Manufacturing and Characterization of Chitin Nanowhisker/Polyolefin Nanocomposites

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
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This thesis discusses the potential large scale production of polymer nanocomposites using polypropylene and high density polyethylene with chitin nanowhiskers (CNW). Fabrication of the nanocomposites with and without compatibilization were prepared over a range of CNW loading through melt compounding. The processing techniques tested included direct melt compounding, and a two step masterbatch dilution process. Three studies were investigated to build an understanding of the composite structure-property relationship based on morphological, thermal, water barrier, mechanical, and rheological properties. The addition of CNW and compatibilizer provided mechanical reinforcement and improvements in water barrier. However, the CNW significantly affected the crystallinities of the composites, which impacted its overall properties. Finally, the masterbatch diluted composites maintained good mechanical and water barrier compared to the neat polymer, but the directly compounded composites were still better. Therefore, further optimization of this process is required to maximize CNW dispersion, which also greatly affected the composite properties.
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List of Abbreviations

AFM: Atomic Force Microscopy
CNP: Chitin Nanoparticle
CNW: Chitin Nanowhisker
DSC: Differential Scanning Calorimetry
HDPE: High Density Polyethylene
LLDPE: Linear Low-Density Polyethylene
MAPE: Maleated Polyethylene
MAPP: Maleated Polypropylene
MWCNT: Multi-Walled Carbon Nanotube
PHB: Poly(3-hydroxybutyrate)
PLA: Polylactic Acid
PP: Polypropylene
PVA: Polyvinyl Alcohol
SEM: Scanning Electron Microscopy
TGA: Thermogravimetric Analysis
WVP: Water Vapor Permeance
WVT: Water Vapor Transmission
Chapter 1  Introduction

1.1 Preamble

Polymer nanocomposites with natural fillers has been of great interest in the recent years to satisfy the need for environmentally sustainable and safe materials. Especially in the packaging industry, nanocomposites consisting of inorganic and carbon fillers are common but dangerous in comparison to the potential use of natural fillers. Although many small scale processing techniques have proven that natural fillers are capable in serving high performance nanocomposites, it has not shown efficiency in its implementation into an industrial scale. More recently, a few studies have began to apply scalable processes in fully biodegradable filler-polymer systems, however, insufficient research has been performed on alternative polymer systems, which are less susceptible to degradation issues the experienced by biodegradable polymers during processing. As a result, these issues can interfere with understanding some of the underlying reasons behind properties that the composites exhibit. This research looks to use CNWs in enhancing the thermal, mechanical, and water barrier properties of polymer nanocomposites such that they are comparable to non biodegradable systems.

1.2 Research Objectives and Contributions

This research explores two different composite systems that combines polypropylene with chitin nanowhiskers, and high density polyethylene with chitin nanowhiskers through two different melt blending processes. Little to no studies have considered the water vapor barrier properties of melt blended polymer nanocomposites with CNWs, therefore this thesis aims to counter the use of inorganic and carbon nanofillers by examining the physical effects of CNWs and compatibilizer on PP and HDPE nanocomposites. An advantage of using CNWs is that it can also potentially impart antimicrobial properties into the composite.[1] The main objectives of this research based on the testing of two polymer systems is to:

1. Develop value-added products from CNWs, which is typically considered as a waste material, by incorporating them into polymer to enhance its properties.
2. Fabricate CNW/polymer nanocomposites through direct melt compounding to analyze its structure to property relationships and determine its optimal composition.

3. Investigate the feasibility of using the CNW/polymer nanocomposites as a masterbatch material to tailor the properties of the polymer nanocomposites after a dilution processes using melt blending.

Currently, no studies have processed polymer nanocomposites using unmodified CNWs combined with PP or HDPE through melt compounding. Furthermore, the capabilities of these polymer nanocomposites as masterbatches have not been previously considered. This research will provide a better understanding of the thermal, mechanical, and water barrier properties of the polymer nanocomposites processed based on their morphology and rheological properties. This research will also address the factors affecting particular material properties and challenges in processing to help future advances in the development of CNW/polymer nanocomposites and other polymer nanocomposites containing natural fillers.

1.3 Thesis Organization

This thesis is organized into 6 chapters starting with Chapter 1, which describes the motivation behind this research and the goals that this research aims to achieve. Chapter 2 will provide a background on the target applications and materials used in this thesis along with literature review from previous and recent studies that will address the properties and processing of polymer nanocomposites. Chapter 3 will discuss the effects of CNW loading and compatibilizer on the morphological, thermal, water barrier, mechanical, and rheological properties of CNW/PP composites. Another investigation of the same effects and properties will be presented in Chapter 4 but in a HDPE polymer system. Chapter 5 will utilize the findings from Chapter 3 and Chapter 4 to evaluate the suitability of using CNW/PP and CNW/HDPE composites in large scale production through a masterbatch dilution process. Lastly, Chapter 6 is the final chapter that will provide a summary the whole thesis and considerations for future work.
Chapter 2  Background and Literature Survey

2.1 Polymer Composite Packaging

The current market for polymer nanocomposites in the packaging industry are high demanding due to their superior barrier, mechanical, and other properties compared to its base polymer alone. Especially, the use of inorganic nanofillers in polymer nanocomposite films and coatings have dominated the packaging industry and continue to expand through seeking more environmentally viable options by using biopolymers[2]. Even though employing biopolymers can improve its environmental impact, the use of inorganic filler is still questionable. Traditional fillers such as talc[3-5], mica[6-8], montmorillonite[9-11], calcium carbonate[4], calcium sulfate[12-14], and zinc oxide[9, 15] have shown to enhance mechanical, thermal, and barrier properties when added into a polymer matrix. However, using these inorganic nanofillers poses environmental and health hazards for humans through exposure during processing or usage.[16] Therefore there is a drive towards safer additives and fillers that are less hazardous, biodegradable, and abundant.

2.2 Chitin Nanowhiskers

Chitin is the second most abundant natural polymer that can be sourced from shells of arthropods, such as crabs, shrimps, fish, lobster, fish, and insects, and is a sustainable resource for biomedical, packaging, and industrial applications due to its biodegradability, biocompatibility, low toxicity, and renewability.[17-19] In its nanowhisker form, it can provide exceptional mechanical properties due to its high aspect ratio and crystallinity.[20] Chitosan, a derivative of chitin, has been widely study due to its effective antimicrobial properties as a matrix or even when incorporated into various polymer matrices.[21-24] Nonetheless, very limited studies have investigated the potential of CNW in high performance composites despite showing antimicrobial activity and superior mechanical properties to chitosan due to its crystallinity.[18, 25, 26] The major issue with the composite processing of natural nanofillers such as cellulose or chitin is its incompatibility with commonly used polymers due to their differences in polarity. Chitin, as its chemical structure is shown below in Figure 2-1, has many
hydroxyl groups, therefore is hydrophilic and tends to self-agglomerate by forming hydrogen bonds in a dehydrated state.

![Chemical structure of chitin](image)

**Figure 2-1 Chemical structure of chitin.**

As a result, previous studies have focused on the incorporation of natural nanofillers in either hydrophilic polymers to match the polarities of the filler-matrix system[27, 28] or PLA with compatibilizers to account for a fully biodegradable and biocompatible composite.[29-31] However, the most frequently used industrial polymers, such as polyethylene, PP, polystyrene, and PLA, are all hydrophobic polymers.[32] Moreover, there are drawbacks of using PLA as it is brittle and has its limited applications due to its low service temperature and its susceptibility to degradation. A common approach taken to accommodate for the filler-matrix incompatibility is to strengthen the filler-matrix interaction by introducing surfactants or modifying filler surfaces.[33-36] Through the incorporation of surfactants, the fillers are able to disperse better throughout the matrix, but can in return degrade the polymer matrix. Furthermore, surface treatment of fillers can be performed to make them behave more hydrophobic so that they can adhere better to hydrophobic matrices. Although both techniques have shown to improve mechanical properties based on tensile and dynamic mechanical analysis, the main disadvantage with adding surfactants and surface modifications of fillers is that they can alter the biodegradability and properties of the overall composite.

### 2.3 Processing and Properties of Polymer Composites with Bio-Fillers

The use of chitin as reinforcement in matrices such as PVA[37] and carrageenan[38] have shown to be effective since it has good compatibility with hydrophilic polymers. An enhanced filler-matrix interfacial interaction improved stress transfer from the matrix to the CNWs resulting in an increase in tensile strength and elastic modulus. The addition of CNWs also helped increase the crystallinity of PVA by inducing chain orientation and decreased the water vapor permeability of carrageenan composites. However, PVA and carrageenan are water soluble
polymers, therefore have limited applications. Another study presented the use of CNP, which has a lower crystallinity than nanowhiskers, in a potato starch matrix to evaluate its mechanical and water barrier properties.[28] Similar with the studies mentioned previously, an increase in tensile strength and water vapor permeability was observed due to the addition of CNP. When the lowest water vapor permeability was reached, further addition of CNP caused it to increase due to the agglomeration of the chitin particles. Moreover, fully biodegradable composites such as chitosan/PHB[39], nanocellulose/PLA[40], and CNW/PLA[29, 30] have been previously investigated. The thermal stabilities of these composites tend to drop with increasing filler content, but exhibited improvements in tensile stiffness and strength. However, due to the limitations of PHB mass production and low service temperature of PLA, therefore either they are not suitable for industrial production or incorporation into a wide range of applications.

Although some of the studies have shown significant improvements with the incorporation of chitin, as a result of good bonding and dispersion, but as mentioned before, the ability to transition these processing techniques to an industrial scale is more challenging compared to conventional polymer composite processing such as melt blending. A study on chitosan/LLDPE composite film prepared by melt compounding and film blowing showed potential for packaging applications.[41] The addition of a maleated compatibilizer helped improve the interaction between LLDPE and chitosan as it increased the tensile strength, but was lower when compared to the neat polymer. Furthermore, no significant effects of the compatibilizer on the water and oxygen barrier properties were observed, but the incorporation of chitosan decreased the oxygen permeance while increasing the water vapor permeability. The increase in water vapor permeability was explained by the water absorption of chitosan promoting the transmission of water molecules.

In order to overcome the ability to disperse the fillers for the ease of processing, dried forms of bio-nanofillers were developed through various drying processes such as freeze drying, spray drying, and supercritical drying[42], and attempts have been made to directly melt compound them with polymer. However, due to the agglomeration issue stated earlier, it was found that the hydrogen bonds formed between dried bio-nanofillers are difficult to redisperse and breakdown.[43] This was further correlated to the deteriorating mechanical properties and poor resistance against water vapor diffusion. Alternatively, processing these natural nanofillers in a hydrated state, by solvent casting, has been previously studied due to the ability of achieving a
good dispersion of the nanofillers within a matrix.[27, 28, 44] As a result, significant improvements in mechanical, barrier properties were obtained, but solvent casting is not a process that can currently be implemented into an industrial scale for mass production. Additionally, a problem associated with solvent casting is the effects of solvent on the overall properties of the end product and efficiency of solvent removal. Another method that has shown to produce well dispersion of bio-nanofillers in PLA through electrospinning, but more investigation is needed for the optimization of its properties.[26, 43]

More recently, to address the complications of dispersing dried fillers and scalability of processing, melt mixing of bio-nanofiller suspensions in PLA have been previously examined to analyze filler dispersion, and thermal and mechanical properties.[29-31] Nanowhisker loadings ranging from 0.5 to 5 wt% were investigated. Thermal degradation was found to be an issue during processing as a result of the solvolytic degradation of N,N-dimethylacetamide, which was used as a swelling and separation agent, and hydrolysis of PLA. Morphology of the composites revealed some dispersion of nanowhiskers accompanied by agglomerates. There was a noticeable change in the size of the agglomerates as they increased with nanowhisker loading. Some improvements in the elastic modulus and tensile strength were observed with the addition of the nanowhiskers, however, addition of certain compatibilizers and modifications had also caused weakening of the neat matrix. Since PLA is a common polymer used for packaging, barrier properties is an important aspect of the material that should be examined, but it was not reported in these studies.

2.4 Water Vapor Barrier Properties of Polymer Composites

It is generally found that the incorporation of fillers into polymers lead to an increase in the degree of crystallinity of the composite because the fillers can influence the nucleation of crystals.[30, 45, 46] Furthermore, previous studies have investigated the effects of crystallinity on the diffusion of water vapor and discovered that a rise in crystallinity can reduce the diffusion coefficient of water vapor.[47, 48] This was explained by the structure of crystalline domains and the orientation of polymer chains, which in turn affects the mobility of water vapor through the composite. Additionally, putting fillers into a polymer forms a more tortuous path for water vapor to travel across the composite. As a result, nanocomposites usually show better water vapor resistance than the neat polymer matrix by itself, but is also dependent on the type of
filler.[28, 49, 50] Poor filler-matrix interfacial properties results in air gaps within the composite that allows water vapor to diffuse easily through the material. A past research studied the water absorption of composites with macro sized chitin waste incorporated into PP and showed an increase in water absorption with increasing chitin loading as expected from the hydrophilicity of chitin.[51] Fillers that can absorb, interact, or react with the permeating gas molecule can have an effect on promoting or resisting the diffusion of vapor permeance through the composite.

2.5 Polypropylene Composites

Polypropylene has good mechanical and barrier properties and is commonly used in packaging applications [52, 53]. Many studies in the past have found to further enhance its properties by incorporating nanofillers. More specifically, nanoclay/PP composites have been a widely studied system that has shown improvements in thermal, mechanical, and barrier properties. A study on melt blended organoclay/PP nanocomposites with and without compatibilizers at 5 to 15 wt% nanoclay loadings for analyzing thermal, mechanical, and barrier properties found improvements in degradation and melting temperature, tensile strength, and decrease in oxygen permeability.[50] This showed that nanoclay is an effective filler for packaging materials. Another study analyzed the thermal stability of nanoclay-polypropylene composites using TGA and DSC and showed an increase in thermal stability, which was a result of the nanoclay providing a stabilizing effect on the polypropylene.[54]

As discussed previously, the incorporation of additives into polymer is known to help maximize its crystallinity due to the ability of additives to act as nucleating sites for crystallization. One of many studies examined the effects of the addition of nanotubes on its crystallization and thermal stability of PP nanocomposites [45]. As expected, the crystallinity and crystallization temperature was found to increase with the addition of the nanotubes. Moreover, the composites with nanotubes showed slight improvement in thermal stability based on TGA. This may have been caused by the barrier effects of nanotubes, which reduced the speed at which the volatile products escaped.

Furthermore, a study examined the thermal and mechanical properties of melt blended chitosan/PP composites and an improvement in thermal stability and crystallinity was observed with the incorporation of chitosan.[46] Another study investigated unidirectionally aligned chitosan fiber/PP prepared by sandwiching the fibers between PP sheets through compression
molding.[55] In both these studies, an increase in tensile strength and elastic modulus were observed. Moreover, the addition of chitosan resulted in a faster water uptake by the composites. On the other hand, a decrease in crystallinity of PP was revealed from a study when incorporating dried nanocellulose fibers [56]. However, the mechanical properties were improved and its water absorption was also higher compared to the pure PP. The combination of chitosan and cellulose nanocomposite films have been studied lots previously, but there is limited research in the use of CNWs.

2.6 High Density Polyethylene Composites

One of the most commonly used polymer for such application is high density polyethylene (HDPE). HDPE is a rigid polymer that has good water vapor barrier and chemical resistance against strong acids and alkalis, but poor gas barrier properties.[57] As a result, HDPE is commonly used in bottle packaging, pipes, and industrial containers. Many studies have investigated the effects of incorporating conventional fillers such as montmorillonite[58, 59], chrysotile[60], calcium carbonate[61], and talc[62] into HDPE composites to optimize oxygen barrier and mechanical properties. However, the main concern of using these inorganic fillers is the negative health and environmental impacts since they are not biodegradable and renewable.[16]

2.6.1 Effects of Crystallinity on the Properties of HDPE

In order to understand some of the factors that control the properties of HDPE, a previous study proposed that the film crystalline structure, melt relaxation rates of molten polyethylene, and physical properties are some factors that can affect oxygen and moisture barrier of HDPE films.[63] The crystalline structure of the films has an impact on the permeability of water and oxygen because the size of the molecules can easily diffuse through amorphous regions, but are too small to penetrate crystalline domains. Since HDPE has a high density due to its minimal branching between polymer chains leading to a closed packed structure, therefore it is known to have a high degree of crystallinity and good barrier properties.[64] Moreover, a recent study examined co-extruded multilayered film systems to analyze the crystalline morphology of HDPE at different layer thickness under confinement.[65] The confined spherulite morphology generated provided a tortuous path for water and gas diffusion, hence enhancing barrier properties. The correlation between crystallinity and barrier properties has also been observed
with other polymers including PLA[47] and PP[66]. Additionally, the stress relaxation rate of the polymer melt determines orientation of the crystalline domains as a faster rate will result in a more random orientation, which improves barrier properties.[63] Two of many polymer properties that can affect barrier properties include melt index and density. Melt index is a measure of the melt flow rate of a polymer on a mass per time basis. An increase in the melt index of HDPE will reduce the water vapor transmission rate because it causes faster relaxation times. Lastly, as mentioned earlier, polymers with a higher density will provide a more optimal water vapor and oxygen barrier oppose to low density due to the direct correlation between density and crystallinity.

2.6.2 Effects of Fillers on the Crystallinity and Properties of HDPE

One way to maximize crystal formation is through incorporating fillers, that can act as nucleating agents, in polymer to promote crystallization.[62] The addition of fillers can also help reinforce the matrix to enhance mechanical properties.[67] However, HDPE is known to be a hydrophobic polymer and does not interact well with many conventional fillers, therefore the use of surface modified fillers[68, 69] and polymers[70-72] have been previously tested so that they can interact with each other better. Between the two, the most common and easy to scale is the modification of the surface of polymers since the functional groups on fillers can vary greatly and may be difficult to modify. More specifically, maleic anhydride is typically grafted onto polymers as a coupling agent because it is easy to graft.[73] It also provides the appropriate functional groups to accommodate for the polarity differences between the filler and matrix improve the bonding between the two. The addition of a maleated compatibilizer can show strong adhesion through the observation of the morphology of the composite.[71, 74] From a visual inspection of the fracture surface of a composite, evidence of poor interfacial adhesion includes voids and the pull-out of fillers whereas a strong interfacial adhesion would show some plastic deformation and coating of the matrix onto the fillers. By increasing the filler-matrix interfacial interaction, stress experienced by the matrix can be transferred to the filler for improving the strength of the composite. Furthermore, enhancement in intermolecular interaction can suppress crystallization and disrupt the original crystal structures of polymers.[39]

As a result of some of the effects mentioned, the use of fillers, such as cellulose fiber[74], carbon nanotube[75], and nanoclay[70] in HDPE composites have found to be effective in enhancing
When low loadings of these filler were added to the HDPE, a slight increase in crystallinity was observed, but decreased at higher filler loadings. The decrease in crystallinity at higher filler loadings was explained by the fillers restricting mobility of the polymer chains. Despite the decrease in crystallinity, the oxygen permeability was still lower compared to the unfilled HDPE as a result of the fillers providing a tortuous path for the gas molecules. Furthermore, any filler and matrix interaction with permeants will also affect the permeability since it can cause the composite to be more absorbent to certain molecules passing through the material. Additionally, an increase in storage modulus was observed with increasing filler content. However, reduction in stiffness was observed with the addition of a compatibilizer due to plasticizing effects, but elongation at break and toughness were increased.

### 2.6.3 Effects of Filler Dimensionality and Orientation on Crystallinity of HDPE

In addition to the filler-matrix interaction the dimensionality and orientation of the fillers also has an effect on crystallinity, and mechanical and oxygen barrier properties. A study investigated the effects of carbon nanofiller dimensionality on the isothermal and non isothermal crystallization of HDPE. One of the main differences between isothermal and nonisothermal crystallization was the crystallization mechanism. For the case of the isothermal condition, a nucleation-controlled mechanism applied whereas for the nonisothermal condition, crystal growth was more dominant. Moreover, it was found that the orientation of the fillers from processing the composites had an effect on crystallinity as well. Biaxially stretched composites had fillers exhibiting a preferred orientation and resulted in higher crystallinity than compared to compression or blow molded films. The addition of compatibilizer was not found to have an effect on the filler orientation.

### 2.7 Masterbatch Dilution of Polymer Composites

In the recent years, masterbatch dilution of composites has been a popular processing technique applied in research to investigate the ability to promote filler dispersion due to agglomeration of fillers that can reside in the melt after a single step direct compounding process. The production of a masterbatch can help with the ease of processing composites industrially to avoid the need to deal with fillers that are difficult to incorporate into polymers. Moreover, the
properties of composites can be tailored by blending different additives and polymers with the masterbatch. One of the most studied polymer composites with masterbatch dilution involves the use of MWCNT in PP.[49, 79-81] Generally, the addition of MWCNT resulted in an increase in crystallinity, elastic modulus, yield stress, storage modulus, viscosity, and a decrease in ductility of the composites. The further of the addition of a compatibilizer improved filler-matrix interaction and also increased mechanical properties, but it hindered the increase in dispersion, crystallinity, and viscosity. It was suggested that a polarity mismatch between the polar regions of the compatibilizer and the nonpolar base matrix caused difficulties in dispersion. The compatibilizer also interfered with the stacking of PP chains causing some decrease in crystallinity compared to MWCNT without the compatibilizer but still higher than neat PP. However, the studies found that existing agglomerates from the masterbatch could not be effectively dispersed in the dilution process. In addressing the effects of dispersion, one study examined the dispersion of MWCNT in PLA under different processing conditions for masterbatch production and its dilution process.[78] It was determined that a twin screw extruder operating at a faster screw speed of generated composites with better dispersion and less number of agglomerates. This was consistent for the dilution process as well, therefore it proved that the extra step in diluting a masterbatch can help with increasing dispersion and minimizing agglomerates. The initial dispersion of MWCNT in the masterbatch also had an effect on how well dispersed they were in the composite was after dilution.

Other masterbatch studies of nanoclay[49, 82-84], graphite[85, 86], layered silicate[87], and carbon black[88] polymer composites have also been tested and showed improvements in electrical, mechanical, thermal, barrier and flame retarding properties. However, the demand for environmentally sustainable composites have triggered investigations in the development of masterbatches using natural and biodegradable fillers such as cellulose, chitosan, and chitin in PLA and polyethylene.[89-91] Masterbatch dilution of these composites have been previously evaluated based on thermal, mechanical, and barrier properties. In regards to thermal properties, the thermal stabilities tend to drop due to natural fillers being more susceptible to degradation than the polymer itself, but the crystallinity increases as a result of crystal nucleation from the fillers. Tensile modulus and strength also increase since the fillers help reinforce the polymer, though the presence of a compatibilizer can have slight drawbacks. However, the barrier properties of the composites have either found to deteriorate or not greatly affected by the fillers.
All of these studies showed the comparisons of the diluted composites relative to its neat polymer matrix, but did not show the value of using a masterbatch dilution over directly compounded composites. Therefore, to evaluate the effectiveness in masterbatch dilution, the mechanical properties of directly compounded CNW/PLA composites[92] have been compared to diluted CNW/PLA[89] composites. Both composites are found to have higher elastic modulus and tensile strength than pure PLA, but the directly compounded CNW/PLA composites had slightly better mechanical properties than diluted composites, but it was also important to note that the diluted composites also contained talc. Although PLA has advantage over other polymers due to its biodegradability, there still exist degradation issues when processing at high temperatures with aqueous solutions and solvents.[29-31]

2.8 Summary

This chapter provided an outline of various polymer nanocomposite systems and processing techniques that have been previously studied. The complications in processing natural fillers over conventional fillers have also been addressed. Also, the importance of nanofiller dispersion and its effects on polymer crystallinity has also been discussed relative to the properties of the nanocomposites. Moreover, masterbatch dilution, which is process applicable towards large scale production, has been reviewed based on existing research. The following sections will give a thorough analysis of the relationship between the structure and properties of the composites processed by the different methods applied in this thesis.
Chapter 3  Chitin Nanowhisker/Polypropylene Composites

The combination of various studies has shown the potential of bio-nanofillers to replace existing inorganic fillers as they are able to provide effective enhancement in different material properties. However, current studies lack the examination of CNW composites in a polymer matrix that is not susceptible to degradation and the investigations of water vapor barrier properties, which is crucial to many applications. This study aims to explore the use of direct melt blending of CNW/PP composites to analyze the effects of the incorporation of CNW and compatibilizer into polypropylene on its thermal, barrier, mechanical, and rheological properties. Moreover, connections between the properties at high and low weight percentages of CNW will be detailed to provide a better understanding of the behaviors that they exhibit. Lastly, the scalability of the process based on the performance of the composites will be evaluated.

3.1 Materials and Methods for Fabrication of CNW/PP Composites

3.1.1 Materials for CNW/PP Composite Fabrication

CNW suspension supplied by BOCO Technology Inc. was used as the composite filler and its chemical structure is provided in Figure 2-1. Its aspect ratio (L/W) is approximately 20-50 and density is 1.45 g·cm⁻³. The composite matrix used in this study was a homopolymer PP (ExxonMobil Achieve™ 3854) with a density of 0.9g·cm⁻³ and the compatibilizer was a maleated PP (Eastman™ G-3003 Polymer).

3.1.2 Fabrication of CNW/PP Composites

A co-rotating twin screw micro compounder (DSM Xplore® MC 15) was used to melt blend the CNW/PP composites. The PP and MAPP were mixed with the CNWs and fed into the compounder operating at 170°C and 200 rpm. Moreover, the amount of CNW suspension added was based on its concentration, which was used to determine its dried weight percent, and the four main compositions processed were 1, 2, 5, and 10 wt% CNW in PP. Additionally, two sets of the four compositions, with and without compatibilizer, were prepared to investigate both the effects of the CNW and the compatibilizer on the composite. In this study, the composites with
and without compatibilizer are denoted by CNW/PP and CNW/MAPP respectively following their weight percentages. A set of neat PP was also processed before testing to have consistent thermal and processing history with the other compositions for comparison. The compounded material extruded from the compounding was then pelletized for further processing.

The pelletized compound containing CNW and PP were either compression molded using a hydraulic hot press (Carver, Inc.) or injection molded using a micro injection molding machine (DSM Xplore® IM 5.5). Composite films, less than 200 µm in thickness, were prepared by compression molding at 180°C and 1000 psi in a thin mold for water barrier testing. The samples for rheological testing were also compression molded under the same conditions but slow cooled and using a different mold that provided rectangular samples with the dimensions of 10 mm by 18 mm by 0.7 mm. For mechanical testing, the samples were prepared by injection molding at 180°C and 100 psi to produce type IV specimens. A schematic of all the processing methods used in this study are shown in Figure 3-1.

![Figure 3-1 Schematic of melt compounding (a), compression molding (b), and injection molding (c) processing methods.](image)

3.1.3 Characterization of CNW/PP Composites

3.1.3.1 Morphological Analysis

Morphology of the CNWs and melt compounded CNW/PP and CNW/MAPP composites were analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM) to see
the dispersion of the CNWs in the PP matrix. An ultra-high resolution SEM (Hitachi UHR-SEM SU8230) was used for examining dried CNWs and nitrogen fractured cross section surfaces of the composites. The specimens were sputter coated with platinum prior to SEM imaging to minimize charging at the surface of the sample. An atomic force microscope (Bruker) was used to further confirm observations from the SEM imaging for the dried CNWs and microtomed cross sections of the composites.

3.1.3.2 Thermal Analysis

The thermal stability of the PP and CNW/PP composites were observed through TGA by using the TGA Q50 (TA Instruments) under nitrogen atmosphere. Samples were heated at a rate of 20°C/min. from room temperature (25°C) to 600°C to ensure complete thermal degradation. The degradation temperatures of each composition were determined from the weight change curves. Further thermal analysis of the PP and CNW/PP composites were performed through DSC by using the DSC Q2000 (TA Instruments) under nitrogen atmosphere. This helped measure the enthalpy of fusion, and melting and crystallization temperature of the composites. A heat-cool cycle between room temperature (25°C) and 200°C at a rate of 10°C/min. was used so that the composites were tested below their degradation temperatures.

3.1.3.3 Water Vapor Barrier Analysis

Water permeance of the CNW/PP and CNW/MAPP composite films were measured using the water method mentioned in ASTM E96 by monitoring the weight change the test dishes over a period of one to three weeks to ensure steady weight loss was achieved. Each test dish contained the same volume of water to begin with and had the compression molded films mounted on top of them. The test dishes were kept in an incubator at a controlled temperature and humidity, which were 50°C and 0% RH respectively, throughout the duration of the test. Three samples of each composition were prepared for comparison and the rate of water loss was extracted from a linear fit of the plot of weight change with respect to time at the end of each test. Further calculations were performed to obtain the values for water vapour transmission and permeance.

3.1.3.4 Mechanical analysis

The Microtester 5848 (Instron) was used for tensile testing based on ASTM D638 standard using a Type IV tensile specimen. An average of four to six samples for each composition was taken to
ensure consistency of the results. The elastic modulus, ultimate tensile strength, and elongation strain at break were extracted from the tensile curves for comparison.

### 3.1.3.5 Rheological analysis

A extensional viscosity test was performed on the ARES rheometer (TA Instruments) with the extensional viscosity fixture, was used to measure the extensional viscosity of the composites at a temperature and strain rate of 180°C and 1.0s⁻¹ respectively. An average of three samples for each composition was taken for the test.

### 3.2 Results and Discussion of CNW/PP Composites

#### 3.2.1 Morphology of CNW and CNW/PP Composites

Morphological analysis of the composites was important because it provided information on the quality of the material produced from the specified processing method based on filler dispersion. It also helped predict some of the material properties. The initial AFM and SEM images shown in Figure 3-2 presents the dried form of CNW fillers used in this study.

![AFM and SEM images of dried CNWs](image)

**Figure 3-2** AFM (a) and SEM (b) images of the morphology of dried CNWs.

The height image from the AFM of the dried CNWs confirmed the nanoscale of the nanowhiskers based on their observed high aspect ratios. A higher magnification of the dried CNWs under SEM showed the agglomeration of the CNWs as stated before from the hydrogen bonds that they form with each other when dehydrated, hence a fibrous mat is formed.

As for the AFM of the CNW composites, a constant force, that was able to deform the PP matrix, was applied throughout the sample to perform a modulus mapping of the surface since it was
known that the modulus of CNWs is higher than neat PP. This helped confirm the existence of the CNWs and its dispersion observed in the SEM images of the composites. Comparisons between the morphologies of the various CNW/PP compositions using AFM and SEM are shown below in Figure 3-3.

**Figure 3-3 AFM images of the cross sections of neat PP (a), 2% (b), 5% (c), and 10% (d) CNW/MAPP, and SEM images of the cross sections of 2% (e), 5% (f), and 10% (g) CNW/MAPP, and 10% CNW/PP.**

In the AFM images, the light and dark areas indicated higher and lower modulus respectively. Since CNWs have a higher modulus, therefore, they appeared as the lighter areas where as the darker areas were representative of the PP matrix. AFM of the neat PP was provided as a control sample to verify the integrity of what is observed in the composites containing CNWs. The AFM images of Figure 3-3(b), (c), and (d) corresponded to the SEM images of Figure 3-3(e), (f), and (g). In the AFM images, it was evident that the dispersion of the CNWs were not completely uniform and slight agglomeration of the CNWs had occurred. In the SEM images, the CNW agglomerates appeared as nanosized circular particles because of two possible reasons. The first being that the agglomerates are seen as the cross sections of the CNWs and the second being the actual formation of dried spherical particles as a result of the processing method. The latter reasoning is more likely as it can be explained by the drying of a droplet of CNW
suspension.[42] This is because during melt blending, it was possible for the suspension to break up into droplets from the shear forces and subsequent water removal.

The AFM image of the 2% CNW/MAPP composite did not show any large CNW particles, which suggested a good dispersion but with minimal agglomeration as seen in its SEM image. At 5% CNW loading, a noticeable amount of agglomerates are dispersed throughout the PP matrix, but the size of the agglomerates are still comparable with the agglomerates at 2% CNW loading. In the images of the composites at 10% CNW loading, there was a substantial increase in the size of the agglomerates when compared with the composites at lower CNW loadings, however, dispersion of the agglomerates was maintained.

Between the 10% CNW/MAPP and CNW/PP composites, no significant differences were observed since the dispersion and agglomeration look similar. Moreover, based on the AFM and SEM images, the interfacial interaction between the CNW and PP was difficult to detect due to the limitations of the probe tip size of the AFM and the issues with charging at high magnifications for polymer composites, which are nonconductive, in the SEM. Although a considerable amount of agglomerates were formed, the dispersion of the agglomerates may still serve as an advantage for certain properties. Therefore, the dispersion of the CNWs in the composites is a critical aspect to know as it will be seen the effects it has on the properties addressed in the following sections.

3.2.2 Thermal Properties of CNW/PP Composites

Thermal stabilities of the CNW/PP and CNW/MAPP composites were analyzed using their respective TGA and DSC curves. The onset temperature of degradation was determined using the TA Universal Analysis software. For the analysis of the crystallinity, and melting and crystallization temperatures of the composites, the first heating and cooling curve from the DSC was used for analysis for comparing the materials as processed. The degree of crystallinity of the composites were calculated based on the enthalpy of fusion values obtained from the melting curves of each composition using the TA Universal Analysis software and the following equation:

\[ X_c = \frac{\Delta H_f}{\Delta H_f^0 \cdot W_{PP}} \times 100\% \]  \hspace{1cm} \{1\}
In equation \( \{1\} \), \( X_c \) (\%), \( \Delta H_f \) (J/g), \( W_{PP} \), and \( \Delta H_{f}^{\circ} \) (J/g) are the degree of crystallinity, the enthalpy of fusion of the experimental sample, weight fraction of PP, and the enthalpy of fusion of the 100% crystalline polymer respectively. The enthalpy of fusion of a 100% crystalline polypropylene used in this study was 207 J/g, which was retrieved from the literature.\[93\] Figure 3-4 and Table 3-1 below shows the TGA and DSC curves for analyzing the thermal properties of all the composites.
Figure 3-4 TGA curves for CNW/PP composites (a) and CNW/MAPP composites (b), and heat-cool DSC curves for CNW/PP composites (c) and CNW/MAPP composites (d).

Table 3-1 Thermal properties extracted from TGA and DSC curves.

<table>
<thead>
<tr>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Neat PP</td>
<td>469.37</td>
<td>156.97</td>
<td>109.05</td>
<td>28.79</td>
</tr>
<tr>
<td>1% CNW/PP</td>
<td>481.80</td>
<td>151.67</td>
<td>116.60</td>
<td>37.35</td>
</tr>
<tr>
<td>2% CNW/PP</td>
<td>475.37</td>
<td>151.29</td>
<td>116.59</td>
<td>35.84</td>
</tr>
<tr>
<td>5% CNW/PP</td>
<td>473.10</td>
<td>152.69</td>
<td>116.46</td>
<td>37.96</td>
</tr>
<tr>
<td>10% CNW/PP</td>
<td>471.36</td>
<td>152.70</td>
<td>116.86</td>
<td>39.89</td>
</tr>
<tr>
<td>1% CNW/MAPP</td>
<td>480.80</td>
<td>150.76</td>
<td>115.70</td>
<td>39.01</td>
</tr>
<tr>
<td>2% CNW/MAPP</td>
<td>474.70</td>
<td>151.03</td>
<td>115.66</td>
<td>37.68</td>
</tr>
<tr>
<td>5% CNW/MAPP</td>
<td>472.91</td>
<td>152.94</td>
<td>114.65</td>
<td>37.32</td>
</tr>
<tr>
<td>10% CNW/MAPP</td>
<td>474.19</td>
<td>157.14</td>
<td>114.99</td>
<td>38.77</td>
</tr>
</tbody>
</table>

From the TGA curves, the onset of degradation was at a higher temperature for both the CNW/PP and CNW/MAPP composites in contrast with the neat PP. An increase of up to 12°C
was observed, which may have resulted from the enhanced heat transfer provided by the CNW dispersed within the matrix to help dissipate the heat. This correlated with the rate of degradation that was reduced with the addition of CNW. Therefore, the addition of CNW showed improvements in the thermal stability of the composite, but at CNW loadings greater than 1 wt%, the thermal stability of the composite gradually decreased and approached the thermal degradation properties of neat PP. This was possibly due to agglomeration of CNWs resulting in the dispersion of larger particles, which provided less effective heat dissipation.

Similarly, the crystallization temperature and degree of crystallinity of both the CNW/PP and CNW/MAPP composites were higher than the neat PP. This suggested that the CNWs acted as nucleation sites in promoting crystallization, however, the crystallinity of the composites did not increase after the addition of 1 wt% CNW due to the agglomeration of the CNWs at higher wt%. The ability of fillers to induce crystallization in PP has been shown by past studies through the formation of a transcrysallinity layers at the filler-matrix interface.[94] Since the PP used in this study did not inherently have a high crystallinity, the potential of crystal growth restriction was minimized. Although agglomerates formed at higher wt%, the degree of crystallization still increased because the larger particulates remained as nucleation sites for crystallization. On the other hand, the melting temperature of both the CNW/PP and CNW/MAPP composites decreased when compared to the neat PP. The reason for this is because CNWs can act as impurities in the matrix and allow polymer chains to move more freely, therefore increasing the entropy of fusion of the composite and lowering the melting temperature. Between the CNW/PP and CNW/MAPP composites, no significant differences were observed with the added compatibilizer in terms of the overall thermal properties.

3.2.3 Water Vapor Barrier Properties of CNW/PP Composites

The plots of weight change against time for each set of compositions were generated from the weight measurements gathered and are shown in Figure 3-5(a) and Figure 3-5(b). A linear fit was applied to each set of data and the slope, which represented the rate of water vapor travelling across the film, was obtained for calculations of the WVT and WVP. The equations provided by the ASTM E96 standard to calculate these values are as follows:

\[
WVT = \frac{G}{tA} \quad \{2\}
\]
\[ WVP = \frac{WVT}{S(R_1 - R_2)} \quad \{3\} \]

In equation \{2\}, \( G \) (g) is the weight change, \( t \) (hours) is the time, and \( A \) (m²) is the test area of the specimen. This equation helped determine the rate at which the water vapor was flowing through the sample. In equation \{3\}, \( S \) (Pa) is the saturation vapour pressure at the test temperature, \( R_1 \) is the relative humidity inside the test dish expressed as a fraction, and \( R_2 \) is the relative humidity of the test chamber expressed as a fraction. Similar to equation \{2\}, equation \{3\} quantified the rate of water vapor transmission through the film, but it also considered the pressure difference induced by the temperature and humidity. The water vapor permeance of all the compositions plotted with respect to CNW loading is shown in Figure 3-5.
Figure 3-5 Weight change vs. time curves of CNW/PP (a) and CNW/MAPP (b) composites, and water vapor permeance vs. CNW loading of CNW/PP and CNW/MAPP composites (c).
Based on the water loss curves of both CNW/PP and CNW/MAPP composites, the addition of chitin was observed to decrease the amount of water loss over time. Furthermore, the CNW/MAPP composites showed a smaller decrease overall when compared to the CNW/PP composites. Upon examination of the change in WVP with chitin loading, it was found that the minimum WVP occurred at low weight percentages of CNW and began to increase at higher weight percentages. This was consistent with a previous study that had observed a similar trend in WVP of chitin nanoparticles in starch where the addition of chitin nanoparticles showed a decrease in WVP at low loading and then began to increase, which was explained due to the formation of agglomerates.[28] The optimal WVP of the composites were at 1 and 2% CNW loading for CNW/PP and CNW/MAPP respectively. This can be explained by the dispersion of CNW over a large surface area in the PP impeding the diffusion of water vapor across the film. Additionally, the effects of compatibilizer was not as pronounced at lower CNW loadings whereas the decrease was more significant at higher CNW loadings, which suggested that the compatibilizer was more effective at higher CNW loadings.

From the results obtained, the three main factors that could have contributed to the decrease in WVP of the composites includes the effects of the filler, crystallinity, and compatibilizer. Firstly, the inclusion of the CNW in PP created a more tortuous path for the water vapour to pass through. At higher CNW loadings, the WVP did not continue to reduce due to larger agglomerates of the CNW as observed from the SEM and AFM images shown previously. This lowered the amount of particles, which blocked the paths for water vapor to pass through. Furthermore, CNW is hydrophilic, therefore it was possible for the CNWs entrapped in the matrix to absorb the water vapour as it tried to pass through the composite film. As a result, the rate of diffusion of the water vapour through the composite was reduced. Additionally, the CNW in the PP influenced the crystallization of the polymer causing an increase in the crystallinity of the composite as shown from the DSC data earlier. As mentioned earlier, due to the morphology of crystalline domains, small molecules generally cannot penetrate through them.[47] Since the degree of crystallinity of the composites at higher CNW loading were comparable to the lower CNW loading composites because of the CNW particles inducing crystallization, therefore the WVP remained below the neat PP. Lastly, the addition of the compatibilizer had two possible effects to lower the WVP of the composites. The partial hydrophilic nature of the compatibilizer could have interacted with the water to slow its diffusion pass the composite. Moreover, the
The purpose of the compatibilizer was to help enhance the interaction between the filler and the matrix since poor interaction can lead to interfacial gaps resulting in an increase in WVP. Therefore the compatibilizer indicated improvements in CNW and PP interaction as the WVP of the CNW/MAPP composites were lower than the CNW/PP composites.

3.2.4 Mechanical Properties of CNW/PP Composites

Tensile properties of the CNW/PP and CNW/MAPP composites in terms of elastic modulus, ultimate tensile strength, and elongation strain at break were extracted and plotted against their respective compositions in Figure 3-6.
Figure 3-6 Elastic modulus (a), ultimate tensile strength (b), and elongation strain at break (c) of CNW/PP and CNW/MAPP composites at 1, 2, 5, and 10 wt% CNW loading.
The elastic modulus of both the CNW/PP and CNW/MAPP composites showed an improvement compared to the neat PP. This increase in elastic modulus was expected since it typically improves with the incorporation of rigid fillers in a polymer matrix.[3, 4, 12, 29] The optimal compositions were found to be at 2 and 5 wt% CNW loading for the CNW/PP and CNW/MAPP respectively as an increase of up to 20% in the stiffness was observed. Similarly, the ultimate tensile strength of the CNW/PP and CNW/MAPP composites also showed an increase compared to the neat PP and had the same optimal compositions as the elastic modulus. An increase of 17% in the ultimate tensile strength was observed. The increase in mechanical properties suggested that the CNW showed some reinforcement of the PP from its ability to take on the stress transferred from the matrix. Furthermore, it was possible for transcrystallinity to occur at the CNW-PP interface, which causes crystals to grow perpendicular to the fiber axis, and increase its interfacial strength.[94] It was also suspected that the partially well dispersed CNWs helped strengthen the mechanical properties by forming a stress distribution throughout the composite opposed to one localized area. The low standard deviation within the values for each composition further supported the uniformity of the dispersion of the CNWs throughout the matrix. Moreover, the purpose of adding a compatibilizer was to improve the bonding between CNW and PP and the dispersion of CNW in PP. However, the use of the compatibilizer did not show effective reinforcement until 5 wt% loading, where the elastic modulus and tensile strength surpassed the composite without compatibilizer. At lower CNW loading, the use of compatibilizer seemed to hinder opposed to enhance the mechanical properties of the composite. Additionally, at 10 wt% CNW loading, the elastic modulus and ultimate tensile strength began to greatly decrease due to a rise in agglomeration and agglomerate size acting as stress concentrators and deteriorating the overall mechanical properties of the composites. This was consistent with many other polymer composites studied previously.[21, 29, 30, 50] Although the elastic modulus and ultimate tensile strength at 10 wt% CNW was not at high as the optimal values, the mechanical properties were still comparable to the neat PP possibly due to the partially well dispersed agglomerates.

As for the elongation strain at break, there was a dramatic reduction upon the slightest addition of CNW for both the CNW/PP and CNW/MAPP composites. They continued to decrease with further CNW addition because the composite became rigid and started behaving like a brittle material. There are two different phenomena that can explain this trend. At low CNW loading,
the reinforcing fillers restrained the movement of the matrix causing limited elongation at break. Alternatively, at high CNW loading, the introduction of larger agglomerates created localized stress concentration within the composite, which caused the composite to fail early without exhibiting much reinforcement. Further analysis of the composites was done using a rheological test in the next section to verify some of the behaviors exhibited by the composites.

3.2.5 Rheological Properties of CNW/PP Composites

A uniaxial extension test was performed on the composites to determine their elongation viscosities, which is defined as the extensional stress over the strain rate. The rheological properties of the CNW/PP and CNW/MAPP composites based on elongation viscosity are presented in Figure 3-7.
The extensional viscosity of the CNW/PP composites did not show much change from one composition to another since it is suspected that there were minimal interactions between the hydrophilic CNW and hydrophobic PP. In contrast, extensional viscosity of the CNW/MAPP composites increased with increasing CNW loading. This meant that a higher stress was required for deformation. This indicated reinforcement between the CNWs and PP matrix because of the enhanced interfacial bonding between them with help of the compatibilizer. As a result, the composite showed resistance against flow of the when the strain was applied. Similar to a previous study, comparisons between composites with and without compatibilizers were investigated using a rheological test. No improvements were observed in its rheological properties without the compatibilizer, whereas it improved with increasing filler content of the compatibilized composites. The results from the extensional viscosity test is useful for future development in identifying the optimal processing conditions of the composites. More specifically, it is important for the processing of the composites using fiber spinning, film blowing, or blow molding.

Figure 3-7 Extensional viscosity vs. elongation time curves of CNW/PP (a) and CNW/MAPP (b) composites.
3.3 Summary

In this section, the morphological, thermal, barrier, mechanical, and rheological properties of melt blended CNW/PP and CNW/MAPP composites with CNW loading ranging from 1 to 10 wt% have been investigated. Results have shown the potential of using CNW to replace current inorganic fillers in polymers for packaging applications. These composites are suitable for environmentally friendly industrial packaging applications as proven by its improved thermal stability, water barrier properties, and strength when compared to neat PP. The significant enhancement in the material properties of the composites were supported by the partially well dispersion of CNWs in the PP matrix observed by AFM and SEM and the reinforcement of the CNW and PP bonding through the use of a compatibilizer. Additionally, the CNWs had a positive impact on the degree of crystallinity of the composites, which greatly improved its water vapor barrier properties. Based on the water vapor transmission test results, it was proposed that the water vapor barrier properties of the composites can be tailored via adjusting the CNW loading in the polymer. The mechanical properties of the composites at their optimal compositions exhibited a significant improvement in its elastic modulus and ultimate tensile strength. This was further backed by the rheological test, which revealed an increase in the extensional viscosity with the addition of CNW for the compatibilized composites. It was evident that the addition of CNW and compatibilizer helped strengthen the composite. Although agglomeration was observed at higher CNW loading, the dispersion of the agglomerates. It is possible that further processing, such as a dilution process, can help to break down the agglomerates. Also, since melt compounding is a scalable process, therefore it can be easily incorporated into an industrial scale production. Lastly, through the knowledge obtained from this study, further optimization studies of the composites can be performed to maximize their respective properties for tailoring towards specific applications.
Chapter 4  Chitin Nanowhisker/High Density Polyethylene Composites

In this chapter, melt blended chitin nanowhisker (CNW)/high density polyethylene (HDPE) composites were characterized for their morphological, thermal, barrier, mechanical, and rheological properties. Moreover, the effects of various CNW loadings and the addition of a maleated polyethylene compatibilizer on these properties were investigated.

4.1 Materials and Methods for Fabrication of CNW/HDPE Composites

4.1.1 Materials for CNW/HDPE Composite Fabrication

A homopolymer HDPE (ExxonMobil™ HDPE HD 6908) with a density and melt index of 0.965 g·cm⁻³ and 8.2 g/10 min respectively was used as the matrix. CNW provided by BOCO Technology Inc. with an aspect ratio (L/W) and density of approximately 20-50 and 1.45 g·cm⁻³ respectively was used as the filler. Lastly, a maleic anhydride grafted polyethylene (Westlake Epolene® C-26) with a density and melt index of 0.92g·cm⁻³ and 8 g/10 min respectively was used as the coupling agent for the CNW and HDPE for this study.

4.1.2 Fabrication of CNW/HDPE Composites

CNW/HDPE composites were melt blended using a co-rotating twin screw micro compounder (DSM Xplore® MC 15) at various compositions. The HDPE, MAPE, and CNWs were fed into the compounder, which was operating at a temperature and screw speed of 170°C and 200 rpm respectively. The two main sets of compositions prepared consists of CNW/HDPE composites with and without the addition of a compatibilizer. Furthermore, the two types of composites for with and without compatibilizer are denoted by CNW/HDPE and CNW/MAPE respectively following their weight percentage CNW loading. Within those sets of compositions, a range of CNW loading between 1 to 10 wt% was used.

The composites extruded from melt blending were pelletized and processed further through compression molding using a hydraulic hot press (Carver, Inc.) or injection molding using a micro injection molding machine (DSM Xplore® IM 5.5). Specimens for water vapor
transmission test and rheological testing were prepared using compression molding, and the samples for mechanical testing was prepared using injection molding. For compression molding, molds containing the specified geometries of the specimens were compressed under a temperature and pressure of 180°C and 100 psi respectively and subsequently quenched. The films for water barrier testing were less than 200 µm in thickness and the dimensions of the rheological specimens were a disk with a diameter and thickness of 25 mm and 1.1 mm respectively. Moreover, for injection molding, the samples were formed by molten material at a temperature of 180°C and injected into a mold at a pressure of 100 psi.

4.1.3 Characterization of CNW/HDPE Composites

4.1.3.1 Microscopy Analysis

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used for cross sectional analysis of the composites for observing its morphology and dispersion of CNWs in the HDPE matrix. The samples for AFM (Bruker) were prepared using a microtome to flatten the cross section prior to imaging. On the other hand, SEM was performed using the Quanta FEG 250 ESEM (FEITM) and the samples were prepared by nitrogen fracturing and gold sputter coated prior to imaging. The coating was required for dissipating the charge build up at the surface during imaging.

4.1.3.2 Thermal Testing

TGA and DSC were used for the thermal analysis of HDPE and CNW/HDPE composites. The TGA Q50 (TA Instruments) was used under nitrogen atmosphere with a temperature ramp of 20°C/min from room temperature (25°C) to 600°C for examining thermal stabilities of the composites. Moreover, the DSC Q2000 (TA Instruments) was used under nitrogen atmosphere with a heat-cool cycle between room temperature (25°C) and 200°C at a heating and cooling rate of 10°C/min for determining the enthalpy of fusion, and melting and crystallization temperature of the composites.

4.1.3.3 Water Vapor Barrier Testing

The water vapor transmission rate of the HDPE, CNW/HDPE and CNW/MAPE composite films were determined by the water method from ASTM E96. Three film samples of each composition were prepared and mounted onto test dishes containing a water level of approximately 1.9 cm
away from the film. The test dishes were placed in an incubator throughout the test at a
controlled temperature and humidity of 50°C and 0% RH respectively. Weight changes of the
test dishes were monitored over a period of one to three weeks until a steady weight loss was
observed. From the constant weight change, the WVT was obtained to calculate for the WVP.

4.1.3.4 Mechanical Testing

Tensile testing of the composites was performed following the ASTM D638 standard through
using Type IV specimens on the Microtester 5848 (Instron) machine. An average from four to
six specimens for each composition was tested. Stress-strain curves were obtained from the
testing and were further analyzed to determine the elastic modulus, ultimate tensile strength, and
elongation strain at break.

4.1.3.5 Rheological Testing

Rheological measurements were gathered using the ARES rheometer (TA instruments) with a
parallel plate geometry. A strain sweep was first tested on the HDPE at a temperature, frequency,
and strain rate range of 160°C, 0.99 rad/s, and 0.01 to 100% respectively. This was used to
determine the strain rate at which the material was within its linear viscoelastic region and was
evaluated to be 6%. The dynamic frequency sweep test was then performed on all the composites
at a temperature, strain rate, and frequency range of 160°C, 6%, and 0.1 to 200 rad/s
respectively. An average of three specimens for each composition were tested.

4.2 Results and Discussion of CNW/HDPE Composites

4.2.1 SEM and AFM of CNW/HDPE Composites

Morphology of the CNW/HDPE and CNW/MAPE composites were analyzed using the SEM and
AFM images depicted in Figure 4-1. More specifically, the focus was to examine the dispersion
of CNWs in the HDPE matrix. The use of AFM helped confirm the CNW dispersion observed in
the SEM images through mapping the modulus at a constant force applied over a cross sectional
area of the composites.
Figure 4-1 AFM and SEM images of the cross sections of neat HDPE (a), 2% CNW/MAPE (b and e), 5% CNW/MAPE (c and f), 10% CNW/MAPE (d and g), and 10% CNW/HDPE (h).

The AFM images of the composites provided are accommodated by their respective SEM images. In the AFM images, the differences in modulus is represented by the dark and light colors showing low and high modulus respectively. Although no agglomerates were detected in the AFM image of the 2% CNW/MAPE composite, the SEM image presented dispersion of CNW agglomerates with sizes ranging from approximately 0.3 to 1 µm in diameter. This suggested that the CNW was only partially dispersed in the HDPE matrix and the shear forces from melt compounding did not further break down the agglomerates or prevent agglomeration from occurring. Furthermore, the SEM image of the 5% CNW/MAPE composite also showed more dispersed CNW agglomerates of a similar size as the ones found in 2% CNW/MAPE.

At 10% CNW loading, it was evident from the AFM image that the CNWs had formed agglomerates in the HDPE matrix. Furthermore, the SEM shows clusters of agglomerates scattered in the matrix. It appeared that in the 10% CNW/HDPE composite that there were not many observable CNW agglomerates, but it may have been caused by the inconsistent sizes of agglomerates, as seen in 2% CNW/MAPE, in randomly dispersed areas. Lastly, the interface between the CNW and HDPE could not be resolved due to the limitations of the resolution for
AFM and SEM. Therefore the CNW-HDPE compatibility was not evaluated between the CNW/HDPE and CNW/MAPE composites based on the AFM and SEM images.

4.2.2 TGA and DSC of CNW/HDPE Composites

The thermal properties of CNW/HDPE and CNW/MAPE composites were examined the curves attained from TGA and DSC. All the properties were determined and extracted using the TA Universal Analysis software. These properties included the onset temperature of degradation, enthalpy of fusion, and melting and crystallization temperatures. Additionally, the enthalpy of fusion obtained from the first melting peak of the first DSC heating curve was used for further calculation of the degree of crystallinity. The crystallinity was calculated using equation \{3\} from section 3.2.2 and in combination with the enthalpy of fusion of 293 J/g of a 100% crystalline polyethylene, which was obtained from the literature.\[93\] The TGA and DSC curves used for analysis are presented below in Figure 4-2 and Table 4-1.
Figure 4-2 TGA curves for CNW/HDPE composites (a) and CNW/MAPE composites (b), and heat-cool DSC curves for CNW/HDPE composites (c) and CNW/MAPE composites (d).

Table 4-1 Thermal properties of all the compositions obtained from the TGA and DSC curves.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Neat HDPE</td>
<td>485.58</td>
<td>135.85</td>
<td>118.41</td>
<td>84.44</td>
</tr>
<tr>
<td>1% CNW/HDPE</td>
<td>487.19</td>
<td>131.51</td>
<td>120.38</td>
<td>67.32</td>
</tr>
<tr>
<td>2% CNW/HDPE</td>
<td>488.79</td>
<td>133.21</td>
<td>119.56</td>
<td>65.26</td>
</tr>
<tr>
<td>5% CNW/HDPE</td>
<td>472.37</td>
<td>132.84</td>
<td>120.63</td>
<td>62.33</td>
</tr>
<tr>
<td>10% CNW/HDPE</td>
<td>486.02</td>
<td>133.64</td>
<td>120.39</td>
<td>67.27</td>
</tr>
<tr>
<td>1% CNW/MAPE</td>
<td>485.65</td>
<td>136.09</td>
<td>118.14</td>
<td>64.26</td>
</tr>
<tr>
<td>2% CNW/MAPE</td>
<td>485.07</td>
<td>132.11</td>
<td>120.35</td>
<td>60.44</td>
</tr>
<tr>
<td>5% CNW/MAPE</td>
<td>485.14</td>
<td>132.84</td>
<td>121.07</td>
<td>61.68</td>
</tr>
<tr>
<td>10% CNW/MAPE</td>
<td>483.66</td>
<td>132.5</td>
<td>122.24</td>
<td>67.35</td>
</tr>
</tbody>
</table>
The onset of degradation temperature between the pure HDPE, CNW/HDPE, and CNW/MAPE composites did not show significant changes. For the CNW/HDPE composites, the degradation temperature increased between 1 to 3°C by adding CNWs with the exception of a discrepancy at 5 wt% CNW/HDPE. Although there was a slight increase in the degradation temperature, a greater percentage weight drop was observed from the onset of degradation temperature until about 485°C when compared to neat HDPE. The weight drop was more significant at higher CNW loading. Beyond 485°C, the degradation rate reduced with respect to the neat HDPE. In contrast, when the coupling agent was added, the degradation temperature proceeded to decrease with the addition of CNWs. Furthermore, the effect of degradation rate for the CNW/MAPE composites showed the same trend as the CNW/HDPE composites, but not as prominent. This trend can be explained by the CNWs being less thermally stable, which was also observed from previous studies.[29, 30]

A decrease in the melting temperature was shown with by adding CNWs for both the CNW/HDPE and CNW/MAPE composites. The introduction of CNW into the matrix disturbed the uniformity of the polymer chains in the matrix and causing an increase in entropy resulting in a lower melting temperature. On the other hand, the crystallization temperature increased with CNW loading for both the composites with and without compatibilizer, which was expected since CNWs can act as promoters for crystal nucleation. However, the degree of crystallinities of all the compositions containing CNWs showed down to a 30% decrease when compared to the neat HDPE. One of the possible reasons for this occurrence is the restricted crystal growth caused by the enhanced filler-matrix interaction with a compatibilizer.[70] Moreover, due to the inherently high crystallinity of HDPE, the addition of fillers can disrupt the uniformity of the crystalline structures within the polymer.[75] At higher CNW loadings, the further reduction in degree of crystallinity resulted from the increased amount of CNW and larger CNW agglomerates impeding crystal growth. The addition of compatibilizer into the matrix did not have a great impact on the thermal properties of the composites.

4.2.3 Water Vapor Transmission Test of CNW/HDPE Composites

The weight change, which was based on water loss, of the test dishes plotted over time for the various CNW/HDPE and CNW/MAPE compositions are shown in Figure 4-3(a) and Figure 4-3(b). Comparisons were made with respect to neat HDPE, and CNW loadings and
compatibilizer effects. The equations \(2\) and \(3\) from section 3.2.3 were used to calculate the WVT and WVP. The WVP of all the compositions plotted with respect to CNW loading is shown in Figure 4-3(c).

(a)

(b)
Figure 4-3 Weight change vs. time curves of CNW/HDPE (a) and CNW/MAPE (b) composites, and WVP vs. CNW loading of CNW/HDPE and CNW/MAPE composites.

The slope of the linear regressions from the water loss to time plots show the rate of water diffusion through each composite film. A steeper slope indicates a higher water transmission through the film and vice versa. In many cases, the incorporation of fillers in a polymer matrix helps to decrease water vapor permeance since it promotes crystallinity and creates a more tortuous path for the water vapor molecules.[40] However, even though the CNWs showed dispersion within the HDPE matrix, an increase in WVP was observed with the addition of CNWs. One main reason for this trend was the decrease in the crystallinities of the composites, which were determined earlier by DSC. The major drop in crystallinity when the CNWs were added to the HDPE allowed for more amorphous regions for the water molecules to easily travel through. Despite a decrease in crystallinity of up to 25%, the water vapor permeance at low CNW loadings did not differ by too much when compared to neat HDPE. This signified a countering effect of the CNWs helping to block the path of the water vapor. Another indication of this effect was at higher CNW loadings, where a slight decrease in WVP was observed from 5% to 10% CNW loading. This same trend was observed for the CNW/MAPE composites.
It was proposed that the addition of compatibilizer should help reduce the water vapor permeance by enhancing the filler-matrix interaction and minimizing interfacial gaps, which can in turn allow water to diffuse through easier. Nevertheless, the water vapor permeance of the CNW/MAPE composites showed a an even greater increase than the CNW/HDPE composites. On top of the reduction in crystallinity from the CNWs, a further decrease in crystallinity was suspected as a result of the compatibilizer, which was explained in the previous section.

Aside from the crystallinity of the composites, the fillers and compatibilizer themselves have possible effects on the WVP. Since the CNWs used were water sensitive and can absorb water, this could have helped to slow down the water loss as the water vapor passed through the film. This was supported by the composites at the highest CNW loading in this study, but the WVP of these composites were still higher than the neat HDPE. Moreover, the compatibilizer also has hydrophilic properties, so it could have contributed to the reducing the mobility of the water. Lastly, the compatibilizer should have improved the interaction between the CNWs and the HDPE matrix in order to prevent voids at the interface to decrease water transport. Although these factors could have potentially minimized the WVP, they were not sufficient enough to overcome the crystallinity effects.

4.2.4 Tensile Test of CNW/HDPE Composites

The elastic modulus, ultimate tensile strength, and elongation strain at break of the CNW/HDPE and CNW/MAPE composites at different CNW loading were extracted from stress-strain curves and are displayed in Figure 4-4.
Figure 4-4 Tensile properties of the CNW/HDPE and CNW/MAPE composites based on elastic modulus (a), ultimate tensile strength (b), and elongation strain at break (c).

When adding a rigid filler into a polymer matrix, the elastic modulus usually increases since the stiff filler has a higher modulus itself.\cite{96} So as expected, the elastic modulus increase up to 20\% and 15\% by adding CNWs for both the CNW/HDPE and CNW/MAPE composites respectively compared to the neat HDPE. Moreover, the partially dispersed CNWs observe from the cross sectional images of the composites contributed to the increase in elastic modulus. The maximum elastic modulus for both sets of composites occurred at 10 wt\%, which was the maximum CNW loading in this study. As a result, an even higher elastic modulus could potentially be found with CNW loading greater than 10 wt\%. The addition of a compatibilizer to the composite did not show enhancements in its elastic modulus when compared to the composites without the compatibilizer. This may have been a caused by the poor mechanical properties of the compatibilizer that had transferred into the composite. Therefore the compatibilizing effects was not as pronounced.

On the other hand, the ultimate tensile strength of both sets of composites decreased with the addition of CNW except at 10 wt\% CNW loading when compared with neat HDPE. Two
contributing factors for this decrease can be explained by the lack of reinforcement between the CNW and the HDPE, and the density of the composites. The former is relatively straightforward since the absence of filler-matrix interaction can prevent stress transfer from the HDPE to CNW and result in interfacial gaps causing stress concentrations for early failure. As for the former reasoning, although not investigated in this study, the density of the composites could have caused the reduction in ultimate tensile strength. This was as a result of the drop in density of the composites due to the lowering of the degree of crystallinity with the addition of CNWs and the addition of a compatibilizer with a lower density. Since crystallinity is related to density because polymer chains in the crystalline region can pack better than in the amorphous region, therefore it was predicted that the density had decreased as well, which can affect the decrease in ultimate tensile strength. However, the effects of compatibilizer on the reinforcement of the composite was observed as the ultimate tensile strength of the CNW/MAPE composites were slightly higher than the CNW/HDPE composites.

A gradual reduction in the elongation strain at break was seen with the CNW/HDPE composites as the amount of CNW loading increased. The elongation strain at break was also continuously lower than that of neat HDPE. In contrast, the addition of the compatibilizer showed a higher elongation strain at break at 1 and 2 wt% CNW loadings and then proceeded to decrease with increasing CNW loadings with respect to neat HDPE. Overall, the CNW/MAPE composites showed a greater elongation strain at break compared to CNW/HDPE, which suggested that the compatibilizer exhibited a plasticizing effect enabling the composite to become more flexible. This also supported the slight decrease observed in elastic modulus since the reduction in crystallinity allows for the ease of access of diluents into the amorphous regions to lower the stiffness of the composites.

4.2.5 Rheology Test of CNW/HDPE Composites

Rheological properties of the CNW/HDPE and CNW/MAPE composites were evaluated using a parallel plate geometry with an applied shear force over a range of frequencies. The storage modulus and complex viscosity results are shown in Figure 4-5.
(a) Storage Modulus [Pa] vs. Frequency [rad/s] for HDPE, 1% CNW/HDPE, 2% CNW/HDPE, 5% CNW/HDPE, and 10% CNW/HDPE.

(b) Storage Modulus [Pa] vs. Frequency [rad/s] for HDPE, 1% CNW/MAPE, 2% CNW/MAPE, 5% CNW/MAPE, and 10% CNW/MAPE.
Figure 4-5 Storage modulus and complex viscosity of CNW/HDPE (a and c) and CNW/MAPE (b and d) composites with respect to frequency.
In theory, the reinforcing effect of fillers in a polymer matrix should reveal an increase in storage modulus and complex viscosity especially at low frequencies.[97] This is because the dependence of these properties at low frequencies decline as the compatibility between the filler and matrix improve. Therefore, the lack of improvement in the storage modulus of the CNW/HDPE was expected since CNW is not compatible with each other due to their differences in polarity and the ultimate tensile strength results from the previous section did not increase. Further analysis of the CNW/MAPE composites showed no improvements in the storage modulus either. The reason for this was due to the inefficiency of the compatibilizer in enhancing the CNW-HDPE interaction and the compatibilizer exhibiting a plasticizing behavior from the mechanical properties. Both of these factors will cause a decrease in the storage modulus because it enables polymer chains to flow more freely past each other. This was reminiscent of the behavior observed in previous studies on CNW/PLA composites.[29, 30]

Similar to the storage modulus, the complex viscosity is expected to increase with filler addition given that successful enhancement of the filler and polymer matrix interaction is achieved. However, for the same reasons as the minor changes in storage modulus, the complex viscosity did not differ by a lot either. Although a small increase was observed for the CNW/HDPE composites, it was suspected as a result of the dispersion of the small CNW agglomerates in the HDPE. The CNW/MAPE composites had a further reduction in the complex viscosity, which was believed to be as a result of the compatibilizer. Overall, the rheological measurements were consistent with the observed mechanical properties of the composites.

4.3 Summary

This paper examined the morphological, thermal, water barrier, mechanical, and rheological properties of CNW/HDPE and CNW/MAPE composites at different CNW loadings processed through melt compounding. The purpose was to investigate the possibility in using CNW/HDPE composites to outperform existing solutions of composites of nanoclay and carbon nanofillers in HDPE for mainly mechanical and water barrier properties. The addition of CNW promoted crystal nucleation and increased the crystallization temperature, but decreased in melting temperature and caused the composite to become less thermally stable. Despite an observable dispersion of CNWs in HDPE and increase in elastic modulus, the compatibility between the filler and matrix remained an issue and caused a drop in ultimate tensile strength and water vapor
resistance. This was verified by the storage modulus and complex viscosity of the composites, which were determined to have a similar trend compared to neat HDPE over a range of frequencies, signifying poor compatibility between the CNW and HDPE. Furthermore, using CNW in HDPE restricted the crystal growth in the composites and reduced its crystallinity, which affected the ability of the composite to resist water diffusion. At low CNW loading, the crystallinity of the composite seem to have countered the effects of the fillers for the water barrier properties. On the other hand, at higher CNW loading, the effects of the fillers on the improving water barrier properties became more prominent. Based on the results from this study, it is evident that further investigation is required in optimizing processing methods to minimize CNW agglomeration and maintain or increase the crystallinity of the HDPE composites. Considerations need to be taken to examine the water absorption and oxygen barrier properties of the composites.
Chapter 5  Chitin Nanowhisker/Polyolefin Composite Masterbatches

This study uses a two step approach in processing CNW/polymer composites to investigate the masterbatch dilution of these composites in two different polymer systems, which includes PP and HDPE. Examination of their morphological, thermal, water barrier, mechanical, and rheological properties will help evaluate its the feasibility in producing diluted composites with enhanced properties for industrial scale processing. Not only can chitin and its derivatives substitute the use of inorganic fillers, it also has the edge over cellulose in potentially replacing hazardous metallic fillers used in medical applications for antimicrobial properties.[98] Moreover, water barrier is an integral material property for packaging applications that many studies lack to examine.

5.1 Materials and Methods for Fabrication of Masterbatch and Diluted CNW/PP and CNW/HDPE Composites

5.1.1 Materials for Fabrication of CNW/PP and CNW/HDPE Composites

The CNW provided by BOCO Technology Inc. had an aspect ratio (L/W) and density of approximately 20-50 and 1.45 g·cm⁻³ respectively. It was used as the filler for preparing the composite masterbatch along with homopolymers of PP (ExxonMobil Achieve™ 3854) and HDPE (ExxonMobil™ HDPE HD 6908), and their respective compatibilizers of maleated PP (Eastman™ G-3003 Polymer) and maleated HDPE (Westlake Epolene® C-26). The homopolymers of PP and HDPE had densities of 0.9 g·cm⁻³ and 0.965 g·cm⁻³ respectively.

5.1.2 Preparation of Masterbatch and Dilution of CNW/PP and CNW/HDPE Composites

CNW/PP and CNW/HDPE composites were prepared by a two stage melt compounding process with a co-rotating twin screw micro compounder (DSM Xplore® MC 15). In the first stage, two sets of masterbatches, with and without compatibilizer, of the PP and HDPE composites at a 10 wt% CNW loading were processed in the compounder operating at 170°C and 200 rpm. The masterbatches were then processed again under the same conditions but diluted using their
respective base polymers to produce composites containing 1 and 2 wt% CNW loading. The four sets of composites investigated in this study are denoted by CNW/PP and CNW/MAPP for the PP composites, and CNW/HDPE and CNW/MAPE for the HDPE composites.

The composites were further processed using compression molding and injection molding to prepare specimens for testing. A hydraulic hot press (Carver, Inc.) operating at 180°C and 1000 psi was used to create composite films with less than 200 µm in thickness for water barrier testing, and disks with 25 mm in diameter and 1.1 mm in thickness for rheological testing. On the other hand a micro injection molding machine (DSM Xplore® IM 5.5) operating at 180°C and 100 psi was used to produce type IV tensile testing specimens for mechanical testing.

5.1.3 Characterization of Masterbatch and Diluted CNW/PP and CNW/HDPE Composites

5.1.3.1 Morphology

Analysis of the cross sectional morphology of the masterbatch and diluted CNW/PP and CNW/HDPE composites were performed by scanning electron microscopy (SEM) using the Quanta FEG 250 ESEM (FEITM). The samples for imaging were prepared by nitrogen fracturing and gold sputtering to prevent the sample from charging and being damaged from the electron beam.

5.1.3.2 Thermal Behavior

The thermal degradation, crystallization, and melting temperature of the diluted CNW/PP and CNW/HDPE composites were determined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA Q50 (TA Instruments) was used for thermal degradation analysis under nitrogen conditions at a temperature ramp of 20°C/min. from room temperature (25°C) to 600°C. The DSC Q2000 (TA Instruments) was used for melting and crystallization analysis under nitrogen conditions through a heat-cool cycle between room temperature (25°C) to 200°C at a rate of 10°C/min..

5.1.3.3 Water Vapor Barrier

Diluted CNW/PP and CNW/HDPE composite films prepared from compression molding were mounted onto a test setup, which contained water with a fixed initial height relative to the film.
The test setups were prepared based on the water method stated in the ASTM E96 standard and for this study were kept in a Forma™ Series II Water Jacket CO₂ incubator (Thermo Scientific™) under constant temperature and humidity conditions of 50°C and 0% RH respectively. They were also weighed at least 7 times over a period of one to two and a half weeks to record its changes in weight. An average of three films for each composition were taken into account to ensure consistency of the results.

5.1.3.4 Mechanical Behavior

Mechanical properties of the composites were measured through uniaxial tensile testing using the Microtester 5848 (Instron) machine to obtain stress-strain curves. The composite samples were prepared by injection molding to create Type IV specimens specified by ASTM D638 standards. Six specimens for each composition were tested and their ultimate tensile strengths, elastic moduli, and elongation strains at break were averaged for analysis.

5.1.3.5 Rheological Behavior

Rheological properties, including storage modulus and complex viscosity, were determined using a parallel plate geometry fixture for the ARES rheometer (TA instruments). In making sure that the tests were performed within the linear viscoelastic region of the composites, an initial strain sweep test was ran to obtain a proper strain rate to be used for running the dynamic frequency sweep tests. Three samples for all the compositions were used to carry out the dynamic frequency sweep tests with the operating temperature, strain rate, and frequency range of 160°C, 6%, and 0.1 to 200 rad/s respectively.

5.2 Results and Discussion of Masterbatch and Diluted CNW/PP and CNW/HDPE Composites

5.2.1 SEM Morphology of Masterbatch and Diluted CNW/PP and CNW/HDPE Composites

Cross sections of the masterbatch and diluted CNW/PP and CNW/HDPE composites taken from SEM are shown below in Figure 5-1. The morphology and CNW dispersion in the polymer matrices can be observed from these images.
Figure 5-1 SEM images of 10% CNW/MAPP (a), 2% diluted CNW/MAPP (b and c), 10% CNW/HDPE (d), and 2% diluted CNW/MAPE (e and f) composites.

A well CNW dispersion was observed in the 10% CNW/MAPP masterbatch but with notable agglomeration. After the dilution process, the size of the agglomerates did not reduce in size as shown in the morphology of the 2% diluted CNW/MAPP composites in Figure 5-1(b). Furthermore, a closer magnification of the 2% diluted CNW/MAPP composite revealed the existence of CNW agglomerates up to the size of 1 μm as shown in Figure 5-1(c). Operating at a faster screw speed could potentially reduce the size of the agglomerates as identified by a previous study, but the high shear can also cause degradation of the CNWs.[78] Although, the CNW agglomerates are shown to be relatively well dispersed in the PP matrix, it was not representative of the bulk morphology of the material as localized dispersion of the CNWs was observed. This could have been as a result of reduced interaction between the slight hydrophilic nature of CNW/MAPP masterbatch not being able to well disperse within the hydrophobic PP matrix.[80]

In contrast, a well dispersion of much smaller agglomerates were seen in the 10% CNW/HDPE masterbatch. Moreover, the relative sizes of the agglomerates were also retained after the dilution process as shown in Figure 5-1(f and g). The average sizes of the agglomerates were identified to range from 30 to 100 nm. Since the diameter of the CNWs are in the range of 10 to 20 nm, it was possible that some of the particles observed in the SEM images are cross sections of the CNWs. It was also observed in Figure 5-1(g) that there are regions where there were
higher densities of CNWs, so the dispersion of the CNWs were not uniform throughout the whole matrix as explained previously with the diluted CNW/MAPP composites.

5.2.2 TGA and DSC of Diluted CNW/PP and CNW/HDPE Composites

TGA and DSC curves obtained from thermal testing were analyzed using the TA Universal Analysis software and are shown in Figure 5-2. The software helped determine the onset temperature of thermal degradation, crystallization temperature, and melting temperature of the diluted CNW/PP and CNW/HDPE composites. From the first DSC heating curve, the enthalpy of fusion measured by the software was attained for the further calculation of the degree of crystallinity of the composites using equation {1} from section 3.2.2.
(b) Weight Change [%] vs Temperature [°C]

- Neat HDPE
- 1% Diluted CNW/HDPE
- 2% Diluted CNW/HDPE
- 1% Diluted CNW/MAPE
- 2% Diluted CNW/MAPE

(c) Heat Flow [W/g], Exo Up vs Temperature [°C]

- Neat PP
- 1% Diluted CNW/PP
- 2% Diluted CNW/PP
- 1% Diluted CNW/MAPP
- 2% Diluted CNW/MAPP
Figure 5-2 TGA curves for CNW/PP composites (a) and CNW/MAPP composites (b), and heat-cool DSC curves for CNW/PP composites (c) and CNW/MAPP composites (d).

Table 5-1 Thermal properties extracted from the TGA and DSC curves.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Neat PP</td>
<td>469.37</td>
<td>156.97</td>
<td>109.05</td>
<td>28.79</td>
</tr>
<tr>
<td>1% Diluted CNW/PP</td>
<td>481.80</td>
<td>151.55</td>
<td>113.86</td>
<td>39.93</td>
</tr>
<tr>
<td>2% Diluted CNW/PP</td>
<td>477.61</td>
<td>152.46</td>
<td>112.68</td>
<td>39.94</td>
</tr>
<tr>
<td>1% Diluted CNW/MAPP</td>
<td>480.80</td>
<td>151.56</td>
<td>117.42</td>
<td>39.26</td>
</tr>
<tr>
<td>2% Diluted CNW/MAPP</td>
<td>477.57</td>
<td>150.55</td>
<td>114.02</td>
<td>40.68</td>
</tr>
<tr>
<td>Neat HDPE</td>
<td>485.58</td>
<td>135.85</td>
<td>118.41</td>
<td>84.44</td>
</tr>
<tr>
<td>1% Diluted CNW/HDPE</td>
<td>488.35</td>
<td>132.80</td>
<td>120.20</td>
<td>63.98</td>
</tr>
<tr>
<td>2% Diluted CNW/HDPE</td>
<td>485.48</td>
<td>135.51</td>
<td>119.40</td>
<td>71.60</td>
</tr>
<tr>
<td>1% Diluted CNW/MAPE</td>
<td>486.31</td>
<td>133.31</td>
<td>119.39</td>
<td>64.81</td>
</tr>
<tr>
<td>2% Diluted CNW/MAPE</td>
<td>485.60</td>
<td>131.81</td>
<td>120.12</td>
<td>58.68</td>
</tr>
</tbody>
</table>
The thermal stabilities of the diluted CNW/PP composites were improved with CNW since the onset temperature of degradation were shown to be higher than neat PP. Furthermore, the rate of degradation was also reduced, with the exception of a discrepancy at 1% diluted CNW/PP composite, which showed a faster rate of degradation. A slower degradation rate can be explained by the CNWs acting as a source of material to conduct heat. Similarly, the thermal stability of the diluted CNW/HDPE composites also improved slightly, but not as pronounced as observed with CNW/PP composites. The addition of a compatibilizer showed no effects on the thermal degradation temperature since the curves corresponding to a particular diluted CNW loading composition had close overlaps with each other.

A decrease in melting temperature was discovered upon the DSC analysis of both the diluted CNW/PP and CNW/HDPE composites relative to the neat base polymers. This decrease can be explained by the CNWs disrupting polymer chain movement and encouraging the formation of randomly oriented structures. As a result, the entropy of the composite system increased and the melting temperature of the composites were reduced. Moreover, the introduction of CNW into PP and HDPE showed an increase in crystallization temperature relative to the neat polymer itself. This was be explained by the known concept that fillers in a polymer can induce crystal nucleating effects.[99]

However, a significant difference in the effects of CNW on the degree of crystallinity between the two polymer systems was observed. For the diluted CNW/PP composites, there was an increase of at least 10% in crystallinity when compared to neat PP. On the other hand, there was a decrease of 20% or more in crystallinity for the diluted CNW/HDPE composites compared to neat HDPE. In both polymer systems, the CNWs promoted crystallization as mentioned earlier, however, crystal growth was identified as the limiting factor accounting for their differences under the non-isothermal conditions of this study.[77] This suggested that the CNWs had different impact on the crystallization of PP and HDPE since all the composites were processed in the same manner. In this study, the PP used had a much lower initial crystallinity than the HDPE, therefore the CNW allowed for more crystal formation in PP with minimal restriction in crystal growth. On the other hand, the HDPE used had a higher initial crystallinity, therefore the CNW greatly suppressed free volume and mobility of the polymer chains to minimize their ability in forming ordered crystals.[100] For both polymer systems, the addition of a compatibilizer in the composites showed minimal effects on its overall thermal properties.
5.2.3 Water Barrier Properties of Diluted CNW/PP and CNW/HDPE Composites

The water barrier properties of the diluted composites were compared with their respective pure base polymer matrix. From a linear fit of the weight loss due to water permeation through the film over time, the water vapor transmission (WVT) of the composites could be attained. The water vapor permeance (WVP) was also calculated using to account for the temperature and humidity conditions during the test. Both values were evaluated based on ASTM E96 standard. These values determined helped express the rate in which water diffused through the composite films. The WVP of the diluted composites were plotted with respect to CNW loading and are presented in Figure 5-3.
Figure 5-3 WVP vs. CNW loading of CNW/PP and CNW/MAPP (a), and CNW/HDPE and CNW/MAPE (b) composites.

The WVP of diluted CNW/PP composites was observed to be lower when compared to neat PP as a result of the increase in crystallinity and the CNWs providing tortuous path for the water molecules. The crystallinity of a polymer has an impact on its water barrier properties because of the packing of the crystal structures that can stop water vapor from penetrating through it.[47] It was believed that the diluted CNW/MAPP would have an even lower WVP due to the enhanced filler-matrix interaction to mitigate water travelling through poor interfaces. However, the WVP of diluted CNW/MAPP composites were higher than the diluted CNW/PP composites but still below neat PP. Although a better filler-matrix interface with the compatibilizer may have existed, a previous study had concluded that the incompatibilities between the masterbatch and the polymer for dilution can prevent good dispersion.[80] In this study, the CNW/MAPP masterbatch, which had a more polar behavior, combined with the nonpolar PP could have potentially reduced the proper dispersion of the CNW in the composite causing localized areas of dispersion from the masterbatch. The dispersion of CNW is an important factor in reducing WVP because a better the dispersion covers a larger surface area of obstacles in impeding the
diffusion of water across the composites. An optimal WVP was observed at 1% and 2% for the
diluted CNW/PP and CNW/MAPP composites respectively. Despite diluted CNW/PP and
CNW/MAPP composites showing a lower WVP than neat PP, it was still much higher in
comparison to the as compounded CNW/PP and CNW/MAPP composites from Chapter 3 even
though they had a slightly higher degree of crystallinity. This was due to the residual
agglomerates that were not further broken down after the dilution process on top of the
suboptimal CNW dispersion in the PP matrix.

On the other hand, a higher WVP was seen for the diluted CNW/HDPE composites compared to
neat HDPE due to the significant decrease in crystallinity, which dominated the effects of the
CNWs as the source of blocking agent for water vapor diffusion. The loosely packed amorphous
structures in the polymer allowed water to move freely through the composite films. Similar with
the diluted CNW/MAPP composites, the diluted CNW/MAPE composites also had a higher
WVP compared to the diluted CNW/HDPE at 1% CNW loading, but was slightly lower at 2%
CNW loading. As with the diluted CNW/MAPP composites, the opposition in the polarities of
the CNW/MAPE masterbatch and HDPE could have hindered the dispersion of the CNWs.
However, the 2% diluted CNW/MAPE composite was not expected to have a lower WVP than
the 2% diluted CNW/HDPE composite since it had a much lower crystallinity. Therefore it was
suggested that the compatibilizer had some influence on lowering the WVP. Furthermore, the
diluted CNW/HDPE and CNW/MAPE composites had a higher WVP when compared to the as
compounded CNW/HDPE and CNW/MAPE composites. This was consistent with what was
observed earlier with the diluted CNW/PP composites, therefore it was also suspected that the
lack of proper dispersion contributed to the increase in WVP.

5.2.4 Tensile Testing of Diluted CNW/PP and CNW/HDPE Composites

Three main tensile properties, which includes elastic modulus, ultimate tensile strength,
elongation strain at break, of the diluted CNW/PP and CNW/HDPE composites will be analyzed
in this section. They have been plotted with respect to their compositions and are displayed in
Figure 5-4.
Figure 5-4  Elastic modulus (a & b), ultimate tensile strength (c & d), and elongation strain at break (e & f) of CNW/PP, CNW/MAPP, CNW/HDPE and CNW/MAPE composites.
For the diluted CNW/PP composites, the elastic moduli and ultimate tensile strengths were observed to be similar to neat PP and without much improvement, though the elastic modulus at 2% CNW loading had a much greater increase due to the rigidity of the CNWs. This showed evidence that there was little to no reinforcement between the CNW and PP. Moreover, the CNW caused a slight increase in elongation strain at break at 1% CNW loading but then a dramatic drop occurred at 2% CNW loading. This suggested that the lack of reinforcement and agglomerates within the matrix induced localized stress for early failure. In contrast, despite the WVP of diluted CNW/MAPP composites being higher than the diluted CNW/PP composites due to its suboptimal CNW dispersion within the matrix, the addition of a compatibilizer to the composite resulted in a greater increase in elastic modulus and ultimate tensile strength than the diluted CNW/PP composites. This was explained by the reinforcing effect that the compatibilizer exhibited in enhancing the interaction between the CNW and PP. However, the elastic modulus and ultimate tensile strength did not further increase after 1% CNW loading, therefore it was proposed that the optimal properties occurred at 1% CNW loading or less, but lower weight percentages were not tested in this study. By comparing the diluted and as compounded CNW/PP and CNW/MAPP composites, the as compounded composites had slightly better mechanical properties as expected due to the existence of larger CNW agglomerates mentioned earlier.

As for the diluted CNW/HDPE composites, although they displayed smaller agglomerates that were better dispersed than in PP and has a notable increase in elastic modulus as a result of the incorporation of a stiff filler, but its ultimate tensile strength and elongation strain at break did not show significant changes compared to neat HDPE. Even with the addition of a compatibilizer, the elastic modulus was much lower compared to the diluted CNW/HDPE composites though still higher than the neat HDPE. Furthermore, the diluted CNW/MAPE composites also had the same trend where its ultimate tensile strength and elongation strain at break remained relatively the same as neat HDPE. One possible explanation for this behavior may have been caused by the substantial drop in crystallinity, which resulted in return can affect the density and tensile strength of the composite. Therefore, it was believed that the crystallinity effects had counteracted any potential reinforcement that the compatibilizer may have expressed. The reduction in the crystallinity when adding fillers to HDPE has been a phenomenon observed by many other studies.[101-103] It has also shown very minimal improvements in mechanical
properties as was observed in this study. As for the comparisons between the diluted and as compounded CNW/HDPE and CNW/MAPE composites, the mechanical properties were consistent between the two. This may have been due to the smaller agglomerates seen in the CNW/HDPE composite masterbatches, therefore it had a less effect on the mechanical properties after dilution.

5.2.5 Rheology of Diluted CNW/PP and CNW/HDPE Composites

The storage modulus and complex viscosity measurements of the diluted CNW/PP and CNW/HDPE composites with respect to a range of frequencies were graphed and depicted in Figure 5-5.
(b) Storage Modulus [Pa]

(c) Complex Viscosity [Pa·s]
Figure 5-5 Storage modulus (a and b) and complex viscosity (c and d) of diluted CNW/PP, CNW/MAPP, CNW/HDPE, and CNW/MAPE composites.

The storage modulus and complex viscosity at low frequencies were expected to increase with the addition of a filler and compatibilizer due to the reduced dependency on the interaction between the filler and matrix at those frequencies. The storage moduli and complex viscosities of the diluted CNW/PP composites at low frequencies were similar to neat PP, which was expected since the concentration of fillers were relatively low, the CNW dispersion observed from the SEM images were not optimal, and the poor interfacial interaction between CNW and PP. However, a decrease in the storage moduli and complex viscosity was unexpected since there were improvements in mechanical properties. In order to evaluate this result, it was possible that the incompatibility between the compatibilized masterbatch with the neat PP, as mentioned earlier, could have caused this reduction in addition with the CNW agglomerates.

On the other hand, a slight increase in the storage moduli and complex viscosities of the diluted CNW/HDPE composites was seen at low frequencies. The increase in these properties can be explained by the better dispersion of CNWs providing a greater specific surface area for hydrodynamic interactions between them.
elastic modulus. However, similar with the diluted CNW/MAPP composites, the CNW/MAPE composites had a decrease in both storage modulus and complex viscosity even though they were observed to have a better CNW dispersion. The issue with incompatibilities between the masterbatch and the neat HDPE was also an applicable explanation for this case. Although no significant enhancements in the interactions between the CNW and polymers were observed based on the rheological behaviors presented, the crystallinity effects were not accounted for since the composites were tested in a molten state.

5.3 Summary

The process of masterbatch dilution was tested in this section with the use of CNWs in PP and HDPE by melt compounding. Morphological, thermal, water barrier, mechanical, and rheological analysis were performed to evaluate quality of the diluted composites. The focus of this study was to examine if masterbatch dilution is a suitable technique for the future development of biocomposite materials to minimize the current use of carbon and inorganic filler based polymer composites for industrial packaging applications. With the addition of CNW to PP, an enhancement in thermal stability, crystallinity, elastic modulus, tensile strength, and water barrier properties relative to neat PP were observed. Even though the addition of a compatibilizer showed some hindrance in the dispersion of the CNWs causing slight reductions in water barrier properties, it is proposed that the dilution process can be further optimized for better dispersion. In contrast, the addition of CNWs to HDPE had opposite effects where only slight improvements in thermal stability and mechanical properties were achieved, but a decrease in crystallinity and water barrier properties was also observed. Similar with the diluted CNW/MAPP composites, dispersion of the diluted CNW/MAPE still remained a challenge, but the CNW agglomerate sizes observed were much smaller. The mechanical and water barrier properties of both composite systems were found to be highly governed by the crystallinity of the composites with the incorporation of CNWs. It can be concluded that there is potential for CNW/PP masterbatches to be implemented for industrial scale processing. As for the CNW/HDPE masterbatches, further investigations would be needed to optimize its crystallinity because it has a significant impact on many of its properties. Moreover, controlling the crystallization process of HDPE is known to be difficult.
Chapter 6  Conclusions and Future Work

The purpose of this research was to evaluate the potential in using CNWs in polymer nanocomposites for large scale production in packaging applications. Results from all the studies are summarized in this chapter and recommendations for further investigations to build upon the existing conclusions from this research have been suggested.

6.1 Conclusions

1. Morphological studies of the CNW/PP and CNW/MAPP composites revealed good dispersion of CNWs within the polymer matrix, which translated into improvements in elastic modulus, ultimate tensile strength, and water barrier properties. These results were further supported by thermal and rheological properties showing increase in crystallinity and extensional viscosity of the composites respectively. Moreover, the addition of a compatibilizer suggested reinforcement and enhanced interaction between the CNW and PP as a significant improvement in water barrier properties was observed. Based on results, the multiple properties that were explored in this study can be tailored with the addition of CNWs, which is a biodegradable filler, for various sustainable packaging and industrial applications.

2. Although the CNW/HDPE composites exhibited good dispersion of CNW agglomerates with an increase in elastic modulus, a decrease in ultimate tensile strength and increase in water vapor permeance was observed. The incorporation of CNWs was found to significantly decrease the crystallinity of CNW/HDPE composites, which affected its overall properties. Furthermore, the addition of the compatibilizer showed some plasticizing effects oppose to reinforcing effects. These results were also confirmed through the minimal changes in storage modulus and complex viscosity of the composites.

3. Improvements in thermal, water barrier, and mechanical properties were observed for the CNW/PP composites processed through masterbatch dilution. On the other hand, the diluted CNW/HDPE composites had minimal improvements in thermal and mechanical properties, but reduction in water barrier properties. The addition of CNWs showed great impact on the crystallinities of the composites, which translated into the behaviors
exhibited by the composites. Furthermore, the rheological properties of the composites revealed some issues for potential improvements and optimization in the processing technique.

6.2 Future Work

1. Despite the CNW dispersions observed from SEM and AFM, future imaging using a transmission electron microscope would provide a better resolution for the relative sizes of the CNW agglomerates.

2. As a result of the minimal increases in storage moduli and complex viscosities observed from the rheological properties of the nanocomposites, a parametric study of different combinations of CNWs and compatibilizer is needed to determine the proper ratios to optimize the filler and matrix interaction to enhance the properties of the PP and HDPE nanocomposites. Also, processing parameters for preparing the polymer nanocomposites should be tested to further optimize CNW dispersion. This applies particularly for the nanocomposite masterbatches since it has a direct effect on the properties of the nanocomposites after the dilution process.

3. For more in depth analysis of the crystallinity of the polymer nanocomposites using wide angle X-ray scattering and polarized light microscopy are suggested in the future to determine crystal orientation and crystal size as it correlates to the water vapor barrier properties of the composites.

4. In addition to the water vapor barrier tests performed in this study, water absorption tests should be performed since it has an effect on the water permeability through the composite films. Moreover, oxygen barrier tests and optical measurements should also be examined for future development of the nanocomposites in the packaging industry.

5. Transitioning the manufacturing process of the nanocomposites on a larger scale equipment should be considered in the future. This would provide greater quantities of materials to test with proper film production processes.
References


[92] N. Herrera, A. M. Salaberria, A. P. Mathew and K. Oksman, "Plasticized polylactic acid nanocomposite films with cellulose and chitin nanocrystals prepared using extrusion and


