THE USE OF WASTE FROM ORANGE JUICING FOR FOOD PACKAGING APPLICATIONS

By

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ABSTRACT

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Utilization of orange juicing waste (OP) as a filler material within a polymer matrix can add value to this agricultural waste and reduce dependency on non-renewable resources. This study aims to study the impact of OP filler's physical characteristics including size, loading, and retention or removal of zest on the properties of linear low density polyethylene (LLDPE) and to produce LLDPE/OP films by blown-film extrusion. LLDPE/OP sheets with zest exhibited decreased thermal stability, larger OP agglomerates, worsened dispersion, and darker yellower colors and can act as UV- and light-absorbers. Larger OP particles increased air bubble formation, decreased mechanical properties, worsen dispersion, and produced darker yellower composites. Higher OP loadings resulted in LLDPE/OP composite sheets that have darker yellower color, decreased mechanical properties, and increased the size of OP agglomerates, as well as improved distribution and worsened dispersion. LLDPE/OP sheets that had properties most like neat LLDPE were sheets containing OP without zest and smaller particles sizes. This OP was used to determine maximum OP loading for LLDPE/OP films produced by blown-film extrusion. The LLDPE/OP films were subject to a sensory similarity triangle test and a comparison of package acceptance when different OP loading was used. This study found no difference in sensory qualities of bread when packaged in LLDPE/OP to neat LLDPE films. OP loading did not influence consumer perceptions of overall liking, appearance, surface roughness, color, or smell when LLDPE/OP films with 5 and 11.5% OP loadings were compared. This study demonstrates that OP waste can be converted and physically modified into a usable filler for plastic films for food packaging applications without altering the quality of the food product.

Dedicated to my parents
Gary Fehlberg, Joan Kresnak-DiLaura, and Kenneth DiLaura

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Agricultural waste management and disposal has become a growing concern because of the negative effects on the environment [1]. Consequently, several methods have been developed to allow the conversion of these wastes into other reusable formats, such as nutraceuticals, cattle feeds, and food additives [2, 3, 4, 5]. Combining agricultural waste with petroleum-based plastics for development of packaging materials is an easy way to add value to a renewable waste while reducing the consumption of a non-renewable resource by replacing a portion of this. This fully aligns with current societal trends that have moved towards the use of renewable packaging materials because of increasing environmental awareness, decreasing oil reserves, and meeting the demands of legislative authorities [6]. Consequently, extensive research has been conducted to evaluate the addition of agricultural wastes into petroleum-based polymer matrixes. Examples of agricultural wastes investigated include fish gelatin [7,8], chitosan from blue crabs [9], grape pomace, turmeric shavings, coffee grounds, apple peels, sugar cane bagasse [10], and orange peels (OP) [10, 11,12, 10, 13].

OP waste has gained a lot of attention due to substantial worldwide production of oranges (over 66,974 metric tons in 2016) that are converted into orange juice [14] since 50 - 60% of each orange juiced becomes waste [15]. OP waste is generally converted to citrus pulp pellets for cattle feed [15] or discarded in landfills [16]. Innovative ways to use OP waste have led to exploring its integration into plastics to add value to the waste while reducing the plastic source similar to other agricultural wastes. Iyer et al. (2015) after combining LDPE with 8% OP powder by single screw extrusion and compression molding found that OP powder behaved like a thermo-oxidative stabilizer enhancing the reprocessing and recycling by suppressing LDPE chain scission and branching [13]. OP was compounded into high density polyethylene (HDPE) at 5, 10, 15, 20, and 25% OP loadings in a two roll mill and then thermoformed with a hydraulic press, which resulted in composite sheets with increased tensile strengths and stiffnesses [11]. Abass (2015) observed a similar increased tensile strength in plate casted films when 10% of OP was combined with NYCIL 6043 polyester resin and methylethylketone peroxide catalyst (MEKP) compared to the pure polyester resin and MEKP [17]. Compression molded LDPE combined with 5% OP and ferric salt increased photo-oxidative degradation rates of the composite sheets compared to neat LDPE [12].

Based on the above studies, OP waste can be used as a filler, thermo-oxidative stabilizer, colorant, UV- absorber, light-absorber, antimicrobial, and antioxidant for plastics. This impressive list shows significant upside potential for OP waste in food packaging. Though composites containing OP have been produced using compression molding and plate casting, these processes are not as widely used to manufacture packaging materials for food applications, like that of blown film extrusion. The effects of the OP filler's physical characteristics on the properties of a polymer matrix have not been investigated yet. This information is crucial for the successful development of materials (e.g., films, sheets, and bottles) that can be used for food packaging applications, one of the largest markets for plastics. This study aims to fill gaps of knowledge by studying the impact of OP filler's physical characteristics including size, loading, and retention or removal of zest on plastic properties of interest for food packaging applications. This study also aims to produce composite films containing OP using blown film extrusion and to determine the maximum amount of OP that can be incorporated into a plastic. LLDPE was selected as the polymer matrix due to its substantial growth and widespread use in food packaging [18].

1.2 Objectives

The overall goal of this study is to develop plastic composite sheets and films incorporated with OP for food packaging applications through standard packaging industry processes. Specific objectives include:

1. Develop a filler from OP to create plastic composite materials for food packaging applications
2. Determine the effects of OP powder’s physical properties (e.g. retention/absence of zest, particle size, and loading) that affect the characteristics of plastic composites
3. To produce OP composite films using blown film extrusion and determine maximum loading
4. To evaluate consumer sensory perceptions of a food product packaged in a film containing OP including product quality and material likeness

1.3 Hypotheses

The hypotheses of this study are: (1) OP waste can be converted into a usable filler for plastic films for food packaging, (2) the OP filler's physical properties (absence/presence of zest, particle size, and loadings) when mixed with the plastic will have an influence on the composite's characteristics, (3) OP composite films can be produced blown film extrusion, and (4) OP composite films can be used for food packaging applications without affecting food product's shelf life compared to neat films.

1.4 Structure of thesis

The first chapter of the thesis introduces the rationale of this research. Chapter 2 is a background on polymer composites and additives, in addition to previous research of agricultural fillers that have been introduced into petroleum-based polymer matrices. The process of OP conversion into a usable filler format and its characteristics that affect the characteristics of LLDPE are and discussed in chapter 3. Chapter 4 explores the maximum amount of OP loading in LLDPE films produced by blown film extrusion, as well as evaluates bread packaged with LLDPE/OP films by sensory evaluation. Chapter 5 gives the summary of the findings inferred from the experimental data and proposed future works.

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CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

Consistent with the scope of this study, a background and literature review on the current use of agricultural waste as a filler for plastic polymer composites for food packaging applications are presented in this chapter. The review focuses on processing techniques used to manufacture composites containing agricultural wastes, specifically produced from orange juicing waste.

2.2 Polymer composite

Polymer composites are a heterogeneous material comprising of different (nongaseous) phase domains in which at least one phase domain is a continuous or polymer phase [1]. Composites are made of two constituent materials are significantly different in physical or chemical properties that, when combined produce a material with characteristics different from the individual components; the individual components remain separate and distinct within the final composite structure [2,3]. Polymer composites have been used for a wide range of industries including aerospace, construction, and automotive industries for their light weight and high specific stiffness and strengths [4]. Common production methods for polymer composites include extrusion, injection molding, injection blow molding, compression molding, co-extrusion process, and thermoforming processes [5,6,7]. Whichever method used to produce polymer composite, two constituents are required: a polymer matrix and reinforcement filler.

2.3 Components of polymer composites

2.3.1 Polymer

International Union of Pure and Applied Chemistry (IUPAC) defines polymer as a substance made of large molecules that is characterized by the multiple repetition of one or more group of atoms (called monomers or constitutional units) linked to each other covalently in amounts sufficient to provide a set of properties that do no vary markedly with the addition or removal of one or a few of the constitutional units [8]. There are different types of plastic polymers including plastics low-density polyethylene, high-density polyethylene, polypropylene, polyvinyl alcohol, etc. [9]. This research will be focusing on LLDPE.

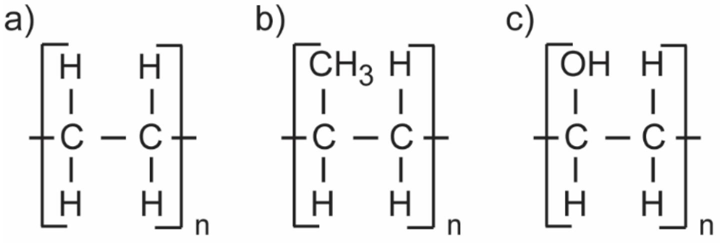

Figure 2.1 Chemical structures of a) polyethylene, b) polypropylene, and c) polyvinyl alcohol.

2.3.1.1 Linear low density polyethylene

LLDPE is a copolymer which is polymerized with comonomer alkenes such as butene, hexene, and octene (Table 2.1) and stereo-specific catalyst [9]. The density of the polymer depends on the amount of comonomer, the higher amounts of comonomer the lower the density of the copolymer [9]. Packaging applications of LLDPE is are stretch/cling film, grocery sacks, and heavy-duty shipping sacks [9]. Comparisons of LLDPE properties with other petroleum-based polymers properties are displayed in Table 2.2.

Table 2.1 LLDPE comonomer alkenes molecular formulas [9].

Comonomer alkenes	Molecular formula
Butene	$H_2C = CH\ CH_2\ CH_3$
Hexene	$H_2C = CH\ (CH_2)_3\ CH_3$
Octene	$H_2C = CH\ (CH_2)_5\ CH_3$

Table 2.2 Comparison of LLDPE properties with other petroleum-based polymers common properties [9,10,11,12,13].

Properties	**LLDPE**	**LDPE**	**PET**	**PS**	**PP**
T_g (°C)	-5	-5	75	105	-10
Density	0.9	0.9	1.3	1.1	0.9
Ultimate tensile strength (MPa)	31.0	19	55	45	31
Tensile Modulus (GPa)	0.22	0.17	2.76	2.90	0.90
Elongation at break (%)	745	500	130	7	120
Water vapor permeability at 23°C ($x10^{-15}$ $kg*m/m^2*s*Pa$)	2.2	1.5	1.1	6.7	2.3

2.3.2 Reinforcement fillers

Generally, fillers are non-plastic substances incorporated into a plastic to reduce its cost or improve its performance [9,14]. They can be used to improve the mechanical, thermal, barrier, etc. properties of plastics. There is a significant diversity in chemical structures, forms, shapes, sizes, and inherent properties of fillers [14,15]. Though there are a vast variety of fillers, they can be categorized into two major groups, inorganic and organic.

2.3.2.1 Inorganic fillers

Inorganic is defined as being or composed of matter other than plant or animal [16]. The most widely used inorganic filler for plastic polymers is calcium carbonate [9]. Other inorganic fillers include carbon fibers, alumina trihydrate, silica, talc, etc. Inorganic composite materials have wide applications in many higher end industries such as sporting facilities, medical, aerospace, turbines, and indoor decorations [17].

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2.3.2.3 Organic fillers

The Webster's Dictionary defines organic is defined as of, relating to, or derived from living organisms [18]. Organic fillers consist of graphite fibers and flakes, cellulose fibers, wood flour, flax, cotton, sisal, etc. [15]. One area of organic fillers that have gained attention for the past few decades are those produced from agricultural wastes.

2.4 Agricultural wastes

Agricultural wastes can be natural (organic) and non-natural (e.g. packaging materials, plastics, tires, and oil) wastes and used to describe wastes produced through farming activities, such as dairy farming, horticulture, seed growing, livestock breeding, grazing land, etc. [19]. The wastes produced from agriculture have proven to have detrimental effects on the environment and are major sources of pollution to land and water resources [20]. Rotten agricultural wastes produce methane and leach ate, and open burning by farmers to clear their lands produced carbon dioxide and local pollutants [21]. Examples of natural agricultural wastes are Tunisian vine stem wastes, cotton burr [23], grape pomace, coffee grounds, turmeric wastes [24], chitosan from blue crabs [25], sugar cane bagasse, apple peels [26], OP [24,25,26,27,28], etc. To see the positives and negatives effects of agricultural fillers in plastics, please refer to Table 2.3.

Table 2.3 Examples and properties of plastics affected by agricultural fillers.

Polymer	Filler	Loading (%)	Processing	Improvements	Negatives	Source
LDPE	Tunisian vine stem wastes	30	Compression molding	Melting (T_m) and glass transition (T_g) temperatures remained constant as filler loading increased Crystallization increased as filler loading increased Increased Young's modulus strength resulting in 3 times higher strength	Elongation at break decreased as filler increased Stiffer Increased water uptake as filler loading increased	[22]
LDPE	OP grape pomace (GW) coffee grounds (CG) turmeric wastes (TW)	8 OP 4 GW 12 CG 8 TW	Single screw extrusion, compression molding	Enhanced reprocessing and recycling by behaving like a thermo-oxidative stabilizer that suppressed chain scission and branching	Reduction of elongation at break	[24]
LDPE	OP with ferric salt	5	Compression molding	Increased photo-oxidative degradation rate		[29]
LDPE PLA	Cotton Burr	10 20 30	Injection molding	PLA T_g decreased as filler loading increased.	LDPE Crystallinity decreased as filler increased Decreased tensile strength, elongation, Young's modulus as filler loading increased Rough SEM PLA Decreased tensile strength, elongation, and Young's modulus decreased Smoother SEM (when compared to LDPE)	[23]
HDPE	OP in their carbonized and uncarbonized forms	5 10 15 20 25	Compression molding	Tensile strength, stiffness, hardness increased with amts to 25% where it decreased dramatically	Decreased strain at failure as filler loading increased resulting in a stiffer material	[30]
PP	Rice husk ash	5 10 20 30 40	Injection Molding	Increase in Young's Modulus Increase in yield strength No changes to T_c and crystallinity Increased thermal degradation temperature	Decrease in elongation at break Increase in hardness	[31]

Table 2.3 (con't)

Polymer	Filler	Loading (%)	Processing	Improvements	Negatives	Source
Maleated (5%) PP	Olive stone flour	Up to 70	Injection molding	Increase in Youngs modulus as filler loading increased, however 70% without compatibilizer decreased Compatibilizer improved dispersion	Decreases in impact and flexural strength at filler loading increased, resulting in a stiffer material Increase water absorption properties as filler loading increased	[32]
PVOH	Apple pomace (AP)	1 5 10 30	Plate casting	Improved antioxidant properties and reduced lipid oxidation of soybean oil	Decreases in tensile strength and elongation at break, and transparency as filler loading increased. Rougher surfaces Increased oxygen transmission rates at 10% filler loading	[33]
PVOH Corn Starch 22% glycerol, urea, water	Sugarcane bagasse, apple and orange waste	Up to 22	Compression molding	PVOH and starch with apple and sugarcane bagasse inc. hardness than OP No effect on degradation of lignocellulos fibers		[26]
Poly(3-hydroxybutyrate-co-valerate) and polylactic acid (PLA) blends (60:40 wt%)	Soy hull, switchgrass miscanthus	30	Injection molding	Increased Flexural Modulus No changes melting peak, melting enthalpy and crystallinity	Lower tensile strength and elongation at break due to poor adhesion between fiber and matrix Lower impact strength Increased water absorption	[34]
Poly (butyleen adipate-co-terphthalate	Coffee grounds, untreated and torrefied (heated to removed water and volatiles)	10 20 30	Batch cast film extrusion	Filler behaved as a nucleating agent producing higher crystallization No changes in T_g, except PBAT/CG30-270C were T_g increased Increases in wettability as untreated filler loading increased	Increased Tm and ΔH_m slightly Decreased tensile strength and strain at break as filler loading increased Worsened dispersion and increased voids within polymer as filler loading increased	[35]
Polyester	OP	2 4 6 8 10	Plate Casting	Increases in impact strength, hardness, and tensile strength filler loading increased	Stiffness increased	[36]
PLA	Wheat straw, corn stover, soy stalks	30, 10 hybrid combination	Injection molding	Increased density Reduced molecular weight 20-30% No effect T_g and T_m Reduction in ΔH_m and H_c Decreased T_c	Increased stiffness, reduced toughness, and elongation SEM showed voids and fiber pullout that may have contributed to the observed reduction in tensile, flexural, and impact strength	[37]

2.4.1 Agricultural wastes from oranges

Valencia oranges (*Citrus sinensis*) are round fruits that grow on small trees or shrubs, and have leathery and oily rinds and edible, juicy inner flesh [38]. The chemical make up of Valencia oranges are displayed in Table 2.4 [39]. Generally, orange flesh is used for flavoring agents, jams, marmalades, or fresh juice [40]. The main orange wastes are obtained from the orange juicing industry. In 2016, about 67 million tonnes of oranges were produced worldwide, the world's leading producers of oranges are Brazil, United States, Egypt, Spain, China, and India [41]. A substantial portion of orange's are converted into juice (e.g., approx. half of the oranges harvested in the United States) and when juicing, the 50-60 percent of the OP becomes wastes in the form of peels, seeds, and membranes.

Table 2.4 Valencia orange's percentage composition of chemical constituents identified in hexanic extracts [39].

Compound	Chemical constituents (%)	Compound	Chemical constituents (%)
Hydrocarbons		**Aldehydes**	
Monoterpenes		***Monoterpenes***	
α-Pinene	0.24	Dodecanal	0.02
Sabinene	0.12	**Ketones**	
β-Myrcene	0.96	Nootkatone	0.47
α-Phellandrene	0.01	**Alcohols**	
δ -3-Carene	0.01	***Monoterpenes***	
D-Limonene	96.47	Linalool	0.48
cis-Ocimene	0.07	α-Terpineol	0.06
α-Copaene	0.01	Geraniol	0.02
Calarene	0.02	Elemol	0.01
trans-Caryophillene	0.01	1-Octanol	0.07
epi-*byciclo* Sesquiphellandrene	0.02	Linalyl acetate	0.01
Valencene	1.04	Limonen-10-ylacetate	0.01
δ -Cadinene	0.02	**Oxides**	
Citronellal	0.02	***Monoterpenes***	
Z-Citral	0.02	Trans limonene oxide	0.02
E-Citral	0.03	**Others**	
Octanal	0.1	Oxacycloheptadec-8-en-2-one	0.02
Decanal	0.12		

2.4.1.1 Orange Waste Reuse

Generally, the wastes produced from orange juicing is dried and pelletized to produce a low value cattle feed called citrus pulp pellets or discarded in the land fill [42]. For orange juice waste, less common applications include the production of limonene, ethanol, molasses [43], and adsorbents for water treatment [44,45].

2.5 Composites produce with orange wastes

Some research has focused on the use of OP waste within a polymer matrix. Iyer et al. reported the effectiveness of OP powder within low density polyethylene (LDPE), and found that the OP powder performed better than a synthetic antioxidant at suppressing LDPE chain scission and branching, which improved reprocessing and recycling [24]. LDPE films containing OP combined with ferric salt exhibited increased photo-oxidative degradation rates than that of plain LDPE films [29]. OP were used to reinforce high density polyethylene in their carbonized and uncarbonized forms to produced molded composites that displayed increased hardness, tensile, and bending strengths [30].

2.6 Agricultural waste composites with food packaging applications

Casted films produced from Kluai Namwa banana flour and chitosan, a byproduct from the shrimp industry, were used to package asparagus, baby corn, and Chinese cabbage [47]. These films exhibited antimicrobial capabilities and extended shelf life of fruits and vegetables. Food packaging films were produced from polyvinyl alcohol (PVA) combined with apple pomace, a byproduct from apple juice industry, to reduce lipid oxidation of soybean oil [32]. Hanani et al. (2018) produced films by combining the fruit peel powders of pomegranate, papaya, and jackfruit with a fish gelatin/polyethylene bilayer for active packaging to effectively improved the antimicrobial and antioxidant properties [48,49]. Mango peel extract incorporated into fish gelatin films was developed for active food packaging and was found to decrease the water vapor permeability, and increased concentration of mango peels extract improved free radical scavenging activity [49]. Films were casted from a solution of chitosan extracted from blue crab and pectin from OP, and when compared to commercial films of pectin and chitosan with no significant effect to degree of swelling and water vapor permeability and the blended films were less stiff than films based on only one biopolymer [50].

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CHAPTER 3

PRODUCTION AND CHARACTERIZATION OF LLDPE/OP COMPOSITES

3.1 Materials and methods

3.1.1 Development and characterization of orange peel powder

3.1.1.1 Material

Valencia oranges (*Citrus sinensis*) were purchased from a local supermarket (Meijer, MI, USA). This orange variety was chosen because it is the most common variety for juicing worldwide.

3.1.1.2 Juicing processes that resemble the orange juicing industry

Purchased oranges were washed to remove debris and divided into two groups with the same number of oranges. The oranges from one group had their zest (outermost part of the OP) removed by a peeler (IKEA, MI, USA) while this was kept in the oranges of the other group. Subsequently, all oranges were cut in half using a kitchen knife and pressed to remove membranes and juice using a Breville 800CPXL Die-Cast Stainless-Steel Motorized Citrus Press (Melbourne, Australia). The resulting rinds with and without zest were cut into quarters for further processing using the aforementioned knife.

3.1.2 Orange peel powder production

The rind quarters obtained in section 3.1.1.2 were dried using a freeze dryer (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 brittle OP were run through a hammer mill (Whirlpool Corp, MI, USA) with a screen (040 1A) to obtain a powder. The OP powder was then sifted through a series of standard sieves (Dual Manufacturing Co., IL, USA) with different pore sizes (75, 177, 300, 355, and 420 µm) to separate its particle sizes. The sizes retained for further investigation were those between the range of 75-177 and 355-420 µm. The different OP powder samples (75-177 µm with zest, 75-177 µm without zest, 355-420 µm with zest, 355-420 µm without zest) were placed into LDPE Ziploc® bags and stored in a desiccator to prevent the powders form absorbing moisture.

3.1.3 Thermal analysis of OP powder

The procedure to determine OP powder thermal stability and material loss for composite development was in accordance to methods described by Morais et al. [1] with modifications. Thermogravimetry was performed using a TGA Q50 thermogravimetric analyzer (TA instruments, DE, USA) under a nitrogen-air flow of 40-60 mL per min. Between 7 to 8 mg of each OP powder was placed in a standard aluminum pan (TA Instruments, DE, USA) and heated from 25 to 400 °C at a rate of 10 °C per min.

3.2 Production and characterization of LLDPE/OP Powder composite sheets

3.2.1 Materials

Linear low density polyethylene (LLDPE; Dowlex 2045G; density = 0.920; melt index = 1 g per 10 min) was provided by DOW Chemical (MI, USA) and the OP powders were produced in section 3.1.2.

3.3 Production of LLDPE/OP powder composites

3.3.1 Production of LLDPE/OP powder composite sheets

Specific masses of the four OP powder samples produced in 3.1.2 and of LLDPE were measured using an analytical balance (Voyager, Ohause, NJ, USA) with an accuracy of +/- 0.0001 g to produce different composites (Table 3.1). The two materials in the amounts presented in Table 3.1 were combined in a 250 mL Pyrex beaker (Corning, NY, USA), stirred by a metal rod for 30 seconds, and then placed in a co-rotating segmented twin-screw mixer (TSE DSE 25, C.W. Brabender Instruments Inc., NJ, USA) operating at 140°C and 30 RPM for 3 minutes. A total of 6 different composites were produced with at least three replicates of each type. Composites differed in OP powder loading (0.4-0.5 vs. 1.0 g), particle size (75-177 vs. 355-420 µm), and zest (yes vs. no). Controls were obtained by weighing 10 g of LLDPE 3 times with the aforementioned analytical balance and placing each of these in the twin-screw mixer.

Table 3.1 Amounts of LLDPE and OP powder used to produce the neat LLDPE (control) and LLDPE/OP powder composites (treatments).

Materials		**Formulations**	
		Wt. (%)	**Mass (g)**
	Control		
LLDPE		100	10.0 ± 0.0
	Treatments		
LLDPE		95-96	10.1 ± 0.2
OP powder	Zest	5	0.5 ± 0.0
	No zest	4	0.4 ± 0.1
LLDPE		90	9.1 ± 0.2
OP powder	Zest	10	1.0 ± 0.2
	No zest	10	1.0 ± 0.2

3.3.2 Characterization of LLDPE/OP Powder composite sheets

The composites produced in section 3.3.1 were placed between two sheets 30.48 x 30.48 x 0.00762 cm of aluminum (Strongsville, OH, USA) and flattened with a hydraulic press (Model-M, Carver Laboratory Press, Carver Inc., IN, USA) set at 140 °C and 137.9 +/- 6.9 MPa for 3 minutes. The resulting LDPE/OP powder composite sheets were then cooled at room temperature (23 °C) for 15 minutes, prior to removing the aluminum sheets. The resulting composite sheets were then cut into 17.78 x 2.54 cm strips by a combination of a JDC precision sample cutter (Thwing-Albert Co., NJ, USA) and a paper cutter (Premier Brand, NJ, USA; Figure 3.1). The thicknesses of resulting 3 to 4 strips were measured in three locations, along their length, using a digital micrometer (TMI Group of Companies, DE, USA). The average thickness of the strips was 0.322 +/- 0.023 mm.

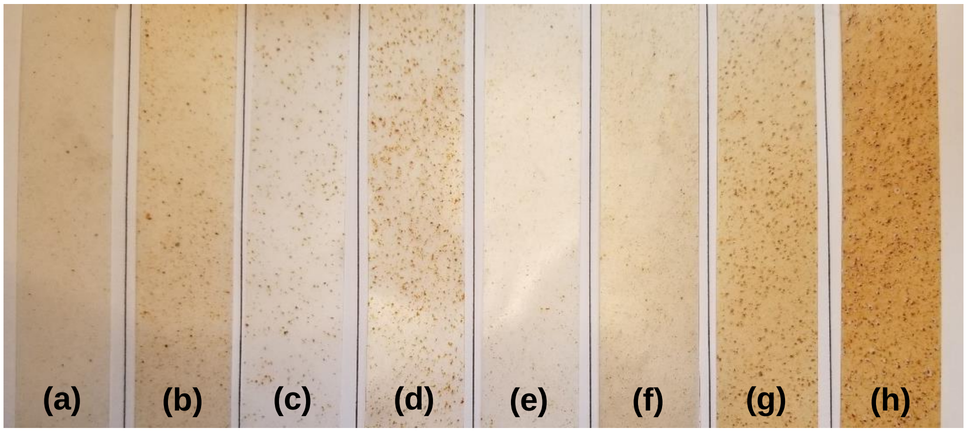

Figure 3.1 LLDPE/OP sheets (a) no zest 75-177 µm 0.4g (b) no zest 75-177 µm 1g, (c) no zest 355-420 µm 0.4g, (d) no zest 355-420 µm 1g, (e) zest 75-177 µm 0.4g, (f) zest 75-177 µm 1g, (g) zest 355-420 µm 0.4g, and (h) zest 355-420 µm 1g.

3.3.3 Number of air bubbles per gram of OP powder

Photos of three random locations of each replicate produced in section 3.3.1 were taken using the micro-optics image system of an Olympus SZX-ZB12 microscope (Tokyo, Japan) at 7x magnification. A photo of a clear metric ruler was taken in the same way. The photos were saved in a computer using Magnafire SP (Olympus; Tokyo, Japan). Photoshop (Adobe Systems, CA, USA) was used to embed the ruler's image within the sample's images to obtain the field of view of 12.3 x 10 mm. The air bubbles present in the aforementioned area were counted by eye. The number of air bubbles was divided by the amount of OP powder (g) used to produce the composite in order to determine the effects of OP powder loading, OP powder size, and presence or absence of zest in the OP powder on the number of bubbles formed. The results are presented as number of air bubbles per g of OP powder.

3.3.4 Average size of OP agglomerates and number of OP agglomerates per mm2 of composite sheet

The effects of OP powder loading, OP powder size, and presence or absence of zest in the OP powder on the average size of the OP agglomerates and on the number of OP agglomerates per mm^2 of composite sheet were determined using Adobe Photoshop (Adobe Systems, CA, USA) and Java-based image processing software ImageJ (National Institutes of Health, MD, USA). Adobe Photoshop was used to correlate ImageJ pixels and mm (105 pixels = 1 mm) and after the scale was set in ImageJ, the photos used in section 3.3.3 had their contrast and brightness adjusted, as well as their backgrounds subtracted. Next, the photos were converted into 8-bit files and the threshold settings were adjusted between a range of 0 and 200 units. Additionally, for image analysis, the particle size was set from 0 to infinity mm^2, with the circularity of the particles ranging from 0.05 (least like a circle) to 1.00 (perfect circle). The software counted the number of OP agglomerates and measured their sizes (area). The information was used to determine the number of OP agglomerates per mm^2 of composite sheet and the average size of OP agglomerates. The results are presented as μm^2 for average size of OP agglomerates and the number of OP agglomerates per mm^2 of composite sheet.

3.3.5 Distribution and dispersion

Adobe Photoshop (Adobe Systems, CA, USA) in combination with Excel (Microsoft, WA, USA) were used to determine OP agglomerate dispersion and distribution as affected by OP powder loading, OP powder size, and presence or absence of zest in the OP powder. Each of the three composite sheets per treatment produced in section 3.3.1 had photos taken at three different points. Using Adobe Photoshop, each photo was covered with a black foreground containing four square windows of 152 by 152 pixels each to allow the random selection of one photo portion using Excel. The obtained portions were then grouped according to the OP powder loading, OP powder size, and presence or absence of zest in the OP powder of the initial composite sheets. An example of the grouping of the nine portions per treatment is shown in Figure 3.2(a). The portions that did not match the overall trend of the same treatment were removed as represented in Figure 3.2(a) by the use of crosses. OP agglomerate dispersion in each group was determined by measuring the largest agglomerates found in each of the portions with a ruler to the nearest +/- 0.1 mm as shown by the circles in Figure 3.2(a). Next, the groups were ranked from best dispersion (smallest agglomerate size) to worst dispersion (largest agglomerate size). OP agglomerate distribution was determined by visually comparing each of the portions of the group with the scale shown in Figure 3.2(b), which ranged from 1 (poor distribution) to 5 (excellent distribution). Due to space limitation, a portion that represents the OP agglomerate dispersion and the OP agglomerate distribution within the same treatment is presented in the results.

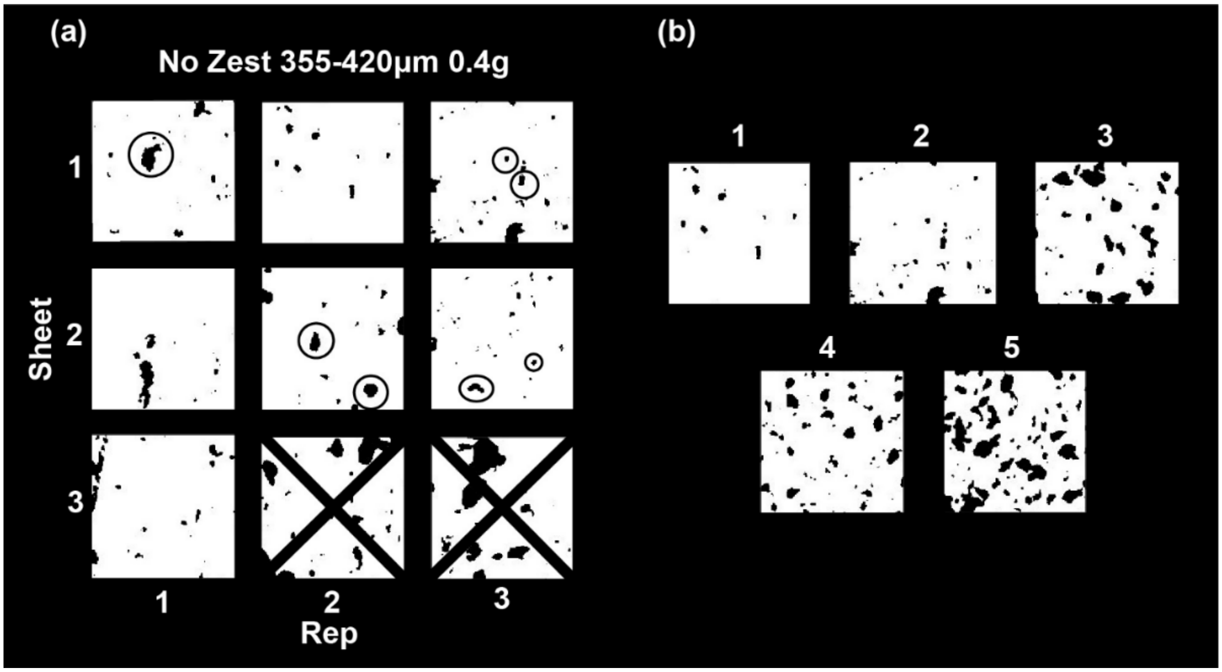

Figure 3.2 (a) Example of grouping of portions per treatment and (b) scale used to measure OP agglomerate distribution.

3.3.6 Mechanical properties

The effects of OP loading, OP size, and presence or absence of zest in the OP on the tensile strength at yield and modulus of elasticity (MOE) of the composite sheets was determined using a 5565P6021 Instron Universal Testing Machine (Instron Engineering Corporation, MA, USA) according to the ASTM D882-18[3]. Samples produced in section 3.3.2 were tested with a cross head's initial grip separation of 50 mm and a rate of grip separation of 500 mm/min. Results are given in MPa for tensile strength at yield and GPa for MOE. Five replicates with were tested, at least 1 sample from each LLDPE and LLDPE/OP sheet.

3.3.7 Water vapor barrier

The water vapor permeability coefficients of the LLDPE/OP sheets with closer mechanical properties to those of the neat LLDPE sheets were calculated with a Mocon Permatran-W Model 3/33 (USA) according to the ASTM F1249-13 [4]. Samples from each sheet replication, produced in section 3.3.2, were cut from random film locations with scissors and masked with 101.6 µm-thick aluminum foil adhesive backed (McMaster-Carr, IL, USA) with a testing area of 0.79 cm^2 prior to being placed into the equipment's permeation cells. At least one sample from each film replication was tested at ambient conditions ($23^{\circ}C$ and 50% RH). Results are given in $kg*m/m^2*Pa*s$. Five replicates were tested, with at least 1 sample from each LLDPE and LLDPE/OP sheet.

3.3.8 Color

The effect of OP powder loading, OP powder size, and presence or absence of zest in the OP powder on the color of the composite sheets was determined using a spectrophotometer (LabScan XE, Hunter Associates Laboratory, Inc., VA, USA). The samples produced in section 3.3.1 were placed over a view plate area of 3.2 mm^2 and their CIELAB color coordinates L* (brightness), a* (+ red to - green), and b* (+ yellow to - blue) were recorded using the EasyMatchQC application software. a* and b* were used to calculate Hue angle (h*), which was adjusted in the case of negative a* values in accordance to McLellan et al. [2]. The color results are presented as h* vs. L*.

3.3.9 Transmittance

The effect of OP powder loading, OP powder size, and presence or absence of zest in the OP powder on the transmittance of the composite sheets was evaluated with an UV/vis spectrophotometer (Lambda 25 Perkin Elmer Instruments, MA, USA) coupled to a computer with the UV WinLab application software. The samples produced in section 3.3.1 were place in an aperture with a 1.0 slit, and were then measured within spectral ranges of 190 to 900 nm with a scan speed of 480 nm per min.

3.4 Statistics

Each of the three to four sheets (replicates) of each type of LLDPE/OP powder composite was measured in three to four different locations (blocks). Outliers within the same type and amount of OP powder were removed before data analysis using the Modified Thompson-Tau test [5]. The factor color wavelength range (i.e., 380-450 nm is violet) was also taken into consideration for outlier removal in the case of the parameter transmittance. For statistical analysis, MINITAB 17 (Statistical Software for PC/Windows, Minitab Inc., PA, USA) was first used to average the repeated measurements (across composite sheets and locations) resulting from the effect of the OP powder's factors zest (yes vs. no), loading (0.4-0.5 vs. 1.0 g), and particle size (75-177 vs. 355-420 µm) to obtain a descriptive summary (including the mean and standard error) of the parameters OP powder thermal stability, OP powder material lost at 150 °C, number of air bubbles per gram of OP powder, average size of OP agglomerate, number of OP agglomerates per mm^2 of composite sheet, distribution, dispersion, color, and transmittance. Subsequently, a general liner modeling (GLM) approach to the analysis of variance (ANOVA) of three-way factorial designs with the Tukey Method [6] for all pairwise comparisons (controlling the family-wise error rate of 0.05) was used to examine the main effects and interactions of OP powder's loading, particle size, and presence or absence of zest on the aforementioned parameters. Moreover, to gain a better understanding of the influence of small particles on air bubbles, further statistical analysis of interaction assessment was performed to determine if there was any combined effect of zest and loading conditional on the 75-177 μm range of OP powder. Note that the assumptions of normality, independence, and homogeneity for random errors are considered in all analyses for estimation (maximum likelihood) and interference (generalizability).

3.5 Results and discussion

3.5.1 Thermogravimetric analysis of OP powder

The effects of both zest and particle size on OP powder's degradation temperature were studied to determine their impact on composite processing. The zest () had a significant effect ($P = 0.002$; Table 3.3) on the temperature at which the OP powder degraded, irrespective of particle size. Its removal from the OP resulted in an OP powder more resistant to higher temperatures (147-148 vs. 141-143 °C for OP powder without and with zest, respectively). This could be attributed to the zest's components having lower thermal stability compared to those of the white spongy portion of the OP left behind after zest removal (albedo). For example, the orange zest possesses oil sacs that contain oils like trans-caryophillene and α-pinene [7] with boiling points close to 140 °C [8]. Furthermore, the removal of the zest results in an OP power with less water content and the weight loss of the OP towards 150 °C has been associated with water loss [1]. In agreement with the previous statements, the OP powder without zest had about 3% less material loss than the OP powder with zest (Figure 3.3) ($P = 0.000$; Table 3.3). Regarding particle size, this did not affect ($P > 0.05$; Table 3.3) either the degradation temperature of the OP powder or the amount of material lost from it. Based on these results, the OP powder without zest is a better option for the formation of plastic composites because it exhibits better thermal stability and losses less material at 150 °C. However, LLDPE composites containing OP powder with zest were produced in order to thoroughly investigate the effect of retaining versus removing the zest on properties of the composite sheets that may be crucial to develop novel packaging materials.

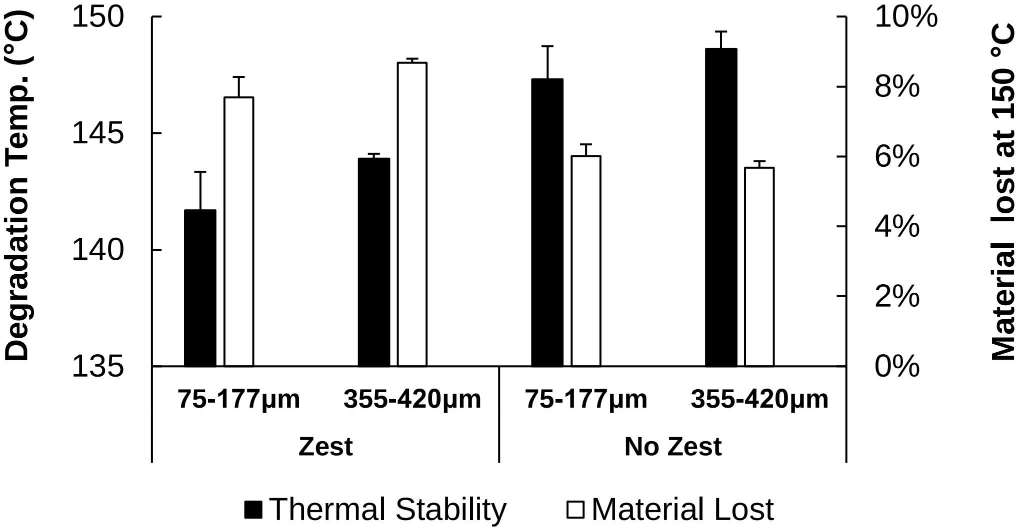

Figure 3.3 Effect of presence/absence of zest and particle size on OP powders' thermal stability and material loss at 150 °C.

3.5.2 Number of air bubbles per gram of OP powder

The effect of presence/absence of zest, particle size, and loading of OP powder on air bubble formation within the LLDPE/OP powder composite sheets is presented in Figure 3.4. The particle size of the OP powder affected the number of air bubbles (P = 0.000; Table 3.3). The smaller the particle size, the lesser the number of air bubbles formed (3 air bubbles per g of OP powder for 75-177-µm particle size vs. 22 air bubbles per g of OP powder for 355-420-µm particle size). Since particle size had no effect on the loss of moisture or volatiles (Figure 3.4), the differences in air bubble counts could be attributed to the different amounts of entrapped air within the OP powders. The OP particles ranging between 75-177 µm had less entrapped air because of the lesser free volume within them due to the relative close proximity caused by their smaller sizes, in comparison to the larger particle sizes 355-420 µm. Cinelli et al. attributed the irregularity of the air bubbles present in composites containing poly(vinyl alcohol), starch, OP, and glycerol to temperature fluctuations or entrapped air, however, the authors related the formation of the bubbles to the release of water vapor from processing [9]. For the larger OP particles (355-420 µm) (Figure 3.4), both OP powder loading and presence/absence of zest influenced the formation of air bubbles within the LLDPE/OP powder composite sheets. A 34 % air bubble reduction occurred when more OP powder was used (1 g) (2-way interaction between particle size and loading; P = 0.001; Table 3.3). This reduction could be explained by the displacement of air from the OP agglomerates due to the weight resulting from the combination of larger particle size and more particles. A further air bubble reduction (46 %) occurred when the more OP powder (1 g) contained zest (3-way interaction between particle size, loading, and zest; P = 0.024; Table 3.3), which could be attributed to the displacement of more air during the formation of the agglomerate because of the cohesion of the OP particles to each other due to the oils in their zests. For the smaller OP particles (75-177 µm) with or without zest (Table 3.3), an effect of OP loading (P = 0.000; Table 3.3) was found. Almost 5 times more air bubbles were produced at higher loadings of OP powder, which could be attributed to the smaller particles not being big enough in mass to displace entrapped gases, unlike the larger OP particles when forming agglomerates. Overall, the best composite sheets in terms of low bubble presence (2 or less air bubbles) were formed when using lower loadings (0.4 - 0.5 g) of OP powder with a smaller particle size (75-177 µm).

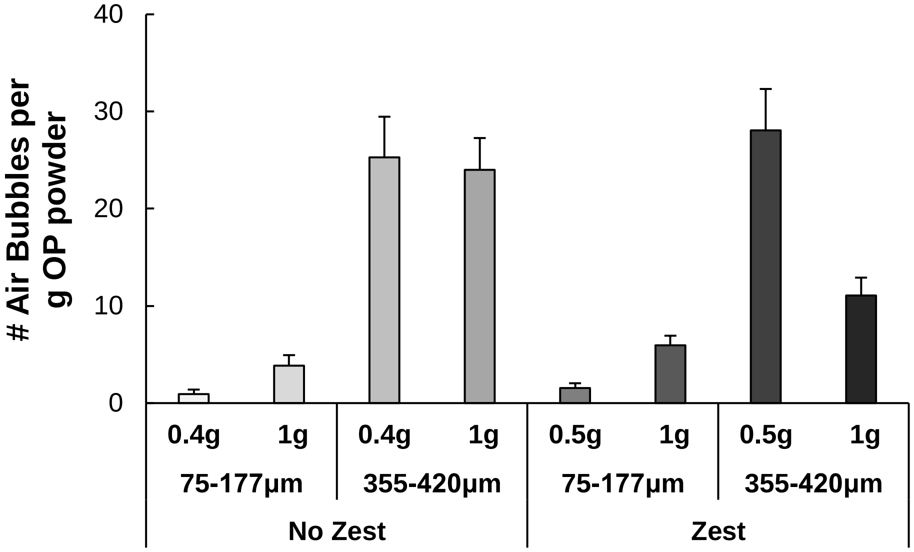

Figure 3.4 Effect of presence/absence of zest, particle size, and loadings of OP powder on the number of air bubbles per gram of OP powder.

3.5.3 Average size of OP agglomerates

The OP particles combined to form OP agglomerates. The average size of these agglomerates within the LLDPE/OP powder composite sheets ranged from 1,500 to 5,250 µm^2 as conveyed in Figure 3.5 OP powder with zest resulted in larger OP agglomerates (DIFF = 2,307 µm2; P = 0.000; Table 3.3). This could be attributed to cohesion between the zest components (e.g., oils). The cohesion of components by weak physical interactions to form agglomerates has been previously reported[10]. The formation of these larger OP agglomerates in the presence of zest occurred regardless of the size of the OP particles (2-way interaction between particle size and absence/presence of zest; P = 0.009; Table 3.3). Larger OP agglomerates were also the result of higher loadings of OP powder (P = 0.000; Table 3.3), which was most likely because fillers tend to associate to form agglomerates, especially at higher filler loadings[11]. This is reinforced by a 2-way interaction between OP powder loading and particle size (P = 0.005; Table 3.3) showing that larger OP agglomerates were produced at higher OP powder loadings for both particle sizes. Therefore, smaller OP agglomerates were formed when OP powder without zest was used in lesser loadings regardless of its particle size.

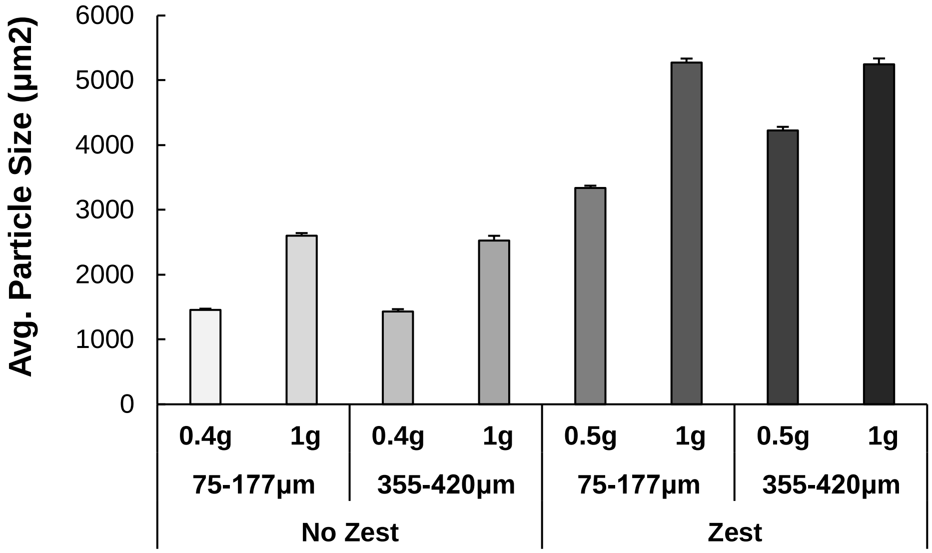

Figure 3.5 Effect of presence/absence of zest, particle size, and loading of OP powder on the average size of OP agglomerates.

3.5.4 Number of OP agglomerates per mm2 of composite sheet

The number of OP agglomerates per mm^2 of composite sheet ranged between 13 and 25. Presence/absence of zest, particle size, and loading of OP powder contributed to this variation as shown in Figure 3.6. Overall, smaller particles produced more OP agglomerates per mm^2 of composite sheet than larger particles (DIFF = 2 OP agglomerates per mm^2; P = 0.019; Table 3.3). A 2-way interaction between particle size and loading (P = 0.018; Table 3.3) led this to occur at higher loadings (1 g), but not lower loadings (0.4 g) of OP powder. Similarly, Payne and Whittaker[12] observed denser populations of agglomerates when combining carbon black and rubber using smaller particles with higher loadings compared to the use of larger particles and lower loadings. The presence of zest produced a greater number of OP agglomerates per mm^2 of sheet (28% increase; P = 0.000; Table 3.3). As explained in section 3.5.3, the zest’s components facilitated adhesion between the OP particles. This is reinforced by a 2-way interaction between zest and loading (P = 0.005; Table 3.3) showing that more OP agglomerates per mm^2 of sheet were produced (DIFF = 12) in the presence of the zest regardless of the loading of OP powder. A 2-way interaction between zest and OP powder particle size (P = 0.000; Table 3.3) led to this increase in the presence of zest to occur in larger particles only. This can be attributed to the bigger surface area of the larger particles that allowed for more interaction between the zest's components. Therefore, the higher the structure, the easier larger particles disperse while mixing [13]. Generally, the lowest number of OP agglomerates per mm^2 of composite sheet was obtained when larger particles without zest were used regardless of their OP loading.

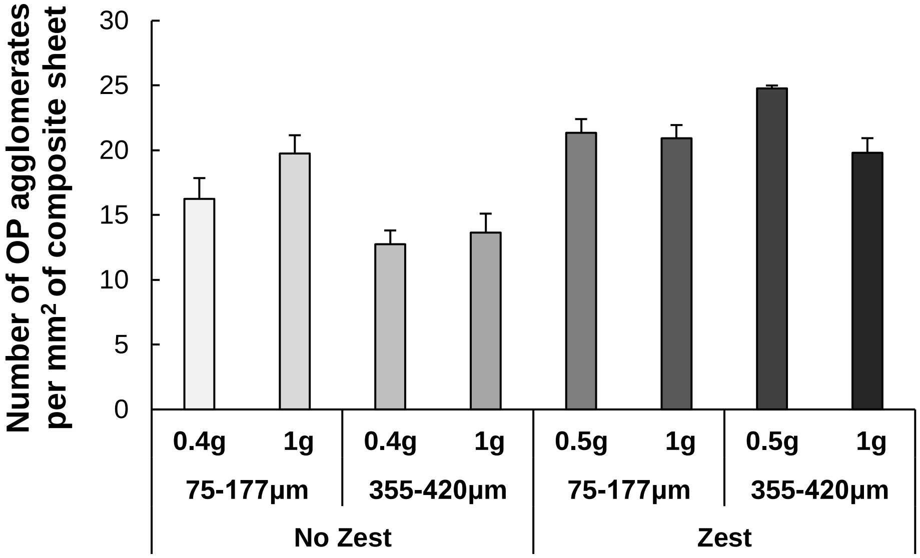

Figure 3.6 Effect of presence/absence of zest, particle size, and loading of OP powder on the number of OP agglomerates per mm^2 of composite sheet.

3.5.5 Distribution and dispersion

The effects of OP powder's presence/absence of zest, loading, and particle size on the distribution and dispersion of the OP agglomerates in the LLDPE/OP powder composite sheets are shown in Figure 3.7(a) and (b). Distribution can be defined as how well particles equally disperse and space one another throughout the polymer matrix. Composites containing OP powder with zest produced a better distribution of the OP agglomerates (Figure 3.7(a)). This could be attributed to oils within zest that behaved as a dispersing agent [13], which improved the separation between the OP powder and LLDPE during compounding. Overall, greater loadings also improved the distribution of the OP agglomerates in the LLDPE/OP powder composite sheets. Similar results were found by Chen et al.[14] when combining polyurethane and metal salts. Overall, particle size did not have a major influence on distribution. In contrast, Chan et al.[15] observed that particles of copper- and silver- nanoparticle-filled epoxy composites presented better distribution when smaller the particles were in size. In summary, OP powder with zest and higher loadings exhibited better distribution.

Dispersion in this context refers to methods for wetting out and reducing size of agglomerates and aggregates of the additive either in the dry form or within a masterbatch[16]. Zest had the largest impact on dispersion. LLDPE/OP powder composite sheets produced using OP powder without zest showed the best dispersion. This could be attributed to the lack of cohesion between zest's components that reduced OP powder agglomeration and facilitated the formation of agglomerates similar in size and shape during mixing. According to Ogbobe[16], the cohesive properties of the additive powder determine its level of agglomeration. In agreement with these dispersion results, section 3.5.3 reports the formation of larger OP agglomerates with OP powder with zest. The OP powder was generally better dispersed into the LLDPE when used in lower loadings. In agreement, section 3.5.3, reports the formation of larger OP agglomerates as a result of higher loadings of OP powder. Supporting these results, Wang[11] reported that fillers tend to associate to form agglomerates, especially at higher filler loadings. Generally, the reduction of the particle size improves the dispersion of the OP powder as well. This could be because smaller OP particles move through polymer chain voids freely while larger OP particles are trapped, which facilitates formation of larger agglomerates due to proximity. Two 2-way interactions between loading and particle size (No Zest 355-420 µm 0.4 g and No Zest 75-177 µm 1g) resulted in the LLDPE/OP powder composite sheets with the best dispersion. Similarly, Karásek and Sumita[17] observed that the dispersion of carbon black into a rubber matrix can be improved by using smaller particles and higher loadings. In summary, OP powder with a smaller particle size, in combination with lesser loadings, and absence of zest produced better dispersions. Based on the above results, the sample that proved the most promising in terms of distribution and dispersion would be No Zest 75-177 µm 1g because it exhibited a decent distribution and the second-best dispersion.

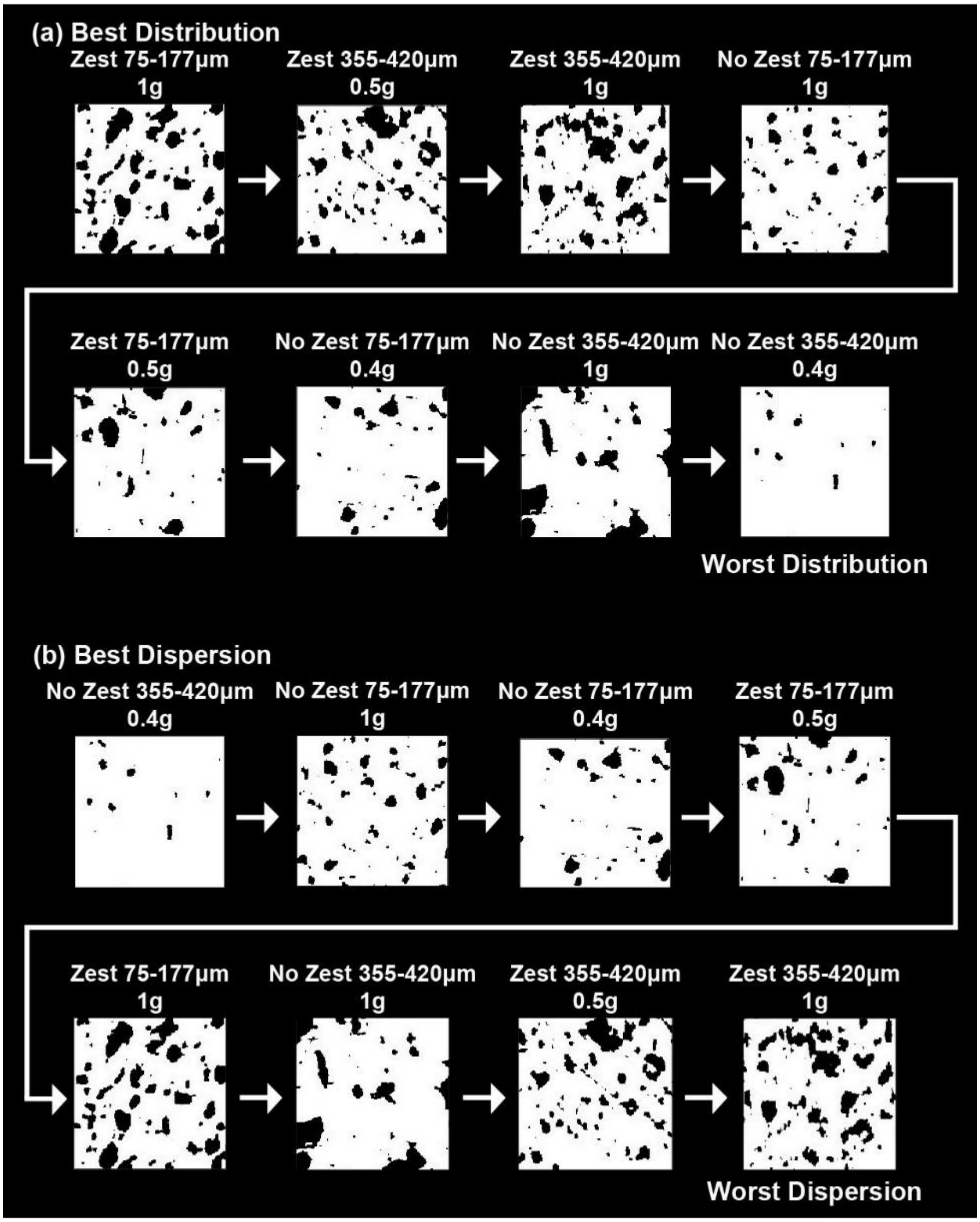

Figure 3.7 Effect of presence and absence of zest, particle size, and loading of OP powder on (a) distribution and (b) dispersion. Ordered from best to worst.

3.5.6 Mechanical properties

The tensile strength at yield of the LLDPE/OP sheets ranged from 8.6 to 13.6 MPa as shown in Figure 3.8. The values recorded for the neat LLDPE sheets are in accordance to the literature [19]. Tensile strength at yield was affected by particle size and loading but not by presence/absence of OP zest ($P = 0.152$; Table 3.4). As OP particle size increased from 75-177 to 355-420 μm, the tensile strength at yield of the composite sheets decreased by 13.7% ($P = 0.001$; Table 3.4). According to Kitey and Tippur (2005), filler particle sizes influence the fracture cracking behavior because larger particles are poorly adhered to the matrix [22]. A similar decrease (11.6%) in tensile strength at yield was observed as OP loading increased from 0.4-0.5 to 1.0 g ($P = 0.004$; Table 3.4). A 2-way interaction between zest and particle size showed that LLDPE/OP sheets with larger OP particle sizes were easier to break than those with smaller OP particles only when zest was present ($P = 0.047$; Table 3.4). The 2-way interaction observed between particle size and loading (355-420 μm and 1g) resulted in weaker LLDPE/OP sheets ($P = 0.033$; Table 3.4). Among all the LLDPE/OP sheets, only sheets containing zest, OP particle size 355-420, and 1 g OP loading differed in tensile strength at yield with the neat LLDPE sheets ($P \leq 0.05$; Table 3.4).

LLDPE/OP sheets' MOE ranged from 0.13 and 0.21 GPa as shown in Figure 3.8 The values recorded for the neat LLDPE sheets are in accordance to the literature [20]. There was no effect zest on MOE within the LLDPE/OP sheets ($P = 0.124$; Table 3.4). However, as OP particle size increased from 75-177 to 355-420 μm, a 10% decrease in MOE was observed for the LLDPE/OP sheets ($P = 0.005$; Table 3.4). Increased OP loading within LLDPE/OP sheets decreased MOE by 11% ($P = 0.003$; Table 3.4). This could be due to the OP filler is stiffer than the LLDPE matrix and it deforms less, causing a reduction in matrix strain, resulting in a stiffer material [21]. A decrease in MOE was observed for LLDPE/OP sheets with zest and 355-420 μm (2-way interaction between zest and particle size; $P \leq 0.05$; Table 3.4). The 2-way interaction between particle size and OP loading decreased MOE for samples containing larger OP particles and higher loadings ($P = 0.028$; Table 3.4). When LLDPE/OP sheets were compared to the control, a difference in MOE was observed only for the LLDPE/OP sheets containing zest, 355-420 μm OP particle size, and 1 g OP loading ($P \leq 0.05$; Table 3.4).

LLDPE/OP sheets' elongation at break ranged from 66.5 and 123.1 % as shown in Figure 3.8. The neat LLDPE sheets presented an elongation at break of 771.8 % and this value is in accordance to the literature [20]. As OP particle size increased, elongation at break decreased by 23% ($P = 0.044$). The increase of OP loading decreased elongation at break by 23% ($P = 0.047$). A 2-way interaction between particle size and loading showed that larger OP particle size decreased elongation at break more than the smaller OP particle size ($P = 0.009$). Decreases of elongation at break due to the increase of OP particle size could be associated to larger particles having a weak adhesion to LLDPE polymer matrix [22]. Onuoha et al. (2017) observed similar decreases when combining recycled polypropylene with larger particles and loadings of periwinkle shells [23].

Overall, LLDPE/OP sheets with larger OP particles and greater loadings were weaker and stiffer. The decreases in tensile strength at yield, elongation at break, and MOE of the LLDPE/OP sheets containing greater loadings and larger particle sizes of OP could be explained by the OP's poor adhesion to LLDPE that increased the number of stress concentrators, resulting in more brittle and stiffer composites. Mechtali et al. (2015) and Richard et al. (2016) each observed similar decreases tensile strength, elongation at break, and MOE when combining almond shells with polypropylene and rice husk with Sree polyester polymer, respectively [21,24].

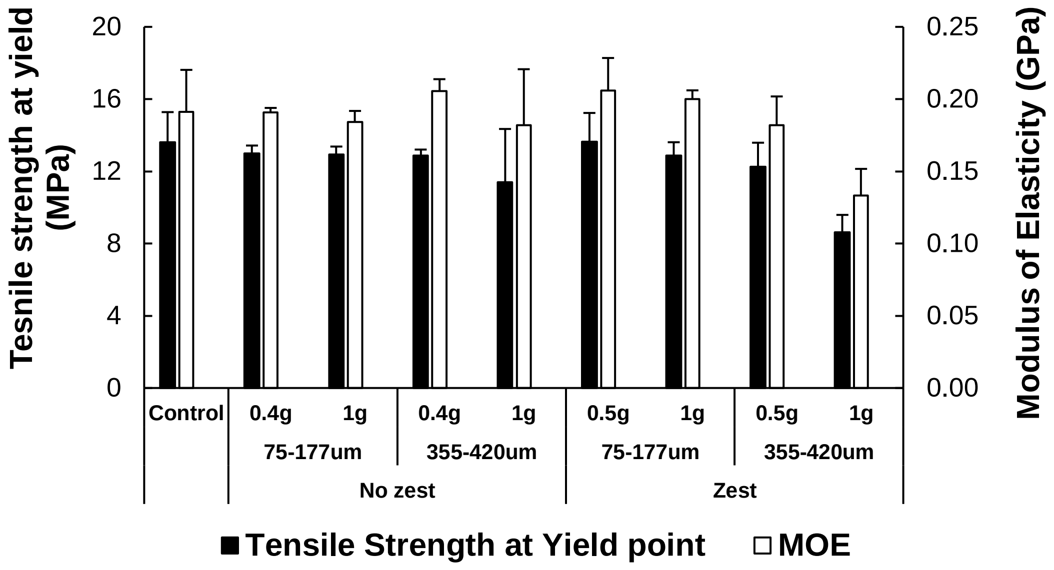

Figure 3.8 Effects of zest, particle size, and loading on the tensile strength at yield and the MOE of the LLDPE/OP sheets.

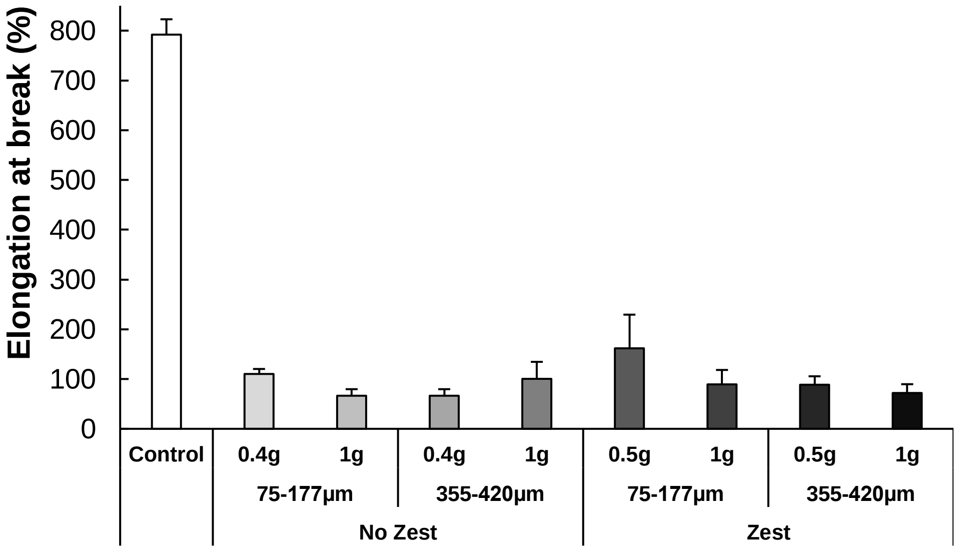

Figure 3.9 Effects of zest, particle size, and loading on the elongation at break (%) of the LLDPE/OP sheets.

3.5.7 Permeability properties

The permeability coefficients of the LLDPE/OP sheets at 23 °C and 50% RH ranged from 6.2 to 6.7 x10^{-15} kg*m/m^2*s*Pa as shown in Table 3.6. Xie et al. (2016) and Kumar et al. (2019) reported the permeability coefficients of LLDPE to be 3.7 and 7.7 x10^{-15} kg*m/m^2*s*Pa, respectively, in agreement with those measured for the neat LLDPE sheets [19,26]. There was no difference between the water vapor permeability coefficients of the neat LLDPE and the composite sheets ($P > 0.05$;). The content of OP powder with or without zest was not enough to change permeability coefficients because LLDPE is a non-polar polyolefin, which is good barrier to water vapor [27].

Table 3.2 Water vapor permeability coefficients of LLDPE/OP with and without zest 75-177 µm 0.4-0.5g sheets at 23 °C and 50% RH. Values with different letter code are significantly different ($P \leq 0.05$).

LLDPE/OP sheet type	**Permeability x10^{-15}** (kg*m/m^2*s*Pa)
Control	6.2 ± 0.4^a
No zest 75-177 µm 0.4g	6.7 ± 0.4^a
Zest 75-177 µm 0.5g	6.2 ± 0.5^a

3.5.8 Color

The color coordinates hue angle (h*) and lightness (L*) of the LLDPE/OP powder composite sheets as affected by OP powder presence/absence of zest, loading, and particle size are shown in Figure 3.10. The control sheet, neat LLDPE, was greenish yellow in color. The use of OP powder with zest produced composite sheets yellower than the control sheets ($P = 0.000$; Table 3.3). This could be attributed to the presence of carotenoids in the zest, which are yellow-to-orange in color[18]. Larger particle size also produced yellower LLDPE/OP powder composite sheets (P = 0.000; Table 3.3), which could be explained by the more carotenoid content due to the increased particle surface. According to Mulholland, the final color of a plastic depends on the particle size of the colorant's pigment used [28]. Greater loadings of OP powder also resulted in yellower LLDPE/OP powder composite sheets (P = 0.000; Table 3.3). In agreement, our distribution results show that the LLDPE/OP powder composite sheets with better distribution (Figure 3.7) are the yellowest LLDPE/OP powder composite sheets (Figure 3.10). A 2-way interaction between particle size and loading (P = 0.043; Table 3.3) showed that greater loadings in combination with the larger particle size resulted in yellower LLDPE/OP powder composite sheets. This can be attributed to a synergetic effect on yellow color of the larger particle sizes and higher loadings. A 3-way interaction between zest, loading, and particle size (P = 0.003; Table 3.3) shows that samples with zest in greater loadings and with larger particle sizes produced the yellowest composite sheets. This can also be attributed to a synergetic effect on yellow color that occurred due to the greater quantity of OP agglomerates and greater surface area of OP agglomerates that contain carotenoids. Overall, the h* of the LLDPE/OP composite sheets closest in resemblance to the control was the OP powder no zest with a smaller particle size regardless of loading.

For L*, the samples closest in resemblance (P > 0.05; Table 3.3) to the control were no zest in lesser loadings of OP powder (Figure 3.10). OP powder's presence of zest, larger particle size, and greater loadings each individually produced darker LLDPE/OP powder composite sheets (P = 0.000; Table 3.3). 2-way interactions show significant effects (P = 0.000; Table 3.3) between zest and loading as well as particle size and loading. The presence of zest darkened the LLDPE/OP powder composite sheets when OP powder was used in lesser loadings only. The combination of larger particle sizes of OP powders in greater loadings had a synergism that resulted in darker LLDPE/OP powder composite sheets. Ahmed et al.[29] found a similar decrease in L* when polycarbonate was combined with colorants with greater loadings and larger particle sizes. This is reinforced by a 3-way interaction between zest, particle size, and loading (P = 0.000; Table 3.3) that shows that LLDPE/OP powder composites sheets with larger particle size and higher loadings produced the darkest sheets regardless of the presence or absence of zest. In summary, the samples that best resembled the control in h* and L* (P > 0.05; Table 3.3) were No Zest 75-177 µm 0.4 g, No Zest 75-177 µm 1 g, and No Zest 355-420 µm 0.4g.

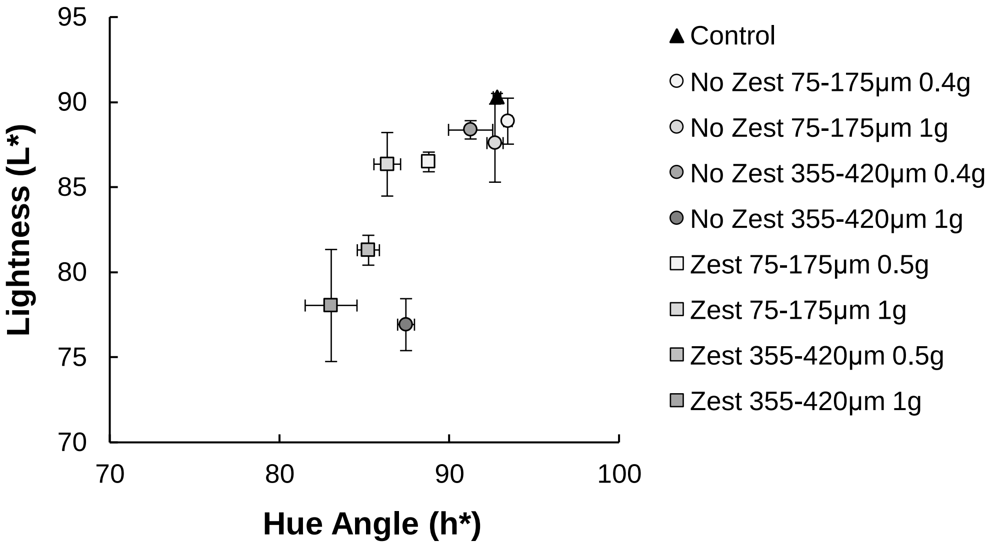

Figure 3.10 Effect of presence/absence of zest, particle size, and loading of OP powder on h* and L*.

3.5.9 Transmittance

Transmittance results are conveyed in Figure 3.11(a) and (b). Both zest and particle size changed the transmittance of the LLDPE/OP powder composite sheets at shorter wavelengths. The presence of zest in LLDPE/OP powder composite sheets decreased transmittances ($P \leq 0.05$; Table 3.5) up to 470 nm (blue), except for the sample composed with smaller OP particle size and lower loading, as seen in Figure 3.11(a). This could be because samples with zest contain carotenoids and these have been shown to absorb and protect against UV and photooxidant damage during photosynthesis[30]. Chedea et al. also observed that carotenoids absorbed light between 400 and 450 nm [18]. An effect particle size was observed at 300 nm (ultraviolet; $P = 0.002$; ; Table 3.5) and 420 nm (violet; $P = 0.028$; ; Table 3.5). The smaller OP particle size had increased transmittances at these wavelengths. This could be due to the improved dispersion of the OP agglomerates produced with smaller OP powder observed in section 3.5. Goh et al. [31] observed a similar trend whereas particle size decreased, transmittance increased. Supporting the above results, when the LLDPE/OP powder composite sheets were compared to the plain LLDPE sheets (control) at 300 nm (ultraviolet), they had similar transmittances except Zest 355-420 µm 0.5g and Zest 355-420 µm 1g that had lower transmittances than the control ($P \leq 0.05$; Table 3.5). In summary, the control and the LLDPE/OP powder composite sheets exhibited the same transmittances at wavelengths above 470 nm. Below 470 nm, the LLDPE/OP powder composite sheets with zest better scattered ultraviolet, violet, and blue lights and those with smaller particle size scattered ultraviolet and violet lights, all compared to the control.

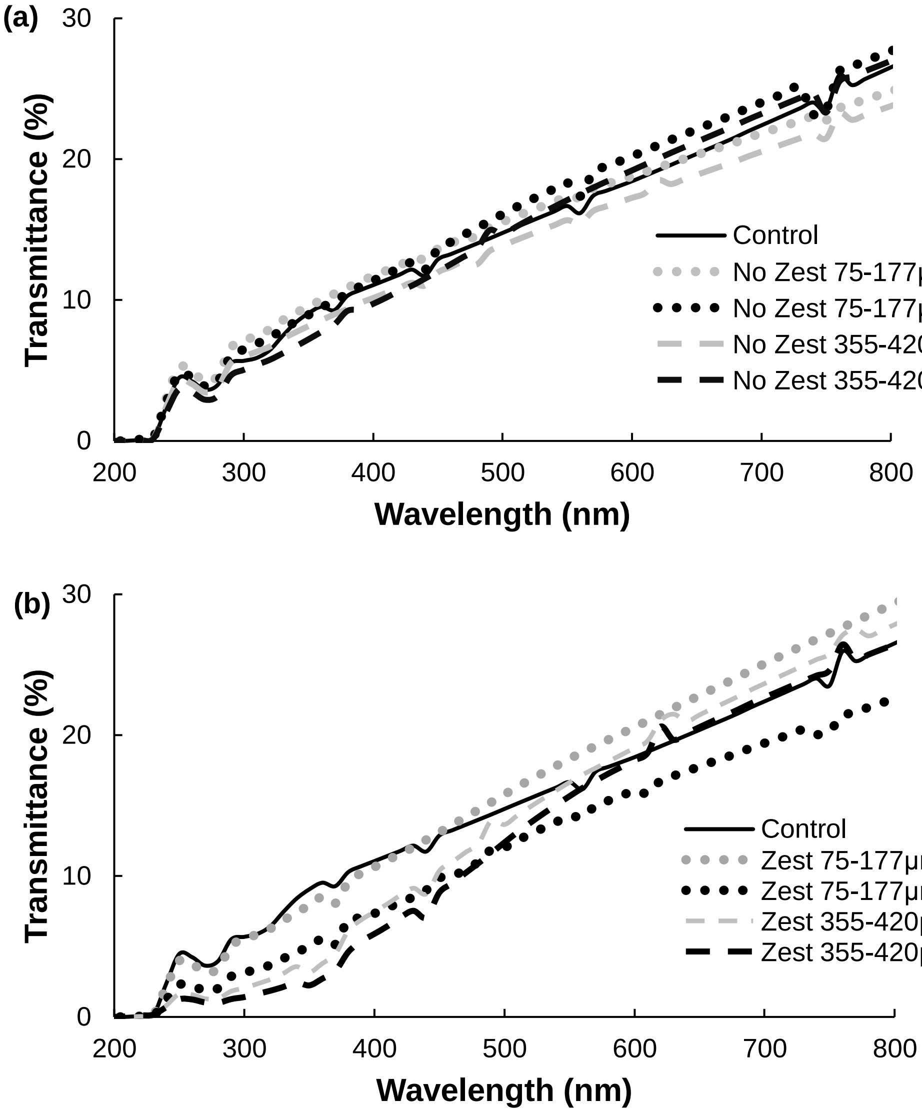

Figure 3.11 Effect of (a) presence and (b) absence of zest, particle size, and loading of OP powder on transmittance (%) from 190 nm to 800 nm.

APPENDIX

APPENDIX

Table 3.3 P-values from the general liner modeling approach using a three-way interaction ANOVA with Tukey Pairwise Comparisons (*P ≤ 0.05 indicates effect of factor (single or combined (interaction)) on each variable.

Factors	Variable						
	TGA					Colorimetry	
	Degradation temp.	Material lost at 150°C	Air bubbles per g of OP powder	Avg. agglomerate size	Number of OP agglomerates per mm^2	Hue	Light
Zest	0.002*	0.000*	0.319	0.000*	0.000*	0.000*	0.000*
Particle Size	0.165	0.375	0.000*	0.887	0.019*	0.000*	0.000*
Loading	-	-	0.144	0.000*	0.816	0.000*	0.000*
Zest x Particle Size	0.708	0.096	0.087	0.009*	0.000*	0.511	0.750
Zest x Loading	-	-	0.059	0.999	0.005*	0.931	0.000*
Particle Size x Loading	-	-	0.001*	0.005*	0.018*	0.043*	0.000*
Zest x Particle Size x Loading	-	-	0.024*	0.858	0.742	0.003*	0.000*

Table 3.4 P-values from the general liner modeling approach using a three-way interaction ANOVA with Tukey Pairwise Comparisons (*P ≤ 0.05 indicates effect of factor (single or combined (interaction)) on tensile strength at yield, MOE, elongation at break, and water permeability.

Factors	Variable			
	Mechanical properties			
	Tensile strength at yield	MOE	Elongation at break	Water vapor permeability
Zest	0.152	0.124	0.162	0.332
Particle Size	0.001*	0.005*	0.044*	-
Loading	0.004*	0.003*	0.047*	-
Zest x Particle Size	0.047*	0.000*	0.100	-
Zest x Loading	0.149	0.343	0.106	-
Particle Size x Loading	0.033*	0.028*	0.009*	-
Zest x Particle Size x Loading	0.455	0.322	0.649	-

Table 3.5 P-values from the general liner modeling approach using a three-way interaction ANOVA with Tukey Pairwise Comparisons (*P ≤ 0.05 indicates effect of factor (single or combined (interaction)) on transmittance wavelengths (nm).

Factors	Transmittance wavelengths (nm)									
	190	300	420	470	530	580	610	690	800	900
Zest	0.128	0.000*	0.008*	0.037*	0.200	0.424	0.647	0.866	0.925	0.601
Particle Size	0.806	0.002*	0.028*	0.078	0.247	0.442	0.537	0.749	0.883	0.820
Loading	0.239	0.057	0.101	0.173	0.345	0.461	0.551	0.572	0.575	0.551
Zest * Particle Size	0.241	0.173	0.650	0.978	0.644	0.507	0.516	0.435	0.475	0.750
Zest * Loading	0.131	0.535	0.171	0.123	0.084	0.063	0.077	0.036*	0.024*	0.096
Particle Size * Loading	0.176	0.480	0.542	0.480	0.366	0.294	0.355	0.246	0.257	0.409
Zest * Particle Size * Loading	0.794	0.306	0.491	0.457	0.380	0.316	0.347	0.235	0.206	0.450

Table 3.6 Effect of presence/absence of zest, particle size, and loading on LLDPE/OP sheets' tensile strength at yield, MOE, elongation at break, and water vapor permeability at 23 °C and 50% RH. Values with different letter code are significantly different (treatments with control; P ≤ 0.05).

			Mechanical properties			Water barrier
Zest	**OP particle size**	**Loading**	**Tensile Strength at yield** (MPa)	**MOE** (Gpa)	**Elongation at break** (%)	**Permeability x10^{-15}** (kg*m/m2*s*Pa)
No Zest	**75-177 µm**	**0.4g**	13.00 +/- 0.43^{a}	0.19 +/- 0.00^{a}	110.19 +/- 10.03^{bc}	6.7 ± 0.4^{a}
		1g	12.92 +/- 0.45^{a}	0.18 +/- 0.01^{a}	66.46 +/- 13.18^{c}	-
	355-420 µm	**0.4g**	12.88 +/- 0.33^{a}	0.21 +/- 0.01^{a}	66.46 +/- 13.18^{c}	-
		1g	11.39 +/- 2.96^{ab}	0.18 +/- 0.04^{a}	100.41 +/- 34.14^{bc}	-
Zest	**75-177 µm**	**0.5g**	13.63 +/- 1.60^{a}	0.21 +/- 0.02^{a}	161.75 +/- 67.63^{b}	6.2 ± 0.5^{a}
		1g	12.87 +/- 0.75^{a}	0.20 +/- 0.01^{a}	89.29 +/- 28.96b^{c}	-
	355-420 µm	**0.5g**	12.25 +/- 1.33^{a}	0.18 +/- 0.02^{a}	88.58 +/- 16.94b^{c}	-
		1g	8.62 +/- 0.97^{b}	0.13 +/- 0.02^{b}	72.01 +/- 17.67^{c}	-
LLDPE			13.61 +/- 1.67^{a}	0.19 +/- 0.03^{a}	791.99 +/- 30.87^{a}	6.2 ± 0.4^{a}

Table 3.7 Effect of presence/absence of zest and particle size on OP powders' thermal stability and material loss at 150 °C. Values with different letter code are significantly different (2-way interaction zest and particle size; $P \leq 0.05$).

		Thermal Gravimetric analysis	
Zest	**OP particle size**	**Degradation Temperature** (°C)	**Material lost at 150°C**
No Zest	**75-177µm**	147.30 +/- 1.43^{a}	6.02 +/- 0.33^{b}
	355-420µm	148.62 +/- 0.73^{a}	5.68 +/- 0.18^{b}
Zest	**75-177µm**	141.68 +/- 1.66^{b}	7.69 +/- 0.59^{a}
	355-420µm	143.90 +/- 0.21^{ab}	8.68 +/- 0.11^{a}

Table 3.8 Effect of presence/absence of zest, particle size, and loading on LLDPE/OP sheets' number of air bubbles per g of OP, average agglomerate size (μm^2), and agglomerates per mm^2. Values with different letter code are significantly different (3-way interaction zest*particle size*loading; $P \leq 0.05$).

				Morphology	
Zest	**OP particle size**	**Loading**	**# of air bubbles per g of OP**	**Avg. agglomerate size** (μm^2)	**Agglomerates per mm^2**
No Zest	**75-177 µm**	**0.4g**	0.93 +/- 0.46^{b}	1456.75 +/- 18.71^{e}	16.25 +/- 1.60^{cd}
		1g	3.85 +/- 1.08^{b}	2602.12 +/- 40.16^{bc}	19.75 +/- 1.41^{abc}
	355-420 µm	**0.4g**	25.28 +/- 4.18^{a}	1432.14 +/- 36.26^{de}	12.75 +/- 1.06^{d}
		1g	24.00 +/- 3.27^{a}	2527.33 +/- 72.95^{cd}	13.65 +/- 1.46^{d}
Zest	**75-177 µm**	**0.5g**	1.55 +/- 0.49^{b}	3338.54 +/- 35.59^{bc}	21.35 +/- 1.06^{ab}
		1g	5.95 +/- 0.99^{b}	5274.06 +/- 61.48^{a}	20.93 +/- 1.02^{abc}
	355-420 µm	**0.5g**	28.06 +/- 4.26^{a}	4226.75 +/- 55.08^{b}	24.78 +/- 0.22^{a}
		1g	11.07 +/- 1.84^{b}	5247.29 +/- 90.38^{a}	19.81 +/- 1.13^{bc}

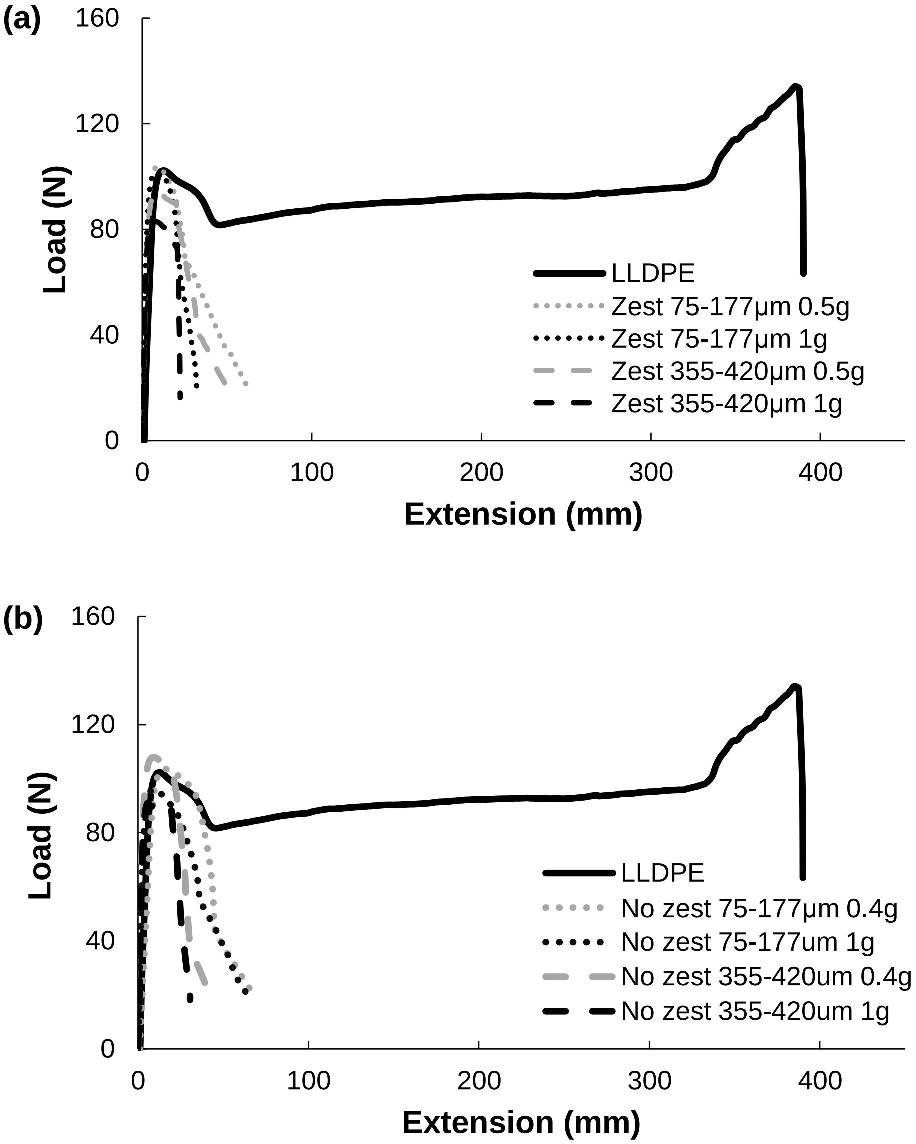

Figure 3.12 Effects of (a) presence and (b) absence of zest, particle size, and loading on the load and extension of LLDPE/OP sheets.

Table 3.9 Effect of presence/absence of zest, particle size, and loading on LLDPE/OP sheets' hue angle and lightness. Values with different letter code are significantly different (treatments with control; $P \leq 0.05$).

			Color	
Zest	**OP particle size**	**Loading**	**Hue angle (h*)**	**Lightness (L*)**
No Zest	**75-177 µm**	**0.4g**	93.46 +/- 0.25^{ab}	88.88 +/- 1.35^{ab}
		1g	92.69 +/- 0.48^{abc}	87.59 +/- 2.30^{abc}
	355-420 µm	**0.4g**	91.26 +/- 1.30^{ab}	88.37 +/- 0.54^{ab}
		1g	87.45 +/- 0.50^{e}	76.92 +/- 1.53^{e}
Zest	**75-177 µm**	**0.5g**	88.80 +/- 0.14^{bc}	86.48 +/- 0.58^{bc}
		1g	86.35 +/- 0.79^{c}	86.35 +/- 1.87^{c}
	355-420 µm	**0.5g**	85.23 +/- 0.65^{d}	81.29 +/- 0.88^{d}
		1g	83.04 +/- 1.53^{e}	78.04 +/- 3.29^{e}
LLDPE			92.81 +/- 0.22^{a}	90.29 +/- 0.57^{a}

Table 3.10 Effect of presence and absence of zest, particle size, and loading of OP powder on transmittance (%) from (a) 190 nm to 530 nm and (b) 580nm to 800 nm. Values with different letter code are significantly different in transmittance (%) (treatments with control; $P \leq 0.05$).

(a)

			Wavelength (nm)				
Zest	**OP particle size**	**Loading**	**190**	**300**	**420**	**470**	**530**
No Zest	75-177 µm	0.4 g	0.00 +/- 0.00^{a}	7.09 +/- 0.29^{a}	12.46 +/- 0.40^{a}	14.41 +/- 0.43^{a}	16.63 +/- 0.51^{a}
		1 g	0.01 +/- 0.00^{a}	5.98 +/- 0.70^{a}	10.86 +/- 0.81^{a}	12.73 +/- 0.82^{a}	14.97 +/- 0.86^{a}
	355-420 µm	0.4 g	0.01 +/- 0.00^{a}	6.50 +/- 0.99^{ab}	12.26 +/- 1.47^{ab}	14.63 +/- 1.61^{a}	17.47 +/- 1.82^{a}
		1 g	0.00 +/- 0.00^{a}	5.05 +/- 0.51^{ab}	10.64 +/- 0.88^{ab}	13.07 +/- 1.09^{a}	16.17 +/- 1.40^{a}
Zest	75-177 µm	0.5 g	0.00 +/- 0.00^{a}	5.50 +/- 0.51^{ab}	11.61 +/- 0.88^{ab}	14.18 +/- 1.09^{a}	17.34 +/- 1.40^{a}
		1 g	0.00 +/- 0.00^{a}	2.05 +/- 1.58^{bc}	8.63 +/- 2.56^{ab}	11.68 +/- 2.98^{a}	15.51 +/- 3.49^{a}
	355-420 µm	0.5 g	0.01 +/- 0.01^{a}	3.14 +/- 0.45^{c}	8.17 +/- 0.56^{ab}	10.50 +/- 0.55^{a}	13.42 +/- 0.60^{a}
		1 g	0.00 +/- 0.00^{a}	1.41 +/- 0.59^{c}	7.06 +/- 1.64^{b}	10.21 +/- 1.96^{a}	14.44 +/- 2.17^{a}
		LLDPE	0.00 +/- 0.00^{a}	5.69 +/- 1.80^{ab}	11.79 +/- 2.38^{ab}	13.63 +/- 1.95^{a}	15.92 +/- 1.39^{a}

(b)

			Wavelength (nm)				
Zest	**OP particle size**	**Loading**	**580**	**610**	**690**	**800**	**900**
No Zest	75-177 µm	0.4 g	18.23 +/- 0.59^{a}	19.09 +/- 0.62^{a}	21.54 +/- 0.77^{a}	24.81 +/- 1.01^{a}	27.03 +/- 0.85^{a}
		1 g	16.65 +/- 0.91^{a}	17.58 +/- 0.95^{a}	20.21 +/- 1.08^{a}	23.77 +/- 1.30^{a}	27.01 +/- 1.45^{a}
	355-420 µm	0.4 g	19.48 +/- 2.09^{a}	20.60 +/- 2.28^{a}	23.66 +/- 2.86^{a}	27.67 +/- 3.68^{a}	28.15 +/- 0.26^{a}
		1g	18.40 +/- 1.73^{a}	19.62 +/- 1.97^{a}	22.83 +/- 2.59^{a}	26.98 +/- 3.50^{a}	30.50 +/- 4.26^{a}
Zest	75-177 µm	0.5 g	19.68 +/- 1.73^{a}	21.02 +/- 1.97^{a}	24.64 +/- 2.59^{a}	29.36 +/- 3.50^{a}	33.43 +/- 4.26^{a}
		1 g	18.14 +/- 3.94^{a}	19.59 +/- 4.21^{a}	23.24 +/- 4.93^{a}	27.85 +/- 5.80^{a}	30.97 +/- 6.43^{a}
	355-420 µm	0.5 g	15.36 +/- 0.69^{a}	15.89 +/- 0.16^{a}	19.11 +/- 0.89^{a}	22.60 +/- 1.02^{a}	24.96 +/- 0.05^{a}
		1 g	17.27 +/- 2.22^{a}	18.72 +/- 2.20^{a}	22.28 +/- 2.21^{a}	26.43 +/- 2.34^{a}	29.82 +/- 2.47^{a}
		LLDPE	17.75 +/- 1.24^{a}	18.82 +/- 1.23^{a}	22.00 +/- 1.32^{a}	26.52 +/- 1.48^{a}	30.60 +/- 1.61^{a}

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CHAPTER 4

PRODUCTION AND VALIDATION OF LLDPE/OP BLOWN FILM COMPOSITES

4.1 Materials and methods

4.1.1 Development of orange peel powder

4.1.1.1 Materials

Orange juicing waste composed of Valencia orange (*Citrus Sinensis*) peels and debris (OP) was sourced from a juicing company located in Florida (USA) after the OP were dried in gas-oven rotating driers at 82°C for 10 mins.

4.1.1.2 Particle size reduction and separation

The OP from section 4.1.1.1 were freeze dried for 72 hours using a Virtis Genesis 25XL Bulk Drying Lyophilizer (SP Scientific, NY, USA) equipped with a Wizard 2.0 Controller (sample chamber pressure: 1333 Pa; shelf temperature: 25 °C; condenser temperature: -80 °C). The brittle OP was processed through a hammer mill (Whirlpool Corp, MI, USA) with a screen (040 1A) to obtain a powder. The particles of the OP powder were separated by size using a RO-TAP Sieve shaker (W.S. Tyler Mentor, OH, USA) with sieves with ascending pore sizes: 75, 106, 150, 250, 500 µm. About 200 g of OP powder were shook for 10 minutes per run. The 75-106 µm size was retained and stored in LDPE Ziploc® bags within a desiccator to prevent the powder form absorbing moisture. The OP power size selection was made based on previous findings (Chapter 2).

4.1.2 Production of LLDPE/OP composite film

4.1.2.1 Materials

Linear low density polyethylene (LLDPE; Affinity 1880G; density = 0.902 g/cm^3; melt index = 1 g per 10 min) was kindly donated by DOW Chemical (MI, USA). The OP powder (density = 0.732 g/cm^3) was produced as reported in section 4.1.1.2. The bulk density of OP was determined by filling 10 mL of OP into a 50-mL Pyrex glass beaker and weighing this with an analytical balance (Voyager, Ohause, NJ, USA).

4.1.2.2 Production of LLDPE/OP masterbatch

A co-rotating twin screw extruder with an aspect ratio of 48:1 equipped with a side feeder and two gravimetric stock feeders (Leistritz Extruder, Nuremberg, Germany) was used. The twin screws had a diameter of 27 mm and a speed of 100 RPM. The extruder had its 11 heating zones set to 135°C. LLDPE was dispensed at zone 1 a 52.2 g/min by a K-tron soder Model KCLKQX4 (Coperion, NJ, USA). Every minute, 15.1 g of OP was weighed with a scale (±0.1; Adventurer Pro AV8101, NJ, USA) and placed into the side feeder with a screw diameter of 23 mm and a speed of 100 RPM located at zone 5. The powder was placed in an oven (Thermo Scientific Precision model 664, OH, USA) at 80 °C for at least 24 hours prior to processing. Zone 11 was fitted with a 0.5-cm diameter circular die to produce LLDPE/OP masterbatch ribbons. These were cut to 2 m in length and removed from the die by hand to be air cooled. Each of the ribbons was further cut into 4- to 5-cm pellets with a Scheer Bay Pelletizer (MI, USA). The settings of the pelletizer were 2, 2, and 9.1 m per min for the feed roll speed, cutting wheel speed, and line speed, respectively. The final LLDPE/OP masterbatch pellets contained 22.44% OP.

4.1.2.3 Production of LLDPE/OP composite films

The LLDPE/OP masterbatch pellets produced in section 4.1.2.2 were dried 24 hours in advance in the aforementioned oven prior to being combined with neat LLDPE to produce LLDPE/OP composite films differing in OP powder content (Table 4.1 Formulations of the LLDPE/OP films used in the study.. A Killion KLB 100 blow film extruder (Davis-standard LLC, CT, USA) with an aspect ratio of 24:1 and equipped with a 3-horse power motor and with a 25.4 mm diameter screw and a 50.8 mm diameter annular die with a 0.75 mm gap was used to produce the films. The temperature profile of the extrusion process was 150-150-150-150-151.1-151.1-151.1 °C for barrel zones 1, 2, 3, clamp ring, adapter, die 1, and die 2, respectively. The screw speed and take up speed were 7 RPM and 0.762 m/min, respectively. The blow-up ratio of the film was calculated as 1.5. Three replications of each of the LLDPE/OP composite films (0 to 12.5%) were produced.

Table 4.1 Formulations of the LLDPE/OP films used in the study.

g of OP per g of LLDPE (%)	**LLDPE/OP - 22.4% masterbatch** (g)	**Neat LLDPE** (g)
0	0	500
5	107	393
10	210	290
11.5	230	270

Figure 4.1 LLDPE/OP-5% film.

Figure 4.2 LLDPE/OP-10% film.

Figure 4.3 LLDPE/OP-11.5% film.

4.2 Sensory evaluation

4.2.1 Materials

Neat LLDPE, LLDPE/OP-5%, and -11.5% blown films with thicknesses ranging from 35.48 and 42.27 μm produced from section 4.1.2.3 were used. Brownberry 100% whole wheat pre-sliced bread loafs (Bimbo Bakeries USA, Inc. Horsham, PA, USA) were purchased locally from Meijer (Okemos, MI, USA). This bread was selected because it does not contain artificial preservatives and has an expected shelf life of 10 days. The bread's ingredients are as followed: whole wheat flour, water, bulgur wheat, sugar, soybean oil, wheat gluten, honey, yeast, whole wheat cultured wheat flour, salt, soy lecithin, grain vinegar, natural flavors, citric acid, soy whey.

4.2.2 Preparation of LLDPE/OP pouches and bread samples for sensory study

Neat LLDPE, LLDPE/OP-5, and -11.5% tube roles produced in section 4.1.2.3 were cut into 18.4 x 15.9 cm rectangles that were paired and laid on top of one another. Then, 3 sides of the paired films were sealed 0.6 cm from the edge with an impulse heat-sealer (Technopack, Sunrise, FL, USA) with a cool time setting of 6 and sealing time setting of 3. Ten days prior to sensory evaluation, two slices of bread from section 4.2.1 were packaged and sealed with aforementioned heat sealer inside the neat LLDPE, LLDPE/OP-5%, and -11.5% pouches. The resulting pouches of bread were stored in a controlled storage chamber at 23° C and 50% RH for 10 days. On the day of evaluation, the bread was removed from the pouches, crust removed and cut into 1.5 x 1.5 cm square pieces with a knife. The pieces were placed in the appropriately three-digit code PET plastic cups and then covered with plastic lids (Meijer, MI, USA). Maximum time of 10 minutes spent the bread pieces in the presentation cup.

4.2.3 Panelists

Eighty-six panelists were recruited from the university and the surrounding area using an online research participation (SONA) system (Figure 4.5). Potential panelist provided their demographic and other consumer information to the SONA pool. Those who met the testing recruiting requirements (18 years and older, eats bread regularly, and not allergic to oranges) were contacted via email through the SONA system. On the day of the sensory evaluation, panelists were provided a consent form and an overview of the experimental protocol (Figure 4.6). The protocol used in this study was approved by the Institutional Review Board of Michigan State University (Figure 4.7). Each panelist received a free ice cream coupon for the MSU dairy store for their participation.

4.2.4 Testing conditions and questionnaire

Evaluation was conducted in a single session in one day. Panelists were seated in individual sensory booths with controlled lighting and environmental conditions within the Michigan State University Sensory Lab (East Lansing, MI, USA). Instruction, questions, and response inputs were given to the panelists through SIMS 2000 Sensory Evaluation Testing Software (Sensory Computer Systems, NJ, USA). For the first similarity triangle test, panelists were served a white tray, a cup of purified water, and a random set of bread pieces from the neat LLDPE and LLDPE/OP-5% pouches placed in the aforementioned PET cups produced in section 4.2.2. The panelists were then asked to taste, smell, and observe the bread pieces to identify the odd sample of bread. This procedure was repeated for a second similarity triangle test, but for the bread pieces packaged in the neat LLDPE and LLDPE/OP-11.5% pouches. Next the panelists were given either pouch of LLDPE/OP-5 or -11.5% containing two bread slices as produced in section 4.2.2. The panelists were given a prompt from the aforementioned software, “The bread you sampled was packaged with materials that contained OP, an agricultural by-product from the orange juicing industry that is generally discarded. The incorporation of the OP reduces the amount of non-renewable petroleum-based plastics needed for packaging film production. Both packages are the same common bread packaging material combined OP. The only difference is the amount of OP combined within the plastic." Then the panelists were asked to evaluate the overall liking, appearance, color, transparency, surface roughness, and smell of the pouch with a nine-point Likert scale ranging from dislike extremely (1) to like extremely (9). This procedure was repeated, but panelists received the LLDPE/OP pouch not given first. This was followed by a demographic questionnaire about the panelists' age, gender, education, ethnicity, environmentally conscious, bread consumption, purchase frequency, and purchase influence.

4.3 Statistics

For each of the similarity triangle tests, the panelist responses were collected by SIMs 2000 and were analyzed with a t-test that using an $\alpha = 0.20$, $\beta = 0.05$, and proportion of distinguisher of 20%, meaning this would require a minimum of 33 out of the 86 panelists to identify the odd sample for each of the similarity triangle tests to determine significant difference. For the second portion of the sensory evaluation, the data collected in SIMs 2000 was analyzed using MINITAB 17 (Statistical Software for PC/Windows, Minitab Inc., PA, USA). This software was used to average the panelists repeated responses from the nine-point Likert scales of overall liking, appearance, color, transparency, surface roughness, and smell for each type of pouch. Subsequently, a general liner modeling (GLM) approach to the analysis of variance (ANOVA) of 2-way factorial design between population segments (i.e., age, gender, education, ethnicity, environmentally conscious, bread consumption, purchase frequency, or purchase influence) and perceptions of the packages (i.e., overall liking, appearance, color, transparency, surface roughness, and smell). Then ignoring population segments, LLDPE/OP-5% and 11.5% pouches were subject to a similar general linear model to be compared against each other for overall liking, appearance, color, transparency, surface roughness, and smell. Specifically, the Tukey Method was use for all pairwise comparisons (controlling the family-wise error rate of 0.05) to examine the effect of bread packaged in LLDPE/OP pouches on panelists Likert scale results [2]. Note that the assumptions of normality, independence, and homogeneity for random errors are considered in all analyses for estimation (maximum likelihood) and interference (generalizability).

4.4 Results and discussion

4.4.1 Production of LLDPE/OP composite films

This study shows that LLDPE/OP composite films can be produced through the processing technique blown film extrusion. The use of the parameters listed in section 4.1.2.3 (processing temperature of 150-151 °C, screw speed of 7 RPM, take up speed of 0.762 m/min, and blow up ratio of film of 1.5) results in a maximum amount of OP powder incorporated into LLDPE of 11.5%. LLDPE/OP composite films produced with more than 11.5% OP powder were unable to reach blow-up ratio of 1.5 because of film holes and polymer tearing Figure 4.4 . Films with higher OP loading could most likely be produced through blown film extrusion using different processing parameters. This is beyond the scope of this study, however it is worth it to be investigated in the future. Blown LLDPE/OP composite films with 0, 5, and 11.5% OP powder were produced and a sensory study was performed to investigate the effect of OP loading on consumer perception of bread packaged in pouches made of blown LLDPE/OP composites as well as consumer acceptance of the two composites as food packaging materials.

Figure 4.4 LLDPE/OP film tearing due to OP filler, produced by blown film extrusion.

4.4.2 Panelists

Eighty-six participants that purchase bread frequently and above the age of 18 took part in the study. The demographic breakdown of the panelists including their bread purchase frequency is presented in Table 4.2. The average age of the panelists were 36 ± 14 years old, Caucasian (62.8%), female (66.3%), and purchased bread 3-4 times a month (33.7%). Gül1 et al. (2003) found that the minimum amount of bread consumed daily was half a loaf day so frequent bread purchasing would be expected, however in their study most respondents were male [3]. In our study, the higher female representation could be attributed to more females than males being enrolled in universities [4]. As well as, generally more women than men participate and sensory panels [5].

Table 4.2 Panelists demographics.

Variable	Definition	Panelists (n=86)
Sex (%)	Female	66.3
	Male	33.7
Age group (%)	Under 25	23.3
	25 -35	38.4
	35 and older	38.5
Race/Ethnicity (%)	White	62.8
	Hispanic, Latino Spanish	7.0
	Black or African American	2.3
	Asian or Asian Indian	26.7
	American Indian or Alaska Native	1.2
Education (%)	Less than high school	0
	High school graduate	4.7
	Some college	5.8
	2-year degree	5.8
	4-year degree	36.0
	Masters	39.5
	Doctoral	5.8
	Professional Degree	2.3
Frequency of bread purchasing (%)	1-2 times a month	9.3
	3-4 times a month	36.0
	Once a week	19.9
	Twice a week	29.1
	More than 3 times a week	5.8
Bread Consumption (%)	Less than once a week	3.5
	1-2 times	22.1
	3-4 times	33.7
	5-6 times	18.6
	Everyday	22.1
Purchase influence (%)	I don't have an influence	4.8
	Someone else has majority	5.8
	I share influence	22.1
	I have majority	30.2
	I have all the influence	37.2

4.4.3 Overall response

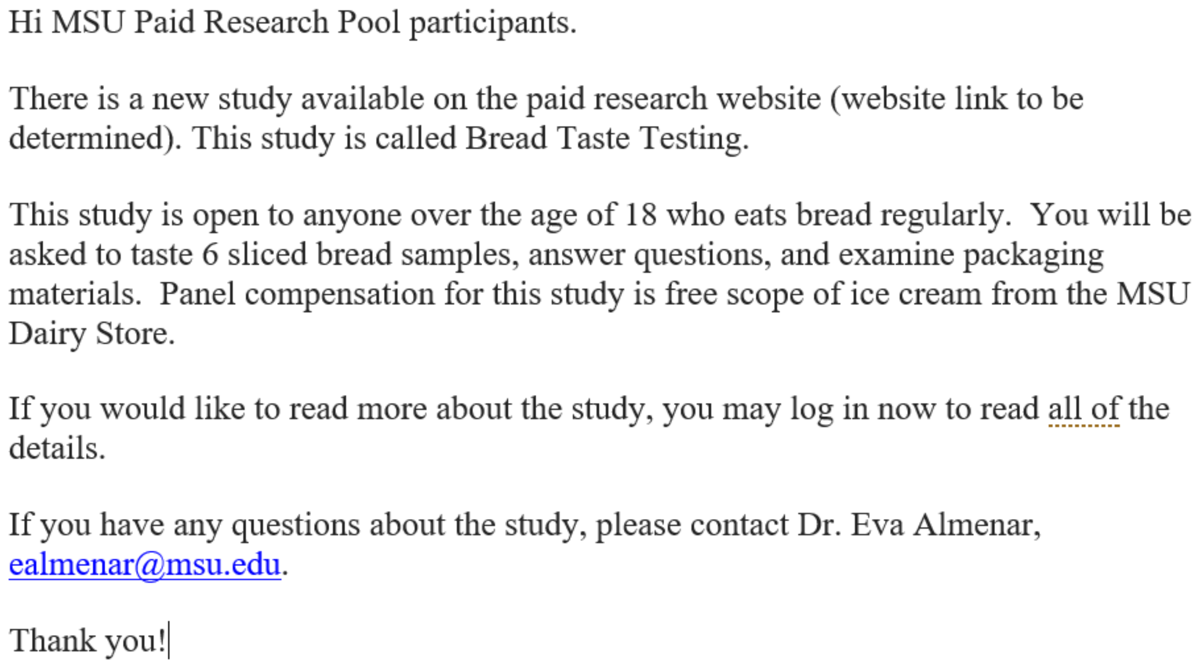
For the each of the two similarity triangle tests, after panelists tasted, smelled, and observed the bread, they were not able to detect a difference between bread packaged in neat LLDPE pouches and the bread packaged in LLDPE/OP -5 or -11.5% pouches. For the LLDPE/OP -5 and -11.5%, only 32 and 29 out of the 86 panelists, respectively, were able to detect a difference. The presence of OP powder in LLDPE did not affect the sensory characteristics of bread, so LLDPE/OP composites have the potential to be used for food packaging application. For the second portion of the sensory evaluation, when the panelists were given the LLDPE/OP-5% pouch, no effect was found for the populations segments of age, gender, education, ethnicity, environmentally conscious, bread consumption, purchase frequency, or purchase influence on their perception of the packages' overall liking, appearance, color, transparency, surface roughness, and smell found no difference among the population segments ($P > 0.05$;). Similarly, no effects were observed for the bread packaged in the LLDPE/OP-11.5% film ($P > 0.05$). However, when the LLDPE/OP -5 and 11.5% are compared, ignoring population segments, the panelists preferred the transparency of the LLDPE/OP-5% pouch ($P = 0.003$; Table 4.3). The preferred transparency of the LLDPE/OP-5% to -11.5% could be attributed to the general consumer preference to have full transparency in order to see a product inside its packaging (Sabo, 2017). Overall panelists responses were between indifferent and like slightly when comparing the LLDPE/OP-5 and 11.5% packages (Table 4.3).

Table 4.3 LLDPE/OP-5 and 11.5% package comparison and the panelists Likert scale responses (Avg. ± S.D.). Values with different letter code are significantly different ($P \leq 0.05$).

Package	Overall Liking	Appearance	Color	Transparency	Surface Roughness	Smell
LLDPE/OP-5%	6.17 ± 1.76^{a}	5.88 ± 1.87^{a}	5.29 ± 1.85^{a}	5.97 ± 2.03^{a}	5.87 ± 1.79^{a}	5.98 ± 1.43^{a}
LLDPE/OP-11.5%	5.95 ± 1.87^{a}	5.57 ± 1.92^{a}	4.88 ± 1.96^{a}	5.07 ± 1.84^{b}	5.51 ± 1.70^{a}	5.80 ± 1.43^{a}

APPENDIX

APPENDIX



Hi MSU Paid Research Pool participants.

There is a new study available on the paid research website (website link to be determined). This study is called Bread Taste Testing.

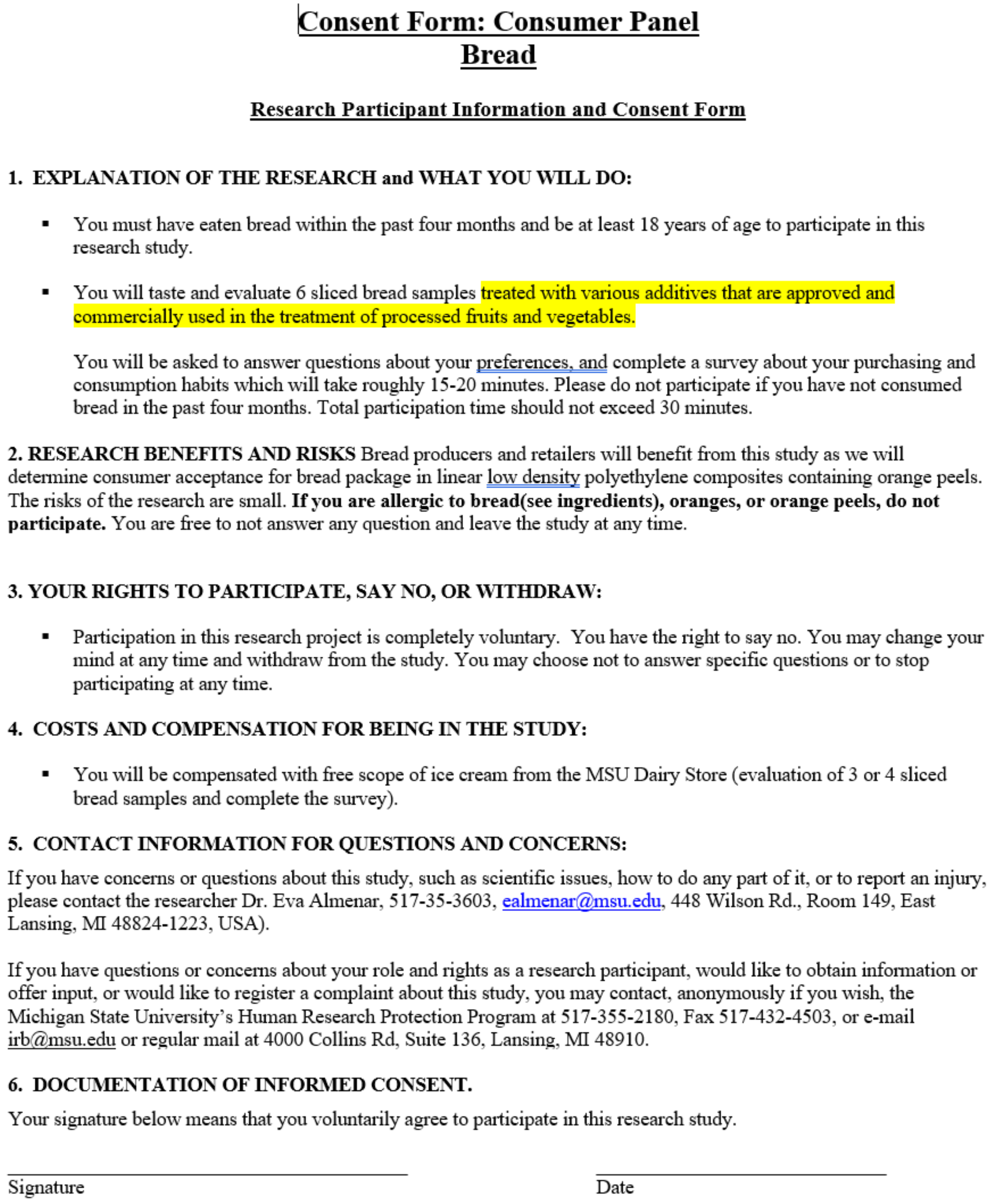
This study is open to anyone over the age of 18 who eats bread regularly. You will be asked to taste 6 sliced bread samples, answer questions, and examine packaging materials. Panel compensation for this study is free scope of ice cream from the MSU Dairy Store.

If you would like to read more about the study, you may log in now to read all of the details.

If you have any questions about the study, please contact Dr. Eva Almenar, ealmenar@msu.edu.

Thank you!

Figure 4.5 LLDPE/OP bread sensory study advertisement.



Consent Form: Consumer Panel
Bread

Research Participant Information and Consent Form

1. EXPLANATION OF THE RESEARCH and WHAT YOU WILL DO:

- You must have eaten bread within the past four months and be at least 18 years of age to participate in this research study.
- You will taste and evaluate 6 sliced bread samples treated with various additives that are approved and commercially used in the treatment of processed fruits and vegetables.

  You will be asked to answer questions about your preferences, and complete a survey about your purchasing and consumption habits which will take roughly 15-20 minutes. Please do not participate if you have not consumed bread in the past four months. Total participation time should not exceed 30 minutes.

2. RESEARCH BENEFITS AND RISKS Bread producers and retailers will benefit from this study as we will determine consumer acceptance for bread package in linear low density polyethylene composites containing orange peels. The risks of the research are small. **If you are allergic to bread(see ingredients), oranges, or orange peels, do not participate.** You are free to not answer any question and leave the study at any time.

3. YOUR RIGHTS TO PARTICIPATE, SAY NO, OR WITHDRAW:

- Participation in this research project is completely voluntary. You have the right to say no. You may change your mind at any time and withdraw from the study. You may choose not to answer specific questions or to stop participating at any time.

4. COSTS AND COMPENSATION FOR BEING IN THE STUDY:

- You will be compensated with free scope of ice cream from the MSU Dairy Store (evaluation of 3 or 4 sliced bread samples and complete the survey).

5. CONTACT INFORMATION FOR QUESTIONS AND CONCERNS:

If you have concerns or questions about this study, such as scientific issues, how to do any part of it, or to report an injury, please contact the researcher Dr. Eva Almenar, 517-35-3603, ealmenar@msu.edu, 448 Wilson Rd., Room 149, East Lansing, MI 48824-1223, USA).

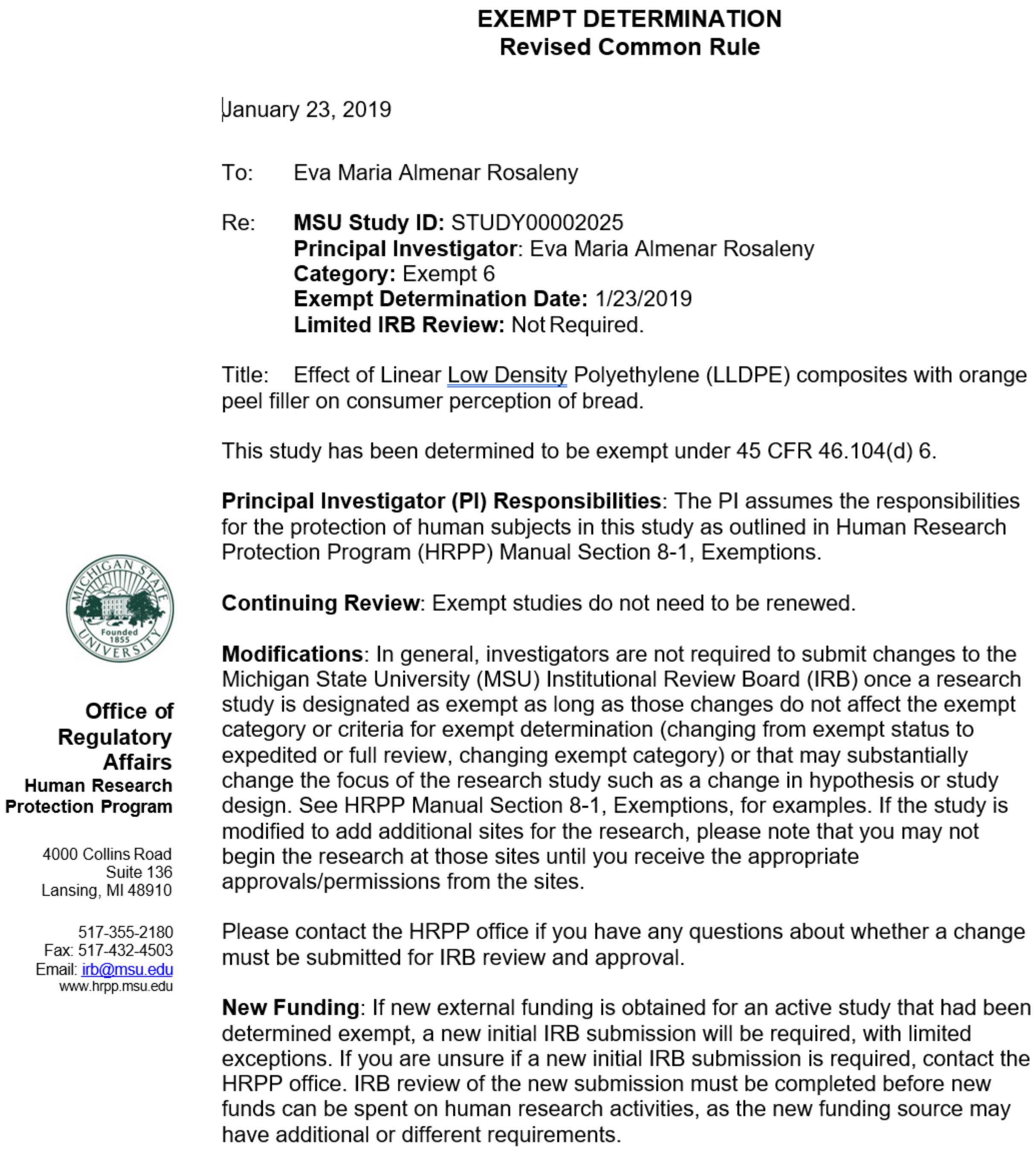
If you have questions or concerns about your role and rights as a research participant, would like to obtain information or offer input, or would like to register a complaint about this study, you may contact, anonymously if you wish, the Michigan State University's Human Research Protection Program at 517-355-2180, Fax 517-432-4503, or e-mail irb@msu.edu or regular mail at 4000 Collins Rd, Suite 136, Lansing, MI 48910.

6. DOCUMENTATION OF INFORMED CONSENT.

Your signature below means that you voluntarily agree to participate in this research study.

______________________	______________________
Signature	Date

Figure 4.6 LLDPE/OP bread sensory panelist consent form.



EXEMPT DETERMINATION
Revised Common Rule

Office of Regulatory Affairs
Human Research Protection Program

4000 Collins Road
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Lansing, MI 48910

517-355-2180
Fax: 517-432-4503
Email: irb@msu.edu
www.hrpp.msu.edu

January 23, 2019

To: Eva Maria Almenar Rosaleny

Re: **MSU Study ID:** STUDY00002025
Principal Investigator: Eva Maria Almenar Rosaleny
Category: Exempt 6
Exempt Determination Date: 1/23/2019
Limited IRB Review: Not Required.

Title: Effect of Linear Low Density Polyethylene (LLDPE) composites with orange peel filler on consumer perception of bread.

This study has been determined to be exempt under 45 CFR 46.104(d) 6.

Principal Investigator (PI) Responsibilities: The PI assumes the responsibilities for the protection of human subjects in this study as outlined in Human Research Protection Program (HRPP) Manual Section 8-1, Exemptions.

Continuing Review: Exempt studies do not need to be renewed.

Modifications: In general, investigators are not required to submit changes to the Michigan State University (MSU) Institutional Review Board (IRB) once a research study is designated as exempt as long as those changes do not affect the exempt category or criteria for exempt determination (changing from exempt status to expedited or full review, changing exempt category) or that may substantially change the focus of the research study such as a change in hypothesis or study design. See HRPP Manual Section 8-1, Exemptions, for examples. If the study is modified to add additional sites for the research, please note that you may not begin the research at those sites until you receive the appropriate approvals/permissions from the sites.

Please contact the HRPP office if you have any questions about whether a change must be submitted for IRB review and approval.

New Funding: If new external funding is obtained for an active study that had been determined exempt, a new initial IRB submission will be required, with limited exceptions. If you are unsure if a new initial IRB submission is required, contact the HRPP office. IRB review of the new submission must be completed before new funds can be spent on human research activities, as the new funding source may have additional or different requirements.

Figure 4.7 IRB approval documentation.

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CHAPTER 5

CONCLUSIONS

5.1 Conclusions

This study demonstrates it is possible to produce a usable OP filler material for plastics intended to be used for food packaging applications from OP waste. OP's physical characteristics significantly altered the properties of the resulting biocomposite plastic. Using OP with zest results in LLDPE/OP composite sheets with decreased thermal stability, larger OP agglomerates, worsened dispersion, and darker yellower colors that can act as UV- and light-absorbers. In contrast, OP without zest produces LLDPE/OP composite sheets with improved distribution and transmittances and color most similar to neat LLDPE. As for the effect of particle size, larger particle sizes increase air bubble formation, decreased tensile strength at yield and modulus of elasticity, worsen dispersion, and produce darker yellower composites that can decrease transmittance from 300 to 400 nm. Using higher OP loadings result in LLDPE/OP composite sheets that have darker yellower color, decreased tensile strength at yield and modulus of elasticity and present OP agglomerates with an increased average size, as well as improved distribution but worsened dispersion. Overall, the most promising OP to be used as filler for the production of a biocomposite plastic close to neat LLDPE for packaging applications would be No Zest 75-177 µm 0.4 g. This filler exhibits higher thermal stability, less air bubble formation, smaller OP agglomerates, a decent agglomerate dispersion, transmittance, color, mechanical, and water barrier properties similar to that of neat LLDPE. However, OP Zest 355-420 µm 1 g should be used as filler if UV-absorbance capabilities and natural coloring of plastic formats are desired for specific packaging applications. This study also demonstrates that LLDPE composites containing OP can be produced through conventional food packaging processes, like blown film extrusion, and that LLDPE/OP films can be used for food packaging applications without shortening a food product's shelf life compared to the neat films. However, LLDPE/OP-5% is was more visually appealing to panelist because it was more transparent than LLDPE/OP-11.5%.

5.2 Future works

Moving forward, it would be advantageous to explore other ways to reduce the OP particle size further to a nanoscale. This could improve the distribution and dispersion of the agro-additive inside the polymer. As well as, finding unique ways to alter the physical properties without the addition of chemicals to improve the composites performance. Further exploration in the types of agricultural wastes and that can be integrated into plastics for food packaging could be done. Another area that needs investigation would be to utilize different packaging processing technologies, such as injection blow molding, cast film extrusion, and thermoforming to produce packaging formats from agro-composites. Finally, a thorough investigation of the interactions that occur between the agro-composite and food product should be conducted, because some agro-waste may have the ability to extend shelf life (e.g., active packaging).