PROCESSING AND PROPERTY EVALUATION OF POLY(LACTIC ACID)/CELLULOSE NANOCRYSTALS EXTRUDED CAST FILMS

By

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ABSTRACT

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Poly(lactic acid) (PLA), a bio-based polymer with poor water and moderate oxygen barrier performance, has become a material of interest in the packaging industry due to its sustainability. Cellulose nanocrystals (CNCs) are added into PLA film to enhance its barrier performance without affecting its transparency. Beside these attributes, heat sealing and mechanical properties are also important features for films intended for packaging applications and need to be investigated. This study assessed the influence of CNC addition (0.5 to 2 wt%) on the surface texture, heat sealing, mechanical and barrier properties of PLA cast films manufactured through a continuous extrusion melt-process. Irrespective of CNC content, the addition of CNC increased the surface roughness of PLA due to the presence of CNC agglomerates indicating a poor dispersion. The sealing performance, i.e., the hot tack strength and seal strength of PLA films as well as the burst pressure of PLA pouches, significantly improved by adding up to 1% CNC into PLA matrix, probably attributed to the increased stress transfer efficiency at the interface. Significant improvements in both the tensile strength and modulus were achieved by adding CNC into PLA matrix, insensitive to CNC content. Nevertheless, these occurred at the expense of ductility since both the elongation at break and the energy to break decreased, results supported by the dart impact strength showing that PLA/CNC composite films were more brittle than neat PLA films. Both water vapor and oxygen permeabilities decreased significantly with the increased CNC content because of the tortuosity effect. The overall performance of the studied PLA/CNC films indicated that they had great potential to be used in packaging applications.

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Chapter 1

INTRODUCTION

1.1 Introduction

Petroleum-based polymers have been widely used in many fields in the United States. However, there are rising demand for bio-based plastics as an alternative to the fossil-derived polymers to alleviate U.S. dependency on foreign oil and environmental concerns associated with production and disposal of petroleum-based polymer [1-4]. The value of bioplastics market is predicted to reach \$34.24 billion globally by 2024 [5]. Poly (lactic acid) (PLA), a polymer derived from sugar beets and corns, has attracted many research and industrial interests due to its bio-based and bio-degradable nature. It has great potentials to serve as a packaging material because of its high stiffness, excellent barrier to aroma and flavor, reasonable strength and bio-degradability [1-4]. In fact, the global PLA market reached \$304.9 million in 2014 and 54.6% of the market shares are garnered by the packaging industry [6,7]. In 2020, the global PLA market is projected to reach \$5.32 billion [8]. Although the increasing demand and attractive properties have shown a promising market for PLA, several drawbacks such as brittleness, low impact resistance, as well as poor water and moderate oxygen barrier properties, have limited its application in the packaging industry [4].

The brittleness and low impact resistance pose challenges in the flexible packaging as the PLA film is subjected to tears and cracks. The barrier properties are important for packaging materials. Water barrier property is crucial to package water sensitive products as moisture uptake or loss by the product will change the texture, deteriorate the quality and shorten its shelf life [9]. Oxygen content within the package is important since excessive or lack of oxygen will impair the

quality of the products. Improving these drawbacks will broaden the PLA films in packaging of food and drugs as well as other engineering applications where toughness, flexibility, and excellent barrier properties are paramount.

The brittleness and impact strength of PLA have been enhanced by modifying its physical properties through several approaches with renewable and biodegradable materials in order to maintain its biodegradation nature [1,2,10-18]. These include copolymerization of lactides with other monomers such as ε -caprolactone [10], foaming [1,11], blending of PLA with a biodegradable second polymer [12-15], and plasticizing with modified vegetable oils [2,16-18].

The barrier properties could be improved by crystallization. Presence of crystallites in the polymer matrix increases the diffusion time of permeants due to a more tortuous diffusion path created. This phenomenon is referred as the tortuosity effect [9,19,20].

Increased crystallinity is achieved through adjusting the processing conditions or modifying the material formulations. As polymer melt exits the die, any stretching in either machine or cross machine direction aligns molecules to create the order, which further increases the degree of crystallinity [21-23]. The cooling rate of polymer melt also affects the crystallization. As the cooling rate decreases, the degree of crystallinity increases as more time is given to form crystallites [23,24].

Another method to increase the crystallinity is to modify the materials' formulations by adding organic and inorganic additives into the polymer matrices. Although inorganic additives such as talc [25,26], calcium carbonate [27], etc. are employed as the nucleating agent to increase the degree of crystallinity of polymers, they could also affect the biodegradable nature of bioplastic like PLA [28] and increase its density. Thus, more attention is currently paid to light weight

organic additives from natural resources such as plant fibers, cellulose nanomaterials [9,19,29], chitosan [30], etc.

Over the past few years, cellulose nanocrystals (CNCs) have attracted many research interests. They are the rod-shaped nanoparticles derived from lignocellulosic plants and are often used as a property enhancer in the bio-based polymer matrix because of its bio-degradability and high surface area and aspect ratio [31-33]. Recent studies have shown that the homogenous dispersion of CNCs in PLA matrix improves the mechanical performance of the composites and this is contributed to efficient stress transfer at the interface [34,35]. Furthermore, the addition of CNCs enhances the water and oxygen barrier properties of PLA/CNC films due to increased crystallinity [19] because CNCs are crystallites and act as the nucleating agent. The improved barrier and mechanical properties have been reported for PLA/CNC films manufactured through solvent casting techniques (a batch process) [32,33,36] and melt-processing (a continuous process) methods [9,19,31,37-39]. All these improvements are achieved without significantly affecting the film transparency [19], making such films ideal for food packing applications.

Although transparency and barrier properties are amongst the important attributes for films intended for packaging applications, films that offer good-sealing strength, high impact strength, and good puncture resistance are also important for food packaging.

For example, packaging pouches, manufactured by heat sealing films, are used in many applications and can have multiple purposes such as to protect products during shipment, extend product shelf life, enhance product presentation, etc. Heat sealing in flexible packaging involves the fusion of one film to another or to a rigid container to create a hermetic seal. Sealing is crucial in packaging because it helps keep product in the package until the consumer or user opens it and protect the product from the outside environment [40]. Poor seals could act as entrances for contaminants, which can lead to the spoilage of packaged food products. In contrast, a good heat seal helps the package provide one of its primary functions of protecting the product. For the packaging of food for example, the seal helps ensure product freshness. While the seal strength is crucial in maintaining the desired shelf life [40], the hot tack strength, i.e., the strength of a polymer in its semi-viscous state, is crucial during the form-fill-seal (FFS) process, to ensure that the seal is strong enough to hold the weight of the product immediately after the seal is made at production speeds [41]. The burst pressure measures the pressure resulting in the failure of a sealed package [2]. This strength is crucial in maintaining the integrity of the packaging system during transportation. During the transportation process, the package may expand to explode when manufactured at sea level and transported to locations with high altitude. Mechanical properties such as the tensile strength and the impact resistance are crucial to packaging industry to maintain the integrity of the packages during transportation and distribution [42]. Therefore, it is important to study the heat sealability and mechanical properties of the films.

Lack of sealing strength, mechanical and barrier properties could lead to the failures of the packages during manufacturing, distribution and transportation process, creating waste of both packaging materials and products. This waste could increase the manufacturing costs, delay the production efficiency, further impair the benefits of stakeholders as well as pose deleterious impacts on the environment. Understanding how the addition of CNCs in PLA cast films affects the packaging performances is of paramount important to avoid such wastes.

To the best of our knowledge, no research has been reported on the influence of CNC addition on the seal strengths, mechanical, and barrier properties of PLA cast films manufactured through a continuous melt-process.

Therefore, the objectives of this study were to manufacture and evaluate the physicomechanical properties, including sealing, mechanical, and barrier properties, of PLA cast films and its composites with various CNC contents to expand the packaging applications of such nanocomposites films.

1.2 Objectives

The goal of this study was to utilize a continuous extrusion process that efficiently incorporates CNCs into a PLA matrix in order to manufacture PLA/CNC cast films for the packaging application. To achieve this objective, the following specific objectives were proposed:

- 1. Manufacture PLA/CNC extruded cast films with various CNC content in the films and characterize their physico-mechanical properties;
- Explore the effect of CNC content on the surface texture of PLA cast films and determine the thickness of neat PLA and composite films;
- 3. Study the effect of CNC content on the water and oxygen barrier properties of PLA extruded cast films to gain an in-depth understanding of the diffusion mechanism with the addition of CNC content;
- 4. Investigate the influence of CNC content on the sealing properties, including seal strength, hot tack performance and burst pressure of PLA cast films;
- 5. Evaluate the effect CNC content on the impact strength, brittleness and other tensile properties of PLA films.

1.3 Hypothesis

This research was intended to test the hypothesis that the addition of a small amount of CNCs into PLA films will enhance its water and oxygen barrier performance without negatively affecting the tensile strength, impact strength, hot tack performance, seal strength and burst pressure of the composite films.

1.4 Structure of thesis

The first chapter of the thesis introduces the rationale of this research. A background on poly(lactic acid), cellulose nanocrystals, their synthesis, properties and blending techniques are reviewed in Chapter 2. The detailed experimental methods, including material specifications, sample manufacturing and property evaluation are described in Chapter 3. The experimental results in evaluating the effect of CNC content on the surface texture, barrier, seal and mechanical properties of neat PLA cast films are discussed in Chapter 4. In Chapter 5, the conclusions summarized from the experimental data and proposed future work are presented.

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Chapter 2

BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

Consistent with the scope of this study, a background and literature review on the current studies of processing poly(lactic acid) (PLA)/cellulose nanocrystals (CNCs) films are presented in this chapter. The review focuses on the effects of CNC addition on the physico-mechanical properties and packaging performances of PLA cast-films; including surface texture, sealing, mechanical and barrier properties, as well as the manufacturing approaches for PLA/CNC composite films.

2.2 Poly(lactic acid)

Poly(lactic acid), a biodegradable and compostable polymer derived from renewable sources, such as sugar beets and corns, belongs to the family of aliphatic polyesters [1]. It is a thermoplastic with reasonable strength, good heat sealability, easy fabrication with existing processing techniques, as well as excellent flavor and aroma barrier properties [2-4].

2.2.1 Synthesis of PLA

Lactic acid (2-hydroxy propionic acid), the basic building block of PLA, has two optical isomers, due to the chirality: L-lactic acid (LLA) and its mirror image, D-lactic acid (DLA) (Figure 2.1) [5].



Figure 2.1: Chemical structure of L(+)- lactic acid and D(-)- lactic acid.

Two ways to produce lactic acid is through fermentative and chemical synthesis [6,7]. The lactic acid with desired stereoisomer can be converted from various carbohydrates sources (corn syrup, cane, whey, etc.) by bacterial fermentation using homolactic organism, such as modified strains of the genus Lactobacilli [7, 8-10]. Bacterial fermentation is commercially used in the industry and can produce both D(-)- and L(+)- enantiomers [10]. The chemical synthesis routes for lactic acid production, including oxidation of propylene glycol, base catalyzed degradation of sugars, hydrolysis of chloropropionic acid as well as reaction of the mixture of acetaldehyde, carbon monoxide and water at elevated temperatures and pressures, only produce the racemic lactic acid [7].

Two most used production techniques to obtain PLA through the polymerization of lactic acid are: (1) direct condensation polymerization; (2) ring-opening polymerization (ROP). The direct condensation method uses solvent under high vacuum and temperatures to remove the water generated in the process, and produce polymer with low to intermediate molecular weight, which can be used or coupled with isocyantes, peroxide to further produce a range of molecular weight polymers [10].

ROP technique, the most commonly used method patented by Cargill Inc., requires catalyst but generates PLA with controlled molecular weight [10,11]. In this method, the lactide is formed by the two lactic acid molecules and has three types of stereoisomers, due to the chirality of lactic acid monomer: L-lactide (two L-lactic acid isomers), meso-lactide (an L-lactic acid and a D-lactic acid isomers) and D-lactide (two D-lactic acid isomers), shown in Figure 2.2 [12,13].



Figure 2.2: Chemical structures of lactide.

PLA can undergo three routes of ring-opening polymerizations: cationic, anionic and coordination-insertion polymerizations. The cationic ROP uses trifluoromethane sulfonic acid (triflic acid) or methyl trifluoromethane sulfonic acid (methyl triflate), as those are the only two cationic initiators to polymerize lactide [8]. The mechanism of the cationic ROP is shown in Figure 2.3.



Figure 2.3: Cationic polymerization mechanism of lactides [1].

Anionic ROP is proceeded through the nucleophilic reaction of the anion with the carbonyl and the acyl-oxygen cleavage [8,14]. Figure 2.4 depicts the anionic initiation process of lactides. It is found that initiator with higher nucleophilicity can initiate the lactide, weaker bases, such as potassium phenoxide, serve as initiator only at high temperatures [8,15]. However, both anionic and cationic ROP, are often performed in the solvent system and susceptible to transesterification, racemization and impurity levels, which are not suitable for mass production for industrial usage.



Figure 2.4: Anionic polymerization mechanism of lactides^[1].

Coordination-insertion ROP, on the other hand, utilizes metal catalysts and forms high molecular weight PLA easily, which is preferred for large-scale commercial use [8,16]. Tin compounds, such as Sn (II), are commonly used as a catalyst in PLA synthesis, because of its low toxicity (FDA approval) and high catalytic activity [8,14]. Figure 2.5 demonstrates the mechanism of coordination-insertion using tin, Sn(II), as a catalyst.



Figure 2.5: Coordination-insertion mechanism of lactides using Sn(II) as a catalyst ^[17].

2.2.2 Properties of PLA

The properties of PLA such as thermal, barrier and mechanical are dependent on PLA's degree of crystallinity and other parameters. The crystallinity of PLA is governed by the types of stereoisomers and its relative amount in the polymer. Poly(L-lactide), the resultant polymer from polymerization of greater than 93% L-lactide content, is semi-crystalline and has very high melting point, high crystallinity and poor processing properties [12,18]. However, when the L-lactide content is between 50 to 93%, the resultant polymer is amorphous [12]. The D,L-PLA, PLA with meso-lactide, is an amorphous polymer with the glass transition temperature (T_g) of 60°C [18]. Due to higher degree of crystallinity, generally, semi-crystalline PLA has higher T_g and melting temperature than amorphous PLA. The thermal properties and melt flow index of different PLA grades are summarized in Table 2.1.

Matariala	D-lactide	MFI ^a	Thermal properties ^b		
Wrater fais	(%) (g/10min)		T _g (°C)	T _m (°C)	χc (%)
PLA 2003D [19]	4-4.5	39.93	61.69	167.03	11.92
PLA 3052D [19]	4	28.80	61.43	165.93	4.12
PLA 4043D [19]	4.8	47.07	62.11	167.68	12.38
PLA 8302D [19]	10	18.47	60.06	-	-
PET [20]	-	-	73-80	245-265	-
PS [20]	-	-	74-105	-	-

Table 2.1: Characteristics of various grades of PLA and petroleum-based polymers.

^aMFI is the melt flow index of different polymers.

 $^{{}^{}b}T_{g}$, T_{m} , and χ_{c} are the glass transition temperature, melting temperature, and percent crystallinity of different polymers.

In general, PLA is more heat sensitive compared to petroleum-based plastics. As shown in Table 2.1, PLA has lower T_g and T_m than that of polyethylene terephthalate (PET) and polystyrene (PS). PLA is susceptible to thermal degradation due to several factors: hydrolysis by slight amount of water; depolymerizaion; oxidative and random main-chain scission; and formation of cyclic oligomers of lactides from intra-molecular transesterification reactions; intermolecular transesterification to monomer and oligomeric esters [21-23].

2.2.2.1 Sealing properties

Heating sealing refers to the process utilizing heat and pressure to seal two structures, where at least one of the structures contains thermoplastic layer [24]. A good seal requires enough molecular entanglement within the polymer chains, between two thermoplastic sealing layers, so that the original interface is destroy to form a homogenous layer, which remains homogenous after cooling [24]. It is important to acquire a good seal to maintain the desired shelf life of the products. Factors such as melting point, viscosity, molecular weight and polarity of the plastics have significant effects on the sealing performance [25].

The performance of a seal can be estimated by measuring the seal strength, the hot tack strength, burst strength, etc. Seal strength reflects the force needed to open a sealed film and can be measured using the peel test after the seal is made and cooled down to the room temperature. Hot tack strength, on the contrary, is a force measured in the polymers' semi-molten state, while the seal remains hot [26]. Hot tack strength is crucial in the vertical form-fill-seal (FFS) process where the product is dropped on the sealed package immediately after it is made. It is essential to ensure the seal is strong enough to hold the weight of the product in this process [25]. The burst pressure measures the pressure resulting in the failure of a sealed package [27]. This strength is

crucial in maintaining the integrity of the packaging system during transportation, and can be measured through the internal burst test. During the transportation process, the package may expand to explode when manufactured at sea level and transported to locations with high altitude.

The sealing properties of PLA have not been extensively studied. Thumsorn and coworkers had investigated the seal characteristic of PLA films and reported that the seal strength of PLA films was from 5.87 to 26.51 N/15 mm for seals made with the heat bar temperature in the range of 90 to 100 °C, and seal time from 0.2 to 2 s with constant seal pressure of 0.2 MPa [28]. Tabasi and coworkers had studied the sealing and mechanical properties of PLA/polycaprolactone (PCL) blends. They found that the hot tack plateau strength of PLA was 800 g/25.4mm under constant pressure and sealing time as 0.5 N/mm² and 1s, respectively. The addition of PCL decreased the sealing and hot tack initiation temperature, while increasing the seal and hot tack strength. Furthermore, PCL act as a plasticizer to increase the elongation at break up to 150% [29].

2.2.2.2 Mechanical properties

The mechanical properties, especially strength, ductility and impact resistance, are crucial in packaging industry to maintain the structural integrity of the package. The package will fail or deform if the tensile strength is not sufficient to hold the weight of the product [30]. Impact resistance is important to maintain the integrity of the package during rough handling conditions.

The mechanical properties of PLA vary in a large range from soft and elastic to stiff and high strength materials as they are dependent on the molecular weight [31,32]. Table 2.2 provides insights of mechanical properties of PLA. The tensile strength of semi-crystalline PLA is between 50-70 MPa, elongation at break of 2-10%, and the elastic modulus is between 3000-4000 MPa [32]. A summary of tensile properties of various PLA grades and that of petroleum-based polymers

is shown in Table 2.2. It is worth mentioning that different methods used in material processing affect the mechanical properties of PLA.

Motoriala	Tensile strength (MPa)		Tensile	Elongation (%)	
Materials	Yield	Break	(GPa)	Yield	Break
PLA 2002D [16]	60	53	3.5	-	6.0
PLA 2100D [16]	62	56	3.5	-	3.0
PLA 4030D [33]	65-72	-	2.11-2.54	4.5-4.7	5.5-10.7
PLA 4031D [34]	-	28.5 ± 3.8	1.7 ± 0.2	-	>100
PLA 4040D [33]	74-84	-	2.31-2.87	3.4-4.2	78.2-96.9
PET [20]	-	48.2-72.3	2.76-4.14		30-3000
PS [20]	-	35.8-51.7	2.27-3.27		1.2-2.5

Table 2.2: Tensile properties of various grades of PLA and petroleum-based polymers.

2.2.2.3 Barrier properties

Barrier properties, the ability of the materials to obstruct the penetration of permeants, are crucial in packaging industry. The barrier properties commonly studied in the packaging field are barrier against water vapor, oxygen (O₂) and carbon dioxide (CO₂). Those properties are extremely useful in determining the applications of polymers in food packaging as well as maintaining the desired shelf life. As most of food products are sensitive to water vapor, O₂ and CO₂, being exposed to those substances may cause off-flavors, loss of crunchiness, mold growth, further deteriorate the quality and shorten the shelf life of packaged products.

Permeability, diffusivity and solubility coefficients are parameters often used to characterize the barrier properties of a plastic. For the materials with identical thickness, higher permeability results in poor barrier properties. Auras and co-workers had studied the barrier properties of films made with two grades of PLA, PLA 4030D with 98% L-lactide and 4040D with 94% L-lactide, and found that the O₂ and CO₂ permeability coefficients of both grades were lower than that of PS, and in a comparable range with PET [33].

Recently, the barrier properties of PLA blown films had also been assessed. Matuana and coworkers had investigated the effect of cellulose nanocrystals (CNCs) on the water vapor transmission rate (WVTR) and O2 transmission rate of PLA blown films, made with semicrystalline PLA 4044D pellets. The water vapor and O2 barrier properties were significantly increased with the addition of 1% CNC. They had further discovered that the relative humidity (RH) and temperature had more influence on the water vapor barrier property of neat PLA blown films than that of PLA/CNC films [37]. The effect of RH on O2 barrier property of neat PLA and modified PLA with hydrophilic additives blown films had been investigated by Kunanusont and coworkers. The O2 permeability of neat PLA blown films, further supported by the contact angle results indicating that the surface of PLA films was slightly hydrophilic (contact angle was less than 900). The O2 permeability of modified PLA, on the other hand, increased with increasing RH [35]. Table 2.3 summarizes barrier properties between different grades of PLA and those of common petroleum-based plastics.

	Permeability					
Materials	O2	CO2	Water vapor			
	(10 ⁻¹⁸ kg-m/m ² -s-Pa)	(10 ⁻¹⁷ kg-m/m ² -s-Pa)	(10 ⁻¹⁴ kg-m/m ² -s-Pa)			
PLA 2003D [35] 23°C, 0%RH 2.49-3.32		-	-			
PLA 3051D [36]	$25\pm1^{o}C$ 4.98 ± 0.16	-	20°C, $50 \pm 2\%$ RH 1.04 ± 0.18			
PLA 4030D [33]	25°C, 70%RH	25°C, 0%RH	37.8°C, 40-90%RH			
	1.21 ± 0.07	2.77 ± 0.05	1.52 ± 0.05			
PLA 4040D [33]	25°C, 70%RH	25°C, 0%RH	37.8°C, 40-90%RH			
	1.39 ± 0.14	1.99 ± 0.06	1.48 ± 0.07			
PLA 4044D [37]	23°C, 0%RH 10.47 ± 2.13	-	23°C, 46%RH 2.08-2.61			
PET [33]	25°C, 70%RH	25°C, 0%RH	25°C, 40-90%RH			
	0.188	0.173	0.11 ± 0.01			
PS [33]	25°C	25°C, 0%RH	25°C			
	27	15.5	0.67			

Table 2.3: Permeability of different grades of PLA and other petroleum-based polymers.

2.3 Processing technologies of PLA

The widely used technique to convert PLA resins to the end products is the melt processing. This process first uses heat to bring PLA resins above its melting point, transferring the resins from the solid to viscous state, in order to reshape into desired format, then cools the resins below its glass transition temperature to stabilize the desired dimensions. Melt processed PLA can be converted into extruded blown and cast films, as well as extruded blow molded bottles. Additionally, the pre-formed parts can be obtained through melt processed PLA and are further processed to form injection stretch molded bottles, and thermoformed containers or cups for packaging applications. This section of the chapter discusses the common processing methods with the emphasis on the cast film extrusion process.

2.3.1 Drying

Prior to melt processing, it is essential to dry PLA sufficiently to avoid loss of physical properties due to the hydrolytic degradation. The drying temperature should be carefully chosen to be below the glass transition temperature (T_g) to prevent sticking of pellets. In general, PLA resins are dried in a chamber with less than 250 ppm moisture presence [38]. As most of the commercial PLA grades are crystalline pellets, they can be dried in a temperature range of 60-90°C [38]. However, a lower temperature range (30-40°C) is needed to dry amorphous PLA pellets due to their low T_g (approximately 60°C) [38]. The drying time can vary, depending on the drying temperature [38].

2.3.2 Extrusion

A homogenous PLA melt can be converted into the end products through extrusion, one of the most common processing techniques. PLA bottles can be formed using blow molding, whereas PLA films and sheets can be obtained through cast or blown film extrusion processes. The key element in the extrusion process is the extruder with three sections: feed, compression and metering. Figure 2.6 is a schematic representation of a conventional extruder. The feed section is where the polymer resins are received and conveyed into the screw. In the compression section, shown as melting region in Figure 2.6, the diameter of screw is increased in order to efficiently compress the polymer pellets. The metering section serves as a pump to meter the desired quantity of polymer to the die region [39].



Figure 2.6: Conventional extruder in extrusion processes ^[40].

The die is another important component in the extrusion process as it shapes the polymer melt into the desired end products. In general, there are three types of dies (Figure 2.7): slit dies (or flat dies) in the cast film extrusion to product films and sheets, annular dies in the blown film extrusion to form tubular films or pipes, and capillary dies for filament and rods [41].



Figure 2.7: Three types of dies used in extrusion processes.

2.3.2.1 Cast film extrusion

Cast film extrusion is one of the most commonly used techniques in the flexible packaging industry. In fact, nearly 12% of all polyethylene films are produced by cast film extrusion [45]. As shown in Figure 2.8, in cast film extrusion, the polymer is melted and extruded through a slit die, in tangentially contact and stretched by the chill rollers to form the film, and collected by the winder. The chill rollers are often water-cooled and have a highly polished smooth surface.


Figure 2.8: Cast film extrusion process.

As illustrated in Figure 2.8, the direction which the extrudate exits the die is often defined as machine direction (MD). The direction perpendicular to the machine direction is referred as cross machine direction (CMD), or transverse direction. When equipped with chill rollers, cast film extrusion process produces the uni-axial oriented films where the polymer melt is stretched in MD resulting in the polymer molecular chain alignment only at that direction. The unbalanced films may have better mechanical properties when tested in MD compared to that tested along the CMD. However, with the addition of the tenter frame at the die exit to stretch the films in CMD, cast film extrusion can also manufacture bi-axially oriented films. The fabrication of film and sheet through cast film extrusion is practically identical. Typically, films are defined as the thickness of end products is below 0.076 mm (0.003in.), whereas, the thickness of the sheets is greater than 0.25 mm (0.01in.) [39]. The thickness of the cast films can be easily controlled through the speed of rotational screw, chill rollers and winders. Due to the tangential contact between extrudate and chill rollers, the thickness of the cast films across the films is more uniform. In addition, compare to other films manufacturing techniques, cast films extrusion process produce films with better transparency as the extrudate is cooled down by the chill rollers allowing less crystallites to form [46]. One of the advantages of cast film extrusion is that it provides ease of processing, thus, it is more suitable to polymers with low melt strength.

PLA with L-lactide contents between 92-98% can be successfully manufactured through cast film extrusion [39]. However, necking likely occurs due to the low melt strength of PLA, which form films with thicker edges and narrower width. Necking can be mitigated by positioning the chill rollers as close as the die exit, or by edge pinning including electrostatic or low pressure air [39]. Additionally, PLA can also be co-extruded with other polymers into multi-layered structures to obtain enhanced properties.

2.3.2.2 Blown film extrusion

In blown film extrusion, after exiting an annular die, the extruded polymer is drawn upward by the take-up rollers with air inside the polymer tube to inflate and form the film [19]. An air ring is used at a certain distance from the die exit to cool the formed polymer tube. The tube is further flattened by the take-up rollers and collected by the winder. Shown in Figure 2.9, the polymer melt is stretched in the machine direction by the take up rollers. As the polymer tube is inflated by the air, which results in the films' orientation in the transverse direction, the bi-axially oriented films with better balance of mechanical properties in both directions are formed.



Figure 2.9: Blown film extrusion process ^[47].

One of major disadvantages of blown film extrusion is that it requires polymers to have moderate or high melt strength. PLA's low melt strength hinders the blown film extrusion process. Melt sag, referring as the accumulation of the polymer near the die exit, likely occurs due to its low melt strength. Other instabilities, such as bubble dancing, draw resonance, also hinder the blown film extrusion process for PLA films. Karkhanis and coworkers had examined the effects of the temperature profile, internal air pressure and processing speed ratio (PSR), which was referred as the speed ratio of the take-up rollers to the rotational screw, on the blow-up ratio (BUR) of PLA blown films. BUR was defined as the ratio of the annular die's diameter to the final film's diameter, and it affected the film thickness. The film became thinner as higher BUR was achieved. A stable PLA blown films was successfully manufactured without using any melt strength enhancers. The instabilities mentioned previously were solved by controlling the internal air pressure and PSR [19].

2.3.2.3 Extrusion blow molding

Hollow products, including bottles or jugs, can be manufactured through extrusion blow molding. In this process, polymer pellets are melted and continuously form a parison by an annular die. The parison is then pinched off from the continuous parison and placed in a mold. As shown in Figure 2.10, air is used to inflate the parison to fill the cavity of the closing mold. The cooling is performed by the direct contact of molten polymer and the mold. The formed part is ejected and trimmed after cooling. Extrusion blow molding process utilizes the blowing air to ensure the stretching of the polymer in the radial direction [48]. This process requires thermoplastic with high melt strength to support its own weight while forming and maintaining a parison until the mold closes around it. Compared to other manufacturing processes for bottles, which will be discussed later in this chapter, extrusion blow molding produces more waste as the bottom of the parison, where the mold closes, needs to be trimmed off (Figure 2.10).



Figure 2.10: Schematic representation of extrusion blow molding ^[49].

2.3.3 Injection

Injection molding is a suitable processing technique to manufacture parts requiring precise dimensions with low tolerances, such as closures. It can also be used to manufacture parts which can be converted into bottles later on through the injection blow molding or injection stretch blow molding process.

Shown in Figure 2.11, the polymer is melted by the heat in the injection unit, which consists of a barrel, screw and nozzle. The screw in the barrel melts, compresses and conveys the polymer to a mold with desired shape through the nozzle. The mold is controlled by the clamping unit and equipped with an ejector pin, which ejects the formed plastic parts from the mold after the molten plastic is solidified. Polymers with low viscosity, which allows ease in flowing and filling the molds, are often used in the injection molding [50].



Figure 2.11: Schematic representation of injection molding^[51].

2.3.3.1 Injection blow molding

Injection blow molding is an alternative to produce hollow shaped containers. This process starts with a pre-formed part from the injection molding process. Shown in Figure 2.12, the length of the preform is the same as the mold and the final product. The preform is re-heated to soften inside a mold cavity. The air is blown into the softened preform in the mold to stretch the preform in the radial direction until filling the mold cavity, thus resulting in an uniaxial orientation. The formed part is ejected after cooling [50]. Compared to the extrusion blow molding process, this process produces higher quality end products with less waste as no parts need to be trimmed. Furthermore, this process is more suitable to manufacture polymer with low melt strength.



Figure 2.12: Schematic representation of injection and injection stretch blow molding.

2.3.3.2 Injection stretch blow molding

The difference between injection stretch blow molding and injection blow molding is the addition of a stretching step. As illustrated in Figure 2.12, the preform with the length shorter than that of the final product, is blown by the air to stretch in the radial direction as well as pulled by a plug to stretch vertically, creating a biaxial orientation. Hence, unlike injection blow molding, this process produces end products oriented in both machine and transverse directions, which offers better balanced mechanical properties in both directions [50].

2.3.4 Thermoforming

Thermoforming is a widely used process to produce rigid containers at low costs. In this process, a sheet is heated to re-shape into a three dimensional article into or around a mold. The molded part is ejected and trimmed after sufficient cooling. PLA can be thermoformed into disposable cups and trays for food packaging applications [41]. Attempts of manufacturing thermoformed containers from PLA and cellulose nanocrystals (CNCs) have also been made. Figure 2.13 shows examples of thermoformed PLA and PLA/1%CNC containers.



Figure 2.13: Thermoformed containers of (a) PLA and (b) PLA/1%CNC.

2.4 Improving PLA's property

As mentioned, PLA's poor water vapor and moderate oxygen barrier properties have limited its application in the packaging industry. The barrier properties can often be improved by increased crystallinity through adjusting the processing conditions (stretching and cooling rates) or modifying the material formulations (use of organic and/or inorganic additives). This study selected cellulose nanocrystals, organic additives from wood, to improve the barrier properties of PLA.

2.5 Cellulose nanocrystals (CNCs)

Cellulose nanocrystals (CNCs), a derivative from lignocellulosic biomass, has attracted many academic and industrial interests, due to their low weight, biodegradability, biocompatibility, low toxicity, high stiffness and tensile strength as well as high surface area [4,54-56]. It has a wide range of applications in a variety of fields including biomedical engineering, wastewater treatment, energy and electronics, packaging, etc. [54].

2.5.1 Extraction of CNCs

CNCs, rod-like nanoparticles often referred as nanowhiskers, nanofibers, microcrystals and micro-crystallites, can be isolated from cellulose. Cellulose, the most abundant natural polymer, is a fibrous, tough and water-insoluble polymer presented in living species, such as algae, fungi, various plants as well as sea animals such as tunicates [57]. The chemical structure of cellulose is shown in Figure 2.14, it is a high molecular weight homopolymer with the repeating unit of cellobiose, a dimer of glucose which consists two glucose residues linked via a β -1,4 glycosidic bond [58,59]. The degree of polymerization varies and can be up to 20,000 depending on the

sources that celluloses are derived. The cellulose molecule chains can form elementary fibrils and further pack into larger microfibrils through hydrogen bonds and van der Waals forces [59,60]. The highly ordered crystalline regions and disordered amorphous regions can both present in the microfibrils [58,59,61]. The characteristic properties, including degree of crystallinity, crystalline state and molecular weight, can be highly variable, depending on the derived sources [62,63].



Figure 2.14: Chemical structure of cellulose with repeating unit of cellobiose ^[57].

The highly crystalline regions from microfibrils can be extracted to form CNCs. The main process to isolate CNCs from cellulose fibers is based on acid hydrolysis. Since the disordered or paracrystalline regions of cellulose are susceptible to acid attack, whereas crystalline regions have a higher resistance to the hydrolysis and more likely to remain intact, cellulose rod-like nanocrystals can be obtained by an acid treatment [57]. Typically, the production of CNCs need to be carried out under strictly controlled conditions of temperature, agitation, and time. Parameters, including the nature of the acid and the acid-to-cellulosic fibers ratios, are also important to the preparation of CNCs. In general, the acid hydrolysis involves the starting material to mix into deionized water with a specific concentration of acid, such as sulfuric, hydrochloric and maleic acids [60]. The mixture is diluted with deionized water to quench the reaction after desired reaction time. This mixture is then treated with a series of separation process, including centrifugation or filtration. Removal of the remaining free acid molecules from the dispersion is achieved through dialysis against distilled water [60]. Sulfuric and hydrochloric acids are extensively used to extract CNCs from the cellulose, however, phosphoric and hydrobromic acids are also reported to achieve such purpose [58]. It is worth mentioning that different acids used in the preparation process may affect the dispersion, thermostability, rheological behavior of CNCs [58].

Due to the abundance of hydroxyl groups at the surface of CNCs, approaches such as esterification, etherification, oxidation, silylation, polymer grafting, etc., have been attempted to chemically modify CNCs. Those chemical modification methods are used to achieve two goals: (1) to obtain a better dispersion by introducing stable electrostatic charges on the CNCs' surfaces and (2) to improve compatibility of CNCs when used in nonpolar or hydrophobic matrices by tuning the surface energy [58].

2.5.2 Properties of CNCs

The aspect ratio of CNCs, defined as the length to diameter ratio (L/D), often determines the reinforcing capability as it is crucial in the formation of percolated networks to control the properties of CNC-based materials [64,65]. CNCs have high aspect ratio, indicating a better reinforcing ability, and the value highly varies depending on the sources [57]. The geometrical dimensions of CNCs also vary widely with the derived sources. In general, the width of CNCs ranges from 10 to 20 nm and length varies to several hundred nanometers [64]. For instance, CNCs from wood are 3-5 nm in width and 100-200 nm in length. Those from cotton are reported to have width of 5-10 nm and length of 100-300 nm [57,58].

The thermal properties of CNCs depend on the particle type and the type of surface modification. In general, the onset of thermal chemical degradation of CNCs can be measured through thermogravimetric analysis (TGA) and is between 200-300°C [60]. CNCs do not have adsorption in the optical range because of the cellulose structure. Nevertheless, the optical properties of CNCs depend on their nanoscale in size, structures, concentration and aspect ratio [60]. Many research interests have been paid to the mechanical properties of CNCs. However, the quantitative evaluation of the tensile modulus and strength of CNCs is challenging due to the limitations in measurements of mechanical properties of nanomaterials along multiple axis [57]. CNCs have good mechanical properties as the elastic modulus ranges between 60-105 GPa in the axial direction and 20-50 GPa in the transverse direction [57,66].

2.5.3 Use of CNCs in bio-based polymers

CNCs have a wide range of applications in the domain of nanomaterials. In general, the application of CNCs can be majorly divided into two broad types: utilizing the functionalized or non-functionalized as-synthesized CNCs, or incorporation with the polymer matrix as a reinforcing agent. As-synthesized CNC itself has great potentials for applications including nanopapers, pH sensors, stabilizing of oil/water interfaces, etc. [57]. Additionally, CNCs have been incorporated into a variety of polymer matrices to form polymer nanocomposite, a multiphase material where a nanomaterial is used to reinforce the polymer phase [57]. Research has reported application of CNCs in the synthetic polymers including poly(vinyl alcohol), poly(vinyl acetate), epoxides, polyethylene, poly(vinyl chloride), polypropylene, polyurethane, as well as biopolymers, such as starch-based polymers, chitosan, poly(lactic acid) [58].

The application of CNCs at low concentration (<30 wt%) as a reinforcing agent in the polymer matrix has been extensively studied [60]. CNCs can be used as the load-bearing constituent in the polymer composite materials to improve the mechanical properties with low

volume fractions. The improvement is attributed to two factors: formation of percolated networktype architecture within the polymer matrix and the aspect ratio [57]. Higher aspect ratio often gives the better reinforcing effect [65].

Furthermore, the addition of CNCs into the polymer matrix can improve the barrier properties of neat polymer films, as CNCs serve as crystallites in the polymer matrix to increase the diffusion time of permeants, resulting in a more tortuous diffusion path, which is referred as the tortuosity effect [37,67,68]. It had reported that both of oxygen and water vapor barrier properties of neat PLA blown films improved significantly with the addition of 1% CNC, attributed to the increased crystallinity as well as the tortuosity effect [37].

It is worth noting that the improved properties can be achieved with good matrix-filler interaction and homogeneous dispersion of nanocrystals within the polymer matrix. However, the good dispersibility of CNCs in the polymer matrix is challenging due to its intrinsically strong interactions [58]. CNCs have a natural tendency to aggregate due to the hydroxyl groups on their surface forming new interparticle H bonds. Agglomeration of CNC is undesirable as it decreases the surface area and further reduces the filler-polymer interactions. It also induces voids and holes in the composite structure [69].

2.6 Processing technologies of composite films

Processing techniques play an important role on the final properties of the composite materials. The dispersion of CNCs is highly dependent on the processing techniques. Other factors related to the intrinsic properties of CNCs, the interfacial characteristics, nature of the polymer matrix, such as solubility and degradation, as well as the properties of the end products, should be taken into considerations when selecting the processing techniques [58]. Composite films can be formed through various processing methods, including casting evaporation, melt processing as well as electrospinning.

2.6.1 Casting-evaporation process

Casting-evaporation process, also known as solvent casting, is one of the most common methods to produce nanocomposite films. Due to the hydrophilic character of CNCs, the watersoluble matrix is the simplest way to incorporate CNCs as a filler in the polymer matrix [58,65]. As illustrated in Figure 2.15, the polymer solution is prepared first by dissolving polymers in the solvent, such as water, alcohol or any organic solvent. The fillers, including natural fibres and CNCs, are mixed with the polymer matrix through mechanical stirring. Enhanced formation or improved properties of the final films are achieved through adjusting the temperature or the pH. The mixture is then casted into a mold or onto a flat surface. The final composite films are obtained after the solvent is removed [70]. This process provides good dispersion of CNCs in the polymer matrix. However, it has various drawbacks as the solvent disposal arouses environmental concerns, and the residual solvent can serve as a plasticizer to reduce the mechanical and barrier properties [67]. In addition, this process is suitable to produce composite materials in the small scale not mass production, which poses difficulties in implementation by the industry [69].



Figure 2.15: Schematic representation of casting-evaporation process^[70].

2.6.2 Melt processing

The melt processing method to prepare cellulose-based composites is quite new with increasing number of publications during the last five to ten years. It has attracted many industrial interests as this approach offers less processing time, ease implementation and does not involve solvent, which is much greener than cast-evaporation method [67,69].

Melt processing requires an extruder. It utilizes the heat to soften the polymer and provides sufficient shear to maximize the dispersion of CNCs in the polymer matrix. It was used along with the solvent casting method to prepare composites in a two-step process. A master batch is prepared using solvent casting technique and then diluted with PLA through melt-compounding by an extruder [71]. Another method to disperse aqueous suspensions of CNCs into the polymer matrix is melt-compounding through liquid feeding in a vented extruder. Attempts in manufacturing PLA and 1% CNC as well as chitin nanocrystal nanocomposites through liquid feeding using a vented twin screw extruder have been made [72]. Although a good dispersion was achieved through

techniques mentioned previously, it has the similar drawbacks including environmental concerns with solvent disposal, as the solvent casting techniques.

Alternatives approaches to manufacture CNCs composites are proposed. Karkhanis and coworkers had investigated two solvent-free approaches to incorporate CNCs into PLA matrix [67]. The first proposed method was to use a three-piece internal batch mixer to achieve homogenous dispersion of CNCs. The second approach used a conventional direct dry-blending, which was more time and energy efficient. Blown films were obtained followed by those two approaches to compare the water vapor barrier property. It was found that both compounding approaches provided good dispersion of CNCs and the water vapor barrier property were improved. However, the blown film from melt-blended process was subjected to more thermal degradation because of the additional heating exposure in the three-mixer prior to the film manufacturing process. The extent of thermal degradation was further quantified by various analytical methods including gel permeation chromatography, Fourier transformation infrared spectroscopy, and differential scanning calorimetry [67].

2.6.3 Electrospinning

Spinning is a process where the polymer melt or solution is pushed through a small orifice, then coagulated in a solution or drying environment. Electrospinning is commonly used to produce fibers for tissue engineering. As shown in Figure 2.16, an insulated syringe is employed to hold the solution mixture of cellulose/polymer. Under pressure and high voltage (10-30 kV), a jet of the solution is accelerated out of the metallic needle toward a collector plate [60]. The solvent is removed through the evaporation during the movement of the solution to form the composites [60].

The electrospinning produces fibers with diameter ranging from less than 100 nm to several micrometers [60].



Figure 2.16: Schematic representation of electrospinning ^[73].

One of the advantages of the electrospinning is that CNCs are oriented along the axis resulting in an uni-axially oriented composites with improved mechanical properties. Electrospinning has been used to incorporate CNCs into polymers including silk fibroin, polyethylene oxide, poly(acrylic acid), poly(lactic acid), poly(methyl methacrylate), poly(vinyl alcohol) and polycaprolactone [59,60,65]. Xiang and coworkers had investigated the mechanical properties of electrospun PLA/CNC fibers, and reported that with the addition of only 1% CNC, the tensile strength was improved significantly due to the increased crystallinity and decreased the diameter of the electrospun fibers [74].

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Chapter 3

EXPERIMENTAL

3.1 Materials

PLA 4044D resin with less than 4% D-lactide content [1] received from NatureWorks LLC (Minnetonka, MN, USA) and Cellulose Nanocrystals (CNCs) (2015-FPL-CNC-071) manufactured in U.S. Forest Service (Madison, WI, USA) were used in this study. CNCs were placed into the blender model MX1050XTS (Conair Corporation, Stamford, CT, USA) to break the CNCs cake into powders for 1 min at the speed of 22,000 rpm. Both materials were dried in the oven at 50°C for at least 24 hours. Prior to film manufacturing, the direct dry blending method were adopted to pre-mix the CNCs into PLA matrix [2,3]. CNC contents at 0.5 wt%, 1 wt% and 2 wt% were compounded with PLA pellets in the mixer at 22,00 rpm for 1 minute. The compounded materials and the control sample (neat PLA) were used in the following cast film extrusion process.

3.2 Sample manufacturing

A conical counter-rotating twin screw extruder (C.W. Brabender Instruments, South Hackensack, NJ, USA) with a length-to-diameter ratio of 13:1 and screw diameter of 32 mm, powered by a 5.6 kilowatt (7.5 hp) Intelli-Torque Plasti-Corder Torque Rheometer (C.W. Brabender Instruments, South Hackensack, NJ, USA) was used to manufacture the neat PLA and its composites cast films. The schematic representation of the cast films extrusion process is shown in Figure 3.1.



Figure 3.1: Schematic representation of the cast film extrusion process.

The extruder was equipped with a slit die of width and measured die gap of 203.2 mm and 3.4 mm, respectively. The temperature profile was set as 180 - 180 - 175 - 155 °C starting from the hopper to the die. Upon exiting the slit die, the extrudate was stretched by the rollers (Randcastle Extrusion system, Inc., Cedar Grove, NJ, USA), which were powered by a speed control drive (Model KBMD-240D, KB Electronics, Inc., Coral Springs, FL, USA) with a 0.06 hp motor (ABB Motors and Mechanical In., Fort Smith, AR, USA) and collected by the winder. The temperature of the rollers was set at 50°C using "LE" series Sentra temperature controller (Advantage Engineering, Inc., Greenwood, IN, USA). The speeds of extruder's rotational screws, chill rollers, and winder were 30 rpm, 20 rpm and 20 rpm, respectively, to achieve the targeted

film thickness of 50 μ m. All film compositions were manufactured employing similar processing conditions to allow comparison between the neat and composites films.

3.3 Property evaluation

3.3.1 Light microscopy

An optical microscope (Olympus BX41, Olympus, Center Valley, PA, USA) with a camera (Olympus Qcolor3) was used to evaluate the distribution and dispersion of CNCs into PLA matrix.

3.3.2 Thickness measurement

Once films were made, their sealing, mechanical and barrier properties were evaluated. In order to evaluate these properties, thickness must first be measured because barrier and mechanical properties are thickness dependent. Two methods were used to measure the thickness of the films, including the digital micrometer method and the density method.

Neat PLA and composite films were cut into strips with dimension of 25.4 mm x 177.8 mm. The thickness of the film strip was first determined by the digital micrometer, followed by the density method. The thickness of six strips per film formulation was assessed. The digital micrometer method was carried out using a digital micrometer (TMI 49-70 Series Micrometers, Testing Machines, Inc., New Castle, DE, USA). To avoid inaccuracy in the thickness of composite films due to their rough surfaces caused by CNC agglomerations, the thickness measurements through density method were performed following the approach described in the literature [4]:

$$\rho_{\text{sample}} = \frac{W_{\text{air}}}{W_{\text{air}} - W_{\text{water}}} \times \rho_{\text{water}}$$
(Equation 3.1)

where ρ_{sample} and ρ_{water} are the densities of the sample and water at room temperature, which was 0.9956502 g/mL at 30°C, respectively; and W_{air} and W_{water} are the sample's weight in air and water, respectively.

The densities of PLA and composite films calculated using the equation mentioned above were then used to calculate their thickness (l) as follows [4]:

$$l = \frac{W_{air}}{A \times \rho_{sample}}$$
(Equation 3.2)

where A is the area of the sample film, which was $4.5 \times 10^3 \text{ mm}^2$.

3.3.3 Profilometry

A surface profilometer (NanoMap 500LS 3D Stylus Surface Profilometer, AEP Technology, Santa Barbara, CA, USA) was used to monitor the surface texture of the neat PLA and its composite films. The scan speed was set to 50 μ m/s with contact force of 5.41 mg. The sample frequency and data resolution were 100 pts/s and 5 μ m, respectively. NanoMap 50 LS software was used to collect and analyze the data. A surface texture profile with Y-axis indicating the amplitude of the surface and X-axis as horizontal scan distance was generated for each scan. Three locations of neat PLA and PLA with 1% CNC films in the machine direction, from left, center and right edges along the width of the films, were scanned with the scan distance of 3 mm.

Two areas from neat PLA and composite films in both machine and cross machine direction were randomly selected for scanning distance of 2 mm.

Two values, Ra and peak-to-peak, were extracted from each surface texture profile generated for each scan. The mean roughness or the roughness average Ra, is the arithmetic average of amplitude in the surface texture profile [5]. Peak-to-peak values (P-t-P) refers to the distance between the highest peak and the lowest valley in the selected scanning range.

3.3.4 Hot tack performance

The hot tack performance was assessed by Lako Tool SL-10 Hot Tack Tester (Testing Machine Inc., New Castle, DE, USA) according to the procedures described in ASTM F1921-98. PLA and PLA/CNC composite films were cut into strips with 342.9 mm length x 25.4 mm width. The pressure and dwell time were maintained as 0.3 N/mm² and 2 s, respectively. Seal was formed at temperature starting from 60°C to 110°C with 5°C increment with the seal area of 25.4 mm x 25.4 mm. Five replicates from each film composition were tested at each sealing temperature to generate a hot tack profile.

An example of a hot tack profile is illustrated in Figure 3.2 where three important parameters could be extracted including (i) hot tack initiation temperature (HTIT), (ii) maximum hot tack strength (MHTS) and (iii) temperature where maximum hot tack strength occurs (T_{MHTS}) [6-8].



Figure 3.2: Hot tack profile showing three important parameters: (i) hot tack initiation temperature (HTIT), (ii) maximum hot tack strength (MHTS) and (iii) temperature where maximum hot tack strength occurred (T_{MHTS}).

Hot tack initiation temperature (HTIT) is the onset temperature where the hot tack strength increases rapidly [6-8]. The maximum hot tack strength (MHTS) is the highest force obtained throughout the tested temperature range whereas the temperature where maximum hot tack strength occurred (T_{MHTS}) is its corresponding temperature. As shown in Figure 3.2, a tangent line

was drawn from the linear portion of the hot tack profile where the temperature increased rapidly and the X-intercept of this tangent line was the estimated HTIT.

3.3.5 Seal strength

The fin seal was made prior to the seal strength test at 130°C, 0.303 N/mm² for 0.5s dwell time with the seal area of 25.4mm x 25.4mm using Lako Tool SL-10 Hot Tack Tester (Testing Machine Inc., New Castle, DE, USA). The sealed samples were placed at the room condition for at least 24 hours for cooling. Seal strength tests of PLA and PLA/CNC composite films were carried out in accordance of the procedures in ASTM F88/F88M using Instron 3345 tensile test machine (Instron, Norwood, MA, USA). The rate of grip separation was set as 254 mm/min and the distance between grips was 25.4 mm. The seal strength was measured using technique A, where the seal area remained unsupported during the tests. Forty samples were tested and the data analyzed through Instron Bluehill 3, version 3.61 software. The load at break and mode of failure were recorded.

3.3.6 Burst pressure

The burst pressure of pouches made with neat PLA and composite films was measured following the procedures described in ASTM F2054/F2054M. Prior to the burst test, the pouch with inside dimensions of 100 mm x 100 mm was formed by assembling two pieces of films, where three sides (two sides and one bottom) were sealed and the forth side remained open. The seals were made with intermittent sealing time of 3 s and cooling time of 3 s, using a table-style pedal impulse sealer (Model MFSA-450, Technopack Corporation, Sunrise, FL, USA) with voltage of 110 v (60Hz) and motor power of 1540 W. Two types of pouch configurations were formed for each formulation depending on the numbers of seals made in machine direction (MD)

and cross machine direction (CMD). As illustrated in Figure 3.3, the first type (type 1) sealed the two sides in MD and the bottom seal was made along CMD, whereas the second type (type 2) had two sides seals form along CMD and the bottom seal in MD.



Figure 3.3: Two types of pouch configurations for the burst test.

After the pouches were made and cooled at the room temperature, the burst pressure was measured using a burst tester (Test-A-Pack Systems 2000, Cobham plc, Dorset, UK) and the pressure causing the failure of the pouch was documented. Eight pouches per type were tested for each formulation.

3.3.7 Tensile properties

The tensile test was performed using Instron 3345 tensile test machine (Instron, Norwood, MA, USA) in accordance of the procedures outlined in ASTM D882. The results were analyzed by the Instron Bluehill 3, version 3.61 software. The distance between grips was 101.6 mm (4 in).

The test was carried out at room condition with the rate of grips separation of 50 mm/min in both the machine and cross machine directions of PLA and its composite films. The films were cut into 152.4 mm long and 25.4 mm wide strips. Tensile strength at yield, tensile strength at break, modulus, energy at break, and percentage of elongation at break were obtained. At least seven replicates of each composition were tested.

3.3.8 Falling dart impact strength

Impact strength of the films was determined using Labthink FDI-01 Falling Dart Impact Tester (Labthink International, Inc., Medford, MA, USA) in agreement with method A described in ASTM D1709 with slight modifications. Two layers of the film specimen were secured using clamps with inside diameter of 76.2 mm. A customized 10 g dart with diameter of 38.2 mm was dropped from a height of 0.33 m (13 in) and the film was assessed as failed or non-failed. "Failure" was defined as film rupture so that the dart penetrates through the film and "non-failure" indicated the situation where the film sustained its integrity to hold the dart. Testing followed a stair-step approach with the increment of dart weight of 5 g, meaning that the weight of the dart increased by 5 g if "non-fail" occurred or decreased by 5 g in case of film failure. At least ten fails and ten non-fails were required to complete a test. Each test generated failure weight as a measurement of impact strength and at least three tests were performed for each film composition.

3.3.9 Water Vapor Permeability (WVP)

Water vapor transmission rates of neat PLA and composite films were measured by the desiccant method described in ASTM E96 at 38°C and 85% RH. Each film specimen was mounted to a vapometer cup (Thwing-Albert Instrument Co., West Berlin, NJ, USA) with 3/4" (19.05 mm) depth. At least nine replicates were tested in the humidity chamber (Model LH 1.5, Associated

Environmental Systems, Ayer, MA, USA) for 24 hours. The cups were weighed before being placed in the chamber. The final weights were measured after 24 hours to obtain the weight gain to calculate WVTR using the following equation:

WVTR =
$$\frac{W/t}{A}$$
 (Equation 3.3)

where W is the weight gain at time t (24 hours), and A is the effective area of exposed film as $31.67 \times 10^{-4} \text{ m}^2$ [2,3].

The water vapor permeability can be calculated from WVTR as follows:

$$WVP = \frac{WVTR \times 1}{\Delta p}$$
(Equation 3.4)

where Δp is the difference in the partial pressure at the testing condition, which is 85% of the saturated water vapor pressure (P_s) at 38°C, and 1 is the thickness of the film measured by the density method. Since P_s at 38°C was found to be 6,626.12 Pa, the Δp was 5,632.20 Pa.

3.3.10 Oxygen Permeability (OP)

Oxygen transmission rate (OTR) was determined through Mocon Ox-Tran 2/22 Model L (Mocon Inc., Minneapolis, MN, USA) according to the procedures described in ASTM D3985 as previously reported [2,3]. At least four replicates were tested at 23°C and 0% relative humidity (RH). The effect of RH on OTRs of neat PLA and PLA with 2% CNC films were tested at constant

temperature of 23°C but at various RH values of 25%, 50% and 75%. At least four replicates were tested at each condition.

Oxygen permeability (OP) can be calculated by normalizing the thickness (l) and difference in partial pressure (Δp) of permeants across the tested films:

$$OP = \frac{OTR \times 1}{\Delta p}$$
 (Equation 3.5)

where Δp was 1 atm, which was 101,325 Pa, and 1 is the thickness of the film measured by the density method.

3.3.11 Statistics

All test results were analyzed based on T Test at 5% significance level using Microsoft Excel 2016.

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Chapter 4

RESULTS AND DISCUSSION

4.1 Effect of CNC content on the surface texture of PLA cast films

Once films were made, their physico-mechanical properties were evaluated, including barrier, tensile, impact strength, hot tack performance, seal strength and burst pressure. In order to evaluate these properties, thickness measurement must first be completed because barrier and mechanical properties are thickness dependent. However, previous studies showed that homogeneous distribution of CNCs in the PLA matrix was successfully achieved but the dispersion of CNCs into blown PLA matrix film was not good since some agglomerates were present in the film. The distribution was measured as the uniformity of CNCs in the PLA matrix, whereas dispersion was defined as the degree of large CNC agglomerates breaking into small particles [1,2]. The neat PLA and PLA/CNC composite films were examined using the light microscopy for distribution and dispersion of CNCs in PLA matrix (Figure 4.1). Shown in Figure 4.1, CNCs were present throughout the PLA matrix for all three PLA/CNC composite films indicating a good distribution of CNCs. However, agglomerations of CNC were observed indicating a poor dispersion.



Figure 4.1: Light microscope images of (a) PLA, (b) PLA/0.5%CNC, (c) PLA/1%CNC and (d) PLA/2%CNC films.

Those agglomerates introduced the surface roughness of PLA/CNC composite films preventing accurate thickness measurement. The profilometer was used to characterize the surface roughness. Shown in Figure 4.2 and Figure 4.3, the amplitude of surface texture (Z-axis) was recorded as a function of scan distance (X-axis). Figure 4.2 shows the surface texture profiles of neat PLA and PLA/1%CNC films with the scan distance of 3 mm at three different locations across the film's width in the machine direction. Large peaks were observed in all three locations of PLA/1%CNC films whereas neat PLA films had a relatively smooth surface within the same scan distance. Irrespective of the sample locations, PLA with 1% CNC films were rougher than neat

PLA films. To further verify the presence of the surface roughness in all composite films, the surface texture profiles of all neat PLA and PLA/CNC composite films were obtained in both machine and cross machine directions (Figure 4.3). As seen in Figure 4.3, large peaks and valleys were present in all PLA/CNC composite films in both machine and cross machine directions at the scan distance of 2 mm. The surface texture profiles indicated that regardless of the film location and direction, the surface of all composite films were rougher than that of PLA films, as more peaks and valleys were observed on the surface of the composite films, attributed to the formation of CNC agglomerates observed in light microscope images (Figure 4.1).



Figure 4.2: Surface texture profiles of (a) neat PLA and (b) PLA/1%CNC films collected at 3 different locations across the film's width: left (a1 and b1); center (a2 and b2); and right (a3 and b3) along the machine direction.



Figure 4.3: Surface texture profiles of neat PLA (first row) and PLA with 0.5% CNC (second row), 1% CNC (third row), and 2% CNC (fourth row). Samples in the left column were tested in the machine direction whereas those in the right column in the cross machine direction.

Surface roughness was further quantified into two parameters: i) roughness (Ra) value, the arithmetic mean of the amplitude [3] and ii) peak-to-peak value (P-t-P), which indicates the distance between the highest and lowest points on the scanned surface. The addition of CNC into the PLA matrix increased both the peak-to-peak and Ra values indicating a rougher surface compared to the surface of neat PLA films (Figure 4.4). Results from profilometry showed that irrespective of the film direction and location, incorporation of CNCs into PLA matrix introduced surface roughness, attributed to the agglomeration of CNC in the PLA matrix. The fact that this roughness existed in different locations throughout PLA/CNC films supported the finding that a good distribution of CNCs in PLA matrix was achieved.



Figure 4.4: Effect of CNC content on roughness (Ra) and peak-to-peak values of PLA cast films.

Since the surfaces of PLA/CNC composite films were found to be rougher than that of neat PLA film, it was more accurate to consider the thickness of PLA/CNC films to be the same as that of neat and smooth PLA films, as films from all formulations were manufactured using identical processing conditions. The results from two thickness measurement methods further confirmed this hypothesis. Shown in Table 4.1, the density method resulted in similar thicknesses for PLA and composite films (~0.042 mm) as expected since all films were manufactured using identical processing conditions. It was worth mentioning that the thickness of neat PLA films measured by the density method was slightly lower than that measured by digital micrometer, attributed to the small peaks observed in the surface texture profiles of neat PLA films in Figure 4.2. Since density method provided more accurate measurements, the thickness obtained from this method was used to calculate the water vapor and oxygen permeability using equations 3.4 and 3.5, respectively.

Motoriala	Thickness* (mm)			
wraterials	Digital micrometer method	Density method		
PLA	$0.052 \pm 0.006^{\rm A}$	$0.042\pm0.004^{\rm A}$		
PLA + 0.5% CNC	$0.078 \pm 0.010^{\rm B}$	$0.042\pm0.005^{\rm A}$		
PLA + 1%CNC	0.079 ± 0.008^{B}	$0.043\pm0.004^{\rm A}$		
PLA + 2%CNC	$0.091 \pm 0.018^{\rm C}$	$0.043\pm0.002^{\rm A}$		

Table 4.1: Thicknesses of neat PLA and composite films measured using digital micrometer and density methods.

*Different superscript letters within the same column are significantly different based on the T Test results at 5% significance level.

4.2 Effect of CNC content on the barrier properties of PLA cast films

Table 4.2 summarizes the effect of CNC content on water vapor permeability (WVP) and oxygen permeability (OP) of PLA films. The addition of CNCs into PLA matrix reduced the WVP and OP significantly. A decrease of approximately 45% in WVP and 49% in OP was observed by adding 2% CNC.

Materials	WVP at 38% (10 ⁻¹⁶ kg-n	C 85% RH [*] n/m ² -s-Pa)	OP at 23°C 0% RH* (10 ⁻²⁰ kg-m/m ² -s-Pa)		
	Average	% Decrease	Average	% Decrease	
PLA	$159.4\pm9.7^{\rm A}$	-	$353.6\pm54.4^{\rm A}$	-	
PLA+0.5%CNC	117.0 ± 4.2 ^B	26.6	267.4 ± 48.4^B	24.4	
PLA+1%CNC	$110.4\pm6.6^{\rm C}$	30.8	$212.1 \pm 25.9^{B,C}$	40.0	
PLA+2%CNC	$87.0\pm8.0^{\rm D}$	45.4	$178.8\pm26.4^{\rm C}$	49.4	

Table 4.2: The effect of CNC content on water vapor permeability (WVP) and oxygenpermeability (OP) of PLA films.

^{*}Different superscript letters within the same column are significantly different based on the T Test results at 5% significance level.

This improvement could be attributed to the increased crystallinity. Crystallites distributed in PLA matrix form impermeable regions. Those impermeable regions create a more tortuous diffusion path for permeants, leading to a slower diffusion process [1,4-8]. Additionally, several studies have shown that CNCs also act as a nucleating agent to induce crystallization which resulted in higher degree of crystallinity [1,9-11]. Karkhanis and coworkers had reported that the addition of 1% CNC in PLA blown films increased the degree of crystallinity based on the results obtained from differential scanning calorimetry [1]. The oxygen permeability (OP) of PLA and PLA with 2% CNC films remained constant as the RH increased from 0% RH to 75% RH at 23°C (Figure 4.5). Similar results were reported by Kunanusont and coworkers [12]. They found that both oxygen permeability and transmission rates of PLA blown films were not affected by the elevating relative humidity. This was due to polarity of films. The contact angle results demonstrated that the surface of PLA films was hydrophilic as the contact angle was less than 90°, thus, more unlikely to be affected by RH [12].



Figure 4.5: Effect of testing relative humidity (RH) on the OP of PLA and PLA/2% CNC

composite films.

4.3 Influence of CNC content on the sealing properties of PLA cast films

The effect of CNC content on the sealing properties was evaluated based on the data obtained from seal, hot tack and burst tests. Figure 4.6 illustrates the experimental hot tack profiles of neat PLA and PLA/CNC composite films where the hot tack strength (force) was graphed as a function of temperature.



Figure 4.6: Experimental hot tack profiles of neat PLA and PLA/CNC composite films.

For all formulations, the hot tack strength increased rapidly starting from 75°C and reached the peak at 85°C. The hot tack parameters estimated from the profiles are listed in Table 4.3. The addition of CNCs into PLA matrix did not affect the HTIT nor temperature where MHTS occurred, which indicated that same sealing conditions could be applied to seal both neat PLA and PLA/CNC composite films. However, the average of maximum hot tack strength (MHTS) increased as the CNC content increased up to 1%.

Table 4.3: The effect of CNC content on the hot tack initiation temperature (HTIT), maximum hot tack strength (MHTS) and temperature where MHTS occurred of PLA films.

Materials	Hot tack initiation temperature [*] (°C)	Temperature where MHTS occurred* (°C)	Maximum hot tack strength [*] (g)
PLA	$74.6\pm0.8^{\rm A}$	$88.0\pm4.5^{\rm A}$	$1,076.8 \pm 244.7^{\mathrm{A}}$
PLA+0.5%CNC	$73.6\pm0.8^{\rm A}$	$86.0\pm2.2^{\rm A}$	$1,\!302.0\pm202.3^{\rm A}$
PLA+1%CNC	$74.5\pm0.7^{\rm A}$	$85.0\pm0.0^{\rm A}$	$1,\!641.6\pm215.9^{\rm B}$
PLA+2%CNC	$73.7\pm0.5^{\rm A}$	$90.0 \pm 11.2^{\rm A}$	$1,\!197.2\pm121.6^{\rm A}$

*Different superscript letters within the same column are significantly different based on the T Test results at 5% significance level.

Incorporating 1% CNC into PLA matrix significantly improved the hot tack strength, which indicated the formation of a stronger seal, probably attributed to the increased stress transfer efficiency at the interface [13]. However, MHTS began to decrease when the CNC content reached 2%, attributed to poor adhesion between interface due to rougher surfaces created by the agglomerations of CNC. As the volume fraction of CNCs increased, the surface became rougher. The surface roughness between sealing interfaces created surface irregularities preventing the intimate direct contact at seal area, further hindering the heat diffusion at the interface and forming a weaker seal [14].

Nevertheless, it is worth mentioning that the average of MHTS for all PLA/CNC composite films was higher than that of neat PLA films. Additionally, once the T_{MHTS} was reached (Figure 4.6), the hot tack strength of PLA and composite films with 0.5 and 1% CNC decreased as the

sealing temperature increased. In contrast, the hot tack strength of composite films with 2% CNC appeared to be not affected by the increasing sealing temperature. As a result, the hot tack force of PLA/2%CNC at 110°C was higher than that of neat PLA and other composite films, implying a broader processing window with the addition of 2% CNC into PLA matrix [14].

The seal strength of neat PLA and PLA/CNC composite films are summarized in Table 4.4. The adhesive failure is defined as the separation of the seal at the interface, whereas cohesive failure occurs when the material breaks before the seal [15]. The addition of CNCs into PLA matrix increased the seal strength significantly, irrespective of CNC content (Table 4.4). As the CNC content increased up to 1%, the cohesive failure was more likely to occur indicating stronger seals formed. This was attributed to the efficient stress transfer in the matrix [13]. However, with the addition of 2% CNC, the mode of failure was less likely to be cohesive. This could be explained as the rough surface preventing the heat diffusion further forming weaker seals.

Materials	Seal strength [*] (N)	% Failure mode
PLA	$8.2\pm5.6^{\rm A}$	85% Adhesive
PLA+0.5%CNC	$14.4\pm9.9^{\text{B}}$	100% Cohesive
PLA+1%CNC	11.8 ± 8.7^{B}	100% Cohesive
PLA+2%CNC	11.9 ± 5.1^{B}	85% Cohesive

Table 4.4: The effect of CNC content on the seal strength of PLA films.

*Different superscript letters within the same column are significantly different based on the T Test results at 5% significance level.

The burst pressures of neat PLA and composite films are shown in Figure 4.7. Type 1 referred to pouches made with two sides sealed along the machine direction (MD) and bottom seal in cross machine direction (CMD). Type 2 defined as pouches with two sides in CMD and bottom seal in MD. As shown in Figure 4.7, regardless of the types of pouches, the addition of CNC content increased the burst pressure, when compared with that of pouches made with neat PLA films, owing to the effective stress transfer between CNCs and PLA matrix [13]. However, as the CNC content increased to 2%, the burst pressure decreased due to the disruption of interfacial adhesion. Incorporating more CNCs may induce microvoids and preventing the efficient stress transfer [14].



Figure 4.7: The effects of CNC content and pouch configuration on the burst pressure of neat PLA films.

Two modes of failures, adhesive and cohesive, occurred during the burst test. As defined previously, the cohesive failure refers to the breakage of the material before the seal, and adhesive failure is defined as the separation of the seal interfaces [15]. The effect of CNCs on the percentage of failure mode of neat PLA films is summarized in Table 4.5. Irrespective of the pouch configurations, majority of failures was cohesive failure, indicating the formation of stronger seals.

Table 4.5 The effect of CNC content on the percentage of failure mode of neat PLA films in burst test.

	PLA	PLA + 0.5%CNC	PLA + 1%CNC	PLA + 2%CNC
Type 1 (MD)	80% Cohesive	100% Cohesive	90% Cohesive	90% Cohesive
Type 2 (CMD)	100% Cohesive	100% Cohesive	100% Cohesive	100% Cohesive

4.4 Effect of CNC content on the tensile and impact properties of PLA cast films

Figure 4.8 illustrates the stress-strain of neat PLA and its composite films when the test was performed along films' machine direction (MD) and cross machine direction (CMD). The tensile property data of each replicate was extracted from those stress-strain curves and summarized in Table 4.6 with averages and standard deviations of tensile strength at yield, tensile strength at break, modulus, energy at break and elongation at break.

The results indicated that increasing CNC content into PLA matrix increased the brittleness of PLA film (Figure 4.8). Shown in Figure 4.8a1, when tested in the machine direction, neat PLA films demonstrated a well-defined yield point and elongation at break reached 91.5% with the tensile strength at break of 41 MPa (Table 4.6). On the other hand, all of the composite films

showed no yielding behaviors and failed at a much lower range of strain (below 4%) with a higher tensile strength at break, when compared with that of neat PLA films. The brittleness of the composite films was attributed to the high degree of brittleness inhered in the cellulose [17].



Figure 4.8: Stress-strain curves of neat PLA films in machine (a1) and cross machine (a2) directions as well as of PLA/CNC composite films in machine (b1) and cross machine (b2)

directions.

Materials	Tensile strength at yield (MPa)	Tensile strength at break [*] (MPa)	Modulus* (GPa)	Energy at break [*] (10 ⁻³ J)	Elongation at break* (%)
		Machine Direc	ction		
PLA	59.9 ± 6.3	$41.0\pm22.7^{\rm A}$	$2.8\pm0.3^{\rm A}$	$4439.7 \pm 1356.3^{\rm A}$	$91.5\pm25.4^{\rm A}$
PLA + 0.5%CNC	-	$115.6\pm12.7^{\text{B}}$	$5.7\pm0.2^{\rm B}$	$209.6\pm37.2^{\rm B}$	3.1 ± 0.4^{B}
PLA + 1%CNC	-	$82.7\pm25.1^{\rm C}$	$5.2\pm0.7^{\rm C}$	$199.4 \pm 131.6^{\text{B},\text{C}}$	$3.4 \pm 1.8^{\rm B}$
PLA + 2%CNC	-	$61.8\pm28.2^{\rm A}$	$4.4\pm0.7^{\rm D}$	151.8 ± 70.0^{C}	$3.2\pm1.3^{\text{B}}$
		Cross Machine D	irection		
PLA	-	$23.4\pm9.6^{\rm A}$	$2.8\pm0.1^{\rm A}$	$16.4\pm5.8^{\rm A}$	$1.1\pm0.2^{\rm A}$
PLA + 0.5%CNC	-	$61.6\pm12.8^{\text{B}}$	$5.6\pm0.1^{\rm B}$	52.7 ± 11.8^{B}	$1.5\pm0.2^{\rm B}$
PLA + 1%CNC	-	$42.6\pm19.0^{\rm C}$	5.9 ± 1.0^{B}	$23.2\pm11.6^{\rm A}$	$1.0\pm0.2^{\rm C}$
PLA + 2%CNC	-	$23.3\pm6.6^{\rm A}$	$3.7\pm0.1^{\text{C}}$	$11.8 \pm 3.2^{\rm C}$	$0.9\pm0.1^{\rm C}$

Table 4.6: The effect of CNC content on the tensile properties of PLA films in both machine and cross machine directions.

*Different superscript letters within the same column are significantly different based on the T Test results at 5% significance level when tested in the same direction.

Additionally, the high elongation at break of neat PLA films was not uncommon, as other investigators reported similar values. Petersson and coworkers reported the elongation at break greater than 100% for PLA films prepared by solution casting [18]. Garlotta also concluded that the elongation at break for high-molecular weight oriented PLA ranged from 15-160% [19]. However, it is worth mentioning that neat PLA films failed at strain of 1.2% with the tensile strength at break of 23.4 MPa in the cross machine direction, which were much lower than that of machine direction, attributed to the uniaxial oriented morphology induced by the stretching in the film manufacturing process [20]. The drawing in the melt state of the polymer may induce a "shish-kebab" structure of PLA chains along the drawing direction, which was the machine direction, further resulting a higher elongation at break and tensile strength in that direction compared to that of the cross machine direction [21-23].

Figure 4.9 illustrates the effect of CNC content on the energy and elongation at break of PLA cast films. In machine direction, the general decrease of both energy (Figure 4.9a1) and elongation (Figure 4.9b1) at break with the addition of CNCs confirmed the brittleness of the composite films, irrespective of CNC content. These properties decreased by adding only 0.5% CNC into PLA and a further increase in CNC content did not change the energy and elongation at break. Interestingly, different trend was observed in the cross machine direction where the addition of up to 0.5% CNC into PLA matrix increased both energy (4.9a2) and elongation (4.9b2) at break of the samples. However, both the energy and elongation at break decreased when the CNC concentration increased above 0.5%.



Figure 4.9: The effect of CNC content on the energy at break in machine (a1) and cross machine (a2) directions as well as on the elongation at break in machine (b1) and cross machine (b2) directions, of PLA cast films.

In contrast, the tensile strength at break and modulus for all of the composite films were higher than that of neat PLA films, indicating the composite films were stronger and stiffer than neat PLA films. Shown in Figure 4.10a and 4.10b, in the machine direction, both of the tensile strength and modulus increased with the addition of 0.5% CNC with a slight drop when the CNC concentration reached 2%. Similar trend was observed in cross machine direction. Irrespective of CNC concentration and testing direction, incorporating CNCs into PLA matrix improved tensile strength as well as the modulus, attributed to the effective stress transfer and the rule of mixtures, respectively [17,24,25]. The slight drop of tensile strength and modulus could be explained as the reduced interfacial adhesion between PLA matrix and CNCs. As CNC content increased from 0.5% to 2%, the intimate interfacial adhesion may be disrupted. The poor dispersion of CNCs facilitated the formation of numerous irregularly shaped microvoids, and further impacted the efficient stress transfer between matrix and CNCs [25].



Figure 4.10: Effect of CNC content on the (a) tensile strength at break and (b) modulus of PLA films along machine direction (MD) and cross machine direction (CMD).

The results from tensile test illustrated that irrespective of CNC concentration, incorporating CNCs into PLA matrix improved the modulus and tensile strength of neat PLA cast films, at the expense of ductility. The brittleness of the composite films was further supported by the results from dart impact test. The impact strength of neat PLA and composite films is summarized in Table 4.7. The failure mass of all composite films was significantly lower than that of neat PLA films, indicative of brittleness in the PLA/CNC composite films.

Materials	Failure mass [*] (g)	% Decrease
PLA	$38.8\pm3.5^{\rm A}$	-
PLA + 0.5% CNC	$33.0\pm2.2^{\rm B}$	14.9
PLA + 1% CNC	33.2 ± 2.4^{B}	14.4
PLA + 2% CNC	32.1 ± 4.7^{B}	17.3

Table 4.7: The effect of CNC content on the impact strength of PLA cast films.

^{*}Different superscript letters within the same column are significantly different based on the T Test results at 5% significance level.

APPENDICES

APPENDIX A

Effect of CNC content on the thickness of PLA cast films

Thickness (l) was calculated using the density method as follows:

$$\rho_{\text{sample}} = \frac{W_{\text{air}}}{W_{\text{air}} - W_{\text{water}}} \times \rho_{\text{water}}$$
(Equation 3.1)

$$l = \frac{W_{air}}{A \times \rho_{sample}}$$
(Equation 3.2)

where W_{air} and W_{water} are the sample's weight in air and in water, respectively, ρ_{sample} and ρ_{water} are the densities of the sample and water at room temperature, which ρ_{water} at 30°C was 0.9956502 g/mL, area (A) was 4.5 x 10³ mm².

Materials -	Water density method				Digital micrometer method
	W _{air} (g)	W _{water} (g)	Density (g/cm ³)	Thickness (mm)	Thickness (mm)
	0.2526	0.0670	1.36	0.041	0.057
	0.2592	0.0601	1.30	0.044	0.056
	0.2386	0.0448	1.23	0.043	0.049
PLA	0.2261	0.0707	1.45	0.035	0.052
	0.2225	0.0102	1.04	0.047	0.051
	0.2373	0.0438	1.22	0.043	0.049
Average	0.2394	0.0494	1.27	0.042	0.052
Std Dev	0.0144	0.0222	0.14	0.004	0.006

Table A.1: Thickness measurement of neat PLA films.

Materials	Water density method				Digital micrometer method
	W _{air} (g)	W _{water} (g)	Density (g/cm ³)	Thickness (mm)	Thickness (mm)
	0.2721	0.1267	1.86	0.032	0.071
	0.2936	0.0914	1.45	0.045	0.081
PLA +	0.2932	0.0864	1.41	0.046	0.081
0.5%CNC	0.2992	0.0904	1.43	0.046	0.082
	0.3187	0.1374	1.75	0.040	0.083
	0.2791	0.0901	1.47	0.042	0.067
Average	0.2927	0.1037	1.56	0.042	0.078
Std Dev	0.0163	0.0223	0.19	0.005	0.010

Table A.2: Thickness measurement of PLA with 0.5% CNC films.

Motoriola	Water density method				Digital micrometer method
Materials	W _{air} (g)	W _{water} (g)	Density (g/cm ³)	Thickness (mm)	Thickness (mm)
	0.2857	0.0785	1.37	0.046	0.071
	0.2697	0.1055	1.64	0.037	0.083
PLA +	0.3186	0.1222	1.62	0.044	0.087
1%CNC	0.2858	0.1040	1.57	0.040	0.079
	0.2948	0.0984	1.49	0.044	0.078
	0.2683	0.0535	1.24	0.048	0.074
Average	0.287	0.094	1.49	0.043	0.079
Std Dev	0.019	0.024	0.15	0.004	0.008

Table A.3: Thickness measurement of PLA with 1% CNC films.

	Water density method				Digital micrometer method
Materials	W _{air} (g)	W _{water} (g)	Density (g/cm ³)	Thickness (mm)	Thickness (mm)
	0.3955	0.1950	1.96	0.045	0.108
	0.3495	0.1680	1.92	0.040	0.089
PLA + 2%CNC	0.3989	0.2113	2.12	0.042	0.079
	0.3433	0.1625	1.89	0.040	0.089
	0.3497	0.1498	1.74	0.044	0.086
	0.4126	0.2063	1.99	0.046	0.095
Average	0.3749	0.1822	1.94	0.043	0.091
Std Dev	0.0307	0.0254	0.12	0.002	0.018

Table A.4: Thickness measurement of PLA with 2% CNC films.

APPENDIX B

Effect of CNC content on the surface texture of PLA cast films

Materials	Location	Ra (µm)	Peak-to-peak (µm)
	Left	0.3581	2.3719
PLA	Center	0.3249	1.9785
	Right	0.3441	2.2905
PLA+1%CNC	Left	1.1177	14.9756
	Center	1.8598	13.0534
	Right	1.3102	11.8594

Table B.1: Surface roughness (Ra) and peak-to-peak values across neat PLA and PLA with 1% CNC films.

CNC content	0%		0.5%		1%		2%	
Direction	Ra (µm)	Peak-to- peak (µm)						
CMD	0.2088	1.8543	0.9051	9.7599	0.9781	6.7811	1.4491	6.8791
MD	0.2868	1.6950	1.1302	7.5198	1.0111	8.8358	1.2174	12.1893
CMD	0.3197	2.0554	1.6460	6.8726	0.9336	7.8103	2.2842	10.6988
MD	0.2269	2.9652	1.3288	7.0541	0.6224	4.4043	0.8189	7.4929
Average	0.2606	2.1425	1.2525	7.8016	0.8863	6.9579	1.4424	9.3150
Std Dev	0.0516	0.5680	0.3143	1.3337	0.1788	1.8978	0.6186	2.5449

Table B.2: Effect of CNC content on the surface roughness of PLA cast films in both machine direction (MD) and cross machine direction (CMD).

APPENDIX C

Effect of CNC content on the water vapor and oxygen barrier properties of PLA cast films

WVP (10 ⁻¹⁶ kg-m/m ² -s-Pa) at 38°C and 85%RH							
CNC content	0%	0.5%	1%	2%			
	153.69	117.72	111.15	101.11			
	162.19	119.68	121.86	91.06			
	163.50	120.99	115.17	92.40			
	168.08	113.80	111.82	92.40			
	169.39	108.56	101.77	73.65			
	168.08	118.37	110.48	87.04			
	159.58	116.41	106.46	85.71			
	149.77	121.64	113.83	85.04			
	140.61	120.34	101.11	76.33			
	-	112.49	-	85.04			
Average	159.43	117.00	110.40	86.98			
Std Dev	9.70	4.22	6.56	7.99			

Table C.1: Effect of CNC content on the water vapor permeability (WVP) of PLA cast films at 38° C and 85%RH.

OP (10 ⁻²⁰ kg-m/m ² -s-Pa) at 23°C and 0%RH							
CNC content	0%	0.5%	1%	2%			
	308.18	246.20	216.48	180.32			
	418.50	228.32	222.60	182.71			
	309.07	319.77	245.03	144.13			
	378.62	319.39	175.58	208.22			
	-	223.33	200.63	-			
Average	353.59	267.40	212.06	178.84			
Std Dev	54.42	48.38	25.88	26.36			

Table C.2: Effect of CNC content on the oxygen permeability (OP) of PLA cast films at 23° C and 0%RH.

OP (10 ⁻²⁰ kg-m/m ² -s-Pa) at 23°C								
RH	0%		25%		50%		75%	
CNC content	0%	2%	0%	2%	0%	2%	0%	2%
	308.18	180.32	376.72	279.85	232.61	121.00	257.87	147.56
	418.50	182.71	324.81	141.34	260.49	111.06	214.77	148.38
	309.07	144.13	277.73	157.16	453.38	133.14	250.81	132.00
	378.62	208.22	279.04	165.23	359.92	123.02	221.33	121.59
	248.83	140.97	-	-	-	150.50	258.93	-
	302.46	132.55	-	-	-	162.72	259.67	-
	293.64	-	-	-	-	-	250.25	-
	294.80	-	-	-	-	-	367.25	-
	289.05	-	-	-	-	-	-	-
	238.91	-	-	-	-	-	-	-
Average	308.21	164.82	314.58	185.90	326.60	135.24	260.11	137.38
Std Dev	54.00	29.94	46.86	63.42	100.65	21.61	46.64	12.94

Table C.3: Effect of testing relative humidity (RH) on the OP of PLA and PLA/2%CNC composite films.

APPENDIX D

Effect of CNC content on the hot tack performance, seal strength and burst pressure of

PLA cast films
									Peak	force	(g)									
CNC content			0%			0.5%				1%					2%					
Temper ature	Number of replicates																			
(°C)	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
60	49	13	0	16	21	28	18	17	16	17	67	18	16	14	14	94	20	19	17	21
65	18	21	21	17	16	12	19	13	21	12	14	16	13	17	9	14	18	17	0	0
70	34	24	26	37	30	20	23	18	21	30	18	15	15	16	24	0	0	18	28	39
75	105	48	40	54	133	65	50	42	64	105	57	51	31	35	60	118	80	81	55	109
80	642	210	174	146	916	632	770	931	1,248	1,085	812	879	447	1,242	1,584	563	544	885	1,121	1,018
85	1,146	859	819	461	1,461	1,290	1,170	1,069	1,544	1,143	1,781	1,638	1,317	1,588	1,884	1,043	1,123	1,188	1,243	1,378
90	1,119	856	882	587	1,202	884	976	1,463	1,218	1,070	1,129	1,390	1,257	1,360	1,557	972	786	992	1144	1,209
95	934	694	642	1,034	850	661	1,037	1,274	783	1,089	1,429	1,037	988	1,178	1,396	981	649	788	892	1,006
100	781	543	359	800	953	897	991	931	766	785	1,099	884	887	962	989	812	749	688	806	908
105	273	209	331	772	523	679	856	1,026	585	598	656	621	536	256	594	817	647	659	797	1,001
110	364	233	244	393	636	492	542	583	313	364	443	297	59	352	160	1,061	546	704	936	929

Table D.1: Effect of CNC content on the hot tack profiles of neat PLA films as temperature increases from 60°C to 110°C.

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		HTI	Г (°С)			Тмнт	s (°C)		MHTS (g)				
CNC content	0%	0.5%	1%	2%	0%	0.5%	1%	2%	0%	0.5%	1%	2%	
	73.94	74.59	74.88	73.79	85	85	85	110	1,146	1,290	1,781	1,061	
	75.40	74.08	74.61	74.42	85	85	85	85	859	1170	1638	1123	
	75.58	73.37	76.54	73.58	90	90	85	85	882	1463	1317	1181	
	74.59	73.57	73.85	73.21	95	85	85	85	1,034	1,544	1,588	1,243	
	73.70	72.50	73.55	73.42	85	85	85	85	1,461	1,143	1,884	1,378	
Average	74.64	73.62	74.69	73.68	88.00	86	85	90.00	1,076.40	1,322.00	1,641.60	1,197.20	
Std Dev	0.84	0.79	1.17	0.46	4.47	2.24	0	11.18	244.75	177.01	215.89	121.56	

Table D.2: Effect of CNC content on the hot tack initiation temperature (HTIT), temperature where maximum hot tack strength occurred (T_{MHTS}), and maximum hot tack strength (MHTS) of neat PLA films at the temperature range of 60°C to 110°C.

CNC content	0%		0.5	%	19	Y0	2%		
	Force (N)	Mode of failure							
-	3.474	Adhesive	10.401	Cohesive	7.315	Cohesive	13.163	Cohesive	
	6.439	Adhesive	40.015	Cohesive	5.773	Cohesive	11.482	Cohesive	
	4.092	Adhesive	16.090	Cohesive	5.201	Cohesive	10.255	Cohesive	
	11.685	Adhesive	7.507	Cohesive	14.641	Cohesive	15.268	Cohesive	
	4.615	Adhesive	24.396	Cohesive	38.548	Cohesive	14.955	Adhesive	
	7.822	Cohesive	9.390	Cohesive	14.492	Cohesive	3.910	Adhesive	
	3.992	Adhesive	13.179	Cohesive	9.907	Cohesive	5.450	Adhesive	
	3.869	Adhesive	3.430	Cohesive	3.323	Cohesive	5.123	Adhesive	
	6.759	Adhesive	27.042	Cohesive	8.570	Cohesive	11.919	Cohesive	
	6.199	Adhesive	10.332	Cohesive	37.524	Cohesive	15.563	Cohesive	
	4.494	Adhesive	10.471	Cohesive	3.099	Cohesive	7.289	Adhesive	
	6.789	Adhesive	9.159	Cohesive	2.799	Cohesive	9.350	Cohesive	
	7.388	Adhesive	9.298	Cohesive	3.599	Cohesive	16.352	Cohesive	

Table D.3: Effect of CNC content on the seal strength of neat PLA cast films.

Table D.3 (cont'd)

6.085	Adhesive	11.144	Cohesive	4.847	Cohesive	26.980	Cohesive
2.681	Adhesive	15.684	Cohesive	8.439	Cohesive	10.731	Adhesive
3.846	Adhesive	8.428	Cohesive	15.700	Cohesive	13.001	Cohesive
4.434	Adhesive	5.374	Cohesive	8.746	Cohesive	14.125	Cohesive
6.041	Adhesive	33.629	Cohesive	9.347	Cohesive	13.227	Cohesive
5.615	Adhesive	5.131	Cohesive	2.605	Cohesive	26.690	Cohesive
7.083	Adhesive	13.499	Cohesive	16.144	Cohesive	14.071	Cohesive
3.463	Adhesive	11.219	Cohesive	15.637	Cohesive	10.561	Cohesive
8.619	Adhesive	7.999	Cohesive	25.542	Cohesive	20.720	Cohesive
11.270	Adhesive	9.921	Cohesive	21.640	Cohesive	9.388	Cohesive
24.412	Adhesive	34.102	Cohesive	5.983	Cohesive	7.267	Cohesive
11.391	Cohesive	14.520	Cohesive	14.611	Cohesive	5.915	Cohesive
12.020	Cohesive	6.727	Cohesive	12.700	Cohesive	10.279	Cohesive
23.675	Adhesive	3.532	Cohesive	3.437	Cohesive	11.673	Cohesive
7.921	Adhesive	7.948	Cohesive	5.619	Cohesive	11.427	Cohesive
3.400	Adhesive	28.051	Cohesive	3.095	Cohesive	5.414	Cohesive

Table D.3 (cont'd)

	7.129	Adhesive	32.975	Cohesive	21.842	Cohesive	9.702	Cohesive
	9.243	Adhesive	27.489	Cohesive	10.658	Cohesive	16.855	Cohesive
	13.046	Adhesive	9.406	Cohesive	8.008	Cohesive	13.677	Cohesive
	8.043	Cohesive	33.157	Cohesive	4.873	Cohesive	12.238	Cohesive
	2.748	Adhesive	8.262	Cohesive	15.901	Cohesive	6.815	Cohesive
	26.894	Adhesive	16.362	Cohesive	14.832	Cohesive	6.015	Cohesive
	9.029	Adhesive	9.353	Cohesive	7.970	Cohesive	13.323	Cohesive
	5.373	Cohesive	5.285	Cohesive	15.358	Cohesive	15.399	Cohesive
	7.110	Adhesive	8.659	Cohesive	11.501	Cohesive	11.937	Cohesive
	7.947	Adhesive	4.883	Cohesive	4.598	Cohesive	8.359	Cohesive
	10.957	Adhesive	13.410	Cohesive	25.443	Cohesive	11.060	Cohesive
Average	8.177	-	14.421	-	11.747	-	11.923	-
Std Dev	5.574	-	9.913	-	8.739	-	5.080	-
% Mode of failure	-	85% Adhesive	-	100% Cohesive	-	100% Cohesive	-	85% Cohesive

				Burst pressu	ure (in. H ₂ O)							
-		Type 1	(MD)		Type 2 (CMD)							
CNC content	0%	0.5%	1%	2%	0%	0.5%	1%	2%				
	51.4	206.7	123.8	54.0	73.7	164.6	37.4	117.6				
	24.8	114.1	202.8	34.7	61.2	141.9	91.7	148.4				
	61.9	93.2	76.0	87.8	67.0	183.2	227.0	128.2				
	48.4	212.4	237.1	26.9	123.9	188.6	197.5	40.5				
	21.9	183.3	222.6	95.9	113	200.2	228.5	220.2				
	36.4	164.1	234.5	160.1	94.4	141.0	196.8	245.6				
	33.8	197.8	207.5	27.9	77.7	176.0	159.7	65.0				
	21.8	148.4	92.8	220.6	133.5	219.3	54.5	70.5				
Average	37.6	165.0	174.6	88.5	93.1	176.9	149.1	129.5				
Std Dev	15.0	43.8	66.2	69.9	27.5	27.2	77.3	73.5				
% Mode of failure	80% Cohesive	100% Cohesive	90% Cohesive	90% Cohesive	100% Cohesive	100% Cohesive	100% Cohesive	100% Cohesive				

Table D.4: Effect of CNC content on the burst pressure of neat PLA cast films.

APPENDIX E

Effect of CNC content on the tensile properties of PLA cast films

	Tensile modulus (MPa)														
-		Machine	direction		Cross machine direction										
CNC Content	0%	0.5%	1%	2%	0%	0.5%	1%	2%							
	2,727.977	5,439.484	4,976.195	5,604.761	2,883.113	5,645.779	3,872.461	3,628.285							
	2,848.442	5,460.088	4,648.636	3,989.295	2,797.365	5,765.433	4,124.440	3,526.297							
	2,811.679	5,497.720	4,997.701	3,839.115	2,770.386	5,228.406	4,673.136	3,546.088							
	3,038.820	5,814.096	5,076.374	4,155.284	2,824.040	5,692.100	5,630.776	3,600.143							
	2,477.109	5,813.165	6,188.784	4,206.754	2,715.320	5,674.032	6,390.407	3,449.277							
	3,356.111	5,771.622	4,375.433	5,540.027	2,872.735	5,700.582	6,790.661	3,679.156							
	2,497.236	5,397.827	4,158.570	4,186.421	2,843.386	5,556.249	5,922.063	3,688.294							
	-	5,930.891	5,188.200	4,137.694	2,836.766	5,611.405	5,821.641	3,654.274							
	-	5,655.476	5,412.282	4,066.708	2,626.055	5,561.038	-	3,788.153							
	-	5,561.696	5,464.273	5,011.173	2,562.660	5,534.997	6,213.452	3,825.936							
	-	6,183.621	6,094.474	5,179.569	-	5,588.850	6,864.387	3,696.433							
	-	-	5,297.119	3,830.017	-	5,624.395	7,681.995	3,671.949							

Table E.1: Effect of CNC content on the tensile modulus of neat PLA cast films in both machine and cross machine directions.

Table E.1 (cont'd)	
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Std Dev	307.233	243.753	659.036	655.145	107.218	137.263	1033.270	106.252
Average	2,822.482	5,684.153	5,219.621	4,430.728	2,773.183	5,559.035	5,915.896	3,646.191
	-	-	-	-	-	5,509.058	-	-
	-	-	-	-	-	5,714.137	-	-
	-	-	-	-	-	5,568.045	-	-
	-	-	-	-	-	5,632.892	-	-
	-	-	-	-	-	5,474.566	-	-
	-	-	-	-	-	5,616.373	-	-
	-	-	-	-	-	5,642.988	-	-
	-	-	-	-	-	5,334.963	6,131.853	-
	-	-	6,539.004	-	-	5,356.586	5,822.125	-
	-	-	5,138.348	-	-	5,335.381	6,008.000	-
	-	-	4,738.920	3,852.644	-	5,489.546	6,791.042	-

	Tensile strength (MPa)																
			N	Iachine o	directi	on			Cross machine direction								
CNC content	0	⁰ ⁄0	0	.5%	1%		2%		()%	0.:	5%	1	0⁄0	2	%	
	Yield	Break	Yield	Break	Yield	Break	Yield	Break	Yield	Break	Yield	Break	Yield	Break	Yield	Break	
	55.546	17.353	_	122.105	-	85.552	-	113.168	-	17.394	_	61.385	_	21.281	-	21.197	
	56.242	28.782	-	82.713	-	80.134	-	70.409	-	20.650	-	64.305	-	26.688	-	30.439	
	61.753	67.324	-	110.308	-	75.358	-	50.556	-	29.965	-	63.300	-	22.544	-	28.958	
	63.495	52.314	-	123.557	-	92.525	-	27.777	-	23.152	-	60.263	-	37.023	-	15.159	
	54.344	27.773	-	116.718	-	122.196	-	64.794	-	11.026	-	79.880	-	65.495	-	15.125	
	71.823	72.578	-	111.219	-	76.730	-	111.322	-	34.541	-	72.005	-	67.963	-	10.268	
	56.289	21.025	-	119.529	-	56.975	-	69.245	-	22.291	-	28.534	-	32.484	-	27.029	
	-	-	-	125.033	-	84.480	-	50.148	-	33.974	-	60.882	-	25.550	-	23.068	
	-	-	-	111.046	-	23.650	-	72.872	-	33.297	-	74.437	-	17.425	-	30.386	
	-	-	-	117.452	-	99.064	-	30.711	-	7.336	-	71.086	-	58.703	-	27.859	
	-	-	-	131.581	-	124.825	-	61.563	-	-	-	64.757	-	29.663	-	23.780	

Table E.2: Effect of CNC content on the tensile strength of neat PLA cast films in both machine and cross machine directions.

Table E.2 (cont'd)	
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	-	-	-	-	-	99.584	-	19.745	-	-	-	74.963	-	77.564	-	26.305
	-	-	-	-	-	62.009	-	60.906	-	-	-	68.870	-	45.453	-	
	-	-	-	-	-	70.424	-	-	-	-	-	63.258	-	40.677	-	
	-	-	-	-	-	87.538	-	-	-	-	-	62.719	-	53.627	-	
	-	-	-	-	-	-	-	-	-	-	-	69.157	-	59.106	-	
	-	-	-	-	-	-	-	-	-	-	-	55.714	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	44.855	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	37.664	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	74.186	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	64.152	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	59.436	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	40.049	-	-	-	
Avg	59.927	41.021	-	115.569	-	82.736	-	61.786	-	23.363	-	61.559	-	42.578	-	23.298
Std Dev	6.255	22.732	-	12.726	-	25.131	-	28.148	_	9.621	_	12.841	-	18.957	-	6.637

	Energy at break (J)								
CNC content		Machine	direction		Cross machine direction				
	0%	0.5%	1%	2%	0%	0.5%	1%	2%	
	2.083	0.230	0.157	0.208	0.009	0.037	0.018	0.017	
	4.800	0.304	0.107	0.093	0.023	0.043	0.010	0.015	
	4.932	0.174	0.456	0.218	0.019	0.044	0.011	0.013	
	3.542	0.193	0.170	0.275	0.010	0.041	0.016	0.010	
	5.330	0.182	0.238	0.103	0.013	0.082	0.037	0.004	
	6.284	0.234	0.101	0.157	0.021	0.058	0.042	0.012	
	4.107	0.215	0.414	0.107	0.010	0.060	0.011	0.011	
	-	0.204	0.103	0.280	0.021	0.057	0.016	0.013	
	-	0.186	0.092	0.106	0.024	0.069	0.013	0.013	
	-	0.178	0.130	0.108	0.014	0.057	0.031	0.011	
	-	0.206	0.198	0.135	-	0.069	0.027	0.010	
	-	-	0.139	0.090	-	0.063	0.044	0.012	
	-	-	0.077	0.094	-	0.050	0.015	-	
	-	-	0.160	-	-	0.039	0.017	-	
	-	-	0.449	-	-	0.046	0.029	-	
	-	-	-	-	-	0.051	0.034	-	
	-	-	-	-	-	0.053	-	-	
	-	-	-	-	-	0.036	-	-	

Table E.3: Effect of CNC content on the energy at break of neat PLA cast films in both machine and cross machine directions.

	-	-	-	-	-	0.040	-	-
	-	-	-	-	-	0.060	-	-
	-	-	-	-	-	0.042	-	-
	-	-	-	-	-	0.059	-	-
	-	-	-	-	-	0.056	-	-
Average	4.4397	0.2096	0.1990	0.1518	0.0164	0.0527	0.0232	0.0118
Std Dev	1.3563	0.0372	0.1310	0.0698	0.0058	0.0118	0.0116	0.0032

	Elongation at break (%)								
CNC content	Machine direction				Cross machine direction				
	0%	0.5%	1%	2%	0%	0.5%	1%	2%	
	43.629	3.365	2.872	3.119	0.903	1.232	1.231	1.067	
	106.202	4.182	2.380	2.380	1.395	1.312	0.737	0.984	
	96.198	2.871	6.644	4.922	1.231	1.394	0.820	0.903	
	77.828	2.873	2.954	5.906	0.902	1.312	0.820	0.821	
	111.945	2.789	3.200	2.462	1.067	1.886	1.149	0.574	
	118.258	3.364	2.379	2.625	1.313	1.558	1.229	0.904	
	86.192	3.199	7.464	2.543	0.903	1.640	0.656	0.821	
	-	2.953	2.215	5.824	1.313	1.559	0.821	0.903	
	-	2.871	2.052	2.543	1.395	1.722	0.821	0.903	
	-	2.789	2.462	2.298	1.067	1.559	1.067	0.821	
	-	2.871	2.873	2.543	-	1.722	0.985	0.820	
	-	-	2.543	2.544	-	1.640	1.149	0.903	
	-	-	1.970	2.461	-	1.476	0.738	-	
	-	-	3.036	-	-	1.315	0.821	-	
	-	-	6.070	-	-	1.394	1.067	-	
	-	-	-	-	-	1.476	1.149	-	
	-	-	-	-	-	1.476	-	-	
	-	-	-	-	-	1.230	-	-	

Table E.4: Effect of CNC content on the elongation at break of neat PLA cast films in both machine and cross machine directions.

Table E.4 (cont'd)

Std Dev	25.426	0.418	1.774	1.347	0.204	0.172	0.194	0.119
Average	91.465	3.102	3.408	3.244	1.149	1.487	0.954	0.869
	-	-	-	-	-	1.560	-	-
	-	-	-	-	-	1.559	-	-
	-	-	-	-	-	1.312	-	-
	-	-	-	-	-	1.559	-	-
	-	-	-	-	-	1.312	-	-

APPENDIX F

Effect of CNC content on the dart impact strength of PLA cast films



Figure F.1: The dart impact test results for neat PLA cast films.



Figure F.2: The dart impact test results for PLA with 0.5% CNC cast films.



Figure F.3: The dart impact test results for PLA with 1% CNC cast films.



Figure F.4: The dart impact test results for neat PLA with 2% CNC cast films.

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REFERENCES

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Chapter 5

CONCLUSIONS

5.1 Conclusions

The aim of this study was to utilize a continuous extrusion process, which efficiently incorporates CNCs into a PLA matrix, in order to manufacture PLA/CNC cast films and further investigate its properties for the packaging application. To achieve this goal, a counter rotating twin-screw extruder was used to manufacture the PLA/CNC cast films. Once the films were made, the distribution and dispersion of CNCs in PLA matrix were examined. As the physico-mechanical properties of neat PLA and its composite films are thickness dependent. The surface texture of PLA and its composite films were determined to assure proper comparison. Two methods, the density and digital micrometer methods, were used to measure the thickness of both neat and composite films to assure the accuracy of the thickness. To expand the packaging application, the effect of CNC content on the hot tack performance, seal strength, and burst strength of PLA cast films was studied. Additionally, this study examined the effect of CNC content on the tensile property and impact strength of PLA cast films. The water and oxygen barrier properties of neat PLA and its composite films were further investigated. The following conclusions were drawn from this study.

- 1. The addition of CNCs into PLA matrix increased the surface roughness of PLA cast films.
 - a. From the images of light microscopy, a homogenous distribution of CNCs into PLA matrix was achieved, however, there were CNC agglomerates indicating a poor dispersion.

- b. The agglomeration of CNCs led to the surface roughness which further verified by profilometry. Results from profilometry showed that irrespective of the film direction and location, incorporating of CNCs into PLA matrix introduced surface roughness, attributed to the agglomeration of CNC in the PLA matrix. The presence of roughness throughout the PLA/CNC films supported the finding that a good distribution was achieved.
- 2. The thickness measurements obtained from the density method showed that there were no significant differences in the thickness between neat PLA and composite films.
 - a. The thickness of neat PLA films obtained from the density method were slightly lower than that measured by the digital micrometer, due to the slight surface roughness supported by the surface profiles from profilometry.
- 3. The addition of CNCs into PLA matrix did not negatively affect the hot tack performance and seal strength.
 - a. Both the hot tack initiation temperature and temperature where the maximum hot tack strength occurred were not affected by the addition of CNC content. In contrast, the maximum hot tack strength appeared to increase with CNC content up to 1% and slightly decreased with further CNC content increase. The optimum maximum hot tack strength occurred with the addition of 1% CNC.
 - b. Incorporating CNCs into the PLA matrix significantly increased the seal strength of PLA cast films, regardless of CNC content.

- c. Regardless of the pouch configuration (sealing directions) and CNC content, the addition of CNCs into PLA matrix increased the burst pressure of the pouches.
- 4. Irrespective of CNC concentration, the addition of CNC content in the PLA matrix improved the tensile strength and modulus of neat PLA cast films, resulting stronger and stiffer composite films. These improvements were achieved at the expense of ductility since both the elongation at break and the energy to break decreased, results supported by the dart impact strength showing that PLA/CNC composite films were more brittle than neat PLA films.
- 5. The addition of CNCs into PLA matrix significantly improved the water and oxygen barrier properties of the films.
 - a. By adding 2% CNC into the PLA matrix, improvements of approximately 45% and 49% in water vapor and oxygen permeabilities of PLA films, were respectively observed. These improvements were attributed to the tortuous diffusion path created by crystallites, as CNCs can serve as both crystallites and a nucleating agent.
 - b. The oxygen permeability of PLA and PLA with 2% CNC films remained constant as the relative humidity increased from 0% to 75% at 23°C.

5.2 Future works

While this study focused on the processing and the physico-mechanical property evaluation of PLA/CNC extruded cast films for the food packaging application, other properties including optical (haze, color, clarity) and thermal (glass transition and melting temperatures, thermal stability) must also be studied. In addition, to ensure the packaging integrity throughout the distribution environment, properties related to vibration and shock absorption, must also be evaluated. As this study showed that stretching in the machine direction at the melt state of PLA had significant effect on the elongation at break of neat PLA films due to the oriented polymer chains alignment, it would be appropriate to further investigate and develop an in-depth understanding of the relationship between tensile properties, melt state drawing and polymer chain alignment. In addition, the effect of melt state stretching on the CNC alignment should also be studied. Furthermore, in order to expand the use of CNCs in PLA extruded cast films for food packaging application, a thorough migration study and shelf life study for PLA/CNC films would be beneficial to carry out using real food products to assure the safety of consuming the products.