BIOBASED NANOCOMPOSITES FOR PACKAGING APPLICATIONS ─ SYNTHESIS USING MELT EXTRUSION OF POLY (LACTIC ACID), POLY (BUTYLENE SUCCINATE) AND/OR STARCH BLENDED WITH NATURAL NANOFILLERS

by

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Abstract

There is a renewed focus on biodegradable polymers in packaging applications due to environmental concerns associated with conventional plastics. Melt extrusion was used to synthesize nanocomposites from poly (lactic acid) (PLA) or poly (butylene succinate) (PBS) blended with natural nanofillers — chitin whiskers (CHW, 1-5%), nanocrystalline cellulose (NCC, 1-5%) or lignin-coated nanocrystalline cellulose (LNCC, 3%). Transmission electron microscopy and x-ray diffraction indicated that the natural nanofillers were uniformly dispersed in the polymer matrix. For PLA based nanocomposites, differential scanning calorimetry showed a decrease in change of heat capacity at glass transition (ΔCp) with increased nanofiller addition, indicating greater confinement of polymer chains. For PBS based nanocomposites, nanofillers acted as nucleating agents and promoted recrystallization of polymer as reflected in increase of degree of crystallinity (Xc) from 65.9-66.8 to 75.6%. By addition of NCC and CHW, tensile strength (TS) of PLA based films increased from 50.2 MPa to 70.9 MPa and 52.1 MPa, respectively, while TS of PBS increased from 23.2-24.9 MPa to 32.9 MPa and 43.6 MPa, respectively. Elongation at break (E%) of nanocomposite films ranged from 9.1 to 15.3, and in general decreased with addition of nanofillers. LNCC did not significantly improve mechanical properties of PBS and PLA films. Additionally, 3% NCC addition reduced oxygen transmission rate (OTR) of PLA from 209.9 to 180.8 cc/m^2/day, which further reduced to 109.3 cc/m^2/day by adding compatibilizer methylene diphenyl diisocyanate (MDI, 4%). Water vapor transmission rate (WVTR) of PLA also reduced from 44.4 to 28.6 g/m^2/day with 3% NCC and 4% MDI addition. Similarly OTR and WVTR of PBS decreased from 737.7 to 280 cc/m^2/day and 83.8 to 49.4 g/m^2/day, respectively with 3% NCC. Use of 4% MDI further reduced OTR and WVTR to 23.8 cc/m^2/day and 30.8 g/m^2/day, respectively.

Use of starch can potentially reduce the costs of bio-based nanocomposites films. Up to 40% starch was incorporated during synthesis of PLA and NCC nanocomposites using solution mixing method. Addition of starch decreased TS from 35.8 MPa to 18.4 MPa and E% from 8.3% to 6.0%. Use of NCC (1%) and MDI (4%) improved the mechanical properties to a certain extent.

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Acknowledgements

Dedication

To my dear parents:

I dedicate my thesis to my dear parents, Ziping Xu and Dongzhi Wang

for their contribution, encouragement, love and support.

Chapter 1 - Food Packaging

1.1. Food packaging

Food packaging, as one of the most important areas in food industry, can maintain food flavor and quality during the period of storage, processing and marketing. The basic functions of food packaging are to confer protection and to maintain nutrition. A good packaging can avoid mechanical damage including abrasion, crush, scratch, shock and vibration during delivery and storage. Also, packaging can support physical barrier to insects and rodents. Packaging can also provide chemical protection from changing of moisture or aroma, or oxygen and light. From biological perspectives, packaging can provide biological barriers to microorganisms. Besides, a good packaging material can even extend shelf life of foods and graphics on the packaging can stimulate consumers to purchase.

Various types of packaging materials are currently available in markets. These materials are mainly made of glass, metal (including aluminum and aluminum foil), plastics and paperboard (Marsh and Bugusu, 2007). Among which, plastics attract more interest than others, due to its desirable designs, low cost and lighter weight. However, these plastics are mainly derived from petroleum and fossil, which has caused serious environmental concerns due to poor degradability, as conventional plastics could not be easily broken down in nature by fungi and bacteria. In addition, even disposal of these materials by burning or melting caused release of carbon dioxide which has also affected environment badly. The advantages of these conventional plastic packaging materials could not hinder and overshadow the disadvantages. Therefore, more recent research has been focused on seeking or developing novel biodegradable materials for the substitution of the traditional plastics.

1.2. Bio-based packaging

Plastics from fossil-chemical processing have been applied in packaging materials for a long period of time, due to their good mechanical properties such as high tensile strength and elongation at break, good barrier performance to water vapor and oxygen, etc. However, the poor biodegradability of these polymers caused serious environmental issues, such as accumulation of wastes which is called "white pollution". Consequently, packaging materials based on biodegradable and renewable sources has been considered as one of the most effective ways to solve this problem. These bio-based polymers have two components, synthetic polymers made from bio-based monomers and natural polymers. Family of synthetic polymers include poly (butylene succinate) (PBS), poly (ethylene succinate) (PES), poly (lactic acid) (PLA), etc (Yang et al., 2007). Natural renewable polymers including starch, cellulose, chitin, chitosan and lignin, and proteins containing gelatin, wool and silk, are naturally carbon-based polymers (Madhavan et al., 2010). As growing attention to environmental policies, biodegradable polymers attract more interest from scientists.

According to various production process and sources, biopolymers can be divided into three categories: polyesters, starch-based polymers, and others (Siracusa et al., 2008). Polyesters can be synthesized from bio-based biomass or bacteria and can directly make the polyesters using the right nutrient sources. Biodegradable polyesters are aliphatic in nature.

The interest and research work related to biodegradable polymer packaging has been there for over twenty years. Several characteristics of biopolymers such as barrier properties and mechanical properties have been summarized as follows. Barrier property of the packaging material in terms of water vapor, aroma and oxygen permeability is evident to package fresh fruits and vegetables. Oxygen and water vapor plays an important role in food preservation. Low

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transmission of oxygen and water or keeping balance of oxygen and water inside and outside will maintain or even extend the shelf life of food. Mechanical properties including tensile strength (TS), elongation at break (E%), storage modulus, flexural modulus and impact modulus are all important parameters to evaluate the quality of the packaging materials. Table 1 shows a brief summary of properties and applications of these biodegradable polymers.

There are two basic requirements of biopolymers as to compete with traditional non-biodegradable polymers. Firstly, biopolymers should cost less compared to traditional petroleum based polymers. However, biopolymers are more costly or cost parity to conventional plastics, therefore, by adding some fillers, cost can be lowered. Secondly, biopolymers should have comparable mechanical properties and barrier properties. Since most of the synthetic polymers are hydrophobic, and some of the natural polymers are hydrophilic, poor interfacial connection between these polymers is always challenging when merging them into each other and cause poor mechanical performance, although many attempts have been engaged to enhance the poor adhesion between hydrophobic and hydrophilic polymers by adding plasticizers like, maleic anhydride, sorbitol and glycerol (Leadprathom et al., 2010). The biggest disadvantages of those biopolymers are their weak barrier and mechanical properties due to their hydrophilic natures. So a novel technology is urgently required to solve this problem.

Table 1.1. Properties and applications of current commercial plastics.

Plastics	Property	Application
High-density polyethylene (HDPE)	Low cost, easily processed; low softening and melting temperature; compatible; translucent; good moisture barrier, poor oxygen barrier	Films: industrial and carry-out bags; drum and box liners; laminates. Household and industrial containers (HIC); tubs (freeze).
Low-density polyethylene (LDPE)	Low cost, easily processed; soft and clear; compatible; fair moisture barrier, poor oxygen barrier; high elongation.	Films: stretch wrap; heat seal films/ coatings; bags and liners; shrink films. Squeezable bottles; caps and closures (high flexibility).
Polypropylene (PP)	Low cost, easily processed, compatible; translucent; clear, stiff and glossy; good moisture barrier, poor oxygen barrier; higher softening point than PE.	Films: food pouches and bags (most snacks); clear wraps; clear label stock; metalized and printed. Dairy tubs, thermoformed; closures; jewel boxes and integral-hinge packs.
Polystyrene (PS)	Hard, brittle, stiff and crystal clear; impact resistance; expanded; poor solvent resistance and poor barrier properties.	Films: mostly in expanded films. Three dimensional: jewel boxes (CD cases); jars, bottles and closures; cosmetic containers; trays and protective packaging; thermoformed or injection cups and tubs.
Polyethylene terephthalate (PET)	High tensile strength; goof moisture and oxygen barrier; low elongation; clear and translucent; crystallized formed at high temperatures.	Films: high strength and applications; oven-able applications. Three dimensional: clear bottle for beverage.

Source: Yang et al., 2007.

1.3. Nanocomposites synthesis and characterization

Nanotechnology is a powerful and innovative tool for development of food packaging. Nanotechnology highly involves exploitation of materials with one or more dimensions that are less than 100nm which can be applied in broad research areas like development, processing, manufacturing, packaging, etc (Mihindukulasuriya and Lim, 2014). This novel and innovative nanotechnology provides efficient and effective ways to enhance the performance of the polymers due to very high surface-to-volume ratio and surface activity of nanomaterials less than 100nm.

Three major nanomaterials packaging involved improved packaging, active packaging and intelligent packaging (Silvestre et al., 2011). The improved packaging refers to addition of nanomaterials to promote barrier and mechanical properties. It has been reported that nanoparticles, like clay (Pluta et al., 2006; Tang, 2008; Keshtkar et al., 2014), nanocrystalline cellulose (Oksman et al., 2003; Kuan et al., 2006; Petersson et al., 2007; Battegazzore et al., 2014), chitin and chitosan (Morin and Dufresne, 2002; Gopalan et al., 2003; Li et al., 2011; Uddin et al., 2012; Huang et al., 2013) have the promising potentials to improve barrier, mechanical and thermal properties of polymers. Active packaging is obtained by incorporating components, such as preservatives, oxygen absorbers, water vapor absorbers into packaging materials, to protect the food packaging system (Mihindukulasuriya and Lim, 2014). Currently, the active packaging technology is mainly applied for antimicrobial packaging. Finally, intelligent packaging is designed to monitor condition around the food (Silvetre et al., 2011). For example, the monitored conditions include oxygen, microorganisms, as well as time, temperature and humidity detections.

Various techniques can be used to manufacture nanocomposites, including melt extrusion, solution mixing, polymerization and intercalation (Tang, 2008). Nanocomposites are usually studied by the following characterizations. Morphological characterizations can be evaluated by x-ray diffraction (XRD) and transmission electron microscope (TEM). Through XRD, it can detect the angles, position and intensity of nanocomposites. Through TEM, it can investigate several inner structure arrangements, such as, intercalation, exfoliation and flocculated nanocomposites. Thermal properties can be evaluated by differential scanning calorimetry (DSC) to study phase transitions.

Additionally, filler are mainly added in polymers to reduce cost in food packaging. Beside nanofillers application in food packaging, nanofillers can also be used as paints and coatings, adhesives, thermosets, thermoplastics, reinforced bio-polymers, synthetic fibers and textiles, cosmetics and pharmaceuticals, optical devices, viscosity modifiers and flow acids, catalysts, flexible displays, printed films (Peng et al., 2011).

1.4. Current development in biodegradable polymers nanocomposites

In the present days, due to development of nanotechnology, the mentioned problems above may be potentially conquered. So far, most of research work was mainly focused on starch and starch relatives, poly (lactic acid) (PLA), poly (butylene succinate) (PBS), polycaprolactone (PCL), poly vinyl alcohol (PVOH).

Starch is a strongly promising material in food packaging area, due to its wide availability and low cost compared to other natural polymers. It is completely degradable in soil and can promote the biodegradability of non-degradable polymers plastics after incorporation. However, starch cannot work alone as a packaging material, due to its hydrophilic nature causing poor barrier and mechanical properties.

PLA derived from fermentation of carbohydrates based substrates has been widely applied. As a food packaging material, PLA attracts lots of interests due to its high tensile stress and compostability under industrial conditions. However, low chemical and heat resistance, and poor barrier properties of PLA limited its usage. Therefore, various nanoparticles have been attempted to blend with PLA to enhance thermal properties, which were as follows: PLA/natural fibers (Oksman et al., 2003); PLA/nano-clay (Pluta et al., 2006); PLA/thermoplastic starch and sorbitol (Li and Huneault, 2011); PLA/starch and chitosan blends (Bie et al., 2013), PLA/nanocrystalline cellulose (Arrieta et al., 2014), etc. However, there is less research work focused on improving poor barrier properties of PLA.

PBS belongs to aliphatic polyesters. It is a promising synthetic polymer due to its high biodegradability and tensile stress and elongation at break. But the soft texture nature, poor barrier properties and high cost of PBS limit its applications. However, tensile strength can be improved by blending with nanoparticles. For instance, it has been reported that, PBS can mix with nanocrystalline cellulose (Lin et al., 2011); jute fiber (Liu et al., 2009); organo-montmorillonite (OMMT) (Phua et al., 2012); palm fiber (Wu et al., 2013); and silica (Jacquel et al., 2014) to enhance its mechanical properties. Also, the cost of PBS films can be lowered by adding nanofillers. However, there is less work focused on improving poor barrier properties of PBS.

PCL is linear polyester obtained from polymerization processing. PCL has high elongation at break, but low modulus and low melting temperature. Mechanical performance of PCL is improved by adding organoclay (Lee et al., 2002) ; and montrollinite (Lim et al., 2002).

PVOH is obtained by hydrolysis of poly vinyl acetate. PVOH has already been studied by diverse researchers because of its highly compatible and mechanical properties. However, barrier

properties of PVOH are really low due to its hydrophilic nature. Some work has been done to promote the poor barrier properties of PVOH by adding nanofillers, for example, PVOH/sodium montmorillinte/starch (Ali et al., 2011) and PVOH/cellulose (Roohani et al., 2008; Pereira et al., 2014).

Nanoparticles were blended with polyethylene terephthalate (PET) and polystyrene (PS) for purpose of improving various properties of these polymers. There are several studies relevant to these polymers, for example, talc/PET (Sekelik et al., 1999) and PS/PLA/thermoplastic starch (Suwanmanee et al., 2013). Nanoparticles showed promising potentials to improve mechanical properties as well as enhanced biodegradability in biopolymers.

1.5. Scope of this study

In this study, research focused on synthesis of nanocomposites based on two basic polymers, PLA and PBS, and nanoparticles which are nanocrystalline cellulose (NCC), chitin whisker (CHW) and lignin-coated nanocrystalline cellulose (LNCC), and studied the effect of nanoparticles on morphological and thermal properties of nanocomposites, also mechanical and barrier properties of nanocomposites films.

Chapter 2 reported preparation and synthesis of nanocomposites of PLA and PBS blended with various concentrations of nanofillers, NCC, CHW and LNCC, respectively. Also, methylene diphenyl diisocyanate (MDI) was added in the blends to study the effect of compatibilizer on various properties of PLA and PBS nanocomposites. TEM and XRD were utilized to study the morphologies of nanocomposites. Thermal properties were evaluated by DSC. Mechanical properties were characterized by Instron and barrier properties including water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) were evaluated.

Chapter 3 presented the introduction of low cost corn starch (CS) adding in PLA and studied thermal and barrier characterizations of PLA/CS films. Also, PLA/CS blends were incorporated with NCC and MDI and thermal and barrier properties were evaluated.

Reference

Ali, S. S., Tang, X., Alavi, S., & Faubion, J. (2011). Structure and Physical Properties of Starch/Poly Vinyl Alcohol/Sodium Montmorillonite Nanocomposite Films. *Journal of Agricultural and Food Chemistry*, *59*(23), 12384–12395.

Arrieta, M. P., Fortunati, E., Dominici, F., Rayón, E., López, J., & Kenny, J. M. (2014). Multifunctional PLA–PHB/cellulose nanocrystal films: Processing, structural and thermal properties. *Carbohydrate Polymers*, *107*, 16–24.

Battegazzore, D., Alongi, J., & Frache, A. (2014). Poly(lactic acid)-Based Composites Containing Natural Fillers: Thermal, Mechanical and Barrier Properties. *Journal of Polymers and the Environment*, *22*(1), 88–98.

Bie, P., Liu, P., Yu, L., Li, X., Chen, L., & Xie, F. (2013). The properties of antimicrobial films derived from poly(lactic acid)/starch/chitosan blended matrix. *Carbohydrate Polymers*, *98*(1), 959–966.

Gopalan, Nair. K., Dufresne, A., Gandini, A., & Belgacem, M. N. (2003). Crab Shell Chitin Whiskers Reinforced Natural Rubber Nanocomposites. 3. Effect of Chemical Modification of Chitin Whiskers. *Biomacromolecules*, *4*(6), 1835–1842.

Huang, Y., Zhang, L., Yang, J., Zhang, X., & Xu, M. (2013). Structure and Properties of Cellulose Films Reinforced by Chitin Whiskers. *Macromolecular Materials and Engineering*, *298*(3), 303–310.

Jacquel, N., Saint-Loup, R., Pascault, J.-P., Rousseau, A., & Fenouillot, F. (2014). Structure-Properties Relationship of In Situ Synthesized Poly(Butylene Succinate)/Silica Nanocomposites. *Macromolecular Materials and Engineering*, *299*(8), 977–989.

Keshtkar, M., Nofar, M., Park, C. B., & Carreau, P. J. (2014). Extruded PLA/clay nanocomposite foams blown with supercritical CO_2. *Polymer*, *55*(16), 4077–4090.

Kuan, C.-F., Ma, C.-C. M., Kuan, H.-C., Wu, H.-L., & Liao, Y.-M. (2006). Preparation and characterization of the novel water-crosslinked cellulose reinforced poly(butylene succinate) composites. *Composites Science and Technology*, *66*(13), 2231–2241.

Leadprathom, J., Suttiruengwong, S., Threepopnatkul, P., & Seadan, M. (2010). Compatibilized Polylactic Acid/Thermoplastic Starch by Reactive Blend. *Journal of Metals, Materials and Minerals*, *20*(3), 87–90.

Lee, S.-R., Park, H.-M., Lim, H., Kang, T., Li, X., Cho, W.-J., & Ha, C.-S. (2002). Microstructure, tensile properties, and biodegradability of aliphatic polyester/clay nanocomposites. *Polymer*, *43*(8), 2495–2500.

Li, H., & Huneault, M. A. (2011). Effect of chain extension on the properties of PLA/TPS blends. *Journal of Applied Polymer Science*, *122*(1), 134–141.

Li, X., Li, X., Ke, B., Shi, X., & Du, Y. (2011). Cooperative performance of chitin whisker and rectorite fillers on chitosan films. *Carbohydrate Polymers*, *85*(4), 747–752.

Lim, S. T., Hyun, Y. H., Choi, H. J., & Jhon, M. S. (2002). Synthetic Biodegradable Aliphatic Polyester/Montmorillonite Nanocomposites. *Chemistry of Materials*, *14*(4), 1839–1844.

Lin, N., Yu, J., Chang, P. R., Li, J., & Huang, J. (2011). Poly(butylene succinate)-based biocomposites filled with polysaccharide nanocrystals: Structure and properties. *Polymer Composites*, *32*(3), 472–482.

Liu, L., Yu, J., Cheng, L., & Qu, W. (2009). Mechanical properties of poly(butylene succinate) (PBS) biocomposites reinforced with surface modified jute fibre. *Composites Part A: Applied Science and Manufacturing*, *40*(5), 669–674.

Madhavan, Nampoothiri. K., Nair, N. R., & John, R. P. (2010). An overview of the recent developments in polylactide (PLA) research. *Bioresource Technology*, *101*(22), 8493–8501.

Marsh, K., & Bugusu, B. (2007). Food Packaging, Roles, Materials, and Environmental Issues. *Journal of Food Science*, *72*(3), R39–R55.

Mihindukulasuriya, S. D. F., & Lim, L.-T. (2014). Nanotechnology development in food packaging: A review. *Trends in Food Science & Technology*, *40*(2), 149–167.

Morin, A., & Dufresne, A. (2002). Nanocomposites of Chitin Whiskers from *Riftia* Tubes and Poly(caprolactone). *Macromolecules*, *35*(6), 2190–2199.

Oksman, K., Skrifvars, M., & Selin, J.-F. (2003). Natural fibres as reinforcement in polylactic acid (PLA) composites. *Composites Science and Technology*, *63*(9), 1317–1324.

Peng, B. L., Dhar, N., Liu, H. L., & Tam, K. C. (2011). Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective. *The Canadian Journal of Chemical Engineering*, *89*(5), 1191–1206.

Pereira, A. L. S., do Nascimento, D. M., Souza Filho, M. de sá M., Morais, J. P. S., Vasconcelos, N. F., Feitosa, J. P. A., Rosa, M. de F. (2014). Improvement of polyvinyl alcohol properties by adding nanocrystalline cellulose isolated from banana pseudostems. *Carbohydrate Polymers*, *112*, 165–172.

Petersson, L., Kvien, I., & Oksman, K. (2007). Structure and thermal properties of poly (lactic acid)/cellulose whiskers nanocomposite materials. *Composites Science and Technology*, *67*(11-12), 2535–2544.

Phua, Y. J., Lau, N. S., Sudesh, K., Chow, W. S., & Mohd Ishak, Z. A. (2012). Biodegradability studies of poly(butylene succinate)/organo-montmorillonite nanocomposites under controlled compost soil conditions: Effects of clay loading and compatibiliser. *Polymer Degradation and Stability*, *97*(8), 1345–1354.

Pluta, M., Paul, M.-A., Alexandre, M., & Dubois, P. (2006). Plasticized polylactide/clay nanocomposites. I. The role of filler content and its surface organo-modification on the physico-chemical properties. *Journal of Polymer Science Part B: Polymer Physics*, *44*(2), 299–311.

Roohani, M., Habibi, Y., Belgacem, N. M., Ebrahim, G., Karimi, A. N., & Dufresne, A. (2008). Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. *European Polymer Journal*, *44*(8), 2489–2498.

Sekelik, D. J., Stepanov, E. V., Nazarenko, S., Schiraldi, D., Hiltner, A., & Baer, E. (1999). Oxygen barrier properties of crystallized and talc-filled poly (ethylene terephthalate). *Journal of Polymer Science Part B Polymer Physics*, *37*(8), 847–857.

Siracusa, V., Rocculi, P., Romani, S., & Rosa, M. D. (2008). Biodegradable polymers for food packaging: a review. *Trends in Food Science & Technology*, *19*(12), 634–643.

Silvestre, C., Duraccio, D., & Cimmino, S. (2011). Food packaging based on polymer nanomaterials. *Progress in Polymer Science*, *36*(12), 1766–1782.

Suwanmanee, U., Varabuntoonvit, V., Chaiwutthinan, P., Tajan, M., Mungcharoen, T., & Leejarkpai, T. (2013). Life cycle assessment of single use thermoform boxes made from polystyrene (PS), polylactic acid, (PLA), and PLA/starch: cradle to consumer gate. *The International Journal of Life Cycle Assessment*, *18*(2), 401–417.

Tang X. (2008). Use of extrusion for synthesis of starch-clay nanocomposites for biodegradable packaging films [M]. *ProQuest*.

Uddin, A. J., Araki, J., Fujie, M., Sembo, S., & Gotoh, Y. (2012). Interfacial interaction and mechanical properties of chitin whisker-poly(vinyl alcohol) gel-spun nanocomposite fibers. *Polymer International*, *61*(6), 1010–1015.

Wu, C.-S., Liao, H.-T., & Jhang, J.-J. (2013). Palm fibre-reinforced hybrid composites of poly(butylene succinate): characterisation and assessment of mechanical and thermal properties. *Polymer Bulletin*, *70*(12), 3443–3462.

Yang, K., Wang, X., Wang, Y., & others. (2007). Progress in nanocomposite of biodegradable polymer. Journal of industrial and engineering chemistry-Seoul, *13*(4), 485.

Chapter 2 - Biodegradable Packaging Films: Nanocomposites Synthesis by Extrusion

Abstract

Due to environmental concerns associated with conventional non-degradable plastics, interest has been increasingly focused on biodegradable polymers. Melt extrusion was used to synthesize nanocomposites from poly (lactic acid) (PLA) or poly (butylene succinate) (PBS) blended with natural nanofillers chitin whiskers (CHW, 1-5%), nanocrystalline cellulose (NCC, 1-5%) or lignin-coated nanocrystalline cellulose (LNCC, 3%). Transmission electron microscopy and x-ray diffraction indicated that the natural nanofillers were uniformly dispersed in the polymer matrix. Differential scanning calorimetry showed as nanofiller content increased in PLA based nanocomposites, the decrease in heat capacity change at glass transition (ΔCp) from 0.50 to 0.39 J/g^{o}C and glass transition temperature (Tg) from 55.4 to 53.2^{o}C signaled greater confinement of the polymer chains. For PBS based nanocomposites, nanofillers acted as nucleating agents and promoted recrystallization of polymer as reflected in the increase in crystallization enthalpy (ΔHc) from 66.0 to 69.2 J/g and degree of crystallinity (Xc) from 65.9-66.8 to 75.6%. Tensile strength (TS) of PLA based films increased from 50.2 MPa to 70.9 MP and 52.1 MPa, respectively, with increase in NCC and CHW content. Similarly in PBS nanocomposites, TS increased from 23.2-24.9 MPa to 32.9 MPa and 43.6 MPa, respectively, with increase in NCC and CHW content. Elongation at break (E%) of nanocomposite films ranged from 9.1 to 15.3, and in general decreased with addition of nanofillers. Use of lignin-coated nanocrystalline cellulose (LNCC, 3%) as nanofiller did not lead to significant improvement in mechanical properties of PBS and PLA based films. Additionally, oxygen

transmission rate (OTR) of PLA reduced from 209.9 to 180.8 cc/m^2/day with the addition of 3%

NCC. Use of methylene diphenyl diisocyanate (MDI, 4%) further reduced OTR to 109.3

cc/m^2/day. Water vapor transmission rate (WVTR) of PLA also reduced from 44.4 to 28.6

g/m^2/day with 3% NCC and 4% MDI addition. Similarly OTR of PBS decreased from 737.7 to

280 cc/m^2/day with 3% NCC and use of 4% MDI further reduced OTR to 23.8 cc/m^2/day.

WVTR of PBS reduced from 83.8 g/m^2/day to 49.4 g/m^2/day with 3% NCC, and 4% MDI

addition further reduced WVTR to 30.8 g/m^2/day.

2.1. Introduction

There has been a growing interest in the application of biodegradable polymers in food packaging due to environmentally-friendly concerns related to some traditional plastics derived from some petroleum and fossil sources which are non-degradable. Biobased polymers are more environmental-friendly than fossil fuel plastics, since bio-based polymer can degrade to carbon dioxide, water and biomass.

Two classifications are concluded in biobased polymers, synthetic polymer and natural polymer. Synthetic polymer contains poly (lactic acid) (PLA), poly (butylene succinate) (PBS), poly (ethylene succinate) (PES), etc (Yang et al., 2007). Natural renewable polymers include starch, cellulose, chitin, chitosan and lignin, and proteins containing gelatin, wool and silk, etc (Madhavan et al., 2010). Among these synthetic polymers, poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) are the most outstanding and the most studied polymers, due to high biodegradability and mechanical properties.

PLA belongs to family of aliphatic polyesters. The fundamental block of PLA is lactic acid, which could be fermented from carbohydrates containing sugars. Commercially, PLA is made of poly (L-lactic acid) and/or poly (D-lactic acid), which is a copolymer. Monomer can also be of renewable origins. PBS can be obtained by polymerization from 1,4-butanediol and succinic acid by biomass fermentation. PLA derived from fermentation of carbohydrates based substrates has been widely applied. As a food packaging material, PLA attracts lots of interests due to its high tensile stress under industrial conditions. However, low chemical and heat resistance, and poor barrier properties of PLA limit its usage. Therefore, various nanoparticles have been attempted to mix with PLA to enhance the mechanical and thermal properties, for example, PLA/natural fibers (Oksman et al., 2003); PLA/nano-clay (Pluta et al., 2006); PLA/organo-montmorillonite (Chow et al., 2009); PLA/thermoplastic starch and sorbitol (Li and

Huneault, 2011); PLA/starch and chitosan blends (Bie et al., 2013); PLA/nanocrystalline cellulose (Arrieta et al., 2014), etc. However, there is less work focused on improving poor barrier properties of PLA.

PBS belongs to aliphatic polyesters. It is a promising synthetic polymer due to its high biodegradability and tensile stress and elongation at break. But the soft texture and poor barrier properties of PBS limit its applications. However, tensile strength can be improved by blending with nanoparticles. For instance, it has been reported that, PBS can mix with nanocrystalline cellulose (Lin et al., 2011); jute fiber (Liu et al., 2009); organo-montmorillonite (OMMT) (Phua et al., 2012); palm fiber (Wu et al., 2013); and silica (Jacquel et al., 2014) to enhance its mechanical properties. However, there is less work focused on improving poor barrier properties of PBS.

Among natural polymers, cellulose is considered as the most common carbohydrates and most abundant natural biopolymers on earth and can be extracted from corn, sorghum, soybean, wheat and even grain residues, especially in plants. Cellulose is a fibrous, rough, water-insoluble substance that plays an important role in maintaining and supporting the structure of plants cell walls (Habibi et al., 2010). Nanocrystalline cellulose (NCC) can be obtained from acid hydrolysis of cellulose fibers. NCC can display high elastic modulus ranged from 100 to 150 GPa according to different sources (Tang and Weder, 2010). The geometrical aspect ratio, length to diameter (L/D), is a major factor that controls the mechanical properties of nanocomposites. Fillers with a high aspect ratio give the best reinforcing effect (Peng et al., 2011). Lignin-coated nanocrystalline cellulose is lignin bonded to cellulose for purpose of improving hydrophobicity of nanocrystalline cellulose.

Chitin is the second most common carbohydrates and second most abundant polymers in nature after cellulose. Chitin can be obtained from various sources of living organisms, for example, shrimp, crab, tortoise and even insects (Zeng et al., 2012). The low crystalline region in structures can be removed by acid treatments, which could be converted in suspension by mechanical shearing, and this is called chitin whiskers (CHW). CHW was incorporated in cellulose and exhibited improvement of tensile strength (TS) and Young's modulus (Huang et al., 2013). Consequently, according to previous study of nanofillers adding in polymer matrix, the addition of CHW, NCC and LNCC in polymers has potential reinforcing effect in mechanical properties.

Also, plasticizers including maleic anhydride, glycerol, sorbitol and compatibilizer including methylene diphenyl diisocyanate (MDI), has already been applied for purpose of improving the poor interaction between hydrophobic and hydrophilic polymers (Zhang and Sun, 2004). Reducing the interfacial tension and enhancing the interaction between polymer phases can transfer the internal stresses from filler to the matrix and thus can improve the strength of the blend (Wang et al., 2001). The isocyanate groups on the surface of MDI is highly reactive with both hydroxyl group on surface of nanofillers and carboxyl group on surface of PLA, thus to form urethane linkage.

CHW, NCC and LNCC at different concentrations were blended with PLA and PBS using melt extrusion. Morphological studies including transmission electron microscope (TEM) and x-ray diffraction (XRD), barrier characterizations of water vapor transmission rate (WVTR) and oxygen transmission rate (OTR), thermal properties and mechanical tests of tensile strength (TS) and elongation at break (E%) were evaluated.

2.2. Experimental

2.2.1. Materials

Poly (lactic acid) (PLA), Nature Works™ 4032D, was supplied by Cargill Dow LLC (Minnetonka, MN, USA). There were two batches of Poly (butylene succinate) (PBS), EnPol G4560-M supplied by SamSung Fine Chemicals (Seoul, Korea) and Bionodle 1001, supplied by Showa Highpolymer Co., Ltd (Tokyo, Japan).

Chitin powder was supplied by Pfaltz and Bauer (Waterbury, CT). Nanocrystalline cellulose was purchased from University of Maine (Orono, ME). Lignin-coated nanocrystalline cellulose was purchased from American Process, INC (Atlanta, GA). Potassium hydroxide (KOH) was purchased from Fisher Scientific (New Brunswick, NJ). Sulphuric acid (H_2SO_4) and chloroform were purchased from chemical store, KSU. Methylene diphenyl diisocyanate (MDI) with purity was over 97%, was obtained from TCI AMERICA (Portland, OR).

2.2.2. Preparation of chitin whiskers

The preparation of chitin whiskers was prepared by acid hydrolysis accordingly (Huang et al., 2013).

The raw chitin powder was boiled in 5% KOH solution for 6hrs to remove most of the protein and then stirred at ambient temperature overnight. After filtration and washing with distilled water, the residue was kept in 5% KOH solution for 48hrs to remove residual protein. It was then centrifuged at 3600 rpm for10 min and dried at 80°C to obtain purified chitin. To prepare chitin whiskers, 10g purified chitin sample was hydrolyzed by 3M H_2SO_4 (30mL/g of chitin) at 70°C for 12 hrs with vigorous stirring and kept in 90°C for 4 hrs. The resultant suspension was diluted with distilled water and centrifuged at 7200 rpm for 15min to discard the supernatant. This process was repeated 12 times to remove excess acid in the supernatant.

Subsequently, the suspension was dialyzed for 2 hrs in running water and then overnight in distilled water, until the pH reached around 6. A further ultrasonic treatment was performed on an ultrasonic cell disruptor for better dispersion of the chitin whiskers in water. Centrifugation of the chitin whisker suspension at 7200 rpm for 15 min was performed again to remove the precipitate. Finally, the chitin whisker suspension was freeze dried.

2.2.3. Synthesis of nanocomposites

PLA and PBS were dried overnight in an air oven at 100°C and 75°C before extrusion, respectively. Chitin whiskers and nanocrystalline cellulose concentration was added from 1%, 2%, 3%, 4% and 5% (w/w polymer basis), and lignin-coated nanocrystalline cellulose was only loaded at 3% (w/w polymer basis) to blend with PLA and PBS, respectively. 4%MDI (w/w polymer basis) was blended with PLA/3%CHW, PLA/3%NCC, PBS/3%CHW and PBS/3%NCC. Blends were mixed in Hobart mixer for 3min using speed setting 1. Nanocomposites blends were processed using a lab-scale twin screw extruder (Micro-18, American Leistritz, Somerville, NJ). Barrel temperature for PLA nanocomposites was 50-100-140-175-175-175 °C. Barrel temperature for PBS nanocomposites was 50-75-95-132-135-137°C.

Table 2.1. Formulation of PLA and PBS nanocomposites.

Nanofiller (wt%)	PLA nanocomposites		PBS nanocomposites	
CHW	**PLA (g)**	**Sample name**	**PBS (g)**	**Sample name**
1%	500	PLA/1%CHW	500	PBS/1%CHW
2%	500	PLA/2%CHW	500	PBS/2%CHW
3%	500	PLA/3%CHW	500	PBS/3%CHW
4%	500	PLA/4%CHW	500	PBS/4%CHW
5%	500	PLA/5%CHW	500	PBS/5%CHW
3% +4%MDI	500	PLA/3%CHW+4%MDI	500	PBS/3%CHW+4%MDI
NCC	**PLA (g)**	**Sample name**	**PBS (g)**	**Sample name**
1%	500	PLA/1%NCC	500	PBS/1%NCC
2%	500	PLA/2%NCC	500	PBS/2%NCC
3%	500	PLA/3%NCC	500	PBS/3%NCC
4%	500	PLA/4%NCC	500	PBS/4%NCC
5%	500	PLA/5%NCC	500	PBS/5%NCC
3% +4%MDI	500	PLA/3%NCC+4%MDI	500	PBS/3%NCC+4%MDI
LNCC	**PLA (g)**	**Sample name**	**PBS (g)**	**Sample name**
3%	500	PLA/3%LNCC	500	PBS/3%LNCC

2.2.4. Transmission Electron Microscope (TEM)

Samples were tested using FEI/Philips CM-100 Transmission Electron Microscope. It has a computer controlled objective stage utilizing joy stick operation. It has a magnification range from 20x to 510,000 and accelerating voltage from 40 to 100kV. The liquid nitrogen-cooled decontaminator in the objective lens area minimizes contamination.

2.2.5. X-Ray Diffraction (XRD)

Samples were tested by Phillips XRG-3100 generator and an APD X-Ray Diffractometer (GBC Scientific Equipment Pty. Ltd., Victoria, Australia). Instrument operating conditions were as follows, the voltage was 35 Kv and current was 20 mA. Step size was 0.02°/2θ, and time/step was 0.6 seconds. Detecting angles start from 5° to 40°.

2.2.6. Thermal characterizations by Differential Scanning Calorimetry (DSC)

Thermal properties were determined by differential scanning calorimetry (DSC Q100, TA Instruments, New Castle, DE, USA). PLA blends were heated from 20 to 190°C at a rate of 10°C/min (1st cycle or 1st scan), cooled to 20°C at a rate of 25°C/min (2nd cycle) and reheated from 20 to 190°C at 10°C/min (3rd cycle or 2nd scan). PBS blends were heated from -80 to 190°C at a rate of 10°C/min (1st cycle or 1st scan), and then cooled it to -80°C at a rate of 25°C/min (cooling scan), and reheated from -80 to 190°C at 10°C/min (3rd cycle or 2nd scan).

PLA Crystallinity calculated as following equation:

$$Xc(\%) = \frac{\Delta Hm - \Delta Hcc}{\Delta Hm1} \times \frac{1}{Wpla} \times 100\%$$

where, ΔHm was the melting enthalpy and ΔHcc was the cold crystallization enthalpy, and ΔHm_1 was the melting enthalpy of pure 100% crystalline PLA which was 93J/g (Fischer et al., 1973 & Arrieta et al., 2014). W_{PLA} = weight fraction of PLA in polymer.

PBS Crystallinity calculated as following equation:

$$Xc(\%) = \frac{\Delta Hm}{\Delta Hm1 \times (1 - Wf)} \times 100\%$$

where, ΔHm was melting enthalpy, and ΔHm_1 was 110.3J/g (Uesaka et al., 2004 & Lin et al., 2011), W_f = nanofiller fraction in polymer.

2.2.7. Film making

Films were made by using Hot-press (Model 3889, 1DI1A09, CARVER, INC). Thickness of shim was 51um. Program was set with force at 2100 lb, and temperatures of up and down hot press plates were 180°C. Hot press was preheated at 180°C for 5min before pressing and total pressing time was 5min.

2.2.8. Mechanical Properties

Films were equilibrated in the humidity chamber for 24hrs, at 23°C and 50%RH before tests. Tensile properties of films were measured using Instron (ChmInstruments, A Chemsultants International Company, US) based on standard method ASTM D882-02 (ASTM 2002). Tensile strength (TS) and elongation at break (E%) were calculated as:

TS=$\frac{Lp}{a}$ × 10^{-6}MPa, where, Lp= peak load (N), a= cross-sectional area (m^2).

E= δL/L×100 (%), where, δL= increase in length at breaking point (mm), L= original length (mm).

2.2.9. Water Vapor Transmission Rate (WVTR)

The water vapor transmission rate was determined gravimetrically according to the standard method E96/E96-05. The water absorption test was using MOCON Permatran W3/31 system (Mocon Inc., Minneapolis, MN, USA). Films were fixed on top of test cells containing a desiccant (silica gel). The amount of water permeating through a sample is filled at constant condition at 90% RH and 37.8°C, with exposed area and thickness of 50cm^2 and 1mm and films were allowed to equilibrate for 30 mins. After steady-state conditions were reached, the weight of cells were measured every 45 mins, detected by a sensor F1249-06.

2.2.10. Oxygen Transmission Rate (OTR)

Films were tested by MOCON model 220 OxTrans analyzer (Modern Controls Inc., USA). The values of oxygen transmission rate of films were permeating through a sample is filled at constant condition at 22.8°C for 30mins, with exposed area and thickness of 50cm^2 and 1mm, respectively. A mixture of 98% N_2 and 2% 0_2 was used as the carrier gas and 0_2 was used as test gas. The films were fixed on the top of the test cell. Firstly, N_2 was passed through both

surfaces to remove any oxygen in the sample. Then, the diffusing oxygen was passed through the sample, and this diffusing oxygen was detected by F2262-08.

2.2.11. Statistical Analysis

All the data were analyzed using SAS.9.4 analysis software. Statistical significance of differences was calculated using Tukey's range test, $P < 0.05$.

2.3. Result and Discussion

2.3.1. Morphological properties of nanocomposites

The morphologies of the nanoparticles and nanocomposites were examined by TEM. CHW, LNCC and NCC presented thread-like structures as shown clearly in figures. After extrusion, CHW was dispersed uniformly in PLA matrix as the nano-particles aggregates. This is because extrusion provides mechanical shearing that nanofillers were broken down into smaller particles mechanically. LNCC was dispersed in PLA matrix. Occasionally, one big aggregates were found out in PLA matrix. NCC was dispersed in PLA matrix as nanoscale particle aggregates. It seems like 3%NCC has better dispersion than 1%NCC and 5%NCC. Similarly, CHW was dispersed uniformly in PBS matrix as nanoparticle aggregates. As increasing CHW loading, CHW was easy to form aggregates, thus it was found out that there was a big aggregates in PBS/5%CHW. LNCC was dispersed in PBS matrix as nanoparticle aggregates. Similarly, NCC was dispersed in PBS matrix as aggregates. As increasing NCC loading, NCC was easy to form aggregates, indicating big aggregates in PBS/3%NCC and PBS/5%NCC.
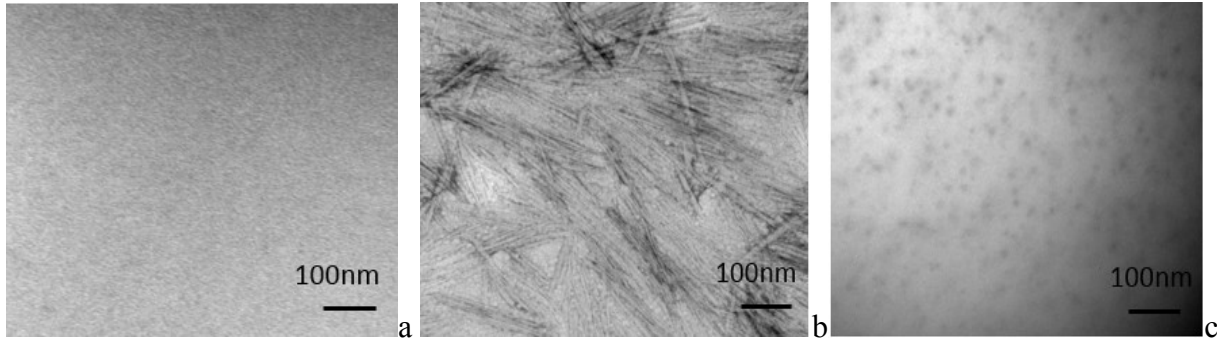
Figure 2.1. TEM image of PLA/CHW nanocomposites. a. PLA. b. CHW. c. PLA/3%CHW. Mag: 64000.

*Due to dark black color of PLA/CHW nanocomposites, only PLA/3%CHW and PLA/3%CHW/4%MDI was selected for further studies, so that is why the reason of missing data.
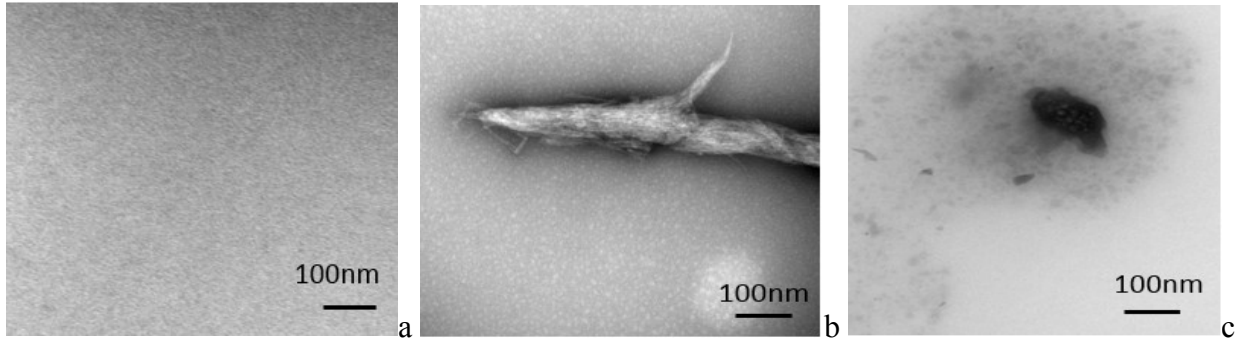
Figure 2.2. TEM image of PLA/LNCC nanocomposites. a. PLA. b. LNCC. c. PLA/3%LNCC. Mag: 64000.
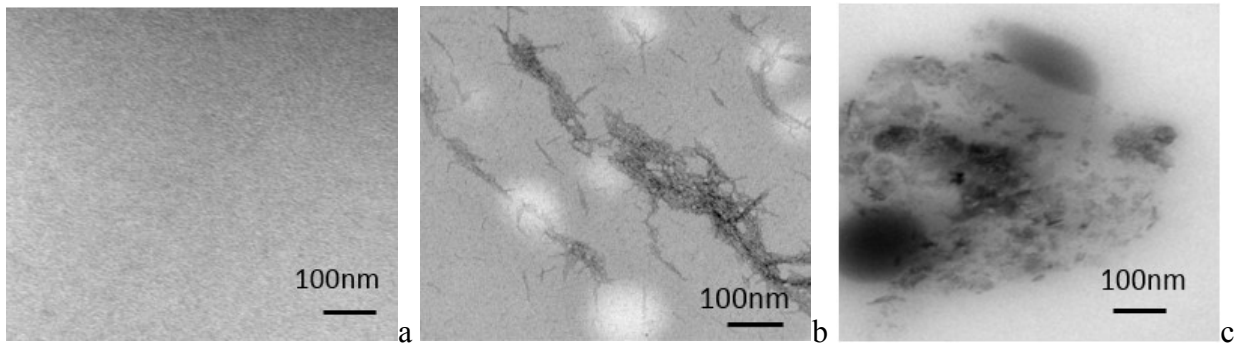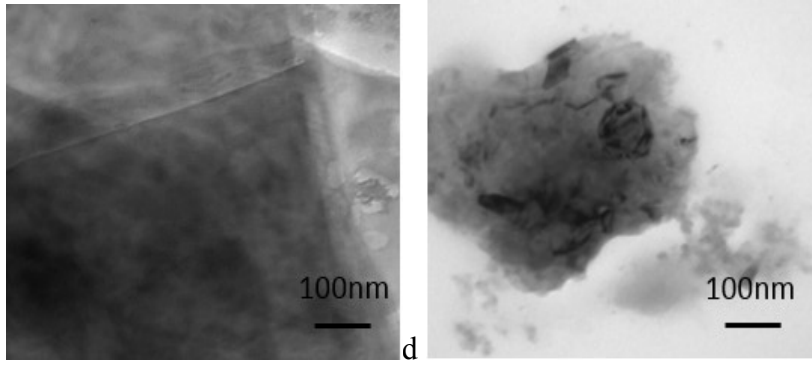
Figure 2.3. TEM image of PLA/NCC nanocomposites. a. PLA. b. NCC. c. PLA/1%NCC. d. PLA/3%NCC. e. PLA/5%NCC. Mag: 64000.
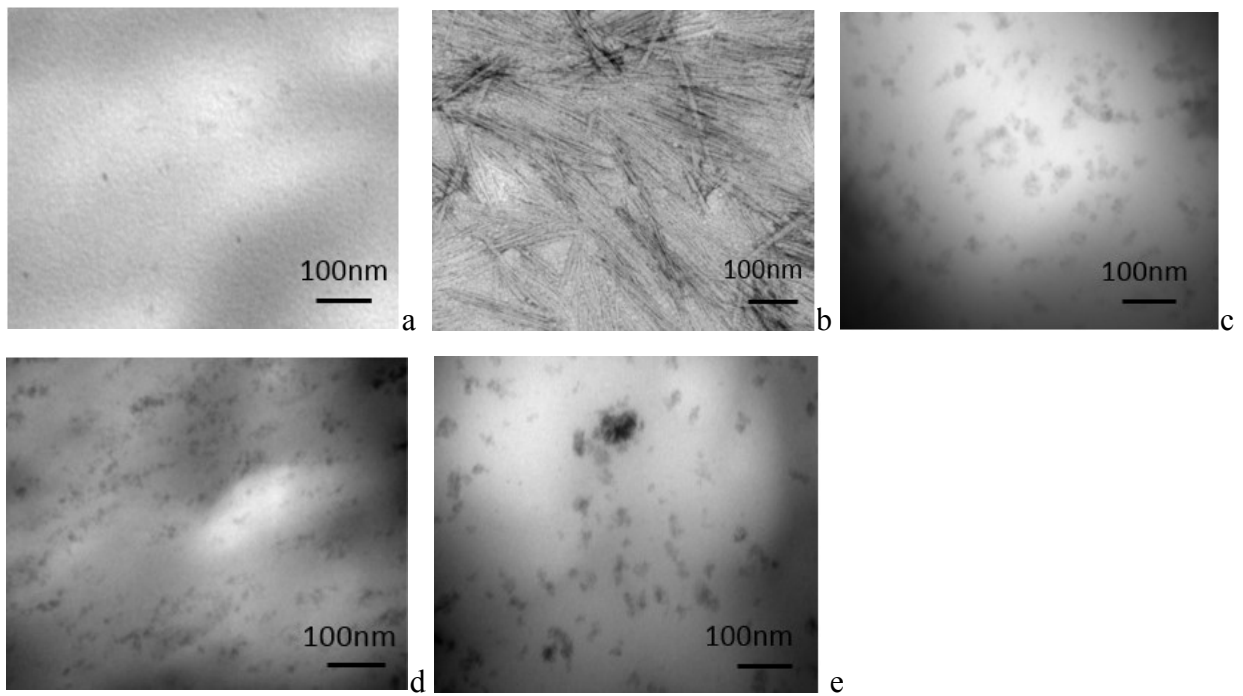
Figure 2.4. TEM image of PBS/CHW nanocomposites. a. PBS. b. CHW. c. PBS/1%CHW. d. PBS/3%CHW. e. PBS/5%CHW. Mag: 64000.
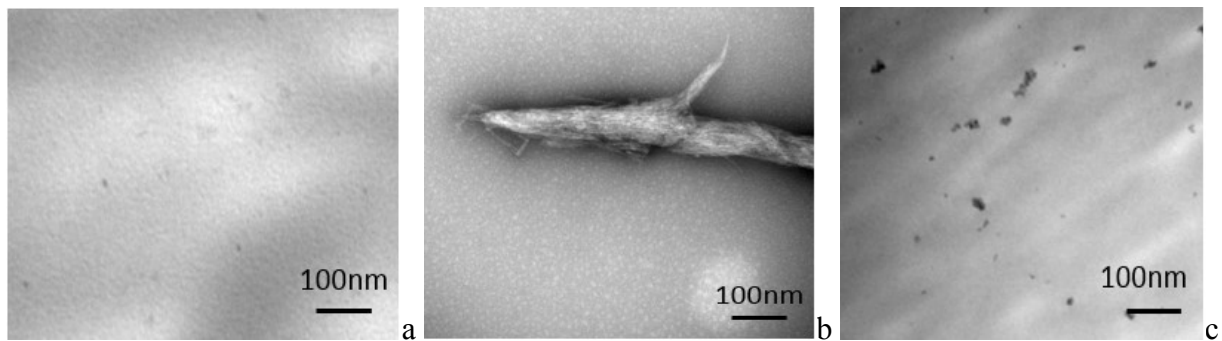
Figure 2.5. TEM image of PBS/LNCC nanocomposites. a. PBS. b. LNCC. c. PBC/3%LNCC. Mag: 64000.
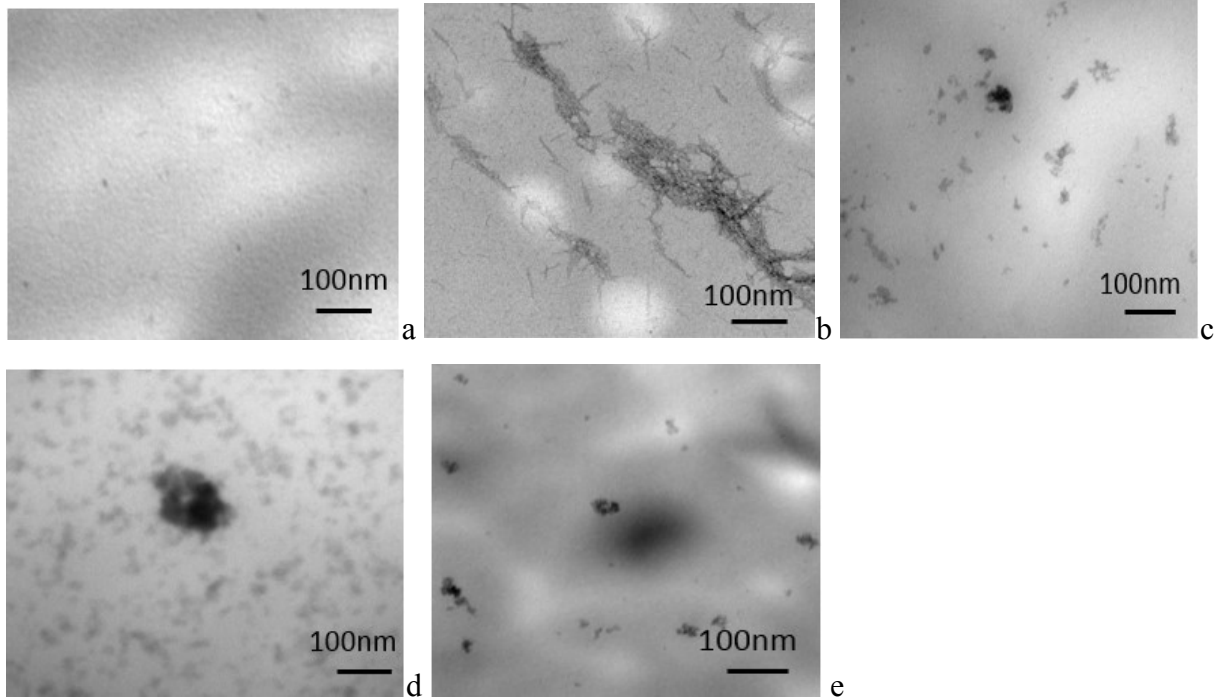
Figure 2.6. TEM image of PBS/NCC nanocomposites. a. PBS. b. NCC. c. PBS/1%NCC. d. PBS/3%NCC. e. PBS/5%NCC. Mag: 64000.

2.3.2. XRD measurements

Untreated PLA and CHW were shown semi-crystalline structure in nature, since both of them have two sharp peaks. LNCC and NCC presented one sharp peak. After blending nanofillers with PLA, XRD cannot detect nanofillers structure, due to low loading concentration of nanofillers and weak intensity. After extrusion, one broad peak of PLA occurred, and the distance between two peaks of PLA became broader, indicating nanofillers were intercalated in the polymer chains. Similarly, there were two sharp peaks of PBS, indicating semi-crystalline nature. After blending nanofillers with PBS, XRD cannot detect nanofillers structure because of low concentration and weak intensity. After extrusion, the distance of PBS peaks became broader, indicating nanofillers intercalated in the polymer chains.
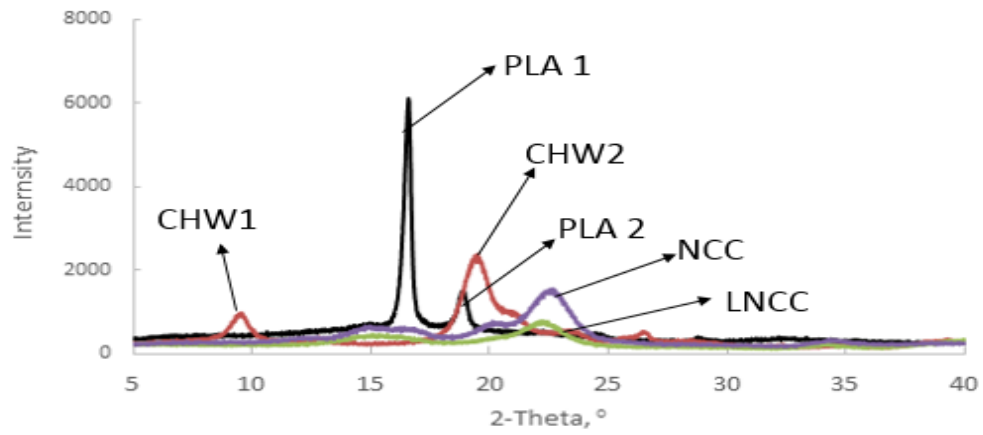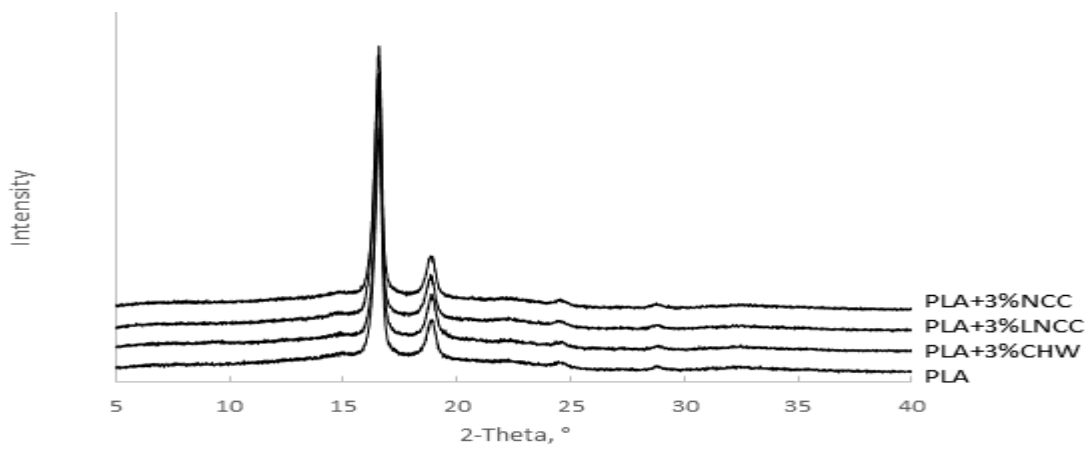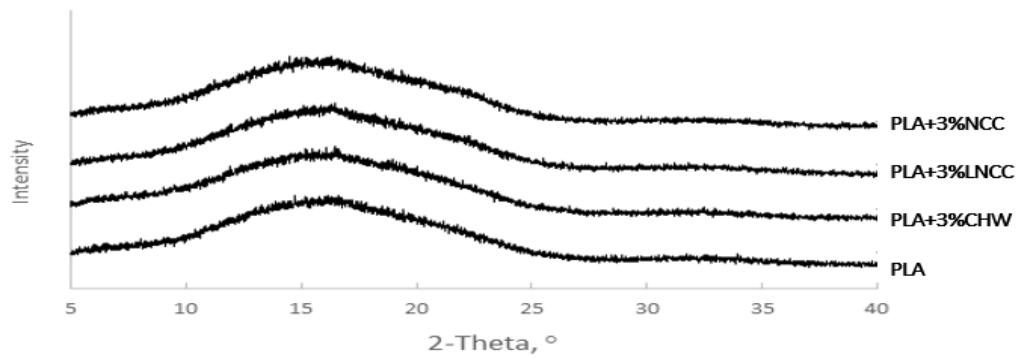
Figure 2.7. XRD pattern of PLA nanocomposites. a. Untreated PLA and nanofillers. b. Unextruded PLA nanocomposites. c. Extruded PLA nanocomposites.
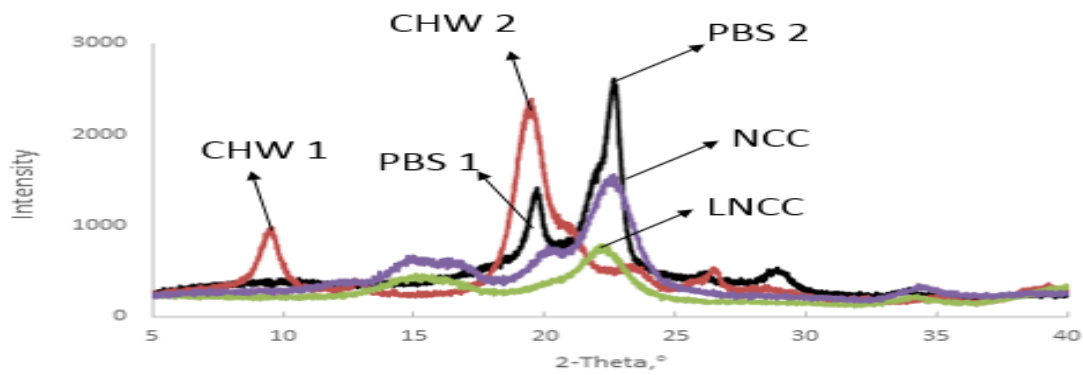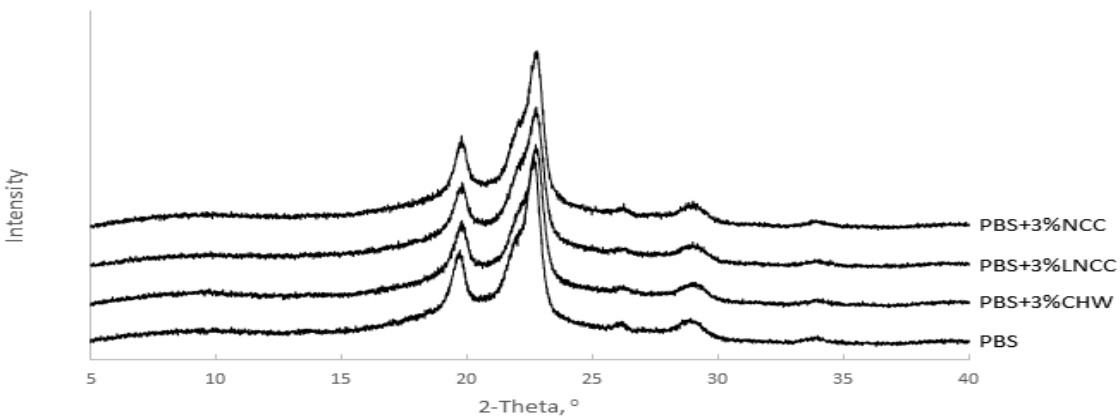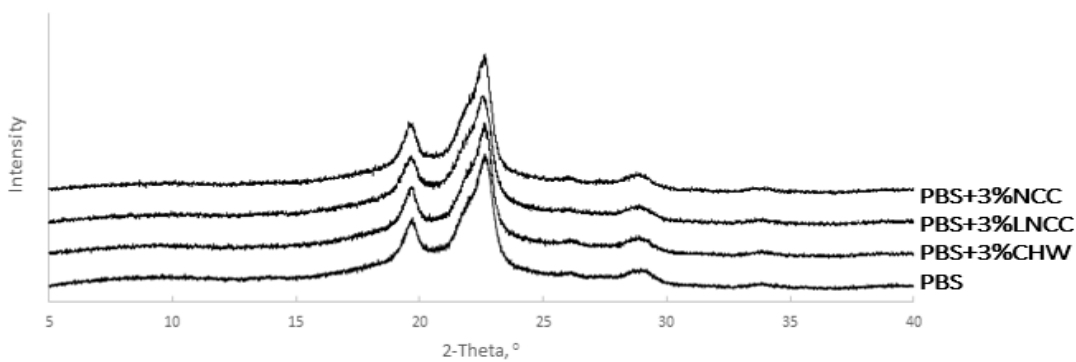
Figure 2.8. XRD pattern of PBS nanocomposites. a. Untreated PBS and nanofillers. b. Unextruded PBS nanocomposites. c. Extruded PBS nanocomposites.

2.3.3. Thermal properties of nanocomposites

A direct proof of polymer miscibility in blend can be obtained by observing the behavior of Tg of the blend composition. If the components (PLA, nanofillers) were totally immiscible, there would observe two glass transition temperatures. In this case, 3%CHW, 3%LNCC and

NCC reduced Tg of PLA, indicating there is miscibility at the interphase of polymers matrix and nanofillers (Cao et al., 2003). Due to large amount of hydroxyl groups on the surface of nanoparticles, it could form hydrogen bonding on the surface of PLA, thus improving compatibility between PLA with nanofillers (Cao et al., 2003). Zhang et al (2009) reported that as more nanofiller introduced into the nanocomposite system, more polymer chains would be confined between polymer and nanofiller, and the value of heat capacity was proportional to the number of degrees of freedom of molecular motion. ΔCp of PLA/CHW and PLA/3%LNCC and PLA/NCC blends decreased slightly with increasing nanofillers concentration, indicating the decreasing number of degrees of freedom of molecular motion, indicating better confinement between PLA and nanofillers (Vyazovkin and Dranca, 2004). MDI addition reduced Tg of PLA/3%CHW and PLA/3%NCC. The possible reason is chain extension by MDI increased the molecular weight and reduced the number of end groups, consequently reduced the free volumes and decreasing Tg (Li and Yang, 2006). According to Fukushima et al (2009), decreasing Tc and increasing ΔHc can indicate nanofillers promotes kinetics and extent of crystallization. However, in this case, there was no significant difference of Tc and ΔHc of PLA nanocomposites. Also, there was no significant difference of Tm and ΔHm of PLA nanocomposites.

There are several forms of nanocomposites, shown in figure 2.9. For phase separation microcomposite, nanofillers are dispersed as aggregates or stacked together, unable to enter in the polymer chains. When polymer chains are inserted into the nanofillers and cause increase in gallery spacing, but nanofillers are still remained their arrays, in this case, the intercalated nanocomposites are formed. For exfoliation nanocomposites, the polymer chains cause the separation of nanofillers and individual nanofiller is dispersed within the polymer matrix. From TEM images, well-dispersed nanofillers in PLA and PBS indicate exfoliation of nanofillers in

polymer matrix. For PLA based nanocomposites, PLA was confined by addition of nanofillers. Due to reinforcement of nanofillers, mechanical properties of PLA will be improved potentially. Also, due to uniform dispersion of nanofillers in PLA matrix, it formed tortuous pathway for water and oxygen molecules, thus increase the effective length for diffusion, therefore reduce the water vapor transmission rate and oxygen transmission rate potentially.

There was no significant difference of Tg and ΔCp of PBS nanocomposites.

Crystallization of PBS was improved by CHW, 3%LNCC and NCC addition, due to slightly increasing Tc and ΔHc of blends (Tang et al., 2014). Increasing Tc and ΔHc indicates nanofillers were the heterogeneous nucleating agent for the polymer and promote recrystallization of polymer. The nucleating agent could provide a surface on which the crystals can grow to form new crystals, thus the energy needed for polymers crystallization will be higher, thus leading to increasing crystallinity (Tang et al., 2014; Wu et al., 2014). MDI addition increased Tc of PBS/3%CHW and PBS/3%NCC, indicating that MDI promoted nucleation of nanoparticles in PBS.

Nucleation of nanocrystals and interactions between nanofiller and matrix are the influencing factors for the Tm, ΔHm and crystallinity of the nanocomposites (Lin et al., 2011). Increase in crystallinity leads to demand for more energy for thermal transformation which results in increase of ΔHm (Lin et al., 2011). Phua *et al* (2012) reported the decreased crystallinity of PBS nanocomposites could result in lower melting enthalpy (Phua et al., 2012). In this case, the crystallinity of PBS blends increased slightly and ΔHm increased slightly with increasing nanofillers concentration. MDI also reduced Tm and increased ΔHm of PBS/3%CHW and PBS/3%NCC, indicating that MDI did not affect interactions between PBS and nanoparticles.

The crystallite formation either on crystalline region of PBS or in amorphous region of PBS will result in polymer chains being restricted in mobility with amorphous region. Figure 2.10 showed the nature of constrained region in semi-crystalline PBS nanocomposites and in amorphous PBS matrix. Consequently, tensile strength will be enhanced by adding nanofillers. Also, these crystallites are the impermeable systems for polymer matrix, from the barrier perspective, therefore, barrier properties will be improved.
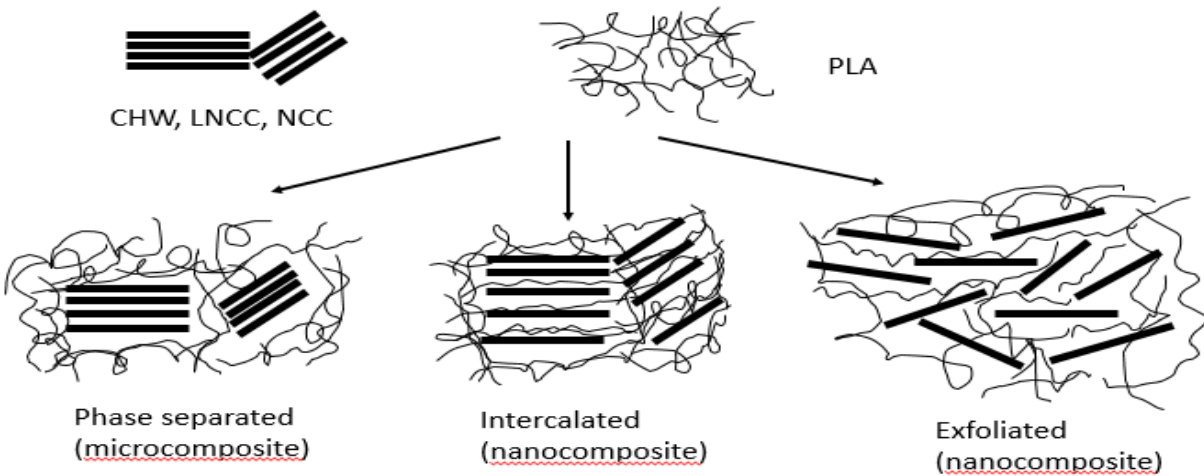
Figure 2.9. Nanocomposoties structure.
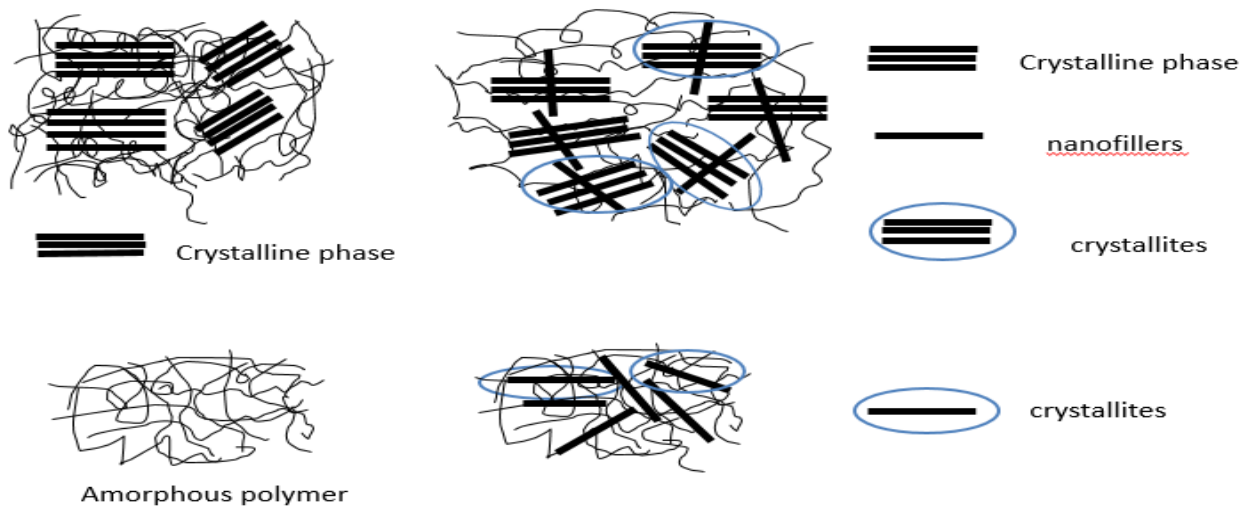
Figure 2.10. Crystallite formation of PBS after adding nanofillers.

Table 2.2. PLA nanocomposites glass transition properties.

NCC	T_g (ºC)	ΔCp (J/gºC)	CHW	T_g (ºC)	ΔCp (J/gºC)
0%	55.41±0.21a	0.50±0.01a	0%	55.41±0.21a	0.50±0.01a
1%	54.99±0.42ab	0.48±0.05a	3%	53.83±0.15b	0.47±0.02a
2%	54.51±0.02ab	0.46±0.02a	3%+4%MDI	53.55±0.03b	0.43±0.06a
3%	54.46±0.42abc	0.40±0.05a			
4%	53.15±0.07c	0.47±0.06a			
5%	53.67±0.13bc	0.39±0.03a			
3%+4%MDI	53.84±0.61bc	0.41±0.08a			
LNCC					
0%	57.86±0.13a	0.40±0.07a			
3%	56.05±0.01b	0.43±0.05a			

*Due to dark black color of PLA/CHW nanocomposites, only PLA/3%CHW and PLA/3%CHW/4%MDI was selected for further studies, so that is why the reason of missing data.
Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different (P<0.05). Comparisons are made within the same column and same nanofillers addition, n=2 for all treatments.

Table 2.3. PLA nanocomposies crystallization properties.

NCC	T_c (ºC)	ΔHc (J/g)	Xc (%)	CHW	T_c (ºC)	ΔHc (J/g)	Xc (%)
0%	98.02±0.25ab	24.55±0.14bc	14.28±1.13a	0%	98.02±0.25a	24.55±0.14a	14.28±1.13a
1%	98.6±0.10a	24.19±0.05c	14.53±0.29a	3%	96.92±0.14b	25.23±0.64a	13.81±1.57a
2%	97.60±0.37abc	25.14±0.98abc	13.36±0.67a	3%+4%MDI	93.72±0.29c	22.71±0.55a	15.85±0.28a
3%	97.17±0.03bc	25.14±0.45abc	14.10±0.05a				
4%	95.86±0.07d	26.02±0.07ab	15.75±1.66a				
5%	96.33±0.28cd	26.4±0.10a	13.37±0.62a				
3%+4%MDI	93.91±0.66e	22.30±0.45d	13.72±1.10a				
LNCC							
0%	101.84±0.03a	25.55±0.45a	8.11±0.25a				
3%	99.25±0.00b	25.23±1.00a	12.06±1.63a				

*Due to dark black color of PLA/CHW nanocomposites, only PLA/3%CHW and PLA/3%CHW/4%MDI was selected for further studies, so that is why the reason of missing data.
Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different (P<0.05). Comparisons are made within the same column and same nanofillers addition, n=2 for all treatments.

Table 2.4. PLA nanocomposites melting properties.

NCC	T$_m$ (ºC)	ΔHm (J/g)	CHW	T$_m$ (ºC)	ΔHm (J/g)
0%	167.65±0.12a	37.83±0.91a	0%	167.65±0.12a	37.83±0.91a
1%	167.44±0.16ab	37.56±0.31a	3%	166.97±0.06b	37.70±0.78a
2%	167.19±0.28ab	37.32±0.37a	3%+4%MDI	165.93±0.03c	36.49±0.31a
3%	166.93±0.49bc	37.87±0.49a			
4%	166.53±0.02c	37.97±0.63a			
5%	166.45±0.06cd	38.55±0.88a			
3%+4%MDI	165.95±0.06d	35.98±1.00a			
LNCC					
0%	168.55±0.26a	33.09±0.21b			
3%	167.63±0.18a	36.12±0.47a			

*Due to dark black color of PLA/CHW nanocomposites, only PLA/3%CHW and PLA/3%CHW/4%MDI was selected for further studies, so that is why the reason of missing data.

Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different (P<0.05). Comparisons are made within the same column and same nanofillers addition, n=2 for all treatments.

Table 2.5. PBS nanocomposites glass transition properties.

NCC	T$_g$ (ºC)	ΔCp (J/g ºC)	CHW	T$_g$ (ºC)	ΔCp (J/g ºC)
0%	-29.58±0.96a	0.15±0.02a	0%	-30.84±0.93a	0.16±0.03a
1%	-29.53±0.74a	0.09±0.00a	1%	-30.75±0.57a	0.15±0.03a
2%	-29.57±0.69a	0.14±0.10a	2%	-31.22±0.06a	0.15±0.02a
3%	-28.56±0.36a	0.11±0.00a	3%	-30.58±0.74a	0.15±0.02a
4%	-29.18±0.66a	0.18±0.05a	4%	-31.42±0.73a	0.12±0.05a
5%	-30.31±0.78a	0.17±0.02a	5%	-32.47±0.69a	0.10±0.01a
3%+4%MDI	-32.59±0.08b	0.14±0.00a	3%+4%MDI	-30.17±0.55a	0.17±0.03a
LNCC					
0%	-30.84±0.93a	0.16±0.03a			
3%	-31.80±0.91a	0.17±0.00a			

Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different (P<0.05). Comparisons are made within the same column and same nanofillers addition, n=2 for all treatments.

Table 2.6. PBS nanocomposites crystallization properties.

NCC	T$_c$ (ºC)	ΔHc (J/g)	Xc (%)	CHW	T$_c$ (ºC)	ΔHc (J/g)	Xc (%)

0%	79.85±1.04b	66.05±0.38c	66.81±0.52d	0%	81.50±0.03b	65.56±1.40a	65.86±0.44d
1%	81.09±1.01b	65.64±0.80c	68.54±1.03cd	1%	81.50±0.16b	65.75±1.46a	65.81±0.45d
2%	81.78±0.05b	66.20±1.04c	69.89±0.26c	2%	81.39±0.01b	65.49±0.40a	67.88±0.11bc
3%	82.03±0.07b	65.45±0.63c	70.33±0.49bc	3%	81.21±0.23b	66.45±0.94a	68.39±0.94b
4%	81.77±0.26b	68.04±0.59bc	71.01±0.35bc	4%	81.55±0.01b	68.36±0.14a	74.20±0.30a
5%	81.69±0.01b	69.17±0.37ab	72.88±0.81b	5%	81.53±0.08b	67.26±1.17a	75.63±0.53a
3%+4%MDI	79.85±1.04b	66.05±0.38c	66.81±0.52d	3%+4%MDI	83.72±0.35a	65.67±1.40a	75.73±0.67a
LNCC							
0%	81.09±0.05a	65.94±0.7a	58.98±0.29b				
3%	78.30±0.26b	63.62±1.17a	69.42±1.84a				

Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different (P<0.05). Comparisons are made within the same column and same nanofillers addition, n=2 for all treatments.

Table 2.7. PBS nanocomposites melting properties.

NCC	Tm (ºC)	ΔHm (J/g)	CHW	Tm (ºC)	ΔHm (J/g)
0%	112.12±0.52a	73.69±0.57b	0%	112.74±0.11a	72.59±0.49c
1%	111.21±0.32ab	74.58±1.13ab	1%	112.35±0.06ab	74.13±.13bc
2%	110.97±0.01ab	75.57±0.28ab	2%	112.06±0.18ab	74.20±1.35bc
3%	111.34±0.16ab	75.32±0.53ab	3%	112.11±0.15ab	75.43±0.23b
4%	110.81±0.22b	75.32±0.37ab	4%	111.64±0.43b	78.69±0.33a
5%	111.19±0.41ab	76.56±0.86a	5%	111.5±0.28b	79.45±0.56a
3%+4%MDI	111.25±0.05a	81.45±0.72c	3%+4%MDI	111.92±0.41ab	78.06±0.70a
LNCC					
0%	110.91±0.13a	65.06±0.35b			
3%	110.43±0.03a	76.21±1.07a			

Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different (P<0.05). Comparisons are made within the same column and same nanofillers addition, n=2 for all treatments.

2.3.4. Mechanical properties

Tensile strength (TS) of PLA increased with CHW, LNCC and NCC addition, indicating that there is a strong interaction between PLA and nanofillers, which was enhanced by the confinement of polymer chains due to nanofillers addition, thus restricting mobility of polymer chains and therefore improving the tensile strength. Also, the load transfer was improved by the

physical bonding between filler and matrix (Kuan et al., 2006). However, nanofillers addition did not affect E% of PLA, and E% values were around 10% which is not significant. MDI addition caused reduction of TS of PLA/3%LNCC and PLA/3%NCC, but a slight increase in E% of PLA/3%CHW and PLA/3%NCC. Previous work reported MDI addition increased mechanical properties of hydrophobic and hydrophilic polymers, for example, PLA/corn starch (Gartner et al., 2015); PLA/starch (Wang et al., 2001; Wang et al., 2002; Zhang and Sun, 2004), etc. Although MDI enhanced the poor interfacial adhesion between hydrophobic and hydrophilic polymers thus to improve TS and E%, it cannot be fit in this case due to low concentration of nanofillers.

In this study, two TS values of PBS were observed as 24.87 MPa and 23.25 MPa because of raw materials obtained from two different sources. As expected, CHW, LNCC and NCC increased TS of PBS, indicating that a strong interactions between nanofillers and polymer matrix, due to the crystallite formation of nanofillers restricted chains mobility. TS of PBS nanocomposites increased with increasing NCC concentration. However, for PBS/CHW films, 1%CHW enhanced TS of PBS most. The similar observation is also reported by Silverajah et al (2012), that over than 1% expoxidized olein palm was added in PLA, a reducing TS was obtained. Above 1%CHW, excess of nanofillers may be dispersed in polymer matrix, which affected its homogeneity and consequently reduced TS of the blends. Reduction of TS above 1% addition may also be caused by agglomeration which leads to poor interaction at the interphase (Pivsa-Art et al., 2013). E% of PBS/NCC was almost similar to neat PBS, and E% values were around 12% which were not significant. However, E% of PBS/CHW reduced, which is possibly due to structural integrity of PBS being destroyed by loading CHW, thus promoting microcracks formation at the interphase area and causing quicker fracture than neat PBS (Liu et al., 2009).

MDI addition increased TS of PBS/3%NCC, but decreased TS of PBS/3%CHW, but both slight

changes were not statistically significant. E% of PBS/3%LNCC and PBS/3%NCC was improved

due to MDI addition.

Due to CHW, NCC and LNCC nanofiller added in PLA and PBS, crystallinity of

nanocomposites increased slightly. Roohani et al (2008) reported reinforcing effect can be

affected by several factors, such as degree of crystallinity and Tg of matrix. It could be ascribed

to increased interactions between nanofillers and PLA or PBS via hydrogen bonding. Decrease in

Tg and ΔCp of PLA nanocomposites resulted in more confinement between PLA and naofillers,

thus corresponds to increasing TS. Increase in crystallinity of PBS nanocomposites increased

hydroxyl groups and the number of hydrogen bonds increased, consequently, resulting in

increase of TS.

When compared TS and E% of PLA and PBS nanocomposites films to commercial

plastics, TS of PLA and PBS nanocomposites films improved significantly. However, E% of

PLA and PLA/NCC films were poor, MDI further improved E% of PLA/3%NCC. E% for PBS

based films were all moderate.

Table 2.8. Effects of nanofillers on TS and E% of PLA and PBS nanocomposites films.

Nanofillers	PLA		PBS	
	TS (MPa)	E%	TS (MPa)	E%
0% NCC	50.25±3.91b	9.60±1.92a	24.87±4.89b	12.80±1.51a
1% NCC	65.47±3.10a	9.80±0.97a	32.13±1.70b	12.30±0.84a
2% NCC	66.58±4.7a	10.00±1.18a	31.21±3.86ab	11.90±1.14a
3% NCC	68.60±4.18a	9.50±0.35a	31.97±2.54ab	12.60±0.82a
4% NCC	69.81±3.75a	9.10±0.89a	32.50±3.19a	12.20±0.91a
5% NCC	70.89±2.83a	9.90±1.19a	32.88±3.70a	10.80±0.84a
3%NCC+4%MDI	49.34±2.07b	11.60±2.01a	34.71±3.34a	15.30±2.93b
Nanofillers	TS (MPa)	E%	TS (MPa)	E%
0%CHW	50.25±3.91b	9.60±1.92a	23.25±2.88c	14.70±3.05ab

1% CHW	-	-	43.65±4.55a	13.20±1.60ab
2% CHW	-	-	37.24±3.98ab	13.10±1.24c
3% CHW	52.1±3.57b	10.60±2.68a	34.63±3.47b	10.80±0.86c
4% CHW	-	-	34.64±1.80b	11.60±0.65c
5% CHW	-	-	33.28±2.10b	12.40±0.82bc
3%CHW+4%MDI	35.00±5.77c	11.90±2.30a	24.49±2.78c	13.50±2.32abc
3%LNCC	53.07±3.54b	10.10±1.24a	25.06±3.28c	9.70±0.97c

* Due to dark black color of PLA/CHW nanocomposites, only PLA/3%CHW and PLA/3%CHW/4%MDI was selected for further studies, so that is why the reason of missing data.
Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different ($P<0.05$). Comparisons are made within the same column, n=5 for all treatments.

2.3.5. Barrier properties

Due to excellent results from PLA/NCC and PBS/NCC tensile tests, barrier tests were mainly focused on nanocomposites of NCC addition. NCC reduced WVTR of PBS, indicating NCC has formed a tortuous pathway for water molecules to traverse film matrix, thus increasing the effective path length of diffusion and reducing WVTR (Tang et al., 2008). Also, NCC both reduced OTR of PLA and PBS films. Nanofillers addition also induced the crystallization of biopolymer, particularly transcrystallinity that blocks the filler matrix interface. It improves the barrier characteristics, since crystals are typically impermeable system (Sanchez-Garcia and Lagaron, 2010). In this study, MDI addition further reduced WVTR and OTR on PLA/3%NCC and PBS/3%NCC, which is an indicator of compatibilizer on barrier properties.

Isocyanate groups on the surface of MDI can both react with hydroxyl groups on the surface of nanofillers and carboxyl groups on the surface of PLA to form urethane group, therefore, leading to good interaction, further to improve E% in mechanical properties and barrier properties.

When compared water barrier of PLA and PBS nanocomposite films to commercial plastics, water barrier of PLA and PBS nanocomposites films were all moderate. Oxygen barrier

of PLA was poor, however, with addition of NCC, oxygen barrier of PLA was enhanced, and

MDI further improved oxygen barrier of PLA/3%NCC. Oxygen barrier of PBS and

PBS/3%NCC was poor, with addition of MDI, oxygen barrier of PBS/3%NCC was improved.
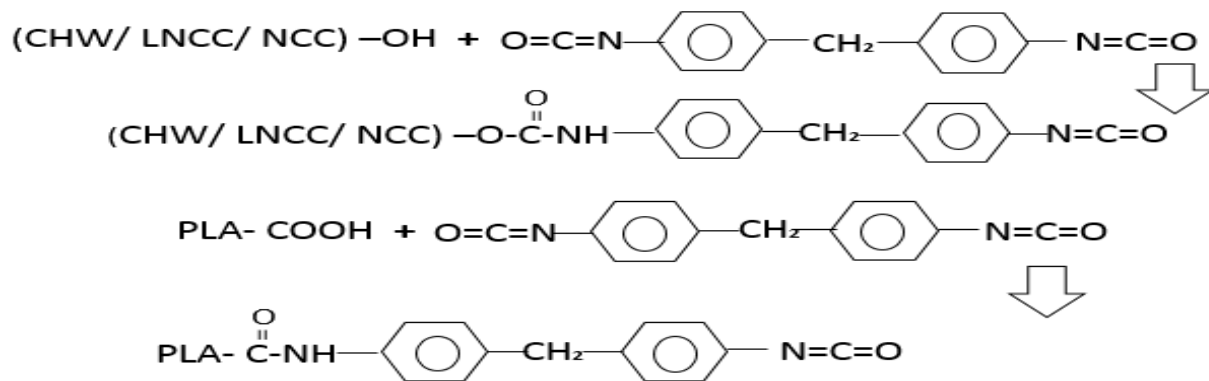
Figure 2.11. MDI react with nanofillers and PLA.

Table 2.9. OTR and WVTR of PLA and PBS nanocomposites films.

Nanofiller	PLA		PBS	
	WVTR $(g/m^2/day)$	OTR $(cc/m^2/day)$	WVTR $(g/m^2/day)$	OTR $(cc/m^2/day)$
0%	44.4	209.9	83.8	737.7
3% NCC	48.5	180.8	49.4	280
3%NCC+4%MDI	28.6	109.3	30.8	23.8

Table 2.10. Comparison of barrier and mechanical properties to commercial plastics.

Material	Preparation	H_2O barrier $(g*mm/m^2*d*kPa)$	O_2 barrier $(cm^3*um/m^2*d*kPa)$	TS (MPa)	E%
Cellophane	Aqueous	Moderate	Good	Good	Good
Cellulose acetate	Extrusion	Moderate	Poor	Moderate	Moderate
Starch/PVOH	Extrusion	Poor	Good	Good	Good
PHB/V	Extrusion	Good	Good	Moderate	Moderate
High Amylose starch	Aqueous	Poor	Moderate	Moderate	Moderate
Zein	95%EtOH	Moderate	Moderate	Moderate	Moderate
Gluten	Aqueous-EtOH	Moderate	Good	Moderate	Moderate
SPI	Aqueous	Poor	Good	Moderate	Moderate
WPI	Aqueous	Poor	Good	Moderate	Moderate
PLA	Extrusion	Moderate	Poor	Moderate	Poor
PLA/3%NCC	Extrusion	Moderate	Moderate	Moderate	Poor

PLA+3%NCC+4%MDI	Extrusion	Moderate	Moderate	Moderate	Moderate
PBS	Extrusion	Moderate	Poor	Moderate	Moderate
PBS/3%NCC	Extrusion	Moderate	Poor	Moderate	Moderate
PBS+3%NCC+4%MDI	Extrusion	Moderate	Moderate	Moderate	Moderate

*WVP and OP were calculated from WVTR and OTR, respectively.

Good: 0.01-0.1	Good: 1-10	Good: >100	Good: >50
Moderate: 0.1-10	Moderate: 10-100	Moderate: 10-100	Moderate: 10-50
Poor: 10-100	poor: 100-1000	poor: <10	poor: <10

Source: Krochta and De Mulder-Johnston, 1997 &
http://www.matweb.com/reference/tensilestrength.aspx.

2.4. Conclusion

Biodegradable nanocomposites were prepared by incorporating nanoparticles in polymer using melt extrusion. TEM and XRD studies indicated nanofillers were broken down into smaller particles mechanically in extrusion processing and dispersed uniformly in both PLA and PBS matrix. Thermal characterization of nanocomposites by DSC proved polymer chains of PLA was confined by nanoparticles. Consequently, mechanical and barrier properties of PLA films were improved by addition of NCC. Also, thermal analysis indicated nanofillers acted as nucleating agents for PBS thus increased crystallinity. Crystallite formation after adding nanofillers increased mechanical and barrier properties of PBS based films. MDI addition further improved barrier properties of PLA/3%NCC and PBS/3%NCC films significantly. MDI addition improved E% in mechanical properties of PLA and PBS films, but not for TS. To summarize, melt extrusion can be used to synthesize biobased PLA and PBS nanocomposites with natural nanofillers. Resultant films have moderate barrier and mechanical properties as compared to commercial films based on synthetic polymers, therefore have potentials to be employed in commercial packaging applications with further improvement.

Reference

Arrieta, M. P., Fortunati, E., Dominici, F., Rayón, E., López, J., & Kenny, J. M. (2014). Multifunctional PLA–PHB/cellulose nanocrystal films: Processing, structural and thermal properties. *Carbohydrate Polymers*, *107*, 16–24.

Cao, X., Mohamed, A., Gordon, S. ., Willett, J., & Sessa, D. (2003). DSC study of biodegradable poly(lactic acid) and poly(hydroxy ester ether) blends. *Thermochimica Acta*, *406*(1-2), 115–127.

Chow, W. S., & Lok, S. K. (2009a). Thermal properties of poly (lactic acid)/organo-montmorillonite nanocomposites. *Journal of Thermal Analysis and Calorimetry*, *95*(2), 627–632.

Gartner, H., Li, Y., & Almenar, E. (2015). Improved wettability and adhesion of polylactic acid/chitosan coating for bio-based multilayer film development. *Applied Surface Science*, *332*, 488–493.

Fischer, E. W., Sterzel, H. J., Wegner G. (1973). Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. *Kolloid-Zeitschrift und Zeitschrift für Polymere, 251*(11): 980-990.

Fukushima, K., Tabuani, D., & Camino, G. (2009). Nanocomposites of PLA and PCL based on montmorillonite and sepiolite. *Materials Science and Engineering: C*, *29*(4), 1433–1441.

Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications. *Chemical Reviews*, *110*(6), 3479–3500.

Huang, Y., Zhang, L., Yang, J., Zhang, X., & Xu, M. (2013). Structure and Properties of Cellulose Films Reinforced by Chitin Whiskers. *Macromolecular Materials and Engineering*, *298*(3), 303–310.

Krochta, J.M., De Mulder-Johnston, C., (1997). Edible and biodegradable polymer films: challenges and opportunities. *Food Technology*, 51(2), 61-64.

Kuan, C.-F., Ma, C.-C. M., Kuan, H.-C., Wu, H.-L., & Liao, Y.-M. (2006). Preparation and characterization of the novel water-crosslinked cellulose reinforced poly(butylene succinate) composites. *Composites Science and Technology*, *66*(13), 2231–2241.

Li, B.-H., & Yang, M.-C. (2006). Improvement of thermal and mechanical properties of poly(L-lactic acid) with 4,4-methylene diphenyl diisocyanate. *Polymers for Advanced Technologies*, *17*(6), 439–443.

Lin, N., Yu, J., Chang, P. R., Li, J., & Huang, J. (2011). Poly(butylene succinate)-based biocomposites filled with polysaccharide nanocrystals: Structure and properties. *Polymer Composites*, *32*(3), 472–482.

Liu, L., Yu, J., Cheng, L., & Qu, W. (2009). Mechanical properties of poly(butylene succinate) (PBS) biocomposites reinforced with surface modified jute fibre. *Composites Part A: Applied Science and Manufacturing*, *40*(5), 669–674.

Madhavan Nampoothiri, K., Nair, N. R., & John, R. P. (2010). An overview of the recent developments in polylactide (PLA) research. *Bioresource Technology*, *101*(22), 8493–8501.

Oksman, K., Skrifvars, M., & Selin, J.-F. (2003). Natural fibres as reinforcement in polylactic acid (PLA) composites. *Composites Science and Technology*, *63*(9), 1317–1324.

Peng, B. L., Dhar, N., Liu, H. L., & Tam, K. C. (2011). Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective. *The Canadian Journal of Chemical Engineering*, *89*(5), 1191–1206.

Phua, Y. J., Lau, N. S., Sudesh, K., Chow, W. S., & Mohd Ishak, Z. A. (2012). Biodegradability studies of poly(butylene succinate)/organo-montmorillonite nanocomposites under controlled compost soil conditions: Effects of clay loading and compatibiliser. *Polymer Degradation and Stability*, *97*(8), 1345–1354.

Pivsa-Art, S., Thumsorn, S., Pavasupree, S., O-Charoen, N., Pivsa-Art, W., Yamane, H., & Ohara, H. (2013). Effect of Additive on Crystallization and Mechanical Properties of Polymer Blends of Poly(Lactic Acid) and Poly[(Butylene Succinate)-co-Adipate]. *Energy Procedia*, *34*, 563–571.

Roohani, M., Habibi, Y., Belgacem, N. M., Ebrahim, G., Karimi, A. N., & Dufresne, A. (2008). Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. *European Polymer Journal*, *44*(8), 2489–2498.

Sanchez-Garcia, M. D., & Lagaron, J. M. (2010). On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. *Cellulose*, *17*(5), 987–1004.

Silverajah, V. S. G., Ibrahim, N. A., Zainuddin, N., Yunus, W. M. Z. W., & Hassan, H. A. (2012). Mechanical, Thermal and Morphological Properties of Poly(lactic acid)/Epoxidized Palm Olein Blend. *Molecules*, *17*(12), 11729–11747.

Tang, X., Alavi, S., Herald, T. J. (2008). Barrier and mechanical properties of starch-clay nanocomposite films. *Cereal chemistry*, *85*(3): 433-439.

Tang, Y.-R., Lin, D.-W., Gao, Y., Xu, J., & Guo, B.-H. (2014). Prominent Nucleating Effect of Finely Dispersed Hydroxyl-Functional Hexagonal Boron Nitride on Biodegradable Poly(butylene succinate). *Industrial & Engineering Chemistry Research*, *53*(12), 4689–4696.

Tang, L., & Weder, C. (2010). Cellulose Whisker/Epoxy Resin Nanocomposites. *ACS Applied Materials & Interfaces*, *2*(4), 1073–1080.

Uesaka, T., Nakane, K., Maeda, S., et al. (2004). Structure and physical properties of poly (butylene succinate)/cellulose acetate blends. *Polymer*, *41*(23): 8449-8454.

Vyazovkin, S., & Dranca, I. (2004). A DSC Study of α- and β-Relaxations in a PS−Clay System. *The Journal of Physical Chemistry B*, *108*(32), 11981–11987.

Wang, H., Sun, X., & Seib, P. (2001). Strengthening blends of poly(lactic acid) and starch with methylenediphenyl diisocyanate. *Journal of Applied Polymer Science*, *82*(7), 1761–1767.

Wang, H., Sun, X., & Seib, P. (2002). Effects of starch moisture on properties of wheat starch/poly (lactic acid) blend containing methylenediphenyl diisocyanate. *Journal of Polymers and the Environment*, *10*(4), 133–138.

Wu, W., Cao, X., Luo, J., He, G., & Zhang, Y. (2014). Morphology, thermal, and mechanical properties of poly(butylene succinate) reinforced with halloysite nanotube. *Polymer Composites*, *35*(5), 847–855.

Yang, K., Wang, X., Wang, Y., & others. (2007). Progress in nanocomposite of biodegradable polymer. Journal of industrial and engineering chemistry-Seoul, *13*(4), 485.

Zeng, J.-B., He, Y.-S., Li, S.-L., & Wang, Y.-Z. (2012). Chitin Whiskers: An Overview.

Biomacromolecules, *13*(1), 1–11.

Zhai, W., Ko, Y., Zhu, W., Wong, A., & Park, C. B. (2009). A Study of the Crystallization, Melting, and Foaming Behaviors of Polylactic Acid in Compressed CO_2. *International Journal of Molecular Sciences*, *10*(12), 5381–5397.

Zhang, J.-F., & Sun, X. (2004). Mechanical and thermal properties of poly(lactic acid)/starch blends with dioctyl maleate. *Journal of Applied Polymer Science*, *94*(4), 1697–1704.

Zhang, X., & Loo, L. S. (2009). Study of Glass Transition and Reinforcement Mechanism in Polymer/Layered Silicate Nanocomposites. *Macromolecules*, *42*(14), 5196–5207.

Tensile Property Testing of Plastics. http://www.matweb.com/reference/tensilestrength.aspx. Retrieved October 25, 2015.

Chapter 3 - Nanocrystalline cellulose effect of Poly(lactic acid)/Starch Polymers

Abstract

Starch is biopolymer that can potentially be used for lowering the costs of biobased nanocomposites for packaging applications. Up to 40% starch was incorporated during synthesis of poly (lactic acid) (PLA) and nanocrystalline cellulose (NCC) based nanocomposites using solution mixing method. PLA/starch blends were detected on thermal analysis and mechanical tests. Addition of starch decreased tensile strength (TS) from 35.8 to 18.4MPa and elongation at break (E%) from 8.3 to 6.0. Use of NCC (1%) or methylene diphenyl diisocyanate (MDI) (4%) did improve the mechanical properties to a certain extent.

3.1. Introduction

The environmental impact on non-degradable plastics derived from petroleum or fossil has stimulated the increasingly interest of seeking for biodegradable polymers substitutes. In the present days, renewable and biodegradable polymers were focused on to replace the conventional plastics. Biodegradable and renewable polymers can not only solve the problems of poor degradation, but also release the burden of petroleum and fossil scarcity. And among those biodegradable polymers, poly (lactic acid) (PLA) which is a synthetic polymer, and starch which is a natural polymer, have the most attractive interests.

PLA is aliphatic hydrophobic polyester. Due to its degradable natures, PLA can be degraded slowly to carbon dioxide, methane and water in the environment from several months to 2 years which has already reduced degradation time compared to conventional plastics with 500-1000 years in nature (Wang et al., 2001). Meanwhile, PLA is widely used due to high tensile strength which is 58.2 MPa (Silverajah et al., 2012). Besides, due to hydrophobic nature of PLA, PLA films are resistant to water molecules, thus providing a good water barrier for most food which are hydrophilic natures potentially.

Starch is a typical hydrophilic, biodegradable, renewable and low-cost polymer in nature. However, starch may cause the problems of poor mechanical characterizations and poor barrier properties due to hydrophilic nature. In this case, the purpose of starch introduced in PLA is to improve the biodegradability and reduce the raw materials cost as well. However, there is one concern when blended hydrophobic PLA and hydrophilic starch that is the poor interfacial interaction.

There are two possible ways to improve the poor interfacial adhesion between hydrophobic and hydrophilic polymers according to preliminary studies. Firstly, a third component can be added in this polymer system in order to reduce the interfacial energy thus to

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improve the poor interfacial interaction (Zhang and Sun, 2004). For example, poly (ethylene glycerol) (PEG) was added in PLA/thermoplastic starch to improve the poor interaction, and the tensile and flexural strength increased significantly (Wang et al., 2013). Secondly, the another possible way is to introduce a third component with functional groups, which is plasticizer, for example, glycerol, sorbitol and maleic anhydride or compatibilizer, for example, methylene diphenyl diisocyanate (MDI), adipate, citrate esters and graphene oxide (GO) which can be reacted with both hydrophobic and hydrophilic polymers to bond together, consequently, to enhance the poor interactions between hydrophobic and hydrophilic polymers (Leadprathom et al., 2010). There are already attempts, for example, dioctyl maleate (DOM) added in PLA/starch (Zhang and Sun, 2004); maleic anhydride (MA) and maleated thermoplastic starch (MATPS) blended with PLA/starch (Jang et al., 2007); glycerol added in PLA/thermoplastic starch (Leadprathom et al., 2010). It has already been reported MDI could react with carboxyl groups of PLA and hydroxyl groups on starch to form urethane group (Wang et al., 2002). Therefore, MDI has the potential to interact PLA and starch to form a good interfacial interaction.

In this scope of study, 1% NCC and 1%NCC with 4% MDI was added in two ratios of PLA/starch blends and evaluated mechanical and thermal characterizations.

3.2. Experimental

3.2.1. Materials

Poly (lactic acid) (PLA), Nature Works^{TM} 4032D, supplied by Cargill Dow LLC, Minnetonka, MN, USA. Corn starch was MELOJEL obtained from National Starch & Chemical Company (Bridgewater, NJ). Nanocrystalline cellulose was purchased from University of Maine (Orono, ME). Methylene diphenyl diisocyanate (MDI) with purity was over 97%, was obtained from TCI AMERICA (Portland, OR). Chloroform was purchased from chemical store, KSU

3.2.2. Blends preparation

Before blending, PLA was heated in air oven overnight under 100°C. There were two ratios of PLA/CS, as 60%/40% and 80%/20%. 1%NCC and 1%NCC/4%MDI of the blends was added in these 80%PLA/20%CS and 60%PLA/40%CS blends. Also, PLA+1%NCC was blended.

Table 3.1. Formulation of PLA/CS blends.

Sample name	PLA/CS (500g)	NCC	MDI
PLA	100/0	-	-
PLA/1%NCC	100/0	1%	-
80%PLA/20%CS	80/20	-	-
80%PLA/20%CS+1%NCC	80/20	1%	-
80%PLA/20%CS+1%NCC+4%MDI	80/20	1%	4%
60%PLA/40%CS	60/40	-	-
60%PLA/40%CS+1%NCC	60/40	1%	-
60%PLA/40%CS+1%NCC+4%MDI	60/40	1%	4%

3.2.3. Thermal characterizations by Differential Scanning Calorimetry (DSC)

Thermal properties were determined via a differential scanning calorimetry (DSC Q100, TA Instruments, New Castle, DE, USA). Samples were heated from 20°C to 190°C at a rate of 10°C/min (1st cycle or 1st scan), cooled to 20°C at a rate of 25°C/min (2nd cycle) and reheated from 20°C to 190°C at 10°C/min (3rd cycle or 2nd scan).

PLA Crystallinity calculated as following equation:

$$Xc(\%) = \frac{\Delta Hm - \Delta Hcc}{\Delta Hm1} \times \frac{1}{Wpla} \times 100\%$$

where, ΔHm was the melting enthalpy and ΔHcc was the cold crystallization , and ΔHm_1 was the melting enthalpy of pure 100% crystalline PLA which is 93J/g (Fischer et al., 1973 & Arrieta et al., 2014), W_{PLA} = weight fraction of PLA in polymer.

3.2.4. Film making

Films were prepared by solvent casting method by using chloroform. 10g polymer was added in 200ml chloroform and stirred for 30mins to get uniform solution. Solutions will be casted on Petri dishes, films will be peeled off till chloroform evaporation.

3.2.5. Mechanical Properties

Films were equilibrated in humidity chamber for 24 hrs, under 23°C and 50%RH before tests. Tensile properties of films were measured using Instron (ChmInstruments, A Chemsultants International Company, US) based on standard method ASTM D882-02. Films were cut into strips (2inch length * 0.5inch width). The crosshead speed was 20inch/min. Tensile strength (TS) and elongation at break (E) were calculated as below:

$TS = \frac{Lp}{a} \times 10^{-6} MPa$, where, Lp= peak load (N), a= cross-sectional area (m^2).

$E = \delta L / L \times 100$, where, δL= increase in length at breaking point (mm), L= original length (mm).

3.2.6. Statistical Analysis

All the data were analyzed using SAS.9.4 analysis software. Statistical significance of differences was calculated using Tukey's range test, $P < 0.05$

3.3. Result and Discussion

3.3.1. Thermal properties

Corn starch addition reduced ΔHc of PLA, which was similar to previous study of PLA/starch blends, indicating starch granules might restrict the molecular motion of PLA matrix and decreased crystallinity (Wang et al., 2001). NCC addition did not affect crystallinity of PLA/CS blends significantly. MDI addition reduced ΔHc of PLA/CS+1%NCC blends slightly.

The possible reason is interfacial interaction between PLA and CS matrix restricted PLA chain orientation (Wang et al., 2001).

Table 3.2. Crystallization properties of PLA/CS blends.

Sample name	Crystallization		
	Tc (°C)	ΔHc (J/g)	Xc (%)
PLA	102.67±0.68a	22.19±0.76a	8.59±1.72a
PLA/1%NCC	102.45±0.84a	23.15±0.16a	10.14±0.35a
80%PLA/20%CS	104.07±1.60a	18.20±1.03c	8.44±0.77a
80%PLA/20%CS/1%NCC	101.93±1.83a	21.48±1.41b	7.87±0.33a
80%PLA/20%CS/1%NCC/4%MDI	90.67±1.27b	18.85±0.11bc	1.05±1.07a
60%PLA/40%CS	103.52±0.62a	16.73±0.05c	9.22±0.22a
60%PLA/40%CS/1%NCC	102.93±0.66a	16.80±0.28c	7.47±0.17a
60%PLA/40%CS/1%NCC/4%MDI	81..02±0.57c	14.00±0.25c	1.99±0.08a

Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different ($P<0.05$). Comparisons are made within the same column, n=2 for all treatments.
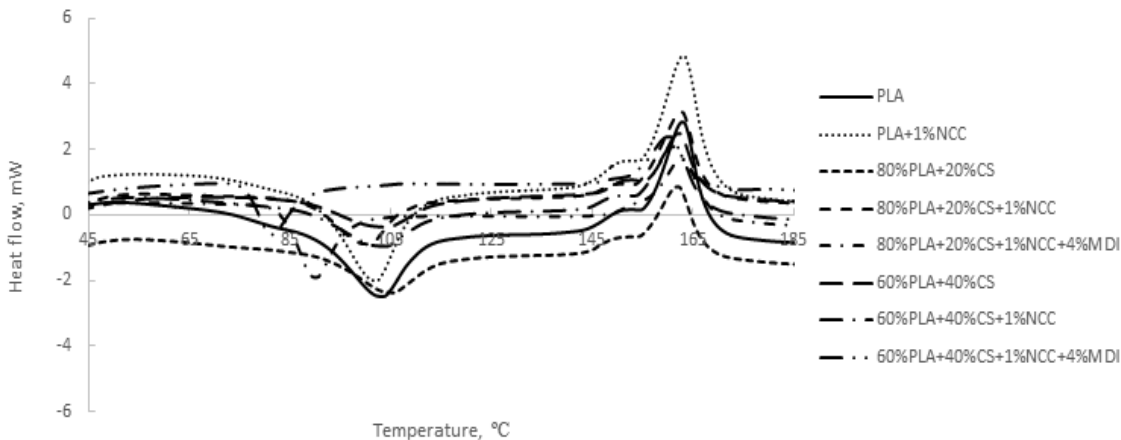
Figure 3.1. DSC thermal graph of PLA/CS blends.

3.3.2. Mechanical properties

Addition of CS to PLA reduced TS indicating poor interfacial adhesion between hydrophobic PLA and hydrophilic CS. This is because of poor interfacial bonding and particles of dispersed starch phase acting as stress concentrators, and decreasing the tensile strength

(Wang et al., 2001). 1%NCC increased TS of neat PLA, which showed similar trends in compressed films, indicating hydrogen bonding was formed due to hydroxyl groups of NCC which enhanced TS. NCC improved TS of PLA/CS films. Also, MDI addition slightly increased the TS of PLA/CS/NCC films slightly.

NCC and MDI addition did not significantly affect E% of PLA/CS blends, except 60%PLA/40%CS/1%NCC. The possible reason is that both PLA and CS was brittle, nanofillers and compatibilizer could not improve the elongations (Jun, 2000). MDI did not affect E% of PLA/CS/NCC films.

Compared TS of PLA/CS films to commercial plastics, TS of PLA/CS films was moderate. But E% of PLA/CS films was lower than commercial films.

Table 3.3. TS and E% of PLA/CS films.

Sample name	TS (MPa)	E%
PLA	35.81±2.32ab	8.3±1.04bc
PLA/1%NCC	41.90±5.14a	7.5±0.94bc
80%PLA/20%CS	30.70±5.76bc	7.90±1.71bc
80%PLA/20%CS/1%NCC	32.19±4.76bc	7.60±0.89bc
80%PLA/20%CS/1%NCC/4%MDI	32.91±3.15bc	10.00±2.72c
60%PLA/40%CS	18.44±2.93e	6.00±0.50c
60%PLA/40%CS/1%NCC	17.83±2.35e	16.10±1.41a
60%PLA/40%CS/1%NCC/4%MDI	22.35±3.54de	6.70±0.70c

Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different ($P<0.05$). Comparisons are made within the same column, n=5 for all treatments.

Good: >100	Good: >50
Moderate: 10-100	Moderate: 10-50
Poor: <10	Poor: <10

Source: Krochta and De Mulder-Johnston, 1997 &
http://www.matweb.com/reference/tensilestrength.aspx.

3.4. Conclusion

Addition of CS to PLA reduced TS due to poor interfacial interaction between hydrophobic PLA and hydrophilic CS. Also, CS addition restricted molecular motion of PLA therefore reducing crystallization enthalpy (ΔHc) of PLA. NCC addition slightly increased the TS of PLA/CS films, and MDI addition further increased TS of PLA/CS/NCC films.

Reference

Arrieta, M. P., Fortunati, E., Dominici, F., Rayón, E., López, J., & Kenny, J. M. (2014). Multifunctional PLA–PHB/cellulose nanocrystal films: Processing, structural and thermal properties. *Carbohydrate Polymers*, *107*, 16–24

Bie, P., Liu, P., Yu, L., Li, X., Chen, L., & Xie, F. (2013). The properties of antimicrobial films derived from poly(lactic acid)/starch/chitosan blended matrix. *Carbohydrate Polymers*, *98*(1), 959–966.

Fischer, E. W., Sterzel, H. J., Wegner G. (1973). Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. *Kolloid-Zeitschrift und Zeitschrift für Polymere, 251*(11): 980-990.

Jang, W. Y., Shin, B. Y., Lee, T. J., & Narayan, R. (2007). Thermal properties and morphology of biodegradable PLA/starch compatibilized blends. *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY-SEOUL-*, *13*(3), 457.

Jun, C. L. (2000). Reactive blending of biodegradable polymers: PLA and starch. *Journal of Polymers and the Environment*, *8*(1), 33–37.

Ke, T., & Sun, X. (2001). Effects of moisture content and heat treatment on the physical properties of starch and poly (lactic acid) blends. *Journal of Applied Polymer Science*, *81*(12), 3069–3082.

Krochta, J.M., De Mulder-Johnston, C. (1997). Edible and biodegradable polymer films: challenges and opportunities. *Food Technology*, 51(2), 61-64.

Kuan, C.-F., Ma, C.-C. M., Kuan, H.-C., Wu, H.-L., & Liao, Y.-M. (2006). Preparation and characterization of the novel water-crosslinked cellulose reinforced poly(butylene succinate) composites. *Composites Science and Technology*, *66*(13), 2231–2241.

Leadprathom, J., Suttiruengwong, S., Threepopnatkul, P., & Seadan, M. (2010). Compatibilized Polylactic Acid/Thermoplastic Starch by Reactive Blend. *Journal of Metals, Materials and Minerals*, *20*(3), 87–90.

Shirai, M. A., Grossmann, M. V. E., Mali, S., Yamashita, F., Garcia, P. S., & Müller, C. M. O. (2013). Development of biodegradable flexible films of starch and poly(lactic acid) plasticized with adipate or citrate esters. *Carbohydrate Polymers*, *92*(1), 19–22.

Silverajah, V. S. G., Ibrahim, N. A., Zainuddin, N., Yunus, W. M. Z. W., & Hassan, H. A. (2012). Mechanical, Thermal and Morphological Properties of Poly(lactic acid)/Epoxidized Palm Olein Blend. *Molecules*, *17*(12), 11729–11747.

Wang, H., Sun, X., & Seib, P. (2001). Strengthening blends of poly(lactic acid) and starch with methylenediphenyl diisocyanate. *Journal of Applied Polymer Science*, *82*(7), 1761–1767.

Wang, H., Sun, X., & Seib, P. (2003). Properties of poly (lactic acid) blends with various starches as affected by physical aging. *Journal of Applied Polymer Science*, *90*(13), 3683–3689.

Zhang, J.-F., & Sun, X. (2004a). Mechanical and thermal properties of poly(lactic acid)/starch blends with dioctyl maleate. *Journal of Applied Polymer Science*, *94*(4), 1697–1704.

Zhang, J.-F., & Sun, X. (2004b). Mechanical Properties of Poly(lactic acid)/Starch

Composites Compatibilized by Maleic Anhydride.

Tensile Property Testing of Plastics. http://www.matweb.com/reference/tensilestrength.aspx. Retrieved October 25, 2015.

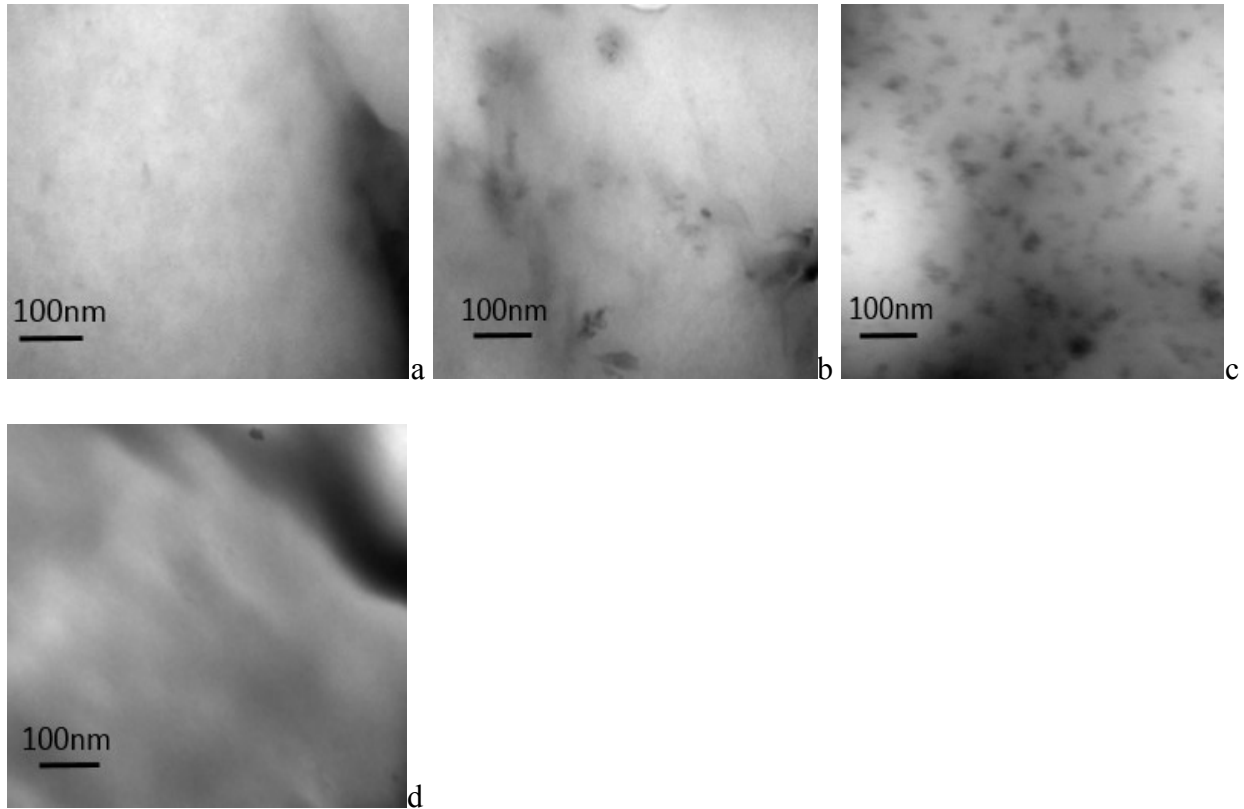# Appendix A - TEM images of MDI addition in PLA and PBS nanocomposites films.

Figure A.1. TEM images of MDI addition in PLA and PBS nanocomposites films. (a). PLA+3%CHW+3%MDI. (b). PLA+3%NCC+4%MDI. (c). PBS+3%CHW+4%MDI. (d). PBS+3%NCC+4%MDI.

Appendix B - Effects of nanofillers on TS and E% of PLA and PBS nanocomposites 75um films.

Table B.1. Effects of nanofillers on TS and E% of PLA and PBS nanocomposites 75um films.

Nanofillers	PLA		PBS	
	TS (MPa)	E%	TS (MPa)	E%
0% NCC	47.80±4.26cd	10.10±1.67a	25.45±3.42c	10.80±1.72b
1% NCC	60.93±2.38a	11.20±3.11a	34.30±3.82b	13.6±0.96ab
2% NCC	58.97±4.04ab	11.40±4.57a	30.86±3.92bc	13.00±1.46b
3% NCC	52.75±5.43abc	10.60±3.90a	33.33±3.50b	11.30±1.04b
4% NCC	51.39±1.62bc	10.00±0.61a	32.41±1.84b	12.20±1.43b
5% NCC	53.93±3.54abc	11.50±3.02a	34.75±2.56ab	12.80±2.49b
3% NCC +4%MDI	35.30±4.60e	11.90±2.30a	40.68±1.64a	16.90±1.78a
Nanofillers	TS (MPa)	E%	TS (MPa)	E%
0%CHW	47.80±4.26cd	10.10±1.67a	27.11±3.27c	16.70±3.68a
1% CHW	-	-	36.13±2.20ab	16.40±2.63ab
2% CHW	-	-	34.38±2.26ab	12.50±0.87bc
3% CHW	49.21±2.33cd	9.40±0.71a	36.59±4.45a	11.90±1.29c
4% CHW	-	-	32.20±4.31abc	11.70±1.44c
5% CHW	-	-	33.40±3.94abc	12.60±1.29bc
3% CHW	40.91±5.86de	11.80±3.03a	31.53±1.62abc	12.90±1.43abc
3%LNCC	53.77±3.07abc	10.50±1.54a	29.87±1.66bc	12.30±1.40c

* Due to dark black color of PLA/CHW nanocomposites, only PLA/3%CHW and PLA/3%CHW/4%MDI was selected for further studies, so that is why the reason of missing data.

Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different (P<0.05). Comparisons are made within the same column, n=5 for all treatments.

Appendix C - Glass transition and melting properties of PLA/CS blends.

Table C.1. Glass transition and melting properties of PLA/CS blends.

Sample name	Glass transition		Melting	
	Tg (°C)	ΔCp	Tm (°C)	ΔHm (J/g)
PLA	40.56±0.04bc	0.36±0.15ab	162.81±0.24ab	30.18±0.84ab
PLA/1%NCC	41.39±0.65abc	0.48±0.05a	164.75±1.03a	32.48±0.16a
80%PLA/20%CS	43.67±0.54ab	0.23±0.07ab	160.99±1.39ab	25.89±0.33cd
80%PLA/20%CS/1%NCC	41.84±0.05b	0.42±0.07a	162.87±0.37ab	28.72±1.62bc
80%PLA/20%CS/1%NCC/4%MDI	39.58±0.60c	0.47±0.00a	163.6±1.10ab	19.76±0.83e
60%PLA/40%CS	44.61±1.61a	0.29±0.13ab	161.88±0.37ab	25.13±0.15d
60%PLA/40%CS/1%NCC	43.70±0.91ab	0.26±0.02ab	161.15±0.25ab	23.68±0.43d
60%PLA/40%CS/1%NCC/4%MDI	42.65±1.58ab	0.08±±0.05b	160.62±0.3ab	15.73±0.18f

Mean± standard deviation of each analysis. Means with the same letter in the same column are not significantly different (P<0.05). Comparisons are made within the same column, n=2 for all treatments.