IMPROVING GAS BARRIER PROPERTIES OF SUGARCANE-BASED LLDPE WITH CELLULOSE NANOCRYSTALS

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ABSTRACT

IMPROVING GAS BARRIER PROPERTIES OF SUGARCANE-BASED LLDPE WITH CELLULOSE NANOCRYSTALS

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This study was aimed at improving the gas barrier property of sugarcane-based LLDPE using cellulose nanocrystals (CNCs). Specifically, this study evaluated the effect of testing methods (isostatic versus gravimetric) on CO_2 permeability coefficient (P_{CO2}) and/or O_2 permeability coefficient (P₀₂) of various bio-PE grades with different densities (LLDPE, LDPE, and HDPE) as well as the effect of CNC content on crystallinity, tortuosity factor, and gas barrier properties of bio-LLDPE sheets and films. The isostatic and gravimetric methods yielded similar P_{CO2}, irrespective of PE grade. However, the P_{CO2} negatively correlated with PE density. All nanocomposites showed considerable improvement in gas barrier irrespective of the CNC content. The P_{CO2} of LLDPE sheets decreased by 36% by adding 10 wt.% of CNCs into the sheet. Similarly, a significant decline in both P_{O2} (about 50%) and P_{CO2} (about 33%) of LLDPE films was obtained by adding 2.5 wt.% of CNCs into the films. Nevertheless, no correlation was established between gas permeability and percent crystallinity of LLDPE sheet since the P_{CO2} decreased almost linearly with increasing CNC content whereas the percent crystallinity of LLDPE increased only up to 2.5% CNC content and remained constant thereafter. In contrast, the tortuosity factors calculated from the diffusion coefficients increased almost linearly with CNC contents and correlated well with the gas permeability improvement in the bio-LLDPE-based nanocomposites. Consequently, the enhanced gas barrier in the nanocomposite was assigned to the tortuosity effect created by the impermeable cellulose nanocrystals rather than the changes in percent crystallinity.

Copyright by MADHUMITHA NATARAJAN 2021 Dedicated to my father Mr. R. Natarajan and my mother Dr. R. Vijayalakshmi

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Most of the plastics used in the industry for various applications including packaging applications are petroleum-based and are obtained from crude oil. However, the use of petroleum-based plastics is a major contributor to global greenhouse gas emissions [1]. Therefore, there is a need for more sustainable, environmentally friendly alternatives like biobased and/or biodegradable polymers [2]. Bioplastics have a smaller carbon footprint compared to petroleum-based plastics [3]. In addition to being sustainable, biobased plastics also have physico-mechanical properties like petroleum-based polymers; and hence are ideal alternative to the latter [4]. Globally, bioplastics was valued at \$4.6 billion in 2019 and is expected to reach \$13.1 billion by 2027[5]. The recent development of sugarcane-based polyethylene is a typical example of more environmentally sustainable plastics. Recently, Braskem, a Brazilian chemical company, has launched a set of biobased polyethylene derived from sugarcane ethanol that have similar properties to their petroleum-based counterparts.

Polyethylene (PE) is one of the most widely used polymers in the plastics industry and has different variants like high density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE). Each variant has its unique properties in terms of appearance, crystallinity, mechanical, and barrier properties. In food packaging, material with transparency is highly desired as it influences packaging aesthetics along with material having good moisture and gas barrier to provide required shelf life for the packaged product. All PE variants have good water barrier, but poor gas barrier and their transparencies vary [6-8].

HDPE has good gas barrier compared to other variants of PE but has a milky white appearance, whereas LDPE has poor gas barrier but has excellent transparency. Since both properties are crucial for packaging applications these drawbacks limit the scope of these polymers in packaging. LLDPE on the other hand has improved regularity in its structure at a low-density making it better than LDPE in most properties especially in terms of its gas barrier properties. LLDPE is also transparent in appearance making it better than HDPE in terms of transparency. Consequently, LLDPE is a suitable polymer for applications requiring both good transparency and good gas barrier like produce bags, frozen food bags, as a protective pallet stretch film, etc. [7-10]. However, when compared to other plastics like EVOH, PET, etc., LLDPE is poor in its gas barrier properties. Further enhancement in gas barrier properties will make it more suitable for a wide range of packaging applications.

Various methods are commonly employed to enhance the gas barrier properties of packaging materials. Coating as well as production of multilayers and laminates structures are few techniques where layers of different materials are combined to achieve desired gas barrier properties of the films [11,12]. Unfortunately, these different layers cannot be easily separated at the end of the material's lifecycle, which leads to problems with recyclability and often a lot of these multilayer films end up in the landfill. Landfill is a major issue with polymers as it is an unsustainable waste management practice.

Manufacture of bio-based composite films of monolayer structure with excellent gas barrier properties could be the solution to a such problems as they are just as recyclable as their neat polymer counterparts [13]. Monolayered nanocomposite films manufactured by incorporating nanoparticles such as nano clay [14], cellulose whiskers [15], cellulose nanofibers (CNFs) [16], cellulose nanocrystals (CNCs) [17-19], etc. into various polymer matrices have been reported to improve the gas barrier properties of the neat polymer counterparts. The improved barrier performance of nanocomposite films has been mainly assigned to the tortuosity effect created by the presence of highly crystalline nanoparticles into the polymeric matrix, which increases the degree of crystallinity of the neat polymer. These crystals increase the effective travel path length for permeants diffusing through the nanocomposites. This reduces the rate of diffusion, thus lowering permeation as reported by others [17-19]. Unfortunately, limited work has been done on nanocomposites based on bio-PE. Recently, Bazan and coworkers investigated the mechanical, thermal properties, and micromechanics of composites made of biobased polyethylene and a combination of natural fibers (e.g., wood flour, coconut shell fibers, and basalt fibers). They reported that hybridization of cellulose fibers with basalt fibers significantly improves the properties compared to adding cellulose fibers alone. Additionally, the accelerated water and thermal ageing of composites samples deteriorated their strength properties compared to unaged counterparts [6].

It is well accepted that gas barrier properties of semi-crystalline polymer filled with nanoparticles is affected not only by the impermeable nanoparticles, but also greatly depends on its crystallinity and crystalline morphology [15-21]. Although a negative correlation between percent crystallinity and permeability coefficients of various permeants has been reported for nanocomposites [15-21], polymer crystallinity is certainly not the only factor influencing its permeability, since no correlation has also been established between level of crystallinity and permeability [22-24]. For example, despite a 27% reduction in crystallinity, the oxygen and carbon dioxide permeability of the polypropylene (PP)/ethylene-propylene-diene rubber (EPDM) blend nanocomposite reduced two-fold by adding only 1.5 vol% montmorillonite-based organoclay into PP/EPDM blend [22]. The increase in barrier property of the nanocomposite blend was attributed to the combination of two phenomena, including (i) the decrease in area available for diffusion, a result of impermeable flakes replacing permeable polymer; and (ii) the increase in the distance a solute must travel to cross the film as it follows a tortuous path around the impermeable flakes [22]. Similarly, a significant decline in both O₂ (about 45%) and CO₂ (about 68%) permeability coefficients of PLA films was obtained by adding 1.37 vol % graphene oxide nanosheets (GONSs) into PLA film, even though all the PLA nanocomposite films were basically amorphous [23]. This large improvement in gas barrier properties of PLA/GONs nanocomposite film was mainly assigned to the impermeable GONSs acting as crystallites and the strong interfacial adhesion between GONSs and PLA matrix, rather than the changes in crystallinity and crystalline morphology of PLA matrix [23]. Therefore, in addition to level of crystallinity, the role of other factors contributing to barrier improvement like the tortuosity factor must also be investigated to understand the mechanisms of barrier improvement in nanocomposites.

1.2 Objectives

Therefore, this study was aimed at improving the gas barrier property of sugarcane-based LLDPE using cellulose nanocrystals (CNCs). Specifically, this study evaluated the effect of CNC content on gas barrier properties of sugarcane-based LLDPE sheets and films. Emphasis was placed on the gravimetric-sorption method to quantify the diffusion and solubility coefficients needed to estimate the tortuosity factor and permeability coefficient, which were correlated to elucidate the mechanism involved in barrier property improvement in nanocomposites. To achieve this objective the following specific objective were proposed:

- Determine the tortuosity factor and gas permeability coefficient of bio LLDPE/CNC composites.
- Correlate the tortuosity factor and gas permeability coefficient in order to elucidate the mechanism involved in barrier property improvement in nanocomposites.

1.3 Hypothesis

This research is intended to test the hypothesis that gas barrier property of sugarcane-based polyethylene can be improved by addition of cellulose nano crystals.

1.4 Structure of thesis

The first chapter of the thesis includes an introduction to rationalize the research. Chapter 2 covers a background on various processing techniques polyethylene, manufacturing of cellulose nano crystals and incorporation techniques. Chapter 3 will cover the material specifications, equipment, and sample manufacturing. The results of permeability coefficient, crystallinity, tortuosity factors, diffusion, solubility of the rigid sample and permeability coefficients for the film sample composites and correlation between the permeability coefficient and tortuosity factor along with its discussion is covered in Chapter 4. Chapter 5 gives the summary of the findings inferred from the experimental data and proposed future.

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CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

This chapter covers the background and literature related to the scope of the research. The synthesis of polyethylene, types of polyethylene, processing techniques of polyethylene will be covered along with the extraction, processing techniques, properties of cellulose nanocrystals and processing technologies of composite films. The different barrier measurement techniques and crystallinity measurement techniques will also be covered.

2.2 Polyethylene

Polyethylene (PE) belongs to the family of addition polymers based on ethylene. Polyethylene can be with linear or branched, it can be copolymers or homopolymers. It is widely used in the polymer industry and is used for a variety of applications like films, containers, pipes, fibers, etc. It is one of the first olefinic polymers to be used in food packaging [1].

2.2.1 Synthesis of polyethylene

Polyethylene is made from gaseous hydrocarbon monomer ethylene (C_2H_4) which is produced commonly from the cracking of ethane. Ethane can be obtained from petroleum or from biobased resources. The ethylene molecule comprises of two methylene units (CH_2) and this is linked together by a double bond. The double bond of ethylene is broken using the polymerization process and the single bond generated is used to link another ethylene molecule and this results in chain of repeating units i.e., a polymeric chain having the following structure [2]. Schematic diagram of structure of polyethylene is shown in Figure 2-1.



Figure 2-1 Structure of polyethylene.^[3]

2.2.2 Petroleum based and biobased polyethylene

Petroleum based polyethylene as the name suggests is developed from ethane obtained from petroleum and natural gas. These are nonrenewable resources and produces synthetic polyethylene. Polyethylene is an important polymer hence these nonrenewable resources are used extensively. However, this petroleum-based polyethylene is not sustainable and contribute to a higher carbon footprint [4,5].

Recently, biobased polyethylene (BioPE) has been developed which is an alternative to the petroleum-based PE as it is more environmentally friendly. These are usually manufactured from biobased and renewable resources like sugarcane, wheat grains and sugar beet, etc. These plant-

based sources are renewable feedstock which consume CO_2 in their annual growth cycle. Hence manufacturing of around 1 Ton of biobased PE from sugarcane would capture around 2.5 Tons of CO_2 from the atmosphere when solar energy is used [6]. This clearly indicates that biobased PE is contributing to a lesser carbon footprint as compared to its petroleum-based counterparts. Also, it is to be noted that BioPE exhibits similar physical and chemical characteristics as their petroleumbased counterparts and can be directly implemented in the manufacturing processes in the industry.

2.3 Variants in polyethylene

There are variants in polyethylene which is produced during the polymerization process depending on the pressure used during the process [5].

2.3.1 Branched polyethylene versus linear polyethylene

The variants produced can be either branched or linear, homopolymer or copolymer. Each variant of polyethylene has its own unique properties. High-density polyethylene (HDPE) and low-density polyethylene (LDPE) are linear and branched variants of polyethylene with 70% to 90% crystallinity and 40% to 60% crystallinity, respectively. HDPE has a linear structure this helps it to have a greater crystallinity producing a tighter packing of molecules which in turn leads to a higher density. Though HDPE is not a good gas barrier it has better gas barrier properties as compared to LDPE and LLDPE due to its dense packing and crystalline structure. The high crystallinity of HDPE also makes it opaque compared to LDPE by giving it a milky white appearance. On the other hand, due to its low percent crystallinity LDPE offers good clarity and

has some unique properties. However, it has poor gas barrier properties due to its low percent crystallinity [1].

2.3.2 Copolymer LLDPE

Linear low-density polyethylene (LLDPE) is linear polymer with very short branch like pendant groups, it is produced by the presence of a comonomer in the polymerization process along with a stereo-specific catalyst. It is also known as ultra-low-density polyethylene (ULDPE), depending on the density achieved during the polymerization process. LLDPE is intermediate in terms of its properties as compared to LDPE and HDPE. In packaging there is a need for both clarity and good gas barrier properties, LLDPE is offers better gas barrier then LDPE but offers more clarity than HDPE hence its preferred in many packaging applications [1]. In this study LDPE has been used to improve its gas barrier properties. Schematic diagram of the structural difference among the polyethylene variants is shown in Figure 2-2.



Figure 2-2 Structure of a) HDPE *b*) LDPE *c*) LLDPE.

2.4 Properties of polyethylene

2.4.1 Low-density polyethylene (LDPE)

LDPE is a branched variant of polyethylene, and the branched structure of polyethylene makes it have desirable properties like clarity, heat sealability, flexibility and ease of processing. LDPE can be used in different processing techniques like cast film, blown film, injection molding, extrusion coating and blow molding. LDPE is majorly used in the flexible packaging industry. Applications of LDPE include bags for clothing and food items, containers, vapor barriers, industrial liners, household products to name a few. LDPE has density of around 0.910 – 0.940 g/cm³ and melting temperature of around 105 – 115°C. It has great properties like good impact strength, machinability, and flexibility. Also due to its lower percent crystallinity LDPE offers good clarity as compared to HDPE but both water and gas barrier is poor compared to HDPE [1,7].

2.4.2 High-density polyethylene (HDPE)

High-density polyethylene (HDPE) is one of most versatile and the second most widely used polymer in the plastics industry. It is produced by the ethylene polymerization in a highpressure reactor using Ziegler - Natta stereo specific catalyst. HDPE has a milky white appearance and is a non-polar linear thermoplastic. Its density usually ranges from 0.940 - 0.965 g/cm³ and its melting point is around 128 - 138°C. Applications of HDPE include manufacture of containers for milk, detergent, bleach, shampoo, pharmaceutical bottles, and flexible packaging applications. It has good processing capabilities and can be used in extrusion blow molding, injection molding, injection blow molding and blown and cast film processes. Other properties like tensile and impact strength changes with molecular weight distribution. One major disadvantage of HDPE is environmental stress cracking which is defined as the failure of a material that is under stress and exposed to a chemical where exposure to either of them alone does not lead to a failure hence for product like detergents are HDPE copolymer is used [1,7].

2.4.3 Linear-low-density polyethylene (LLDPE)

The density of LLDPE is usually 0.916 – 0.940 g/cm³. LLDPE has good mechanical properties as compared to LDPE at the same density due to its high regularity in the structure and narrower molecular weight distribution. LLDPE has a higher melting point as compared to LDPE due to its increased stiffness. LLDPE has higher puncture resistance, tensile strength, tear properties and elongation. Applications of LLDPE include heavy duty shipping sacks, stretch /cling film, grocery snacks [1,7]. The properties of the polyethylene variants are summarized in Table 2-1.

Properties	HDPE	LDPE	LLDPE
Density (g/cm ³)	0.940 - 0.965 ^[1]	$0.910 - 0.940^{\ [1]}$	$0.916 - 0.940^{[1]}$
Crystallinity (%)	70-90 [1]	40-60 [1]	35-60 [8]
Oxygen permeability (10 ⁻¹⁷ × kg·m/m ² sec·Pa)	0.92 – 0.35 ^[9,10]	0.75 - 7.68 ^[9,11,12]	5.16 - 8.33 [13-15]
Carbon dioxide permeability (10 ⁻¹⁷ × kg·m/m ² sec·Pa)	10.9 – 15 ^[9,16]	1.56 - 8.53 ^[9,11,12]	24.99 - 31.9 [13,14,17]
Melting temperature (°C)	128 – 138 [1]	105 – 115 [1]	114 - 160 [18]
Clarity	Milky white in appearance ^[1]	Transparent ^[1]	Translucent ^[1]

Table 2-1 Summary of properties of polyethylene.

2.5 Processing technologies of polyethylene

Polyethylene is produced using melt processing, where the first step is to convert the solid plastics usually in the form of pellets into a melt. The melt is further transformed into desired shape using various processing techniques like blown film extrusion and cast film extrusion processes for film manufacture, extrusion blow molding, compression molding, Injection blow molding, injection stretch blow molding for manufacture of rigid forms of polyethylene [1,19]. This section of this chapter focuses on the processing techniques used for processing polyethylene with special focus on blown film extrusion and compression molding techniques.

2.5.1 Extrusion

Polyethylene is commonly processed using extrusion process to develop desired products from its melt like sheets, film, bottles, etc. The extrusion process is carried out using an extruder. An extruder is used for various machines and applications like making sheets, films, and blow molder of bottles. It is also used as a part of injection molding and injection blow molding machines used in packaging. In all these applications the extruder works similarly and only varies in its shaping operation of the melt. The extruder uses pressure, heat, and shear to uniformly transform the plastic pellets into melt [1].

The extruder comprises of a barrel which is a hollow tube having helical channels called screw. The screw is usually divided into three parts. Firstly, the feed section or solids conveying section then the compression section or melting section and lastly, metering, or pumping section. The standard single screw extruder has a right-hand helix on the screw, and it rotates in the counterclockwise direction. Hopper is another important component of the extruder which helps in feeding the plastic or other components into the extruder from the feed port. The nozzle or die is the component through which the melted plastic exists the extruder [1]. Schematic diagram of the extrusion process is shown in Figure 2-3. There are different types of dies that are used in the extrusion process depending on the desired shape that must be created. Annular die is used for blown film extrusion for production of tubular pipes or films, slit die is used in cast film extrusion to produce sheets and films and capillary die is used for rods and filaments [20].



Figure 2-3 Schematic diagram of extrusion process.

2.5.2 Blown film extrusion

Polyethylene can be made into sheets and film by using blown film extrusion and polyethylene is one of the commonly used polymers in blown film production. Applications where blown film is used generally are bags of all kinds, films for industrial applications like construction and agriculture. In packaging blown films are usually used in packages of cereal, meat, and frozen foods which have multilayers that need to be coextruded and is usually done suing blown film extrusion [1]. Blown film extrusion is a continuous process in which the polymer is melted, and the melt is forced through the annular die and this results into a tube which is inflated with air. This forms a bubble which then cooled. The air is blown inside the bubble to inflate the bubble and for cooling the air is always blown from the outside. In blown film extrusion, the film is biaxially oriented by stretching it both longitudinally and circumferentially during production [1].

The blow-up ratio and the speed control the properties of the blown film. The blow-up ratio is the ratio between the diameter of the final tube of the film and the diameter of the die. Various sizing and guiding devices guide the film in the blown film tower. The stage where the film turns from molten to semi solid is called the frostline. The orientation of the film is completed by this stage though the film may still be deformable. Once the film is cool enough it is deflated using the pinch rollers and plates and then it is wound using the winding roller with or without treatment on the film [1]. Schematic diagram of the blown film extrusion process has been illustrated in Figure 2-4.



Figure 2-4 Schematic diagram of blown film extrusion process.

In blown film extrusion process once the blown film is stable and running there is very less scrap generated as compared to cast film, hence it is good process for a high-volume production. However, film quality is lower than cast films in terms of uniformity of gauge and transparency [1].

2.5.3 Cast film extrusion

Polyethylene sheets and films can be manufactured using the cast film extrusion process. When the thickness of the film is less than 0.010 inch then it is called a film if its more than 0.010 inch then it is a sheet [21]. To produce thinner films the process used is chill roll process or cold cast process. In cast film extrusion the extrudate obtained after extrusion is forced through a slit die. The slit die creates a rectangular profile in which the width is much higher than the thickness. The cast film is produced when the melt passing through the slit die is guided onto chilled chrome rollers which helps the melt cool down to form a film and the rollers help in impact a good surface characteristic to the film [1].

The contact of the extrudate to the first chill roll occurs tangentially and further it typically travels in an S-pattern across two or more rollers. Typically to pin the plastic onto the first chill roller an air knife is used. The dimensions of the film are usually controlled by the various parameters like extrusion rate, die dimensions and take-off speed. For certain applications instead of chill roll process other processes like roll stack and calendaring, quench tank and water bath process are used. Irrespective of the cooling process used, once the plastic is cooled it is wound using the nip rolls and the winder. The nip rolls help the film to get a uniform tension and feeds it to the winder. There are different types of winders available catering to different end needs [1].

2.5.4 Extrusion blow molding

Polyethylene can be made into bottles using the extrusion blow molding process. It is one of the simplest and oldest techniques used to manufacture plastic bottles. The extrusion blow molding process begins with forming a hollow plastic tube in the downward direction. The tube is then closed by the two halves of the mold, cutting it from the extruder. Air is blown into the mold to expand the bubble or parison using a blow pin. The blow pin is inserted in the region that will get cut off from the bottle, so the final forming of the container is done by air only. The mold is cooled using water and then it is opened at a stage when the container can retain its shape without the mold. The excess material called flash, is removed from the container neck and bottom area and from areas like handles and offset necks [1,22].

Extrusion blow molding is especially useful for producing larger bottles with handles or offset necks. It is not very economical for smaller bottles. Also coextruded bottles for different applications are made using extrusion blow molding, like the liquid detergent container with HDPE/regrind-recycle/HDPE bottle structure [1,22].

2.5.5 Compression molding

Polyethylene and polyethylene composites are commonly processed using the compression molding techniques. It comprises of different processes like resin transfer molding process, transfer molding process, compression transfer molding process. The process is chosen depending on the type of product to be fabricated and material used [22]. In compression molding the raw plastic is converted into finished product by compressing them into the desired shape. The machines contain a stationary and a movable mold, the material is placed between them and the mold is closed. Pressure and heat are applied to get a homogenized mixture of the materials used. Figure 2-5 shows the schematic diagram of the compression molding process.



Figure 2-5 Schematic diagram of compression molding process.

The values of applied heat and pressure are decided based of the rheological and thermal properties of the material being used. The machine needs to be preheated to reduce the holding time. Depending on the properties desired for the product either slow cooling or quenching can be applied at the end of the holding time [23].

2.5.6 Thermoforming

Polyethylene is thermoformed for several packaging applications. Thermoforming is one of the least expensive processing techniques compared to injection and blow molding processes. Low pressure is required in the thermoforming process which further brings down the cost as cheaper materials can be used for mold manufacturing. Thermoforming is usually done to obtain smaller sized containers hence the number of packages per cycle is large [1].

Thermoforming process comprises of three basic steps, heating of the sheet, forming the sheet, and trimming the part. Parameters like temperature, cycle time and mold designs used in thermoforming are decided based on the preliminary experimentation based on the polymer being used. The ideal radiant heater temperatures used for polyethylene are around $470 - 630^{\circ}$ C for LDPE and $510 - 630^{\circ}$ C for HDPE. The plastic softened by heat in the first step of thermoforming can be further molded by various methods. The most common three methods are drape forming, vacuum forming and pressure forming [1].

Drape forming uses gravity as the main forming force. A male mold having a positive or convex shape is used and the hot plastic sheet is pulled down towards the mold by the application of vacuum, the hot plastic takes up the mold shape. Vacuum forming uses the air pressure as the main forming force. The mold used in vacuum forming is negative or concave shaped and the hot plastic is forced into the shape of the mold by clamping it onto the mold and applying vacuum. The third type of forming pressure forming as the name suggests uses additional pressure to form the sheet. In this type of forming both positive and negative type of mold can be used [1].

2.6 Drawbacks in polyethylene's property

In packaging there is a need for good gas barrier properties to extend the shelf life of food products along with clarity. As mentioned before, polyethylene is a good water barrier, but has inferior gas barrier compared to other polymers like PET, PP, EVOH [1]. Among the polyethylene HDPE has the best gas barrier, LDPE has the least and LLDPE is intermediate in terms of its gas barrier properties when compared to HDPE and LDPE. In terms of clarity HDPE is milky white, LDPE is transparent and LLDPE is translucent. Hence in this study LLDPE has been chosen as the base polymer for gas barrier property improvement by addition of cellulose nanocrystals (CNCs).

2.7 Cellulose nanocrystals (CNCs)

Cellulose nanocrystals are a type of cellulose nanomaterials extracted from lignocellulosic and is often used in packaging applications [24]. It is used for its desirable properties like renewable nature, biodegradability, low energy consumption, low cost, low-density, and more recyclability compared to inorganic fillers [25,26]. CNCs are used in other applications like wastewater treatment, biomedical industry, and electronics as well [27].
2.7.1 Extraction of CNCs

Bulk cellulose that is naturally occurring in the environment has both crystalline and amorphous regions in them in varying proportions, depending upon the source of cellulose. The highly crystalline regions of the cellulose microfibrils can be extracted from the bulk cellulose if it is subjected to specific combination chemical, mechanical and enzymatic treatments and the extracted highly crystalline regions result in the formation of cellulose nanocrystals (CNCs). CNCs are nearly perfect crystalline structure made up of stiff rod like particles consisting of cellulose chain segments. CNCs are also referred as nanoparticles, whiskers, nanofibers, micro crystallites. CNCs exhibit high specific strength, high surface area, modulus, and unique liquid crystalline properties [26-28]. Schematic diagram of cellulose is shown in Figure 2-6.



Figure 2-6 Schematic diagram of structure of cellulose with repeating unit of cellobiose.^[26,28]

The process of extraction can be mechanical or chemical. Several mechanical processes like high intensity ultrasonic treatments, high pressure homogenization, micro fluidization, cryocrushing, etc., exist and these processes work by producing shear forces which split the cellulosic fibers along the longitudinal axis and help in extraction of cellulose microfibrils. However, the chemical method is better for conversion of cellulose microfibrils into CNCs because it reduces the consumption of energy and produces nanocrystals with improved crystallinity. The mechanical method produces ribbon like nanofiber samples with a lower crystalline fraction usually 0.05 - 0.55 and chemical method produces rod-like nanofiber samples with a crystalline fraction of about 0.6. In chemical process there is strong acid hydrolysis that occurs which removes the amorphous domains that are regularly distributed along the microfibrils. The strong acids have the capability of penetrating easily into the amorphous regions which have a low level of order and hydrolyze them and leave the crystalline regions unaffected. Sulphuric acid hydrolysis is the most used process [28].

2.7.2 Properties of CNCs

CNCs have a highly crystalline structure which makes the structure stiff and hence it has a higher aspect ratio of around 100. Aspect ratio is defined as the ratio of length to diameter, and it helps in determination of the reinforcing capacity, which is crucial in the formation of percolated networks necessary for maintaining the properties of CNC based materials [24,26]. The variables used while manufacturing impact the properties of CNCs, for example the increases in hydrolysis time increases the length of the CNCs. The type of raw material also impacts the dimensions of CNCs for examples, CNCs obtained from wood have a length of 100 - 200 nm and a width of 3 - 5 nm while those obtained from other sources like sea plant have a length of 1000 - 2000 nm and width of 10 - 20 nm. The axial modulus of the CNCs have been reported to be 110 - 220 GPa and the strength of CNCs has been reported to be 7.5 - 7.7 GPa.

2.8 CNCs in bio-based polymers

CNCs has a wide range of applications like synthesis of antimicrobials, use in medical materials, enzyme immobilization, biosensing, green catalysis, etc. In different applications the use of CNCs is of two types, one where it is involves it to be functionalized or nonfunctionalized as synthesized CNCs and the other type is where CNCs are used in polymer nanocomposites and it acts as a reinforcing agent [28].

A polymer nanocomposite is a multiphase material where the nanomaterial reinforces the polymer phase. The nanometric size and the increased surface area of these polymer nanocomposites gives them unique properties. Incorporations of CNCs have significant improvement in the mechanical properties even in low volume fractions. CNCs are also used to impart strength and modulus as it acts as a nanofiller which have a defined morphology. The fabrication of nanocomposites is done by both natural polymers as well as synthetic polymers. Research have been done on natural polymers like starch, chitosan, natural rubber, soy protein and synthetic polymers like polyethylene, polycaprolactone, polyvinyl alcohol, polyvinyl chloride to name a few [24,28].

2.9 Processing technologies of composite films

The final properties of the composite films are impacted by the processing technique used. Hence it is important that the processing techniques are decided based on several factors like the intrinsic properties of the cellulose nano crystals, the nature of the polymer matrix, interfacial characteristic properties of the cellulose nano crystals and the desired final properties of the composite film [29].

2.9.1 Melt processing

Melt processing is an important technique used for preparing nanocomposites. This is very effective method when high volume production is targeted. It is also a cheap and fast processing method. The key principle of melt processing is that the cellulose nanomaterials are dispersed in a thermoplastic polymer melt. This can be done either by batch process or continuous process [30].

In the batch process, small amounts of the materials are added to a processing chamber where it is mixed well for a long period of time using micro extruders. Whereas, in the continuous method the material is fed into a continuous processing unit where the material is melted and mixed. The continuous method is preferred for scaling up as compared to the batch process as it is better at mixing and venting the material [30]. In this study both continuous and batch process has been used.

To make polymer blend in lab scale the batch process is used. Traditionally the Brabender type batch mixing is used. Researchers like Iwatake and coworkers have established that composites prepared by batch process have shown promising results [31]. Another batch process method used for preparing composites is roll-milling process and this is usually used for mixing carbon black and other additives into a rubbery material. Some drawbacks of the batch process are that it can sometimes lead to degradation and discoloration of the polymer or the cellulose. It also takes long processing time. The continuous process uses extruders. These can be counter-rotating or co-rotating twin screw extruders [30].

2.9.2 Solvent casting

Solvent casting is a popular method for preparation of composites. When polar constituents are used, i.e., when a water-soluble polymer is used as a matrices and cellulose nano crystals are used, which are also polar, the interaction between them is strong. When the aqueous suspension containing these two components are mixed, a solid nano composite can be obtained by solvent casting. However, it is difficult to use solvent casting method in circumstances where hydrophilic cellulose and hydrophobic matrices like PE, PP, PCL, and PLA are combined as there is lack of compatibility between them and this leads to poor dispersion. To improve the dispersion various

strategies have been developed like use of surfactants having compatibility on one part with polymeric matrix and another with CN which chemically modifies the interface between them and increases interaction [30].

2.9.3 Electrospinning

Electrospinning also called as electrostatic fiber spinning is another processing method that uses the action of electrostatic forces to process CNs in polymer matrix. But like the solvent evaporation process electrospinning can be a challenging for insoluble polymer matrices. Another variant in the electrospinning process is the "core-in-shell" electrospinning in which an aqueous dispersion of sulfated CNs constitutes the discrete "core" and it is surrounded by the cellulose "shell". Various factors in the spinning process affect the outcome obtained like the distance between the spinning tip and the collector, voltage, flow rate and properties of the spinning solution [30].

2.10 Gas barrier property measurement

In packaging it is very important to measure the gas barrier properties of the packaging material used, as this directly affects the shelf life of the food product. Especially in food and pharmaceutical packaging it is critical that the permeability of the packaging film is in accordance with the expected permeability required by the product. Two critical gases in packaging are oxygen and carbon dioxide and permeability of both gases need to be determined to design a packaging material which has the desired permeability for the given product [32].

The mass transport process in polymeric materials that are important in packaging are permeability, sorption, and migration. Migration is the loss of residues and additives from the polymer and permeation is the exchange of substances through the film. To quantify these mass transport processes at least two of the three coefficients must be determined, permeability coefficient (P), diffusion coefficient (D) and solubility coefficient (S). By using a permeation experiment, the values of these coefficients can be estimated [32].

Various methods are used to measure the gas barrier properties of polymers. In this part of the chapter isostatic permeability method and gravimetric method of permeability measurement will be discussed in detail.

2.10.1 Isostatic permeability method

Isostatic method uses a permeation cell which has two chambers and is separated by the film being tested. One of the chambers is a high concentration chamber (HCC) and the other is a low concentration chamber (LCC). In the HCC, an atmosphere enriched permeant is generated, and these permeant molecules begin to adsorb and diffuse through the polymer till they reach the LCC. The permeant concentration at the LCC is maintained to zero by purging the permeant molecules out of the chamber using an inert gas stream [32].

The permeant flow value is zero initially, and then the permeant flow is measured as a function of time. The permeant flow starts to increase over time and increases until a transition state where it reaches a constant value. At time, the system is at a stationary state and the

experiment is stopped. Using the flow at the stationary state ($F\infty$) the permeability (P) can be determined as follows [32].

$$P = \frac{F_{\infty}l}{A(C_{HCC} - C_{Lcc})} = \frac{F_{\infty}l}{A\Delta c}$$
(2.1)

where the l is the film thickness, A is exposed area, Δc is concentration gradient.

The diffusion coefficient is determined from the data at the transition rate. Following the Pasternak's solution for equation 2.1 and ISO method boundary condition and assuming diffusion coefficient to be independent of permeant concentration the D can obtained using the following [32]:

$$D = \frac{l^2}{7.205 t_{1/2}} \tag{2.2}$$

where $t_{1/2}$ is the time at which the permeant flow is one half of final flow.

Further, using Henry's Law, Solubility can be obtained from the definition of P [32]:

$$P = D.S \to S = \frac{P}{D}$$
(2.3)

Commercial permeability testers like Permatran Mocon use the above-described isostatic method and simplifies it and measures the gas transmission rate as a function of thickness and helps in obtaining the permeability value directly by the following:

$$P_{gas} = \frac{GTR \ x \ l}{\Delta P} \tag{2.4}$$

where GTR is the gas transmission rate, l is the thickness of the film, ΔP is the difference in partial pressure of permeant across the sample [33].

2.10.2 Gravimetric permeability method

The gravimetric or sorption method measures the permeability from the steady state data unlike the isostatic method which measures permeability from the transient data [34]. Sorption experiments estimate the amount of gas absorbed or desorbed in a polymer also known as gas solubility and estimate the rate of gas diffusion also known as gas diffusivity [34-38]. Unlike the isostatic permeability testers which measure the gas transmission rate and directly provides the permeability coefficient, the gravimetric method provides the values of the diffusion coefficient and solubility coefficient which is very important to understand the mechanism of barrier improvement in composites and for quantifying parameters like tortuosity factor [34-38].

Gravimetric method requires a thicker sample like compression molded samples, as compared to isostatic permeability method where thin films are tested. In sorption/desorption experiments the polymer sample to be tested is placed in a chamber and saturated with the testing gas. Once the samples are saturated, it is removed, and the weight gain is measured to see the amount of gas uptake and the percent weight gain can be obtained from the difference of the two weights. The measured solubility of the gas is the maximum amount of absorbed of the gas. To determine the diffusion the desorption process needs to be carried out which determines the amount of gas that is lost. It can be given by the following equation:

$$D = \frac{\pi}{16} \left[\frac{d \frac{M_t}{M_{\infty}}}{d \frac{\sqrt{t}}{l}} \right]^2 \tag{2.5}$$

where, M_{∞} is the mass uptake at infinite time, M_t is the amount of gas uptake at time t and l is the average thickness of the sample. If a curve is plotted for $\frac{M_t}{M_{\infty}} vs \frac{\sqrt{t}}{l}$, the initial gradient of the curve can also be used to calculate the value of diffusion coefficient (D). Experimentally for a system in which the diffusion coefficient is constant, if the half time for desorption or absorption is observed, the value of this constant can be given by [35-38]:

$$D = \frac{0.049}{\left(\frac{\sqrt{t}}{l}\right)^2} \tag{2.6}$$

where, the value of t corresponds to time at which $\frac{M_t}{M_{\infty}} = 0.50$.

Furthermore, Permeability (P) is given by:

$$P = D \cdot S \tag{2.7}$$

where, D is diffusion coefficient and S is solubility coefficient [35-38].

2.11 Crystallinity

Various properties of the polymer like permeability are controlled by the polymer's crystallinity. Polymer molecules prefer to move towards an arrangement that is the lowest possible energy state, which is the crystalline form. Regular repeating arrangement of molecules is called crystallinity. However, crystallization takes place in small regions of the polymer mostly in the order of 1×10^{-9} m. For crystallization to occur the polymer chains should be able to form a parallel array and pack closely. There are various sources of irregularity which prevent the polymer chain from crystallizing like stereochemical irregularity, head-to-head placement of monomer units, branching and copolymers with random placement of comonomers [1].

2.11.1 Measurement techniques

The degree of crystallinity of a polymer reflects the relative of crystalline and amorphous regions. This can be measured using different analytical methods like differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction, nuclear magnetic resonance (NMR), density gradient method to name a few.

2.11.1.1 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a calorimetric technique. It measures the differences in heat flow between a reference and the given sample against the temperature of the sample. It is one of the most accurate methods for estimating changes in heat capacity and enthalpy of samples. DSC is a destructive method of measurement. The DSC has a variety of applications

in different fields like studying corrosion, reduction, oxidation reactions by material scientists, to study physical fundamental properties like boiling point, enthalpy, etc. and polymer chemists often use DSC in measurement of crystallinity, rate of crystallization, polymer degradation, polymerization reaction kinetics, etc. [39].

The DSC measures the degree of crystallinity by determining the enthalpy of fusion from the area under the endotherm. The DSC method involves drawing a linear arbitrary baseline from the first onset of melting to the last trace of crystallinity [40]. The degree of crystallinity is given by:

$$X_c = \frac{\Delta H_f(T_m)}{\Delta H_f^o(T_m^o)}$$
(2.8)

where, X_c is the weight fraction of crystallinity, $\Delta H_f(T_m)$ is the enthalpy of fusion at melting point, $\Delta H_f^o(T_m^o)$ is the enthalpy of fusion of the totally crystalline polymer measured at equilibrium melting point.

2.11.1.2 Fourier transform infrared spectroscopy (FTIR)

FTIR is a nondestructive method of crystallinity measurement. It has a wide range of applications ranging from analysis of small molecules to analysis of cell and tissues. The basic principle of FTIR is that infrared spectroscopy probes molecular vibrations and functional group of the test specimen can be associated with its characteristic infrared absorption bands which further corresponds to the fundamental vibrations of the functional groups [39,41].

The FTIR method helps in identification of almost all chemical groups in one sample. A change in dipole moment of the molecule during vibration makes it absorb incident infrared light i.e., infrared active. Thus, vibrations which are symmetric do not get detected. In contrast, asymmetric vibrations are detected. This lack of sensitivity contributes to the identification of chemical groups in the samples. Especially water and amino acid molecules are not usually identified by other spectroscopy method but FTIR detects them [39,41].

Many researchers have estimated the crystallinity of polymers using the Fourier transform infrared spectroscopy (FTIR) for various polymers like polyhydroxy-alkanoates (PHAs) [42], poly(vinyl alcohol) [43], polyethylene [44], high-density polyethylene [45], polyphenylene Sulfide [46], etc. Cole and coworkers studied results obtained from the FTIR analysis and calorimetric analysis and concluded that both methods showed excellent correlation [46].

2.12 Effect of crystallinity on barrier properties of plastics

In food packaging, gas barrier properties of the films play a crucial part in maintaining and extending the shelf life of products [47]. Different ways have been established to increase the gas barrier properties of the film like laminates and multilayer. Both these methods involve layers of different materials being combined to achieve a desired gas barrier property of the films [15,48]. A major drawback with these methods is that the different layers used in the laminates and multilayers are not easily separated in the end of the materials lifecycle. This often ends in the landfill and leads to an unsustainable waste management practice.

A sustainable and recyclable solution to this problem is the use of monolayer biobased composite films with excellent gas barrier properties [49]. Different types of nano particles are incorporated in the polymer matrix to produce monolayer biobased nanocomposites films. Nanoparticles like nano clay, cellulose nanofibers [50], cellulose nanocrystals [33,51,52], cellulose whiskers [53] are often used. The improved barrier performance has been attributed to the tortuosity effect created by the presence of highly crystalline nanoparticles into the polymeric matrices, which increases the degree of crystallinity of the neat polymer. These crystals increase the effective travel path length for permeants diffusing through the nanocomposites. This reduces the rate of diffusion, thus lowering permeation as reported by other [33,51,52].

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CHAPTER 3

EXPERIMENTAL

3.1 Materials

Sugarcane-based bio-LDPE(STN7006), LLDPE (SLH118) and HDPE (SGD4960) obtained from Braskem Petrochemical (Sao Paulo, State of Sao Paulo, Brazil) were used as polymer matrices. Their respective melt flow indices were 0.6 g/10 min, 1 g/10 min and 0.7 g/10 min whereas their respective densities were 0.924 g/cm³, 0.916 g/cm³ and 0.962 g/cm³. The biobased content of the polymers was 95%, 84% and 96% for LDPE, LLDPE and HDPE, respectively. The CNCs (2018-FPL-CNC-126) used in this study was obtained from the Forest Products laboratory in Madison, Wisconsin, USA. Sulfuric acid hydrolysis was used to produce freeze-dried cellulose nanocrystals around 100 – 300 nm long and a diameter of around 5 nm [1]. CNCs were processed in a high-intensity mixer (MX1050XTS from Waring Commercial Xtreme) for 1 minute at 22,000 rpm to reduce the fiber agglomeration and then oven-dried for at least 24 hours to remove any absorbed moisture.

3.2 Samples manufacture for permeability tests

Two types of barrier measurement techniques were used in this study to understand the mechanism of gas barrier improvement in bio-LLDPE/CNC nanocomposites. The first approach included the gravimetric/sorption method, which measures the amount of gas uptake or lost from the sample. This method required rigid samples of approximately 1.5 mm to 2 mm thick for

performing the tests effectively, which were prepared using compression molding process [2,3]. The second technique involved the isostatic permeability method, which measures the gas transmission rate through the sample and estimates its permeability coefficient. This method required thin film samples for tests to be performed effectively, these were prepared using blown film extrusion. Karkhanis et al. performed isostatic method of permeability measurement successfully for their PLA-CNC nanocomposites using similar sample preparation techniques [4].

3.2.1 Compression molded samples for gravimetric-sorption method

The bio-LLDPE pellets along with dried CNCs were blended in a 60 ml electrically heated three-piece internal mixer/measuring head (3:2 gear ratios) with counter-rotating roller-style mixing blades (C.W. Brabender Instruments, Inc.). The mixer was driven by a 7.5 hp Intelli-Torque Plasti-Corder Torque Rheometer® (C. W. Brabender Instruments, Inc.). The polymer and CNC were mixed for 3 minutes at 170°C. The rotor speed used was 35 rpm and weight charge set at 45 g determined from the preliminary testing. The CNCs contents in the nanocomposites were fixed at 2.5%, 5%, 7.5%, 10%, and 13.5% of total material weight. A 5 kg deadweight was put on the top of the ram throughout the experiments [2,3]. The blended materials were cooled and pressed at 180°C and 5 tons of maximum pressure for 6 minutes using the hydraulic laboratory press (Carver, Model 120-10HC) to a target thickness of 2 mm using a metal spacer while processing. Similar process was utilized to manufacture control samples based on neat LLDPE, neat LDPE, and neat HDPE.

3.2.2 Blown film extrusion for isostatic permeability method

Bio-LLDPE pellets and dried CNCs were blended for 1 min at high intensity setting in a commercial blender (MX1050XTS from Waring Commercial Xtreme). The blended materials were blown into films using a 19 mm single-screw extruder (C.W. Brabender Instruments, South Hackensack, NJ, USA) with a length-to-diameter ratio of 30:1 as previously described [4-6]. The annular die used was of 25.4 mm in diameter and a die-opening diameter of 0.889 mm. The temperature profile of the extruder was set to 185-185-185-185°C from the hopper to die. The speeds of the extruder rotational screw and take up rollers were both set to 20 rpm, while an air pressure of 0.207 kPa (0.030 psi) was used to inflate the film to a blow-up ratio of 3, leading to ~0.062 mm thick films, measured by digital micrometer (model 49-70 from TMI, Ronkonkoma, NY, USA) [4-6].

3.3 Property evaluation

3.3.1 Gas permeability by sorption experiments

The desorption experiments were performed according to the gravimetric method used in previous research work [2,3]. Compression molded samples were cut into 0.5" × 1" rectangular specimens. The samples were weighed using a four-digit precision digital balance, their thickness measured, and they were placed in a chamber that was later pressurized with carbon dioxide (CO₂) at 800 psi and room temperature. The samples were left in the chamber until they were saturated with CO₂ (minimum of 16 hours). At the end of the saturation, the CO₂-saturated samples were

removed from the pressure chamber and weighed again on the balance to determine the amount of CO_2 absorbed or measured solubility. And the solubility coefficient (S) was calculated as follows

$$S = \frac{C_i}{p_i} \tag{3.1}$$

where p_i is the partial pressure of gas and C_i is the solubility of the gas in polymer given by the formula:

$$C_i = \frac{W t_{gas}}{V_p} \tag{3.2}$$

with Wt_{gas} as the weight of the dissolved gas per unit volume of polymer (V_p).

Once the percent weight gain of CO_2 was recorded, desorption process was carried out immediately to determine the amount of gas lost at regular time intervals and estimate the diffusivity of gas (D) in the sample, which is given by the following equation [2,3,7]:

$$D = \frac{\pi}{16} \left[\frac{d \frac{M_t}{M_{\infty}}}{d \frac{\sqrt{t}}{l}} \right]^2 \tag{3.3}$$

where M_{∞} is the mass uptake at infinite time, M_t is the amount of gas uptake at time t and l is the average sample thickness. If a curve is plotted for $\frac{M_t}{M_{\infty}}$ vs $\frac{\sqrt{t}}{l}$, the initial gradient of the curve can also be used to calculate the value of diffusion coefficient (D). Experimentally for a system in which the diffusion coefficient is constant, if the half time for desorption or absorption is observed, the value of this constant can be given by [2,3,7]:

$$D = \frac{0.049}{\left(\frac{\sqrt{t}}{l}\right)^2}$$

where the value of t corresponds to time at which $\frac{M_t}{M_{\infty}} = 0.50$ [2].

Furthermore, Permeability (P) is given by [9]:

$$P = D \cdot S \tag{3.5}$$

(3.4)

where D is diffusion coefficient and S is solubility coefficient.

The solubility (S_c) and diffusion (D_c) coefficients of gas in LLDPE/CNC nanocomposites can also be estimated theoretically in terms of polymer matrix mass fractions using the following equations [2,3,10-12]:

$$S_c = S_p \cdot (1 - \chi) \tag{3.6}$$

$$D_c = D_p \cdot (1 - \chi) \tag{3.7}$$

where S_p and D_p are the solubility and diffusion coefficients of gas in the polymeric matrix and χ is the mass fraction of CNC in the polymer matrix.

3.3.2 Tortuosity factor

The diffusion coefficients obtained from the sorption experiments can be used to calculate the product of Tortuosity Factor (τ), which quantify the hindrances in the diffusion path and immobilization factor (β), which is accounted to the restricted segmental mobility in the amorphous chains. The diffusion coefficient (D) can be expressed as:

$$D = \frac{D_a}{\tau \cdot \beta} \tag{3.8}$$

where D_a is the diffusion coefficient in the amorphous region since crystalline regions act as an impermeable barrier for diffusion, τ is the tortuosity factor, β is the immobilization factor, which is an empirical correction [13].

Both tortuosity factor and immobilization factor increase with crystallinity, hence β can be considered as a constant value for the same crystallinity values [14] and using this assumption some researchers have simplified the equation (3.8) to the following equation [15]:

$$\tau = \frac{D_a}{D_c} \tag{3.9}$$

3.3.3 Gas permeability by isostatic permeability method

The carbon dioxide (CO₂) and oxygen (O₂) transmission rates of films were measured using the permeability testers Mocon, Permatran (Model 4/41) and Mocon Ox-Tran (Model 2/21), respectively. The procedures outlined in ASTM D 1434 and ASTM D3985 were used for the testing procedures of CO₂ and O₂ tests, respectively at room temperature (23 ± 0.1 °C) and 0% relative humidity (RH). Kurek and coworkers established that the CO₂ and O₂ permeability of polyethylene at 0% RH and 95% RH were of the same order of magnitude [16]. Other researchers also had similar observations for polyethylene suggesting that relative humidity does not have a substantial effect on the gas permeability of polyethylene [16-20]. Thus, the isostatic permeation procedure was carried out at room temperature and 0% RH in this study. For each formulation, a minimum of 3 samples were tested with both gases. The gas permeability (P_{gas})was calculated using [4,21].

$$P_{gas} = \frac{GTR \ x \ l}{\Delta P} \tag{3.10}$$

where GTR is the gas transmission rate, 1 is the thickness of the film, ΔP is the difference in partial pressure of permeant (carbon dioxide/oxygen) across the sample which is 101,325 Pa (1 atm).

3.3.4 Crystallinity of nanocomposites

Many researchers have estimated the crystallinity of polymers using the Fourier transform infrared spectroscopy (FTIR) for various polymers like polyhydroxy-alkanoates (PHAs) [22], poly(vinyl alcohol) [23], polyethylene [24], high density polyethylene [25], polyphenylene Sulfide [26], etc. Also, the results obtained from the FTIR analysis have been validated with results of calorimetric analysis, showing an excellent correlation between both the methods [26]. Consequently, FTIR was employed in this study to quantify the percent crystallinity in bio-LLDPE induced by incorporating CNCs into the matrix.

FTIR spectra of compression molded samples were collected using a Shimadzu IR Affinity IS infrared spectrophotometer (Shimadzu Corporation, Kyoto, Japan) in attenuated total reflectance (ATR) mode. The spectra were obtained with triangle apodization using 64 scans in the range of 4000 - 400 cm⁻¹, at a wavelength resolution of 4 cm⁻¹ [5,6]. Spectra were analyzed by WinFIRST software from Thermo Nicolet (Madison, WI).

The crystallinity of PE is given by [24]:

Crystallinity
$$(\chi_c) = \frac{I(722+730)}{I(722+730)+\alpha I(723)}$$
 (3.11)

where 'I' corresponds to the infrared intensity for the band at a certain wavenumber, the peaks at 730 cm⁻¹ and 722 cm⁻¹ correspond to crystalline bands whereas the peak at 723 cm⁻¹ is associated with amorphous component, and $\alpha = \frac{I^{intr}(722+730)}{I^{intr}(723)}$ corresponds to the ratio of intrinsic crystalline to amorphous band intensities of polyethylene [24].

The FTIR spectra of neat sugarcane LLDPE and LLDPE/5% CNC nanocomposite (Fig. 1) in this study showed two crystalline peaks at 718 cm⁻¹ and 729 cm⁻¹, but no amorphous peak was observed at the 723 cm⁻¹ range. Instead, bands associated with the amorphous fraction occurred in the 1400-1250 cm⁻¹ frequency region [24]. Sugarcane-based HDPE also exhibits crystalline peaks at 716-717 cm⁻¹ [27]. Notice that the intensities of bands at 1400 to 1250 cm⁻¹ assigned to the amorphous component in LLDPE as well as those at 1376-1028 cm⁻¹ significantly decreased by adding 5% CNC into the matrix (Fig. 3.1). This result suggests a decrease in the amorphous region of PE was also observed in the frequency range of 1400 - 1250 cm⁻¹ [24], an amorphous peak at 1262 cm⁻¹ (Figure 3-1) was then used to calculate the crystallinity. Consequently, equation (3.11) was slightly modified as follows to determine the percent crystallinity of the neat bio-LLDPE and bio-LLDPE in the nanocomposite samples:

Crystallinity
$$(\chi_c) = \frac{I(718 + 729)}{I(718 + 729) + \alpha I(1262)}$$
 (3.12)

where $\alpha = \frac{I^{intr}(718+729)}{I^{intr}(1262)} = 2.18$, as obtained from the measurement specific to this study.

The crystallinity of sugarcane-based LLDPE in nanocomposites was obtained by performing spectral subtraction. For obtaining the characteristic spectrum of neat LLDPE (i.e., *difference data*) from the spectra of the LLDPE/CNC nanocomposites (i.e., *sample data*), the characteristic spectrum of the cellulose nanocrystal (i.e., *reference data*) was multiplied by the specific percent content of CNCs in the nanocomposite (i.e., *subtraction factor*) for which the crystallinity will be estimated. The obtained spectrum was subtracted from that of its

corresponding nanocomposite for which the crystallinity of its component matrix (neat LLDPE) will be determined. Colomw et al. performed similar procedure for obtaining crystallinity of HDPE from their HDPE/cellulose fiber composites using FTIR [25]. In summary, the following relation was used to extract the characteristic spectrum of neat LLDPE from the spectra of the nanocomposites:

 $Difference \ data = sample \ data - (reference \ data \times subtraction \ factor)$ (3.13)



Figure 3-1 Infrared spectra of sugarcane-based neat LLDPE and LLDPE/5% CNC nanocomposite sheets.

3.3.5 Density measurements

Densities of bio-PEs (LDPE, LLDPE, and HDPE) pellets and LLDPE/CNC nanocomposites were obtained using ColePalmer density gradient apparatus (Cole-Palmer Instrument Company, Vernon Hills, IL, USA). The tests were performed in accordance with the procedure outlined in ASTM D1505-10 (Method C - Continuous filling with liquid entering gradient tube becoming progressively more dense) by observing the level to which a test specimen sinks in a liquid gradient column. The density gradient column was prepared using high pressure liquid chromatography (HPLC)-grade water (750 ml) and isopropanol (500 ml) of densities 0.79 and 1 g/cm³, respectively.

3.3.6 Optical microscopy

Microscope image of bio-LLDPE and bio-LLDPE/CNC nanocomposites were obtained at 12.5X magnification using an Olympus BX41 optical microscope (Olympus, Center Valley, PA) equipped with a camera (Olympus Qcolor3).

3.3.7 Statistical analysis

A one-way t-tests with an α of 0.05 were conducted to compare the permeability coefficients obtained from two different permeability testing methods (isostatic permeability method versus gravimetric method) and three different bio-PE types (LDPE, LLDPE, and HDPE). Similar t-tests were done to assess the effect of CNC content on the crystallinity, diffusion coefficient, solubility coefficient and permeability coefficient of bio-LLDPE.

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CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Effect of testing methods (isostatic versus gravimetric) on CO₂ permeability of PE

Numerous methods, including a gravimetric technique and an isostatic permeation procedure, have been employed for measuring the permeation parameters of various permeants through polymers. Gravimetric permeation is a simple and straight forward method since it allows one to directly calculate both the solubility at steady state (S) and diffusion (D) coefficients from the sorption/desorption curve, from which the permeability (P) coefficient is calculated using equation (3.5). Conversely, the isostatic permeation procedure involves calculation of P at steady state, with D obtained from the transient state portion of the permeability experiment's flux rate profile curve. Once P and D are obtained, then S (transient state) is calculated using equation (3.5) [1-3]. Since the gravimetric approach was selected in this study, the permeability coefficient values determined by these two procedures for the same PE/CO₂ system was compared to validate the selected permeation method.

Table 4-1 lists the CO_2 permeability coefficients of three types of bio-PE determined by a gravimetric procedure and an isostatic permeability technique. Interestingly, the permeability coefficients obtained by the two methods were similar and no statistically significant difference was observed between the two methods, irrespective of PE grade.
Table 4-1 Effect of testing method on the carbon dioxide permeability (P_{CO2}) of various bio-PE grades.

Bio	Densi	ty (g/cm ³)	P _{CO2} (10 ⁻¹⁷ kg·m/m ² s·Pa)								
rolymer types	Provided	Measured	Isostatic ¹	Gravimetric ¹	Literature ²						
LLDPE	0.916	0.915 ± 0.001	27.9 ± 0.70^{a}	$29.3 \pm 1.74^{\rm a}$	31.9 [4]						
LDPE	0.924	0.919 ± 0.001	-	22.9 ± 0.4	17 to 24 ^[5]						
HDPE	0.962	0.951 ± 0.001	8.28 ± 0.4^{b}	8.02 ± 0.42^{b}	10.09 [6]						

¹Similar superscript letters are not significantly different based on the t-test results at a 5% significance level.

²Listed values are for petroleum-based polymers and superscript numbers represent the cited references.

However, the CO₂ permeability was affected by the PE grade, LLDPE showing the highest coefficient permeability and HDPE the lowest. Such a trend was expected and attributed to the difference in density of these three PE (Table 4-1). LLDPE with the lowest density had the highest permeability followed by LDPE and HDPE. The density is approximately inversely proportional to the free volume of the polymer and proportional to the crystallinity of the polymer [7]. Polymers with lower density have poor chain packing and lower crystallinity. Hence it can be inferred that LLDPE having the lowest density (Table 4-1) would have the highest free volume leading to a higher permeability value. Wang and coworkers studied the effect of polyethylene density on gas permeability and reported similar trends [7]. Their results indicated that the permeability of polyethylene decreases by a factor of almost 5-6 for an approximate increase of 5% in density [7]. It is worth mentioning that the CO₂ permeability values of different PE determined by both methods are in accordance with the values reported in the literature (Table 4-1) [4-6], suggesting that that both methods are equally reliable techniques to measure the permeability of polymers. However, the gravimetric method was chosen for further investigation as this method can be used to easily obtain the diffusion coefficient needed to quantify the tortuosity effect in LLDPE/CNC nanocomposites.

4.2 CO₂ barrier improvement and its mechanisms in LLDPE/CNC nanocomposite sheets

4.2.1 Effect of CNC addition on the crystallinity of LLDPE

The crystallinity of LLDPE from the spectra of the LLDPE/CNC nanocomposites obtained by the infrared spectra subtraction method was determined to establish correlation between crystallinity and permeability coefficients. The crystallinity of LLDPE increased with CNC addition level up to 2.5% and remained constant as the CNC content increased further (Table 4-2). The increased crystallinity can be attributed to the highly crystalline CNCs acting as an effective nucleating agent [8-10]. It should be mentioned that all nanocomposites had similar percent crystallinities since the addition of more than 2.5% CNCs did not improve LLDPE crystallinity further probably due to the retarded crystal growth caused by CNC agglomerations at high loading levels [8,9]. A loading level of 2.5% CNC or probably lower appeared to be the maximum concentration of CNC for an effective heterogeneous crystal nucleation in LLDPE matrix. Karkhanis and coworkers reported similar nucleating effect when CNCs were added to PLA matrix [8]. A maximum increase in PLA crystallinity was observed at 1% CNC content in their study and further addition of CNCs to the PLA matrix did not affect the crystallinity [8]. This is in general agreement with the results of Clarkson and coworkers who recently reported similar trends where very small concentrations of CNC (0.05 and 0.55 wt.%) are found effective heterogeneous nucleation agent for PLAs [10]. Other researchers also validated this trend; with the addition of about 1% CNC into the polymer matrix showing improvement in crystallinity, which remained constant thereafter [9,11-13].

CNC content	% χ1	Diffusi (10 ⁻⁷ cm	on ¹ ² /sec)	Tortuosity	Solubil (10 ⁻⁴ g/m	lity ¹ 1 ³ ·Pa)	P_{CO2}^{1} (10 ⁻¹⁷	Percent decrease	
(%)		Experimental	Predicted	Factor (%)	Experimental	Predicted	s·Pa)	in Pco2	
0	50.0 ± 0.0^{a}	5.2 ±0.4 ^a	5.2	100	57.2 ± 1.7^{a}	57.2	$29.3 \pm 1.74^{\rm a}$	-	
2.5	73.7 ± 1.4^{b}	4.9 ± 0.2^{a}	5.1	107 ±5.0	54.3 ±0.9 ^b	52.9	$26.6\pm1.3^{\text{a}}$	9	
5	$73.0\pm0.5^{\text{ b}}$	4.6 ± 0.2^{a}	4.9	114.1 ±4.7	57.1 ± 0.6^{a}	54.2	26.3 ± 1.1^{a}	10	
7.5	$75.3{\pm}0.6^{b}$	4.3 ±0.1 ^a	4.8	120.8 ±3.4	53.1 ± 1.0^{b}	49.1	23.0 ± 0.9^{b}	22	
10	75.3 ± 0.4 ^b	3.7 ±0.2 ^c	4.7	143.9 ±9.6	$50.4 \pm 1.6^{\circ}$	45.4	18.7 ±1.3 ^c	36	
13.5	74.1 ± 0.8^{b}	3.5 ±0.1°	4.5	147.2 ±2.6	55.5 ± 1.1^{b}	48.0	19.6 ±0.4 ^c	33	

Table 4-2 Effect of CNC content on the crystallinity and permeation parameters of compression molded bio-LLDPE sheet.

¹Similar superscript letters in each column are not significantly different based on the t-test results at a 5% significance level.

4.2.2 Effect of CNC addition on the CO₂ diffusion and solubility coefficients of LLDPE

Table 4-2 summarizes the experimentally measured CO_2 diffusion (D) and solubility (S) as well as calculated permeability (P) coefficients of LLDPE and LLDPE/CNC nanocomposites. The S and D coefficients predicted from equations (3.6) and (3.7), respectively, are also listed. The experimental diffusion and solubility coefficients decreased almost linearly as the CNC content increased in the nanocomposites. The reductions in both D and S coefficients were statistically significant (p value < 0.0001). Similar trends were obtained for the S and D coefficients predicted from equations 3.6 and 3.7, respectively. Nevertheless, the theoretically predicted D coefficients were slightly higher and that predicted S coefficients were slightly lower than the experimental ones. The discrepancy between the measured and predicted values increased with CNC content. This could be due to not taking into consideration in equations 6 and 7 the mass fraction of crystals available in LLDPE, which is a semi crystalline polymer, nor accounting for the sorption of gas into CNCs, if any. A poor adhesion between the polymer matrix and cellulosic fibers in composites without coupling/compatibilizer agent also contributes to the difference between the measured and predicted gas sorption parameters in cellulose-based composites [14].

Reductions in both D and S coefficients were expected since these sorption parameters are a function of the polymer matrix mass fraction in the composites [14-19]. Our previous work on cellulosic fiber/plastic composites demonstrated that cellulose fibers reject gas by acting like crystallites and, only the amorphous region in the composite (i.e., polymer matrix) absorbs the gas [14,15]. Not only increasing the fiber contents into the composites reduces the matrix mass fraction available for gas diffusion in the composite, but also the fiber regions in the composites obstruct the movement of gas molecules and, therefore, increase the average length of the paths they must travel [14,15]. Thus, the decrease in the solubility of CO_2 in LLDPE/CNC nanocomposites indicates that the less amorphous is the material, the lower is the gas solubility. Similarly, the diffusion coefficient decreased as the polymer mass fraction decreased in the nanocomposites and that the addition of CNCs increased the CO_2 diffusion time in the nanocomposites, in good agreement with results reported by other investigators [1,20-23].

4.2.3 Correlations between crystallinity, tortuosity factor, and permeability coefficient

Table 4-2 summarizes the CO₂ permeability (P) coefficients and tortuosity factors of LLDPE calculated from equations (3.5) and (3.9), respectively, as a function of CNC contents. As, expected the P coefficients of LLDPE decreased as the CNC content increased due to the decreased in both D and S coefficients as discussed above. This indicates that the permeation process was partly controlled by both solubility and diffusion through the LLDPE matrix. The addition of CNC significantly improved the CO₂ barrier performance of LLDPE sheet up to 10 wt.% content and levelled off above this concentration.

Remarkably, though the crystallinity of bio-LLDPE increased with CNC content up to 2.5% and remained constant thereafter; the CO₂ permeability coefficient in the nanocomposites on the other hand decreased almost linearly with increasing amounts of CNCs (Table 4-2). This suggests that the crystallization of LLDPE matrix caused a decrease of CO₂ permeability, but not

in linear proportion with the decrease in amorphous volume and that the gas permeability in LLDPE appeared to be controlled by other factors in addition to level of crystallinity. In other terms, even though the polymer crystallinity played a role in improving the CO₂ barrier property of bio-LLDPE up to 2.5% CNC, it is certainly not the only factor influencing its gas barrier improvement above this CNC addition level. Our results are in good agreement with those of other investigators who reported no correlation between percent crystallinity and permeability coefficient [20-22]. Indeed, Frounchi and coworkers observed a two-fold reduction in both oxygen and carbon dioxide permeability coefficients of the PP/EPDM blend filled with 1.5 vol% organoclay compared to unfilled PP/EPDM blend, despite a 27% reduction in nanocomposite crystallinity [20]. Similar results have also been observed by other researchers [21,22]. A significant decline in both O₂ (about 45%) and CO₂ (about 68%) permeability coefficients of PLA films was obtained by adding 1.37 vol% graphene oxide nanosheets into PLA film, even though all the PLA nanocomposite films were basically amorphous [21]. Therefore, in addition to level of crystallinity and/or crystal morphology, the role of other factors contributing to barrier improvement like the tortuosity factor must also be investigated to understand the mechanisms of barrier improvement in nanocomposites.

Since the CO_2 permeation process (decreased permeability coefficient) in the nanocomposite was partly controlled by the gas diffusion through the LLDPE matrix, the observed decrease in diffusion coefficient in the nanocomposites indicated an increase in the gas diffusion time as per equation (3.4). The increased diffusion time was attributed to the CNCs acting as impermeable crystals for the movement of gas molecules through the polymer matrix creating a tortuous path for the movement of gas molecules. This mechanism known as a tortuosity effect is

illustrated in Figure 4-1, showing a path A that represents the polymer matrix without CNCs and a path B representing the counterpart with CNCs. The diffusion time in path B will be greater than in path A due to the presence of CNCs. which is creating a tortuous path for the movement of gas molecules, thus increasing its diffusion time. Huang and coworkers attributed the improved gas barrier performance of PLA/graphene oxide nanosheets to the tortuosity effect created by the impermeable graphene oxide nanosheets [21]. Likewise, numerous investigators have claimed this tortuosity mechanism to explain improvement in gas and/or water vapor barrier of various polymers [20-22] but without quantifying it.



Figure 4-1 Schematic diagram of the tortuosity effect.

In this study, the tortuosity effect was quantified as the tortuosity factor according to equation (3.9) (Table 4-2). The effect of CNC content on the tortuosity factor and CO₂ permeability coefficient is illustrated in Figure 4-2. The estimated tortuosity factor increased with the increase in the CNC content in the nanocomposites. This result was expected since CNCs obstruct the movement of gas molecules in the nanocomposites, then more CNCs in the nanocomposites tend

to increase the average length of the paths the gas molecule must travel in the sample; thus, increasing the tortuosity factor. Moreover, samples of nanocomposite sheets and films with various CNC contents were observed under an optical microscope to illustrate the tortuosity effect (Figure 4-3). The images showed an increase in the number of CNC particulates present per unit area with increase in concentration of CNC; thus, the more CNC in the material, the higher is the tortuosity factor. The CO_2 permeability coefficient of LLDPE decreased almost linearly with increasing amounts of CNCs as previously discussed (Table 4-2 and Figure 4-2).



Figure 4-2 Effect of CNC content on tortuosity factor (TF) and CO₂ permeability of bio-LLDPE.



Figure 4-3 Optical microscope images of bio-LLDPE sheets (left column) with various CNC contents: (a) 0%, (b) 2.5%, (c) 7.5% and (d) 13.5% as well as of bio-LLDPE films (right column) with various CNC contents: (a) 0%, (b) 1%, (c) 2.5% and (d) 3.5%.

A strong negative correlation was established between the tortuosity factor and the permeability coefficient. As the tortuosity factor increased the CO_2 permeability coefficient values decreased (Figure 4-4). This correlation showed a good fit with an R² value of approximately 95% (Figure 4-4), clearly indicating that factors other than crystallinity also contribute to gas barrier improvement of polymers.



Figure 4-4 Pco₂ vs tortuosity factor.

4.3 CO₂ and O₂ barrier properties of LLDPE films with CNCs

LLDPE is used in many flexible packaging applications like heavy duty shipping sacks, stretch/cling film, grocery snacks, etc. Hence it is important to investigate the effect of CNCs addition on the gas barrier of bio-LLDPE films, in addition to the nanocomposite sheets discussed previously. The films were studied for their oxygen and carbon dioxide barrier properties, the most important gases crucial for food packaging applications, to understand the effect of CNC addition on LLDPE gas barrier enhancement (Table 4-3).

	0	Gas permeability (10 ⁻¹⁷ kg·m/m ² s·Pa) ¹										
LLDPE composition	P _{CO2}	% decrease in Pco2	P ₀₂	% decrease in Po2								
Control	27.9 ± 0.70^{a}	-	$31.8\pm2.27^{\rm a}$	-								
2.5% CNC	18.7 ± 2.77^{b}	33	$16\pm0.72^{\text{b}}$	50								

Table 4-3 Effect of CNC addition on the CO₂ and O₂ permeability of bio-LLDPE.

¹Different superscript letters in each column indicate that the difference is statistically significant at values of "Prob>|t|" less than 0.05.

As expected, a significant reduction in gas permeability coefficients of bio-LLDPE films was obtained by adding CNCs into the matrix. Both the CO₂ and O₂ permeability coefficients of LLDPE significantly decreased by about 33% and 50%, respectively, by adding only 2.5% CNC. The enhanced gas barrier performance of bio-LLDPE/CNC films is mainly assigned to the efficient nucleating effect of CNCs in the bio-LLDPE matrix along with the tortuosity effect created by the impermeable CNC crystals for the movement of gas molecules. The microscope images in Figure 4-3 clearly show an increase in the number of CNC particulates present per unit area with increase in concentration of CNC, confirming the tortuosity effect. Several studies have reported similar nucleating effect on addition of CNCs to the polymer matrix [8,9]. Furthermore, these results also validate the gas barrier enhancement results achieved in the nanocomposites sheets discussed previously.

Interestingly, the film samples required less amount of CNCs to show a similar improvement in CO₂ barrier as compared to the nanocomposite sheets. The reason for this is unclear now but this could be ascribed to the bi-directionally stretched blown extrusion film having different kinds of crystalline structures compared to uniaxially-stretched compression molding sheets. The voids in compression molded samples could also account for this discrepancy. However, this hypothesis was ruled out since the density of LLDPE/CNC nanocomposites increased with CNC content as expected from the rule of mixtures due to the higher specific gravity of CNC (~1.45) compared to that of LLDPE (0.915). The density of LLDPE increased from 0.915 g/cm³ to 0.925 g/cm³, 0.933 g/cm³, 0.944 g/cm³, and 0.950 g/cm³ by adding 2.5%, 5%, 7.5%, and 10% CNC, respectively into the matrix. The nanocomposite sank to the bottom of the column at 13.5% CNC.

APPENDIX

Samples	Thickness (mm)	CO2TR (cc/m² day)	Permeability (kg·m/m ² sec·Pa)
1	0.0493	7052	7.82E-17
2	0.0493	7185	7.97E-17
3	0.0493	8701	9.65E-17
4	0.0440	7521	7.44E-17
5	0.0486	7807	8.53E-17
Average	4.81E-02	7.65E+03	8.28E-17
SD	2E-03	7E+02	9E-18
COV	0.05	0.09	0.10
SE	1E-03	3E+02	4E-18

 Table A-1 Permeability coefficients of bio-HDPE film obtained using isostatic permeability method.

Table A-2 Permeability, diffusion and solubility coefficients of bio-HDPE using gravimetric method.

Samples	Diffusion Coefficient (10 ⁷ ×cm²/sec)	Solubility Coefficient (g/m ^{3.} Pa)	Permeability (kg•m/m² sec•Pa)
1	4.67	2.10E-03	9.81E-17
2	3.89	2.05E-03	7.98E-17
3	3.13	2.53E-03	7.92E-17
4	2.68	2.30E-03	6.17E-17
5	2.75	2.38E-03	6.55E-17
6	2.79	2.08E-03	5.79E-17
7	4.05	2.26E-03	9.17E-17
8	2.43	2.22E-03	5.39E-17
9	3.99	2.02E-03	8.05E-17
10	4.74	1.98E-03	9.38E-17
11	2.91	2.45E-03	7.12E-17
12	2.30	2.14E-03	4.93E-17
Average	3.65E+00	2.23E-03	8.02E-17
SD	8.02E-01	2.02E-04	1.26E-17
COV	0.22	0.09	0.16
SE	0.27	6.72E-05	4.21E-18

Samples	Diffusion Coefficient (10 ⁷ ×cm ² /sec)	Solubility Coefficient (g/m³·Pa)	Permeability (kg·m/m² sec·Pa)
1	5.43	2.48E-16	
2	4.5	4.72E-03	2.14E-16
3	5.5	4.69E-03	2.57E-16
4	5.3	4.69E-03	2.48E-16
5	5.2	4.60E-03	2.39E-16
6	5.8	4.52E-03	2.60E-16
7	5.0	4.72E-03	2.33E-16
8	4.2	4.54E-03	1.90E-16
9	4.5	4.90E-03	2.20E-16
10	4.3	4.88E-03	2.10E-16
11	4.9	4.94E-03	2.39E-16
12	4.4	5.00E-03	2.20E-16
13	4.6	4.93E-03	2.26E-16
14	4.2	5.18E-03	2.17E-16
15	4.7	4.93E-03	2.19E-16
16	4.8	4.74E-03	2.27E-16
Average	4.53E+00	4.78E-03	2.29E-16
SD	1.30E+00	1.89E-04	1.86E-17
COV	0.287	0.040	0.081
SE	3.25E-01	4.73E-05	4.66E-18

Table A-3 Permeability, diffusion and solubility coefficients of bio-LDPE obtained using
gravimetric method.

Samples	Thickness	CO ₂ TR	Permeability				
Sumples	(mm)	(cc/m² day)	(kg·m/m ² sec Pa)				
1	0.066	17510.39	2.60E-16				
2	0.066	19749.70	2.93E-16				
3	0.071	17703.35	2.82E-16				
4	0.071	17615.00	2.80E-16				
5	0.062	21446.97	2.99E-16				
6	0.064	17776.92	2.57E-16				
Average	0.07	18633.72	2.79E-16				
SD	0.00	1616.12	1.72E-17				
COV	0.05	0.09	0.06				
SE	1.45E-03	6.60E+02	7.01E-18				

Table A-4 CO₂ permeability coefficients of bio-LLDPE film obtained using iso-static permeability method.

Table A-5 CO₂ permeability coefficient values of bio-LLDPE obtained using gravimetric method.

Samples	Diffusion Coefficient (10 ⁷ ×cm ² /sec)	Solubility Coefficient (g/m ³ ·Pa)	Permeability (kg·m/m² sec·Pa)
1	4.8	5.37E-03	2.61E-16
2	5.2	4.91E-03	2.55E-16
3	7.1	5.50E-03	3.93E-16
4	3.3	6.77E-03	2.20E-16
5	4.8	5.92E-03	2.85E-16
6	5.9	5.76E-03	3.41E-16
7	5.3	5.89E-03	3.14E-16
8	4.6	5.78E-03	2.64E-16
9	5.5	5.53E-03	3.05E-16
Average	5.2	5.72E-03	2.93E-16
SD	1.055	5.03E-04	5.21E-17
COV	0.204	8.81E-02	1.78E-01
SE	0.35	1.68E-04	1.74E-17

	LL	DPE	LI	OPE		HI	OPE
Samples	Distance	Density	Distance	Density		Distance	Density
	(in)	(g/cm^3)	(in)	(g/cm ³)		(in)	(g/cm ³)
1	13.000	0.912	12.375	0.915		6.375	0.948
2	12.375	0.915	11.875	0.918		5.625	0.952
3	12.125	0.917	11.375	0.921		5.500	0.952
4	12.375	0.915	11.375	0.921		6.000	0.950
5	12.625	0.914	11.500	0.920		5.625	0.952
6	12.375	0.915	11.500	0.920		5.625	0.952
7	12.375	0.915	11.625	0.919		5.500	0.952
8	12.375	0.915	11.500	0.920		5.625	0.952
Average	12.453	0.915	11.641	0.919		5.734	0.951
Std	0.2582	0.0014	0.3370	0.0018		0.3021	0.0019
COV	0.0207	0.0015	0.0289	0.0020]	0.0527	0.0020
SE	0.09130	0.00049	0.11914	0.00064		0.10679	0.00069

Table A-6 Measured densities of bio-PE obtained using density gradient method.

	2.5%	CNC	5% (CNC		7.5%	CNC		10%	10% CNC	
Samples	es Distance Density Distance Den (in) (g/cm ³) (in) (g/cm ⁴)		Density (g/cm ³)		Distance (in)	Density (g/cm ³)		Distance (in)	Density (g/cm ³)		
1	11.13	0.922	9.00	0.934		6.50	0.947		5.38	0.953	
2	10.33	0.926	8.75	0.935		7.25	0.943		5.63	0.952	
3	10.50	0.925	9.38	0.932		7.63	0.941		7.00	0.944	
Average	10.65	0.925	9.04	0.933		7.13	0.944		6.00	0.950	
Std	0.421	0.002	0.31	0.002		0.57	0.003		0.88	0.005	
COV	0.039	0.002	0.035	0.002		0.080	0.003		0.146	0.005	
SE	0.243	0.001	0.182	0.001		0.331	31 0.002		0.505	0.003	

Table A-7 Measured densities of bio-LLDPE with various CNC contents obtained using density gradient method.



Figure A-1 Effect of CNC content on density of bio-LLDPE/CNC composites.

CNC content	0%	2.50%	5%	7.50%	10%	13.50%	
1	50	76	72	75	75	73	
2	50	75	73	75	76	75	
3	50	71 74		76	75	75	
Average	50	73.7	73	75.3	75.3	74.1	
SD	0	2.4	0.8	1	0.8	1.4	
COV	0	0.032	0.012	0.014	0.01	0.019	
SE	0	1.4	0.5	0.6	0.4	0.8	

Table A-8 Effect of CNC content on crystallinity of bio-LLDPE/CNC composites.

]	LLDPI	E	2.5% CNC			5% CNC				7.5% CNC			10% CNC				13	.5% CI	NC
Sampies		D	S	Р	D	S	Р	D	s	Р		D	s	Р	D	s	Р		D	S	Р
1		4.8	5.4	2.6	5.6	5.3	2.9	5.0	5.7	2.9		4.5	5.4	2.4	3.4	5.4	1.8		3.4	5.7	1.9
2		5.2	4.9	2.5	4.7	5.2	2.5	5.2	5.7	2.9		4.5	5.2	2.4	4.6	4.5	2.0		3.4	6.1	2.1
3		7.1	5.5	3.9	5.2	5.7	2.9	4.4	5.5	2.5		4.5	5.0	2.3	2.6	4.7	1.2		3.3	5.5	1.8
4		3.3	6.8	2.2	4.3	5.5	2.3	5.2	5.7	2.9		4.7	5.8	2.8	4.2	5.1	2.1		3.7	5.4	1.9
5		4.8	5.9	2.9	4.7	5.5	2.6	4.3	5.9	2.6		3.9	5.4	2.1	4.0	5.4	2.1		3.7	5.5	2.0
6		5.9	5.8	3.4				4.1	5.8	2.4		4.1	5.1	2.1	3.9	5.5	2.2		3.8	5.5	2.0
7		5.3	5.9	3.1				4.0	5.5	2.2		4.1	5.4	2.2	3.3	4.5	1.5		3.5	5.3	1.9
8		4.6	5.8	2.6											3.7	5.2	1.9		3.5	5.5	1.9
9		5.5	5.5	3.1															0.2	0.3	0.9
Average		5.2	5.7	2.9	4.9	5.4	2.6	4.6	5.7	2.6		4.3	5.3	2.3	3.7	5.0	1.9		3.5	5.5	1.9
SD	Ī	1.1	0.5	0.5	0.5	0.2	0.3	0.5	0.1	0.3]	0.3	0.3	0.2	0.6	0.4	0.4		0.2	0.3	0.9

Table A-9 CO₂ permeability (P in $10^{-16} \times kg \cdot m/m^2 \sec \cdot Pa$), diffusion (D in $10^7 \times cm^2/sec$), and solubility (S in $10^{-3} \times in g/m^3 \cdot Pa$) coefficients of neat bio-LLDPE and bio-LLDPE filled with various CNC content obtained using gravimetric method.

Samples	Tortuosity Factor							
	2.5% CNC	5% CNC	7.5% CNC	10% CNC	13.5% CNC			
1	0.928	1.039	1.164	1.534	1.516			
2	1.104	1.005	1.147	1.137	1.531			
3	0.994	1.172	1.155	2.005	1.572			
4	1.218	1.006	1.097	1.243	1.421			
5	1.107	1.195	1.337	1.310	1.413			
6		1.261	1.276	1.320	1.385			
7		1.311	1.281	1.575	1.463			
8				1.387				
Average	1.070E+00	1.141E+00	1.208E+00	1.439E+00	1.472E+00			
SD	1.12E-01	1.25E-01	8.89E-02	2.70E-01	6.96E-02			
COV	1.05E-01	1.10E-01	7.36E-02	1.88E-01	4.73E-02			
SE	5.02E-02	4.74E-02	3.36E-02	9.55E-02	2.63E-02			

Table A-10 Tortuosity factor of bio-LLDPE with various CNC contents.

	LLDPE			LLDPE/2.5% CNC		
Samples	Thickness (mm)	CO2TR (cc/m² day)	Permeability (kg·m/m ² ·sec·Pa)	Thickness (mm)	CO2TR (cc/m ² day)	Permeability (kg·m/m ² ·sec·Pa)
1	0.066	17510.39	2.60E-16	0.066	16776.17	2.4903E-16
2	0.066	19749.70	2.93E-16	0.066	13503.62	2.00452E-16
3	0.071	17703.35	2.82E-16	0.062	12975.35	1.8152E-16
4	0.071	17615.00	2.80E-16	0.064	7977.00	1.15183E-16
5	0.062	21446.97	2.99E-16			
6	0.064	17776.92	2.57E-16			
Average	0.07	18633.72	2.79E-16	6.46E-02	1.28E+04	1.87E-16
SD	0.00	1616.12	1.72E-17	1.81E-03	3.63E+03	5.54E-17
COV	0.05	0.09	6.17E-02	0.03	0.28	0.30
SE	1.45E-03	6.60E+02	7.01E-18	9.06E-04	1.82E+03	2.77E-17

Table A-11 CO₂ permeability coefficients of neat bio-LLDPE and bio-LLDPE/2.5% CNC composite films.

	LLDPE			LLDPE/2.5% CNC			
Samples	Thickness	OTR	Permeability	Thickness	OTR	Permeability	
	(mm)	(cc/m² day)	(kg·m/m ² ·sec·Pa)	(mm)	(cc/m² day)	(kg·m/m ² ·sec·Pa)	
1	0.064	4524	2.25E-16	0.064	2421	1.21E-16	
2	0.062	4551	2.19E-16	0.062	3660	1.77E-16	
3	0.062	4741	2.29E-16	0.062	3282	1.58E-16	
4	0.0574	5048	2.25E-16	0.062	3743	1.81E-16	
5	0.061	7512	3.56E-16	0.062	4037	1.95E-16	
6	0.062	9550	4.61E-16	0.062	3419	1.65E-16	
7	0.056	12071	5.26E-16	0.062	4210	2.03E-16	
8	0.054	10556	4.43E-16	0.062	3730	1.80E-16	
9	0.07	5292	2.88E-16	0.062	3447	1.66E-16	
10	0.056	5248	2.29E-16	0.062	3150	1.52E-16	
11	0.057	5714	2.53E-16	0.062	2723	1.31E-16	
12	0.062	6038	2.91E-16	0.062	2688	1.30E-16	
13	0.062	5292	2.55E-16	0.062	2567	1.24E-16	
14	0.055	8312	3.56E-16				
15	0.055	7733	3.31E-16				
16	0.070	5968	3.25E-16				
17	0.072	6976	3.91E-16				
Average	6.10E-02	6.77E+03	3.18E-16	6.22E-02	3313.61	1.60E-16	
SD	5.57E-03	2.24E+03	9.36E-17	5.55E-04	574	2.72E-17	
COV	0.1	0.3	0.3	8.92E-03	0.2	1.70E-01	
SE	 1.35E-03	5.43E+02	2.27E-17	1.39E-04	144	7.28E-18	

Table A-12 O₂ permeability coefficients of neat bio-LLDPE and bio-LLDPE/2.5% CNC composite films.

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CHAPTER 5

CONCLUSION

5.1 Conclusion

This study was intended at improving the gas barrier property of sugarcane-based LLDPE using bio-cellulose nanocrystals (CNCs). Specifically, this study evaluated the effect of testing methods (isostatic versus gravimetric) on CO_2 permeability of various bio-PE grades as well as the effect of CNC content on crystallinity, tortuosity factor, and gas barrier properties of bio-LLDPE sheets and films.

The isostatic and gravimetric permeation methods yielded similar CO_2 permeability coefficients irrespective of PE grade and both methods were concluded to be equally reliable to measure the gas permeability of the polymers. The effect of density on bio-PE permeability coefficient was also established where the PE grade with the lowest density, i.e., bio-LLDPE was observed to have the highest permeability coefficient values among the different PE grades studied.

The crystallinity of bio-LLDPE increased with CNC addition level up to 2.5% and remained constant as the CNC content increased further attributable to the crystal nucleating effect of CNC and the retarded crystal growth caused by CNC agglomerations at high loading levels, respectively. The diffusion and solubility coefficients in bio-LLDPE decreased almost linearly as

the CNC content increased, which caused a decreased polymer matrix mass fraction available for gas diffusion as well as an increased CO_2 diffusion time in the nanocomposites.

The CO₂ permeability coefficient of LLDPE decreased almost linearly with increasing CNC content. A significant decline in CO₂ (about 36%) permeability coefficients of LLDPE sheets was obtained by adding 10 wt. % of CNCs into LLDPE sheet, and P_{CO2} values levelled off above this concentration. No correlation was established between gas permeability and percent crystallinity of LLDPE sheet since the permeability coefficient decreased almost linearly with increasing CNC content whereas the crystallinity of the nanocomposites increased only up to 2.5% CNC content and remained constant thereafter. In contrast, a strong negative correlation was established between the tortuosity factor and the permeability coefficient, clearly indicating that factors other than percent crystallinity also contribute to gas barrier improvement of bio-LLDPE.

The effect of CNC content on the gas barrier properties of bio-LLDPE films was also examined. As expected, a significant improvement in gas barrier of bio-LLDPE films was obtained by adding CNCs into the matrix. The P_{CO2} and P_{O2} coefficients of bio-LLDPE films reduced by 33% and 50%, respectively, when 2.5% of CNC was added into the films, validating the gas barrier enhancement results achieved with nanocomposites sheets.

5.2 Future work

This study investigated the effect of CNC content on the gas barrier properties of sheet and film bio-LLDPE and bio-LLDPE/CNC composites. As discussed, the results showed a significant improvement in gas barrier properties of bio LLDPE by adding CNCs. This improvement will expand their scope in a wide range of packaging applications. However, it would also be appropriate to study the effect of CNC addition on other properties of the resulting composite films/sheets such as optical (haze, color, clarity), thermal properties (glass transition and melting temperatures, thermal stability), mechanical (tensile and impact strength, toughness, creep, resilience, puncture resistance) as well as sealing (seal strength, hot tack). These properties are important parameters to consider while evaluating real world performance of a packaging material and will widen the scope of these composites.