

DEVELOPMENT AND CHARACTERIZATION OF TRAYS MADE OF POLYLACTIC
ACID/ORANGE PEEL COMPOSITE BY DIRECT BLENDING AND MASTERBATCH
PROCESSES FOR FOOD PACKAGING APPLICATIONS

By

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ABSTRACT

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Oranges are a very high production crop that produce a significant amount of waste after juicing. Value can be added to this waste if it can be reused as filler to produce packaging. However, thermoformed trays, which are broadly used in food packaging, have not yet been produced using agricultural waste. The aim of the first part of the study was to develop and investigate the properties of trays containing orange peel powder (OPP) using industrial thermoforming processing. The processing conditions necessities for PLA/OPP tray production were determined and under these conditions, up to 30 wt% OPP was successfully added to PLA for PLA/OPP tray production. Thus, the first part of the study shows that OPP up to 30 wt% can be used for commercial production of thermoformed trays, without compromising most of the properties compared to neat PLA trays, which would reduce agricultural and plastic waste.

Masterbatch process (MB), which improves the performance and properties of the packaging materials, has not been evaluated yet on agricultural waste. The second part of the study was aimed at investigating the effect of masterbatch by developing and comparing (1) trays with increasing amount of OPP produced by MB and (2) trays with the same amount of OPP produced by MB and direct blending. Trays produced using MB had better distribution of OPP that improved processability, which allowed for 5% more OPP (35 wt%) to be used as plastic filler. Therefore, this study shows that the use of MB increased the amount of waste that can be added to the polymer matrix during tray production and improved the properties of the trays compared to direct blending.

Dedicated to my parents, Mr. Pravin Ankush Sawant and Mrs. Manjiri Pravin Sawant

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Agricultural waste is the waste generated during the production of food products and related final goods using agricultural operations (Nagendran, 2011). Oranges, which are mainly used for juice processing, have a global production volume of 46.06 million metric tons (www.statista.com) which has resulted in lot of attention being given to the waste obtained from oranges. The juicing process results in 50-70% of waste generated in the form of peels, segment membranes, pith residues and seeds (Mahato, Sharma, Sinha, & Cho, 2018) (Zema, et al., 2018). Out of the total waste generated, peels contribute to around 40-55% (Sharma & Tripathi, 2008). Value can be added to orange peels from juicing if these are used to produce filler for packaging to improve the properties of a polymer matrix or to simply reduce the amount of polymer. Thus, this waste has been investigated in composite production using non-renewable plastics like low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE) (Banisadr & Asempour, 2012)(Iyer, Zhang, & Torkelson, 2016) (Fehlberg, Lee, Matuana & Almenar, 2020) (Mckay, Sawant, Fehlberg, & Almenar, 2021) (Aigbodion, Atuanya, Igogori, & Ihom, 2013) and renewable plastic like polylactic acid (PLA) (Quiles-Carrillo, Montanes, Lagaron, Balart, & Torres-Ginner, 2018).

PLA has gained enormous attention as a substitute for conventional plastics because it is a bio-based polymer that is biodegradable, compostable, and recyclable. In addition, it has a transparent and glossy finish, heat seal capacity, high tensile strength and modulus of elasticity, decent oxygen barrier, and excellent flavor and aroma barrier. (Almenar & Auras, 2010) (Koutsimanis, Harte, & Almenar, 2015) (Gonzalez-Buesa, et al., 2014) (Perego & Cella, 2010)

(Mallegni, Phuong, Coltelli, Cinelli, & Lazzeri, 2018) (Auras, Harte & Selke, 2004). All the above properties make PLA more attractive than other plastics for production of packaging formats made of composites where agricultural waste is converted into a value-added product. Thus, different types of agricultural waste like cocoa pod husk, peanut shell, argan nut shells, groundnut shells, chestnut shell, olive solid waste, and coconut shell have been used as fillers for PLA to examine the properties of the composites (Sanyang, Sapuan, & Haron, 2017) (Yamoum & Magaraphan, 2015) (Laaziz, et al., 2017) (Olajide, Yaro, Asuke, & Aponbiede, 2017), (Barczewski, Matykiewicz, Krygier, Andrzejewski, & Skorczewska, 2017) (Khemakhem, Lamnawar, Maazouz, & Jaziri, 2016) (Chun, Husseinsyah, & Osman, 2013). A much more significant agricultural waste like orange peel has been mixed with PLA in the form of extract after its freeze-drying, flour or encapsulation into cyclodextrins and pectin in amounts up to 2% (Marinoni, et al., 2018) (Bassani, et al., 2019) (Quiles-Carrillo, Montanes, Lagaron, Balart, & Torres-Ginner, 2018). In addition, there is a patent (Yang et al., 2011) that discloses a degradable packaging material prepared by drying and crushing orange peel dreg particles prior to mixing the particles with an adhesive and injecting the mixture into a forming mold for hot-forming processing (wording extracted from patent). The properties (e.g., barrier, mechanical) of the material are not specified anywhere, which makes hard to evaluate the performance and possible applications of the molded product.

Researchers working with addition of fillers to PLA have been exploring the effect of masterbatch process on the resultant composites (Joo, Auras, & Almenar, 2011). Masterbatch is a process used to improve properties of polymer blends and have been used with different types of polymers like PLA. Despite the improvement of the properties of PLA-based blends with masterbatches, there is no study in the literature that investigates the impact of a masterbatch on the properties of biocomposites made up of PLA and agrowaste. In fact, the authors have not been

able to find any studies investigating the use of a masterbatch in biocomposite formation with agrowaste for other biodegradable polymers or non-biodegradable polymers.

The above studies on biocomposites made of PLA and agricultural waste cover the development of films using solution casting (Sanyang, Sapuan, & Haron, 2017) and of rigid formats using twin-screw extrusion followed by injection molding (Barczewski, Matykiewicz, Krygier, Andrzejewski, & Skorczewska, 2017) (Olajide, Yaro, Asuke, & Aponbiede, 2017) (Laaziz, et al., 2017) (Yamoum & Magaraphan, 2015) (Quiles-Carrillo, Montanes, Lagaron, Balart, & Torres-Ginner, 2018) or mixing followed by compression molding (Chun, Hussein, & Osman, 2013); Yang et al., 2011). To the best of the authors' knowledge, there is no information in the literature about the development and properties of trays made of agricultural waste composites using thermoforming and how these compare with trays made of neat polymer even though thermoforming is broadly used to produce packaging products for the food, medical, and general retail industries. Thermoforming is a manufacturing process used in the plastic packaging industry for shaping thermoplastic sheets and films into packaging products like trays, clamshells, and cups (McCool & Martin, 2011). In 2018, the global market size for thermoformed plastics was valued at 11.69 billion USD and is expected to have a compound annual growth rate of 4.9 % from 2019 to 2025 (www.grandviewresearch.com).

1.2 Objectives

This study has been divided into two parts 1) Developing food packaging trays using industrial thermoforming processing and incorporating different amounts of orange peel into polylactic acid matrix 2) studying the effect of Masterbatch process on the performance of trays made of a mixture of polylactic acid and orange peel (agricultural waste).

The main aim of the first part was to develop trays made of PLA/orange peel powder (OPP) composites using industrial thermoforming equipment. The following sub-objectives were proposed for the study:

1. determine the maximum amount of OPP that can be used as filler to produce thermoformed PLA/OPP trays
2. evaluate the effect of OPP loading on the properties of the thermoformed PLA trays

The main aim of the second part of the study was to develop trays made up of PLA and OPP and to increase the amount of OPP content using a masterbatch and the same processing technology used to produce trays without the masterbatch. The following sub-objectives were proposed for the study:

1. to characterize the trays with increasing amount of OPP to determine improvement in mechanical, thermal, optical, barrier, and physical properties
2. to compare the properties of trays developed using masterbatch and trays developed using without masterbatch (direct blending)

The results obtained from this study will be useful for the sector of the rigid packaging industry with interest in biodegradable and/or compostable packaging and circular economy.

1.3 Hypothesis

The first part of this study is planned to test the hypothesis that OPP can be added as a filler to produce trays using industrial thermoforming equipment. The hypothesis that the addition of OPP will improve the color, barrier, and mechanical properties of the PLA/OPP composite trays compared to neat PLA trays will also be tested in this research.

For the second part of the study, it was hypothesized that the use of a masterbatch can improve the properties of the developed biocomposite PLA/OPP at a same OPP loading and consequently, can allow for more agrowaste to be incorporated without compromising the properties of the biocomposite while maintaining the same processing conditions.

1.4 Structure of Thesis

The rationale of this research has been introduced in the first chapter of the thesis. The Chapter 2 is a literature review that gives a background about polylactic acid, its properties, processing techniques, and about the addition of agricultural waste to PLA and other polymers. Chapter 3 describes the experimental method and results and discussions of the first part of the study, which is focused only on developing trays made of PLA and OPP waste by direct blending process. Chapter 4 is about the experimental methods and results and discussions about the second part of the study, which were focused on using masterbatch to increase the amount of waste that can be added to the polymer matrix and improve properties. Chapter 5 is about the conclusion of the results obtained during this research and proposed future work.

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CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Introduction to Polylactic Acid

Polylactic acid or polylactide (PLA) is a biobased polymer that is biodegradable and made up of natural sources like plants (Pilla, Gong, O'Neill, Rowell, & Krzysik, 2008). It is a good alternative to petroleum-based polymers because it is a biopolymer and has many properties like tensile yield stress, % elongation at break and elastic modulus like other polymers like polyethylene terephthalate (PET), and polystyrene (PS) which are derived from non-renewable resources like oil and natural gas (Auras, Harte, Selke, & Hernandez, 2003). Thus biopolymers make us less dependent on fossil fuels, and also they are CO₂ neutral (Pilla, Gong, O'Neill, Rowell, & Krzysik, 2008). The properties that make PLA desirable for food packaging applications are reasonable strength, high stiffness, excellent flavor and aroma barrier, and good resistance to grease and oil (Karkhanis, Stark, Sabo, & Matuana, 2018).

As PLA is made from bio-based sources like corn, starch, and sugar, it is environmentally friendly, and it can biodegrade into water or soil and without harming the environment because of its non-toxic byproducts. PLA, when exposed to elevated temperatures, undergoes thermal degradation which can be leveraged for recycling of PLA (Tsukegi, Motoyama, & Shirai, 2007) (Fan & Nishida, 2003). But PLA has some disadvantages like its higher cost (avg. cost of 2.2 \$/1 lb.) than many of the traditional polymers like PP, LDPE, and HDPE (0.4-0.5 \$/1 lb.) (Hamad, Kaseem, Gun Ko, & Deri, 2014). Other disadvantages are poor toughness, slow degradation rate, hydrophobicity, and lack of reactive side-chain groups (Farah, Anderson, & Langer, 2016) (Rasal & Hirt, 2008). PLA is always terminated by the OH group, and because of that, it has an affinity to water due to polarity. Thus, it absorbs water, and it becomes difficult to

process, and that is why proper conditioning of PLA resins is always required before performing any tests or processing.

2.2 Synthesis of PLA

The main building block of PLA is lactic acid which can be produced from the fermentation of sugars occurring in renewable sources like corn starch or sugarcane (Garlotta, 2001; Mckeen, 2014). Lactic acid (2-hydroxy propionic acid) is a chiral molecule and thus exists as two optically active configurations, which are L- and D- Lactic acid (Savioli Lopes, Jardini, & Maciel Filho, 2012). Lactic acid is majorly produced by bacterial fermentation of carbohydrates (Hartmann, 1998). Other method to produce lactic acid is by chemical synthesis which include oxidation of propylene glycol, nitric acid oxidation of propylene and reaction of acetaldehyde, carbon monoxide, and water at elevated temperature and pressure (Datta, Tsai, Bonsignore, Moon, & Frank, 1995).

PLA is made from two types of monomers 1) lactic acid or 2) lactide (cyclic di-ester form). One of the methods used to produce PLA is by using metal catalysts for ring-opening polymerization of the lactide. It can also be produced from lactic acid by direct condensation in which there is removal of water due to which the polymerization takes place. It can be produced as an amorphous material as well as semi-crystalline and highly crystalline material.

2.3 Properties of PLA

2.3.1 Thermal Properties

The glass transition and melting temperature of PLA are around 55°C and 175 °C respectively, while the processing temperature is around 180 – 195 °C (Garlotta, 2001). PLA is rubbery above T_g and acts like glass below T_g which has the potential to creep until it is cooled to -45 °C below which it acts like a brittle polymer (Henton, Gruber, Lunt, & randall, 2005).

Compared to other thermoplastics, PLA has high T_g and low T_m (Lim, Auras, & Rubino, 2008). The T_g of PLA is a function of molecular weight and optical purity, as it has been proven that the T_g of PLA can increase based on the L-stereoisomer contents (Lim, Auras, & Rubino, 2008). The T_m of PLA also depends on its optical purity.

2.3.2 Mechanical Properties

The mechanical properties of PLA vary from soft to stiff types of materials according to the grades. But semi-crystalline PLA is preferred when high mechanical properties are required. The tensile modulus and flexural modulus of semi-crystalline PLA are approximately 3 GPa and 5 GPa, respectively, while the tensile strength is around 50 – 70 MPa and elongation at break is 4 % (Farah, Anderson, & Langer, 2016). The impact strength of PLA is low compared to other thermoplastics, and it increases with increase in crystallinity and molecular weight of the polymer (Auras, Harte, & Selke, 2004).

Table 2.1. Physical and mechanical properties of PLA 2003D

PHYSICAL PROPERTIES	
SPECIFIC GRAVITY	1.24
MFR, g/10 min (210°C, 2.16kg)	6
CLARITY	TRANSPARENT
MECHANICAL PROPERTIES	
Tensile Strength @ Break, psi (MPa)	7700
Tensile Yield Strength, psi (MPa)	8700
Tensile Modulus, kpsi (GPa)	500
Tensile Elongation, %	6.0
Notched Izod Impact, ft-lb/in (J/m)	0.3

2.3.3 Barrier Properties

The application of a polymer in food packaging is determined on the basis of its barrier properties as it shows the ability of the polymer to block the flow of gases like oxygen, water vapor and carbon dioxide. The barrier properties of PLA are dependent on crystallinity and are not much affected by the polymer branching or changes in L:D ratio (Dorgan, Lehermeier, & Mang.M., 2000). It has been reported by researchers that the oxygen and carbon dioxide permeability coefficients of PLA are comparable to PET, but lower than PS (Auras, Harte, Selke, & Hernandez, 2003).

Table 2.2. Comparison of properties of PLA with petroleum-based polymers (Auras, Harte, Selke, & Hernandez, 2003) (Cygan, 2009) (Yam, 2009)(Almenar & Auras, 2010)

Properties	PLA	PP	PET	PS
Density (g/cc)	1.24	0.9	1.33	1.05
Tensile Strength at Break (MPa)	53.09	31.03	54.47	44.82
% Elongation	6	120	120	7
Tensile Modulus (MPa)	3447	896	2758	2896
T _g (°C)	55	-10	75	105
Oxygen permeability at 25 °C, 70 % RH (10 ⁻¹⁷ kg.m/(m ² .s.Pa)	0.121	498	0.0188	27
Water vapor permeability at 23 °C (10 ⁻¹³ kg.m/(m ² .s.Pa)	360	225	110	670
Carbon dioxide permeability at 25 °C, 0 % RH (10 ⁻¹⁷ kg.m/(m ² .s.Pa)	2.77	1080	0.173	15.5

2.4 Processing Technologies of PLA

PLA resins are converted into films, sheets, and trays by melt processing. PLA resins are melted by heating them above their glass transition temperatures and then processed into different shapes by different methods like compression molding, thermoforming, injection molding, extrusion, etc. Thermoforming, along with other procedures, are discussed in this section.

2.4.1 Drying

Polyesters are water-sensitive and can absorb moisture from the atmosphere which can affect their processing. As the PLA is also a polyester, it should be dried to avoid hydrolysis (reduction in molecular weight) which can affect the physical properties of PLA (Lim, Auras, & Rubino, 2008). According to Natureworks LLC, PLA should be dried to below 250 ppm moisture content. PLA can be dried using a temperature range of 80-100 °C, with drying time dependent on the temperature used (Lim, Auras, & Rubino, 2008). According to Henton et al., if amorphous PLA is exposed to 60 °C and 80% RH, the molecular weight of PLA can be reduced dramatically (Henton, Gruber, Lunt, & Randall, 2005). Thus, PLA resins can be dried in a vacuum oven with a temperature below its T_g i.e., around 55°C and the vacuum pressure of 20 for 24 hours to sufficiently dry the polymers.

2.4.2 Extrusion

Extrusion is the most used and important method used for melt processing of PLA as the extruder can be connected to different machine systems like blow molding, injection molding, film blowing etc. to convert the PLA melt into sheets, films, or bottles (Lim, Auras, & Rubino, 2008). The conventional screws used to process PLA and other thermoplastics consist of three sections: 1) feeding section where the polymer pellets are fed to the extruder and those pellets are conveyed to the screw of the extruder; 2) transition section designed with gradually decreasing

screw diameter which can compress the pellets enhancing their contact with the extruder's barrel; 3) metering section which has a shallow and constant flight depth acting as a pump to get the required amount of melted polymer (Lim, Cink, & Vanyo, 2010). The shear and residence time of the polymer melt depends on the L/D ratio which is the ratio of length of the screw to its diameter. Screws having large L/D ratio provide better mixing, greater shear heating and longer melt residence time inside the extruder (Lim, Cink, & Vanyo, 2010).

PLA pellets are fed through the hopper which is near the barrel, while the electric or hydraulic powered screw rotates and transports the pellets to the opposite side of the barrel. The temperature of the heater is set at 200-210 °C which is enough to melt all the crystalline phases of PLA and to obtain an optimal melt viscosity (Lim, Cink, & Vanyo, 2010). Higher temperatures can lead to thermal degradation of PLA, resulting in lactide monomers and by-products.

2.4.3. Compression Molding

Compression molding is one of the oldest processing techniques used for plastics and consists of heating the polymer pellets under pressure in a closed mold cavity. The pellets melt and cure because of a chemical reaction caused due to cross-linking of polymer chains (Tatara, 2017). Because of the pressure, the plastic pellets liquify and flow, and take the shape of the cavity, which hardens to form a flat sheet or the product of the desired shape after cooled off (Tatara, 2017). It is suitable to produce different types of consumers, commercial and industrial products like from small to big automobile body parts (Tatara, 2017).

2.4.4 Thermoforming

Containers without any complicated features are commonly formed using thermoforming process, and PLA can be thermoformed into containers of different shapes like single-use food trays, blister packaging, lids, disposable cups, etc. (Lim, Cink, & Vanyo, 2010).

The thermoforming process consists of heating PLA sheet to the temperature above its T_g which is enough to soften the PLA and to prevent it from drooping. This heated PLA sheet is then, mechanically, pneumatically, or hydraulically pressed against the mold, allowed to cool before removing it from the mold, and the thermoformed area is trimmed off to form the final parts (Lim, Auras, & Rubino, 2008). Vacuum or compressed air can be used to thermoform PLA, while depending on the design of the part, pre-stretching or plug-assist stretching can be used (Lim, Auras, & Rubino, 2008).

PLA sheets can be heated during thermoforming by infrared radiation (IR) to a wavelength of 3.2-3.7 μm (Selke, Cutler, & Hernandez, 2004) or using convection or conductive heating to the temperature range of 80-110 $^{\circ}\text{C}$ (Natureworks LLC, 2005) (Bosiers & Engelmann, 2003). Though PLA has lower thermoforming temperatures than other conventional thermoformed plastics like PET and PS, the aluminum molds, ovens, trimming tools designed for PET and PS can be used for forming PLA containers (Lim, Cink, & Vanyo, 2010).

Thermoforming of PLA can lead to certain issues. The toughness of PLA containers depends on the orientation of polymer chains, while the thermoforming behavior of PLA can be affected by the molecular weight of PLA (Lim, Auras, & Rubino, 2008). The regions of PLA sheets that are drawn more are less brittle compared to regions like trims which are subjected to minimal orientation. Researchers have been working on different techniques to solve these issues of thermoforming. Aritake (Europe Patent No. EP1577356A1, 2005) has prepared a composition of PLA with specific amounts of D- and L- isomers that showed good thermoforming characteristics. Researchers have also worked on a technique to induce crystallinity which corresponds to melting enthalpy of approx. 15 J/g by introducing heat to PLA sheet before thermoforming (U.S. Patent No. 2008/0258357A1, 2008).

2.4.5. Other Processing Technologies

2.4.5.1 Cast Film Extrusion

Cast Film Extrusion is a process in which the melted PLA is forced through a flat die, and the film exiting from the die is quenched when it comes in contact with the polished chrome rollers which are cooled off using circulating water (Lim, Auras, & Rubino, 2008). To achieve the desired thickness, the PLA film coming out of the die is stretched in the machine direction between the chill rolls and the die (Al-Robaidi, 2003). The die gap is usually set at 10% or 25-50 μm greater than the targeted thickness of the sheet (Natureworks LLC, 2005). Researchers who have worked on producing PLA films or sheets using cast film extrusion have used temperatures of 160, 180, and 175 °C for the feeding zone, the barrel region and the die region, respectively (Ljungberg, Andersson, & Wesslen, 2003) (US Patent No. 5,484,881, 1996).

One of the main issues with cast film extrusion is necking of the films which results in the final width being smaller than the initial width and this takes place when the film exits the die and touches the chill rolls. The low melt strength of PLA is the reason behind necking and many researchers have worked on adding melt strength enhancers to PLA to avoid necking (25-30) (Mallet, Lamnawar, & and Maazouz, 2016) (Pilla, Kim, Aeur, Gong, & Park, 2009) (Tuominen, Kylma, & Seppala, 2002). PLA has high modulus and good optical properties but has low elongation, burst, and tear strengths (Lim, Auras, & Rubino, 2008). To overcome these drawbacks, PLA can be coextruded with polymers like glycerol fatty acid esters and polyhydroxyalkanoate (PHA) (US Patent No. 7,144,634, 2006) (US Patent No. 6,808,795, 2004).

2.4.5.2. Extrusion Blown Film

The extrusion blown film process consists of molten PLA extruded through an annular die to form a tube that is inflated by blowing air into a thin tubular bubble and cooled off.

The inflated tube is flattened using the nip rolls and winded up by the winder (Lim, Cink, & Vanyo, 2010). Films of different thicknesses and degrees of orientation can be obtained by varying the air pressure, winder speed, screw speed and blow-up ratio (BUR) (Lim, Auras, & Rubino, 2008). Blow-up-ratio is the ratio of the diameter of the bubble to the diameter of the die and researchers have used BUR of 2:1-4:1 while setting the temperature of the die at 190-200 °C for extrusion blown films of PLA (US Patent No. 6,559,244B1, 2003) (US Patent No. 0045940A1, 2006).

The issue with extrusion blowing of PLA is its low melt strength which makes it difficult to form a stable bubble. Therefore, additives like viscosity enhancers are added to PLA while extrusion blown film process to protect it from degradation or to overcome the loss of molecular weight (Lim, Auras, & Rubino, 2008). Commercially available coupling agents made of a copolymer of methyl methacrylate, styrene, and glycidyl methacrylate can be used to increase its melt strength (US Patent No. 0045940A1, 2006). Researchers have also worked to enhance the melt strength of PLA to solve these issues (US Patent No. 6,559,244B1, 2003).

2.4.5.3. Injection Molding

Injection molding is one of the most used processes for producing thermoplastic articles which have complex shapes and required high precision. Injection molding machines consist of an extruder to produce the polymer melt, but it is designed in such a way that the screw can move forward and backward inside the barrel to generate the injection pressure needed to deliver the molten polymer to the mold cavities (Lim, Auras, & Rubino, 2008). Though the reciprocating screw extruders are most commonly used for injection molding of PLA, the two-stage systems which have a shooting pot and extruder, have also been used for injection molding of PLA. The two-stage injection molding system has a shorter cycle time, more consistent shot size and melt quality, and small screw motor drive (Rees, 1995). Polymers having low viscosity

are preferred for injection molding because those polymers can flow easily and fill the molds (Subramanian, 2011). As PLA has low melt strength, it is better suited for injection blow molding compared to extrusion blow molding.

Injection molding process is subdivided into two types which are injection blow molding and injection stretch blow molding.

2.4.5.3.1. Injection Blow Molding

In injection blow molding, a preform of polymer melt is produced which can be blown immediately or at later stages by reheating it. During the blowing stage, the air is blown in the preform after the mold cavity closes around it. Due to the air, the preform is stretched in the radial direction before taking the shape of the mold cavity which is allowed to cool and ejected from the mold. This process is usually used to produce containers with hollow shapes such as bottles. Bottles produced using injection blow molding have higher quality and require less trimming compared to bottles produced using the extrusion blow molding process. This process can be used to produce articles from plastics that have low melt strength.

2.4.5.3.2. Injection Stretch Blow Molding

The difference between injection blow molding and injection stretch blow molding is the additional stretching step. The preform of melt polymer produced in this process is stretched vertically using a plug along with being blown by the air in the radial direction. This orients the final product in both machine and cross directions which results in a better barrier and mechanical properties (Subramanian, 2011).

2.4.5.4. Foaming

PLA has competitive material and processing costs along with good mechanical properties which makes it an alternative option to polystyrene foams which are petroleum-based.

A blowing agent is introduced in the PLA matrix to start the foaming process while inducing the nucleation of bubbles, the pressure is decreased, or the temperature of the process is increased. To stabilize the bubbles, the foam cells are vitrified below the T_g (Lim, Auras, & Rubino, 2008). The low melt strength of PLA results in cell coalescence which affects the cell morphology of the foams and also causes issues to manufacturing PLA foams with low-density (Matuana & Diaz, 2013)

To solve these issues, researchers have worked on adding chain extenders to PLA to avoid cell coalescence, while reducing the foam density and increasing mechanical properties at the same time (Pilla, Kim, Aeur, Gong, & Park, 2009) (Di, Iannace, Di Maio, & Nicolais, 2005). Due to the toxic nature of chain extenders, researchers have also developed a thermodynamic method to increase the melt strength of PLA and control the cell morphology of foams (Matuana & Diaz, 2010)

2.5 Addition of Fillers To PLA

The drawbacks of plastics can be reduced by using proper filler materials. Fillers are materials used to improve the properties of polymers. They can also be used as an alternative to binders to reduce production costs. Some examples of fillers are cellulose nanocrystals, calcium carbonate, talc, fibers, etc. (Dhar, Tarafder, Kumar, & Katiyar, 2015) (Qin, et al., 2014) (Murariu & Dubois, 2016) (Kim, Park, Choi, & Yoon, 2008). These filler materials can interact with the polymer matrix to form composites which can have desirable properties like increase in tensile strength, modulus, barrier properties, etc. (Kim, Park, Choi, & Yoon, 2008) (Qin, et al., 2014)(Dhar, Tarafder, Kumar, & Katiyar, 2015)

There are many types of fillers that are obtained from agricultural waste and can be used to improve the properties of PLA or to reduce the use of polymers. Some of the examples of

agricultural waste used as fillers for PLA are nutshells, coconut shell, cocoa pod husk, peanut shell, olive solid waste, chestnut shells, etc. (Sutivisedsak, et al., 2012)(Chun, Husseinsyah, & Osman, 2013) (Sanyang, Sapuan, & Haron, 2017)(Yamoum & Magaraphan, 2015)(Khemakhem, Lamnawar, Maazouz, & Jaziri, 2016) (Barxzewski, Matykiewicz, krygier, Andrzejewski, & Skorczewska, 2018).

2.6 Orange Peels and Its Waste Generation

Orange is one of the most produced crops in the world and is mostly used for juicing (Banisadr & Asempour, 2012). After juicing, a lot of waste is generated, and out of the total waste, the peels contribute to 40-55% (Sharma & Tripathi, 2008). Though many countries use the orange peels obtained as a waste to produce by-products like flavonides, alcohol, and pectin, most of the waste peels are disposed of without any applications or converted to cattle fodder (Banisadr & Asempour, 2012). Orange peel waste consists of moisture (40.7%), pectin (7.0%), lignin (6.4%), ash (7.39%), crude fiber (7.8%), total sugar (14.08%) and fats (1.85%) (Ahmed, et al., 2016). The minor compounds present in orange peels are essential oils and flavonides, which can be extracted with the help of organic solvents (Banisadr & Asempour, 2012).

2.7 Research on Orange Peel Waste

Due to its large waste generation and the contents present in it, researchers have started focusing on incorporating orange peels into the polymer matrix. There has been work done on adding orange peels extract as a filler for PLA. The extracts obtained from orange peels was blended with PLA to test the migration from it and to test the release of orange extract compounds. (Marinoni, et al., 2018). Orange peel has also been added in the form of flour or by encapsulation into cyclodextrins and pectins (Bassani, et al., 2019) (Quiles-Carrillo, Montanes, Lagaron, Balart, & Torres-Ginner, 2018) and there has been a patent to use crushed orange peel particles to produce

a degradable packaging material (Yang et al., 2011) This waste has also been investigated in composite production using conventional plastics like low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and polyvinyl alcohol (PVOH) (Banisadr & Asempour, 2012) (Iyer, Zhang, & Torkelson, 2016) (Fehlberg, Lee, Matuana & Almenar, 2020) (Mckay, Sawant, Fehlberg, & Almenar, 2021)

2.8 Masterbatch Process

A masterbatch is a plastic formulation containing a high concentration of additives such as fillers, colorants, light stabilizers, antistats, etc., that mixed with the net plastic improves the performance and appearance of the final product (Becker, 2016). While most of the work done with masterbatches has focused on non-biodegradable plastics, including polypropylene (Ahmed, Shamey, Christie, & Mather, 2006), poly(ethylene terephthalate) (Kim, Seo, Hong, & Kim, 1999), and high-density polyethylene (Li & Chen, 2007), in the last decade, research on biodegradable and/or compostable plastics produced from renewable sources has increased significantly. Specifically, polylactic acid (PLA) has been widely investigated. Joo and coworkers observed that films containing 15% cyclodextrins obtained using a masterbatch had better mechanical, thermal, optical, and barrier properties than films containing 15% cyclodextrins obtained from a direct blend of the cyclodextrins with PLA (Joo, Auras, & Almenar, 2011). Byrne et al. (2009) reported an improvement in the impact resistance of PLA when the polymer was blended with four commercially available masterbatches at 1.5 wt.%. Yuan, Liu, & Ren (2009) blended PLA and poly(butylene adipate-co-butylene terephthalate) using masterbatches to improve compatibility between the polymers that resulted in foams with increased cell size and homogenized cell distribution.

2.9 Similar Research Work

Many researchers have worked on adding agricultural waste as byproducts. Egg shells in the form of powder have been used as agricultural waste filler to test the properties of PLA film and after mixing the eggshell powder with PLA it was found that there is an increase in tensile strength while the percent elongation was found to be decreased (Ashok, et al., 2014). There also have been tests performed on PLA in which nutshell of almonds, walnuts, and pistachio in the form of powder were used as a filler (Sutivisedsak, et al., 2012). Addition of nutshells caused a reduction in mechanical and thermal properties which indicated that those composites could be used where cost is a concern.

Lui and coworkers have worked on the effects of inorganic fillers like talc and hydroxyapatite (HA) on the thermal and mechanical properties of PLA. It was found that the blend of PLA with inorganic fillers led to a homogenous mixture, but the molecular weight of PLA was decreased. (Liu, Wang, Chow, Yang, & Mitchell, 2014). When talc was added, the crystallinity of PLA increased while it decreased when HA was added. The tensile strength of the material was dependent on the interfacial properties of PLA and filler and also on the crystallinity of PLA (Liu, Wang, Chow, Yang, & Mitchell, 2014). The toughness of PLA increased due to talc and HA (Liu, Wang, Chow, Yang, & Mitchell, 2014). Sanyang and coworkers have worked on adding cocoa pod husk as a filler to PLA and found that there was an increase in tensile strength of the composite with increasing percentage of CPH to 10 %, but it decreased with filler percentage of 15% (Sanyang, Sapuan, & Haron, 2017). Tensile modulus of the composite also increased from 1.5 MPa to 10.4 MPa, while the elongation at break was found to be reduced from 190 % to 90 % (Sanyang, Sapuan, & Haron, 2017). Effects of oilseed coproducts on PLA were studied by

Finkenstadt and coworkers, where the tensile strength of PLA was found to be decreasing as filler content increased from 0% to 45% by weight (Finkenstadt, Liu, Evangelista, & Willett, 2007).

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CHAPTER 3

DEVELOPMENT AND CHARACTERIZATION OF TRAYS MADE OF POLYLACTIC ACID/ORANGE PEEL COMPOSITE USING INDUSTRIAL THERMOFORMING PROCESS

3.1 Materials and Methods

3.1.1 Materials

PLA 2003D (Specific gravity = 1.24 g/dm³, MFR, g/10 min (210°C, 2.16kg) = 6) was provided by NatureWorks® LLC (Minnetonka, MN). Peels of Valencia orange from the orange juice industry were cut into halves, frozen and shipped to our installations from Bradenton, Florida. The orange peels were converted to a powder form before processing, as explained below.

3.1.2 Methods

3.1.2.1. Preparation of Trays

3.1.2.1.1. Preparation and Characterization of Orange Peel Powder

The orange peels from 3.1.1. were freeze-dried using a lyophilizer (Virtis Genesis 25XL Bulk Drying Lyophilizer SP Scientific, NY, USA) equipped with a Wizard 2.0 Controller (sample chamber pressure: 1333 Pascal; shelf temperature: 25 °C; condenser temperature: -80 °C) for 72 hours. The freeze-dried orange peels were inserted in a hammer mill (Whirlpool Corp, MI, USA) with a screen (040 1A) to be converted into powder. The particle size separation was done with a ROTAP Sieve shaker (W.S. Tyler Mentor, OH, USA) that had sieves of size 75, 105, 180, 250, 500 µm. Around 200 g of orange peel powder (OPP) was shaken for 10 mins per run. The size range of 0 – 180 microns was selected to be mixed with PLA. The selection of this particle size range is discussed under the results. The powder was put in a LDPE Ziploc® bag that was stored in a desiccator to keep away moisture. Before processing, the powder was dried in a vacuum

oven (VWR International, PA, USA) at 102 °C for 4 days. The moisture content of the powder ranged between 1-2 % when determined in an A&D MX-50 moisture analyzer (A&D Company Limited, Tokyo, Japan). The selection of these drying conditions is discussed under results.

The structure and size of dried OPP were characterized using scanning electron microscopy (SEM) (JEOL 6610LV, JEOL, MA, USA). OPP was placed on the sticky patch of the scanning electron microscope sample holder and coated with a layer of 3 nm of gold before the images were acquired using a voltage of 10 kV and a working distance of 19 mm at 500 magnification.

3.1.2.1.2. Mixing with OPP Filler

PLA pellets were conditioned by drying in an oven for 24 hours at 50°C. These pellets were mixed with the OPP from 3.1.2.1.1. using a Brabender mixer (C.W. Brabender® Instruments, Inc.). The OPP proportion was increased by 10 % till the resulting mixture was determined as a failure based on the lack of thermoforming capability of the material. The processing conditions for mixing were determined to be 3 minutes at a temperature of 180 °C and a screw speed of 50 RPM. The selection of these mixing conditions is discussed under results. The Brabender flow curves (graphs of Torque (N · m) vs. Time (mins)) of the PLA/OPP composites during mixing were obtained using Winmix software (C.W. Brabender® Instruments, Inc.). The resulting End Torque values (N · m) for all the samples were recorded to understand the effects of OPP loading and mixing time on the viscosity of the PLA/OPP composite during mixing. The resulting molten mixture was scrapped out. A control sample of 100 % PLA was also produced using the conditions described above. A minimum of four replicates per treatment (mixtures and plain PLA) were made.

3.1.2.1.3. Compression Molding

Each PLA/OPP mixture and plain PLA scrapped out was compression molded to make a flat sheet of the polymer after being placed in between two metal plates wrapped in aluminum foil and then inserted in a compression molding machine (PHI Heated Press, PHI, CA, USA). The temperature of the compression molding machine was set at 170 °C, and a pressure of 9.5 tons was applied. The mixture was preheated for 1 minute and after 3 minutes of compression, the mold was cooled with the help of water till the temperature reached around 65°C and then the sheet was removed from the mold. The selection of these compression conditions is discussed under results.

3.1.2.1.4. Thermoforming

Each of the PLA/OPP composite sheets obtained in 3.1.2.1.3. was inserted in a thermoforming machine (Ceratek, SencorpWhite, MA, USA) to form trays. The oven temperature was set at 260 °C and the heating time was set at 45 seconds. After the sheet softened in the oven, vacuum was used for thermoforming and the tray was formed. The forming time was set at 12 seconds. The selection of these thermoforming conditions is discussed under results.

3.1.2.2. Characterization of Trays

3.1.2.2.1. Physical Properties

3.1.2.2.1.1. Distribution and Dispersion

Distribution was evaluated by observing the way in which the OPP fills the space in the polymer matrix, while dispersion was evaluated by observing the size of the OPP agglomerates. The dispersion and distribution of the OPP in the polymer matrix were observed for four replications of each type of PLA/OPP tray using Scanning Electron Microscopy (JEOL 6610LV, JEOL, MA, USA). Individual pieces were placed horizontally for the top view image

and vertically for the cross-sectional image on the sticky patch of the microscope sample holder and then coated with 3 nm of gold. The images were acquired with an accelerating voltage of 10 kV and a working distance of 19 mm at 50x and 500x magnification for the top view image and at 350x magnification for the cross-sectional view image.

3.1.2.2.1.2. Thickness – Rim, Bottom, Walls, and Corners

The thicknesses of the PLA trays and PLA/OPP trays were evaluated using a digital micrometer (Testing Machines Inc., DE, USA). The thicknesses of different parts of the tray: rim, bottom, walls, and corners were measured. The density gradient method was used to confirm the thicknesses of the different trays, according to Auras (2004). Differences in thickness between the digital micrometer and the density gradient method (up to 32 μm) were used to calculate a conversion factor that was applied to the permeability results. Four replications of each type of tray type were evaluated. The results are expressed in micrometers (μm).

3.1.2.2.2. Mechanical Properties

3.1.2.2.2.1. Crush Resistance Test

The crush resistance test was performed on the PLA trays and PLA/OPP trays to compare the amount of force that the trays can hold without getting damaged. Each tray was fixed in a 5565P6021 Instron Universal Testing Machine (Instron Engineering Corporation, MA, USA) and then the force was applied on it using the compression mode of the machine with a compression speed of 2 mm/s (5 in/min). The compressive extension at maximum compressive load and the maximum compressive load applied on the PLA/OPP trays was obtained as per ASTM D642-00 (ASTM, 2000) and the load was recorded as maximum load before a yield of 10%. Four replications of each PLA/OPP tray type were analyzed. The results are expressed in Newton (N)

and millimeters (mm) for maximum compressive load and compressive extension at maximum compressive load, respectively.

3.1.2.2.3. Barrier Properties

3.1.2.2.3.1. Water Vapor Permeability

The water vapor permeability coefficient of the PLA trays and PLA/OPP trays was measured using a PERMATRAN-W Model 3/34 (MOCON Inc., MN, USA). The equipment's inlet and outlet of gases were connected to a metal block having two holes with help of copper wires. The trays were placed on the metal block in an inverted position so that the holes were covered. The trays were sealed to the metal block using epoxy glue. The trays were placed in room temperature conditions covered with a high barrier plastic bag to obtain 100% RH and 23 °C. The water vapor transmission rate (WVTR) was calculated by the equipment and was expressed as (g/package • day). The water vapor permeability coefficient of the package was calculated as follows:

$$WVP = \frac{WVTR \times L}{\Delta P}$$

where L is the thickness (m) of sheet thermoformed and ΔP is the partial water vapor pressure difference (Pa). Four replications of each type of tray were tested. The results are expressed in kg*m/package*sec*Pa.

3.1.2.2.3.2. Oxygen Permeability

The oxygen permeability coefficient of the PLA trays and PLA/OPP trays was measured using OX-Tran Model 2/22 (MOCON Inc., MN, USA). Samples were cut from the bottom parts of the trays and were then masked using a sticky aluminum foil to obtain testing areas of 0.495 cm². Four samples of each type of tray were tested at 23 °C and 0%RH. The oxygen transmission rate (OTR) was calculated by the equipment and was expressed as (g/m² • day). This

value was multiplied by the surface area of the tray to get the oxygen transmission rate of the whole package (g/package • day). The oxygen permeability coefficient of the package was calculated as follows:

$$OP = \frac{OTR \times L}{\Delta P}$$

where L is the thickness (m) of the sheet thermoformed and ΔP is the partial oxygen pressure difference (Pa). Four replications of each type of tray were tested. The results are expressed in kg*m/package*sec*Pa.

3.1.2.2.4. Thermal Properties

3.1.2.2.4.1. Crystalline Content and Thermal Properties

The effect of OPP loading on the crystallinity of the PLA was evaluated using differential scanning calorimetry (Q100 DSC), TA Instruments, DE, USA). Nitrogen gas, having a flow rate of 70 mL/min was used to purge the DSC cell. A sample weighing 5-10 mg was inserted in the DSC and heated to 220 °C at a constant rate of 10 °C/min, then cooled to 20 °C and again reheated with the same rate to 220 °C. The values of glass transition temperature (T_g), melting temperature (T_m), enthalpy of cold crystallization (ΔH_c), and enthalpy of melting (ΔH_m) were determined using the software Universal Analysis 2000, V4.5 (TA Instruments, DE, USA). The second run was used for analysis to avoid the effect of processing on PLA. Four replications of each type of tray were evaluated. The above values were used to calculate the percentage of crystallinity of each tray as follows:

$$\% \text{ crystallinity} = \frac{\Delta H_m - \Delta H_c}{(1 - \text{filler percentage}) * 93} \times 100$$

As the ΔH_m for PLA is 93 J/g. Results are expressed in °C and percentage.

3.1.2.2.4.2. Thermal Stability

The thermal stability of PLA/OPP trays and PLA trays was compared by performing thermogravimetric analysis (Q50 TGA TA Instruments, New Castle, DE) using a nitrogen flow of 40 in³/min. Samples weighing in the range of 6 and 10 mg were scanned from 25 °C to 600 °C at a constant heating rate of 10 °C/min. The results obtained were in the form of a thermogram depicting the change in residual weight (%) vs. temperature (°C).

3.1.2.2.5. Optical Properties

3.1.2.2.5.1. Color

The walls of the PLA trays and PLA/OPP trays that had thickness closest to the mean thickness of all the walls (16 walls due to the 4 replications per treatment) were selected. These were cut in half horizontally to measure the color values of the two halves using a spectrophotometer (labscan XE, Hunterlab Associates Laboratory, Inc., VA, USA). This was done due to a slight visual color difference found between the top and bottom parts of the walls. The CIELAB color coordinates L*, a* and b* of each tray were recorded by placing the selected half walls on a view plate area of 3.2 mm² and by using the EasyMatchQC software. Hue angle (h*) was calculated using a* and b*. a* was adjusted in case of negative values according to McLellan et al. (1995). Four replications of each type of tray were tested. The color results for each tray are presented as h* vs L*.

3.1.2.2.5.2. Light Transmission

The transmission of light through the PLA trays and PLA/OPP trays was compared by cutting and inserting a small part of the tray wall in a UV-Vis Spectrometer (Lambda 25 UV/VIS Spectrometer, PerkinElmer Instruments Inc., MA, USA) connected to a computer with UV Winlab application software. The samples were inserted in an aperture having a 1.0-mm slit

and the transmittance was measured with a scan speed of 480 nm per min in a spectral range of 200 to 800 nm. Four replications of each type of tray were tested. Light transmissions at selected wavelengths (280 nm, 320 nm, 590 nm, and 600 nm) that cover the UV and visible spectra are presented in %.

3.1.2.2.6. Fungal Resistance

The fungal resistance of the PLA/OPP trays was compared to that of the PLA trays using the method described in Pranata et al. (2019) with a slight modification. Four replications of each type of tray were tested.

3.1.2.2.7. Statistical Analysis

Statistical analysis was performed using MINITAB 19 (Statistical Software for PC/Windows, Minitab Inc., PA). Univariate analysis of variance (ANOVA) and Tukey's method at 0.05 level of significance were used to examine the effect of OPP loading on the aforementioned properties. The effects of tray part (walls, corners, bottoms, and trims) on thickness distribution after thermoforming and of top and bottom part of walls on the L* and h* values were also examined using Tukey's method at 0.05 level of significance.

3.2 Results & Discussion

3.2.1. PLA/OPP Tray Production

Air bubble formation was the problem to overcome during the production of the PLA/OPP trays. Below are the factors producing these bubbles and how the process was optimized until the air bubbles were eliminated entirely.

3.2.1.1. Effects of OPP Properties on PLA/OPP Tray Production

90 wt% PLA and 10 wt% non-dried OPP were mixed in the brabender for 10 minutes at 50 RPM and 180 °C. This mixture was compression molded for 3 minutes with a

pressure of 10 tones. The resulting sheets had big air bubbles where big chunks of OPP were present (Table 3.1). These sheets were not thermoformed. The bubbles were determined as a failure and attributed to the water vapor that came out from the chunks of OPP due to the combination of the pressure and heat applied during compression molding. It is known that OPP has some moisture (Fehlberg J. , Lee, Matuana, & Almenar, 2019). To decrease OPP moisture content, the powder was freeze-dried (till the value reached 0 mTorr). The drying decreased OPP moisture content from 6-7 % to 4.75 %. Parallely, bubble presence was also correlated with OPP particle size. The reduction of particle size by sorting the powder using sieves differing in size (105, 180, 250, 350 and 500 microns) showed that smaller particle sizes led to smaller chunks of OPP due to the better mixing of the agrowaste. There was no significant difference in number of air bubbles between powders in size ranges of 0-105 microns and of 105-180 microns.

Particle load was also noted to have an effect on bubble amount. This effect was determined when producing sheets having 10, 20, 30, and 40 wt.% of the freeze-dried 0-105-micrometer OPP using the processing conditions described in Table 3.1. These sheets were thermoformed into trays using a heating time of 15 – 25 seconds and a forming time of 120 seconds. The heating time was adjusted depending on the sagging of the sheet as sheet strength differed with OPP loading. The air bubbles decreased but were not eliminated. This showed the need for more drying to continue reducing the moisture content in the OPP. Thus, the OPP was dried in a vacuum oven at a temperature of 105 °C and vacuum pressure of 635 mmHg for different time periods to determine optimal drying time. OPP was not sufficiently dried (moisture content > 2 %) after 3 days, as air bubbles were still observed in the developed sheets. OPP dried for 4 days had moisture content ranging between 1-2 % like 7 days that lead to air bubble absence. So, 4 days of drying at the aforementioned conditions were set to get to the minimum moisture content

in OPP for processing. The combination of small particle size and vacuum drying led to a reduction in moisture content sufficient to eliminate bubbles when the appropriate processing conditions (3.2.1.2.) were used. The low moisture content also allowed for higher OPP loadings without any changes in the mixing conditions and tray appearance. Thus, the lower moisture content allowed more waste to replace PLA during tray production.

3.2.1.2. Effects of Processing Conditions on PLA/OPP Trays Production

As insufficient mixing was determined as another reason for air bubbles, processing parameters were also varied to observe any effects on the formation of air bubbles. Initially, different mixing times (15, 20, 25, 30 and 45 minutes) and blade speeds (60, 75 and 100 RPM) were assessed to find out the best mixing conditions using freeze-dried OPP (4.7% moisture) with particle size <105 micrometers. None of the combinations were completely able to remove the air bubbles (Table 3.1). We also found out that an increased mixing time resulted in the breaking of the polymer chains and consequently the loss of molecular weight as the mixture was observed to be less viscous (melted form). Thus, in order to reduce polymer chain breaking, OPP was dried using vacuum oven (1-2% moisture) and processed at lower blade speed (50 RPM) and less mixing time (3, 5 and 7 minutes). The end torque values for the aforementioned mixing times (Table 3.1.) showed that the mixture was more viscous as the end torque value was more. The more viscous mixture suggested less breakage of polymer chains. The highest-end torque values were obtained at 3 minutes as the viscosity decreases due to increasing mixing times and thus, this was the mixing time selected for tray production. The more viscous mixture caused the foils to tear during compression molding and consequently, a preheat time of 1 minute was used to soften the mixture prior to compression molding. This preheat time resulted in the compression molding temperature being reduced from 180 °C to 170 °C and compression pressure being reduced from 10 tones to 9.5

tones. The sheets obtained by using these processing conditions (vacuum oven drying, blade speed 50 RPM and mixing time of 3 minutes) were without any air bubbles and therefore, these sheets were thermoformed by heating at 260 °C for 1 minute and by using forming time of 12 seconds.

Based on the above, the reason for air bubble formation was a combination of the factors OPP particle size, OPP moisture content, OPP loading, and processing mixing time and speed. After the optimization of all these factors, sheets without any air bubbles were successfully developed, which resulted in trays with no holes and perfect mold shape. PLA/OPP sheets without air bubbles were produced with OPP loads up to 50 wt.% using the conditions presented in Table 3.1. For the 50 wt% OPP sheets, the compression pressure was increased to 12 tones as the sheet formed by 9.5 tones was very thick. Higher contents of OPP were not investigated since the PLA/OPP sheets with 35 wt%, 40 wt%, and 50 wt% OPP by weight could not take the form of the mold when using the aforementioned thermoforming conditions. Consequently, only PLA/OPP trays with 0, 10, 20, and 30 wt% OPP by weight were produced (Figure 3.1.) to investigate the effects of OPP loading on tray properties. Studies investigating the processing properties needed to thermoform above 30 wt% OPP by weight are planned in the future since they are out of the scope of this study.

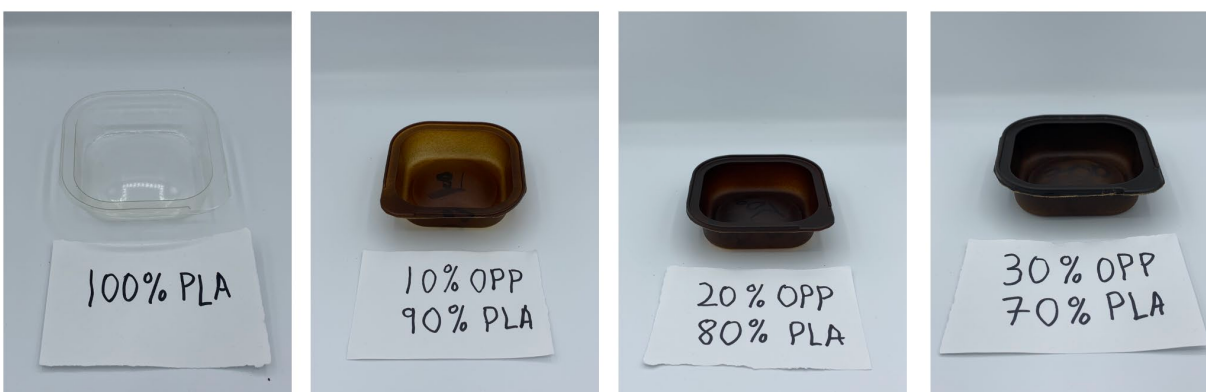


Figure 3.1. PLA/OPP trays with 0, 10, 20 and 30 wt% OPP by weight

Table 3.1. Factors conditioning air bubble amount during PLA/OPP tray production

OPP Factors			Processing conditions						Results			
Dryin g Type (Mois ture conte nt (%))	Parti cle size (μm)	OPP Amo unt (wt %)	Mixing (Brabender)		Compression* (Hydraulic press)		Thermoformin g (Thermoforme r)		Air bubb les	Hol es	Shape	End Torqu e value (N-m)
			Tim e (min s)	RPM	Pres sure (tone s)	Sheet Thickne ss (μm)	Heati ng Time (sec)	Formi ng Time (sec)				
None (6-7)	0- 500	10	10	50	10	600-700	15	120	Not thermoformed due to large air bubbles			Data not obtain ed
Freeze Dryin g (4.75)	0- 105	10	15	60					Yes	No	Good	
			20	75					Yes	No	Good	
			25	100					Yes	No	Good	
			30						Yes	No	Good	
			45						Yes	No	Good	
		20							Yes	No	Good	
		30							Yes	No	Good	
		40							Yes	No	Good	

Table 3.1. (cont'd)

Vacuum oven drying (1-2)	0-180	10	7	50	9.5	600-700	40	12	Few	No	Good	6.9
		10	5			600	60		No	No	Good	7.6
		20				600-620			No	No	Good	6.2
		30	7			700-750			No	No	Good, weak corner sometimes	4.3
		10	3			600-660			No	No	Good	9.0
		20				660-750			No	No	Good	8.3
		30				750			No	No	Good, Weak Corners sometimes	8.9
		40				800-850			No	No	Inconsistent	7.4
		50				850			No	No	Bad	10.6
						12						

*Compression time was 3 minutes for all the samples.

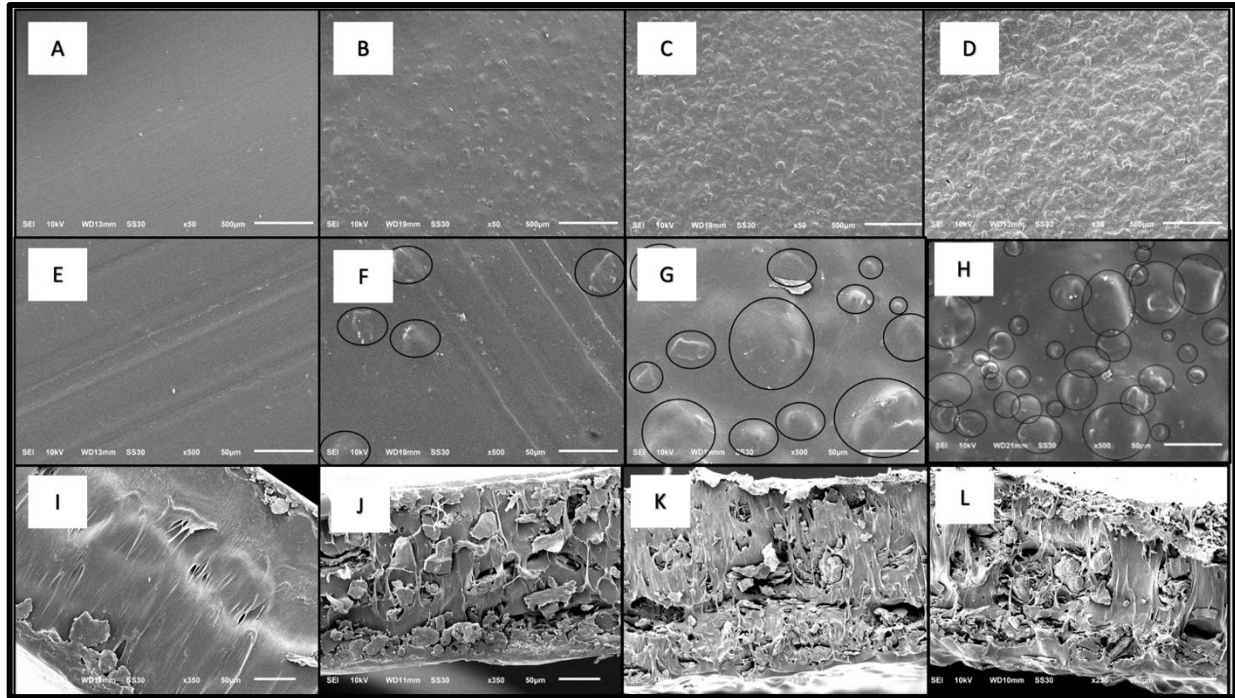
3.2.2. Tray Characterization

3.2.2.1. Physical Properties

3.2.2.1.1. Distribution and Dispersion

The distribution and dispersion of 10, 20 and 30 wt% OPP in the PLA trays are shown in Figure 3.2. A-L. Comparing the location of the OPP agglomerates and the amount of neat PLA that separates these in each composite surface (Figure 3.2.A-D), the increase in OPP loading resulted in a better distribution of OPP. Close-up areas of 253 μm x 189 μm of the composite surfaces (Figure 3.2.E-H) are shown to point out how the agglomerates (black circles) incremented in number and were more equally spaced apart as OPP loading increased. Figure 3.2. I-L, cross-sections of the composites, shows the dispersion of OPP inside the polymer matrix. PLA/OPP 0 wt% trays showed a uniform and smooth structure, while the PLA/OPP 10 wt% trays displayed OPP agglomerates in the range of 5 -66 μm (Appendix 2) that had an average size of 27 ± 15 μm (Table A1). Voids were present in between the polymer and the agglomerates. The PLA/OPP 20 wt% trays had more OPP agglomerates, and these had dimensions in the range of 6-64 μm (Appendix 2) and an average size of 23 ± 13 μm (Table A2). Thus, the increase in OPP content from 10 wt% to 20 wt% resulted in more OPP agglomerates (44 vs 79, respectively), but the size of agglomerates was not significantly different from each other ($P > 0.05$). There was an increase in the number of voids for these trays due to the increase in OPP agglomerates. The PLA/OPP 30 wt% trays had OPP agglomerates in the range of 9-73 μm (Appendix 2) with significantly larger agglomerates ($P < 0.05$) sizing of 36 ± 16 μm (Table A3). Increase in OPP content from 20 wt% to 30 wt% resulted in less OPP agglomerates (79 vs 30 respectively) but the size of agglomerates was significantly larger ($P < 0.05$) for the 30 wt% trays. These trays had larger voids compared to other trays because of the more agglomerates of larger size. The voids in

the polymer matrix indicate poor adhesion and interfacial bonding between PLA and OPP due to the difference in polarity between PLA (non-polar) and OPP (polar). Fehlberg et al. (2019) already reported poor adhesion between orange peel powder and LLDPE due to differences in polarity (Fehlberg, Lee, Matuana, & Almenar, 2019). Researchers working with PLA and other agricultural wastes, including peanut shell, coconut shell powder and argan nutshell to create injection molded and compression molded composites have observed similar poor adhesion and interfacial bonding between PLA and the agricultural waste (Yamoum & Magaraphan, 2015) (Chun, Husseinayah, & Osman, 2013) (Laaziz, et al., 2017).



Micrographs A-D and E-H show 50x and 500x magnification top views, respectively. Micrographs I-L show 350x magnification cross-sectional views. Black circles highlight the OPP agglomerates.

3.2.2.1.2. Thickness – Rim, Bottom, Walls, and Corners

Table 3.2. shows the thicknesses of PLA/OPP composite sheets and trays with 0, 10, 20 and 30 wt% OPP by weight. Sheets and all the tray parts except for the trim increased in thickness with the increase in OPP loading ($P < 0.05$; Table 3.2). This can be attributed to the increase in size of the agglomerates with the increase in OPP loading (section 3.2.2.1.1) that located between the polymer chains increased the resistance to the applied 9.5 tones of compression pressure during sheet forming. The trim thickness ($470 - 530 \mu\text{m}$) did not vary significantly ($P > 0.05$) although the sheet thicknesses did vary ($585 \mu\text{m}$ for 0 wt% while $750 \mu\text{m}$ for 30 wt%) with the increase in OPP loading because the flattening of the future trim section of the sheet was performed by the same part of the thermoformer (i.e., clamp frame).

For a same OPP loading, the different parts of the tray differed in thickness. The corner thicknesses for all the trays and the trim thicknesses only for the trays with 0 and 10 wt% OPP varied significantly ($P < 0.05$) compared to the thicknesses of bottoms and walls (Table 3.2). The corners were observed to be the thinnest ($228\text{-}289 \mu\text{m}$) and this happened because as a sheet is drawn deeper, there is more stretching and excessive thinning in the corners (Martin & Duncan, 2007). The difference between trim and bottom or wall was not observed for the 20 and 30 wt% OPP samples ($P > 0.05$) because as agglomeration increased (section 3.2.2.1.1.), the stretching of polymer chains was reduced, resulting in less thinning of walls and bottoms.

Table 3.2. Effects of OPP loading (wt%) on the thickness profile of PLA sheets and tray parts, agglomerate size, compression strength properties and permeability coefficients.

Properties			OPP content in PLA/OPP composite (wt%)			
			0	10	20	30
Thicknes s (μm)	Sheet		585 ± 44 ^a	650 ± 10 ^{ab}	697 ± 38 ^{bc}	750 ± 0 ^c
	Tray	Wall	355 ± 68 ^{aA}	434 ± 75 ^{abA}	457 ± 101 ^{bA}	502 ± 131 ^{bA}
		Corner	228 ± 24 ^{aB}	237 ± 27 ^{aB}	259 ± 64 ^{abB}	289 ± 65 ^{bB}
		Bottom	379 ± 48 ^{aA}	449 ± 24 ^{abAC}	479 ± 20 ^{bcA}	549 ± 72 ^{cA}
		Trim	530 ± 61 ^{aC}	523 ± 43 ^{aC}	470 ± 10 ^{aA}	510 ± 10 ^{aA}
Agglomerate Size (μm)			N/A	27 ± 15 ^a	23 ± 13 ^a	36 ± 17 ^b
Compres sion Strength	Compressive Extension at Maximum Compressive load (mm)		11.4 ± 1.0 ^a	10.7 ± 0.3 ^a	10.4 ± 0.3 ^a	11.2 ± 0.8 ^a
	Maximum Compressive Load (N)		1108 ± 427 ^a	965 ± 147 ^a	930 ± 142 ^a	1143 ± 195 ^a
Permeabi lity	Oxygen x E-15 (kg.m/package.s.Pa)		1.4 ± 0.1 ^a	1.3 ± 0.0 ^a	0.9 ± 0.1 ^b	1.8 ± 0.2 ^c
Coefficie nts	Water x E-16 (kg.m/package.s.Pa)		1.6 ± 0.3 ^a	1.6 ± 0.2 ^a	1.4 ± 0.1 ^a	1.6 ± 0.4 ^a

Different lowercase letters (a, b, and c) indicate significant differences ($P < 0.05$) among thicknesses, agglomerate size, compressive extension, max compressive load, oxygen permeability and water vapor permeability due to loading percentages of OPP. Different uppercase letters (A, B and C) indicate significant differences ($P < 0.05$) among thicknesses of different parts of a tray. N/A indicates not applicable.

3.2.2.2. Mechanical Properties

3.2.2.2.1 Crush Resistance Test

As shown in Table 3.2., the compressive extensions (10.4-11.4 mm) and the maximum compressive loads (930 – 1143 N) of the PLA/OPP trays with 0, 10, 20 and 30 wt% OPP by weight were not significantly different ($P > 0.05$) from each other. Therefore, 30 wt% OPP can be used to replace PLA without affecting tray resistance to load. The slightly higher-end torque values collected by the Brabender Plastograph, regarded as a formal viscometer (Lee & Purdon, 1969), for the neat PLA trays compared to the composite trays (10 vs. 9-8 Nm) indicate that the addition of up to 30 wt% OPP to PLA did not affect the viscosity of the composite enough to affect tray compression load and extension. The compression strength values reported for PLA trays in other studies (Auras, Singh, & Singh, 2005; Auras, Singh, & Singh, 2006) are not comparable with ours due to the differences in shape and dimensions between the trays. According to Auras, Singh, & Singh (2006), compression strength values of thermoformed plastic containers are a function of the design of the container and material properties.

3.2.2.3. Barrier Properties

3.2.2.3.1 Water Vapor Permeability

Table 3.2. shows the water vapor permeability (WVP) coefficients of PLA/OPP trays containing 0, 10, 20 and 30 wt% OPP. The WVP coefficient of the neat PLA tray, 1.6×10^{-16} kg.m/package.s.Pa, was lower than data reported for PLA pieces of trays and films, 2.0×10^{-14} to 1.1×10^{-15} kg.m/package.s.Pa (Auras, Singh, Singh, 2006; Awalgaonkar, Beaudry, and Almenar, 2020; Joo, Lewandowski, Auras, Harte and Almenar, 2011). This can be attributed to differences in thickness, tested surface area, PLA grade and processing parameters. The WVP coefficient of the neat PLA tray did not change with the addition of up to 30 wt% OPP ($p > 0.05$).

The voids present in the composite trays, which increased in size with the higher OPP loading (Figure 3.2J-L), did not alter the WVP coefficient of the trays because the OPP agglomerates also increased in size, and this allowed for more of the water to move freely through the voids to be absorbed. Other agrowaste can also absorb water when used as plastic fillers for PLA as demonstrated for peanut shell during composting studies (Yamoum & Magaraphan, 2015). The addition of β -cyclodextrin to PLA in amounts like the ones used in our study resulted in composites with poorer barrier to water vapor (Joo, Auras, & Almenar, 2011).

3.2.2.3.2. Oxygen Permeability

Table 3.2. shows the oxygen permeability (OP) coefficients of PLA/OPP trays with 0, 10, 20 and 30 wt% OPP. The OP coefficient of the neat PLA tray, 1.4×10^{-15} kg.m/package.s.Pa, was higher than those reported in the literature for PLA pieces from trays and films, 6.0×10^{-18} to 4.0×10^{-20} kg.m/package.s.Pa (Auras, Singh, Singh, 2006; Joo, Auras, & Almenar, 2011; Auras, Harte, & Selke, 2004; Joo, Lewandowski, Auras, Harte, & Almenar, 2011) due to differences in thickness, PLA grade, tested surface area and processing parameters. The addition of 20 wt% OPP to PLA improved the oxygen barrier of the trays while 10 wt% OPP had no effect and 30 wt% OPP caused barrier reduction. 20 wt% OPP loading produced more and smaller OPP agglomerates that worked better for the obstruction of the flow of the oxygen molecules through the polymer matrix (Figure 3.2.K). The change from 20 wt% to 30 wt% OPP increased the size of the agglomerates and consequently of the voids, as shown in Figure 3.2.L. The larger voids allowed the oxygen molecules to diffuse faster through the polymer matrix. Researchers working with PLA and cellulose nanocrystals (CNCs) observed similar results with improvement of oxygen barrier due to addition of 1% CNCs, but reduction if used 2% CNCs due to the agglomerations of CNC due to the difference in polarity of hydrophilic CNCs and hydrophobic PLA (Dhar, Tarafder,

Kumar, & Katiyar, 2015). Battegazzore et al. (2014) reported that the addition of silica powder from rice husk to PLA improved the oxygen barrier of the polymer while the use of commercial silica, which was larger in size compared to the powder, resulted in barrier reduction (Battegazzore, Bocchini, Alongi, & Frache, 2014).

3.2.2.4. Thermal Properties

3.2.2.4.1 Glass Transition Temperature, Melting Temperature and Crystalline Content

The glass transition temperature, melting temperature and crystalline content of PLA/OPP trays with 0, 10, 20 and 30 wt% OPP by weight are presented in Table 3.3. The composite trays had significantly lower ($P < 0.05$) T_g (56.71 – 58.12 °C) and T_m (145.53 – 147.95 °C) than the neat PLA trays (T_g of 61.18 °C and T_m of 149.12 °C). This can be attributed to the soluble compounds like sugars present in OPP that act as plasticizing agents (Kalajahi, Alizadeh, Hamishekhar, Almasi, & Asefi, 2021). Similarly, (Quiles-Carrillo, Montanes, Lagaron, Balart, & Torres-Ginner, 2018) reported a decrease in T_g of PLA due to the addition of orange peel flour. The T_g of the composite trays decreased significantly ($P < 0.05$) with the increase in OPP loading. In contrast, the T_m of the samples with 30 wt% OPP, 147.95 °C, was significantly higher than the T_m of samples with 10 wt% and 20 wt% OPP, 145.53-146.12 °C. Quilles-Carillo et al. (2018) did not find changes in either T_g or T_m in injected samples made of PLA compatibilized with orange peel flour when the flour increased in amount. The crystalline content of the PLA/OPP trays increased significantly ($P < 0.05$) from 3.68 % to 7.51 % as the amount of OPP increased to 20 wt% and then did not change for 30 wt% OPP. This suggested that OPP has a nucleating agent capacity which induced the crystallization process by providing additional nuclei, thus increasing the crystallinity of PLA. Yamoum & Magaraphan (2015) and (Barczewski, Matykiewicz, Krygier, Andrzejewski, & Skorczewska, 2017) reported an increase in the crystalline content of PLA caused

by the addition of peanut shell and chestnut shell, respectively. In contrast, Quilles-Carillo et al. (2018) reported a reduction in the crystallinity of injected PLA samples with the incorporation of orange peel flour.

Table 3.3. Effects of OPP loading (wt%) on the thermal properties, crystalline content, and light transmission of PLA trays.

Properties		OPP content in PLA/OPP composite (wt%)			
		0	10	20	30
Thermal Properties	T _g (°C)	61.18 ± 0.12 ^a	58.12 ± 0.54 ^b	56.71 ± 0.24 ^c	56.82 ± 0.24 ^c
	T _m (°C)	149.12 ± 0.29 ^a	146.12 ± 0.49 ^b	145.53 ± 0.40 ^b	147.95 ± 0.38 ^c
	Crystallinity (%)	3.68 ± 1.21 ^a	4.92 ± 0.75 ^{ab}	7.51 ± 0.30 ^c	6.25 ± 0.98 ^{bc}
Light Transmission (%)	280 nm	37.83 ± 3.56 ^a	-0.03 ± 0.00 ^b	-0.03 ± 0.00 ^b	-0.04 ± 0.00 ^b
	320 nm	62.19 ± 2.78 ^a	-0.05 ± 0.01 ^b	-0.06 ± 0.01 ^b	-0.05 ± 0.01 ^b
	590 nm	86.25 ± 0.52 ^a	1.37 ± 0.03 ^b	0.15 ± 0.02 ^c	0.01 ± 0.01 ^c
	600 nm	86.41 ± 0.50 ^a	1.50 ± 0.04 ^b	0.18 ± 0.02 ^c	0.01 ± 0.01 ^c

Different lowercase letters (a, b, and c) indicate significant differences ($P < 0.05$) among light transmission, T_g (glass transition temperatures), melting temperatures (T_m), and percentage of crystallinity caused by OPP loading.

3.2.2.4.2. Thermal Stability

Figure 3.3. displays the thermogravimetric curves of the bottoms of the PLA/OPP composite trays with 0, 10, 20 and 30 wt% OPP by weight. There was a loss in weight of 1 % at around 100 °C for the samples with OPP. This can be attributed to the loss of water remaining in the OPP after vacuum oven drying (section 3.1.2.1). There was a gradual weight loss of about 1-3 % for the composite trays for the next 100 °C. This has been attributed to decarboxylation and esterification reaction of OPP (Banisadr & Asempour, 2012). Similar results have been reported for LLDPE/OPP sheets (Fehlberg et al., 2019). In the temperature range 200 – 325 °C, the amount of material loss was proportional to the OPP present in the trays, which indicates the loss of OPP components. As the OPP loading increased, more material loss was observed at the decomposition temperature of hemicellulose (150 – 225 °C) and cellulose (260 – 360 °C) (Zapata, Balmaseda, Fregoso-Israel, & Torres-Garcia, 2009). Approx. 7% weight loss was observed for the neat PLA trays in this temperature range because PLA decomposes between 300 – 380 °C (Yamoum & Magaraphan, 2015) ; Ashok et al., 2014). In the temperature range of 360 – 475 °C, the weight loss was lower as the OPP content in the tray increased. The lower weight loss observed with the increase in OPP could be justified simply with the increase in char from the pyrolysis of the lignin of the OPP since the higher the amount of OPP in the tray the more char that would be produced. The char of orange peel has been shown as remaining % weight loss in the same temperature range during thermogravimetric analysis (Zapata, Balmaseda, Fregoso-Israel, & Torres-Garcia, 2009).

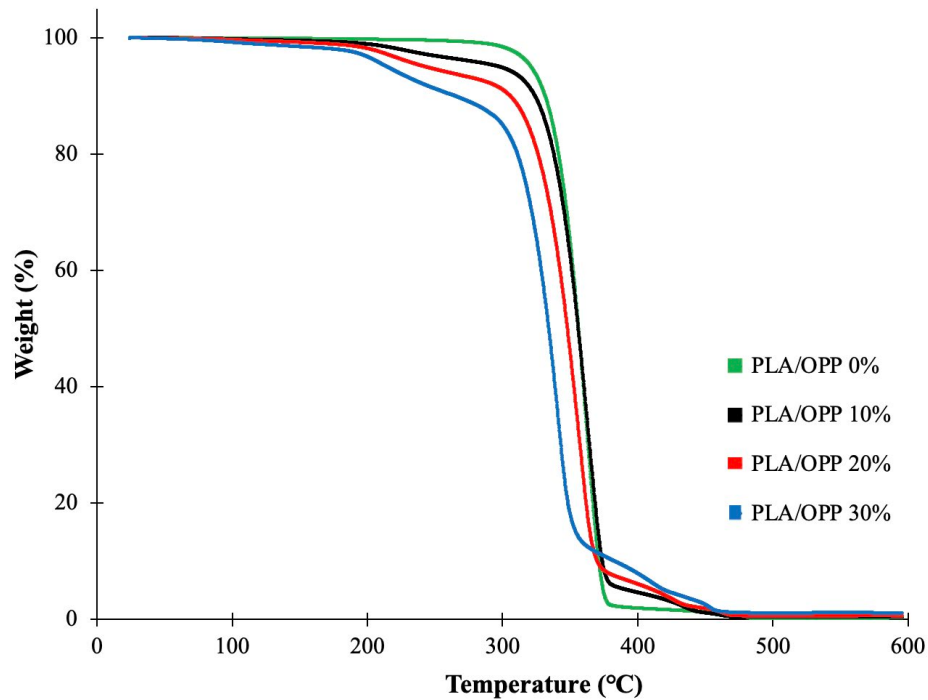


Figure 3.3. Thermogravimetric curves of PLA trays containing OPP loadings of 0, 10, 20, and 30 wt%.

3.2.2.5. Optical Properties

3.2.2.5.1. Color

There was no significant difference ($P > 0.05$) between the color values of the two halves of each wall for the PLA/OPP composite trays with 0, 10, 20 and 30 wt% OPP by weight (data not shown). Thus, the values from the two halves were mixed for data analysis (Figure 3.4). The neat PLA trays (PLA/OPP 0 wt%) were light (90.78) and greenish-yellow (94.23) in color in agreement with the literature (Joo et al., 2011; Pranata et al., 2019). The presence of OPP changed the color of the trays to yellowish-orange ($P < 0.05$; Figure 3.4.). This change in color was due to the carotenoids present in the zest of orange peels, which are yellow to orange in color (Chedea, Kefalas, & Socaciu, 2010). Similar results were reported by researchers who developed LLDPE/OPP composites (Fehlberg J. , Lee, Matuana, & Almenar, 2019) (Mckay, Sawant,

Fehlberg, & Almenar, 2021). As the amount of OPP increased from 10 wt% to 20 wt%, the trays were observed to be more orange in color (h^* changed from 46.5 to 35.1) ($P < 0.05$; Figure 3.5.), which is in agreement with the color change reported by Fehlberg et al. (2019) for LLDPE with the increase of OPP from 0.5 g and 1 g (Fehlberg J. , Lee, Matuana, & Almenar, 2019). However, the increase from 20 wt% to 30 wt% OPP resulted in less orange color trays (h^* changed from 35.1 to 49.7). This could be explained by larger OPP agglomerates in the PLA/OPP composite trays with 30 wt% OPP (section 3.2.2.1.1.) that resulted in some areas of the walls with less OPP and therefore, less orangish color.

The neat PLA trays (PLA/OPP 0 wt%) had a high L^* value (90.8) as reported in the literature (Joo et al., 2011; Pranata et al., 2019). This value decreased ($P < 0.05$; Figure 3.5) due to the presence of OPP. The higher the OPP loading, the darker the tray except for the composite trays with 30 wt% OPP that had L^* values higher (29.8) than those of trays with 10 wt% and 20 wt% OPP, which had L^* values of 22.5 and 21.2, respectively. This can be explained by less OPP in some areas of the walls because larger OPP agglomerates were present in the composite trays with 30 wt% OPP (section 3.2.2.1.1.) that resulted in some areas with less OPP. Addition of fillers other than OPP to PLA also changes PLA color and makes it darker as filler content increased (Joo et al., 2011)(Liu, Liang, Wang, Qin, & Zhang, 2018).

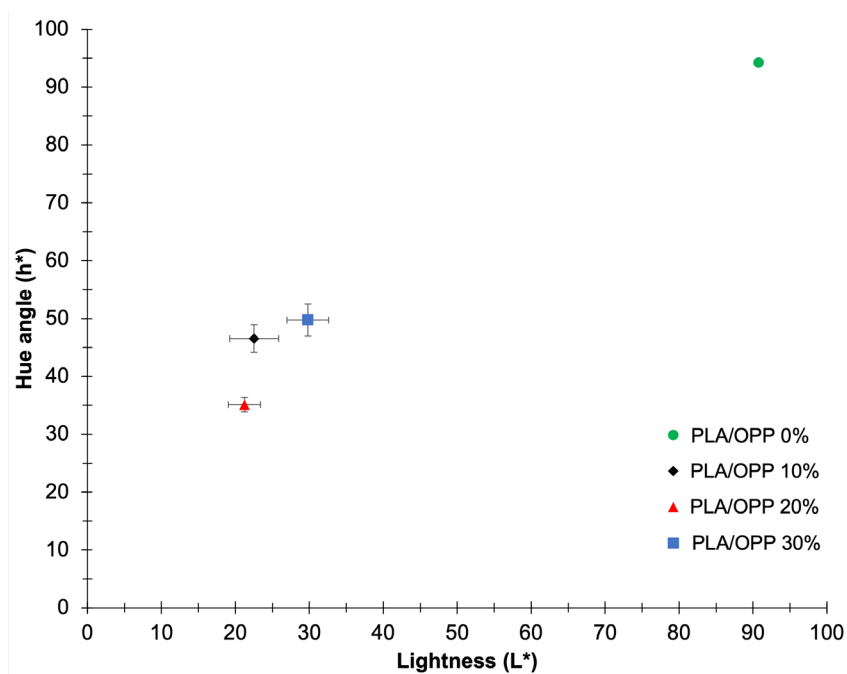


Figure 3.4. Effects of OPP loading (wt%) on the color of PLA trays.

3.2.2.5.2. Light Transmission

Light transmission results are shown in Table 3.3. There was a significant difference ($P < 0.05$) between the light transmission of the neat PLA trays and the PLA/OPP trays for all the selected wavelengths. In the visible region (i.e., 590-600 nm), the neat PLA trays were more transparent than the PLA/OPP trays (e.g., 86.4 % vs. 1.5-0.01 % at 600 nm). This high percentage of light transmission in the visible region for neat PLA has already been reported (Auras, Harte & Selke, 2005; Pranata et al., 2019). The light transmission of the PLA/OPP trays was very low because of the replacement of polymer matrix with OPP, which blocks the light. Similar results were obtained by McKay et al. (2021) for LLDPE/OPP composites. PLA/OPP trays with 20 and 30 wt% OPP had less light transmission than trays with 10 wt% OPP ($P < 0.05$; Table 3.3.) because of the more OPP agglomerates (section 3.2.2.1.1.) blocking the light. Similar results were observed by Fehlberg et al. (2019), who reported that an increase in OPP loading from 0.5 g to 1 g reduced the light transmission of LLDPE/OPP films. The light transmission of the neat PLA

in the UV region (i.e., 280-320 nm) (Table 3.3.) is low compared to the literature (Auras, Harte & Selke, 2005), most likely because the different PLA grades and packaging formats (i.e., tray vs. film). The PLA/OPP composite trays had a light transmission in the UV region even lower than in the visible region. This could be attributed to the carotenoids in OPP that can absorb UV light (Tokarz, et al., 2012). Fehlberg et al. (2019) already reported UV-adsorbing capacity for films containing OPP. OPP loading did not affect the light transmission in the UV region of the PLA/OPP composite trays ($P > 0.05$; Table 3.3.).

3.2.2.6. Fungal Resistance

Figure 3.5. displays the results of the fungal resistance test of the PLA/OPP trays containing 0 wt% and 30 wt% OPP by weight as per ASTM G21-13 (ASTM, 2013b). According to this standard, the test should be terminated for samples having a rating of ‘2’, i.e., 10-30 wt% of the complete area of the petri dish. In the case of *Penicillium* sp., the control trays had a rating of ‘2’ on the sixth day while the PLA/OPP 0 wt% and 30 wt% trays had the same amount of growth on the twelfth and seventh days, respectively. For *A. niger*, the control trays had a rating of ‘2’ on the fourth day, while the PLA/OPP 30 wt% trays had the same amount of growth on the eighth day. The PLA/OPP 0 wt% trays did not grow *A. niger* because of contamination by *Penicillium* sp. Based on the above results, PLA trays with and without OPP were not able to completely stop the growth of *A. niger* and *Penicillium* sp., but were able to delay fungal growth by 1-2 days compared to the control (agar) samples. More molds grew on the PLA/OPP 30 wt% trays than on the PLA/OPP 0 wt% trays because the former had voids that facilitated the diffusion of nutrients through the film, which allowed the mold to grow. Pranata et al. (2019) reported a similar reduction in fungal growth for films made of egg white proteins. In principle, the fungal resistance test results indicate that the PLA/OPP trays can be suitable for dry food products only in the case of long

storage periods. However, (Mckay, Sawant, Fehlberg, & Almenar, 2021) reported that orange peel powder could act as an antimicrobial against *A. niger*, *Botrytis cinerea*, and *Penicillium* sp. at higher OPP concentrations , thus further tray development (e.g., use of compatibilizer to reduce voids and increase the amount of waste) is required for the application of PLA/OPP trays for packaging of moist and semi-moist food products.

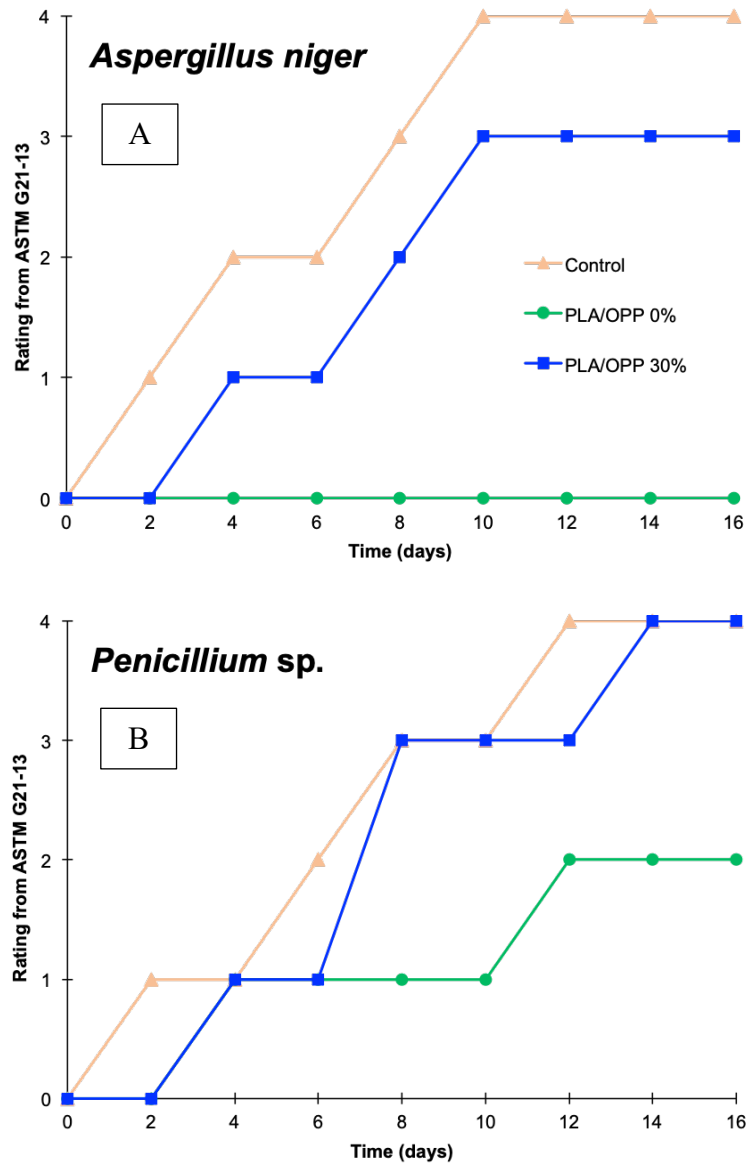


Figure 3.5. Fungal growth ratings as per ASTM G21-13 of the PLA/OPP trays for (A) *Aspergillus niger* and (B) *Penicillium sp.*

APPENDICES

APPENDIX 3A

Effect of Storage Conditions

After drying, the powder was stored in the oven along with PLA resins to keep them away from moisture. But during storage, the PLA resins absorbed some volatiles from the OPP which affected their properties. During processing, it was observed that the PLA was melting more than normal which was because of degradation due to the absorption of volatiles. Also, a color change was observed in PLA as the resins were turning orange in color which indicated the transfer of volatiles from OPP to PLA. Therefore, to avoid this, the PLA resins were dried and stored separately from OPP. This resin was not used.

APPENDIX 3B

Size of OPP agglomerates in the trays.

Due to different OPP loading, the particle size of OPP agglomerates was different for the PLA/OPP trays. The size of OPP agglomerates was measured as shown in the below tables to understand the effect of size of agglomerates on different properties.

Table 3A1. Agglomerate size measurement in cross-sectional area of size 575 x 333 μm for trays with 10 wt% OPP loading

Number of OPP agglomerate	10 wt% 1 (μm)	10 wt% 2 (μm)	10 wt% 3 (μm)
1	57.14	13.51	40.54
2	21.43	18.92	43.24
3	25.00	37.84	16.22
4	23.21	13.51	5.41
5	17.86	27.03	10.81
6	12.50	27.03	10.81
7	53.57	8.11	43.24
8	37.50	37.84	32.43
9	50.00	10.81	29.73
10	66.07	10.81	21.62
11	44.64	27.03	16.22
12	35.71	16.22	37.84

Table 3A1. (cont'd)

13	10.71	8.11	35.14	
14	25.00	18.92	21.62	
15		27.03	27.03	
Average	34.31	20.18	26.13	26.70
STDEV	17.61	9.95	12.54	14.52

Table 3A2. Agglomerate size measurement in cross-sectional area of size 575 x 333 μm for trays with 20 wt% OPP loading

Number of OPP agglomerate	20 wt% 1 (μm)	20 wt% 2 (μm)	20 wt% 3 (μm)
1	19.15	19.15	27.91
2	63.83	17.02	16.28
3	14.89	14.89	23.26
4	10.64	14.89	13.95
5	14.89	14.89	11.63
6	46.81	31.91	18.60
7	34.04	10.64	30.23
8	14.89	21.28	25.58
9	17.02	36.17	25.58
10	34.04	21.28	18.60
11	21.28	6.38	46.51
12	10.64	6.38	27.91

Table 3A2. (cont'd)

13	17.02	14.89	58.14	
14	10.64	8.51	27.91	
15	14.89	36.17	30.23	
16	14.89	38.30	46.51	
17	23.40	17.02	11.63	
18	36.17	17.02	16.28	
19	14.89	53.19	18.60	
20	19.15	21.28	53.49	
21	31.91	4.26	13.95	
22	34.04	4.26	20.93	
23	34.04	17.02	25.58	
24	17.02	21.28	16.28	
25	23.76	12.77	18.60	
26	13.11	6.38	55.81	
27		12.77	34.88	
28		18.52	6.98	
Average	23.76	18.52	26.50	22.77
STDEV	13.11	11.71	13.93	13.03

Table 3A3. Agglomerate measurement in cross-sectional area of size 575 x 333 μm for trays with 30 wt% OPP loading

Number of OPP agglomerate	30 wt% 1 (μm)	30 wt% 2 (μm)	
1	54.05	23.26	
2	37.84	34.88	
3	27.03	13.95	
4	27.03	23.26	
5	72.97	34.88	
6	18.92	25.58	
7	16.22	46.51	
8	21.62	72.09	
9	40.54	46.51	
10	35.14	44.19	
11	45.95	39.53	
12	18.92	37.21	
13		48.84	
14		51.16	
15		60.47	
16		46.51	
17		9.30	
Average	34.68	37.47	36.35
STDEV	16.89	16.62	16.49

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CHAPTER 4

EFFECT OF MASTERBATCH ON TRAYS MADE OF POLYLACTIC ACID AND AGRICULTURAL WASTE

4.1. Material & Methods

4.1.1 Materials

PLA 2003D (Specific gravity = 1.24 g/dm³, MFR, g/10 min (210 °C, 2.16 kg) = 6) was provided by NatureWorks® LLC (Minnetonka, MN). Orange peels resulting from the production of bottled orange juice were obtained from a local supermarket (Fresh Thyme, East Lansing, MI). The peels were converted into powder form before processing, as explained below.

4.1.2 Methods

4.1.2.1. Preparation and Characterization of Orange Peel Powder

A lyophilizer (Virtis Genesis 25XL Bulk Drying Lyophilizer SP Scientific, NY, USA) equipped with a Wizard 2.0 Controller (sample chamber pressure: 1333 Pascal; shelf temperature: 25 °C; condenser temperature: -80 °C) was used to freeze-dried the orange peels for 72 hours. The freeze-dried orange peels were converted into powder form with a hammer mill (Whirlpool Corp, MI, USA) with a screen (040 1A) and a ROTAP Sieve shaker (W.S. Tyler Mentor, OH, USA). The resulting powder with a particle size ranging between 0 and 180 µm as determined in Chapter 3 was placed in a LDPE Ziploc® bag and stored in a desiccator to be protected from moisture. A vacuum oven (VWR International, PA, USA) set at 102 °C for 4 d was used to further remove the moisture from OPP. The final moisture content of OPP was 1-2 % (A&D MX-50 moisture analyzer; A&D Company Limited, Tokyo, Japan).

4.1.2.2. Preparation of OPP Masterbatch And Biocomposites

10 g of PLA pellets conditioned at 50 °C for 24 h (VWR International, PA, USA) were mixed with 15 g of OPP obtained in section 4.1.2.1. in a Brabender mixer (C.W. Brabender® Instruments, Inc.) to prepare a masterbatch that contained 60 wt% of OPP. The mixture was processed for 3 min at 180 °C and at a blade speed of 50 RPM, scraped off with a spatula, cooled down, covered in nylon tissue, and finally broken into small pieces using a hammer. The small pieces were then mixed with neat PLA resin in specific proportions to produce different PLA/OPP biocomposites. Biocomposite components were weighed using OHAUS weighing balance (OHAUS Corporation, NJ, USA). For PLA/OPP biocomposites with 30 wt% OPP (PLA/OPP 30 wt% masterbatch (MB)), 12.5 g of the masterbatch was mixed with 12.5 g of neat PLA using the processing conditions mentioned previously to get a biocomposite containing 7.5 g of OPP, which was 30 wt% of OPP. Similarly, for PLA/OPP biocomposite with 35 wt% OPP (PLA/OPP 35 wt% MB), 14.5 g of masterbatch was mixed with 10.5 g of PLA using the processing conditions mentioned previously. Each control was prepared following a two-step process same as the biocomposites. First, 25 g of PLA was processed in the mixer, cooled down, and converted into small pieces in a similar way as done for the biocomposites. Then, 12.5 g of these pieces was mixed with 12.5 g of neat PLA. Four biocomposites samples of each type and four controls were produced.

4.1.2.3. Preparation of Biocomposites Without OPP Masterbatch

Biocomposites containing 30 wt% OPP (PLA/OPP direct blend (DB)30 wt%) were prepared by a direct blend of OPP with PLA following the procedures laid out in Chapter 3. Briefly, 7.5 g of OPP were mixed with 17.5 g of PLA for 3 mins at 180 °C and at a blade speed of 50 RPM.

4.1.2.4. Preparation of Trays

The PLA/OPP biocomposites obtained in sections 4.1.2.2. and 4.1.2.3. were scraped off, placed between aluminum-foil wrapped metal plates and then inserted in a compression molding machine (PHI Heated Press, PHI, CA, USA). Compression molding took place using the processing conditions reported in Chapter 3. Briefly, the mixture was preheated for 1 min and then compression molded for 3 mins at a temperature of 170 °C and a pressure of 9.5 tons. After 3 mins, water was used to cool down the mold to a temperature of around 65 °C, finally, the biocomposite sheets were removed from the metal plates. Four sheets per treatment were prepared for each test.

The compression-molded biocomposites and controls were thermoformed into trays using a thermoforming machine (Ceratek, Sencorp White, MA, USA). Thermoforming took place using the processing conditions reported in Chapter 3. Briefly, the sheets were first softened at 260 °C for 60 s and were then thermoformed into trays by applying vacuum for a forming time of 12 s. Four trays per treatment were prepared for each test.

4.1.2.5. Characterization of Trays

4.1.2.5.1 Physical Properties

4.1.2.5.1.1. Distribution and Dispersion

The agglomeration of OPP and the location of those agglomerates within the polymer matrix were observed using a Scanning Electron Microscopy (SEM) (JEOL 6610LV, JEOL, MA, USA). The top view images and cross-sectional images were obtained by placing pieces of tray on the sticky patch of sample holder. After coating the samples with 3nm of gold, a working distance of 19 mm and an accelerating voltage of 10 kV was used to obtain the images. For the top view image, magnifications of 50x and 500x were used, while 350x magnification was

used for cross-sectional image. Three replicates of PLA/OPP trays produced with and without the OPP masterbatch were evaluated.

4.1.2.5.1.2. Thickness

Different parts of the PLA trays and PLA/OPP MB trays including walls, corners, bottom, and trim were cut and their thicknesses were measured using a digital micrometer (Testing Machines Inc., DE, USA). To confirm the thicknesses of the trays, density gradient testing was performed according to Auras (2004). The differences observed in the thickness results from the density gradient method and digital micrometer (up to 32 μm) were used for calculation of conversion factor which was later applied to permeability results. For each type of tray, four replicates were evaluated, and their results were expressed in micrometers (μm).

4.1.2.5.2. Mechanical Properties

4.1.2.5.2.1. Torque Values

The viscosity and chain breakage occurred during the mixing of the neat PLA, the PLA/OPP MB and PLA/OPP DB biocomposites were compared by examining their Brabender flow curves (graphs of Torque ($\text{N} \cdot \text{m}$) vs. Time (mins)) obtained using Winmix software (C.W. Brabender[®] Instruments, Inc.). The End Torque values ($\text{N} \cdot \text{m}$) were recorded for four replicates of each type of mixture.

4.1.2.5.2.2. Crush Resistance

The crush resistance of PLA trays and PLA/OPP MB trays was evaluated using a 5565P6021 Instron Universal Testing Machine (Instron Engineering Corporation, MA, USA) to compare the amount of force the trays can hold before any damage. As per ASTM D642-00, the compressive extension at maximum compressive load and the maximum compressive load applied were obtained by recording maximum load before a 10% yield. Four replicates were evaluated for

each type of tray and the results were expressed in millimeters (mm) for compressive extension at maximum compressive load and Newton (N) for maximum compressive load.

4.1.2.5.2.3. Dynamic Mechanical Analysis

The effects of OPP on the movement of polymer chains during the production of the PLA trays, PLA/OPP MB trays and PLA/OPP DB trays were compared using dynamic mechanical analysis. The storage modulus (E') and the damping coefficient ($\tan \delta$) were measured using a dynamic mechanical analyzer (Q800 dynamic mechanical analyzer, TA Instruments, New Castle, DE). The heating rate of the equipment was set at 3 °C/min from 25 to 120 °C and the frequency was set at 1 Hz. Specimens having dimensions 40 mm x 10 mm were cut and inserted into the equipment. Four replicates per type of tray were evaluated.

4.1.2.5.3. Barrier Properties

4.1.2.5.3.1. Water Vapor Permeability

PERMATRAN-W Model 3/34 (MOCON Inc., MN, USA) was used to measure the water vapor permeability coefficients of the PLA trays and PLA/OPP MB trays. The setup for this test and calculations were performed as done in Chapter 3. Four replications of each type of tray were evaluated. The water vapor permeability coefficients were reported as $\text{kg}\cdot\text{m}/\text{package}\cdot\text{sec}\cdot\text{Pa}$.

4.1.2.5.3.2. Oxygen Permeability

OX-Tran Model 2/22 (MOCON Inc., MN, USA) was used to determine the oxygen permeability coefficients of the PLA trays and PLA/OPP MB trays. The test setup, and calculations were performed as done in Chapter 3. Four replications of each type of tray were evaluated. The oxygen permeability coefficient results were expressed in terms of $\text{kg}\cdot\text{m}/\text{package}\cdot\text{sec}\cdot\text{Pa}$.

4.1.2.5.4. Thermal Properties

4.1.2.5.4.1. Crystalline Content and Thermal Properties

Differential scanning calorimetry (Q100 differential scanning calorimeter (DSC), TA Instruments, DE, USA) was used to evaluate the effect of the OPP masterbatch on the crystalline content of PLA. The DSC cell was purged with nitrogen gas having a flow rate of 70 ml/min. Around 7-8 mg of sample was inserted in the DSC. Each sample was heated to 220 °C with a constant rate of 10 °C/min, cooled to 20 °C, and then reheated to 220 °C using the abovementioned rate. The glass transition temperature (T_g), crystallization temperature (T_c), enthalpy of cold crystallization (ΔH_c), melting temperature (T_m), and enthalpy of melting (ΔH_m) for the second run of four replicates of each type of tray were determined. The percentage of crystallinity of the PLA trays and PLA/OPP MB trays was calculated as done in Chapter 3. Results were expressed in °C and percentage.

4.1.2.5.4.2. Thermal Stability

Thermogravimetric analysis was used to evaluate the changes in weight of the PLA trays and the PLA/OPP MB trays with temperature using a thermogravimetric analyzer (Q50 thermogravimetric analyzer, TA Instruments, New Castle, DE) with a nitrogen flow of 40 in³/min. Samples between 7-8 mg were heated from 25 °C to 600 °C at a constant heating rate of 10 °C/min. The results were presented in the form of a thermogram that depicts a change in residual weight (%) vs. temperature (°C).

4.1.2.5.5. Optical Properties

4.1.2.5.5.1. Color

The walls of the PLA trays, PLA/OPP MB trays, and PLA/OPP DB trays that had their thicknesses closest to the mean thickness of all 12 walls (4 replications per treatment) were

selected. These walls were horizontally cut in half to get two halves that were measured separately due to the slight visual color difference observed along each wall. Each wall half was placed on a view plate area of 3.2 mm² and their CIELAB color coordinates L*, a* and b* were recorded using a spectrophotometer (labscan XE, Hunterlab Associates Laboratory, Inc., VA, USA) with an EasyMatchQC software. The a* and b* values were used to calculate the Hue angle (h*), which was adjusted in case of negative a* values as per McLellan et al. (1995). Four replicates for each half wall of each tray type were evaluated and the results were presented as h* vs L*.

4.1.2.5.5.2. Light Transmission

The walls of the PLA trays and PLA/OPP MB trays were cut and inserted in a UV-Vis Spectrometer (Lambda 25 UV/VIS Spectrometer, PerkinElmer Instruments Inc., MA, USA) connected to a computer with an UV Winlab application software. Walls of four replicates of each type of tray were inserted in a 1.0-mm slit aperture and the light transmission was measured in a spectral range of 200 – 800 nm with a scan speed of 480 nm per min. The light transmissions of each type of tray at wavelengths that cover the UV and visible spectra: 280 nm, 320 nm, 590 nm, and 600 nm are presented in %.

4.1.2.5.6. Fungal Resistance

The fungal resistance of the PLA trays and PLA/OPP MB trays was determined following the procedure described in (Pranata, et al., 2019) with a slight modification. Four replicates were evaluated per type of tray.

4.1.2.5.7. Statistical Analysis

MINITAB 19 (Statistical Software for PC/Windows, Minitab Inc., PA) was used to perform statistical analysis. Univariate analysis of variance (ANOVA) and Tukey's method at 0.05 level of significance were used to analyze a change in the studied properties caused by i)

processing (masterbatch vs. direct mixing) and ii) different OPP loadings in the masterbatch. The effect of top and bottom halves of wall on the h^* and L^* values and effect of different tray parts (trims, bottoms, walls, and corners) on thickness distribution after thermoforming was also analyzed using Tukey's method at 0.05 level of significance.

4.2 Results and Discussion

4.2.1. Effect of Masterbatch On PLA/OPP Tray Production

Research done during the Chapter 3 of this study shows that 30 wt% OPP is the maximum amount of powder that can be directly blended with PLA without the use of a compatibilizer to produce trays that thermoform properly. In this study, the use of a masterbatch of PLA and OPP allows to produce properly thermoformed trays with up to 35 wt.% OPP. This can be attributed to the similar agglomerate size for 35 wt% MB OPP and 30 wt% DB OPP which resulted in increase in extra 5 wt.% OPP that can be added to PLA using masterbatch. Hence, more OPP can be used to replace polymer matrix using a masterbatch, which adds more value to the agrowaste.

4.2.2 Tray Characterization

4.2.2.1. Physical Properties

4.2.2.1.1. Distribution and Dispersion

Figure 4.1.A-L shows the distribution and dispersion of OPP in the PLA/OPP MB trays. Panels A-D, which display the surfaces of the biocomposites, show the location of the agglomerates and thus, the distribution of OPP in the trays. The PLA/OPP MB trays containing 30 wt% and 35 wt% OPP show good distribution with OPP agglomerates located everywhere. The increase in loading from 30 to 35 wt% had no effect on the good distribution of OPP. The comparison between PLA/OPP 30 wt% MB and PLA/OPP 30 wt% DB shows that OPP had worse

distribution in PLA/OPP 30 wt% DB than in PLA/OPP 30 wt% MB. This can be better observed in Figure 4.1.E-H due to the close-up of the aforementioned panels (area of 253 μm x 189 μm at 50x magnification). Panel G shows OPP agglomerates located everywhere, while panel H shows OPP agglomerates in specific locations and different empty spaces in between. This demonstrates the better distribution resulting from the masterbatch process. The dispersion of OPP in the PLA trays can be observed in the aforementioned close-up images as well as in the cross-section images shown in Figure 4.1.I-L. Panels F and G show that the increase in loading from 30 to 35 wt% resulted in significantly larger agglomerates. The size of the OPP agglomerates ranged from 5 to 47 μm (Appendix 2) with an average size of 18 ± 11 μm (Table A4) for PLA/OPP 30 wt% MB and from 13 to 75 μm (Appendix 2) with a significantly larger ($P < 0.05$) average agglomerate size of 32 ± 13 μm (Table A5) for PLA/OPP 35 wt% MB (Figure 4.1.J-K and Table 4.1). Consequently, the voids surrounding the OPP agglomerates were a little bit larger size in the PLA/OPP 35 wt% trays. These voids were formed due to poor interfacial bonding and adhesion between PLA and OPP caused by a difference in polarity (Fehlberg, Lee, Matuana, & Almenar, 2020). The same voids have been observed when PLA has been mixed with other types of agricultural waste like peanut shells (Yamoum & Magaraphan, 2017). Panel I show neither voids nor OPP agglomerates for the PLA/OPP 0 wt% MB trays. The comparison between PLA/OPP 30 wt% MB trays and PLA/OPP 30 wt% DB shows significantly larger OPP agglomerates (size range 9-73 μm , Appendix 2) ($P < 0.05$) for direct blending as the average size was 36 ± 16 μm (Table A3). The number of voids observed for PLA/OPP 30 wt% MB and PLA/OPP 30 wt% DB were similar to each other, but these were larger in the case of direct blending.

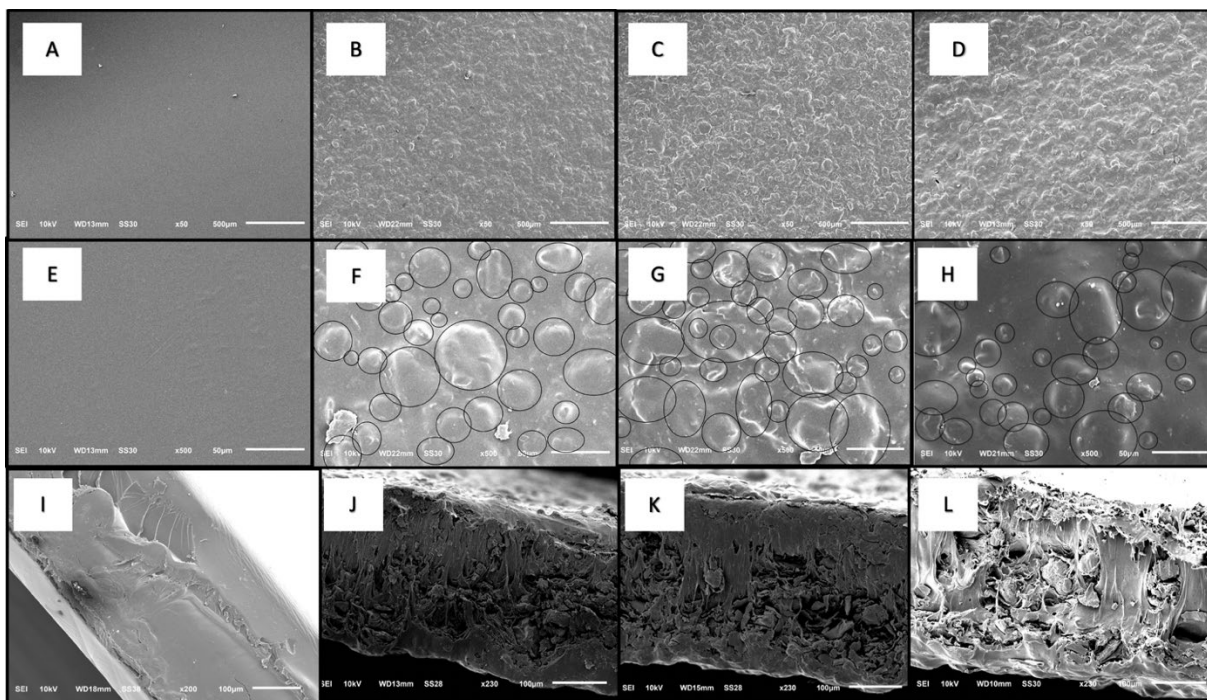


Figure 4.1. Scanning electron micrographs of PLA/OPP composite trays with 0 wt% MB (A, E, I), 30 wt% MB (B, F, J), 35 wt% MB (C, G, K) and 30 wt% DB (D, H, L) OPP by weight.

Micrographs A-D and E-H show 50x and 500x magnification top views, respectively. Micrographs I-L show 350x magnification cross-sectional views. Black circles highlight the OPP agglomerates. The images used for 30% DB samples (D, H, L) have been retrieved from Chapter 3.

4.2.2.1.2. Thickness

Table 4.1. shows the thicknesses of sheets and trays made of PLA/OPP MB containing 0 wt%, 30 wt% and 35 wt% OPP and PLA/OPP DB containing 30 wt% OPP. The thicknesses of the sheets (614 – 633 μm) and the tray bottoms (423 – 441 μm) and trims (460 – 498 μm) were the same ($P > 0.05$) among the PLA/OPP 0 wt% MB, PLA/OPP 30 wt% MB and PLA/OPP 35 wt% MB. In contrast, either sheets or trays parts made of PLA/OPP biocomposites by direct blending showed an increase in thickness as agrowaste loading increased. Therefore, the use of a masterbatch allows for OPP to produce plastic sheets and trays closer in thickness to the trays made of neat PLA. Congruently, the comparison between the biocomposites PLA/OPP 30 wt% MB and PLA/OPP 30 wt% DB showed that the latter was significantly thicker ($P < 0.05$) in terms of sheet and all tray parts except for the walls. This occurred because of the extra processing for the PLA/OPP 30 wt% MB trays. The extra processing results in breaking of polymer chains which causes the mixture to be softer and easier to compress compared to PLA/OPP 30wt% DB trays. Corner thicknesses varied significantly ($P < 0.05$) among the different trays (PLA/OPP 0 wt% MB < PLA/OPP 30 wt% MB < PLA/OPP 30 wt% DB) as well as varied significantly ($P < 0.05$) when compared with other parts of the tray. The reason behind corners being thinnest in a tray is the more sheet stretching when this is drawn deeper during thermoforming (Martin & Duncan, 2007). The bottom, walls and trim of each tray did not vary significantly ($P > 0.05$) except in the case of the PLA/OPP 0 wt% MB trays. Differences were also found between the bottoms and trims of neat PLA trays in Chapter 3.

Table 4.1. Thickness profile of sheet and trays and agglomerate size of OPP in the trays containing different OPP loadings produced by masterbatch production.

Properties			OPP content in PLA/OPP composite (wt%)			
			0 MB	30 MB	30 DB*	35 MB
Thickness (μm)	Sheet		632 ± 28 ^a	633 ± 24 ^{aα}	750 ± 0 ^β	614 ± 21 ^a
	Tray	Wall	364 ± 42 ^{aA}	404 ± 65 ^{abAα}	502 ± 131 ^{AB}	438 ± 64 ^{bA}
		Corner	256 ± 25 ^{aB}	226 ± 27 ^{bBα}	289 ± 65 ^{Bβ}	263 ± 32 ^{aB}
		Bottom	423 ± 13 ^{aC}	440 + 21 ^{aAα}	549 ± 72 ^{AB}	441 ± 36 ^{aA}
		Trim	498 ± 39 ^{aD}	460 ± 10 ^{aAα}	510 ± 10 ^{AB}	490 ± 36 ^{aA}
Agglomerate Size (μm)			N/A	18 ± 13 ^{aα}	36 ± 16 ^β	31 ± 13 ^b

Different lowercase letters (a and b) indicate significant differences ($P < 0.05$) among thicknesses and agglomerate size caused by OPP loading. Different uppercase letters (A and B) indicate significant differences ($P < 0.05$) among thicknesses of different parts of a tray. Different Greek letters (α and β) indicate significant differences ($P < 0.05$) among thicknesses caused by processing (masterbatch vs. direct mixing). *Data retrieved from Chapter 3. N/A indicates not applicable.

4.2.2.2 Mechanical Properties

4.2.2.2.1. Torque Values

The end torque values of the PLA/OPP MB mixtures containing 0 wt%, 30 wt% and 35 wt% OPP and the PLA/OPP DB mixture containing 30 wt% OPP are displayed in Table 4.2. The end torque values of the PLA decreased significantly ($P < 0.05$) with the addition of OPP. This indicates that the PLA/OPP MB mixtures are less viscous than the plain PLA (~6 (N.m) vs. 9.2 (N.m)). However, the increase of OPP from 30 wt% to 35 wt% increased ($P < 0.05$) the end torque value from 5.7 (N.m) to 6.7 (N.m). The higher amount of OPP resulted in OPP agglomerates with bigger size (Table 4.9) that provided resistance to the blades of the Brabender. The comparison of end torque values between the PLA/OPP 30 wt% MB mixture and the PLA/OPP 30 wt% DB mixture shows that the latter had higher ($P < 0.05$) end torque values (8.7 N.m). This difference can be attributed to the extra processing of the masterbatch samples, which causes more breaking of chains. Also, the smaller size of the OPP agglomerates (Figure 4.1) in the PLA/OPP 30 wt% MB mixture could have contributed to the lower end torque values.

Table 4.2. Effects of OPP loading (%) in PLA trays produced by masterbatch production on the water vapor and oxygen permeability coefficients, compression strength properties and end torque values

Properties		OPP content in PLA/OPP composite (wt%)			
		0 MB	30 MB	30 DB*	35 MB
End Torque values		9.2 ± 0.3^a	5.7 ± 0.3^{bA}	8.7 ± 0.2^B	6.7 ± 0.1^c
Compression Strength	Compressive extension at Maximum Compressive load (mm)	11.9 ± 0.8^a	8.1 ± 1.3^{bA}	11.2 ± 0.8^B	9.1 ± 0.8^b
	Maximum Compressive load (N)	972 ± 227^a	605 ± 148^{bA}	1144 ± 196^B	743 ± 31^{ab}
Permeability Coefficients	Oxygen x E-16 (kg.m/package.s.Pa)	7.5 ± 0.2^a	5.1 ± 0.4^{bA}	17.6 ± 2.0^B	8.8 ± 0.6^c
	Water x E-16 (kg.m/package.s.Pa)	1.5 ± 0.2^{ab}	1.0 ± 0.3^{aA}	1.6 ± 0.4^A	1.7 ± 0.5^b

Different lowercase letters (a, b, and c) indicate significant differences ($P < 0.05$) on water vapor and oxygen permeability coefficient, end torque values and compression strength properties caused by OPP loading. Different Uppercase letters (A, B and C) indicate significant differences ($P < 0.05$) on water vapor and oxygen permeability coefficient, end torque values and compression

strength properties caused by masterbatch process and direct blending process. *Data retrieved from Chapter 3.

4.2.2.2.2. Crush Resistance

Table 4.2. displays the compressive extension at maximum compressive load and maximum compressive load results of PLA/OPP trays produced by masterbatch processing (0 wt%, 30 wt%, 35 wt%) and by direct blending (30 wt%). Due to the addition of OPP, the compressive extension of trays decreased significantly ($P < 0.05$) from 11.94 mm, for the PLA/OPP 0% MB trays, to 8.13 and 9.14 mm for PLA/OPP 30 wt% and 35 wt% MB trays, respectively, while the maximum compressive load decreased significantly ($P < 0.05$) from 972 N, for the 0 wt% MB trays, to 605 N and 743 N for PLA/OPP 30 wt% and 35 wt% MB trays, respectively. This decrease can be justified by the change in the end torque values of the neat PLA trays with the addition of OPP (Table 4.2.). As the end torque values decreased, the maximum compressive load also decreased because the compressive strength of the trays was affected by the breaking of the PLA chains. The decrease in maximum compressive load resulted in a lower compressive extension at maximum compressive load. When the compression properties of the PLA/OPP 30 wt% MB trays were compared with those of the PLA/OPP 30 wt% DB trays, the latter had statistically higher ($P < 0.05$) values of compressive extension and maximum compressive load. This can be justified by the higher end torque values of the PLA/OPP 30 wt% DB trays. The extra processing for the PLA/OPP 30 wt% MB trays caused a decrease in compressive properties. Compression strength values reported in the literature for PLA trays (Auras, Auras, Singh, 2005) (Auras, Singh, Singh, 2006) cannot be used for comparison purposes since the compression strength of thermoformed plastic containers depends on container design (Auras, Singh, Singh, 2006).

4.2.2.2.3. Dynamic Mechanical Analysis

Figure 4.2. displays the storage modulus (E') and tan delta of PLA/OPP trays produced by masterbatch processing (0 wt%, 30 wt%, 35 wt%) and by direct blending (30 wt%) as a function of temperature. Figure 4.2A shows that the trays with OPP had higher E' than the PLA/OPP 0 wt% MB trays (2.1-2.5 GPa vs. 1.65 GPa) in the temperature range around 55 °C, which is the glassy region (Cristea, Ionita, & Iftime, 2020). The higher E' resulted from the incompatibility between PLA and OPP that caused the movement of PLA chains being restrained due to OPP agglomerates. E' increased with the amount of OPP loading. This is in agreement with the results observed for PLA mixed with different cyclodextrin loadings (Joo, Auras, & Almenar, 2011) (Almenar, Auras, Harte, & Rubino, 2009). The use of the masterbatch had an effect on E' . The PLA/OPP 30 wt% MB trays had lower E' compared to PLA/OPP 30 wt% DB trays in the glassy region because of better distribution and dispersion, leading to less restraining of PLA chains. In contrast, the use of the masterbatch had no effect on the E' of PLA mixed with cyclodextrins (Almenar, Auras, Harte, & Rubino, 2009). E' of all the trays dropped starting at 55 °C due to the increase in mobility of segments of the PLA chains at temperatures close to the PLA T_g . The curves shifted for the trays with OPP having lower E' than PLA/OPP 0 wt% MB. This is in agreement with the decrease in T_g of the trays with OPP reported in Table 4.3. An increase in E' was observed for the samples with OPP in the temperature range above 80 °C, which is the region of cold crystallization as per Cristea, Ionita, & Iftime (2020). The same increase in E' was observed for neat PLA samples at around 100 °C. The PLA/OPP 30 wt% DB trays had the highest E' in the cold crystallization region while the PLA/OPP 0 wt% MB trays had the lowest compared to the other PLA/OPP trays, which is in agreement with the % crystallinity reported in Table 4.3. PLA/OPP 30 wt% MB and 35 wt% MB trays had very similar E' in this region, which is shown

as non-significant differences in crystallinity (Table 4.3). Therefore, although the polymer chains were restrained (less elasticity) as OPP loading increased, the use of the masterbatch process resulted in less restrained chains and thus more OPP added without affecting the tray shaping compared to direct blending.

The tan delta results are displayed in Figure 4.2B. The PLA/OPP 0 wt% MB trays had no obstruction of movement of its polymer chains and thus, the curve of this type of trays displays a very intense and sharp peak which is in agreement with results obtained by other researchers working with neat PLA (Huda, Mohanty, Drzal, Schut, & Misra, 2005). The height of the tan delta peak of the PLA/OPP 0 wt% MB tray (3.4) was reduced with an increase in OPP loading (1.8 – 2.1), which confirms the obstruction in chain mobility due to the presence of OPP. A similar height reduction have been reported for films made of PLA and cyclodextrins (Joo, Auras, & Almenar, 2009). In contrast, Quiles-Carrillo et al. (2018) reported higher tan delta peaks for injected pieces of PLA mixed with orange peel flour than for the same pieces when made of neat PLA. The PLA/OPP 30 wt% MB trays had less PLA chain movement reduction (tan delta value of 2.1) than the PLA/OPP 30 wt% DB trays (tan delta value of 2.0). This proves that the better distribution and dispersion of OPP due to the masterbatch process (Figure 4.1) resulted in better chain mobility and consequently better processability (shaping of the trays) at higher OPP loading. This was in agreement with the results obtained by other researchers who observed that there was less reduction in the height of the tan delta peaks of the PLA/ cyclodextrins mixture obtained by the masterbatch process compared to direct blending (Joo, Auras, & Almenar, 2009).

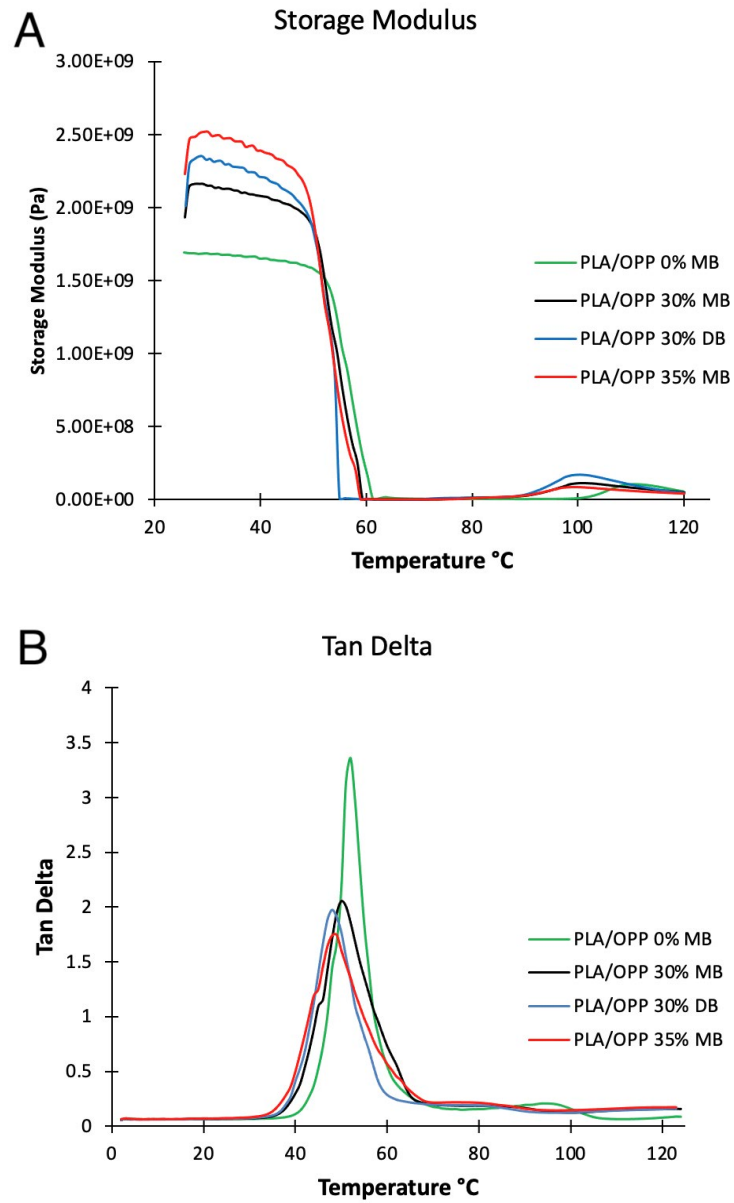


Figure 4.2. Storage Modulus (A), and Tan Delta (B) of PLA trays containing different OPP loadings by masterbatch production.

4.2.2.3. Barrier Properties

4.2.2.3.1. Water Vapor Permeability

Table 4.2. displays the water vapor permeability (WVP) coefficients of PLA/OPP MB trays with 0 wt%, 30 wt% and 35 wt% OPP and PLA/OPP DB trays with 30 wt% OPP. The PLA/OPP 30 wt% MB trays had better water vapor barrier ($P < 0.05$) than PLA/OPP 35 wt% MB trays (1.0×10^{-16} (kg.m/package.s.Pa) vs. 1.7×10^{-16} (kg.m/package.s.Pa)), but the WVP for both types of trays was not statistically different ($P > 0.05$) than the PLA/OPP 0 wt% MB trays (1.5×10^{-16} (kg.m/package.s.Pa)). No statistical differences in water vapor permeability of PLA/OPP trays due to addition of OPP by direct blending have been reported. This indicates that the blending of OPP with PLA does not affect the water vapor barrier of PLA. This could be explained by the OPP particles being able to absorb some of the water vapor molecules moving freely through the polymer matrix. The difference in WVP coefficients of PLA/OPP 30 wt% MB and 35 wt% MB was observed because of the increase in the size of voids with the increase in OPP as shown in Figure 4.1. The WVP coefficient of the MB tray without OPP was observed to be lower compared with the literature, 2.0×10^{-14} (kg.m/package.s.Pa) to 1.1×10^{-15} (kg.m/package.s.Pa) (Awalgaonkar, Beaudry, & Almenar, 2020) (Joo, Lewandowski, Auras, Harte, & Almenar, 2011)(Auras, Singh, & Singh, 2006). The difference could be attributed to the different tested surface area, extra mixing due to the masterbatch process, and different thickness. The comparison between the PLA/OPP 30 wt% DB trays and PLA/OPP 30 wt% MB trays shows that the latter had greater barrier ($P < 0.05$). This can be explained by the better distribution of OPP in the polymer matrix that absorbed the water molecules passing through the different areas of the tray.

4.2.2.3.2. Oxygen Permeability

The oxygen permeability (OP) coefficients of PLA/OPP MB trays with 0 wt%, 30 wt% and 35 wt% OPP and PLA/OPP DB trays with 30 wt% OPP are presented in Table 4.2. The OP coefficients of the PLA/OPP 0 wt% MB trays, 7.5×10^{-16} (kg.m/package.s.Pa) , were higher than those reported in literature for neat PLA trays and films, 6.0×10^{-18} (kg.m/package.s.Pa) to 4.0×10^{-20} (kg.m/package.s.Pa) (Joo, Lewandowski, Auras, Harte, & Almenar, 2011)(Auras, Singh, & Singh, 2006). This difference can be explained by the different PLA grade, thickness, tested surface area and extra processing due to the masterbatch process. The barrier of the trays improved significantly ($P < 0.05$) with the addition of 30 wt% OPP as the OPP were able to obstruct the flow of oxygen molecules through the polymer matrix. Similarly, PLA mixed with silica powder extracted from rice husk had an improved OP coefficient (Battezzato, Bocchini, Alongi, & Frache, 2014). However, the addition of 35 wt% OPP caused an increase in permeability ($P < 0.05$) that can be attributed to the increase in the size of the voids present in the PLA/OPP 35 wt% MB compared to PLA/OPP 30 wt% MB (Figure 4.1). Similarly, Dhar et al. (2015) reported that the addition of 1% CNC to PLA resulted in an improved oxygen barrier, but the addition of 2% CNC resulted in an increase in oxygen permeability (Dhar, Tarafder, Kumar, & Katiyar, 2015). The comparison between the PLA/OPP 30 wt% MB trays and PLA/OPP 30 wt% DB trays shows that the former had significantly lower OP coefficients ($P < 0.05$). This can be explained by the better mixing and distribution of OPP, resulting in a better barrier material.

4.2.2.4. Thermal Properties

4.2.2.4.1. Glass Transition temperature, Melting temperature and Crystalline Content

The glass transition temperature, melting temperature and crystalline content of PLA/OPP MB trays containing 0 wt%, 30 wt% and 35 wt% OPP and PLA/OPP DB trays

containing 30 wt% OPP are shown in Table 4.3. The T_g of the PLA/OPP 0 wt% MB trays was observed to be 61.2 °C and it decreased ($P < 0.05$) to 58.7 °C and 57.6 °C for the PLA/OPP 30 wt% MB and PLA/OPP 35 wt% MB trays, respectively. Researchers working with PLA and orange peel flour have also observed a decrease in T_g of the composite (Quiles-Carrillo, Montanes, Lagaron, Balart, & Torres-Ginner, 2018). The reason behind this can be the presence of soluble compounds in OPP like sugars which have plasticizing effects (Kalajahi, Alizadeh, Hamishekhar, Almasi, & Asefi, 2021). Furthermore, the agglomerates increased chain separation that facilitated chain mobility when temperature was near T_g (Figure 4.1). The PLA/OPP 30 wt% DB trays had a significantly ($P < 0.05$) lower T_g , 56.8 °C, than the PLA/OPP 30 wt% MB trays because of the chain separation caused by the bigger agglomerates present in the DB samples. The T_m of the PLA/OPP MB trays with 30 and 35 wt% OPP was slightly less ($P < 0.05$), 147.5 °C and 147.7 °C, respectively, than that of the 0 wt% MB trays, which had a T_m of 149.7 °C. In contrast, (Quiles-Carrillo, Montanes, Lagaron, Balart, & Torres-Ginner, 2018) reported no statistical differences in the T_m of injected PLA due to addition of orange peel flour (Quiles-Carrillo, Montanes, Lagaron, Balart, & Torres-Ginner, 2018). There was no statistical difference ($P > 0.05$) between in T_m of the PLA/OPP 30 wt% MB and 30 wt% DB trays (148.0 °C in both cases) because the same amount of PLA was present in both types of trays. The crystalline content of the samples increased significantly ($P < 0.05$) with the addition of OPP for the MB trays. This indicates that OPP acted as a nucleating agent. When the PLA/OPP 30 wt% MB trays were compared with the PLA/OPP 30 wt% DB trays, there was no significant difference ($P > 0.05$) in crystalline content because the same amount of OPP was present in both types of trays. Similarly, researchers working with additives other than OPP observed an increase in the crystalline content of PLA when this was

blended with the additives under study (Joo, Auras, & Almenar, 2011) (Yamoum & Magaraphan, 2017) (Almenar, Auras, Harte & Rubino, 2009).

Table 4.3. Effects of OPP loading percentage in PLA trays produced by masterbatch production on light transmission, thermal properties, and crystalline content

Properties		OPP content in PLA/OPP composite (wt%)			
		0 MB	30 MB	30 DB*	35 MB
Thermal Properties	T _g (°C)	61.2 ± 0.2 ^a	58.7 ± 0.5 ^{bA}	56.8 ± 0.2 ^B	57.6 ± 0.2 ^c
	T _m (°C)	149.7 ± 0.3 ^a	147.5 ± 0.3 ^{bA}	148.0 ± 0.4 ^A	147.7 ± 0.3 ^b
	Crystallinity (%)	1.7 ± 0.4 ^a	5.1 ± 1.0 ^{bA}	6.3 ± 1.0 ^A	6.0 ± 1.0 ^b
Light Transmission (%)	280 nm	36.67 ± 9.37 ^a	-0.03 ± 0.01 ^{bA}	-0.04 ± 0.00 ^{bA}	-0.03 ± 0.01 ^b
	320 nm	59.02 ± 7.15 ^a	-0.06 ± 0.01 ^{bA}	-0.05 ± 0.01 ^{bA}	-0.06 ± 0.01 ^b
	590 nm	84.03 ± 2.44 ^a	0.04 ± 0.03 ^{bA}	0.01 ± 0.01 ^{bA}	0.01 ± 0.01 ^b
	600 nm	84.22 ± 2.41 ^a	0.06 ± 0.04 ^{bA}	0.01 ± 0.01 ^{bA}	0.01 ± 0.01 ^b

Different lowercase letters (a, b and c) indicate significant differences ($P < 0.05$) among light transmission, T_g (glass transition temperatures), melting temperatures (T_m), and percentage of crystallinity caused by OPP loading. Different Uppercase letters (A, B and C) indicate significant differences ($P < 0.05$) among light transmission, T_g (glass transition temperatures), melting temperatures (T_m), and percentage of crystallinity caused due to Masterbatch process and direct blend process. *Data retrieved from Chapter 3.

4.2.2.4.2. Thermal Stability

The thermogravimetric curves of the bottoms of trays made of PLA/OPP MB containing 0 wt%, 30 wt% and 35 wt% OPP and PLA/OPP DB containing 30 wt% OPP are presented in Figure 4.3. The first weight loss of approximately 1% occurred around 100 °C for all the biocomposite trays. This mass loss has been attributed to water loss (Fehlberg, Lee, Matuana, & Almenar, 2020); Zapata, Balmaseda, Fregoso-Israel, & Torres-Garcia, 2009). The next weight loss of around 2% for all the biocomposite trays was observed in the range of 100 – 175 °C. This has been attributed to the decarboxylation and esterification reactions occurring in OPP (Banisadr & Asempour, 2012) and has also been observed by other researchers working with OPP (Fehlberg, Lee, Matuana, & Almenar, 2020). The weight loss of approximately 12% in the region of 175 – 300 °C for the PLA/OPP trays indicates the loss of the hemicellulose and cellulose present in OPP as the degradation temperature of hemicellulose and cellulose has been reported to be in the range of 150 – 225 °C and 260 – 360 °C, respectively (Zapata, Balmaseda, Fregoso-Israel, & Torres-Garcia, 2009). The 1-2% weight loss difference within the exothermic peaks of the two PLA/OPP MB trays corroborates the more OPP loading of the PLA/OPP trays with 35 wt% OPP. A major weight loss (approx. 70%) for the biocomposites was observed in the range of 300 – 360 °C. This can be attributed to the loss of PLA (Yamoum & Magaraphan, 2017), which was approx. 50% in this temperature interval, along with the loss of cellulose and lignin (approx. 20% in this temperature interval). The last weight loss of 12-15% for the biocomposite trays was observed in the range of 360 – 475 °C. This has been correlated to the degradation temperature of lignin and char or tar residues (Zapata, Balmaseda, Fregoso-Israel, & Torres-Garcia, 2009). In this temperature range, the PLA/OPP trays with 35 wt% OPP had approx. 5% less weight loss than those with 30 wt% OPP, which according to other researchers (Chun, Husseinsyah, & Osman,

2013) will show the better resistance of the PLA/OPP biocomposite to thermal decomposition with higher OPP content. Similar results were obtained by in Chapter 3 where the reason was attributed to the lower weight loss observed with the increase in OPP to simply the increase in char from the pyrolysis of the lignin present in the OPP. When the thermogravimetric curves of 30 wt% DB and 30 wt% MB were compared, the curves were observed to be similar due to the same amount of OPP being present in the two types of trays.

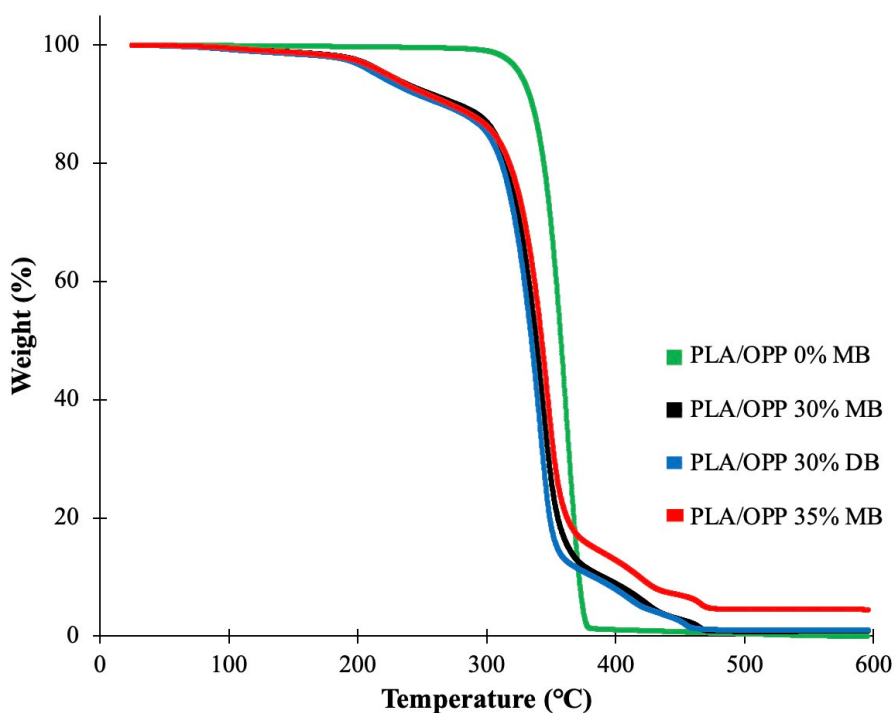


Figure 4.3. Thermogravimetric curves of PLA trays containing different OPP loadings by masterbatch production.

4.2.2.5. Optical Properties

4.2.2.5.1. Color

Figure 4.4 shows the color of trays made of PLA/OPP MB trays containing 0 wt%, 30 wt% and 35 wt% OPP and PLA/OPP DB trays containing 30 wt% OPP. The PLA/OPP 0 wt% MB trays were light (88.05) greenish yellow (92.78) in color. The slightly different L^* and h^* values compared with neat PLA from the literature (Auras, Harte, & Selke, 2004; Pranata et al., 2019) can be attributed to the several mixing processes that PLA was exposed to simulate the masterbatch process of the biocomposites. All the biocomposite trays were opaque yellowish-orange in color due to the presence of carotenoids in the OPP (Chedea, Kefalas, & Socaciu, 2010). This yellowish orange color has previously been reported for other plastic biocomposites containing OPP (Fehlberg, Lee, Matuana, & Almenar, 2020) (Mckay, Sawant, Fehlberg, & Almenar, 2021). The PLA/OPP 30 wt% MB trays had lower lightness ($P < 0.05$) and were less orange in color ($P < 0.05$) than the PLA/OPP 30 wt% DB trays (Figure 4.2). This can be attributed to the trays turning brownish in color due to the extra processing time in the masterbatch process. Joo et al. (2011) observed that a biocomposite made of PLA and β -cyclodextrin had lower lightness when produced by masterbatch processing compared to direct blending due to a slightly reduced crystalline content. Table 4.4 shows that the lightness of the top and bottom parts of the walls of PLA/OPP MB trays did not show significant differences ($P > 0.05$) except for the PLA/OPP 35 wt% MB trays which had statistically different ($P < 0.05$) L^* values for top and bottom parts of the walls. The polymer chains in the PLA/OPP 35 wt% MB trays couldn't be stretched easily during thermoforming due to the higher amount of OPP present in this biocomposite, which resulted in a difference in the lightness values of the top and bottom parts of the walls. The h^* value of the top and bottom parts of the walls of the trays (Table 4.4) produced

using the masterbatch showed no significant difference ($P > 0.05$). The increase in OPP (PLA/OPP 30 wt% MB trays vs. 35 wt% MB trays) did not impact ($P > 0.05$) the L^* and h^* values of either top or bottom parts of the walls showing that the addition of 5 % more OPP did not affect the color of the trays. In contrast, it was observed in Chapter 3 that a difference in lightness ($P < 0.05$) when OPP % was increased from 20 wt% to 30 wt% and a difference in h^* value ($P < 0.05$) was observed for each increment of 10 wt% OPP from 0 wt% to 30 wt%. The difference can be attributed to a better distribution of OPP due to masterbatch processing.

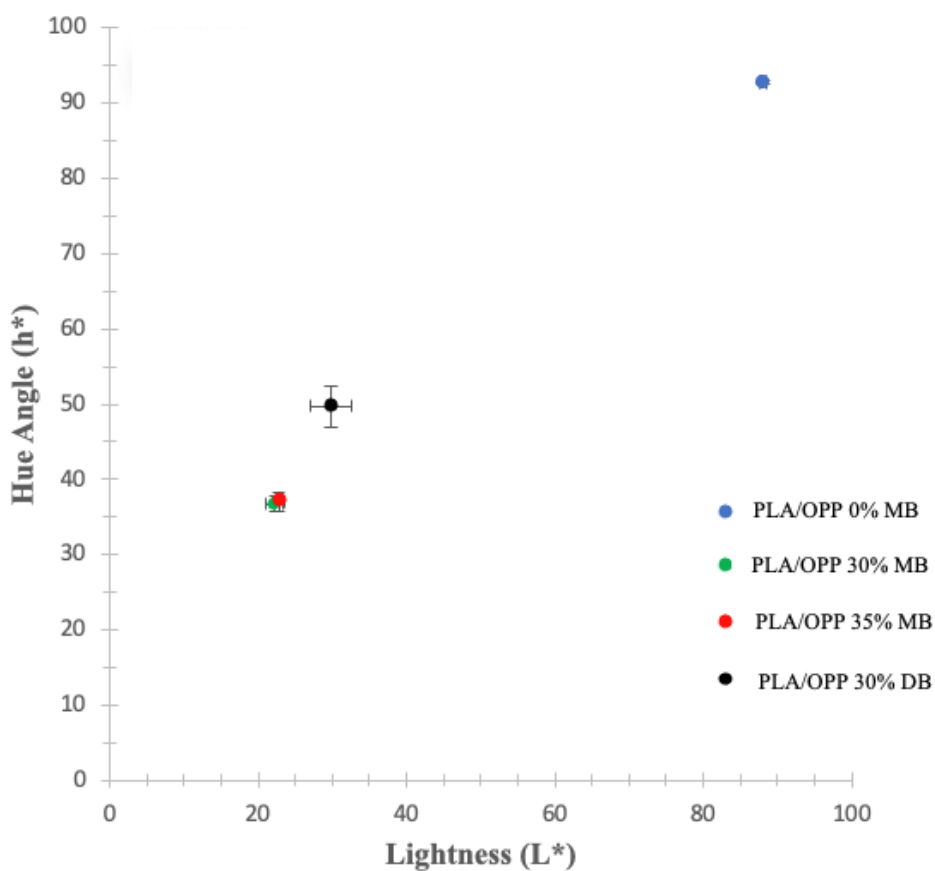


Figure 4.4. Effects of OPP loading percentage in PLA trays produced by masterbatch production on L^* (Lightness) and h^* (hue angle) values.

Table 4.4. Effects of OPP loading percentage and difference in L* and h* values of top and bottom parts of walls of PLA trays produced by masterbatch production.

OPP content in PLA/OPP biocomposite (wt%)	L* D65/10 Top	L* D65/10 Bottom	h* D65/10 Top	h* D65/10 Bottom
0 MB	87.76 ± 0.21 ^{aA}	88.34 ± 0.32 ^{aA}	92.70 ± 0.15 ^{aA}	92.86 ± 0.31 ^{aA}
30 MB	21.27 ± 0.79 ^{bAα}	23.18 ± 0.41 ^{bAα}	36.32 ± 1.13 ^{bAα}	37.17 ± 0.89 ^{bAα}
30 DB*	28.14 ± 2.82 ^{Aβ}	31.47 ± 1.91 ^{Aβ}	48.27 ± 3.22 ^{Aβ}	51.19 ± 1.50 ^{Aβ}
35 MB	22.13 ± 0.06 ^{bA}	23.51 ± 0.19 ^{bB}	36.61 ± 1.71 ^{bA}	37.42 ± 0.52 ^{bA}

Different lowercase letters (a and b) indicate significant differences ($P < 0.05$) among Lightness and Hue angle caused by OPP loading. Different uppercase letters (A and B) indicate significant differences ($P < 0.05$) among Lightness and Hue angle of different parts of a tray. Different Greek letters (α and β) indicate significant differences ($P < 0.05$) among Lightness and Hue angle caused by processing (masterbatch vs direct mixing).

4.2.2.5.2. Light Transmission

Table 4.3. presents the light transmission of trays made of PLA/OPP MB containing 0 wt%, 30 wt% and 35 wt% OPP and PLA/OPP DB containing 30 wt% OPP. The PLA/OPP 0 wt% MB trays had the same high light transmission as that reported in the literature for the PLA film (Pranata, et al., 2019). The trays with OPP had lower light transmission. The presence of the OPP in the polymer matrix blocked the light as reported previously in Chapter 3. Similarly, Fehlberg, Lee, Matuana, & Almenar (2020) reported a reduction in light transmission in LLDPE/OPP sheets when OPP loading increased from 0.5 g to 1 g. The authors attributed the reduction to the fact that the carotenoids present in OPP can absorb UV light.

The MB trays with 30 wt% and 35 wt% OPP had the same ($P > 0.05$) light transmission in the visible and ultraviolet regions. This light transmission was significantly lower ($P < 0.05$) than that of trays without OPP. Similarly, it was observed in Chapter 3 that a large decrease in light transmission for PLA/OPP trays were obtained by direct blend. Light transmission reduction in the presence of agrowaste has also been reported for other plastic/waste combinations. For example, Dixit & Yadav (2019) reported a reduction in the light transmission of a multilayer film made of PP and PE with the addition of wheat straw. The light transmission of PLA/OPP 30 wt% DB trays and PLA/OPP 30 wt% MB trays did not differ ($P > 0.05$) because PLA containing OPP does not change its light transmission when OPP is present in amounts of 20 wt% or higher.

4.2.2.6. Fungal Resistance

Figure 4.5 represents the results of the ASTM G21-13 fungal resistance test (ASTM, 2013b) for the PLA/OPP MB trays. According to the test, 28 days without fungal growth implies fungal resistance. However, if there is fungal growth, the test has to be terminated when a sample gets a

rating of '2', i.e., fungal growth of 10-30% of the total area of the petri dish, for comparison between control and treatments. Figure 4.5 shows that both, control (agar) and PLA/OPP 35 wt% MB trays, received a rating of '2' for *A. niger* on the fourth day while the PLA/OPP 0 wt% MB trays had same amount of fungal growth on the sixth day. Figure 4.5 also shows that the control and PLA/OPP 0 wt% MB trays received a '2' rating for *Penicillium* sp. on sixth day while the PLA/OPP 35 wt% MB trays received a '2' rating on fourth day. Based on the above results neither the trays containing OPP, nor the trays made of neat PLA show fungal resistance. In principle, the neat PLA show have acted as a barrier to the transfer of nutrients from the media that are essential for the fungi to growth. However, the PLA/OPP 0 wt% MB trays showed fungal growth. This could be due to the presence of imperfection (e.g., cracks and pinholes) that allowed the transfer of nutrients to the surface of the samples to feed the fungi. These should have been nanosized imperfections because these are not observed in Figure 4.1. The higher fungal growth on the PLA/OPP 35 wt% MB trays compared to the PLA/OPP 0 wt% MB trays can be explained by a change in contact angle for the drop of solution placed on the PLA/OPP 35 wt% MB samples that caused the drop to spread on the agar. This allowed the fungi to grow faster because of the more access to nutrients. These results indicate that the PLA/OPP MB trays may be suitable for dry/solid food packaging rather than liquid or semi-liquid food and the trays needs to be improved to avoid the transfer of nutrients.

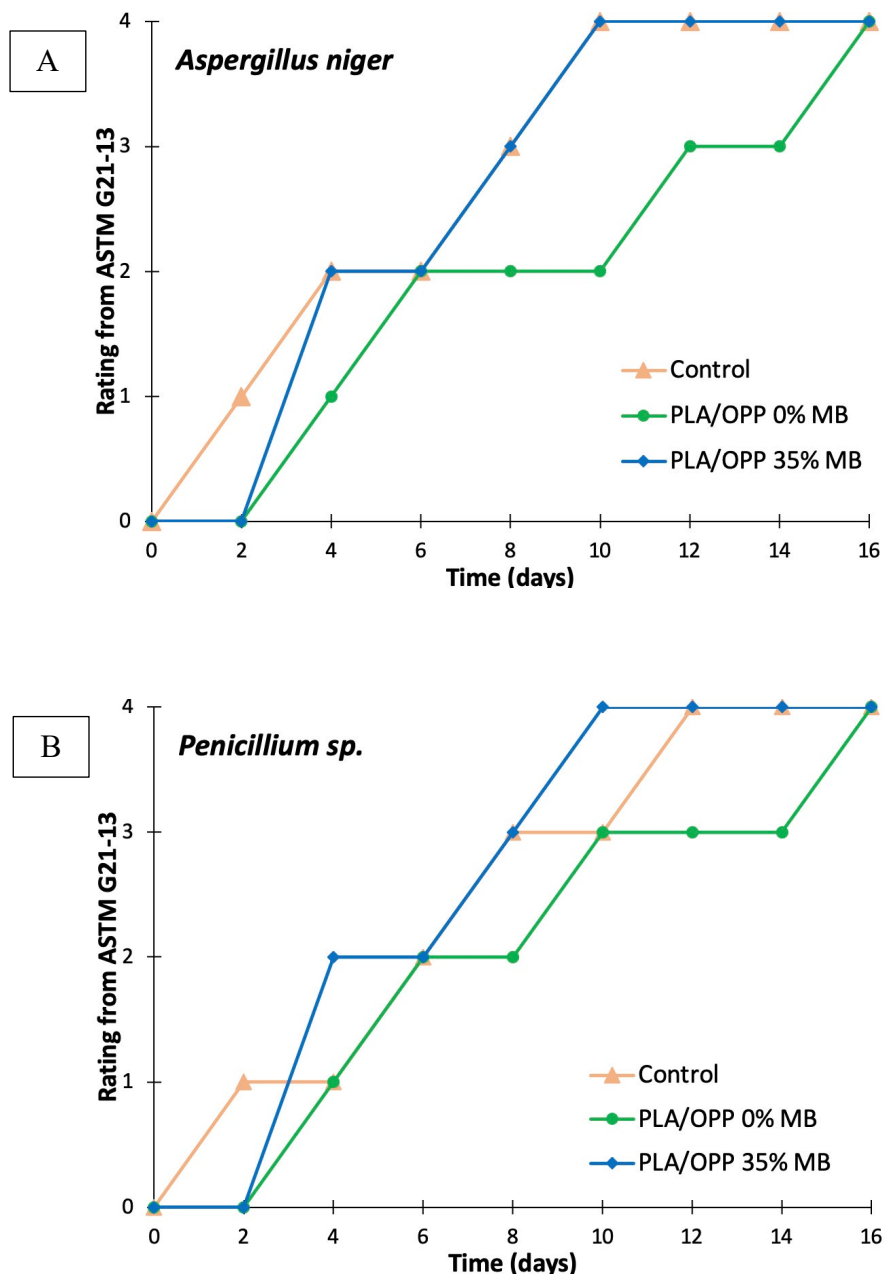


Figure 4.5. Fungal growth ratings as per ASTM G21-13 of PLA/OPP MB Trays for (A) *Aspergillus niger* and (B) *Penicillium sp.*

APPENDIX

APPENDIX

Size of OPP agglomerates in the MB trays.

Due to different OPP loading, the particle size of OPP agglomerates was different for the PLA/OPP trays. The size of OPP agglomerates was measured as shown in the below tables to understand the effect of size of agglomerates on different properties.

Table 4A1. Agglomerate measurement in cross-sectional area of size 575 x 333 μm for trays with 30 wt% MB OPP loading

Number of OPP agglomerate	30 wt% MB 1 (μm)	30 wt% MB 2 (μm)	30 wt% MB 3 (μm)
1	16.28	11.63	10.64
2	9.30	30.23	10.64
3	11.63	13.95	19.15
4	6.98	16.28	36.17
5	25.58	11.63	29.79
6	18.60	34.88	12.77
7	6.98	6.98	23.40
8	13.95	9.30	10.64
9	34.88	13.95	38.30
10	23.26	39.53	12.77
11	9.30	16.28	17.02
12	23.26	4.65	29.79
13	6.98	6.98	38.30

Table 4A1 (cont'd)

14	4.65	9.30	6.38	
15	11.63	25.58	8.51	
16	9.30	6.98	6.38	
17	16.28	9.30	19.15	
18	46.51	9.30	10.64	
19	16.28	37.21	25.53	
20	46.51	37.21		
21	32.56	11.63		
22	6.98	13.95		
23	16.28	13.95		
24	27.91	20.93		
25	11.63	6.98		
26		11.63		
Average	20.57	16.55	19.26	17.85
STDEV	17.00	10.67	10.86	11.05

Table 4A2. Agglomerate measurement in cross-sectional area of size 575 x 333 μm for trays with 35 wt% MB OPP loading

Number of OPP agglomerate	35 wt% MB 1 (μm)	35 wt% MB 2 (μm)	35 wt% MB 3 (μm)
1	34.88	20.93	25.53
2	12.77	34.88	25.53
3	23.40	46.51	23.40
4	19.15	30.23	29.79
5	14.89	27.91	23.40
6	23.40	34.88	17.02
7	29.79	30.23	23.40
8	14.89	25.58	34.04
9	14.89	25.58	19.15
10	46.81	23.26	21.28
11	14.89	27.91	27.66
12	25.53	27.91	21.28
13	36.17	39.53	29.79
14	14.89	41.86	74.47
15	19.15	48.84	27.66
16	27.66	54.05	23.40
17	29.79	54.05	36.17
18	21.28	37.84	25.53
19	19.15	40.54	

Table 4A2 (cont'd)

20	53.19	48.65		
21	46.81	67.57		
22	31.91	29.73		
23		29.73		
24		48.65		
25		56.76		
26		48.65		
27		37.84		
Average	26.15	38.50	28.25	31.79
STDEV	11.59	11.69	12.51	13.01

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CHAPTER 5

CONCLUSION

5.1 Conclusion

This study demonstrates that OPP can be used as plastic filler in commercial tray production since trays made of PLA and OPP were successfully produced using industrial thermoforming processing. Air bubble formation was the problem to overcome during the production of the PLA/OPP trays. The factors producing these bubbles were identified as larger particle size of OPP, higher moisture content and higher mixing times and overcame when using OPP having an average particle size of below 180 microns, drying the OPP using a vacuum oven to reduce its moisture content below 2 %, and by setting the mixing time, temperature, and speed at 3 minutes, 180 °C and 50 rpm respectively. The compression conditions determined to thermoform the composites allowed for a maximum amount of OPP as filler of 30% by weight since over this amount led to trays not taking the shape of the mold properly. The increase in OPP loading resulted in the formation of OPP agglomerates and voids which led to an increase in thickness UV and visible light blocking capacity, crystalline content, and a decrease in thermal stability, T_g , T_m and fungal resistance. The water vapor permeability and compression strength results were not affected statistically due to the addition of OPP. The PLA/OPP 20wt.% trays had the best dispersion due to which it had better oxygen barrier properties and darker color than the rest of the samples. Thus, the results obtained from this study proved that OPP could be blended into PLA to produce trays using industrial thermoforming equipment which will allow for reduction in plastic and agricultural waste and consequently, environmental pollution.

Additionally, the masterbatch process was used, which allowed higher incorporation of agricultural waste as plastic filler in PLA matrix. The maximum amount of OPP

that can be added to PLA was increased from 30 wt.% (by direct blending) to 35 wt.% (by masterbatch). This was caused by the production of smaller agglomerates with a better distribution that improved processability (higher tan delta). The use of MB also resulted in trays that had improved oxygen barrier, higher T_g , less thickness, and darker color that did not change in thermal stability, visible and UV light blocking capacity, T_m and crystalline content, thickness, and water vapor barrier. However, the MB trays showed a decreased compression strength because of the extra processing. Increasing the OPP content from 30 wt.% to 35 wt.% for the MB trays resulted in a decrease in processability (tan delta), T_g , oxygen and water vapor barrier, thermal stability, and fungal resistance due to increased sizes of agglomerates and voids while thickness, color, visible and UV light blocking capacity, T_m , crystallinity, compression strength and crystalline content were maintained. Therefore, the trays produced from PLA and OPP biocomposites using the masterbatch process showed that more agrowaste could be added to the polymer matrix while improving some properties, thus replacing more plastic with waste for producing packages.

5.2 Future Work

This study focused on developing trays made from PLA and OPP waste and increasing the amount of OPP that can be added to the polymer matrix. Compatibilizers were not used during this study mainly due to cost addition but could be used in further studies to investigate the possibility of the addition of more OPP to the polymer matrix when producing trays. The composite trays were not tested for any specific applications like food packaging etc. Shelf-life studies on food products by packaging in these trays can be performed in the future. Also, the tray can be claimed to be biodegradable based on the biodegradable nature of materials used to prepare them which are PLA and OPP, but any biodegradability tests were not performed during this study and can be performed in the future to prove if the packages are biodegradable or not.