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A Study of poly lactic acid bio-polymer for cereal packaging

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A STUDY OF POLY LACTIC ACID BIO-POLYMER FOR CEREAL PACKAGING

By

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A Thesis

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College of Applied Science and Technology

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Rochester Institute of Technology

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CERTIFICATE OF APPROVAL

M. S. DEGREE THESIS

The M.S. degree thesis of George A. Tuszkiewicz
has been examined and approved
by the thesis committee as satisfactory
for the thesis requirements for the
Master of Science Degree

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DEDICATION

This thesis is dedicated to my family: My wife Lisa, and children Nicole, and Paige Tuszkiewicz, who provided continuous encouragement and had to experience many family sacrifices while I pursued this career goal. Without their unwavering love, support, understanding, and compromises, I would not have been able to achieve this milestone.

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ABSTRACT

The aim of this research has provided a technical framework for evaluating Co-Ex film structures of Poly Lactic Acid (PLA) and High Density Polyethylene (HDPE) for Read to Eat (RTE) cereal primary packaging. This was accomplished through increased percentages of PLA content in each identified film candidate. The foundation for this research is that Bio Polymers are gaining market popularity as a result of the increasing world demand on plastics. As a result of plastics high market volatility and the strain on fossil fuel it has created focused research on Bio Polymers. However, it is widely known there are intrinsic performance deficiencies with Bio Polymers that have been developed over the last decade that specifically, compete with polyolefin's. PLA a hydrophilic polymer is one of the most widely evaluated and commercialized of the renewable polymers. In order for PLA to shift demand from polyolefin's and be widely used as a RTE cereal packaging film there are economic barriers and market dynamics that need to be overcome. The study provided technical learning's on the critical moisture and oxygen barrier, physical, mechanical material performance properties and the impact on environmental sustainability for RTE cereal film. Presented are the key findings for the cereal industry and suggested future research.

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1.0 INTRODUCTION

RTE cereal packaging has changed over the last 100 years and so has the importance of packaging. Packaging needs to provide product protection, containment, identification, marketing, and the distribution of the product to consumers. The packaging system consists of the primary, secondary and tertiary package. The typical primary package is a plastic film pouch that provides the following:

- Contains the product
- Isolates the product from contamination
- Functional barrier (moisture and oxygen) and mechanical properties for the product requirements

The secondary package which is normally a paperboard folding carton provides the following:

- Structure for the consumer package
- Contains graphics for labeling of nutritional and brand information
- Provides structural integrity for the primary package contents

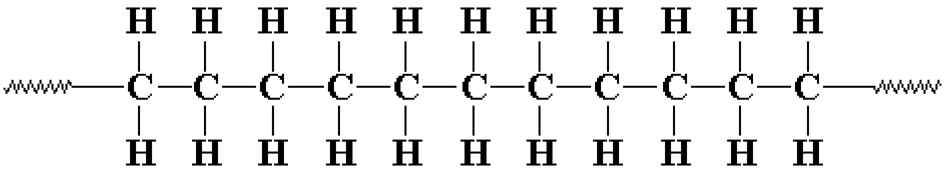
The tertiary package which is normally a corrugated container provides the following:

- Means to consolidate secondary packaged product
- Provides efficient distribution of the packaged product through the supply chain
- Product identification for the customer

The majority of RTE cereal packaging consists of the primary, secondary and tertiary packaging system components. However, there are a few market introductions of RTE cereal products that have eliminated the secondary package in the case of the folding carton. The primary package is produced using one of several film making processes: Blown Co-Extrusion, Biaxial Cast Orientated Co-Extrusion and or Cast Co-Extrusion. Co-Extruded films are engineered with as few as two up to thirteen layers to achieve the desired performance properties. The various layers can consist of different types of polymers, varying percentages of the polymers in each distinct layer, tie layers to provide appropriate bond strength between each layer, and unique polymer sealants depending on the specific application for sealing the package. Bio Polymers in which the feedstock comes from a renewable source have become increasingly important with the gaining of consumer advocacy. However, it is widely known there are intrinsic performance deficiencies with Bio Polymers which have been developed over the last decade specifically, hydrophilic Bio Polymers that compete with the polyolefin's that are hydrophobic. PLA which accounts for approximately 43% of the total Bio-Polymer volume is one of the most widely evaluated and commercialized of the Bio Polymers. The aim of this research will provide a technical framework for evaluating the Co-Ex structure of Bio-Polymer PLA combined with HDPE the most common petroleum based polymer, in the primary packaging film for RTE cereal. Specifically, the study will focus on the critical barrier, physical material performance properties and the impact on environmental sustainability for RTE cereal as the percentages of HDPE and PLA for each structure is varied. The sealant layer was not included in Co-Ex structure candidates and was not part of this study

1.1 Petroleum Polymers for cereal film

Petroleum based Polyolefin's are the most commonly used polymers for RTE packaging. Polyethylene (PE) chemical backbone is made of Hydrogen and Carbon atoms with an infinite monomer chain length and variation of multiple densities. HDPE and Low Density Polyethylene (LDPE) are two of the most common petroleum based polymers used for the primary packaging film for RTE cereals. HDPE is a nonpolar, linear branched thermoplastic that posses a much more linear structure than LDPE. It has up to 90% crystallinity, whereas LDPE exhibits crystallinity as low as 50%.[1] HDPE as result does not exhibit a lot of perpendicular branching and thus greater packing of chains can occur providing for an increased polymer density of 0.941 g/cc. LDPE does exhibit greater perpendicular branching and less packing of chains can occur providing for a reduced polymer density to 0.910–0.940 g/cc. The branching produces tensile toughness for LDPE and the reduced branching produce greater stiffness for HDPE which makes for an excellent combination for multilayer Co-Extruded film structure. The morphology of HDPE of the chain packing and increased density has provided for its excellent moisture barrier properties.



Source: Society of Plastic Engineers

Figure 1. Diagram of the Polyethylene molecule

Consumer Product Goods Companies (CPG’s) are seeking Bio Polymer packaging films that are viable alternative solutions to non renewable petroleum based polymer films which reduce the dependency on fossil fuels. Crude oil and natural gas are the main feedstock’s used to produce Polyolefin’s. There is a direct relationship to the feedstock and the economic relationship on packaging films. Polyolefin’s have been optimized over many decades of commercial experience which is the major packaging film consumables. CPG’s are turning to Bio Polymers with the issue of escalating cost of crude oil, market sensitivity, long term availability, environmental impact of pollution, and social economic concern of increasing packaging waste of petroleum based polymer films. The economic affect on petroleum polymers that stem from political unrest, conflicts, natural disasters, as well as, supply and demand fluctuations is well documented. This continues to present questions for CPG’s to accelerate the assessment and development renewable Bio Polymer films that have the ability to negate these challenging requirements.

2.0 BRIEF REVIEW OF FILM PROCESSING

There are many different processing methods to produce films and film structures. It is important to recognize that there are two distinct categories for consideration. The first method is laminated films which are composed of multiple individual films that are brought together through a variety of laminating processes. The second method is the extrusion process whereby the complete film is made up of many layers through a combination of polymers.

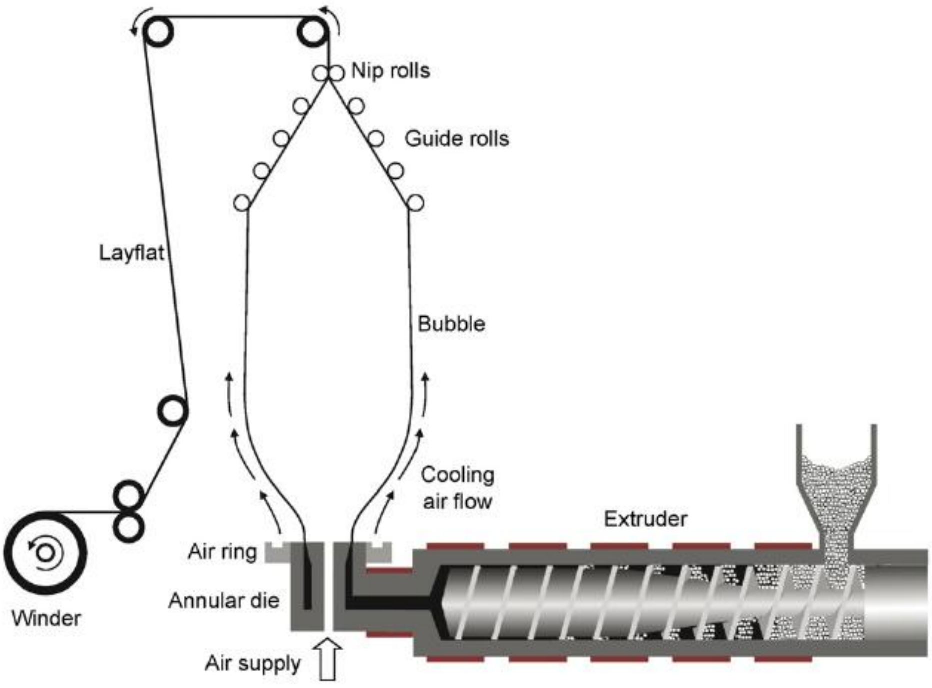
The laminated film process may include an adhesive and or a molten extrusion polymer to join the films. Lamination adhesives can consist of solvent, water based, solventless - 100% solids and or bio based formulations. Lamination by extrusion is the process of bonding two or more films with a polymer web which is produced by the extrusion process.

The extrusion film making process consists of one or more layers of polymers that are extruded through the use of a common die. The resultant film can consist of multiple polymer types with varying thicknesses and polymer tie layers for inner layer bonding. The extrusion film process can consist of different approaches which include blown Co-Extrusion single and double bubble, cast Co-Extrusion and biaxial Co-Extrusion film.

Laminated films are acknowledged as an important approach to producing packaging film structures but this research will be focused on the extrusion film making process. The films that have been produced and tested have been constructed with the cast Co-Extrusion process. However, for high volume RTE cereal film the commonly preferred method to produce the film structure is using the blown Co-Extrusion process.

2.1 Blown Co-Ex Films

Blown Co-Extrusion film method is a common manufacturing process to produce primary packaging film structures.



Source: Process in Polymer Science

Figure 2. Diagram of the blown film converting process

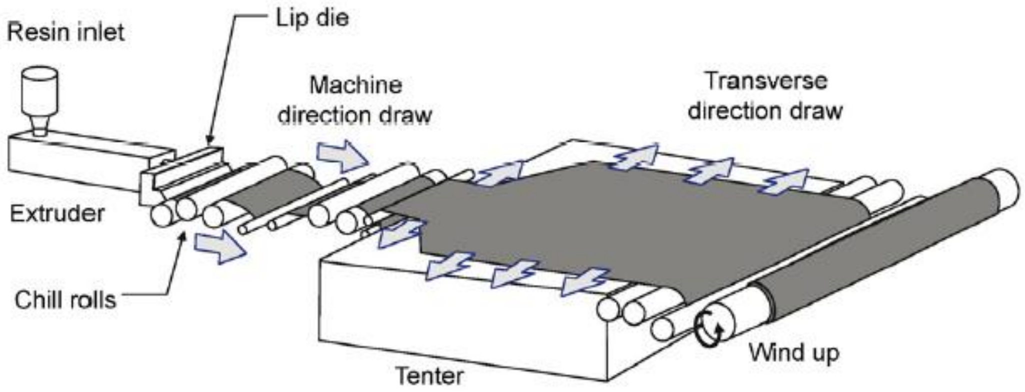
Blown Co-Extrusion film structures are engineered with as few as two up to eleven layers to achieve the desired performance properties. The function of the various layers can have different types of polymers, varying percentages of the polymers in each distinct layer, tie layers to provide bond strength between each layer, and unique polymer sealants depending on the specific application for sealing the package. In the Co-Extrusion blown film process, polymer resin is heated to a molten state and extruded to form a tube using an annular multilayer die. By blowing air through the die head, the tube is inflated into a thin tubular bubble. The tube is greatly orientated in the machine direction (MD) and partially in the cross direction (CD) and then cooled. The tube is then flattened by nip rolls and taken up by the winder. The ratio of the bubble diameter to the die diameter is called the blow up ratio (BUR). BUR ratios of 2:1-4:1 By varing the BUR, screw speed, air pressure,and winder speed, films of different thicknesses (10-150 µm) and degree of orientation can be achieved.[2] Collapsing the roll in the nip can pose a challenge of producing winkles in the finished film. Calcium Carbonate ($CaCO_3$) in small amounts can be added in the process to reduce the anti adhesion of the film when winding the film.

Blown Film Co-Extrusion Process Material Advantages

- Controlled MD and CD orientation means the film will have good tensile and elongation strength.
- Orientation process yields slow cooling, higher molecule alignment and controlled crystal growth. This influences higher moisture barrier, gas and higher stiffness properties.
- Lower clarity due to greater crystalline structure.
- The rotating die on a blown film extruder distributes any gauge variations evenly across the width of the roll to avoid gauge bands.
- Blown film can be the most economical method for producing films from 0.001” – 0.010” thick.
- Edge trim waste associated with production process reintroduced into the film.

2.2 Biaxial Orientated Co-Ex Films

Biaxial Orientated Cast Co-Extrusion film method is common manufacturing process to produce primary packaging film structures.



Source: Process in Polymer Science

Figure 3. Diagram of the biaxial cast orientated tenter frame film converting process

The polymer resin is feed into an extruder which is heated to become molten and extruded through a multilayer die to reach its glass transition temperature. The extrusion film is stretched in longitudinal (MD) and transverse (CD) direction to attain a required film dimension. Typically film is stretched 4X in the MD to 8X in the CD. The film is then processed either sequentially or simultaneously in order to obtain a very thin highly orientated film. Sequential lines first stretch the cast film in MD direction through a series of rollers. This stretching is achieved by different speeds between groups of rollers. The film then enters the tenter oven like device, which uses two endless chains to grip and stretch the web in CD direction on driving rails. The simultaneous process is a combination converting where the film is stretched in both directions at the same time. After the film is stretched the polymer orientation is fixed. The film is then quenched to room temperature and wound onto the master roll. The films typically produced using the biaxial orientation process is often laminated to other print or barrier films which then complete the total film structure.

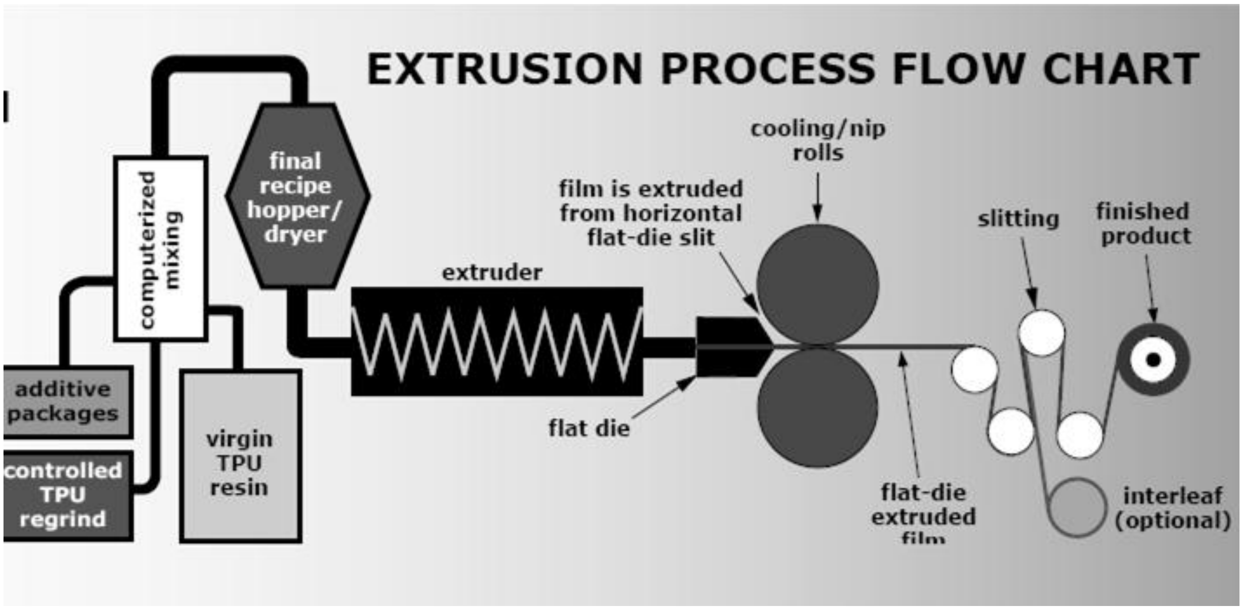
Biaxial Orientated Tenter Frame Co-Extrusion Film Process Material Advantages

- High levels of orientation both MD and CD yield strongest mechanical properties puncture, tensile and modulus possible of film processes.
- Highly organized crystalline structure creates higher moisture and gas barrier properties.
- Cost competitive only at high utilization rates typically 15-20 million pounds annually and higher.
- Excellent gauge consistency possible on long production campaigns.
- Heat setting process for highly crystalline films with dimensionally stable up to 150° C.
- Ability to producer flatter films.
- Ability to produce very clear films.

2.3 Cast Co-Ex Films

Cast Co-Extrusion film method is common manufacturing process to produce primary packaging films. The cast Co-Extrusion film includes the following processing equipment.

- Extruder
- Feed block
- Flat sheet die
- Chill roll unit
- Thickness gauge instrumentation
- Winder



Source: www.Argotec.com

Figure 4. Diagram of the cast Co-Extrusion film converting process

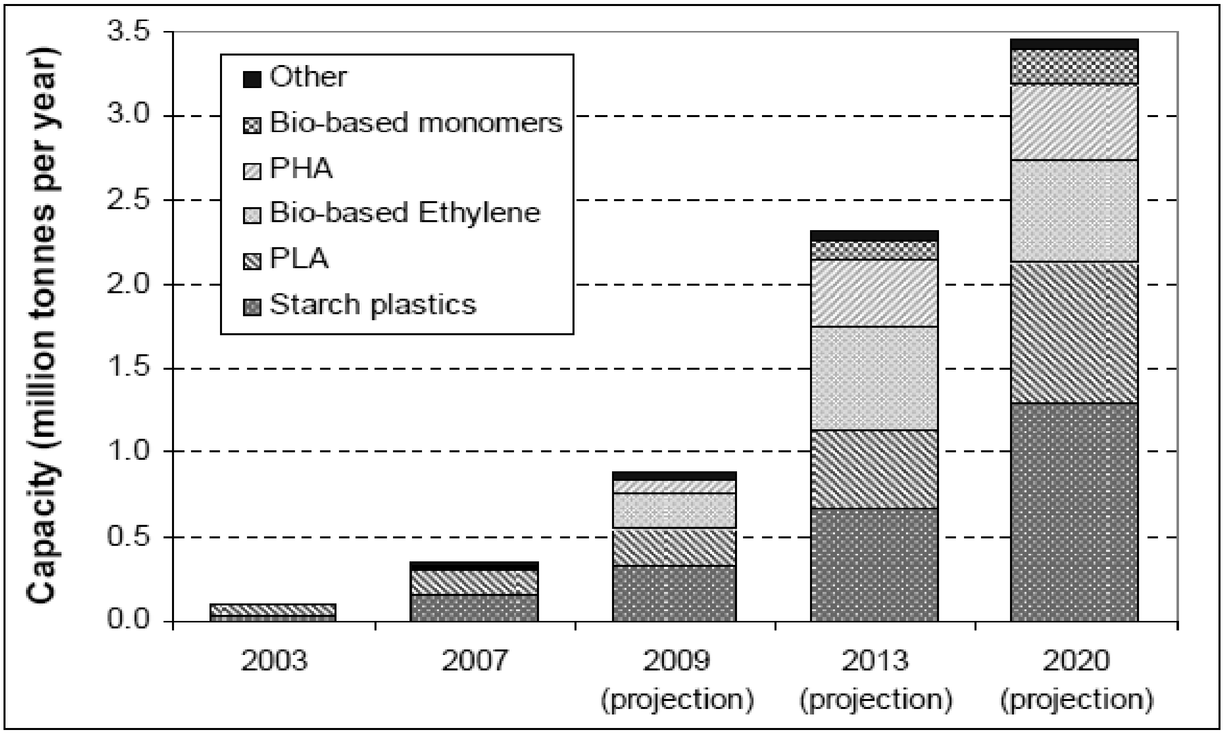
The resin is feed into an extruder which is mixed by the rotation of the extruder screw and heated to become molten. The resin is extruded through a feed block die. The feed block die provides the proper layering of polymers for the film structure. The film is extruded onto the chill roll which quenches the film instantaneously. This instantaneous quenching of the polymer structure provides outstanding film clarity and dimensional consistency. After the chill rolls the material is wound onto to large rolls for further processing as needed.

Cast Co-Extrusion Film Process Material Advantages

- Highly cost effective film processing due to rapid cooling of structure.
- Higher amorphous and lower crystalline structure which provide higher moisture, gas permeation.
- Less stiffness properties.
- Ability to easily incorporate additives for processing and performance.
- Higher levels of orientation in machine direction MD and low CD direction.
- Excellent gauge consistency possible with long extended campaigns.
- Ability to produce very clear and glossy films due greater amorphous regions.
- Thin films as low as 0.0002” can be produced.

3.0 COMMON BIO POLYMERS FOR FILMS

Bio Polymers in which the feedstock comes from a renewable source have become increasingly important with the gaining of consumer popularity. The current demand for Bio Polymers is very low compared to the petroleum based polymer films. While currently only representing 2% of the total petroleum based polymer volume Bio Polymers are expected to rapidly expand capacity and increase in demand over the next decade. As a result of the increasing world demand on fossil fuels, and the high volatility, Bio Polymers are of great interest to researchers. They provide an alternative packaging solution to a highly volatile and sensitive petroleum based polymer market. The market for renewable plastics has been experiencing rapid growth. From 2003 to the end of 2007 the global annual growth rate was 38%. The growth rate in Europe was 48% as compared in the same period. The world wide average growth rate is expected to be 19% through 2020. The starch based polymers in particular are predicted to enjoy significant growth in the immediate future. The potential substitution opportunity for Polyethylene petroleum based polymers is quite high at a level of 90%. This presents a significant market opportunity. There are technical issues with scale up with Bio Polymers and consistent availability of feedstock. However, the opportunity cost for growth and share switching from the petroleum based polymer films remain high with a projected growth of Bio Polymers of 4 million tons by 2020.



Source: 2009 European Science and Technology Observatory

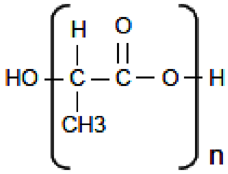
Figure 5. Projected worldwide supply of renewable polymers

Starch based plastics, PLA and renewable based PE, and polyhydroxyalkanoate (PHA) are anticipated to lead the renewable polymer surge in growth. “Starch based polymers are projected to grow at a rate of 38%, PLA 24%, bio based PE 18%, and PHA13%, bio based monomers 6%, and 2% respectively.” [3] The uncertainty of the amount of fossil fuel for petroleum based films lends a favorable opportunity to renewable films. Unlike the petroleum feedstock which has many global factors which are outside of the supply and demand of the market for films do not present the same market dynamic for renewable polymers. For Bio Polymers there still is a dependency on the petroleum industry including growing the feedstock, harvesting, energy to process the resin and transportation to the market. However, the feedstock availability and volatility is not driving force. The packaging film cost to the CPG's should be void of wide swings in feedstock market price fluctuations.

In the last decade PLA has made significant inroads into various markets while competing with well established commodity based petroleum polymers. Specifically, Bio Polymers in the polyester family have been developed over the last decade.

There are many challenges associated with Bio Polymers as well, from market availability, economics, infrastructure capacity, impact on the food supply, and its ability to deliver against demanding material properties. In order for PLA as a polymer to be more commercially viable as a packaging film the material performance and barrier properties need to be improved. Balancing all these challenges within an emerging polymer technology can pose great difficulty as well as present market opportunities. The major focus area that is of particular interest of food companies is the material performance. Compared to Polyolefin polymers PLA does not provide comparable moisture, and oxygen barrier performance. In order for PLA to become a viable option for food packaging films there needs to be additional technologies considered to enhance the barrier properties. Increasing world population and providing longer shelf life products to reach more consumers are compelling to accelerate the rate of the basic research. With this goal in mind CPG's have the responsibility as providers to participate in leading the industry research and helping the commercialization of the technology.

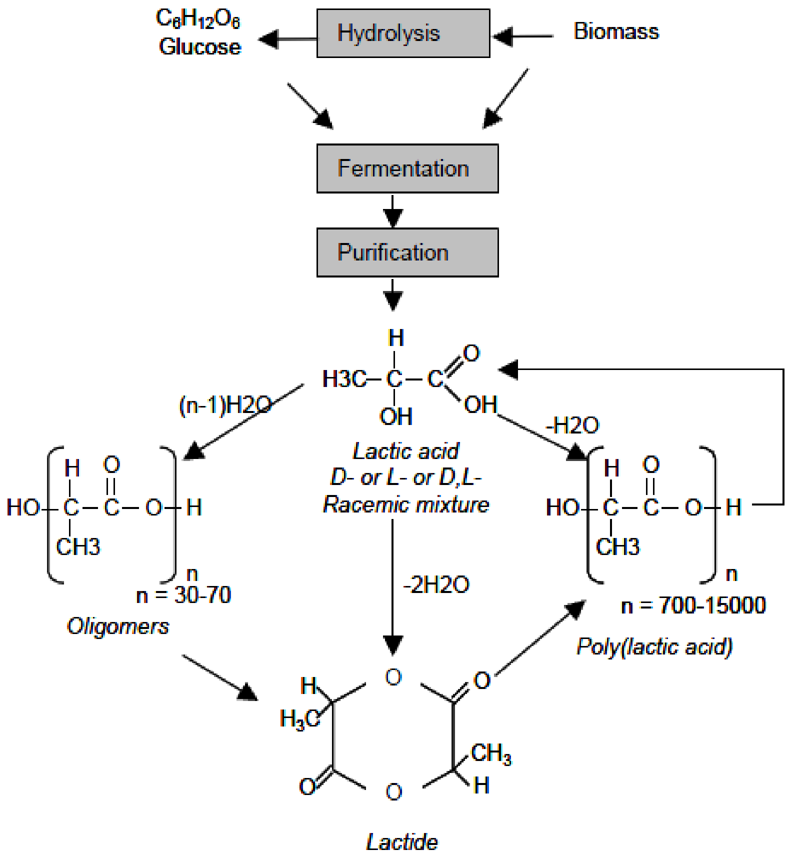
PLA is synthesized from L-and D-lactic acid, which are produced from fermentation of sugar and (poly) saccharides such as sugar feedstock and corn, wheat, rice and other starch sources, either by ring-opening polymerization or by condensation polymerization.[4] In the future it is expected to hydrolysis of lignocellulosics – i.e. woody or herbaceous biomass originating from wood , straw, corn stover and sugarcane byproducts – will become a viable pathway through technological advances (enzymatic processes), together with the pressure on resources driving the increased utilization of agricultural waste.[3] The feed stocks are abundant and renewable which makes PLA an attractive packaging film.



$$HO-\left[\overset{H}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-O\right]_n-H$$

Figure 6. PLA molecule 700 – 15000 Dalton

PLA was discovered over 150 years ago however as a result of low cost well established petroleum polymers and technical properties that had inferiority there was no immediate application until in the 1960’s were then medical applications became possible. During the 1980’s and 1990’s DuPont, Coors Brewing (Chronopol), and Cargill were focused on the commercialization of the polymer as a low cost commodity resin. The efforts of DuPont and Chronopol soon failed as significant research dollars were committed. However, Cargill did finally develop a continuous process for high purity PLA production using the distillation reactive process.



Source: Utrecht University

Figure 7. Shows the Nature Works LLC PLA production process from bio mass

Nature Works PLA resin uses a continuous process of a ring opening polymerization (ROP) of lactide. Condensation of aqueous lactic acid produces low molecular PLA pre-polymer (<5000 Dalton). The pre-polymer is then depolymerized by increasing the polycondensation temperature and lowering the pressure, resulting in a mixture of lactide stereoisomers. As organometallic catalyst tin octoate, is used to enhance the rate and selectivity of the intermolecular crystallization reaction. The molten lactide mixture is then purified by vacuum distillation. In the final step, high molecular weight PLA (>100,000 Dalton) polymer is produced by catalyzed ring-opening polymerization in the melt. Any remaining monomer is removed under vacuum and recycled to the start of the process. By controlling the rate of polymerization (ROP) process chemistry it is possible to select the stereoisomer of the lactide intermediates and thereby also the properties of the resulting PLA. Usually, high purity L.L-lactide is the desired intermediate for the production of PLLA.[3]

4.0 CEREAL PROPERTIES

RTE cereals continue to gain in popularity due to their convenience, economical, nutritional health benefits. The increasing need for high fiber, lower fat and whole gains in our diets makes for a high market demand for RTE cereal. In addition, to the documented nutritional benefits RTE breakfast cereal studies have shown to positive cognitive benefits for adults and children. The diversity and product forms present for some interesting technical challenges concerning product preservation. For CPG's that produce RTE cereal they rely heavily on the packaging system to help provide the best possible quality product for their consumers. The packaging system comprises of many functions from the production of the product, packaging, storage and warehousing, distribution to customers, and the overall consumer experience. Once the product has been manufactured and packaged the shelf life has commenced. Shelf Life is defined as the amount of available days the product meets all physical and organoleptic quality requirements by the CPG's. The objective of defining the shelf life is to optimize the performance parameters of the package to improve the quality of the product offering, and to extend the consumption time in a cost effective manner. The shelf life of RTE cereal depends to a large extent on the content and quality of the oils contained in them. Thus, cereal products made with low oil content such as wheat, barley, rice, and maize grits (oil content: 1.5% to 2.0%) have a longer Shelf Life than products made from oats (oil content: 4% to 11%, average 7%). Although whole corn has high oil content (4.4%), most of the oil is contained in the germ, which is removed in making grits.[5]

When considering the appropriate packaging materials for RTE cereal there are five modes of product failure which are listed as follows:

Table 1.1.

Modes of failure for RTE cereal

Product Characteristics	**Resulting**	**Affect**
Textural Change of Crispness	➡	Moisture Gain or Loss
Rancidity Off Flavors	➡	Lipid Oxidation
Nutritional Change	➡	Vitamin Loss
Aesthetic Compromise in Physical Appearance	➡	Product Breakage
Degradation of Flavor	➡	Aroma Loss

4.1 Textural Changes

Packaging of RTE cereal is traditionally packaged in a secondary package which is typically a paperboard folding carton which provides structural integrity, nutritional content and consumer product information about the product. The primary package which is normally a plastic film liner or pouch has direct contact with the cereal and has the greatest impact on the modes of product failure. In a few cases where the cereal product is not hydroscopic or retains a satisfactory texture when in equilibration with the ambient atmosphere, a liner may not be needed for moisture protection and may even serve to entrap rancid aromas. Where this is the case, either no liner or one which is vapor permeable may be used.[6] The majority of the RTE cereal is hydroscopic and requires a primary package such as a plastic liner for extending the Shelf Life. During the distribution and storage of the product , due to the difference between the water activity inside and outside the package, water molecules permeate through the package leading to an increase of the internal water content. This causes an increase of the water content of the packaged product and consequently a decrease of its quality.[7] The lower the water activity (a_w) of a product the greater likely hood that the product will gain moisture over the shelf life period. The resulting product is some way has been compromised in its final texture. The consumer perception of this textural change can lead to an undesirable eating quality such as chewy, sticky, soggy or staling of the product. When fruit particulates are incorporated with cereal the a_w of the cereal needs to be manipulated in order for the cereal to remain crisp and the fruit to remain succulent. In some cases the cereal may have a different starting a_w and it continues to equilibrate closer to the fruit a_w over time through the shelf life of the product. This is a moisture management of the internal environment to the plastic liner.

4.2 Rancidity and Off Flavors

Plant based lipids contain hydrocarbon chains of fats typically unsaturated which are susceptible oxidation. The primary mode of chemical deterioration in dry cereal is lipid oxidation and two reasons have been advanced for this. First the a_w of dry cereals is at or below the monolayer, which essentially stops all other types of deteriorative reactions. Second, unsaturated fats are required in lipid oxidation, and the grains used in breakfast cereals have a high ratio of unsaturated to saturated fats.[8] Oxidation of lipids creates rancidity and off flavor in RTE cereal however, most do not develop rancidity at an accelerated rate. Generally for off-odors to be detected less than 1% of the unsaturated lipid needs to be oxidized. It is possible at higher temperatures during storage conditions with an extended shelf life to develop rancidity. Temperature and relative humidity are the extrinsic factors having greatest effect on the oxygen permeability of packages.[9] The critical function of the primary package is to reduce or prevent oxygen permeation during shelf life. Thus to prevent resulting lipid oxidation as an essential attribute for providing desirable product. Excluding oxygen may be of limited assistance in extending shelf life although oxygen is almost never rate limiting.[5] There are circumstances where some products need to breathe due to the out gassing of volatile compounds during the cooking of the grains. In some extreme cases although not typical where there can be ingress of odors into the package due to outside aromatic content which would require some oxygen barrier. For this reason most CPG's do not require an ultra high oxygen barrier packaging plastic liner. Noted but generally not a major concern is the light transmission of the primary package. The secondary package since it is typically a paperboard this provides a significant light barrier for the product and this is usually not a concern for the product. However, where there are packaging designs in which the secondary package has been eliminated then primary package incorporates a high level opacity for reduced light transmission.

4.3 Nutritional Change

Vitamin fortification is a common practice in the RTE cereal category. This micronutrient strategy is part of the production of the cereal where vitamins are incorporated through a variety of methods into the product during processing. This allows CPG's to enhance the nutritional content of the cereal in delivering vital nutrients as well as target vitamins that may be deficient in some diets. In some cases this can prove to be an important product differentiation from one brand vs. another. Nutritional labeling and the requirements are very specific in several countries including the United States. For this reason it is important to preserve nutritional value and maintain the compliance with the nutritional content on the declaration of the label. In some cases depending on the sensitivity of the vitamin there may be an overage used to minimize problems with label claims. There are two major factors in vitamin loss which are the temperature of the product, in particular to the storage conditions and oxygen permeation. One hypothesis is due to the kinetics of permeation. As the storage temperature raises the permeation rate increases thus accelerating the ingress of oxygen to deteriorate oxygen sensitive vitamins. The second hypothesis is related to the effects of temperature which are the change or delta T, and length of time. A temperature change of 10°C has a two -three fold kinetic change on the rate of oxidation. The packaging cannot prevent the temperature change however, it must perform under the know storage and distribution conditions. In a product study conducted on the effects of micronutrient loss during processing and storage it was concluded that the affect on shelf life was not significant. It was noted however, the possible exception of vitamin A and to a slight extent, vitamin C. Vitamin A survived for 6 months (average distribution of time) at room temperature with no measureable loss.[8] For this reason the distribution and storage of the finished product is handled in ambient conditions.

4.4 Aesthetic Compromise

Physical properties of cereal include product fragility, abrasiveness, its ability to flow and the density. The product appearance is tied to several factors one which is not related to the primary package or the plastic liner. The secondary package however, plays a vital role in maintaining product integrity. The compression strength and impact resistance of the paperboard carton is critical to protecting the product through the normal distribution and handling of the product. Product breakage in RTE cereal is not a significant concern and the insignificant amount of product finds (broken pieces of cereal) due to handling is acceptable to consumers. The packaging liner plays an insignificant role in product breakage.

4.5 Degradation of Flavor

The loss of aroma can be a challenge with certain RTE cereals where they have a high aromatic flavor. This is typical of some of the fruiter type cereals where the strong aroma is precursor to an intense flavor. These typically have volatile compounds that are difficult to maintain in the plastic liner. In some cases consumers perceive the loss of flavor with an out of date product and in fact opposite is also perceived by the same consumers. A study evaluating two typical cereal liner materials (HDPE and glassine) found that the permeability coefficients of *d*-limonene (a common flavor component in citrus products) in the HDPE liner were three to four orders magnitude higher than that in glassine. It was also found that the solubility of *d*-limonene in the glassine liner was substantially lower than in the HDPE liner for the same vapor pressures.[10] The sealant layer of the plastic film which is in direct contact with the cereal can have a significant effect on the scalping kinetics of the volatile flavors. It should be noted there are barrier strategies that can be developed to prevent the scalping of volatile compounds. Where this is a product requirement the film structure is developed with an aroma barrier property.

5.0 DEFINITION OF TERMS

Polymers

BUR – Blow Up Ratio

Biax – Bi-Axial

Co-Ex – Co-Extrusion

CD – Cross Direction

$CaCO_3$ – Calcium Carbonate

EVA – Ethylene Vinyl Acetate

I/O – In to Out

O/I – Out to In

LDPE – Low Density Polyethylene

LLDPE – Linear Low Density Polyethylene

HDPE – High Density Polyethylene

MD – Machine Direction

PE – Polyethylene

PHA – Polyhydroxyalkanoate

PLA – Poly Lactic Acid

PLLA – Poly-L-Lactide Acid

ROP – Ring Opening Polymerization

Cereal Terms

CPG’s – Consumer Package Goods Company

RTE – Ready to Eat

a_w - Water Activity

Test Methods and Instrumentation

> – Greater Than

< – Less Than

C – Celsius

COF – Coefficient of Friction

ASTM – American Society for Testing and Materials

DOE – Design of Experiment

DSC – Differential Scanning Calorimetry

Gms - Grams

MVTR – Moisture Vapor Transmission Ratio

Mills - .001”

T– Temperature

Tensile Strength

MD/CD Secant Modulus

Notched and Un-Notched Tear Resistance

In and Out Puncture Resistance

PSI – Pounds per Square Inch

OTR – Oxygen Transmission Ratio

ROP – Rate of Polymerization

µm – Micron

Software

Net Stat – Statistics Software

Savvy Pack® – Sustainability Software (Allied Development™)

Sustainability

CO_2 – Carbon Dioxide Emissions

GHG’s – Green House Gases

MSI – One thousand square inches

MJ – Mega Joules

6.0 RESEARCH METHODOLGY

Methodology

The methodology used was both quantitative and qualitative research methods. The sample size was set at five for each analytical test due to economic constraints of cost of analytical time. Additionally there was a low standard deviation of each sample set which provided additional confidence. However, Water Vapor Transmission Ration (WVTR), Oxygen Transmission Ratio (OTR) sampling was limited to two samples due to normal industry sampling practices and as well as low standard deviation of results.

1. Design of Experiment consisted of the following:
    a. Controls – included 100% HDPE and 100% PLA as respective resin films.
    b. Six structure variables – included progressively increasing percentages of PLA and reducing percentages of HDPE resins in the films.
2. Mean and standard deviation were determined for each viable sample set and film test.
3. Comparative means from two or more samples for each film test variable.
4. Mean values were plotted with a progression trend line for each film test variable.

The procedure

1. Samples were TAPPI conditioned at 73 ° F and 50% RH for 48 hours.
2. Samples were taken from the beginning middle and end of the 200 ft of film that was produced for each test film structure variable.

3. All films samples were prepared in accordance per ASTM standard methodology for each individual test method.

7.0 TEST METHODS & INSTRUMENTATION

Table 1.2.

ASTM test methods performed on test film

Test	**Units**	**Method**	**Equipment**
Coefficient of Friction Static – I-I/O-O Kinetic – I-I/O-O	u_S,u_K	ASTM D1894	Testing Machines Inc 32-06
Clarity	%	ASTM D1003	Byk-Gardner Haze-Gard Plus
Haze	%	ASTM D1003	Byk-Gardner Haze-Gard Plus
Density	gms/cc	ASTM-D1505	
Gauge	mils or .000"		Micrometer - Emveco 210A
High Speed Puncture Multiaxial Impact	ft/lb Newton’s- Peak Load Joules- Energy	ASTM D3763	Instron- Dynatup
OTR	cc/100 in²/24 hr	ASTM D3985	MOCON OX- TRAN 2/20
Propagation Tear Resistance Notched/Un Notched MD/CD	gms	ASTM D1922	Thwing-Albert Elmendorf
Secant Modulus MD /CD	psi	ASTM D882	Instron - 5566
Tensile Strength @ Break MD/CD	%	ASTM D882	Instron - 5566
Tensile Elongation @ Break MD/CD	%	ASTM D882	Instron - 5566
Melting Point	ºC	ASTM E 794-98	Seiko - RDC 220
WVTR	gms/100 in²/24 hr	ASTM F1249	MOCON PERMATRAN-W® Model 3/33

8.0 MATERIAL SELECTION

The following polymers were used in this body of research:

Polymer: PLA - 4042D (NatureWorks®)

Polymer: HDPE - MarFlex® 9608XD (Chevron Phillips)

Impact Modifier: Biomax® 120 (DuPont®) added 10% by weight to the PLA

Tie Layer: ADMER® SF600 (Mitsui Chemicals America)

Test structures consisted of a 3 layer Co-Ex: Resin A /Tie/ Resin B without the sealant layer

Film thickness .002”

8.1 Material Variables

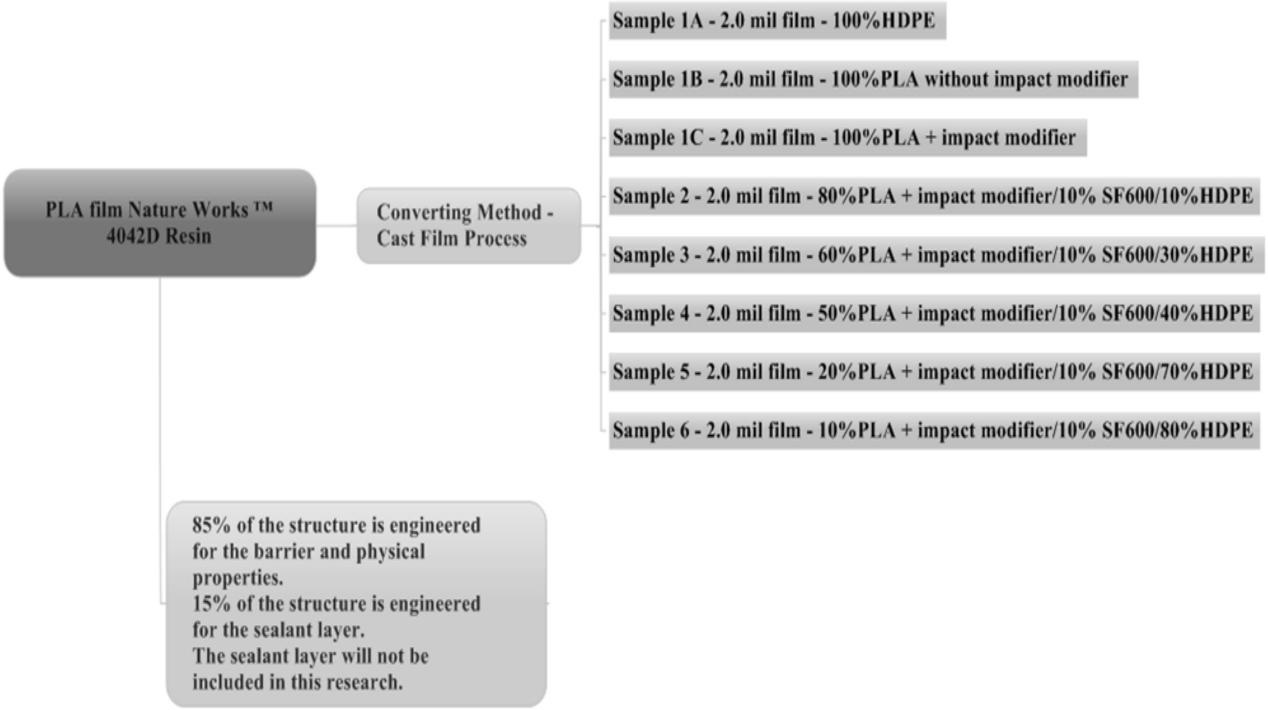


Figure 8. Test film structure variables

Table 1.3.

Film structure observed measurements vs. actual physical material measurements

Units - Mils =.001”

Layer Observed	1A	1B	1C	2	3	4	5	6
PLA	0	1.92	2.01	1.38	1.98	1.02	0.47	0.30
Tie	0	0	0	0.33	0.30	0.24	0.23	0.19
HDPE	2.00	0	0	0.53	0.26	0.80	1.24	2.14
Total	2.00	1.92	2.01	2.24	2.54	2.06	1.94	2.63
Micro Reading	1A	1B	1C	2	3	4	5	6
PLA	0	1.92	2.01	1.21	1.71	0.92	0.42	0.30
Tie	0	0	0	0.29	0.26	0.22	0.20	0.19
HDPE	2.00	0	0	0.47	0.22	0.72	1.10	2.12
Total	2.00	1.92	2.01	1.97	2.19	1.85	1.72	2.61
Layer % Observed	1A	1B	1C	2	3	4	5	6
PLA	**0**	**100**	**100**	**61.60**	**78.00**	**49.50**	**24.20**	**11.40**
Tie	0	0	0	14.70	11.80	11.70	11.90	7.20
HDPE	100	0	0	23.70	10.20	38.80	63.90	81.40

The test material was run on a pilot lab scale Cast Co-Ex film line. The Cast line was chosen due to the ability to run Co-Ex material with multiple die layer capabilities. In preparation the PLA was dried down to 250 ppm in moisture content prior to feeding the resin into the hopper. The Biomax® 120 (DuPont®) was added 10% by weight to the PLA to provide flexibility to the PLA when proceeded. The HDPE did not go through any pretreatment set up.

8.2 Extruder Conditions

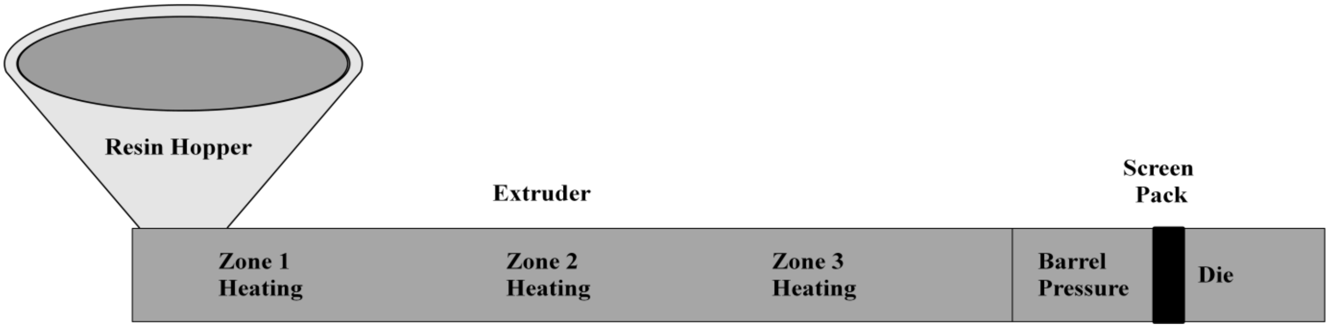


Figure 9. Single extruder design

Table 1.4.

Extruder operating conditions

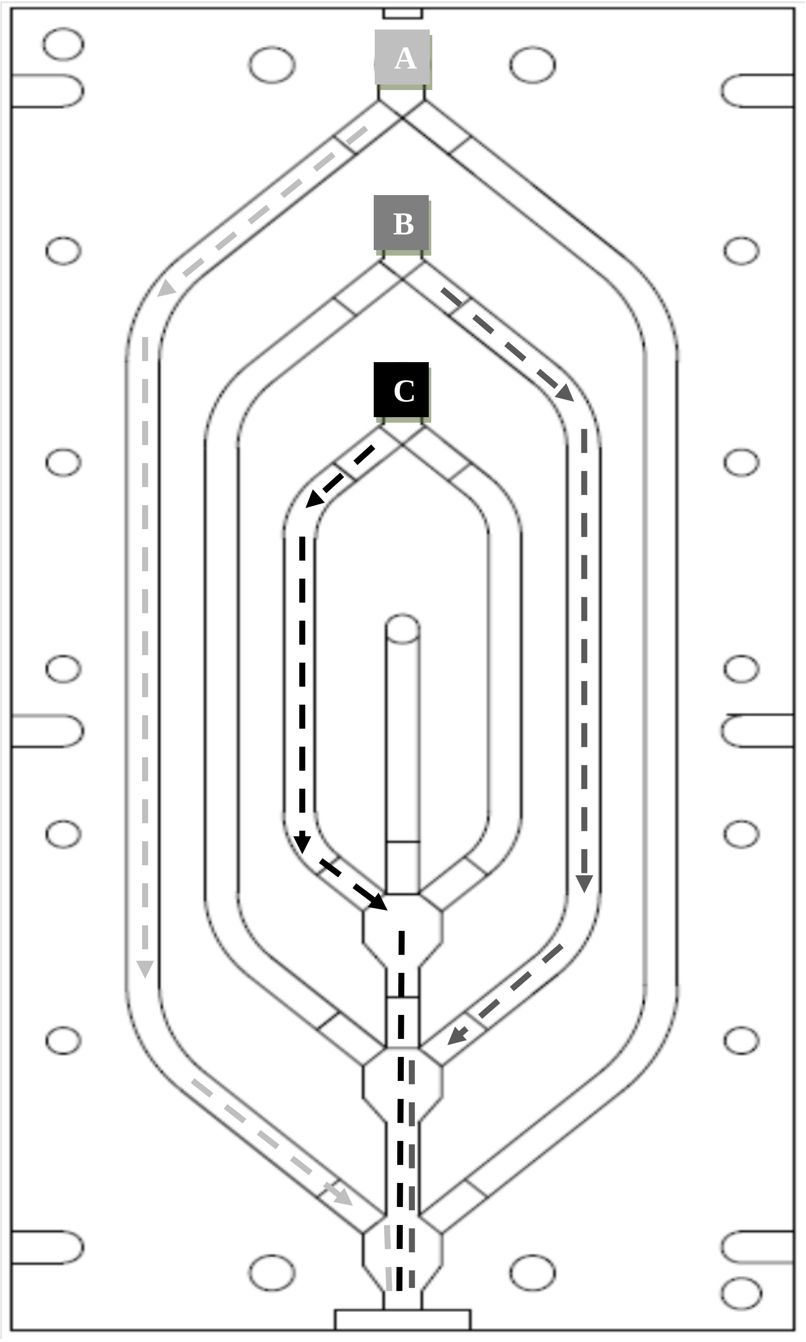
Extruder	**Zone 1 – Temp** **F°**	**Zone 1 – Temp** **F°**	**Zone 1 – Temp** **F°**	**Barrel Pressure** **PSI**
A – HDPE	400	450	450	1000
B – PLA	350	440	450	500
C – Tie Layer	235	440	440	770

The pilot Cast Co-Ex line is composed of three extruders each with a resin hopper that processes each material individually. The three extruders used in the test are the following:

- 2- 1 ¼” extruders are model KTS-125 24:1 L/D, barrier screws w/ Maddox mixers, 10 Horse Power DC Drive
- 1- 1” extruder is a Killion (Davis Standard) model KTS-100, 24:1 L/D, general purpose screw, 5 Horse Power DC Drive.

The individual extruders consist of a barrel and screw, three heating zones, and a screen pack shown in Figure 9. The two 1 ¼” A/B extruders (HDPE and PLA) respectively are fitted with a melt pump to control the flow of resin. The barrel pressure was monitored before and after the melt pump for fluctuations. The flow of resin was metered by the melt pump that was controlled by a variable speed DC motor with controller. The melt pump provides for a uniform and consistent resin flow that is independent of extruder fluctuations. Once the resin reached the screen pack and fee of debris, the molten resin flows into the feed block. The feed block maintains the resin laminar flow to the coat hanger die which prevents resin mixing shown in Figure 10. The coat hanger die maintains the laminar flow and laterally spreads the resin from the inlet of 3/4" to 14" through the die lip. The extruded Co-Ex film is metered onto a quenching chill roll which sets up the crystallization structure of the film. The film was then wound onto a master roll for material analysis.

Feed Block Diagram



Extruder A – PLA, Extruder B – HDPE, Extruder C – Tie Layer

Figure 10. Feed block die resin flow

9.0 ANALITICAL RESULTS AND FINDINGS

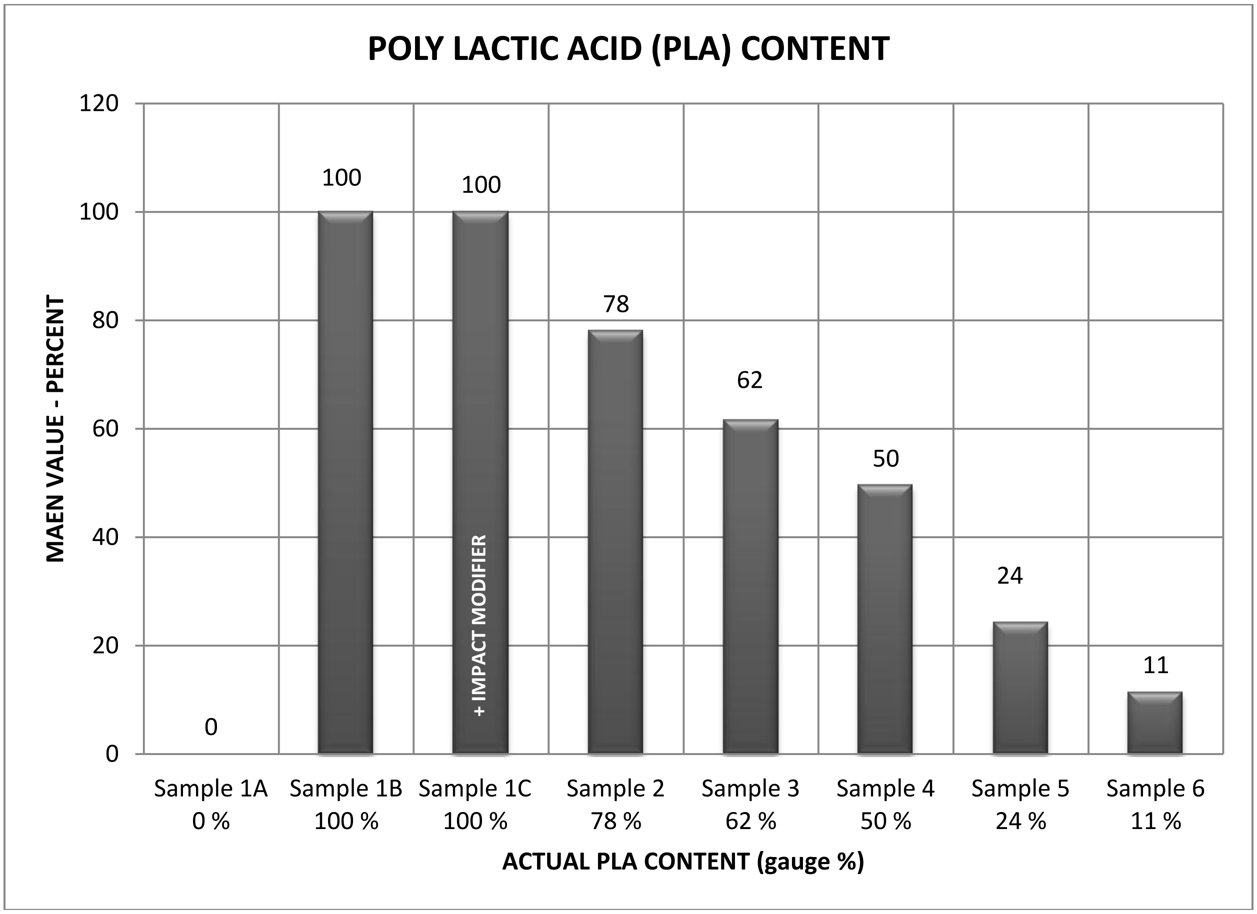


Figure 11. Poly Lactic Acid percent content in film structure

In Figure 11 it is noted that the PLA content of each film structure variable is expressed as a percentage of the total thickness of the film. The percentage of PLA content was determined by two methods. The first method determined the percentage content by microtoming the sample and then viewing it under a microscope. The software (Image Pro Plus) was used to derive the measurements from the microtome samples. The second method used a micro gauge reading which is the actual overall thickness determined when measuring the sample with a micrometer. Both measurement techniques were used to provide the greatest level of accuracy since the film was highly compressible. It is noted the actual measured percentage of PLA content per film structure variable is slightly different than the DOE test plan in Figure 8.

9.1 Clarity

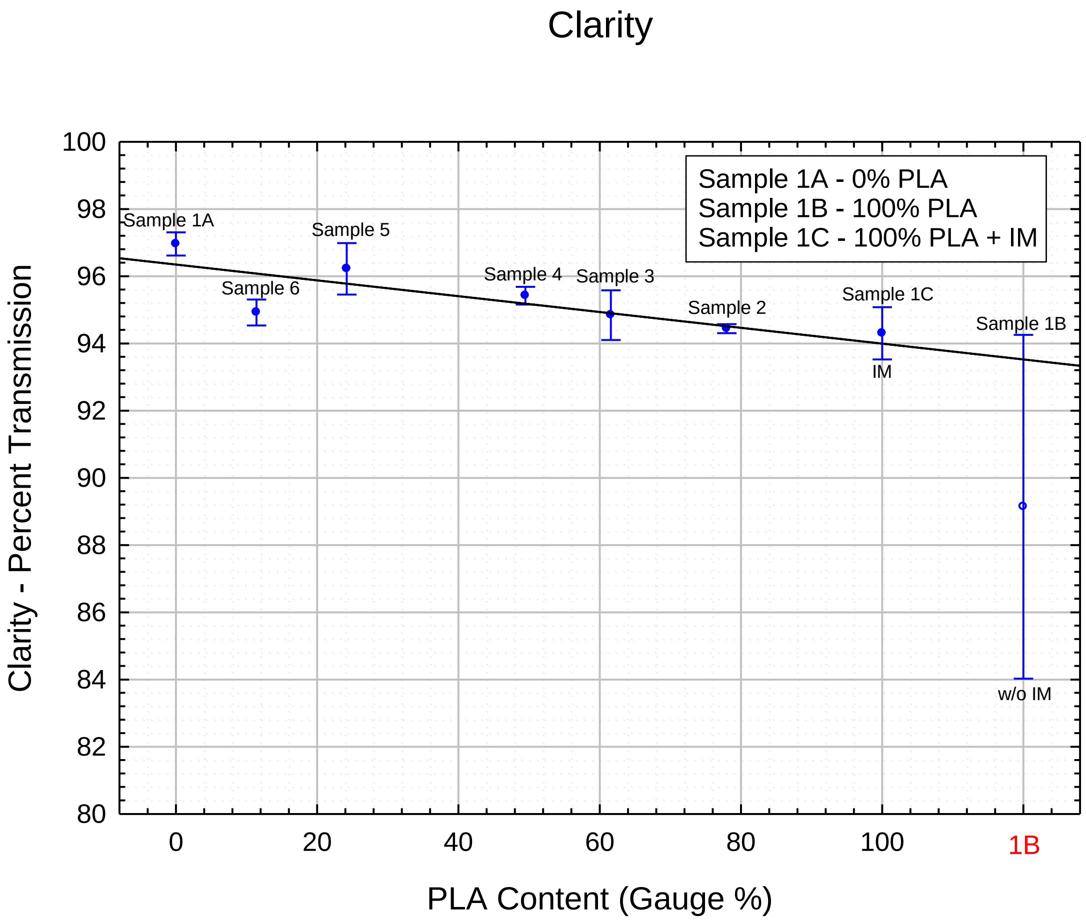


Figure 12. Percent light transmission in film structure

In Figure 12 the film structures were tested for percent clarity in accordance with ASTM D1003 method using a Byk-Gardner Haze-Gard Plus lab tester. The percentage of narrow angle light transmission through the film of sample 1A which is 100% HDPE allowed for the greatest light transmission of all the sample structures. Sample 1B which is 100% PLA had demonstrated less light transmission through the film compared to sample 1A and was statistically significant. Samples 2-6 showed no significant difference in light transmission through the film compared to sample compared to 1A and 1C. A trend showed as the percentage of PLA content was increased and HDPE content reduced the light transmission level reduced linearly. Sample 1C with the 10% impact modifier added did show a statistically significant difference in light transmission compared to sample 1B. Sample 1C demonstrated an increase in the amount of light transmission through the film. PLA without an impact modifier is a highly crystalline structure which contributes to the scattering of light in the polymer. It was anticipated when adding the impact modifier that it created an increased amorphous polymer matrix. This created smaller and fewer crystalline sites which reduced diffraction of light contributing to the increase in transparency through the film.

9.2 Haze

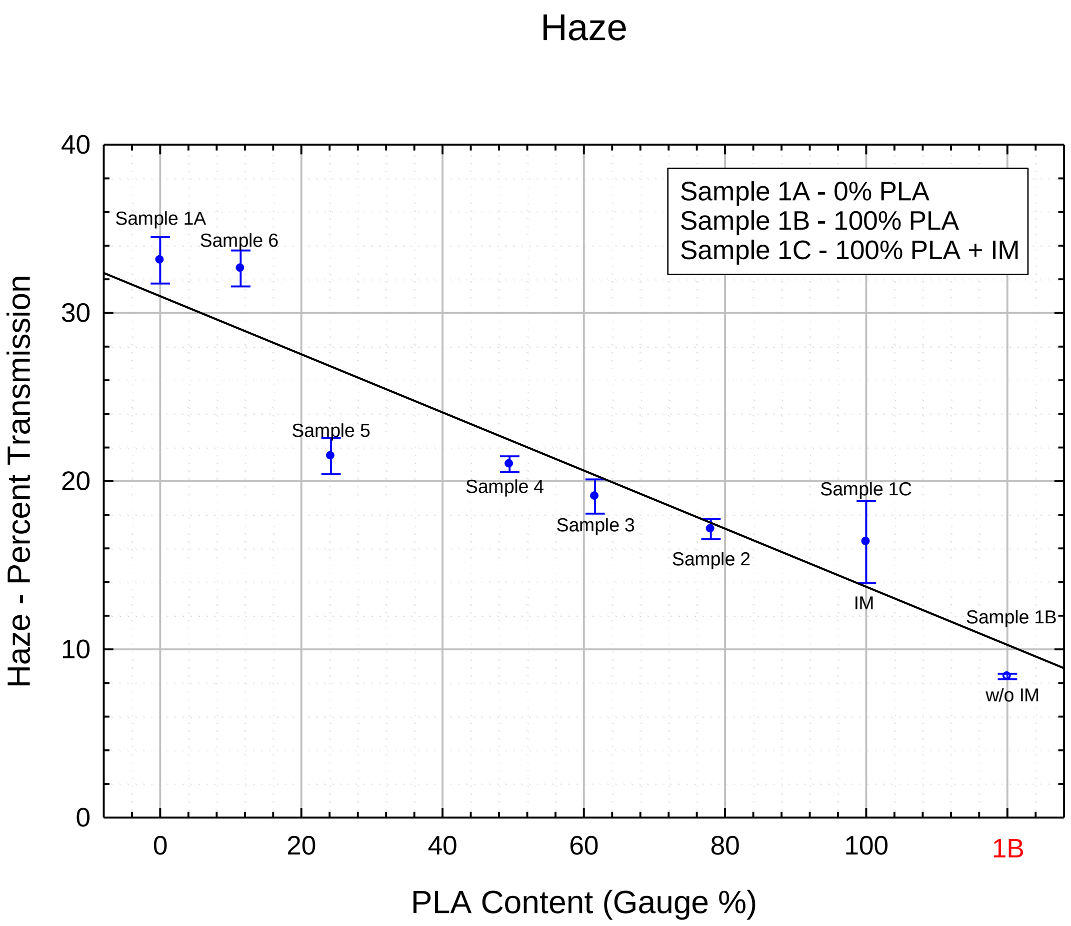


Figure 13. Percent haze in film structure

In Figure 13 the film structures were tested for percent haze in accordance with ASTM D1003 method using a Byk-Gardner Haze-Gard Plus lab tester. The percentage of wide angle light transmission through the film with sample 1A which is 100% HDPE allowed for the greatest percent haze of all the sample structures. Sample 1B which is 100% PLA had demonstrated the least amount of percent haze which was statistically significant compared to sample 1A. Samples 2-5 showed a statistically significant difference in haze compared to sample

1A. The trend showed as the percentage of PLA content was increased and HDPE content reduced the percentage of haze reduced linearly.

9.3 Coefficient of Friction (Inside/Inside)

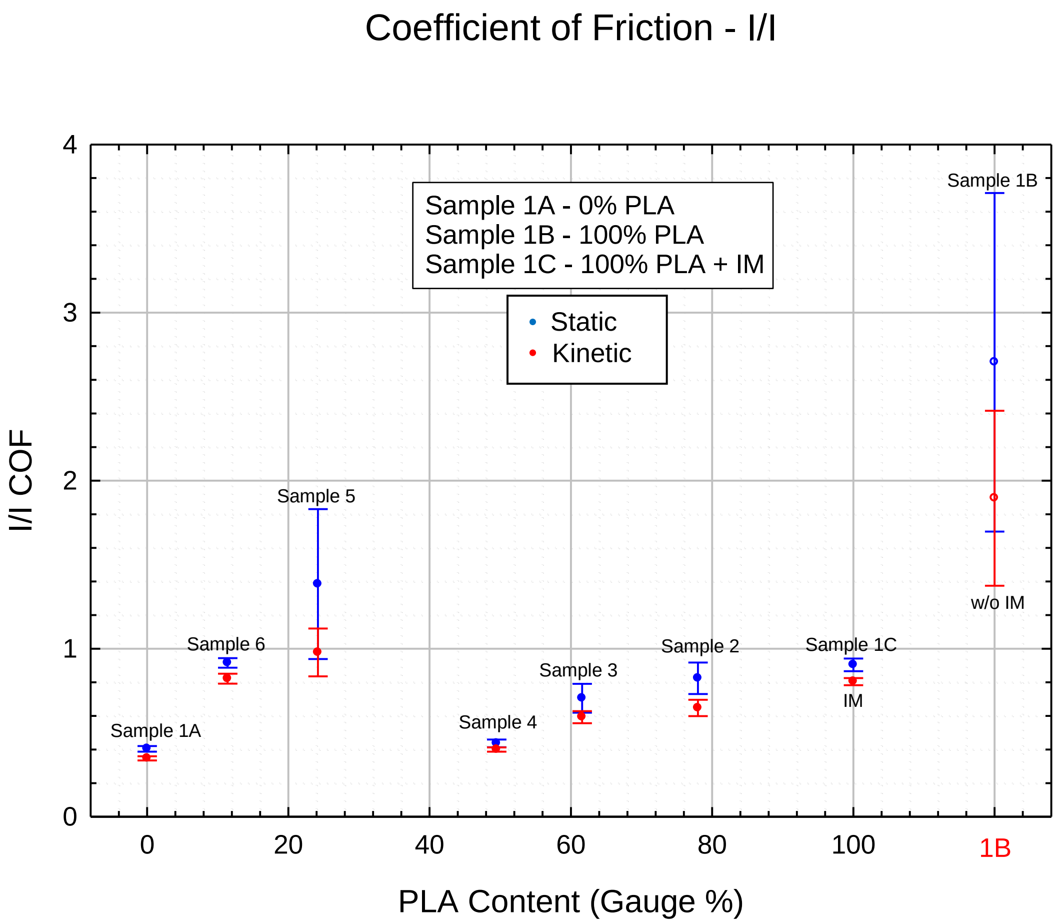


Figure 14. Inside COF of film structure variables

In Figure 14 the film structures were tested for static and kinetic inside COF in accordance with ASTM D1894 method using the Testing Machines Inc 32-06 lab tester. No slip additives were incorporated into the film structure. As expected, there was a difference between the static and kinetic COF within each film structure variable. The static COF was higher in all cases compared to the kinetic COF. Sample 1A which is 100% HDPE showed the overall lowest static and kinetic COF of all film structure variables. Sample 1B which was 100% PLA demonstrated the highest both static and kinetic COF values that was statistically significant compared to all samples. Samples 2-4 showed a trend that as the PLA content was increased the COF values both static and kinetic both slightly increased. However, sample 5-6 showed just the opposite trend. It may be noted that the COF results were somewhat inconclusive and there would need to be additional testing particularly when lower percentages of PLA were used in the film structure variables.

9.4 Coefficient of Friction (Outside)

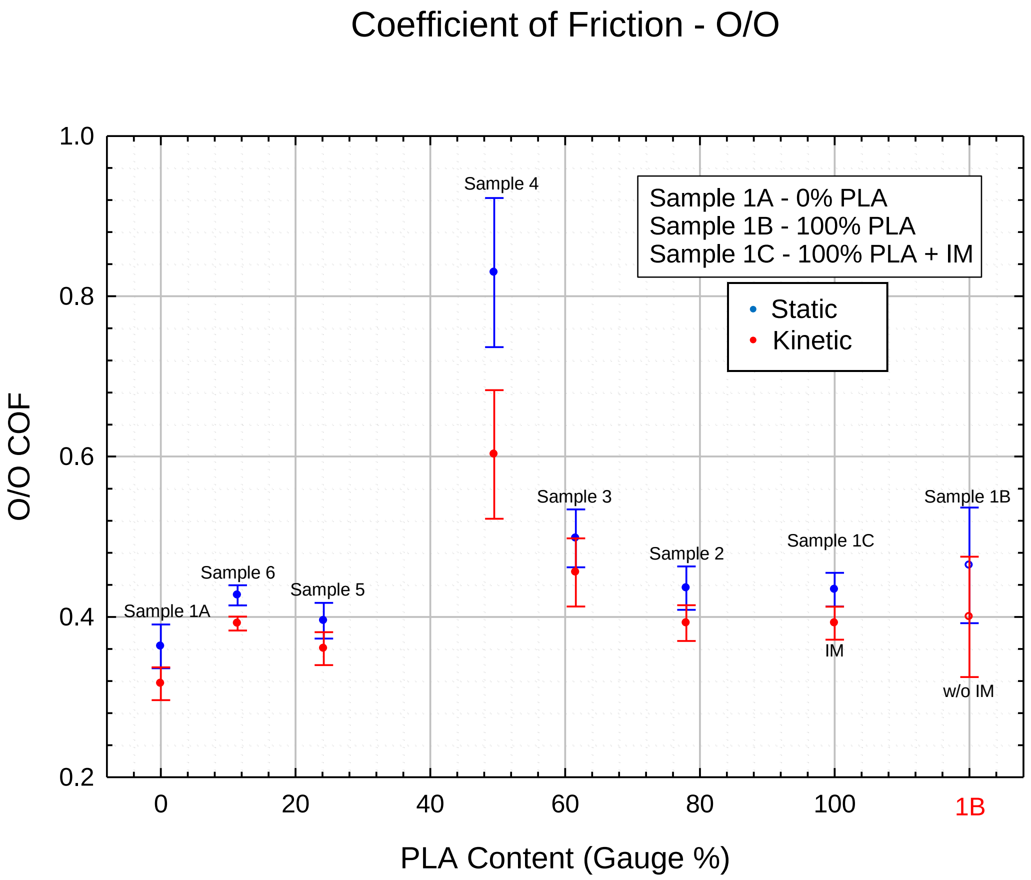


Figure 15. Outside COF of film structure variables

In Figure 15 the film structures were tested for static and kinetic outside COF in accordance with ASTM D1894 method using the Testing Machines Inc 32-06 lab tester. No slip additives were incorporated into the film structure. As expected, there was a difference between the static and kinetic COF within each film structure variable. The static COF was higher in all cases compared to the kinetic COF. Sample 1A which is 100% HDPE showed the overall lowest static and kinetic COF of all film structure variables. Sample 1B which was the 100% PLA demonstrated slightly higher both static and kinetic COF values but was not statistically significant compared to all samples. Samples 2,3,5,6 showed a trend that as the PLA content was increased the COF values both static and kinetic remained consistent to each other. However, sample 4 showed just the opposite trend. Sample 4 was 50% PLA and it demonstrated the highest static and kinetic COF of all film structure variables.

9.5 Tear Resistance (Notched)

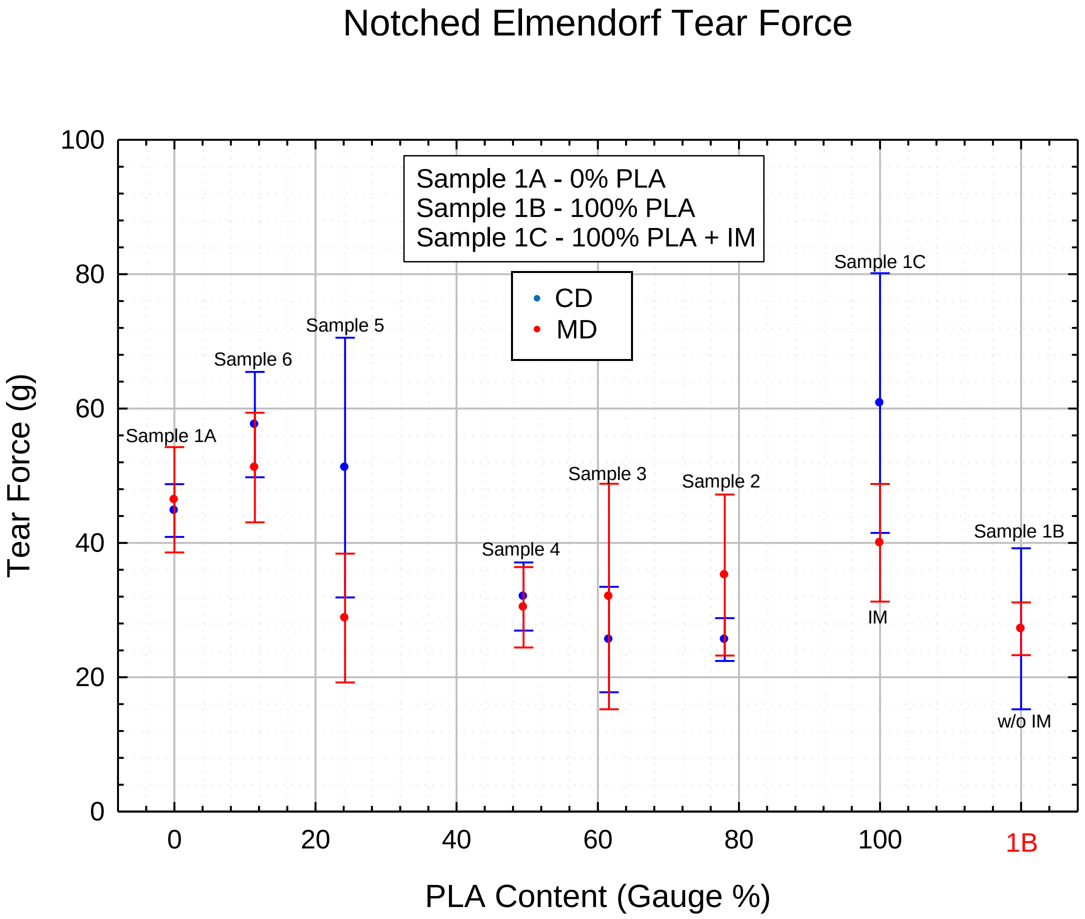


Figure 16. CD & MD notched tear resistance of film structure variables

In Figure 16 the film structures were tested for notched CD and MD tear resistance in accordance with ASTM D1922 method using the Thwing-Albert Elmendorf lab tester. Sample 1A which was 100% HDPE showed consistent tear resistance force both MD and CD. Sample 1B which was 100% PLA showed consistently low tear resistance force both MD and CD. This was to be expected with the crystalline structure of PLA the polymer once the tear propagation was initiated it facilitated propagation to tear. This was validated in Sample 1C with a less crystalline film structure when the impact modifier was added and the tear resistance force increased significantly in both but particularly in the CD direction. However, with the exception of sample 6 when the PLA content was increased and the HDPE content reduced the tear resistance force remained similar. Once the film structure is notched it takes on the tear characteristics of the weaker material in this case PLA.

9.6 Tear Resistance (Un-Notched)

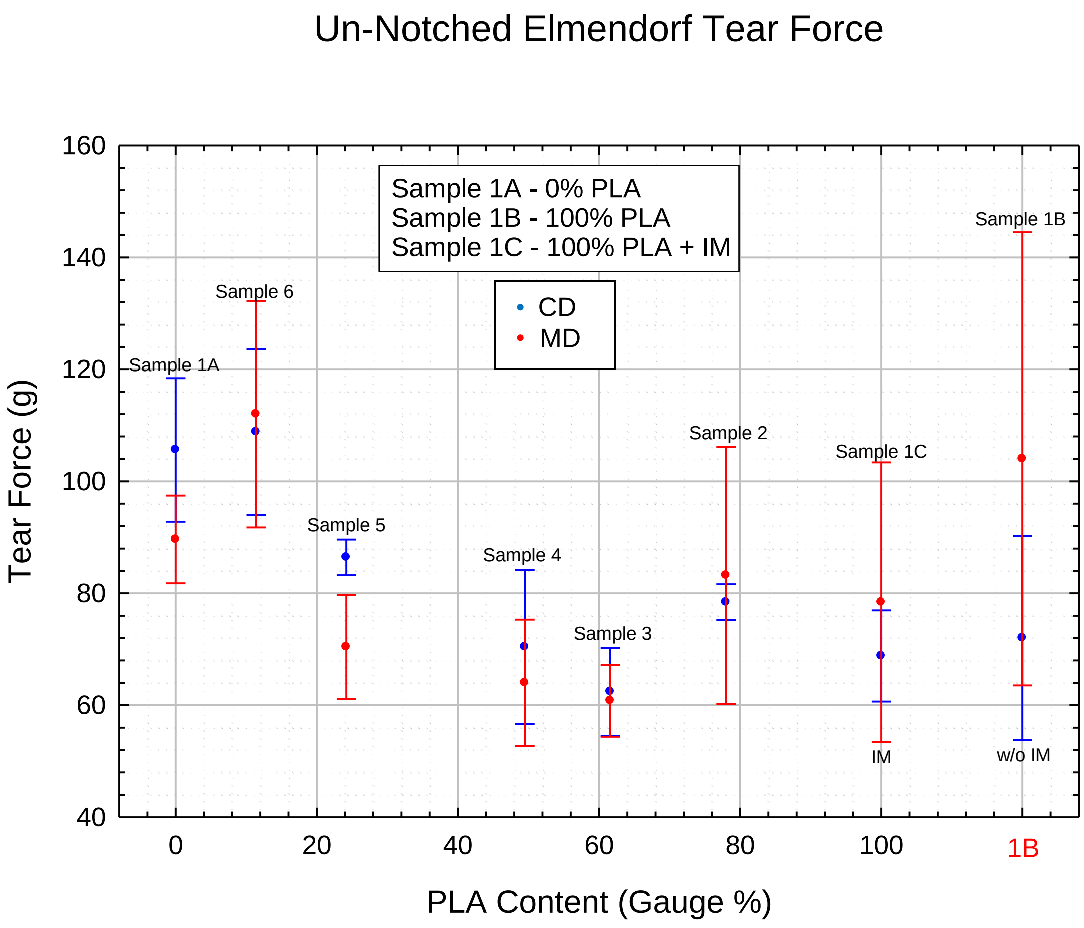


Figure 17. CD & MD un-notched tear resistance of film structure variables

In Figure 17 the film structures were tested for unnotched CD and MD tear resistance in accordance with ASTM D1922 method using the Thwing-Albert Elmendorf lab tester. Sample 1A which was 100% HDPE demonstrated high tear resistance force both MD and CD. Sample 2-5 which showed un-notched tear resistance force both MD and CD to be similar and lower. This was to be expected as the PLA content was increased the tear resistance to force reduced. This was due to the more non crystalline structure of HDPE polymer that is more resistance to tear.

9.7 Puncture Resistance

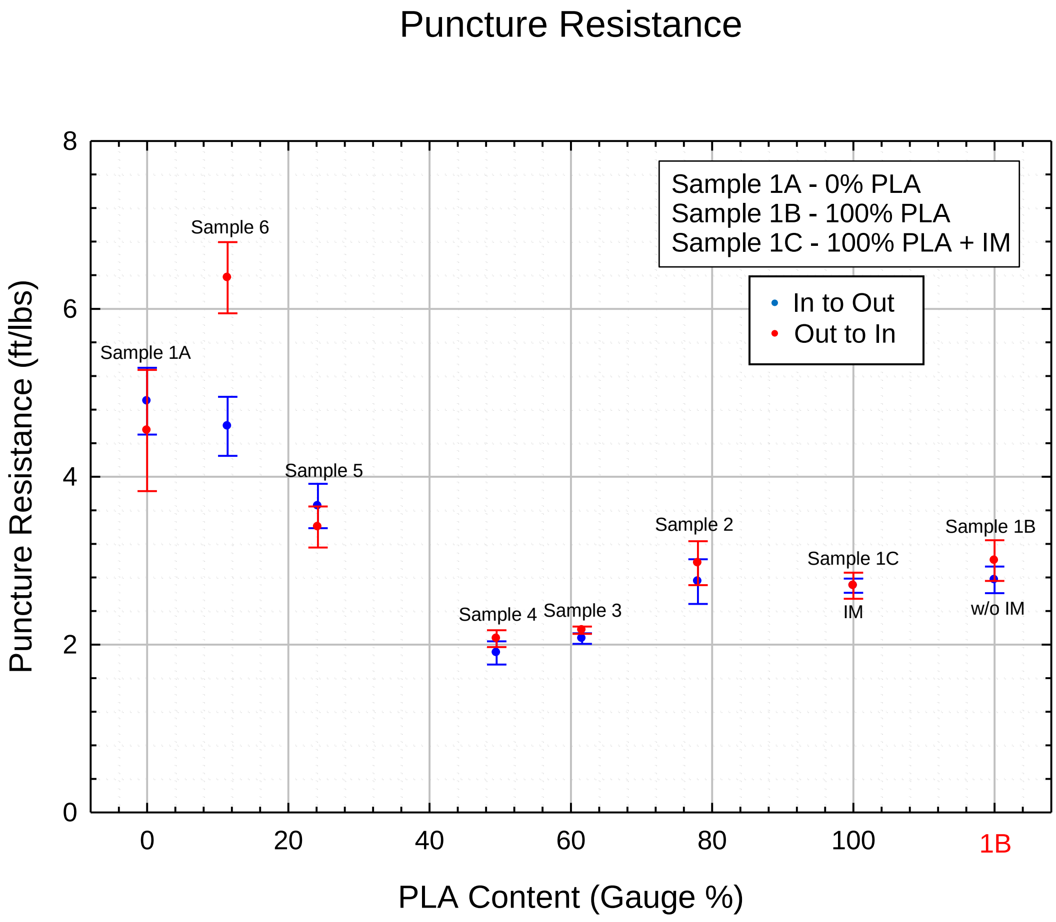


Figure 18. Maximum puncture resistance of film structure variables

In Figure 18 the film structures were tested for maximum puncture resistance in accordance with ASTM D3763 method using the Instron- Dynatup lab tester. Sample 1A like Sample 6 both showed the highest resistance to puncture compared to the rest of the samples.

The trend demonstrated was as the PLA percent content increased the puncture resistance reduced. Conversely as the HDPE content increased the puncture resistance increased.

9.8 Secant Modulus (MD)

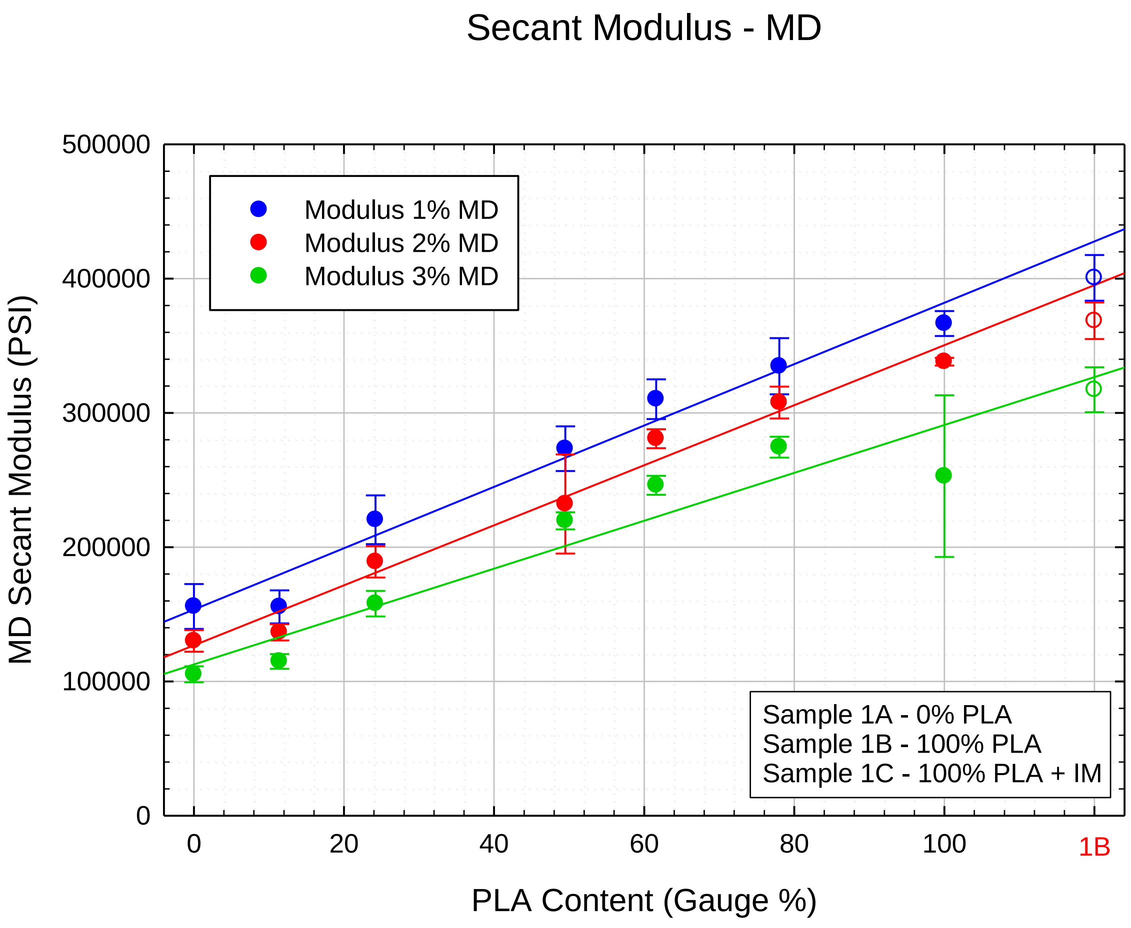


Figure 19. Machine direction secant modulus of film structure variables

In Figure 19 the film structures were tested for 1%-3% MD modulus in accordance with ASTM D882 method using the Instron – 5566 lab tester. Sample 1A like Sample 6 both showed the lowest MD modulus compared to the rest of the samples. The trend demonstrated as the PLA content increased the MD modulus increased proportionally. PLA is a more crystalline polymer and as expected the stiffness which directly impacted the increased modulus.

9.9 Secant Modulus (CD)

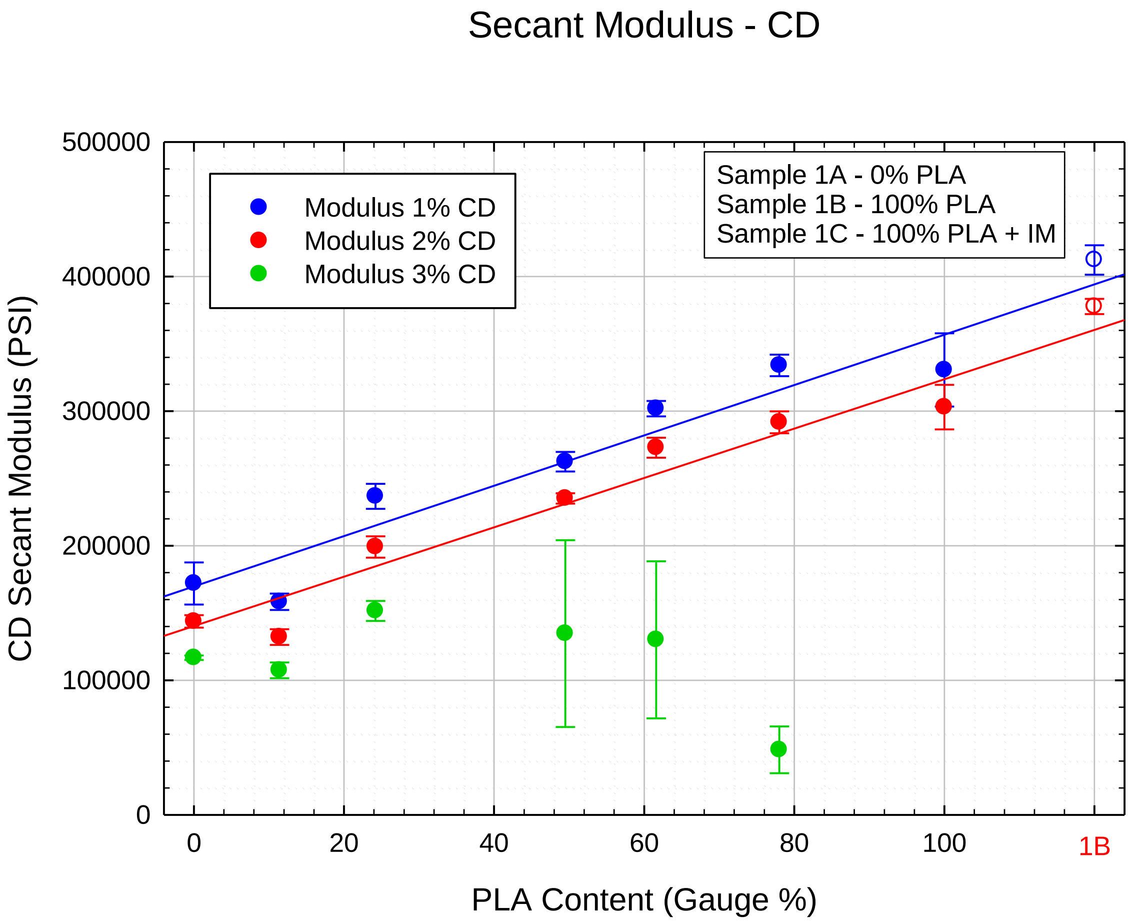


Figure 20. Cross direction secant modulus of film structure variables

In Figure 20 the film structures were tested for 1%-3% CD modulus in accordance with ASTM D882 method using the Instron – 5566 lab tester. Sample 1A like Sample 6 both showed the lowest CD modulus compared to the rest of the samples. The 1% modulus trend was inconclusive however, the trend of 2%-3% modulus demonstrated as the PLA content was increased the CD modulus increased proportionally. This was to be expected as PLA is a more crystalline polymer which would directly affected the modulus. There was a noted difference between the MD and CD modulus with the MD modulus having slightly higher values overall which resulted from the cast film orientation process.

9.10 Tensile (MD)

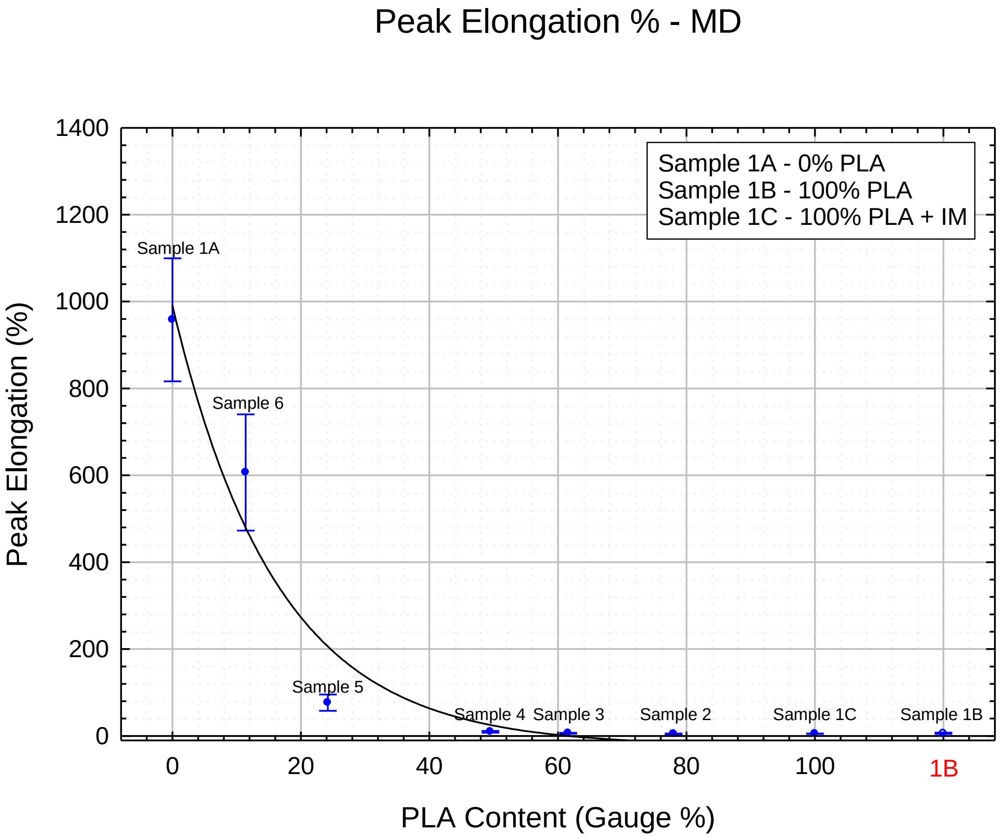


Figure 21. Machine direction peak percent elongation of film structure variables

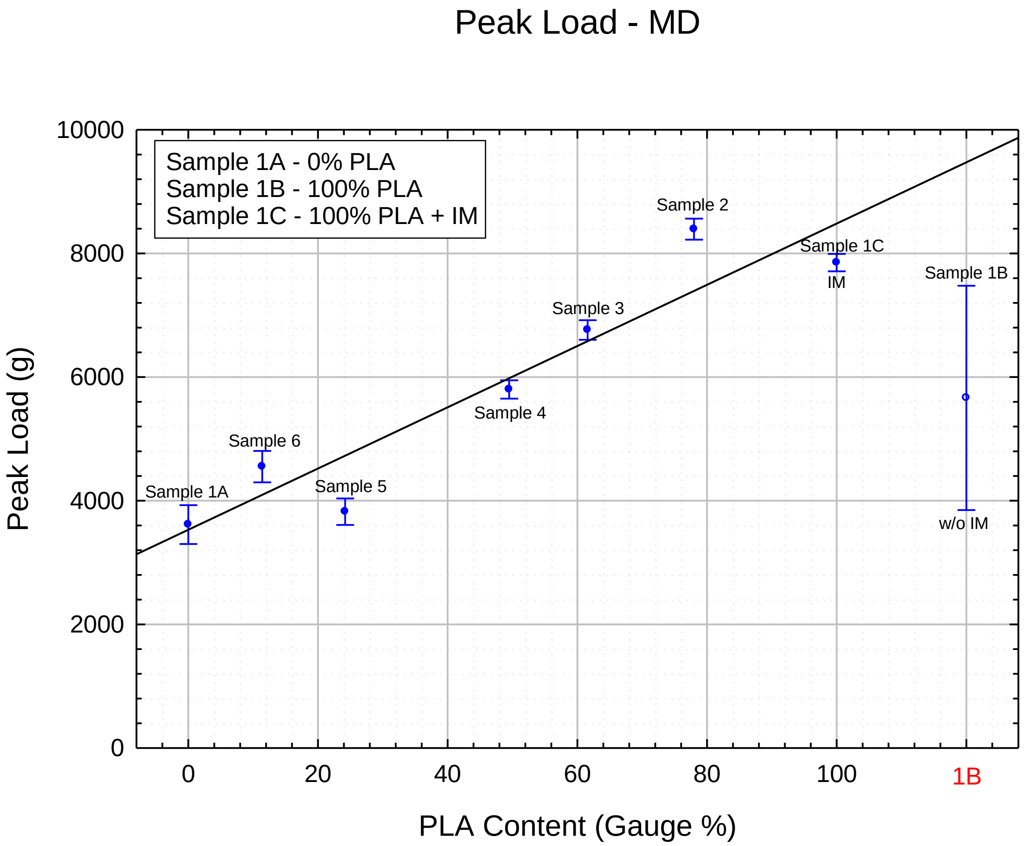


Figure 22. Machine direction peak load of film structure variables

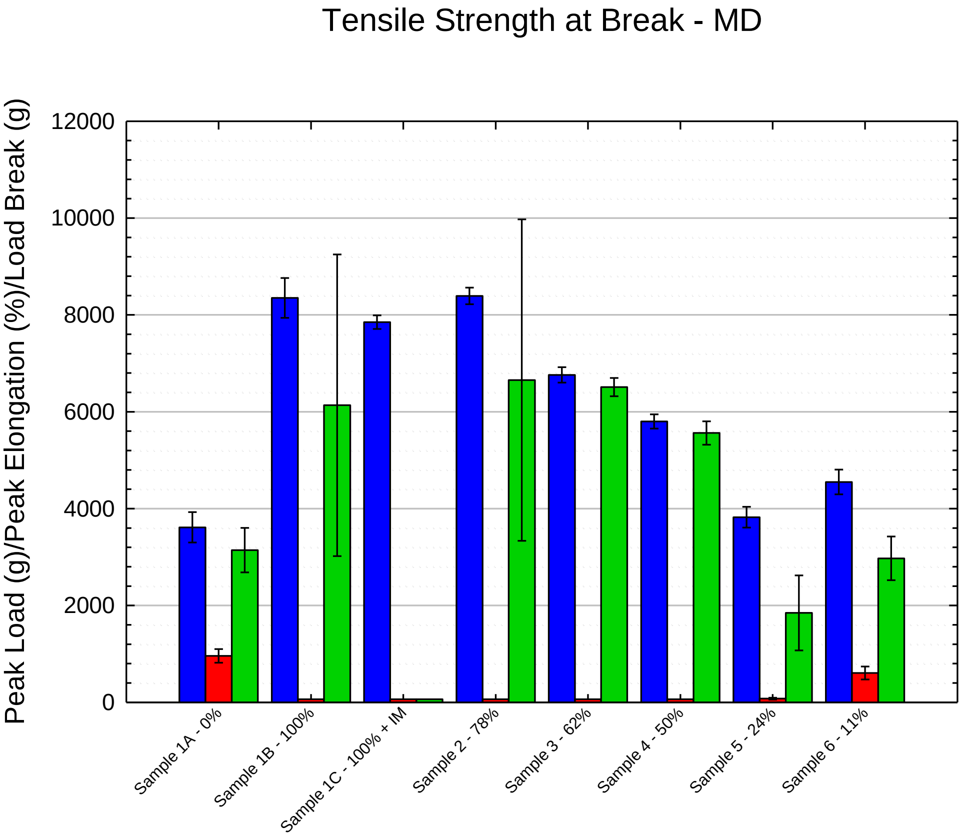


Figure 23. Machine direction tensile strength at break of film structure variables

In Figure 23 the film structures were tested for MD tensile load in accordance with ASTM D882 method using the Instron – 5566 lab tester. Sample 1A like Sample 6 both showed the highest MD peak elongation compared to the rest of the samples. The samples that contained higher percentages of PLA demonstrated very low levels of peak elongation. The film samples rather than elongating failed at high levels of peak load and load at break. When the PLA content was increased the peak load and load at break increased respectively. Sample 2 which was a high percentage of PLA showed the highest of level of peak at load and load at break of all film structure candidates.

9.11 Tensile Strength (CD)

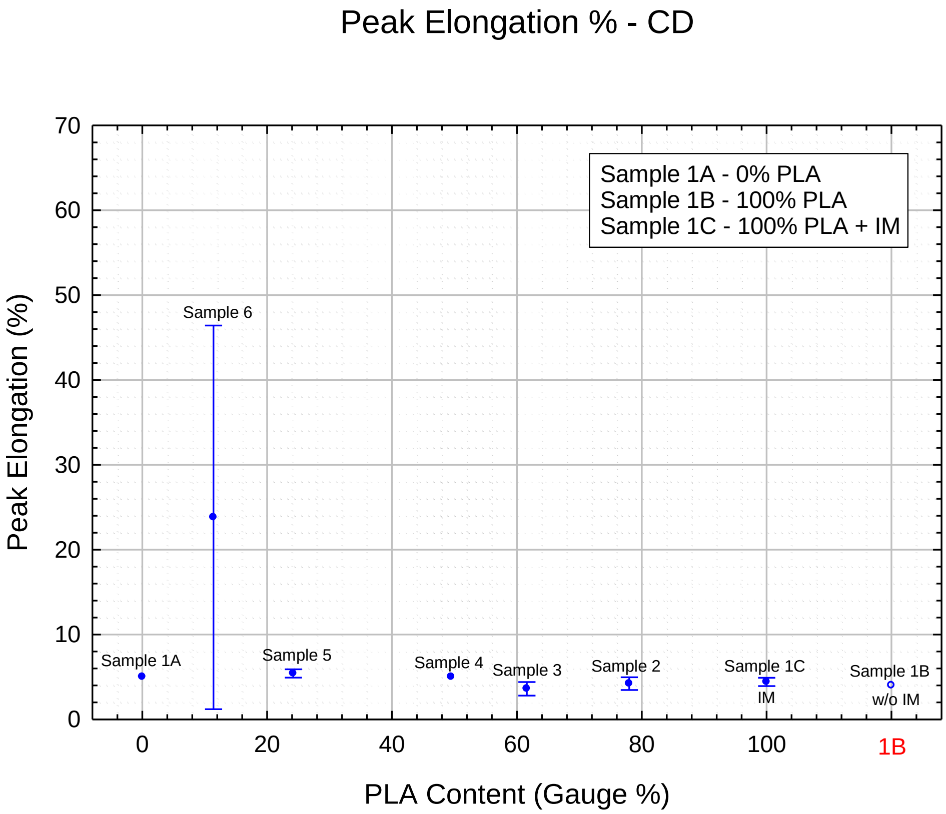


Figure 24. Cross direction peak elongation of film structure variables

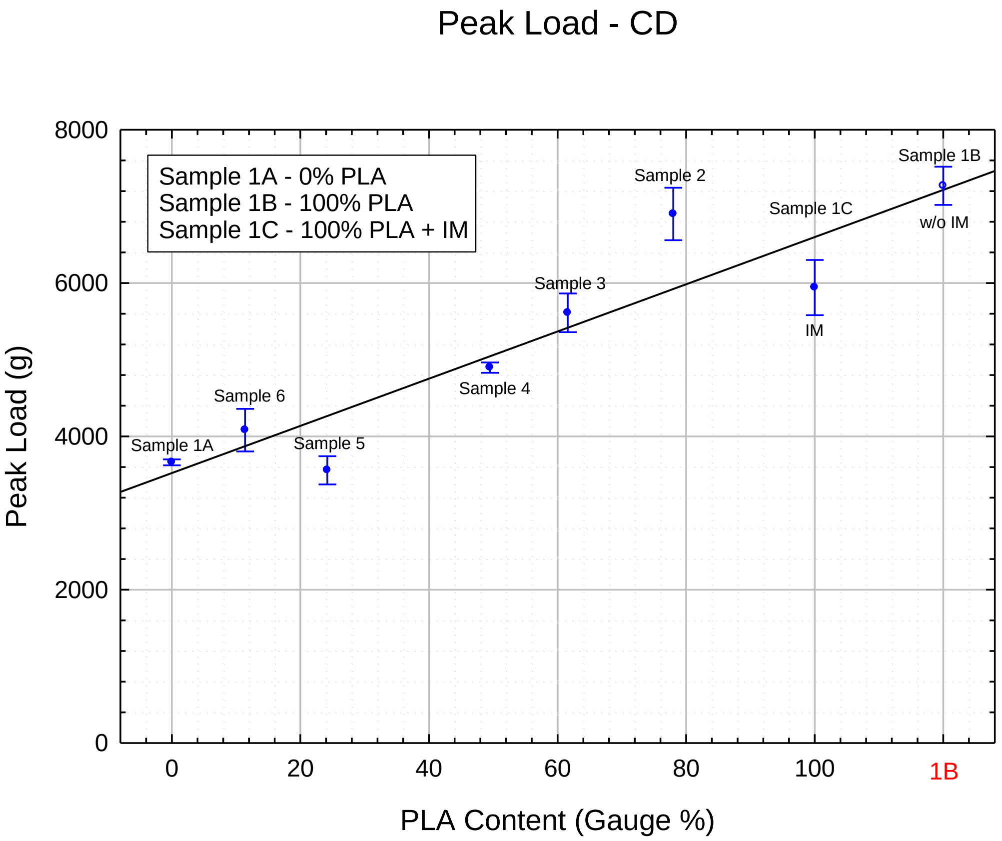


Figure 25. Cross direction peak load of film structure variables

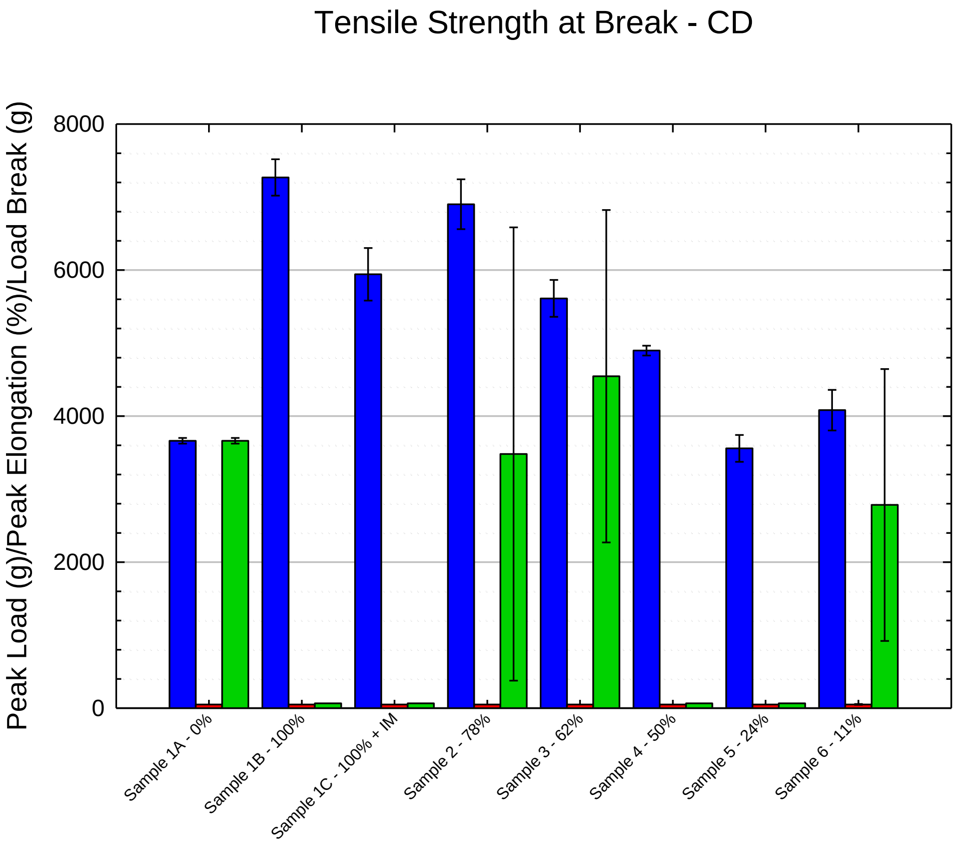


Figure 26. Cross direction tensile strength at break of film structure variables

In Figure 26 the film structures were tested for CD tensile load in accordance with ASTM D882 method using the Instron – 5566 lab tester. All samples demonstrated low peak CD percent elongation with the exception of sample 6. This was likely a result to the low CD film orientation in the cast film process. The film samples rather than elongating failed at high levels of peak load and load at break. As PLA content increased the peak load and load at break increased respectfully. Sample 1B which was the 100% PLA did show the highest CD peak to load of any of the film structure variables. Samples 2, 3, and 6 showed unusually high standard deviation due to small size and single data points that were significant different from the group.

9.12 OTR Permeation

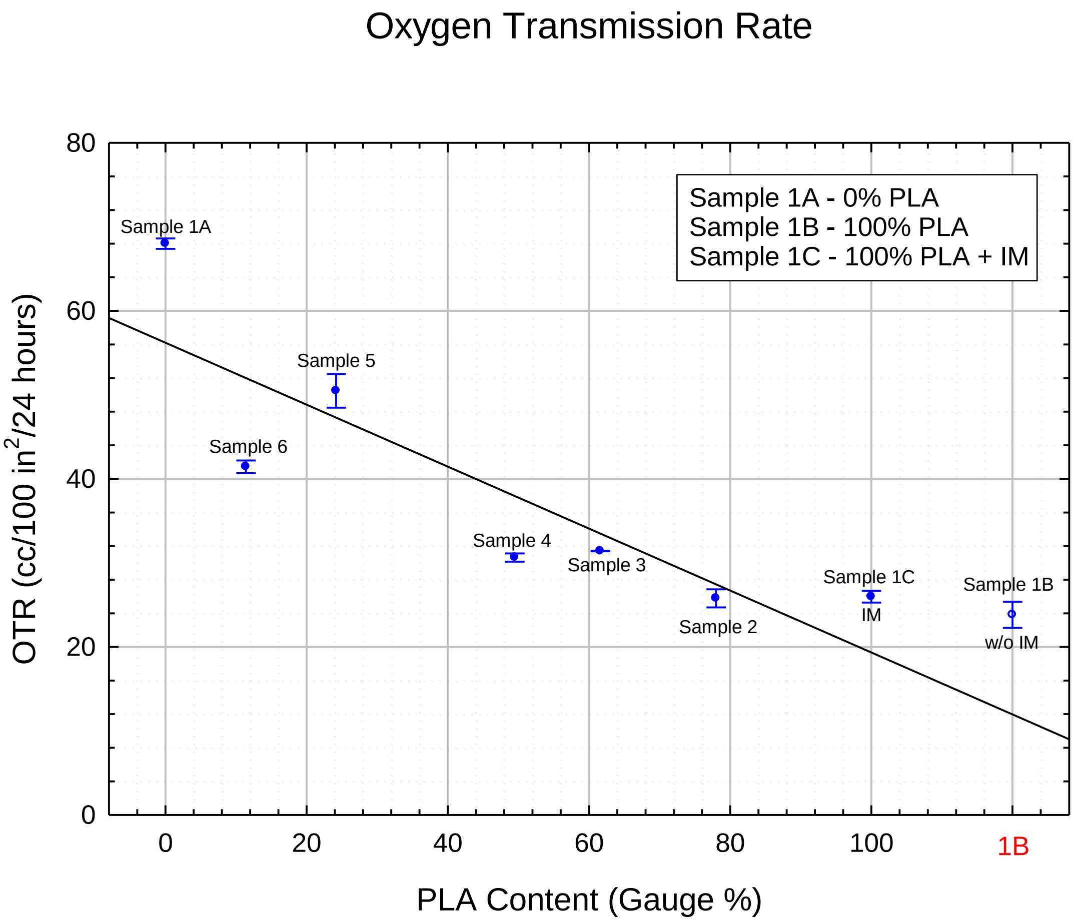


Figure 27. Oxygen transmission permeation rate of film structure variables

In Figure 27 the film structures were tested for oxygen transmission in accordance with ASTM D3985 method using the MOCON OX- TRAN 2/20 lab tester. Sample 1B that is a 100% PLA film structure demonstrated the lowest level of permeation of all the film structure variables. Sample 1C with the impact modifier actually had a negative impact on barrier as it reduced the amount of PLA as a percentage in the overall total thickness. As expected, HDPE polymer is a non polar and oxygen gas is a non polar molecule. The polymer polarity of HDPE readily absorbs non polar molecules such as oxygen. Demonstrated as the HDPE content increases the oxygen permeability increases. PLA polymer is polar polymer and the polymer demonstrates a reduction in permeability of oxygen as a non polar gas.

9.13 WVTR Permeation

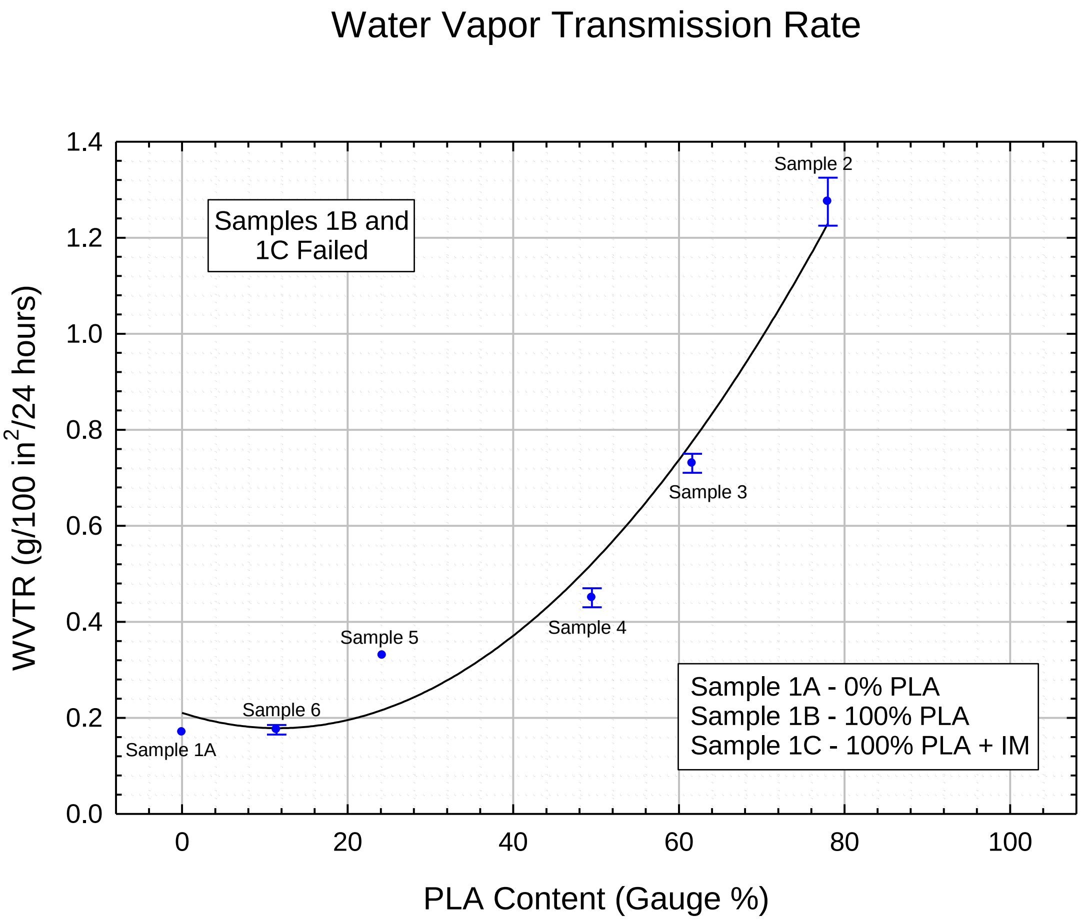


Figure 28. Water vapor transmission rate of film structure variables

In Figure 28 the film structures were tested for moisture transmission in accordance with ASTM F1249 method using the MOCON PERMATRAN-W® Model 3/33 lab tester. Sample 1B and 1C that is 100% PLA and 100% PLA plus impact modifier respectfully failed since the moisture permeation was elevated for the testing apparatus. PLA is a polar hydrophilic polymer which inherently has infinity to moisture. Sample 1A and 6 both demonstrated the lowest moisture permeation performance of all film structure variables. As expected, HDPE is a non polar hydrophobic polymer which provides a reduction in permeation to the polar water molecule. The trend demonstrated moisture permeation decreases as the percent of HDPE content increases and the PLA percent content decreases.

9.14 Summary of Properties

C0-EX FILM PROPERTIES

Table 1.5.

Film Property Values

		Samples (%PLA)							
Typical Values	**Units**	**1A-0%**	**1B -100%**	**1C-100%**	**2 -78%**	**3 -61.6%**	**4 - 49.5%**	**5 - 24.2%**	**6 - 11.4%**
Clarity (Clear Film)	%	97	94	89	94	95	95	96	95
Haze(Clear Film)	%	33	8	16	17	19	21	21	33
Coefficient of Friction Static & Kinetic	uS	.36/.32	.46/.40	.43/.39	.44/.40	.50/.45	.83/.60	.40/.36	.43/.40
Elmendorf Tear Strength Notched MD & CD	gms	46/45	27/27	40/61	36/26	32//26	30/32	29/51	51/58
Elmendorf Tear Strength Un Notched MD & CD	gms	90/106	104/72	78/69	83/78	61/62	64/70	70/86	112/109
High Speed Puncture Multiaxial impact (Dynatup) I/O	ft/lbs	4.9/4.6	2.8/3.0	2.7/2.7	2.8/3/0	2.1/2.2	1.9/2.1	3.7/3.4	4.6/6.4
Secant Modulus MD & CD 1%	psi	156000 172000	401,000 412,000	366,000 330,000	334,000 334,000	310,000 302,000	273,000 262,000	220,000 237,000	156,000 158,000
Tensile Elongation @ break MD & CD	%	958 5	6 4	5 4	5 4	6 4	9 5	77 5	607 24
Tensile Strength @ break MD & CD	%	3143 3661	7667 16	17 13	8311 5793	6509 5678	5562 11	2190 9	2972 2782
OTR	cc/100 in² /24 hr.	68	23.1	26	26	31.4	31	50	41.4
WVTR	g/100 in² /24 hr.	0.17	F	F	1.28	0.73	0.45	0.33	0.18

In Table 1.5 the film structures were tested for typical properties. The chart provides qualitative values for each sample tested as comparative samples.

10.0 SUSTAINABILITY

10.1 Energy

All the analysis was conducted using the software program (Savvy Pack®) from Allied Development™. The evaluated categories that were considered were the following: Green House Gas, Water Usage, Waste, and Energy. Green House Gas (GHG) and Energy were the two focused categories that were evaluated. The inputs for Energy and GHG were the following: Raw materials, Raw materials packaging, Raw materials and packaging transport, processing, distribution packaging, distribution transport, and transport to customer. The individual film structures were analyzed using the assumptions listed below from industry data.

Assumptions and example for analysis:

- 2.2 mil film structure (including sealant layer)
- Produced by one supplier and one production location
- Shipped maximum 1000 miles to CPG's by truck
- Annual film volume - 9,870,429 ft^2
- Annual converted number of packages
- Example: package size – 20" roll width, 10" cut off = 200 in^2 or 1.38 ft^2 →7,1524,848 total packages
- 12 packages per container = 5,960,404 cases - @ 6MM case annual volume

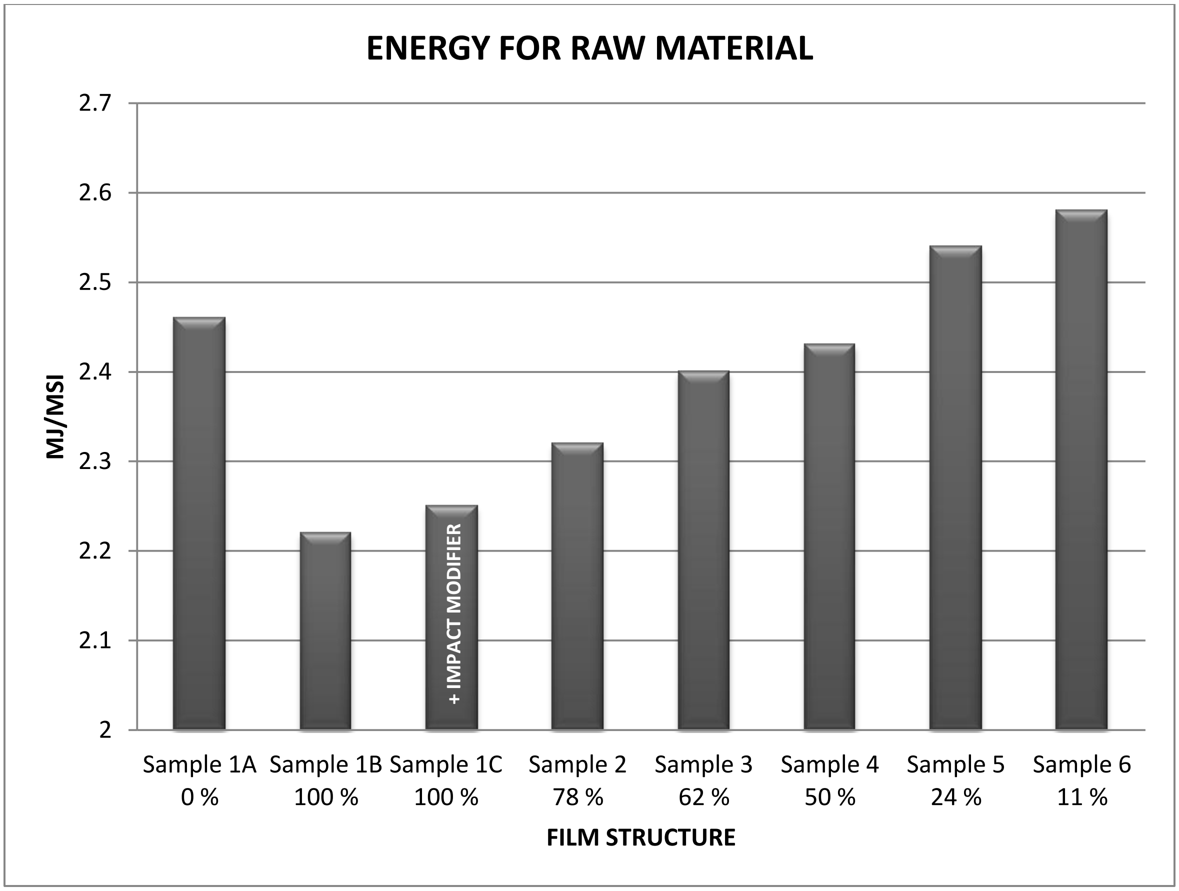


Figure 29. Mega Joules of energy / MSI of raw materials for each film structure

In Figure 29 the film structures were evaluated based on the mega joules of energy per thousand square inches (MSI) of film. The raw materials consist of all the combined resins to convert the individual film structures which include HDPE, tie layer, PLA, LDPE, and Ethylene Vinyl Acetate (EVA). Another factor such as packaging materials and transport of incoming materials is not factored into the number. The trend that is demonstrated for the raw material energy is that as PLA resin content decreases in the film structure the MJ/MSI increases.

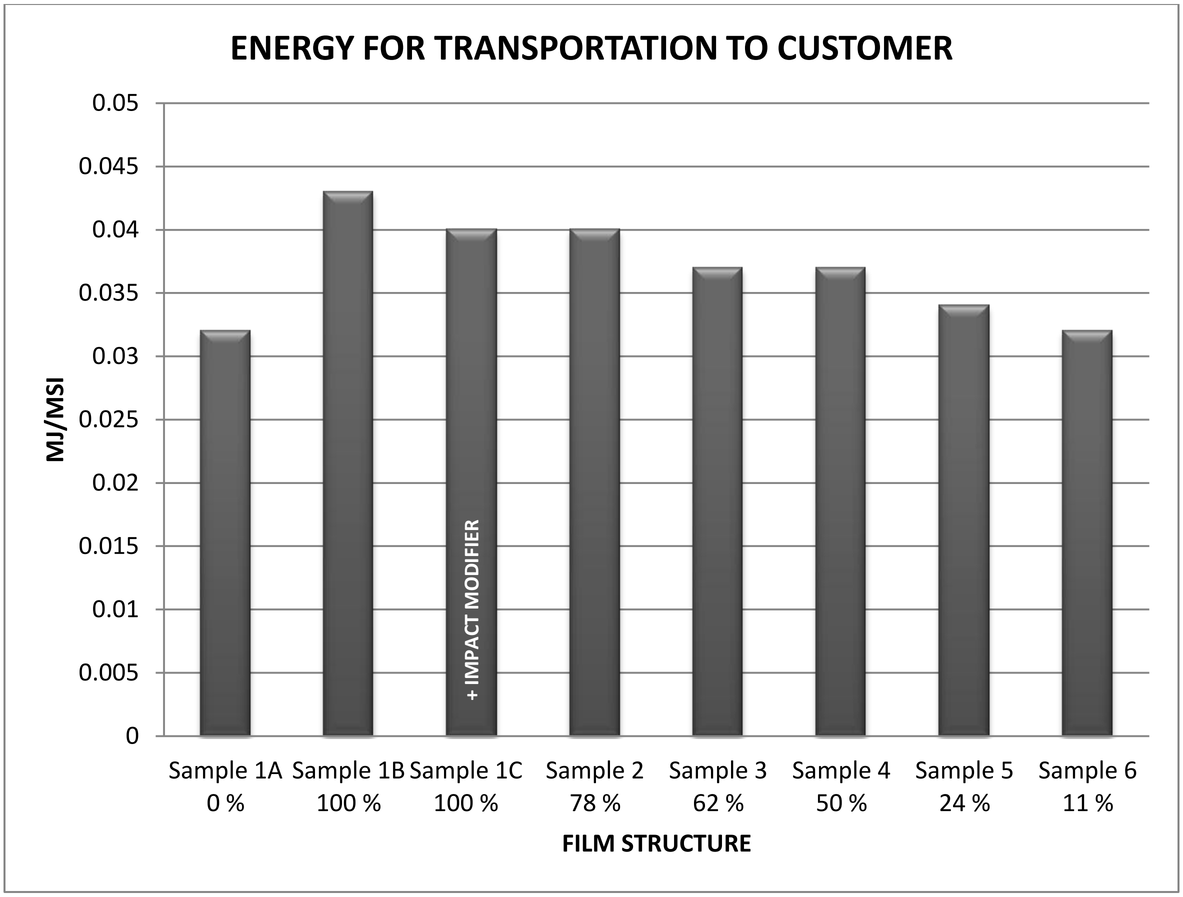


Figure 30. Mega Joules of energy / MSI of transportation for each film structure

In Figure 30 the film structures were evaluated based on the mega joules of energy per MSI of film. The energy for transportation to the customer consisted of the finished film material shipped to the CPG Company. The trend that is demonstrated for the transportation energy is that as PLA resin content increases in the film structure the MJ/MSI increases. This is a result of the density increase of PLA compared to HDPE. The density change per same film thickness causes for additional weight per roll of film thus an increase in transportation energy per MSI.

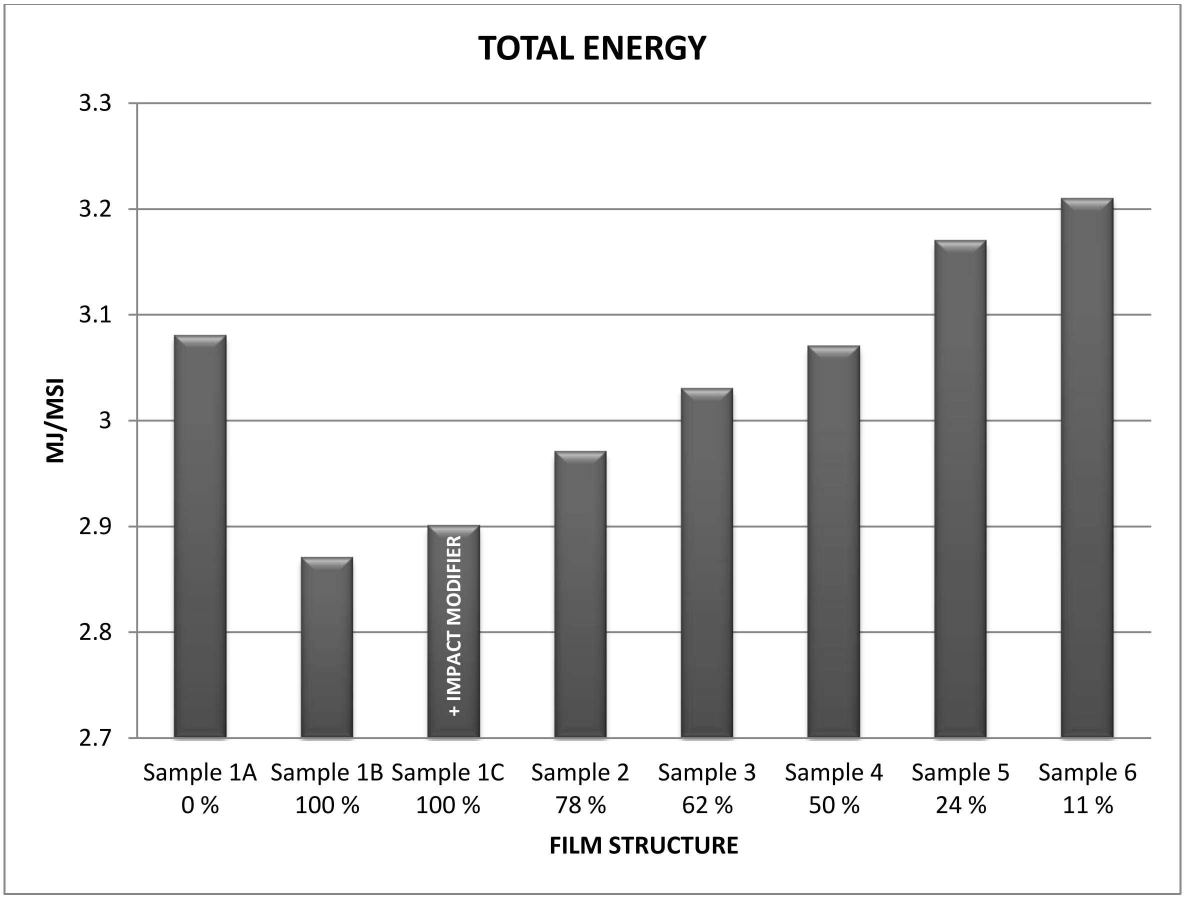


Figure 31. Mega Joules of energy / MSI of total energy for each film structure

In Figure 31 the film structures were evaluated based on the mega joules of energy per MSI of film. The total energy inputs were the following: Raw materials, raw materials packaging, raw materials and packaging transport, processing, distribution packaging, distribution transport, and transport to customer. Despite the impact of the significant transportation energy of raw materials and the transportation energy of the converted materials to the CPG's a trend demonstrated as PLA resin content decreases in the film structure the MJ/MSI increases. The incoming resin and the additional weight per roll resulting from the PLA resin density increase caused a significant increase in transportation energy per MSI. However, overall on a total percentage the energy of the raw material had the greatest affect on the MJ/MSI basis.

10.2 Green House Gas

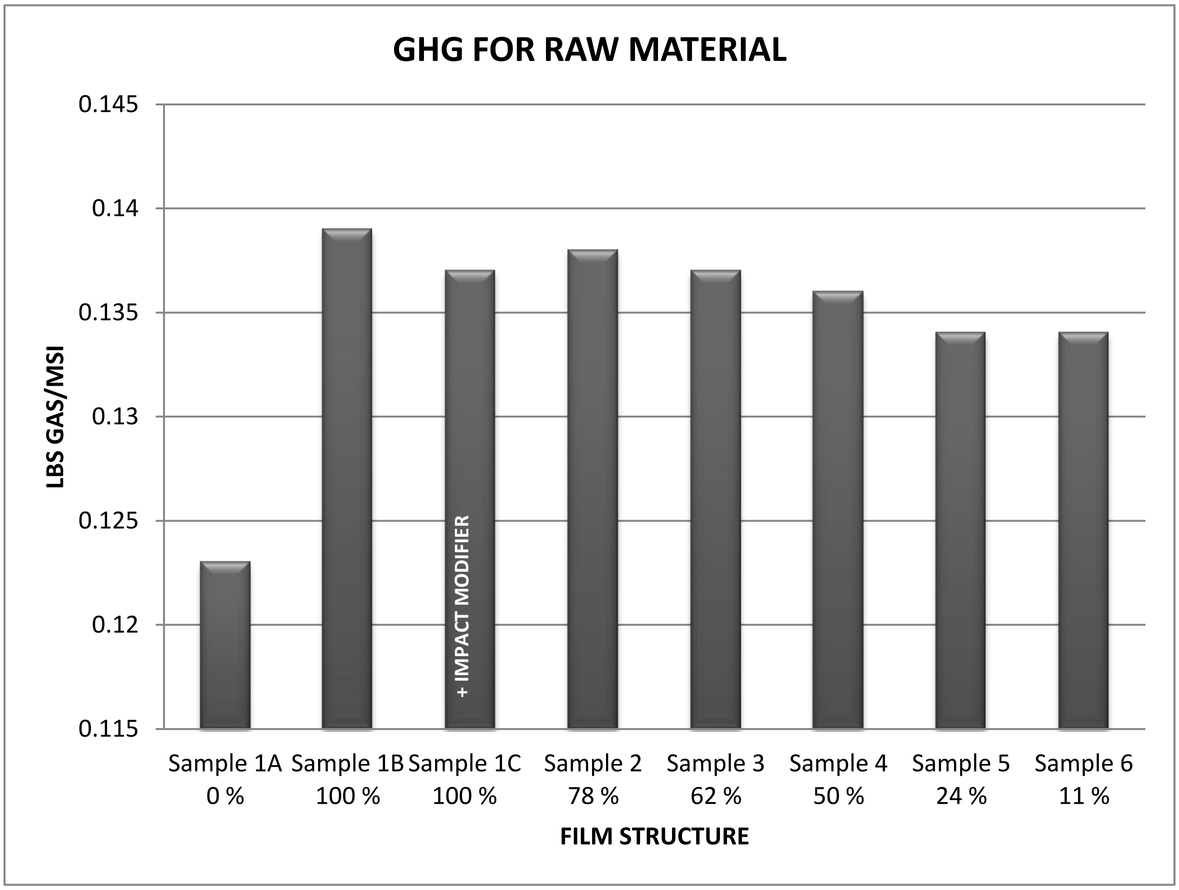


Figure 32. LBS of GHG / MSI of raw materials for each film structure

In Figure 32 the film structures were evaluated based on the LBS of gas per MSI of film. The raw materials consist of all the combined resins to convert the individual film structures which include HDPE, tie layer, PLA, LLDPE, and EVA. Another factor such as packaging materials and transport of incoming materials is not factored into the number. The trend that was demonstrated for the raw material GHG is that as PLA resin content decreases in the film structure the LBS of GAS/MSI decreases.

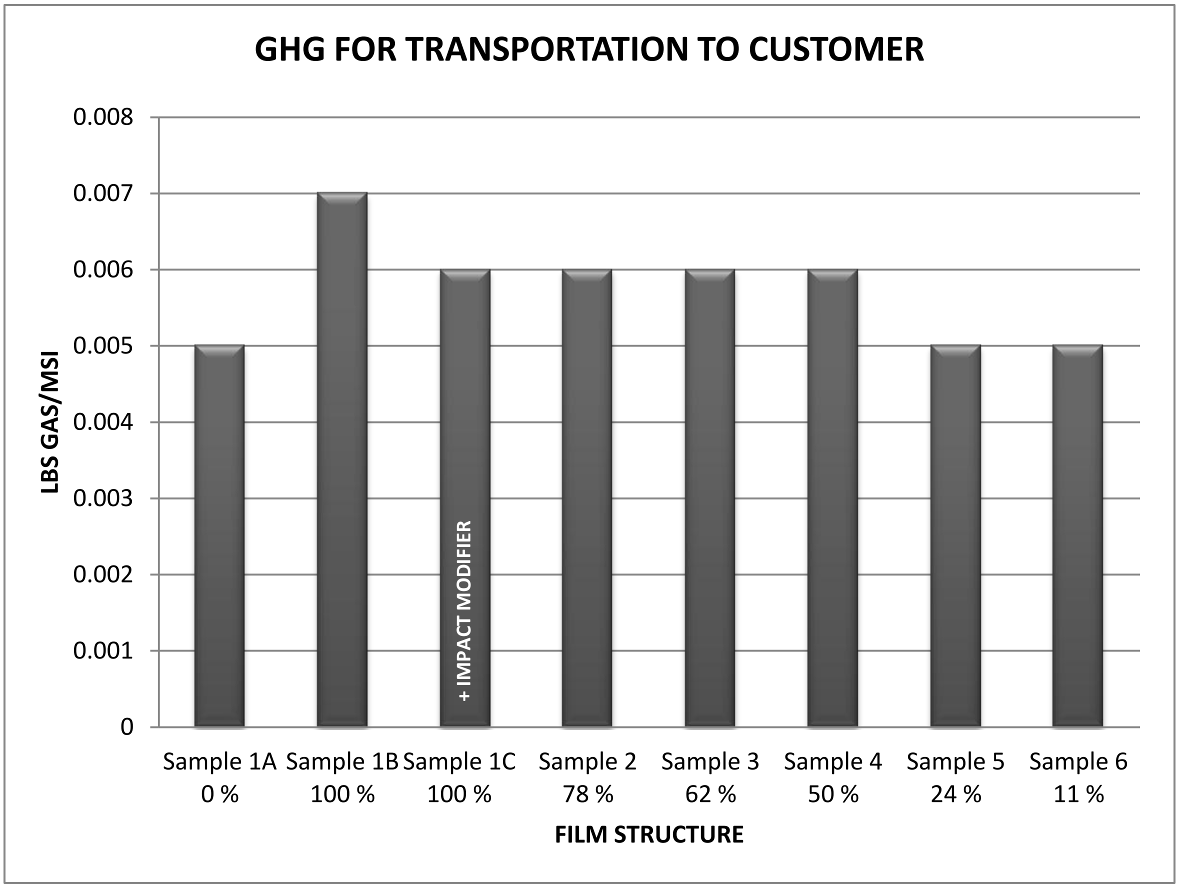


Figure 33. LBS of GHG / MSI of transportation for each film structure

In Figure 33 the film structures were evaluated based on the LBS of GAS per MSI of film. The GHG for transportation to customer consisted of finished film materials shipped to the CPG's. The trend that was demonstrated for the transportation GHG is that as PLA resin content increases in the film structure the LBS of GAS /MSI increases. This is a result of the density increase of PLA compared to HDPE. The density change per same film thickness causes for additional weight per roll of film thus an increase in transportation GHG per MSI.

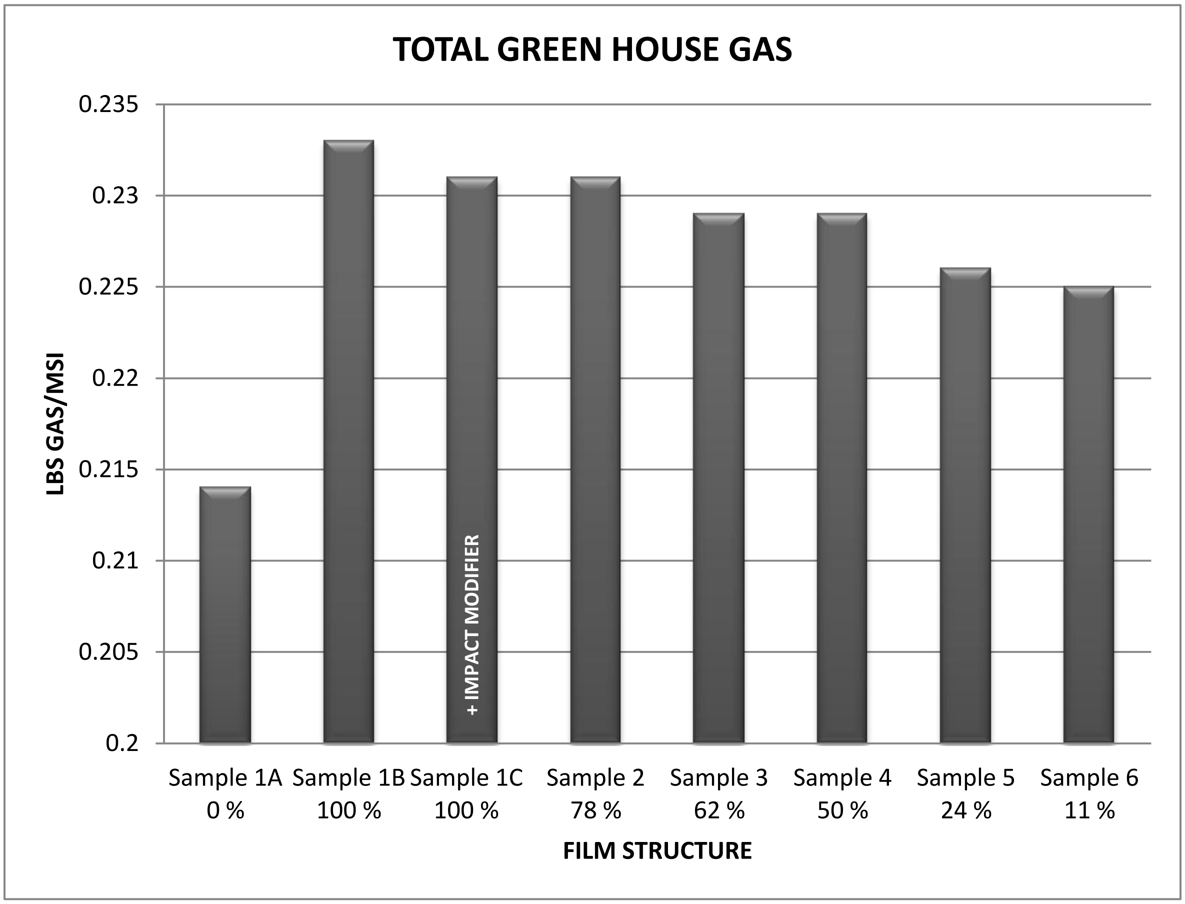


Figure 34. LBS of GHG / MSI of total GHG for each film structure

In Figure 34 the film structures are evaluated based on LBS of GAS per MSI of film. The total GHG inputs were the following: Raw materials, raw materials packaging, raw materials and packaging transport, processing, distribution packaging, distribution transport, and transport to customer. The impact of the raw material GHG, the transportation GHG of raw materials and the transportation GHG of the converted materials to the CPG's demonstrated the trend as PLA resin content decreases in the film structure the LBS of GAS /MSI decreases. It should be noted the total percentage the GHG of the raw material had the greatest affect on the LBS of GAS /MSI basis.

11.0 CONCLUSIONS

Consumers are interested in doing their part in controlling Carbon Dioxide Emissions (CO_2) however they are not supportive of rising food prices. Consumers when asked do support the effort of Bio Polymers and understand the importance of bio based materials but do not see the burden being placed on them. They see this as industry responsibility to figure out how to make this affordable to consumers. Bio Polymers have made significant progress with respect to development and commercialization. The environmental impact in reduction of CO_2, GHG and the reduction in energy from fossil fuels to produce the polymer through the supply chain are significant advantages.

PLA is a highly versatile polymer as one of its major benefits is that it can be processed using conventional infrastructure of equipment with minimal investments. The systems that are used to convert traditional polyolefin films are the same systems that are used for PLA films. The polymer has been continually modified in order to be processed efficiently but has significant development needs to be on par with some of competitive polyolefin films i.e. Polyethylene. The following are some of the technical barriers that continue to challenge the increased commercialization of PLA: downstream processing of lactic acid, alternative feedstock materials, processing, economics, and material property enhancements.

The feedstock for PLA is corn and sugar beets which is the main source of sugar. The feedstock in general has been an advantage for PLA since it comes from a renewable source and is abundant. This has however, not materialized as an economic advantage in the market place with respect to reduced film costs. The film costs have actually been significantly higher than competitive polyolefin films. Since cost is an important consideration for producers of PLA there is ongoing research to explore the use of cellulose as an alternative feedstock. In order to use cellulose feedstock there needs to be further research to convert it to fermentable type sugar at high yields that are economical. This is an important next step since feedstock will cause an upset in balance as more acreage is taken away from the food chain. The opportunity of low value biomass will be pivotal to the long term success of this material. The economics will continue to play an important role as the film moves through the commercialization cycle. The industry has several collaborative models that can potentially provide a means to driving the cost of the polymer to be competitive with petroleum films. The ability to reach back as far into the supply chain will play a significant role in helping to reduce waste in the system which is ultimately cost.

11.1 Impact on the Cereal Industry

In the last decade there has been significant market progress in the strengthening of renewable materials. The market projections for renewable packaging materials and substitution rate acceptance of materials are supporting the evolutionary journey for continued shifts. The dynamic market forces demonstrate that more cost competitive pricing is inevitable for the renewable packaging materials. However, there will need to be additional work conducted to better understand the price elasticity of the market. If PLA films are to be successful there will need to be some key advancements:

1. More companies need to enter the market for alternative bio based feedstock, to increase capacity and drive the resin cost down compared to non renewable petroleum resins. Bio based resin costs are not on par with HDPE which would lead to a loss in margin. The cost of resin is dynamic and fluctuates based on market conditions however, with the cost assumption of the price of $.85/ lb for film grade HDPE resin and $1.05/lb for film grade PLA there is a 19% increase in resin cost. This is not the total cost to the CPG's as the film will need to be converted and there is conversion cost, which also includes a waste factor. The waste which is inherent in the process cannot be used in the structure since the polymers are immiscible. This would add an incremental cost to the film of 2-4% as the waste cannot be added into one of the layers which are typical for homogeneous Co-Ex films.
2. Targeted technical material enhancements for some of the key material property shortcomings. One of the most critical properties for cereal is the prevention of moisture gain. PLA resin demonstrated an increase in moisture permeation with an increased content in the film structure. Co-Ex film sample # 6 with 11% PLA content showed the greatest potential to meet the WVTR permeation requirements for high barrier performance when compared to 100% HDPE. Depending on the type of cereal the shelf life may be reduced. The cereals that are oxygen sensitive when the PLA resin was incorporated in the film structure variables they demonstrated a significant reduction in oxygen permeation. This would be an advantage for the high lipid based cereals to reduce rancidity. Film tear resistance property is also critical for when consumers open the package. This can help to prevent the film structure from splitting and causing the contents from spilling out. PLA demonstrated a significant decrease in tear resistance

with increased content in the film structure. However, Co-Ex film sample # 6 with 11% PLA content showed a significant increase in tear resistance in the MD and an insignificant increase in the CD over 100% HDPE. Puncture resistance is another critical attribute as the product is packaged and shipped through the supply chain. If the cereal itself or if there are sharp inclusions they may puncture through the package liner. The increased content of PLA demonstrated a significant decrease in puncture resistance. However, Co-Ex film sample # 6 with 11% PLA content showed a significant increase in puncture resistance in the out to in puncture direction and a insignificant increase puncture resistance in the in to out puncture direction over 100% HDPE. Stiffness of film is important for handling the package once the package is filled and for further downstream package conversion. The increased content of PLA demonstrated a significant increase in film stiffness. Co-Ex film sample # 6 with 11% PLA content demonstrated a similar stiffness compared to 100% HDPE.

3. The need for “Consumer pull (demand) for environmentally friendly films” packaging which has tangible benefits that is meaningful. Consumers desire positive sustainable materials however are not willing to absorb the increased cost.
4. The package sustainability metrics need to be evaluated individually. The total energy of MJ/MSI is reduced as PLA content is increased in the film structure which is a positive. However, the total GHG of LBS of GAS / MSI is increased as the PLA content increased in the structure which is a negative.

12.0 FUTURE RESEARCH

The continued research in renewable polymers will be necessary. The market dynamics for CPG food companies will continue to evolve with time. The influence of consumer's trends, market competitors, renewable material advancements, reduction of CO_2 and GHG's, state and federal public policies, and social economics will all contribute to the acceleration and the further adoption of renewable packaging materials. CPG's are in an interesting position and will continue to play a valuable role in the supply of renewable materials but are only a portion of the total economic system. The limited supply of fossil fuel as feedstock and with a global population demanding more petroleum products will continue to be a motivating denominator. Suggested future research may include the following:

1. Evaluation of PLA resin as a CO-EX film structure with the use of micro layer die technology to understand the impact on the mechanical properties.
2. The incorporation of additives that are compounded into the PLA resin in a Co-Ex film structure to understand the influence on moisture and oxygen barrier properties.
3. The incorporation of a renewable non polar polymer in a Co-Ex film to understand the effects on moisture and oxygen barrier properties.
4. Evaluation of sustainability metrics for GHG and Energy through additional commercial software programs for comparative analysis.

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