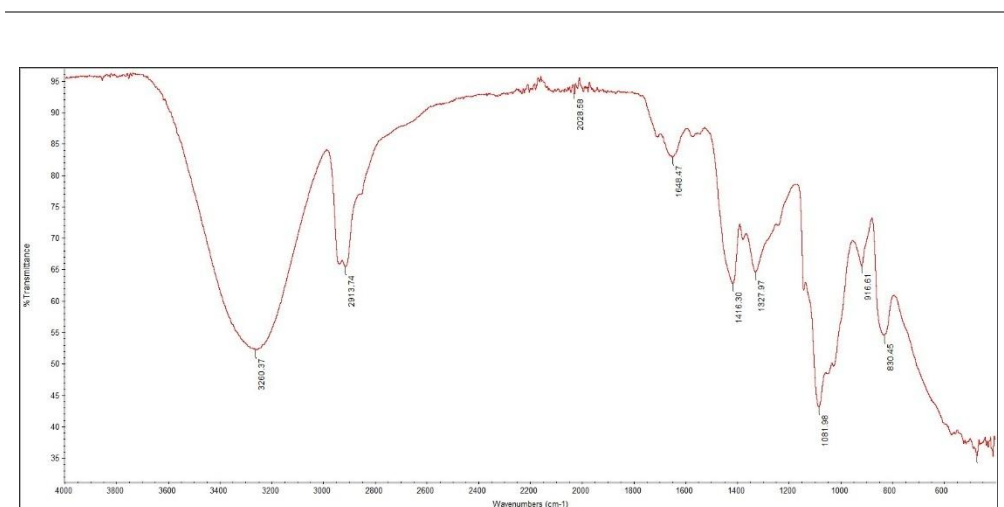
Formulation 4 (1.0:1)



Formulation 5 (1.5:1)

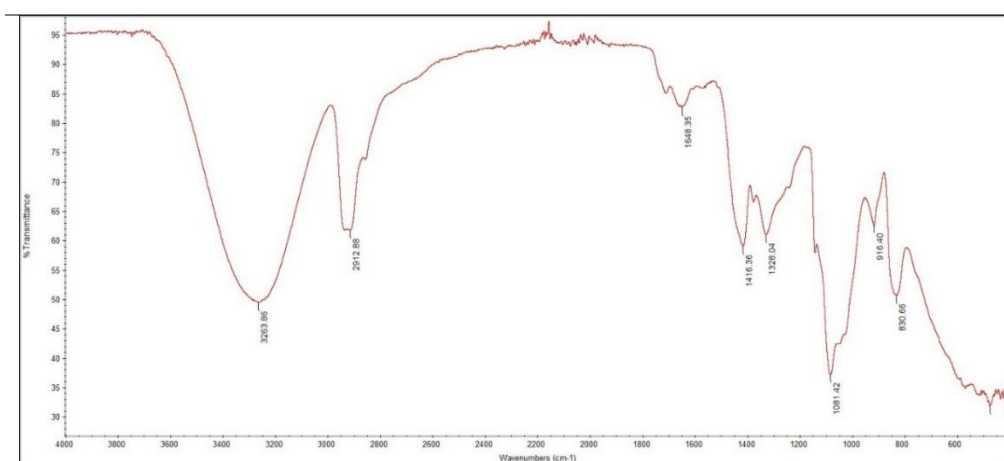


Formulation 6 (2.0:1)

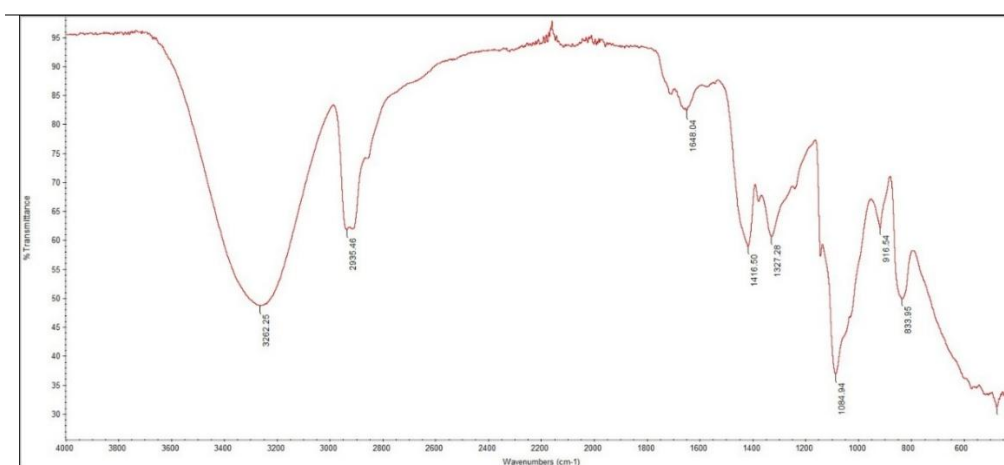


Appendix 2: SET 2: Experiment 4, 5 and 6 (0.2g MWCNTs)

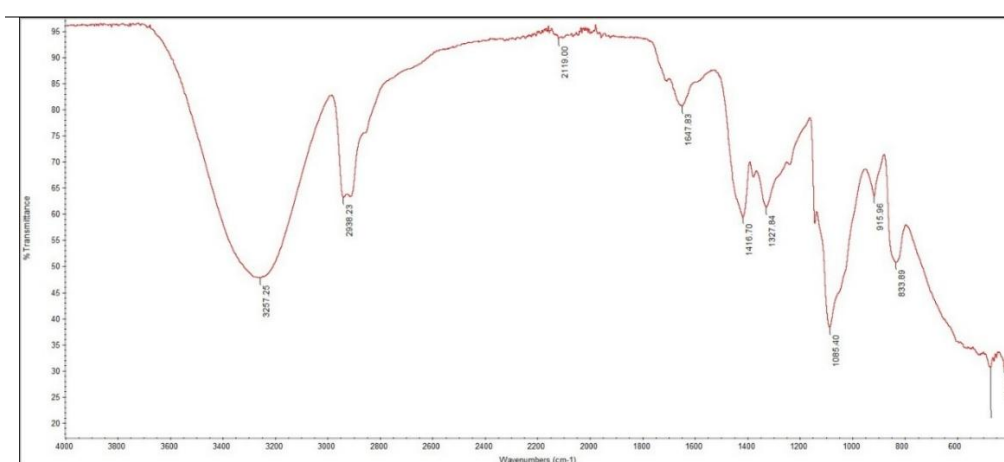
Formulation 7 (1.0:1)



Formulation 8 (1.5:1)



Formulation 9 (2.0:1)



Appendix 3: SET 3: Experiment 7, 8 and 9 (0.3g MWCNTs)