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Mechanical characterization of commercial biodegradable plastic films

Joseph Robert Vanstrom
Iowa State University

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Mechanical characterization of commercial biodegradable plastic films

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Presented by

Joseph R. Vanstrom

Major: Industrial Technology

Program of Study Committee

Major Professor:
David Grewell, Iowa State University

Committee Members:
Michael Kessler, Iowa State University
Raj Raman, Iowa State University
Carl Bern, Iowa State University

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The faculty and staff of
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And all my friends through the years

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Key Terms and Abbreviations

Material testing

Differential Scanning Calorimetry	DSC
Thermogravimetric analysis	TGA

Units of measure

Megapascals	MPa
Joules	J
Newtons	N

Material property notation

Ultimate tensile strength	UTS
Melt temperature	T_m
Glass transition temperature	T_g
Melt Enthalpy	ΔH_m
Molecular weight	M_w
Crystallinity temperature	T_c
Degree of crystallinity	W_c

Abstract

Polylactic acid (PLA) is a biodegradable plastic that is relatively new compared to other plastics in use throughout industry. The material is produced by the polymerization of lactic acid which is produced by the fermentation of starches derived from renewable feedstocks such as corn. Polylactic acid can be manufactured to fit a wide variety of applications.

This study details the mechanical and morphological properties of selected commercially available PLA film products. Testing was conducted at Iowa State University and in conjunction with the United States Department of Agriculture (USDA) BioPreferred Program®. Results acquired by Iowa State were compared to a similar study performed by the Cortec Corporation in 2006. The PLA films tested at Iowa State were acquired in 2009 and 2010. In addition to these two studies at ISU, the films that were acquired in 2009 were aged for a year in a controlled environment and then re-tested to determine effects of time (ageing) on the mechanical properties. All films displayed anisotropic properties which were confirmed by inspection of the films with polarized light.

The mechanical testing of the films followed American Society for Testing and Materials (ASTM) standards. Mechanical characteristics included: tensile strength (ASTM D882), elongation of material at failure (ASTM D882), impact resistance (ASTM D1922), and tear resistance (ASTM D4272). The observed values amongst all the films ranged as followed: tensile strength 33.65 – 8.54 MPa; elongation at failure 1,665.1% – 47.2%; tear resistance 3.61 – 0.46 N; and puncture resistance 2.22 – 0.28 J. There were significant differences between the observed data for a number of films and the reported data published by the Cortec Corp. In addition, there were significant differences between the newly acquired material from 2009 and 2010, as well as the newly acquired materials in 2009 and the aged 2009 materials, suggesting that ageing and manufacturing date had an effect on the mechanical properties.

The morphological properties were tested using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The material properties examined were: glass transition temperature (T_g), degree of crystallinity (W_c), and material composition in terms of inorganic content. Results from DSC testing revealed that the glass transition temperatures ranged from 43.2 – 52.2 °C, the degree of crystallintiy ranged from 4.1 – 13.8%, and material composition of the films ranged from 89.9 – 100% organic materials. The morphological examination of the polymers also indicated that the mechanical properties of the films may have been altered by the manufacturing and processing of the film material or by the addition of filler or plasticizers.

Chapter 1. Introduction

In 2009, the average Municipal Solid Waste (MSW) generated per person each day in the U.S. was 4.34 pounds before recycling, corresponding to 243 million tons of MSW, annually. Plastics represent approximately 12.3% (29.9 million tons) of the total waste generated. With current recycling methods unable to meet the rate of waste production, 66.2% of MSW (82 million tons) was not recycled or recovered. Either the waste is discarded in landfills (54.3%) or used as fuel for combustion (11.9%) as detailed in Figure 1 [1]. Both of these lead to concerns with soil and air pollution. It is obvious that plastics represent a significant environmental concern in terms of waste.

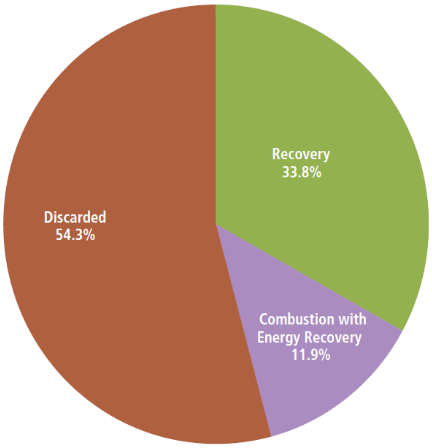


Figure 1) Management of MSW in the United States 2009 (by percentage) [1]

Greenhouse Gas Emissions

Currently, the United States is regulating greenhouse emission by charging for the release of these emissions to minimize greenhouse gas (GHG) emissions. This has been labeled by most as “carbon credits”. Programs such as Regional Greenhouse Gas Initiative [2], Western Climate Initiative [3], Chicago Climate Exchange [4], and California AB 32 [5] have been developed to curb and or reduce the total amount of GHG released into the atmosphere.

Globally, the most comprehensive international policy has been the Kyoto Protocol (KP). This act binds 37 industrialized countries (not including the US) into achieving GHG emission targets. Each country that agreed to the conditions of the protocol was given a target level based on the country’s corresponding 1990 emission level. The KP parties are to achieve these targets in a five year period between 2008 and 2012 [6]. As of 2005, the countries that agreed to the Kyoto Protocol were on track to, or have already met their predetermined emission targets. As of latest calculations, KP parties are collectively predicted to meet the target of a 4.2% reduction of GHG emissions by 2010. The United States, which is not a KP party but was given a target emission level, has seen an increase in emissions by 13% since 1990 [7].

It is important to note that GHG emissions do not solely consist of carbon dioxide (CO_2). In regards to the Kyoto Protocols, greenhouse gases targeted in the accord refer to the following emissions: CO_2, methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6) [6]. Table 1 describes the CO2 equivalencies for each GHG emission [8].

Table 1) Greenhouse Gas CO_2 Equivalents

Greenhouse Gas (GHG)	Molecular Symbol	GHG CO_2 equivalents
Methane	CH_4	21x
Nitrous Oxide	N_2O	310x
Hydrofluorocarbon	HFC	11,700x
Perfluorocarbon	PFC	6,500x
Sulfur Hexafluoride	SF_6	23,900x

Carbon Cycle

In partial response to the rising concerns regarding GHG emissions, institutions and corporations in the U.S. are considering alternatives to petroleum based products that contribute to high levels of GHG. These companies have begun developing lignocellulosic-based products through the use of naturally occurring polymers and those that can be derived from renewable feed stocks. The use of renewable feed stocks has the potential to create a closed loop in the carbon cycle.

The carbon cycle theory was developed in 1999 by the U.S Global Change Research Program (USGCRP) [9]. The concept of closed loop carbon cycle assumes that carbon acquired through lignocellulosic materials is used to create products which were previously produced using petroleum feedstocks. This concept details the use of carbon from surface sources (organic carbon) and limits the removal of carbon through crude oil and other fossil fuels. By maintaining a balance of carbon removal/replenishment, i.e., the harvesting and planting of renewable feed stocks, the closed carbon loop has the potential of reducing the global warming trends that are seen today.

Feedstocks with high starch content are being utilized in the production of biodegradable plastics such as PLA. Some of the important applications of biodegradable plastics include packaging, such as trash and carry bags and temporary wrappings. The existing market offers a narrow range of biodegradable films and plastic sheet products from various manufacturers.

Polymers

The word "polymer" is derived from the Greek *poly* (many) and *mer* (parts or units). Polymers are made up of a series of repeating molecular units to form chain-like structure. Polymer chains are constructed around a "backbone" that repeats throughout the polymer. In the case of the polyethylene polymer, (C_2H_4), there is a common backbone of carbon atoms, Figure 2.

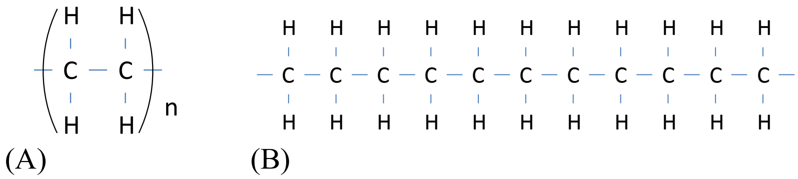


Figure 2) (A) Repeating polyethylene polymer unit; (B) Polyethylene polymer chain

Polymers can be classified into three groups: thermoplastic polymers (TP), thermosetting polymers (TS), and elastomers (E).

Polymer chains are held together by a system of force interactions between the repeating units of the chain. These forces allow the material to coalesce to form a ductile material that can be used to manufacture products.

In the case of thermoplastics these interactions largely consist of van der Waals forces and molecular entanglement between the molecules. These relatively weak interactions of the molecules allow the molecules to flow similar to a viscous material when energy (heat) is introduced into the system. This allows the polymers to be reshaped to form new products.

For thermosetting polymers, actual cross-linking bonds (primary bonds) form between the chains which lock the polymer into its molecular structure. This prevents the polymer from being reshaped when the material's temperature is raised. The polymer will degrade rather than flow. Polylactic acid is an example thermoplastic polymer.

As the polymeric chains of thermoplastics bond together, there can be areas in which the chain can fold back on itself multiple times to form a crystalline structure. The number and degree of these structures is called "packing" and define the materials molecular density. It is important to note that this folding occurs in a three dimensional fashion, resulting in large crystalline structures in an amorphous matrix. As crystalline chains build, they form layers. These layers of crystalline polymers are lamella, Figure 3.

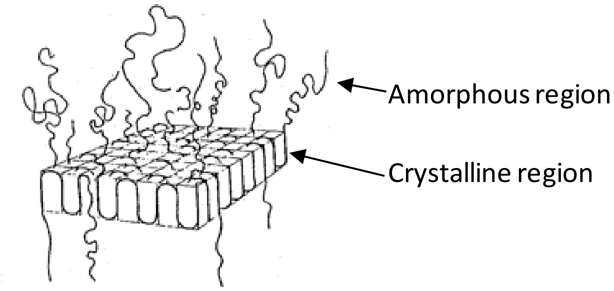


Figure 3) Lamellar Polymer Chain [10]

Biodegradable Polymers

Biodegradable polymers are described by the International Standards Organization (ISO) and American Society for Testing and Materials (ASTM) as follows:

> ISO 472: 1988 – A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastics and application in a period of time that determines its classification. The change in chemical structure results from the action of naturally occurring microorganisms.
>
> ASTM sub-committee D20.96 proposal – Degradable plastics are plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which leads to fragmentation or disintegration of the plastics.

Biodegradable polymers are classified as: polysaccharides, polypeptides, polycaprolactones, polyesters, polyamides, polyurethanes and polyureas, polyanhydrides, poly(amide-enamine)s, poly(vinyl alcohol) and poly(vinyl acetate), and polyacrylates. PLA is classified as polyester.

Some biopolymers can degrade through the same pathways as composting of organic waste. Microorganisms, such as bacteria or fungi, are able to break down these polymers through hydrolysis. The organisms are able to hydrolyze the material through enzymatic digestion of the polymer, resulting in degradation of the polymer matrix. It is important to note that not all bio-polymers are degradable, for example, polyethylene derived from sugar cane [11]. Another pathway, not directly related to PLA, is radiation degradation, such as UV, and oxidation. Because these are the primary degradation pathways for PLA they are not detailed in here.

Polylactic Acid Polymers

Polylactic acid (PLA) has been utilized for various applications such as sutures in the medical industry and as disposable utensils and containers in the food and beverage industry.

Polylactic acid is currently synthesized by polymerizing lactic acid produced from fermentation of sugars derived from renewable feedstocks, such as starch from corn or sugar from sugar cane. Lactic acid commonly occurs in two optical arrangements: L- and D- lactic acid. L-lactic acid is the preferred monomer for industrial production of PLA because it provides higher yields and better material properties [12]. Bacterial strains that are identified to produce either the L- or D- lactic acid chains are highly valuable. *Lactobacillus bulgaricus* [13] and *Lactococcus lactis* are widely used bacterial strains for industrial fermentation of cellulosic glucose and fructose into lactic acid [14].

Polylactic acid is a highly hydrophobic polymer. During the polymerization of two lactic acid monomers, a single water molecule is produced which opposes and resists direct polymerization. If the moisture is not removed, the result will be low molecular weight PLA (low MW PLA), which has limited mechanical strength, which is undesirable for industry purposes.

The direct condensation process creates low MW PLA and coupling agents in a secondary process are used to join the low MW PLA chains together to form high MW PLA, Figure 4. The polycondensation polymerization method [15] will remove the moisture generated during the polymerization process, thereby enabling the production of a more desirable high molecular weight (high MW) PLA.

Another process that creates high MW PLA uses low MW PLA to create lactide rings. After applying a ring-opening process, these lactide rings form chains of high MW PLA. These polymer chains are significantly more stable and of higher quality than the polymer strains created using direct condensation, Figure 4.

An alternative process creates high MW PLA through a one-step process. The process of azeotropic dehydration condensation uses chemical distillation to eliminate any byproducts that would damage the PLA chains, Figure 4 [16].

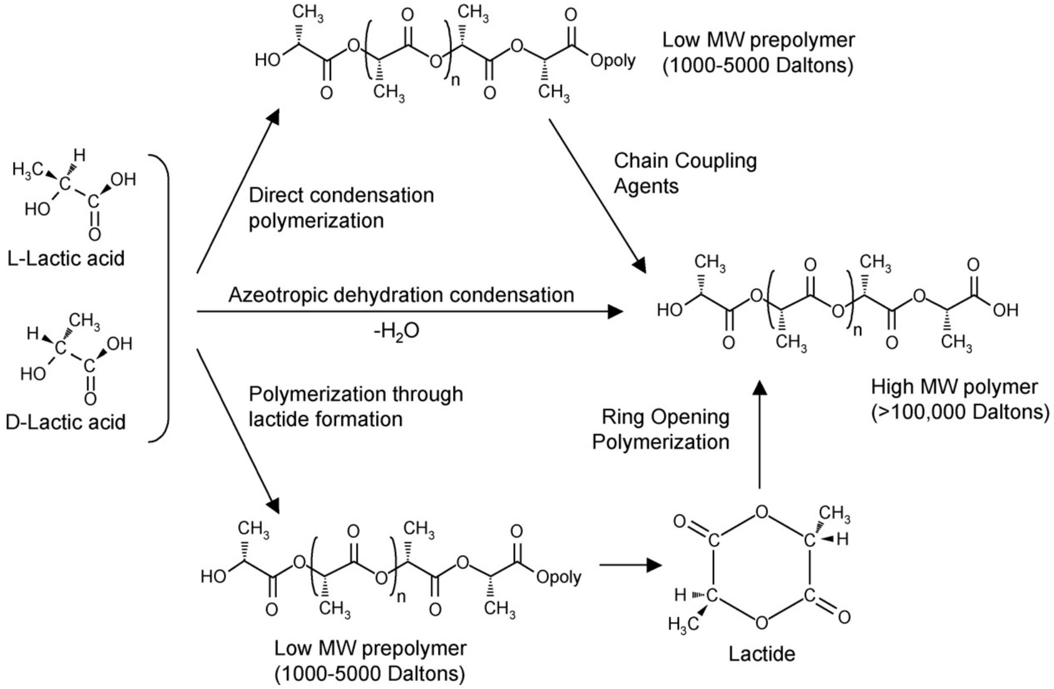


Figure 4**)** Lactic acid molecular progression to the formation of PLA polymers [17]

The complete potential of PLA is yet to be realized and there is ongoing research into compounding the polymer matrix with property enhancing additives.

These various polymerization techniques all produce high MW PLA. The variety of processing methods may affect the material properties of the end material.

Manufacturing of Polylactic Acid Polymer Films

Once the PLA resin is produced, further processing is required to create specific products. As with petroleum thermoplastics, PLA can be processed with a wide range of polymer processing techniques to produce various products. Some of the prominent examples include filament spun PLA for medical sutures [17,20], injection molded and thermoformed PLA sheets for food grade utensils and beverage containers, respectively [17,23], as well as polylactic acid films that can be formed through blown film extrusion, slit-die extrusion, or calendering. These processes are detailed in the following. It is important to note that each of these processes may alter the PLA's mechanical and morphological properties compared to virgin PLA [18].

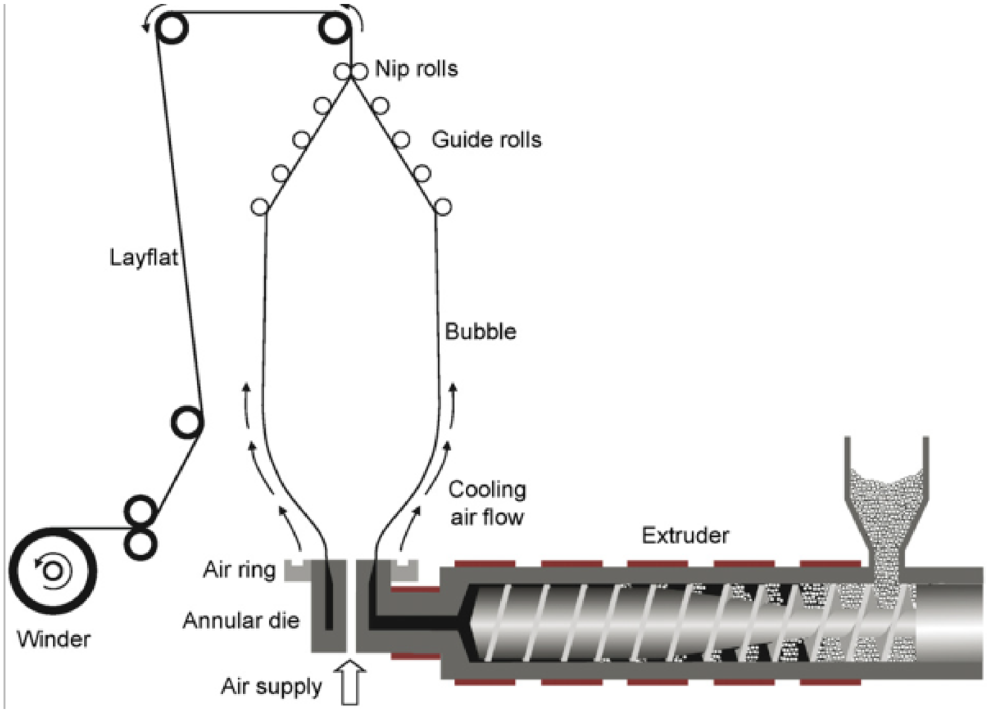


Figure 5) Blown film extrusion system [17]

Blown film extrusion is the preferred process to make films for bags and related products. In blown film extrusion, PLA is plasticized in an extruder and forced through a pipe die (donut shaped opening) to form a straw-like extrusion as shown in Figure 5. Air is passed through the hollow PLA extrudate. This allows the relatively thick-walled polymer straw to expand and create a bubble. In order to maintain a proper thickness of the inflated material, the air pressure within the bubble must remain constant. This factor affects a steady frost line and maintains uniformity in the quality of the bags [23]. The ratio of the bubble diameter to the die diameter is called blow-up-ratio (BUR) [17]. BUR ratios of 2:1–4:1 with the die temperature of 190–200 °C have been used for extrusion blowing of PLA films [19,20]. The final diameter is typically determined at the "frost line". This is the point at which the polymer solidifies and can no longer stretch. The balloon is then slit open into flat films and trimmed to predetermined widths. These films are then heat sealed to form bags. It is important to note that the film can be enhanced through heat treatment and stretching as detailed in the following text.

PLA's relatively high density of 1.24 g/cm^3 (0.94 g/cm^3 for polyethylene) and viscosity of 3460 Pa-s at 150 °C [21] (115 Pa-s at 151 °C for polyethylene [23]) can pose a potential problem for current infrastructure of film manufacturing. Most extrusion screw systems are designed for processing of materials with much lower viscosity at their melt temperature. If the motors driving the screws are operating at near capacity, the added stress of processing a much denser material may cause the system to "jam-up" and/or burnout the motors of the extrusion system [22]. Additives and copolymers may provide a solution, as these materials tend to have different melt flow properties, particularly melt temperatures, and may be easier to process.

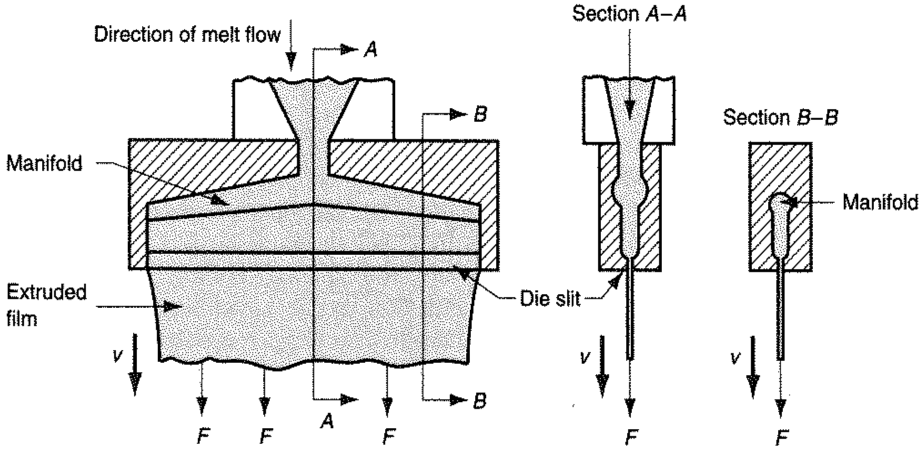


Figure 6) Cross sectional view of slit-die extrusion [23]

Slit-die extrusion allows for production of polymer sheets widths that meet commercial requirements. In a sheet extrusion process, the molten material from the extruder, is passed through a manifold that evenly distributes the polymer across the die, forcing it through a rectangular die opening to form the sheet, Figure 6. The die opening may vary in geometry but is traditionally rectangular and can range up to multiple meters wide and fractions of millimeters thick. This determines the initial size and thickness of the films. As the material passes through the die opening, tension is typically applied uniformly across thicknesses. It defines the final thickness of the film which cooled immediately in either a bath or by contact with cold rollers, Figure 7. As the sheet is processed through the slit-die mold, it is pulled through sets of rollers with sequentially decreasing gap widths. Meanwhile, tension can be applied both along the perpendicular direction to induce orientation, improving the physical properties of the polymer. This makes the final dimensions and properties of the material more predictable [17,23]. Additional steps can be taken in order to impart further material properties to the film. Ou and Cakmak subjected the film to an annealing process in order to promote crystallinity [24].

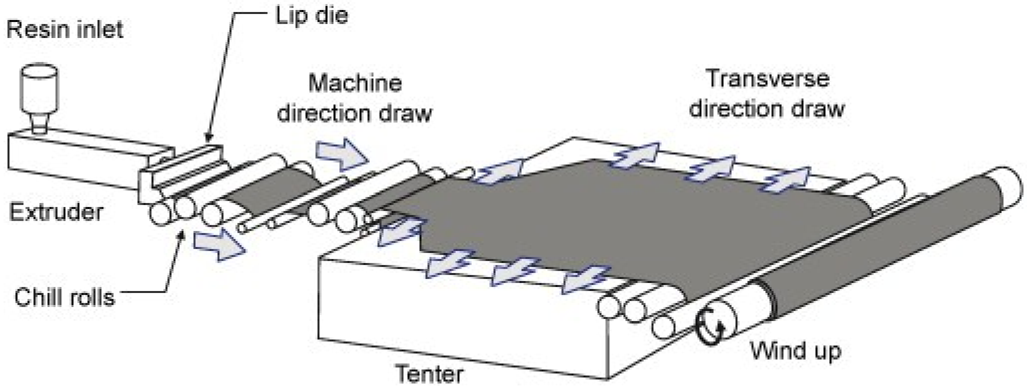
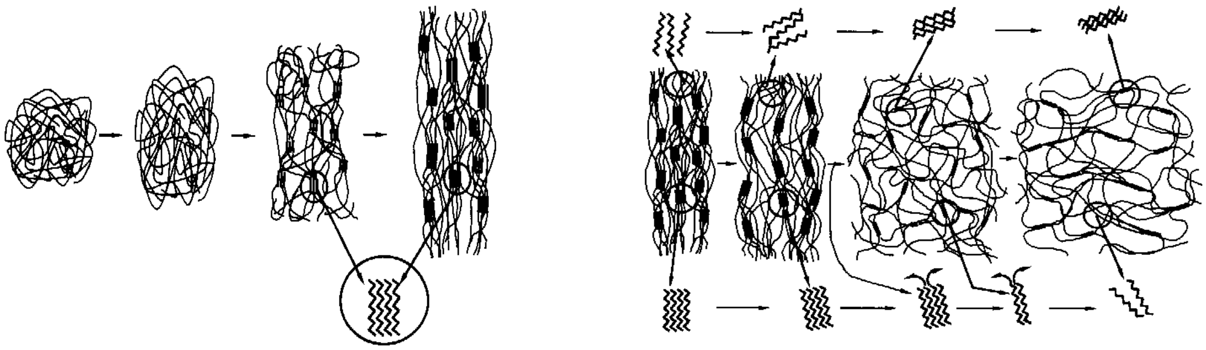


Figure 7) Cast film/slit-die extrusion [17]

As the material is processed through chilled rollers, the mechanical properties of the polymer can be altered. Through the drawing of the film in the calender rollers, the polymer can be oriented uniaxially along the machine draw direction, Figure 7. As tension is applied to the material, the polymer chains tend to align in the machine draw direction. This drawing of the polymer can enhance the impact resistance and thermal properties of the plastic material [17]. As the polymer chains are uniaxially stretched, crystallization of the polymer chains can be induced, Figure 8 [25]. The increased crystallization enhances the mechanical properties when tested along the direction of machine draw. A secondary stretching process that is applied transversely to the initial machine drawing can reduce the concentration of crystallized areas of the polymer and therefore reduce effectiveness of the crystallization that was initially created by the drawing of the film.



(A) (B)

Figure 8) (A) Polymer chain alignment due to calendering along machine direction; (B) Polymer chain alignment due to stretching perpendicular to machine drawn direction [25]

In both the processes, once the desired material thickness is reached, the polymer is cut to length and processed into bags.

USDA BioPreferred Program®

The United States Department of Agriculture (USDA) has established a program that identifies and promotes the use of bio-based products.

This study was in partial response to a published report by Cortec Corporation (White Bear Lake, MN) in 2006 on the mechanical properties of commercially available PLA [26]. In conjunction with the USDA BioPreferred Program®, an independent third party, Iowa State University repeated the testing as well as further characterized the morphological properties of biodegradable polymers.

Chapter 2. Literature Review

The material properties of unaltered or "neat" polylactic acid have been extensively tested and documented. General material properties confirmed through various sources are listed in Table 2 [12,17,27,43,44].

Table 2) Material properties of neat polylactic acid; compiled from several sources

Material Properties of neat Poly(L-, D- lactic acid)			
Specific Density		1.24	g/cm^3
Molecular weight (Highly oriented poly(L-lactic acid)	M_w	190,000	g/mol
Tensile strength	σ	66	MPa
Elongation at break	ε	56	%
Glass transition temperature	T_g	55	°C
Melting temperature	T_m	150	°C
Melt enthalpy	ΔH_m	93.1	J/g

PLA has been utilized in the medical industry, food barrier packaging, transportation padding and wrappings, and refuse bags [17]. PLA is a perfect fit for of the previously mentioned applications due its quality of compostability.

The medical field has utilized PLA in several areas. First, it was used in suturing wounds and incisions made inside the body [28]. Upon degradation, the human body readily absorbs the lactic acid molecules released by the polymer. This made patient recovery much more expedient because there were no follow up procedures to remove the sutures.

Another medical application is bone regeneration. Here, PLA is combined with calcium oxidate to form a lattice network (scaffold). The scaffold serves as a structural component during healing and the calcium oxidate serves as a bone growth enhancer. . The environment of the body would naturally dissolve the PLA and the bone and marrow tissue would grow and replace the scaffold-like material [28,29].

Polylactic acid is also used for rate release medication delivery, for example, for over-the-counter cold gel-tablets. The waxy coating on the outside of the pill is commonly made of PLA. After the PLA casing is degraded, the drug is released to the body. Depending on the thickness of the PLA casing, the pill can be engineered to only release once it reaches a particular area of the body [30]. This type of treatment constitutes a much less invasive method of treating some illnesses.

Because PLA can be processed in many forms and techniques, additives are relatively easily incorporated in the neat resin; this includes medical drugs to accelerate the healing of patients. This can also be engineered to release the drug evenly over a set period of time or release larger dosages over a period of time [30]. The benefit of a PLA pill for medical drug delivery is that, as the PLA degrades, it turns into simple lactic acid strains that the human body naturally generates, creating a non-toxic by-product.

The biodegradability of PLA was the main driver for its inception and its use by industry. The rate of PLA’s degradation is dependent on the humidity and temperature. Immersed in water and held at various temperatures, PLA degrades predictably over a given time. While maintaining a mean temperature of 13 °C, PLA begins to fragment at 25 months and degrade at 48 months; at 25 °C, PLA will fragment at 6 months and degrade at 11.4

months [31]. This is a critical point of comparison as it shows a discrepancy between the interaction of the materials and the environment as it pertains to the materials ability to maintain its structural integrity beyond the 12 month timeframe.

The ability of PLA to serve as a structural material is highly contested and will be studied in this study. It is common for PLA to be compounded with additives to increase its material properties. Additives can alter the mechanical properties of PLA and increase its load bearing capabilities and other mechanical capabilities. Mixing PLA with various other types of polymers such as elastomers [32], thermoplastic starch [33], poly(ethylene glycol) (PEG) [33,34,35], triacetin and tributyl citrate [34,36,37] and polyhydroxyalkanoates (PHA) [38,39]. Other bio-renewable and natural materials, such as nanoclays [46], kenaf and rice husk fibers [45], talc and bamboo fibers [40], flax fibers [47], wood flour [48], and glycerol [41] have also been used to enhance the material properties of PLA resins. In many cases, these additions have not only enhanced the polymer's mechanical properties but also improved the rheological properties to ease in PLA production.

Chapter 3. Objectives

The questions that will be answered in this study are:

- Is there a significant difference between the mechanical properties of PLA films that were tested by the Cortec Corporation in 2006 and the same materials acquired and tested by Iowa State University?
- Is there a significant difference in the mechanical properties of PLA films before and after a period of ageing for 1 year?
- Is there a significant difference in the mechanical properties of PLA films from varied production times as well as the ageing of films?

Chapter 4. Experimental Procedures

A series of mechanical and morphological tests were performed on a range of films that were provided by selected manufacturers.

The mechanical testing consisted of the following standard tests recommended by the American Society of Testing and Materials (ASTM):

- ASTM D882 (Tensile Test)
- ASTM D1922 (Tear Propagation Test)
- ASTM D4272 (Dart Drop Puncture Test)

Additional tests to study the morphology and composition of the materials were also conducted. These tests consisted of:

- Differential Scanning Calorimetry (DSC)

- Thermogravimetric Analysis (TGA)

The DSC tests characterize the material for phase changes over a range of temperatures including glass transition temperature (T_g), crystallization temperature (T_c), and melt temperature(T_m).

Thermogravimetric analysis (TGA) determined the composition of the materials in terms of organic and inorganic components. This effectively determines thermal degradation of the material as a function of temperature and measuring the mass change during the heating process.

It is important to note that morphology and chemical attributes depend on

- Raw material composition
- Processing of the material
- Ageing of the material

Analytic studies were used to characterize these effects. In more detail, TGA and DSC studies were completed to explain any discrepancies between the results found between Cortec and ISU reports and ageing studies. The mechanical properties and material characteristics of the PLA films have been made available to the USDA as well as those companies who agreed to participate (supplied samples) towards this study.

Chapter 5. Materials

The biodegradable polymer that was used in this study was poly-lactic acid (PLA).

Six PLA films were tested as detailed in Table 3. Several of the manufacturers of materials that were tested in the 2006 Cortec Corporation report have discontinued certain films from production or did not participate in this study. Replacement films were identified based on their similar specifications compared to the original materials and verified by the USDA for this study (identified by *).

Table 3) Table of materials studied (ordered by polymer thickness)

Brand	Reference ID for study	Polymer thickness (mil)	Manufacturer of material
*EcoWorks 45	EcoWorks 45	12.0	Cortec Corp.
BioTuf Trash Bags	Heritage	1.0	Heritage
BioCorp	Indaco	1.0	Indaco Corp.
Ecofilm	Ecofilm	1.0	Cortec Corp.
*BioBag Lawn and Leaf	Biobag L	0.75	BioBag USA
BioBag Kitchen	Biobag K	0.66	Biobag USA

To determine whether the films have an axial orientation, each film was examined with polarized microscopy to identify the degree and angle, if any, of molecular orientation within the film [42]. This aided in determining if the samples were isotropic or anisotropic and in preparing the samples for testing. Visual inspection of the materials indicated that all of the films were uniaxially oriented. Because all films displayed anisotropic properties, each material was tested in both the parallel and perpendicular to the machine direction.

In order to reduce any atmospheric effects, all the films were stored, for 30 days, in their packaging prior to testing. This storage simulated the environment and time in which the product could be packaged and shipped from the manufacturing facility to the store and ultimately, to the consumer. The environmental conditions were maintained at 25 °C ±5 °C and 30 % ±10 % relative humidity. The conditions were monitored twice a week.

The materials were tested at three separate times. The first set of testing was performed on the films that were acquired from manufacturers in 2009 and were tested after the conditioning period, herein referred to as *2009*. The second set of testing was conducted after the balance of materials acquired in 2009 were stored for one year at the conditions previously described. These materials were re-tested to determine if the mechanical properties were altered after a period of time, herein referred to as *2009+1 year*. A third set of tests were conducted on materials that were acquired in 2010, herein referred to as *2010*. This was used to determine whether films acquired in 2009 were similar to those manufactured in 2010.

Testing that required orientation to be identified and tested separately was randomized to minimize any variations with the apparatus. A randomization order was developed to minimize variations between samples from the different films. This also eliminated any variation between samples from the same film based on the orientation of each film. A sample from each film was tested for each round of testing. The table was developed for the ASTM D882 (Tensile Test) and the ASTM D1922 (Tear Propagation Resistance Test). The randomization order can be seen in Table 4. The samples that were perpendicular to the machine direction were labeled as *Even* and the samples that were parallel to the machine direction were labeled as *Odd.*

Table 4) Randomization order for mechanical testing

Material	Sample number									
	1	2	3	4	5	6	7	8	9	10
Biobag L	Even	Even	Odd	Odd	Odd	Odd	Odd	Even	Even	Even
Biobag K	Odd	Odd	Even	Odd	Even	Even	Even	Even	Even	Odd
Ecofilm	Even	Odd	Odd	Even	Even	Odd	Odd	Even	Even	Odd
EcoWorks 45	Odd	Even	Odd	Odd	Even	Even	Even	Odd	Even	Odd
Heritage	Odd	Odd	Even	Even	Odd	Even	Even	Even	Odd	Odd
Indaco	Even	Even	Odd	Odd	Odd	Even	Even	Odd	Even	Odd

Chapter 6. Results and Discussion: Mechanical Testing

Because many of the PLA applications are in packaging, those properties that are critical, namely tensile, tear resistance and impact strengths (similar to the Cortec report [26]), were characterized. It is important to note that the impact resistance test (ASTM-D4272) that was performed in this test, while very similar, differs from the test performed by the Cortec Lab (ASTM-D3420). The alternative method was chosen due to the availability of the dart drop testing apparatus; however, it produces similar impact resistance data. The within the ASTM D420 it is stated that, "…Test Method D 4272 is initiation plus completion energy. Some films have shown consistency when the initiation energy was the same as the total energy." The appendix X2 in ASTM D3420 standard shows the relationship between the two standards.

Samples were cut from sheets of PLA provided by each company participating in this evaluation. The samples were characterized according to the previously stated ASTM standards. Each standard is described in detail, followed by the results of the testing performed at Iowa State. A comparison of all materials and all standards is presented at the conclusion of this work.

ASTM D882 (Tensile Test)

Tensile testing determines the amount of stress each material can sustain prior to failure as well as the amount of elongation at the time of failure.

Each tensile test specimen followed the guidelines according to the ASTM D882:

"6.1 The test specimen shall consist of strips of uniform width and thickness at least 50mm (2 in.) longer than the grip separation used.

6.2 The nominal width of the specimens shall not be less than 5.0 mm (0.20 in) or greater than 25.4 mm (1.0 in).

6.3 A width-thickness ratio of at least eight shall be used. Narrow specimens magnify effects of edge strain or flaws, or both."

Each specimen measured 50 mm (2.0 in) x 12.7 mm (0.5 in) at the gauge length and was cut from supplied films using hand shears.

The tests were conducted using an Instron Tensile Tester with a crosshead speed of 500 mm/min (ASTM D882: Table 1).

The ASTM standard requires a minimum of ten replications for anisotropic films to be tested. Because the materials displayed anisotropic properties, 5 specimens each were selected from the material drawn in machine and perpendicular to the machine direction. The Cortec report [26] did not detail data variation such as standard deviation.

The reported values included ultimate tensile strength (MPa) and elongation at failure (%).

It is important to note that in order to assure clarity, the experimental procedures and results are combined for the various tests. That is to say, not all of the procedures and all of the results are collected into separate sections.

ASTM D882: Ultimate Tensile Strength

The ultimate tensile strength of the materials was calculated using the maximum force the sample experienced during testing by the cross sectional area of the sample. The cross sectional area was measured as the gage width by the average thickness of the material. The thickness of the material was averaged by measuring each set of five oriented samples with an accuracy of 0.01mm.

Figure 9 details tensile strength of the materials studied. Part A and B contain data from all three ageing conditions, as well as the data from the 2006 Cortec report [26]. It can be seen that for the various materials, the results vary between the ISU data and the Cortec data. However, there is no clear trend. For example, while the perpendicular data for the Indaco material shows that the initial ISU data (2009) is significantly higher (41 MPa) compared to the Cortec data (24.5 MPa), after one year of ageing, it is seen that ISU 2010 (perpendicular) results are very similar to the Cortec results. In contrast, the results from the balance of the materials follow other trends. For example, in the case of the Biobag K, the Cortec results are higher compared to the ISU data. However, it is seen that in general, the material properties tend to degrade after a year of ageing (*2009* to *2009 +1 year*) except for the EcoWorks 45 material. This is most likely the result of polymer degradation such as hydrolysis of the polymer chains and loss of molecular weight.

Figure 10 details the difference between the highest value that was recorded during the Iowa State tensile testing and the corresponding value that was reported by Cortec Corp. [26]. Lines are added to the graph, connecting the corresponding data points, for visualization reasons. In addition, standard deviation bars are not included to reduce "clutter" however, the statistical analyses is completed in a separate section. In more detail, a material was given a positive value, if it exhibited higher tensile strength as measured by ISU researchers compared to the value reported in the Cortec report. Correspondingly, negative values indicate that the properties measured by ISU researchers were lower than those reported in the Cortec report. While there were differences between the ISU and Cortec data, the differences are relatively material dependent. For example, with regard to perpendicular tensile strength, ISU data consistently reported lower strength values compared to the Cortec report. In contrast, Indaco property values were generally higher in the ISU reported data. This suggests that while the materials were manufactured and supplied by the same company, there were differences with each material type. While it is not possible to determine what actually caused these differences, they may have been caused by manufacturing, storage, and/or composition.

It is interesting to note that in the direction parallel to machine direction, all materials follow a similar trend with a saddle point (low point for the "*2009+1*" showing the lowest strength, suggesting that ageing had an effect on the mechanical properties). While not as obvious, a similar trend is seen in the results perpendicular to machine direction. These trends also suggest that manufacturing date had an effect on the mechanical properties.

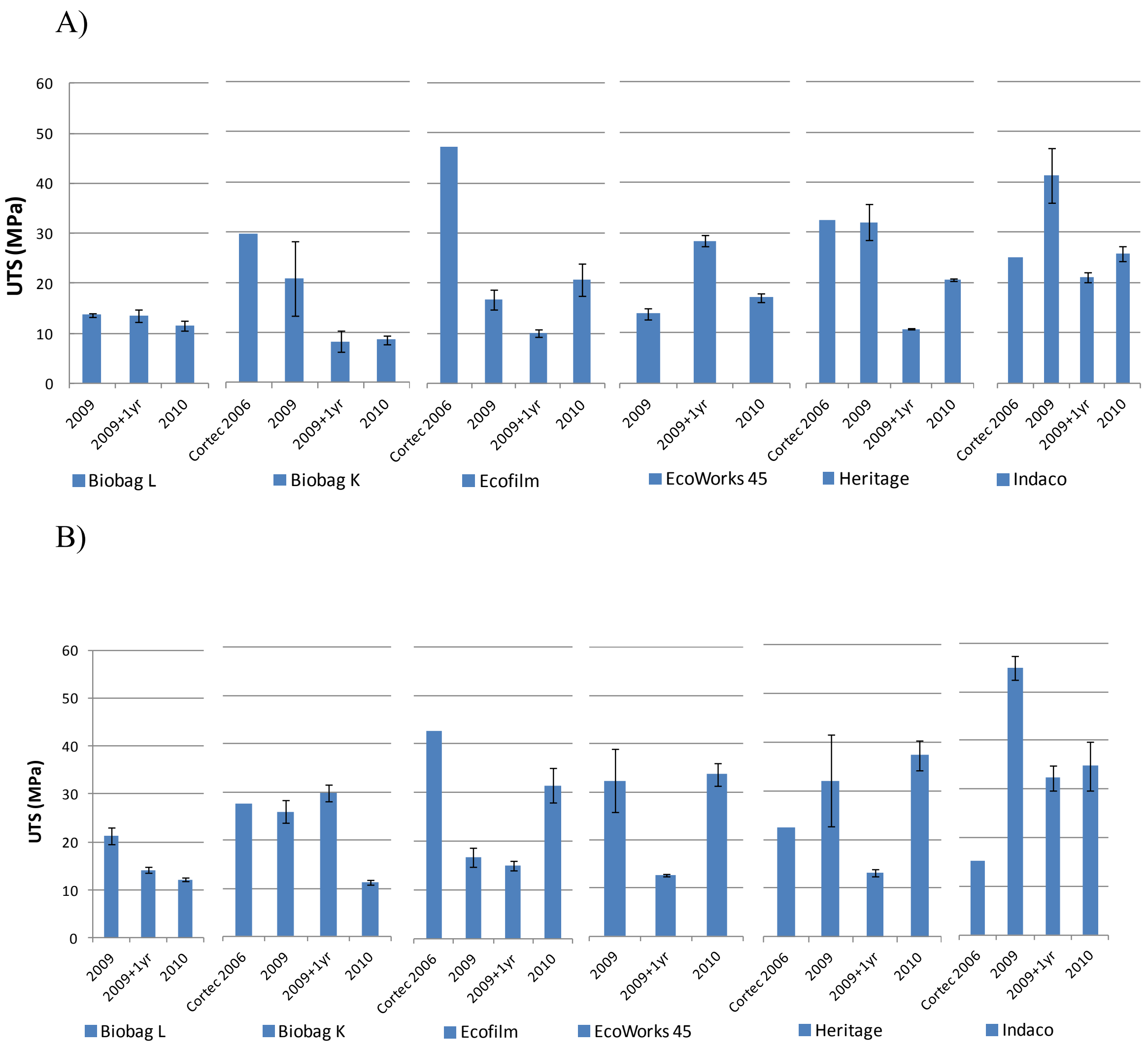


Figure 9) ASTM D882 Tensile testing results, ultimate tensile strength compared to 2006 Cortec Report; (A) Perpendicular to machine direction; (B) Parallel to machine direction

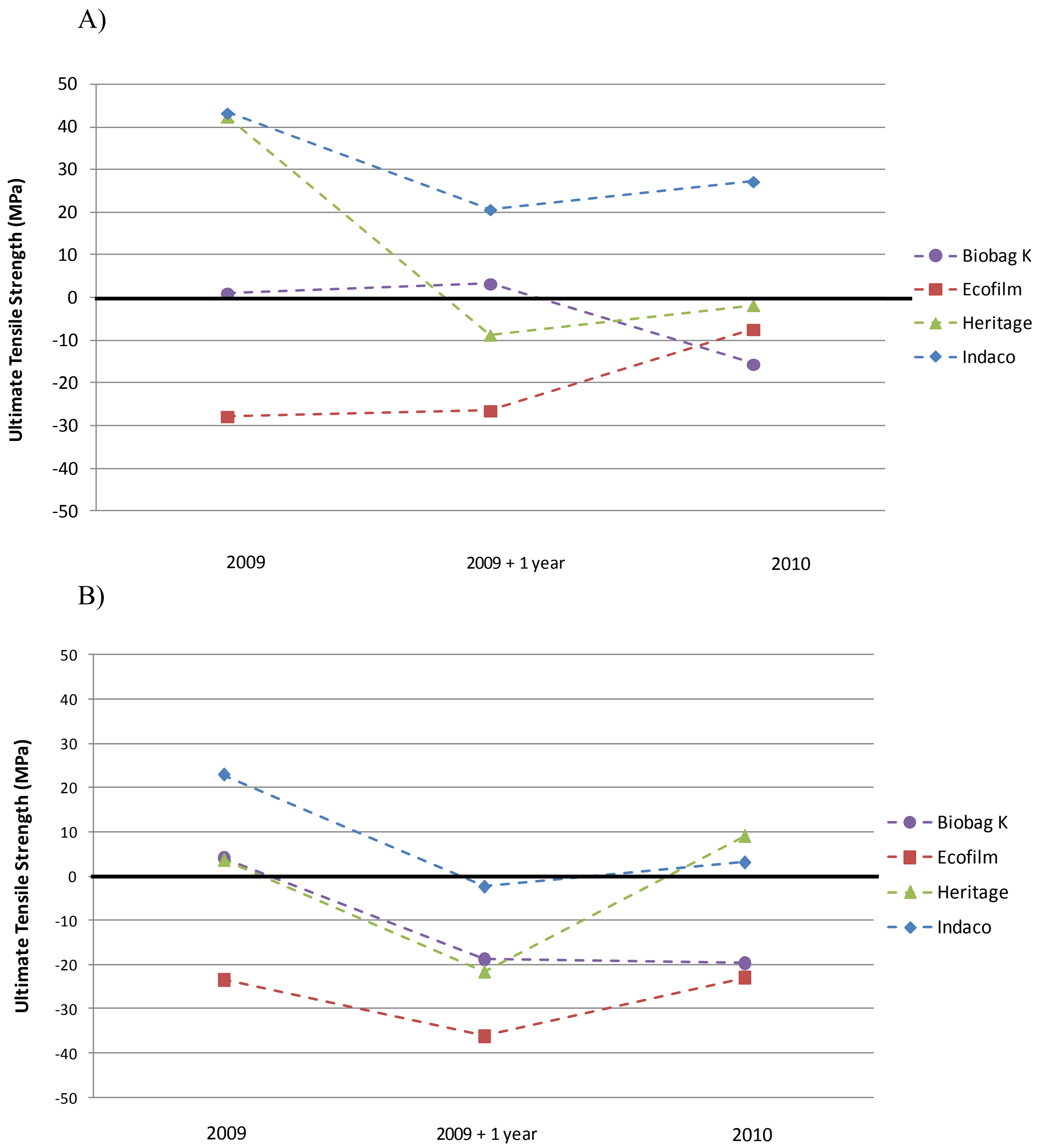


Figure 10) Difference between 2006 Cortec reported stress values and ISU recorded stress values; (A) Perpendicular to machine direction, (B) Parallel to machine direction

Statistical Analysis of Ultimate Tensile Strength (ASTM D882)

Perpendicular to machine direction

In order to determine the statistical difference of the data acquired by the testing performed at Iowa State and the data reported within the Cortec report [26], P- tests were completed using JMP software. These analyses compared the material ultimate tensile strength perpendicular to the machined direction of the material.

The first set of analyses, as seen in Table 5, compares the data from the material acquired in 2009 to the 2009+1 year material; as well as the newly acquired material from 2009 to the new material acquired in 2010. Comparisons of ultimate tensile strength (UTS) for the perpendicular to machine direction were made for the following populations and detailed in Table 5:

- Sample mean of new materials tested in 2009 (x_{2009}) compared to
  Sample mean of 2009 materials after 1 year of storage (x_{2009+1})
- Sample mean of new materials tested in 2009 (x_{2009})compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 5) Statistical analysis of ASTM D882, perpendicular to machine direction (A) comparison of sample means of 2009 to 2009 aged material; (B) comparison of sample means from 2009 to 2010 material

A)

Ultimate tensile strength statistical analysis: perpendicular to machine direction (MPa)					
Null Hypothesis (H_o): $x_{2009} = x_{2009+1}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2009+1}$					
	x_{2009}	σ_{2009}	x_{2009+1}	σ_{2009+1}	95% confidence
Biobag L	13.7	0.42	13.6	1.19	Not significantly different
Biobag K	20.9	7.42	8.2	2.06	Significantly different
Ecofilm	16.7	1.93	10.0	0.73	Significantly different
EcoWorks 45	13.9	1.11	28.3	1.09	Significantly different
Heritage	32.1	3.69	10.8	0.12	Significantly different
Indaco	41.3	5.41	21.0	0.99	Significantly different

B)

Ultimate tensile strength statistical analysis: perpendicular to machine direction (MPa)					
Null Hypothesis (H_o): $x_{2009} = x_{2010}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2010}$					
	x_{2009}	σ_{2009}	x_{2010}	σ_{2010}	95% confidence
Biobag L	13.7	0.42	11.5	0.91	Significantly different
Biobag K	20.9	7.42	8.5	0.82	Significantly different
Ecofilm	16.7	1.93	20.7	3.24	Significantly different
EcoWorks 45	13.9	1.11	17.0	0.93	Significantly different
Heritage	32.1	3.69	20.6	0.25	Significantly different
Indaco	41.3	5.41	25.7	1.47	Significantly different

The statistical comparison determined that the ultimate tensile strength of each material in the perpendicular direction to the machined axes is significantly different in all populations, except for the comparison of new 2009 Biobag L material and the same material aged for a year. This again suggests that the manufacturing date had a significant effect on the mechanical properties. In addition, it is seen that ageing (*2009* compared to *2009+1*) had a significant effect on the mechanical properties.

The second set of analyses, as seen in Table 6, uses the values published by Cortec Corp. as the population mean to compare the newly acquired materials from 2009 and 2010 [26]. Comparisons of ultimate tensile strength (UTS) for the perpendicular to machine direction were made for the following populations and detailed in Table 6:

- Reported data from the Cortec Report (x_{Cortec}) compared to
  Sample mean of new materials tested in 2009 (x_{2009})
- Reported data from the Cortec Report (x_{Cortec}) compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 6) Statistical analysis of ASTM D882, perpendicular to machine direction (A) comparison of sample means of 2009 material to Cortec reported data; (B) comparison of sample means from 2010 material to Cortec reported data

A)

Ultimate tensile strength statistical analysis: Perpendicular to machine direction (MPa)				
Null Hypothesis (H_o): $x_{Cortec} = x_{2009}$ Alternative Hypothesis (H_A): $x_{Cortec} \neq x_{2009}$				
	x_{cortec}	x_{2009}	σ_{2009}	95% confidence
Biobag K	29.6	20.9	7.42	Not significantly different
Ecofilm	47.1	16.7	1.93	Significantly different
Heritage	32.5	32.1	3.69	Significantly different
Indaco	24.9	41.3	5.41	Significantly different

B)

Ultimate tensile strength statistical analysis: Perpendicular to machine direction (MPa)				
Null Hypothesis (H_o): $x_{Cortec} = x_{2010}$ Alternative Hypothesis (H_A): $x_{Cortec} \neq x_{2010}$				
	x_{cortec}	x_{2010}	σ_{2010}	95% confidence
Biobag K	27.3	8.5	0.82	Significantly different
Ecofilm	47.1	20.7	3.24	Significantly different
Heritage	32.5	20.6	0.25	Significantly different
Indaco	24.9	25.7	1.47	Significantly different

The statistical comparison determined that the ultimate tensile strength of each material, perpendicular to machine direction, is significantly different to the results reported in the Cortec report [26] in all material populations except for the Biobag K material when compared to the new 2009 material. In addition, it is seen that the property values for all materials are significantly different between the Cortec report and the materials tested in 2010 in the perpendicular direction.

Parallel to machine direction

In order to determine the statistical difference of the data acquired by the testing performed at Iowa State and the data reported within the Cortec report [26], P- tests were completed using JMP software. These analyses compare the material as it was tested parallel to the machined direction.

The first set of analyses, as seen in Table 7, compares the data from the material acquired in 2009 to the same material that was aged for a year; as well as the newly acquired material from 2009 to the new material acquired in 2010. Comparisons of ultimate tensile strength (UTS) for the parallel to machine direction were made for the following populations and detailed in Table 7:

- Sample mean of new materials tested in 2009 (x_{2009})compared to
  Sample mean of 2009 materials after 1 year of storage (x_{2009+1})
- Sample mean of new materials tested in 2009 (x_{2009})compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 7) Statistical analysis of ASTM D882, parallel to machine direction (A) comparison of sample means of 2009 to 2009 aged material; (B) comparison of sample means from 2009 to 2010 material

A)

Ultimate tensile strength statistical analysis: Parallel to machine direction (MPa)					
Null Hypothesis (H_o): $x_{2009} = x_{2009+1}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2009+1}$					
	x_{2009}	σ_{2009}	x_{2009+1}	σ_{2009+1}	95% confidence
Biobag L	21.2	1.72	14.1	0.65	Significantly different
Biobag K	25.9	2.32	29.7	1.70	Significantly different
Ecofilm	16.8	1.87	15.0	1.01	Not significantly different
EcoWorks 45	32.4	6.62	12.7	0.31	Significantly different
Heritage	57.1	9.39	13.7	0.82	Not significantly different
Indaco	55.0	2.47	32.3	2.52	Significantly different

B)

Ultimate tensile strength statistical analysis: Parallel to machine direction (MPa)					
Null Hypothesis (H_o): $x_{2009} = x_{2010}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2010}$					
	x_{2009}	σ_{2009}	x_{2010}	σ_{2010}	95% confidence
Biobag L	21.2	1.72	12.2	0.91	Significantly different
Biobag K	25.9	2.32	11.2	0.59	Significantly different
Ecofilm	16.8	1.87	31.5	3.58	Significantly different
EcoWorks 45	32.4	6.62	33.7	2.44	Not significantly different
Heritage	57.1	9.39	37.3	3.07	Not significantly different
Indaco	55.0	2.47	34.7	4.96	Significantly different

The statistical comparison determined that the ultimate tensile strength of each material in the parallel direction of the machined axes is significantly different in all populations except for the Ecofilm and Heritage material when comparing the new 2009 material and the same material aged for a year; as well as the EcoWorks 45 and Heritage material when comparing the 2009 material and the material acquired in 2010. Again, this suggests that there are ageing and production date effects on the mechanical properties of the films.

The second set of analyses, as seen in Table 8, uses the values published by Cortec Corp. as the population mean to compare the newly acquired materials from 2009 and 2010 [26]. Comparisons of ultimate tensile strength (UTS) for the parallel to machine direction were made for the following populations and detailed in Table 8:

- Reported data from the Cortec Report (x_{Cortec})compared to
  Sample mean of new materials tested in 2009 (x_{2009})
- Reported data from the Cortec Report (x_{Cortec})compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 8) Statistical analysis of ASTM D882, parallel to machine direction (A) comparison of sample means of 2009 material to Cortec reported data; (B) comparison of sample means from 2010 material to Cortec reported data

A)

Ultimate tensile strength statistical analysis: parallel to machine direction (MPa)				
Null Hypothesis (H_o): $x_{Cortec} = x_{2009}$ Alternative Hypothesis (H_A): $x_{Cortec} \neq x_{2009}$				
	x_{cortec}	x_{2009}	σ_{2009}	95% confidence
Biobag K	27.5	25.9	2.32	Not significantly different
Ecofilm	42.7	16.8	1.87	Significantly different
Heritage	22.5	57.1	3.39	Significantly different
Indaco	15.2	55.0	2.47	Significantly different

B)

Ultimate tensile strength statistical analysis: parallel to machine direction (MPa)				
Null Hypothesis (H_o): $x_{Cortec} = x_{2010}$ Alternative Hypothesis (H_A): $x_{Cortec} \neq x_{2010}$				
	x_{cortec}	x_{2010}	σ_{2010}	95% confidence
Biobag K	27.5	11.2	0.594	Significantly different
Ecofilm	42.7	31.5	3.578	Significantly different
Heritage	22.5	37.3	3.073	Significantly different
Indaco	15.2	34.7	4.960	Significantly different

The statistical comparison determined that the measured results of ultimate tensile strength of each material in the parallel direction of the machined axes was significantly different to the results reported in the Cortec report [26] in all populations, except for the Biobag K when compared to the new 2009 material and the Heritage material when comparing the new 2009 and 2010 material. In addition, it is seen that all material property values are significantly different between the Cortec report and the materials tested in 2010 in the parallel direction.

ASTM D882: Elongation at Failure

Figure 12 details the elongation at failure for the various materials, orientation/direction, and ageing condition. The data is reported as a percentage of its original length as measured through head displacement of the grips, Figure 11.

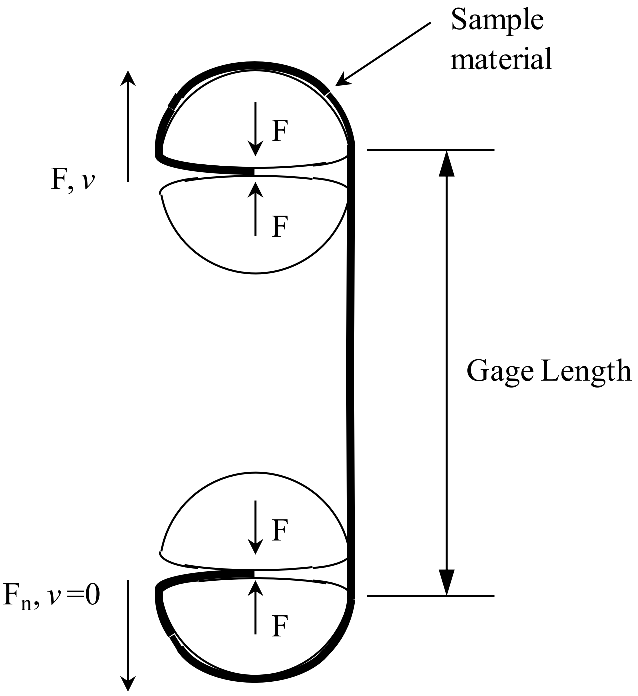


Figure 11) Tensile testing grip apparatus

It is seen that there are large variations within the groups as well as individual data points and it is difficult to identify any general reason. For example, the Ecofilm brand exhibits similar strain in the parallel direction (395% or 3.95 $^{mm}/_{mm}$) compared to the Cortec results (393% or 3.93$^{mm}/_{mm}$). However, after a year of ageing, the strain in the parallel direction had more than tripled (1,328% or 13.28 $^{mm}/_{mm}$). This is counter intuitive as ageing usually promotes embrittlement and loss of elongation at failure due to leaching of plasticizers. It may be the result of polymer chain scission, possibly hydrolysis, resulting in small chains that act as plasticizers.

In the parallel direction, the year old Heritage material displayed the lowest variation at 0.050 $^{mm}/_{mm}$. The Biobag K and Biobag L material were more consistent from the initial test to the year old testing, with a difference in their standard deviation of 0.009 $^{mm}/_{mm}$ and 0.107 $^{mm}/_{mm}$, respectively, while the Indaco and Heritage materials showed the largest difference from the initial testing in 2009 to the testing after a year of ageing, with a difference in their standard deviation of 3.538 $^{mm}/_{mm}$ and 0.605 $^{mm}/_{mm}$, respectively.

In the perpendicular direction, the year old Biobag L material displayed the lowest variation at 0.031 $^{mm}/_{mm}$. The Heritage and Biobag K material were more consistent from the first to the year old testing, with a difference in their standard deviation of 0.095 $^{mm}/_{mm}$ and 0.062 $^{mm}/_{mm}$, respectively, while the Ecofilm and Indaco materials showed a largest difference from the initial testing in 2009 to the testing after a year of ageing, with a difference in their standard deviation of 0.412 $^{mm}/_{mm}$ and 0.380 $^{mm}/_{mm}$, respectively.

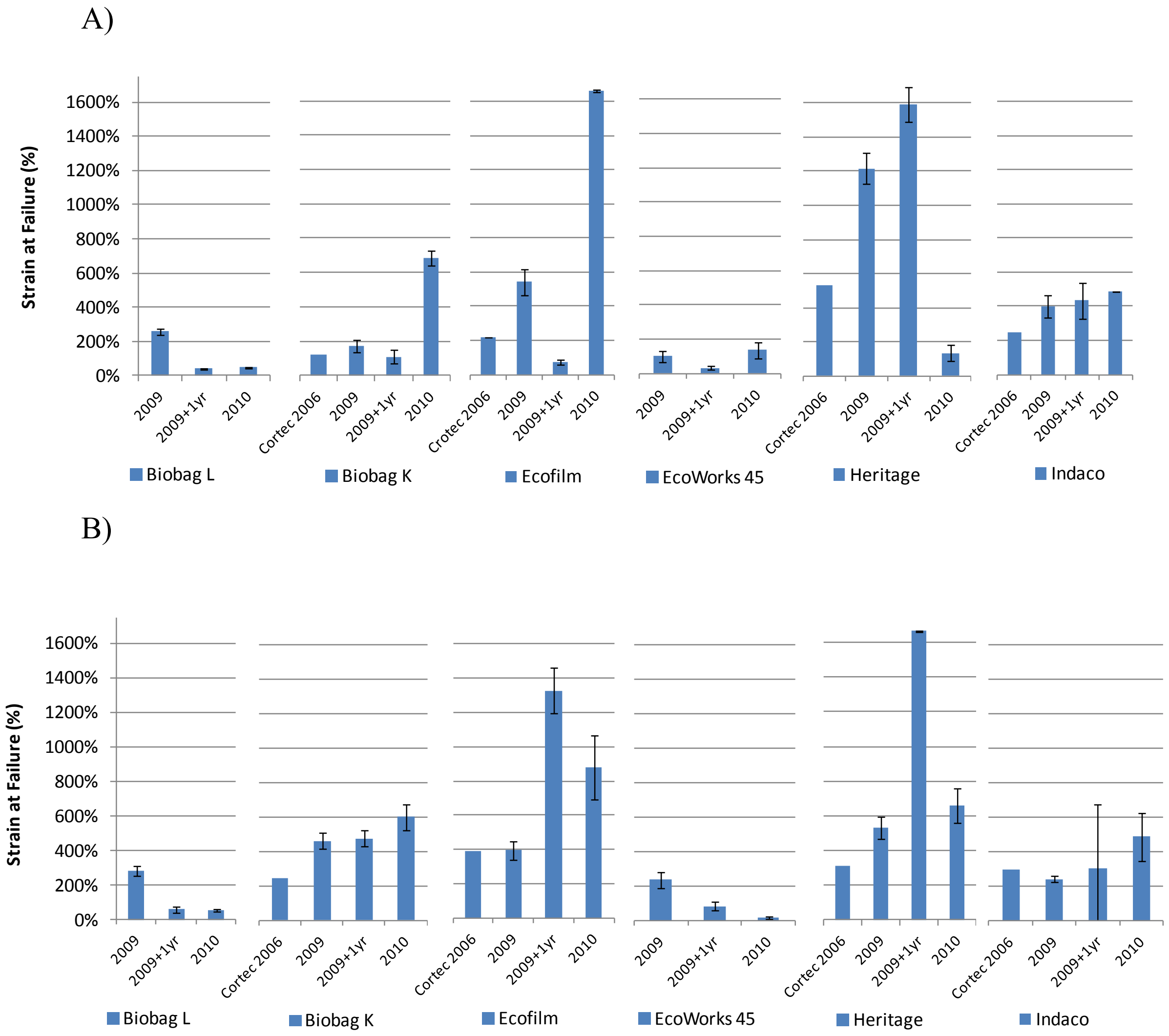
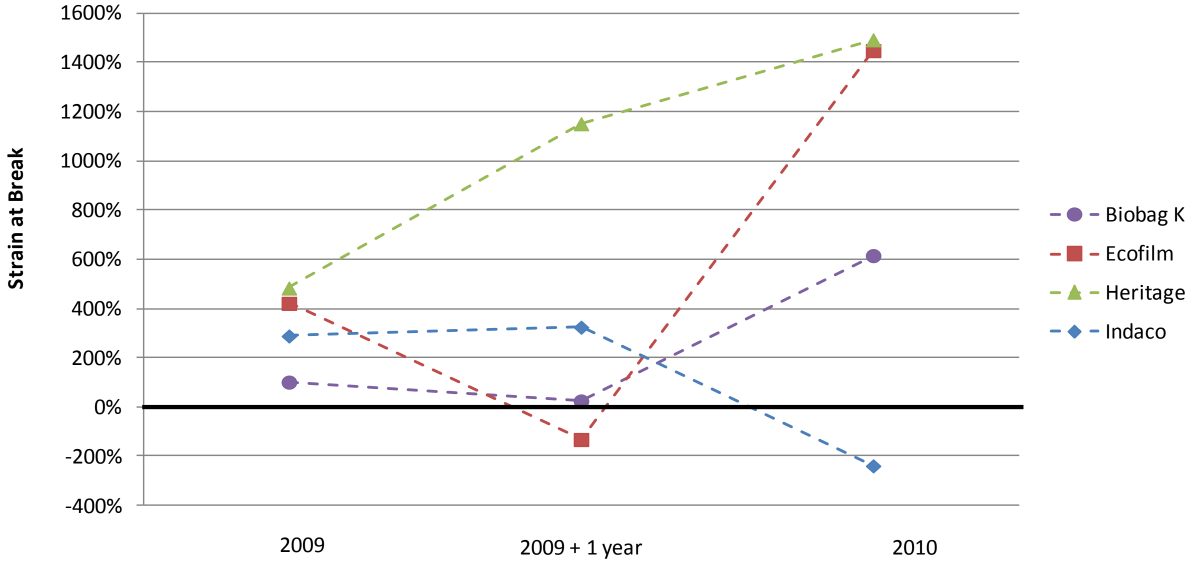


Figure 12) ASTM D 882 tensile testing results, strain at failure (%) compared to 2006 Cortec Report; (A) Perpendicular to machine direction; (B) Parallel to machine direction

A)



B)

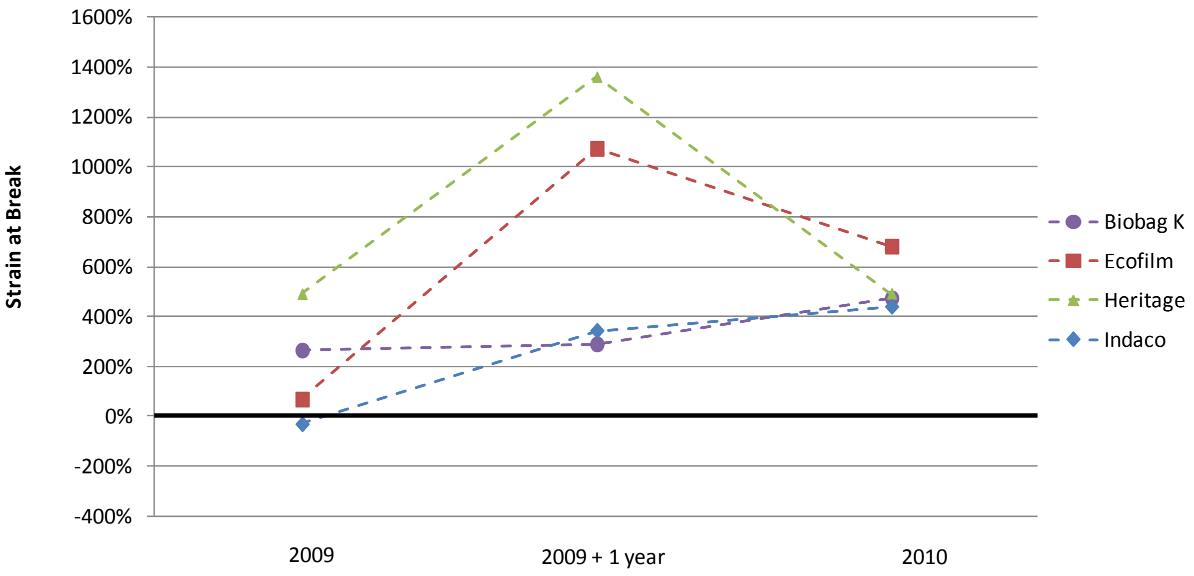


Figure 13) Difference between 2006 Cortec reported strain values and ISU recorded strain values; (A) Perpendicular to machine direction; (B) Parallel to machine direction

Statistical Analysis of Strain at Break

Perpendicular to Machine Direction

In order to determine the statistical difference of the data acquired by the testing performed at Iowa State, P- tests were completed using JMP software. These analyses compare the material as it was tested in the perpendicular direction to that of the machined direction of the material.

The first analysis, as seen in Table 9, compares the data from the material acquired in 2009 to the 2009+1 year material; as well as the newly acquired material from 2009 to the material acquired in 2010. Comparisons of strain at break for the perpendicular to machine direction were made for the following populations and detailed in Table 9:

- Sample mean of new materials tested in 2009 (x_{2009}) compared to
  Sample mean of 2009 materials after 1 year of storage (x_{2009+1})
- Sample mean of new materials tested in 2009 (x_{2009}) compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 9) Statistical analysis of ASTM D882, perpendicular to machine direction (A) comparing sample means of 2009 to 2009 aged material; (B) comparing sample means from 2009 to 2010 material

A)

<table>
<tr><td colspan="6">Strain at break statistical analysis: perpendicular to machine direction
(mm/mm)</td></tr>
<tr><td colspan="6">Null Hypothesis (H_o): $x_{2009} = x_{2009+1}$
Alternative Hypothesis (H_A): $x_{2009} \neq x_{2009+1}$</td></tr>
<tr><td></td><td>x_{2009}</td><td>σ_{2009}</td><td>x_{2009+1}</td><td>σ_{2009+1}</td><td>95% confidence</td></tr>
<tr><td>Biobag L</td><td>2.6</td><td>0.21</td><td>0.4</td><td>0.31</td><td>Significantly different</td></tr>
<tr><td>Biobag K</td><td>1.7</td><td>0.34</td><td>1.1</td><td>0.40</td><td>Significantly different</td></tr>
<tr><td>Ecofilm</td><td>5.4</td><td>0.77</td><td>0.7</td><td>0.15</td><td>Significantly different</td></tr>
<tr><td>EcoWorks 45</td><td>1.0</td><td>0.32</td><td>0.3</td><td>0.09</td><td>Significantly different</td></tr>
<tr><td>Heritage</td><td>5.3</td><td>0.92</td><td>12.2</td><td>1.01</td><td>Significantly different</td></tr>
<tr><td>Indaco</td><td>4.0</td><td>0.68</td><td>4.3</td><td>1.06</td><td>Not significantly different</td></tr>
</table>

B)

<table>
<tr><td colspan="6">Strain at break statistical analysis: perpendicular to machine direction
(mm/mm)</td></tr>
<tr><td colspan="6">Null Hypothesis (H_o): $x_{2009} = x_{2010}$
Alternative Hypothesis (H_A): $x_{2009} \neq x_{2010}$</td></tr>
<tr><td></td><td>x_{2009}</td><td>σ_{2009}</td><td>x_{2010}</td><td>σ_{2010}</td><td>95% confidence</td></tr>
<tr><td>Biobag L</td><td>2.6</td><td>0.21</td><td>0.5</td><td>0.07</td><td>Significantly different</td></tr>
<tr><td>Biobag K</td><td>1.7</td><td>0.34</td><td>6.9</td><td>0.42</td><td>Significantly different</td></tr>
<tr><td>Ecofilm</td><td>5.4</td><td>0.77</td><td>16.7</td><td>0.07</td><td>Significantly different</td></tr>
<tr><td>EcoWorks 45</td><td>1.0</td><td>0.32</td><td>1.4</td><td>0.47</td><td>Not significantly different</td></tr>
<tr><td>Heritage</td><td>5.3</td><td>0.92</td><td>15.9</td><td>0.49</td><td>Significantly different</td></tr>
<tr><td>Indaco</td><td>4.0</td><td>0.68</td><td>0.1</td><td>0.01</td><td>Significantly different</td></tr>
</table>

The statistical comparison determined that for each material, the strain at break in the perpendicular direction to that of the machine axes was significantly different in all populations, except for the Indaco material compared to the new 2009 material and the same material aged for a year; as well as the EcoWorks 45 material compared to the new 2009 material and the 2010 material. This again suggests that the manufacturing date had a significant effect on the mechanical properties. In addition, it is seen that ageing (2009 compared to 2009+1) had a significant effect on the mechanical properties.

The second analysis, as seen in Table 10, uses the values published by Cortec Corp. as the population mean to compare the newly acquired materials from 2009 and 2010 [26]. Comparisons of strain at break for the perpendicular to machine direction were made for the following populations and detailed in Table 10:

- Reported data from the Cortec Report (x_{Cortec})compared to
  Sample mean of new materials tested in 2009 (x_{2009})
- Reported data from the Cortec Report (x_{Cortec}) compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 10) Statistical analysis of ASTM D882, perpendicular to machine direction (A) comparing sample means of 2009 material to Cortec reported data; (B) comparing sample means from 2010 material to Cortec reported data

A)

Strain at break statistical analysis: perpendicular to machine direction (mm/mm)				
Null Hypothesis (H_o): $x_{Cortec} = x_{2009}$ Alternative Hypothesis (H_A): $x_{Cortec} \neq x_{2009}$				
	x_{cortec}	x_{2009}	σ_{2009}	95% confidence
Biobag K	48.9	1.7	0.34	Significantly different
Ecofilm	68.4	5.4	0.77	Significantly different
Heritage	47.1	5.3	0.92	Significantly different
Indaco	36.1	4.0	0.68	Significantly different

B)

Strain at break statistical analysis: perpendicular to machine direction (mm/mm)				
Null Hypothesis (H_o): $x_{Cortec} = x_{2010}$ Alternative Hypothesis (H_A): $x_{Cortec} \neq x_{2010}$				
	x_{cortec}	x_{2010}	σ_{2010}	95% confidence
Biobag K	42.9	6.9	0.42	Significantly different
Ecofilm	68.4	16.7	0.07	Significantly different
Heritage	47.1	20.6	0.25	Significantly different
Indaco	36.1	0.1	0.01	Significantly different

The statistical comparison determined that the strain at break of each material in the perpendicular direction of the machine axes was significantly different to the results reported by Cortec [26]. In addition, it is seen that all materials show significant differences between the Cortec report and the materials tested in 2010 in the perpendicular direction.

Parallel to Machine Direction

In order to determine the statistical difference of the data acquired by the testing performed at Iowa State, P- tests were completed using JMP software. These analyses compare the material as it was tested perpendicular to the machine direction of the material.

The first set of analyses, as seen in Table 11, compares the data from the material acquired in 2009 to the 2009+1 year material; as well as the newly acquired material from 2009 to the new material acquired in 2010. Comparisons of strain at break for the parallel to machine direction were made for the following populations and detailed in Table 11:

- Sample mean of new materials tested in 2009 (x_{2009}) compared to
  Sample mean of 2009 materials after 1 year of storage (x_{2009+1})
- Sample mean of new materials tested in 2009 (x_{2009}) compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 11) Statistical analysis of ASTM D882, parallel to machine direction (A) comparing sample means of 2009 to 2009 aged material; (B) comparing sample means from 2009 to 2010 material

A)

Strain at break statistical analysis: parallel to machine direction (mm/mm)					
Null Hypothesis (H_o): $x_{2009} = x_{2009+1}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2009+1}$					
	x_{2009}	σ_{2009}	x_{2009+1}	σ_{2009+1}	95% confidence
Biobag L	21.2	1.72	14.1	0.65	Significantly different
Biobag K	4.6	0.46	4.8	0.47	Not significantly different
Ecofilm	4.0	0.56	13.3	1.33	Significantly different
EcoWorks 45	2.4	0.45	0.8	0.25	Significantly different
Heritage	7.5	0.66	16.7	0.05	Significantly different
Indaco	2.4	0.17	3.0	3.71	Not significantly different

B)

Strain at break statistical analysis: parallel to machine direction (mm/mm)					
Null Hypothesis (H_o): $x_{2009} = x_{2010}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2010}$					
	x_{2009}	σ_{2009}	x_{2010}	σ_{2010}	95% confidence
Biobag L	13.7	0.42	11.5	0.91	Significantly different
Biobag K	4.6	0.46	6.0	0.73	Significantly different
Ecofilm	4.0	0.56	8.8	1.87	Significantly different
EcoWorks 45	2.4	0.45	0.2	0.09	Significantly different
Heritage	7.5	0.66	6.6	1.00	Not significantly different
Indaco	2.4	0.17	4.9	1.42	Significantly different

The statistical comparison determined that the strain break of each material in the parallel direction of the machined axes is significantly different in all populations except, for the Biobag Kitchen and Indaco materials compared to the new 2009 material and the same material aged for a year; as well as Heritage material compared to the 2009 material and the material acquired in 2010. This again suggests that the manufacturing date had significant effect on the mechanical properties. In addition, it is seen that ageing (2009 compared to 2009+1) had a significant effect on the mechanical properties.

The second set of analyses, as seen in Table 12, uses the values published by Cortec Corp. as the population mean to compare the newly acquired materials from 2009 and 2010 [26]. Comparisons of strain at break for the perpendicular to machine direction were made for the following populations and detailed in Table 12:

- Reported data from the Cortec Report (x_{Cortec})compared to
  Sample mean of new materials tested in 2009 (x_{2009})
- Reported data from the Cortec Report (x_{Cortec}) compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 12) Statistical analysis of ASTM D882, parallel to machine direction (A) comparing sample means of 2009 material to Cortec reported data; (B) comparing sample means from 2010 material to Cortec reported data

A)

Strain at break statistical analysis: parallel to machine direction (mm/mm)				
Null Hypothesis (H_o): $x_{Cortec} = x_{2009}$ Alternative Hypothesis (H_A): $x_{Cortec} \neq x_{2009}$				
	x_{cortec}	x_{2009}	σ_{2009}	95% confidence
Biobag K	2.4	4.6	0.46	Significantly different
Ecofilm	3.9	4.0	0.56	Not significantly different
Heritage	3.1	7.5	0.65	Significantly different
Indaco	2.9	2.4	0.17	Significantly different

B)

Strain at break statistical analysis: parallel to machine direction (mm/mm)				
Null Hypothesis (H_o): $x_{Cortec} = x_{2010}$ Alternative Hypothesis (H_A): $x_{Cortec} \neq x_{2010}$				
	x_{cortec}	x_{2010}	σ_{2010}	95% confidence
Biobag K	2.42	6.0	0.73	Significantly different
Ecofilm	3.9	8.8	1.87	Significantly different
Heritage	3.1	6.6	1.0	Significantly different
Indaco	2.9	4.9	1.42	Significantly different

The statistical comparison determined that the strain break of each material parallel to the machine direction was significantly different to the results presented in the Cortec report [26] in all populations, except for the Ecofilm materials when compared to the new 2009 material. In addition, it is seen that there were significant differences for all material property values between the Cortec report and the materials tested in 2010 in the parallel direction.

ASTM D1922 (Tear Propagation Resistance Test)

The tear propagation test simulates a pre-existing tear in the film and determines the amount of energy that each material is able to absorb before it fails (catastrophic tear growth).

All samples were cut using a template designed according to the dimensions specified by the ASTM standard. Figure 14 details the design of the samples for a constant radius testing length along the upper portion of the sample. There was a 20 mm (0.80 in) slit cut at the midpoint of the base.

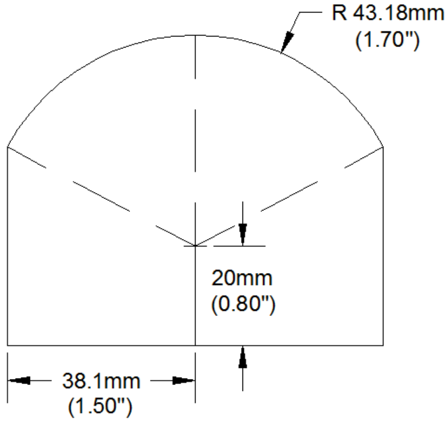


Figure 14) ASTM D 1922 Tear propagation template

All materials displayed anisotropic properties; therefore 5 specimens each were selected from the perpendicular and the parallel direction in relation to the machining direction.

The test was performed using an Oakland Instruments Pendulum Tear Tester Series ME (Minneapolis, MN), with an 800 g test pendulum. Each test specimen was placed in a split-vise, one side being attached to the pendulum the other to the stationary base. As the pendulum was released, the film absorbs the kinetic energy of the falling pendulum. The indicator on the side of the pendulum displayed the amount of energy absorbed as a percentage corresponding to the mass and height of the pendulum and was correlated to the tear force.

The average tearing force for each film was calculated using the following Eq.1 (ASTM D1922; Sec. 11.1.1):

$$\text{Average Tearing Force (N)} = \frac{\text{\% of Energy Absorbed} \times \text{mass of pendulum(g)} \times \text{graviational constant(9.81)}}{1000}$$

Eq. 1

This calculation assumes that air resistance and friction within the system are negligible. The resulting average tear force for each film was calculated and reported in Table 13. In this table the standard deviation (SD) is also noted for the data. It is important to note that the Cortec report did not detail this material property and thus is not included in the table. It is seen that there are relatively large variations between the materials as well as the direction. For example, there is a fivefold difference between the parallel and perpendicular direction for Biobag (L) in 2009. In addition, ageing of this material reduced its tear resistance in both directions. This trend is generally true for most of the materials studied. However, in selected materials, such as Heritage and Indaco films, the films retained their tear resistance over the one year ageing period. This is consistent with the findings for the elongation at break testing described previously, Figure 12. These two materials exhibited an increase in extension to failure after ageing, suggesting that the two materials do not become more brittle with ageing. Again, this is counterintuitive and there is no clear evidence of the underlying mechanisms, but perhaps the result of polymer chain scission (possibly hydrolysis) resulting in small chains that act as plasticizers. This would also help explain why these materials also exhibited a relatively large reduction in tensile strength with ageing.

Table 13) Tear propagation resistance (ASTM D1922) data

Tear propagation resistance test (ASTM D1922)		2009		2009+1		2010	
Material	Direction	Resistive force (N)	SD	Resistive force (N)	SD	Resistive force (N)	SD
Biobag L	Parallel	0.96	0.40	0.19	0.12	2.73	0.58
	Perpendicular	4.55	0.51	1.10	0.60	5.52	0.39
Biobag K	Parallel	2.86	0.52	1.07	0.37	0.86	0.16
	Perpendicular	2.42	0.63	2.51	0.12	4.03	0.55
Ecofilm	Parallel	0.52	0.07	1.11	0.37	0.69	0.15
	Perpendicular	2.53	0.23	1.76	0.14	2.24	0.14
EcoWorks 45	Parallel	0.09	0.04	0.19	0.04	0.25	0.10
	Perpendicular	0.52	0.12	0.85	0.17	0.46	0.12
Heritage	Parallel	3.63	0.24	3.72	0.66	3.61	0.51
	Perpendicular	5.12	0.45	5.13	0.49	5.09	0.43
Indaco	Parallel	0.36	0.12	0.38	0.07	0.41	0.10
	Perpendicular	0.52	0.04	0.49	0.07	0.46	0.07

Figure 15 details the tear propagation resistance force for the various materials. Both graphs in Figure 15 contain data collected from all 3 testing sessions. Note that there were no tear propagation test results published in the 2006 Cortec report [26]. A comparison of the results of testing in both directions shows that generally the materials absorb more force before fracturing in the perpendicular direction than in the parallel direction. In reference to both testing directions, the Heritage and Indaco films display the most consistency through all 3 testing runs. Results for the Heritage material were differentiated by only 0.11 N in the parallel direction and 0.04 N in the perpendicular direction from year to year. Indaco material results were separated by 0.05 N and 0.06 N in the parallel and perpendicular directions, respectively.

Some of the materials showed an increasing or decreasing trend in certain directions of testing. Biobag K (perpendicular), EcoWorks 45 (parallel), and Indaco (parallel) showed an increasing resistance to tearing through the testing sequence. Biobag K (parallel) and Indaco (perpendicular) displayed a decreasing resistance to tearing.

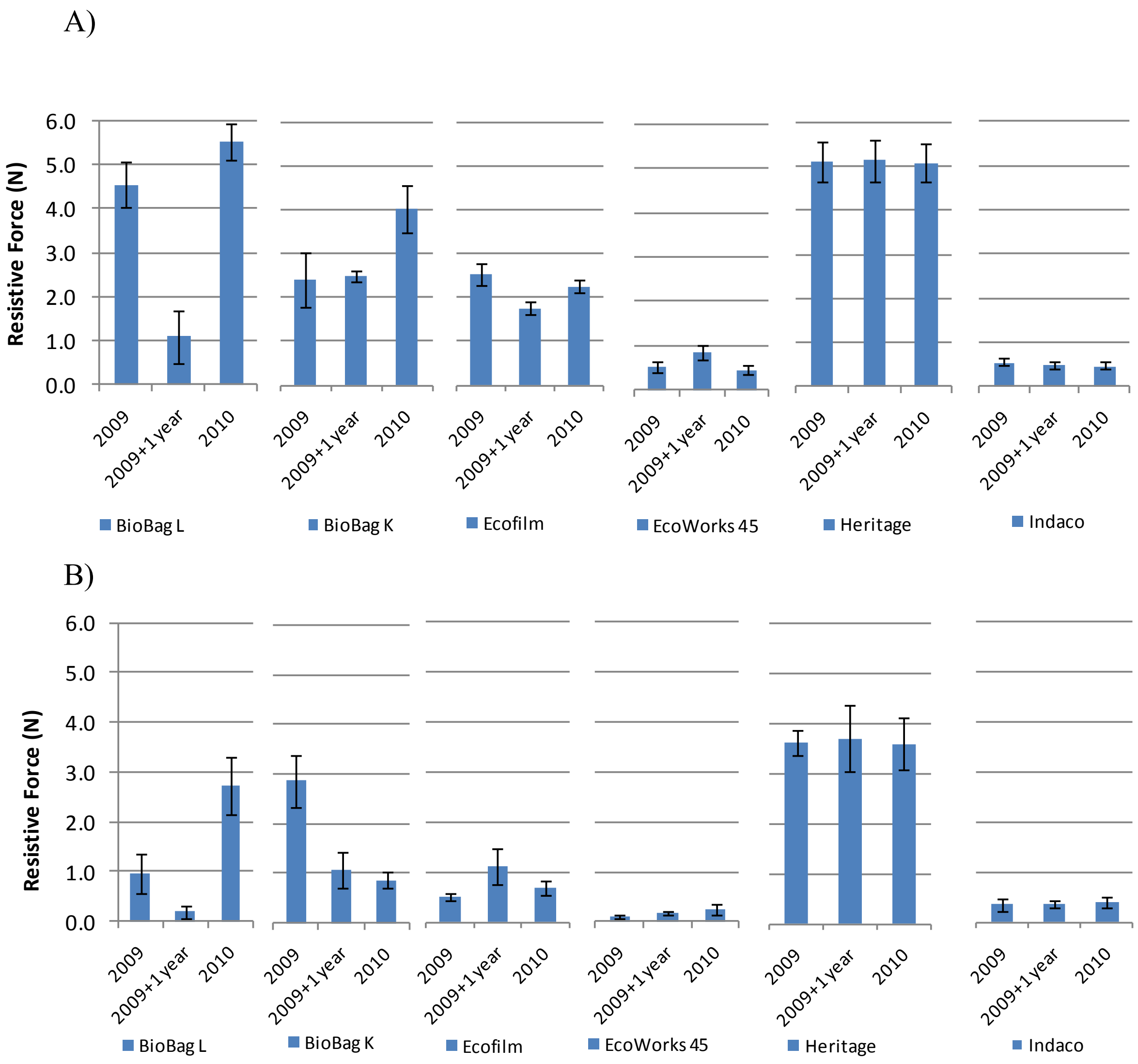


Figure 15) ASTM D1922 tear propagation resistance testing results, resistive force (N); (A) perpendicular to machine direction, (B) parallel to machine direction

Statistical Analysis of Tear Propagation Resistance

Perpendicular to Machine Direction

In order to determine the statistical difference of the data acquired by the testing performed at Iowa State and the data reported within the Cortec report [26], P- test was completed with using JMP software. These analyses compare the material as it was tested perpendicular to the machine direction of the material.

The analysis seen in Table 14 compares the data from the material acquired in 2009 to the 2009+1 year material; as well as the newly acquired material from 2009 to the new material acquired in 2010. Comparisons of strain at break for the perpendicular to machine direction were made for the following populations and detailed in Table 14.

- Sample mean of new materials tested in 2009 (x_{2009}) compared to
  Sample mean of 2009 materials after 1 year of storage (x_{2009+1})
- Sample mean of new materials tested in 2009 (x_{2009}) compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 14) Statistical analysis of ASTM D1922, perpendicular to machine direction (A) comparing sample means of 2009 to 2009 aged material; (B) comparing sample means from 2009 to 2010 material

A)

Tear Propagation Resistance: Perpendicular to Machine Direction (N)					
Null Hypothesis (H_o): $x_{2009} = x_{2009+1}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2009+1}$					
	x_{2009}	σ_{2009}	x_{2009+1}	σ_{2009+1}	95% confidence
Biobag L	4.6	0.51	1.1	0.60	Significantly different
Biobag K	2.4	0.63	2.5	0.12	Not significantly different
Ecofilm	2.5	0.23	1.8	0.14	Significantly different
EcoWorks 45	0.5	0.12	0.9	0.17	Significantly different
Heritage	5.1	0.45	5.1	0.49	Not significantly different
Indaco	0.5	0.04	0.5	0.07	Not significantly different

B)

Tear Propagation Resistance: Perpendicular to Machine Direction (N)					
Null Hypothesis (H_o): $x_{2009} = x_{2010}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2010}$					
	x_{2009}	σ_{2009}	x_{2010}	σ_{2010}	95% confidence
Biobag L	4.6	0.51	5.5	0.40	Significantly different
Biobag K	2.4	0.63	4.0	0.55	Significantly different
Ecofilm	2.5	0.23	2.2	0.14	Significantly different
EcoWorks 45	0.5	0.12	0.8	0.17	Significantly different
Heritage	5.1	0.45	5.1	0.43	Not significantly different
Indaco	0.5	0.04	0.5	0.07	Not significantly different

The statistical comparison determined that the resistance to tear propagation of each material in the direction perpendicular to the machined axes is significantly different in all populations, except for the Heritage and Indaco materials compared to the new 2009 material and the same material aged for a year as well as the materials acquired in 2010. This again suggests that the manufacturing date had significant effect on the mechanical properties. In addition, it is seen that ageing (2009 compared to 2009+1) had a significant effect on the mechanical properties.

Parallel to Machine Direction

In order to determine the statistical difference of the data acquired by the testing performed at Iowa State and the data reported within the Cortec report [26], P-tests were completed using JMP software. These analyses compare the material tested in the direction parallel to the machine direction.

The analysis seen in Table 15 compares the following populations of data for the material acquired in 2009 to the 2009+1 year material; as well as the newly acquired material from 2009 to the new material acquired in 2010.

- Sample mean of new materials tested in 2009 (x_{2009}) compared to
  Sample mean of 2009 materials after 1 year of storage (x_{2009+1})
- Sample mean of new materials tested in 2009 (x_{2009}) compared to
  Sample mean of new materials tested in 2010 (x_{2010})

Table 15) Statistical analysis of ASTM D1922, parallel to machine direction (A) comparing sample means of 2009 to 2009 aged material; (B) comparing sample means from 2009 to 2010 material

A)

Tear Propagation Resistance: Parallel to Machine Direction (N)					
Null Hypothesis (H_o): $x_{2009} = x_{2009+1}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2009+1}$					
	x_{2009}	σ_{2009}	x_{2009+1}	σ_{2009+1}	95% confidence
Biobag L	1.0	0.51	0.19	0.12	Significantly different
Biobag K	2.9	0.52	1.1	0.37	Significantly different
Ecofilm	0.5	0.07	1.1	0.37	Significantly different
EcoWorks 45	0.1	0.04	0.2	0.43	Significantly different
Heritage	3.6	0.24	3.7	0.66	Not significantly different
Indaco	0.4	0.12	0.4	0.07	Not significantly different

B)

Tear Propagation Resistance: Parallel to Machine Direction (N)					
Null Hypothesis (H_o): $x_{2009} = x_{2010}$ Alternative Hypothesis (H_A): $x_{2009} \neq x_{2010}$					
	x_{2009}	σ_{2009}	x_{2010}	σ_{2010}	95% confidence
Biobag L	1.0	0.51	2.7	0.58	Significantly different
Biobag K	2.9	0.52	0.9	0.16	Significantly different
Ecofilm	0.5	0.07	0.7	0.15	Significantly different
EcoWorks 45	0.1	0.04	0.2	0.04	Significantly different
Heritage	3.6	0.24	3.6	0.51	Not significantly different
Indaco	0.4	0.119	0.4	0.10	Not significantly different

The statistical comparison determined that the resistance to tear propagation of each material in the direction parallel direction of the machine axes is significantly different in all populations, except for Heritage and Indaco materials comparing the new 2009 material to the same material aged for a year as well as the material acquired in 2010.

ASTM D4272 (Dart Drop Puncture Test)

This impact resistance test simulates an object imparting a sudden force onto the film and determines the amount of energy each material can absorb.

The specimen for the puncture resistance test was a disk with a diameter of 154.2 mm (6.0”).

The test was performed on an Oakland Instruments Dart Drop Tester Series 8000 (Minneapolis, MN) with a variable mass dart as seen Figure 16.

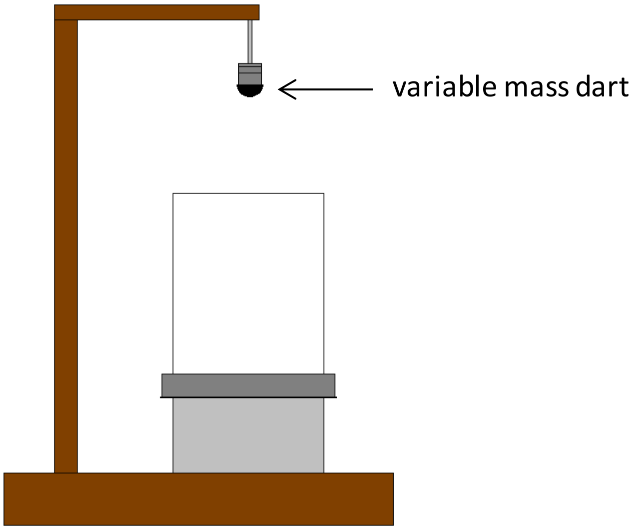


Figure 16) Dart drop impact resistance testing apparatus

Each sample was placed in a circular grip and a dart with a hemispherical diameter of 50 mm (2.0 in) was dropped at a height of 584 mm (23 in). The film was then inspected for integrity. In more detail, the condition of the film was determined using the following criteria:

- **Pass:** The dart did not create a hole in the film upon impact.

  Result: Increase weight of the dart by 5 g.

- **Failure:** The dart did create a hole in the film upon impact.

  Result: Decrease weight of the dart by 5 g.

Because the failure weight of the material is initially unknown, a set of pre-test drops was conducted (screening experiments) prior to testing. The screening test drops included a series of large weight step adjustments. In more detail, the highest dart weight is used (360 g of mass (3.5 N)). If the material failed, the mass of the dart was reduced by half. It is important to note that none of the materials tested withstood initial drop. This iterative approach of the testing continues in the same manner as described above with the weight of the dart changing in increments of half of the previous weight, until the incremental change is 5 g. These screening experiments ensure that the mass of the dart was relatively close to the failure weight of the film.

To calculate the failure weight of each film, Eq.2 was used, where increment of mass change is 5 g, *N* is the total number of failures, and A is the sum of the weighted scores:

$$\text{Total Failure Weight (gf)} = 38.2\text{g} + (\text{Lowest Failure Weight}) + (\text{Increment of mass changes}) \times \frac{\text{A} - 1}{\text{N} - 2}$$

Eq. 2

The amount of energy that the film absorbed before failure is calculated using Eq. 3, where the total failure weight is taken from Eq. 2:

$$\text{Energy at Failure (J)} = \text{Total Failure Weight (gf)} \times .001 \times 9.81\, {}^{\text{m}}\!/_{\text{s}^2} \times \text{Drop distance of the Dart (m)}$$

Eq.3

Figure 17 details the dart impact resistance for all 3 testing conditions (2009, +1 year and 2010) as well as the data from the Cortec report. Most materials had a relatively small change (±10 % or less) from the initial testing (2009) to the following year (2009+1 year) after ageing (Biobag K (-3.72 %), Heritage (-3.31 %) and Ecofilm (5.67 %). The materials that experienced a large change (±10 % or more) from 2009 to a year later were Biobag L (-10.34 %), EcoWorks 45 (-39.52 %), and Indaco (24.99 %). Again it is seen that the Heritage and Indaco both demonstrated a relatively high energy absorbance. This is in agreement with the results for extension to failure and tear resistance.

In comparing the Cortec values to the values that were recorded by ISU Figure 18, it is seen that generally the ISU values were higher for the Heritage and Indaco films and similar for the balance of the films. In more detail, the Biobag K and Ecofilm products showed the least amount of variation compared to the Cortec values. The 2010 testing showed that the impact resistance of Biobag K material exhibited 0.005 J (0.88 %) difference from the Cortec value and the Ecofilm material exhibited 0.05 J (8.3 %) difference from the Cortec value. In comparison, the impact resistance values for Heritage and Indaco films were 1.9 J and 0.9 J (641 % and 89 %) higher than the Cortec values reported for their brands.

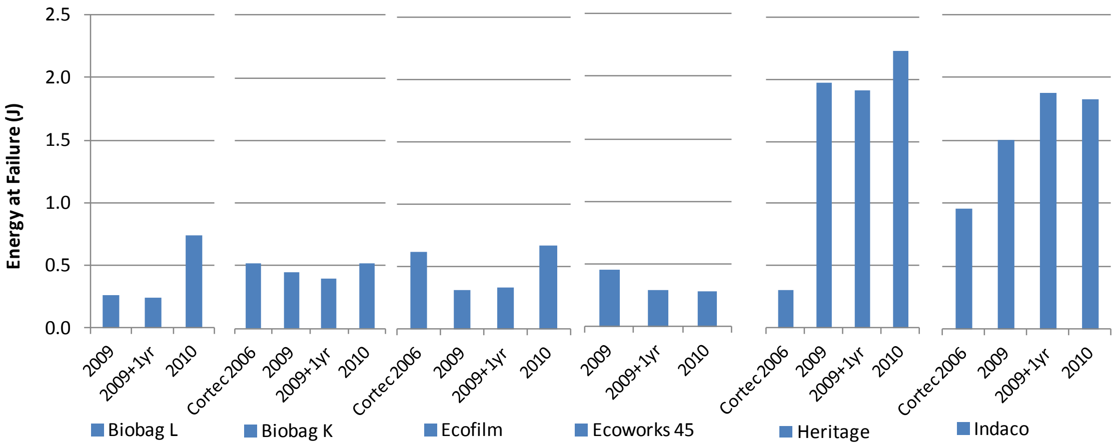


Figure 17) ASTM D4272 dart drop impact resistance testing results compared to Cortec report (ASTM D3420)

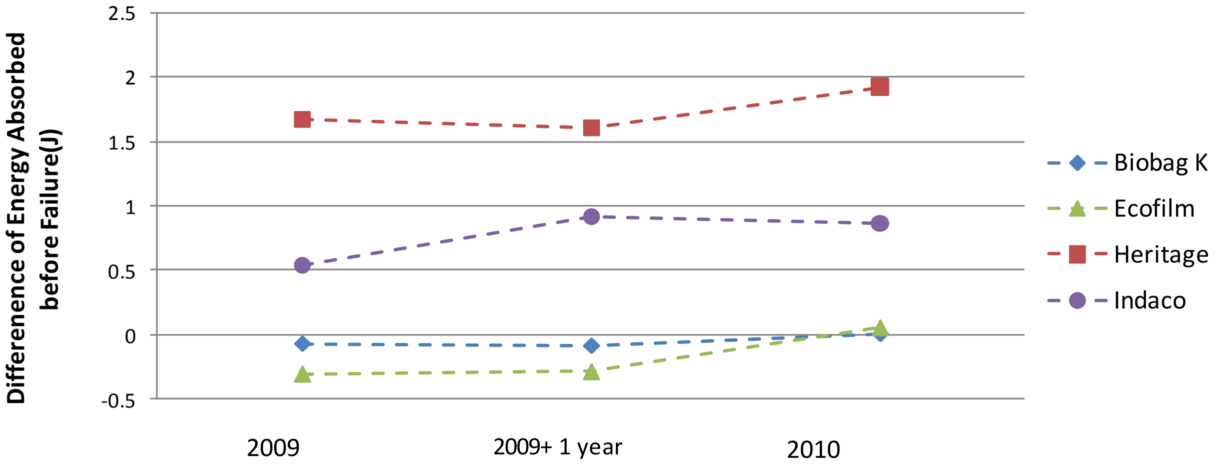


Figure 18) Difference between 2006 Cortec reported values and ISU recorded values

Chapter 7. Morphological Testing

In order to better understand the behavior of the materials, further analysis was done to determine if there were any contributing factors to variations seen between the different testing scenarios.

Differential Scanning Calorimetry (DSC)

A differential scanning calorimetry (DSC) test was used to estimate the processing history of each material based on morphology. Two samples of 3-5 mg of each material were tested in order to account for variations. The sample was heated to promote phase changes and determine phase change temperatures, such as glass transition temperature, melt temperature, and any other possible endo- or exo- thermic reactions of the film.

The initial temperature was 10 °C; the temperature was increased to 200°C at a rate of 10 °C/min. Once the maximum temperature was reached, the sample was cooled rapidly back to 10 °C using liquid nitrogen. The thermal cycling was completed three times per sample in order to clearly identify whether any additional physical properties were induced to the material due to the production/processing of the film as well ageing and other effects (such as storage).

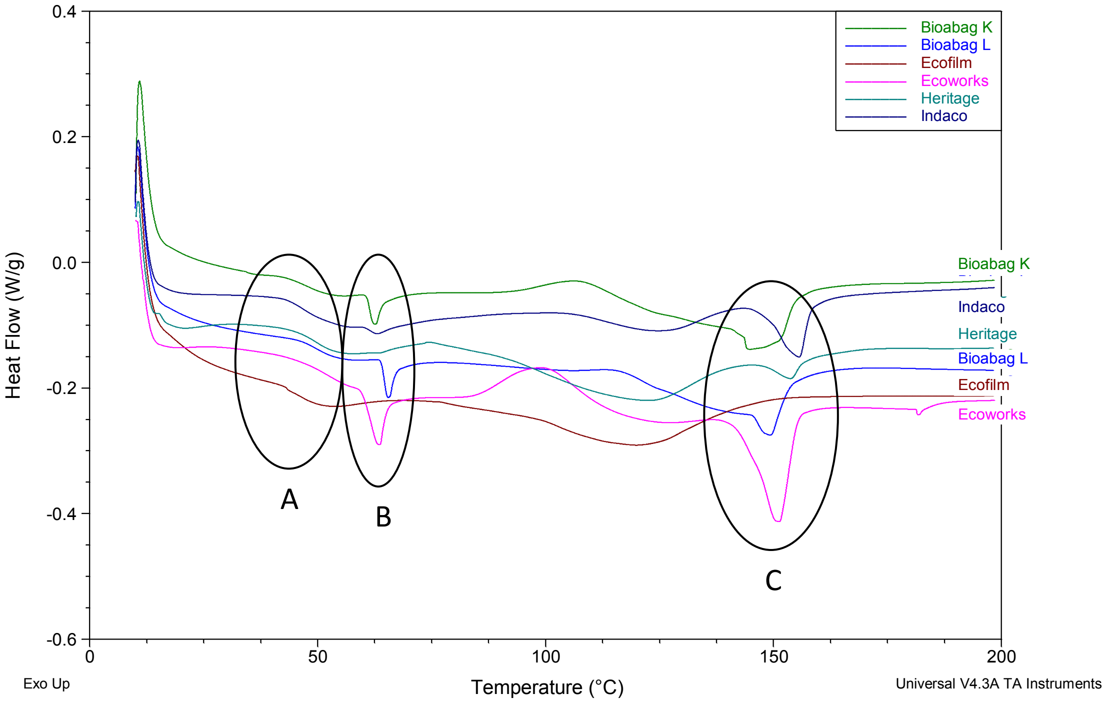


Figure 19) Results of 1st DSC heating cycle for all materials; (A) The glass transition areas during the initial heating cycle are easily identifiable due to the sharp change in slope of the curve; (B, C) The melt points of the material can be identified by deep valley-like shapes along the curve

Figure 19 shows the initial heating cycle for all materials. Each valley-like feature represents an endothermic reaction correlating to a phase change in the material. There are variations and similarities between each polymer. The melting temperature of neat PLA, as described by Lim et Al., ranges between 150 and 200 °C [17]. All materials show phase changes at similar temperatures; however, the amount of energy required to melt each sample and the number of melting points vary from material to material. For example, EcoWorks 45, Biobag L, and Biobag K experienced two melting points during the first heating cycle. The fact that these materials display multiple melting curves in the first heating cycle may indicate that the material underwent some pre-processing before its final production steps.

The glass transition (T_g) temperature for virgin PLA ranges from 50 to 70 °C [17,43,44]. This is consistent with the observed data for the 2nd and 3rd heating cycles. All materials displayed a glass transition near this point, as detailed in "A" of Figure 19. Some of the materials had an initial T_g at slightly lower temperatures than that reported by Das [44] (Table 16); however, the difference is minimal.

By measuring the melting enthalpies of each material it is possible to calculate the degree of crystallinity (W_c) for each material by using Eq. 4. Where ΔH_m^0 is the enthalpy of PLA (91 J/g) and ΔH_m is the melting enthalpy observed during the DSC testing [46].

$$w_c = \frac{\Delta H_m}{\Delta H_m^0}$$

Eq. 4

Table 16) ISU results of DSC testing of PLA films, glass transition

	Tg (°C)		
Material	1st cycle	2nd cycle	3rd cycle
Biobag K	47.88	57.29	55.36
Biobag L	49.53	60.9	61.73
Ecofilm	43.23	50.74	57.69
Ecoworks	52.23	57.55	57.37
Heritage	49.53	57.65	54.88
Indaco	46.68	60.87	61.83

Table 17) Melt enthalpy and degree of crystallinity for PLA films

Material		1st cycle	2nd cycle	3rd cycle
Biobag K	ΔH (J/g)	6.55	5.25	5.79
	Wc	7.2%	5.8%	6.4%
Biobag L	ΔH (J/g)	12.53	7.13	6.69
	Wc	13.8%	7.8%	7.3%
Ecofilm	ΔH (J/g)	11.12	12.03	11.13
	Wc	12.2%	13.2%	12.2%
Ecoworks	ΔH (J/g)	7.97	12.46	11.34
	Wc	8.8%	13.7%	12.5%
Heritage	ΔH (J/g)	11.55	1.09	1.23
	Wc	12.7%	1.2%	1.4%
Indaco	ΔH (J/g)	3.70	5.02	5.19
	Wc	4.1%	5.5%	5.7%

The melting enthalpy and degree of crystallinity for each material after each heating cycle is detailed in Table 17**.** As the materials undergo the DSC heating cycles, most materials seem to lose crystallinity after the quenching process (Biobag K, Biobag L, and Heritage). In EcoWorks 45 and Indaco materials the crystallinity increased, while in Ecofilm material it stayed relatively constant throughout testing. This is expected because quenching during the cooling prevents crystallization. It is seen that the Biobag L, Ecofilm, and Heritage had the highest level of crystallinity as received.

After the heating cycles, the samples were quenched with liquid nitrogen. Each material appears to have gone through an exothermic reaction. But as the cooling process was performed manually, data was not taken during this step of the process.

In a closer examination of the heating portion of the second cycle, the materials produced a different curve than the initial heating cycle in Figure 19. There are no melting points at the lower temperatures and the glass transition temperatures have been depressed slightly.

The third and final heating cycle of the DSC yielded curves more similar to the second heating cycle than to the initial heating cycle. Again, the melting points that appeared in the initial heating cycle, Figure 19(B), are absent, while the melting temperatures that occurred at the higher range of the test are still present. This would indicate that there are no other phases that may have been induced because of the films' processing history.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed in order to determine the organic and inorganic composition of the films as well as degradation temperatures. Figure 20 displays several points where the material degrades. In order to accurately determine these degradation points, a derivative (%/C) of the TGA curve as a function of temperature with respect to the percent of weight loss is seen in Figure 20 to determine the onset, ending, and percentage of material degradation. The points of inflection on the derivative curve pinpoint the onset and ending of each degradation point.

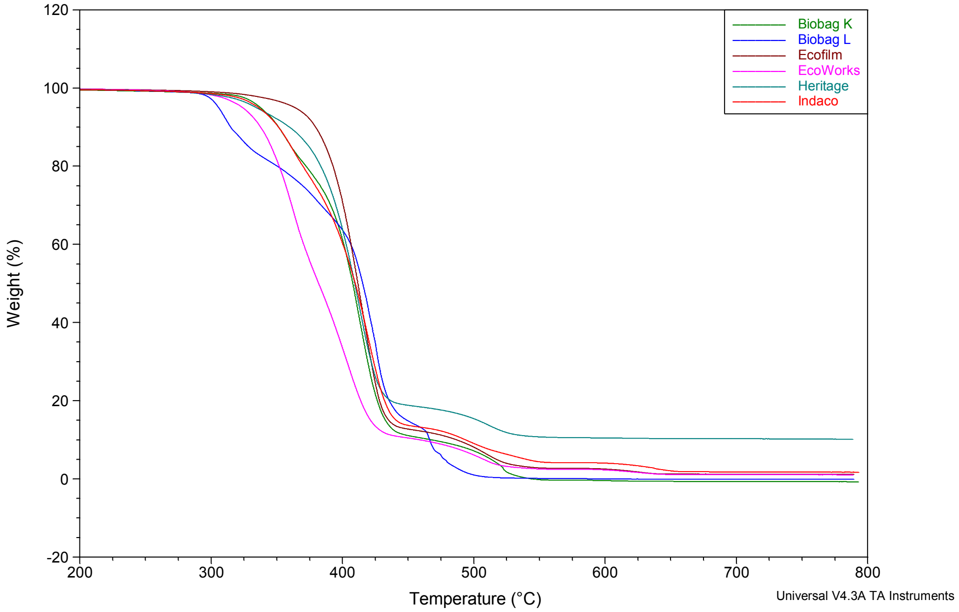


Figure 20) TGA characterization of commercially available PLA films; weight loss (%) vs. temperature (°C)

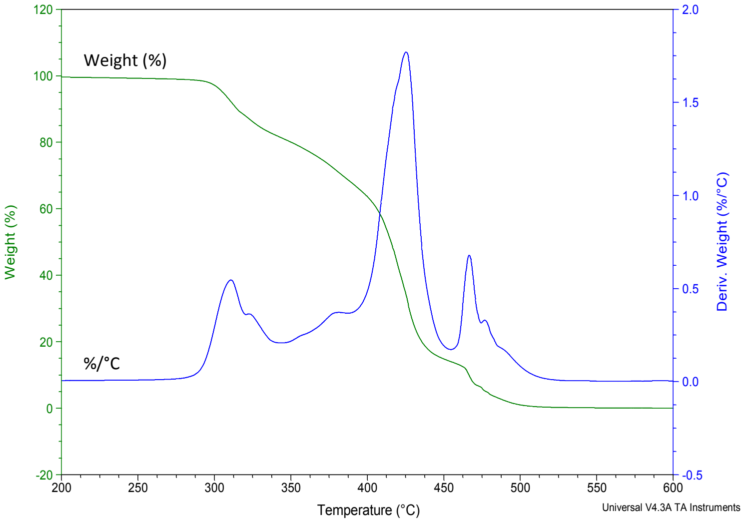
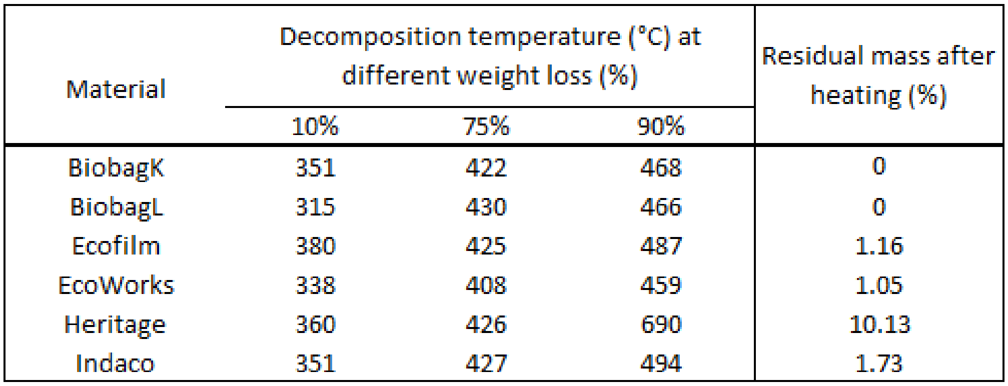


Figure 21) TGA characterization of commercially available PLA films temperature (°C) as a function of weight loss (%) compared to derivative of weight

All curves reveal relatively substantial material degradation between 300 °C and 450 °C, as seen in Table 18. This is in contrast to the reported degradation temperature of PLA by Yussuf [45].Degradation of neat PLA was reported as 10 % degradation occurring at a temperature of 327 °C and 75% degradation occurring at 360 °C. Any degradation points beyond 360 °C are considered to be non-cellulosic materials [45]. This suggests that the materials studied in this report where more thermally stable and may have had additives to promote thermal stability.

Table 18) Material degradation temperatures at given percentage of weight loss



Material	Decomposition temperature (°C) at different weight loss (%)			Residual mass after heating (%)
	10%	75%	90%	
BiobagK	351	422	468	0
BiobagL	315	430	466	0
Ecofilm	380	425	487	1.16
EcoWorks	338	408	459	1.05
Heritage	360	426	690	10.13
Indaco	351	427	494	1.73

After each sample was heated to 800 °C, some of the films had a residual amount of mass remaining, indicating inorganic components. It is seen that the highest amounts of inorganic components are found in the Heritage and Indaco films. These are the two films that had the highest strain at failure and tear resistance properties, suggesting that they contained an inorganic or thermally stable organic plasticizer. Yussuf added Kenaf and rice husks to PLA fibers and produced similar TGA plots [45]. Similar results were also observed when electro spun PLA fibers mixed with clay nanocomposites underwent similar TGA testing [46]. A PLA-flax seed composite was prepared with other compounds, including benzilic acid, mandelic acid, zein, and dicumyl peroxide; these composites also displayed similar TGA plots [47]. A study of the effect of wood flour, talc, and silane composites with PLA also revealed similar TGA results [48].

Chapter 8. Results and Conclusion

The results of tensile testing are shown in Table 20. Overall, the tensile strength was observed to be higher when tested in the parallel direction to the machine direction, which is consistent with molecular alignment. The materials with the highest tensile strength in the parallel direction were: Indaco *2009* (55.0 MPa), Indaco *2009 +1 year* (32.3 MPa) and Heritage *2010* (37.3 MPa). The materials with the highest tensile strength in the perpendicular direction were: Indaco *2009* (41.3 MPa), EcoWorks 45 *2009 +1 year* (28.3 MPa), and Indaco *2010* (25.7 MPa).

Overall, the elongation of the materials was observed to be higher when tested in the parallel direction to the machine direction. The materials with the highest elongation before failure in the parallel direction were: Ecofilm *2009* (544 %), Heritage *2009 +1 year* (1665 %), and Ecofilm *2010* (1665 %). The materials with the highest elongation before failure in the perpendicular direction were: Heritage *2009* (532 %), Indaco *2009 +1 year* (1217 %), and Ecofilm *2010* (878%).

The results of tear propagation test are shown in Table 13. Overall, the tear resistance was higher when tested in the parallel direction to the machine direction. The materials that had the highest tear resistance in the parallel direction were: Heritage *2009* (3.63 N), Heritage *2009 +1 year* (3.72 N), and Heritage *2010* (3.61 N). The materials with the highest tear resistance in the perpendicular direction were: Heritage *2009* (5.12 N), Heritage *2009 +1 year* (5.13 N), and Biobag L *2010* (5.52 N).

The results of the dart drop impact test are shown in Table 22. The materials that were able to absorb the most energy before failure were: Heritage *2009* (1.97 J), Heritage *2009 +1 year* (1.91 J), and Heritage *2010* (2.22 J).

The results of mechanical testing suggest that there is generally a significant difference between the *2009* materials and the *2009+1 year, 2010* materials in the tested properties of: ultimate tensile strength, strain at break, resistance to tearing, and impact resistance. These properties were tested at various stages of the materials' life and between periods of manufacturing.

As these biodegradable films age, the materials tend to become more brittle and lose the ability to withstand both shear and tensile stresses. This is consistent with what Lunt observed in neat PLA [31]. The comparison of the new materials to the same materials after ageing for one year showed a general trend of declining tensile strength.

The mechanical properties of materials that were tested at Iowa State were shown to be significantly different than the material properties that were reported in the Cortec Corp. report [26]. Despite these findings, it is difficult to draw an equal comparison between the values reported by the Cortec Corp. in 2006 and the results that were observed by the testing completed by Iowa State University over the past 2 years. The materials that were tested at ISU were produced in 2009 and 2010. There were significant increases in property values for all materials when comparing the Cortec Corp. and the 2009, 2010 materials. This difference in manufacturing dates makes a direct comparison between the two difficult. By taking the results as a timeline it is possible to view the history and development of the materials and how the bags have evolved over that short period of time. For example, the Indaco material's impact resistance has increased from 0.96 J in 2006 to 1.50 J in 2009, and 1.82 J in 2010.

Differential scanning calorimetry showed that there was preprocessing induced morphologies in some materials. This was evident by the multiple phase changes in the first heating cycle during testing. These phase changes were not seen in subsequent heating cycles and appeared to be in agreement with literature that states that unprocessed/virgin PLA has a glass transition temperature of approximately 51 °C and a melting temperature of approximately 150 °C.

The thermogravimetric analysis revealed that some of the materials contained inorganic materials (evidence was the residue remaining after the samples were heated to 800 °C). It is unclear what exactly these additive compounds are without further testing.

Table 19 contains the data of the highest and lowest performers observed during the testing of the materials acquired during 2010. Overall, Heritage brand was the top performer in 3 categories: tensile strength (parallel), tear resistance (parallel), and puncture resistance.

Overall, the results of the ISU study showed higher mechanical properties compared to the Cortec report. This is consistent with the observed trend in the 2009 and 2010 materials.

Table 19) Tabulated results for materials (2010)

		Highest	Lowest
Tensile strength (parallel)	MPa	Heritage 33.65	Biobag K 11.24
Tensile strength (perpendicular)	MPa	Indaco 25.72	Biobag K 8.54
Elongation (parallel)	%	Ecofilm 1665.1%	Indaco 10.0%
Elongation (perpendicular)	%	Ecofilm 877.6%	Biobag L 47.2%
Tear resistance (parallel)	N	Heritage 3.61	EcoWorks 45 0.25
Tear reistance (perpendicular)	N	Biobag L 5.52	EcoWorks 45, Indaco 0.46
Puncture reisistance	J	Heritage 2.22	EcoWorks 45 0.28
Wc (1st cycle)	%	Biobag L 13.8	Indaco 4.1
Non-Organic Residue	%	Heritage 10.13	Biobag L, Biobag K 0.00

Appendix: Raw Data

The following are selected results obtained from testing:

ASTM D882: Tensile Testing

Table 20 contains the results obtained from the tensile testing performed on all materials and in all conditions. The tensile strength of the Indaco and Heritage films tended to outperform the other materials. The materials that displayed the best elongation properties were the Ecofilm and Heritage brands.

Table 20) ASTM D882: Tensile testing results

Tensile Test (ASTM D 882)			2009				2009 +1year				2010			
Material	Thickness (mm)	Direction	Ultimate Tensile Strength (MPa)	SD	Elongation at Break (%)	SD	Ultimate Tensile Strength (MPa)	SD	Elongation at Break (%)	SD	Ultimate Tensile Strength (MPa)	SD	Elongation at Break (%)	SD
Biobag L	0.02	Parallel	21.21	1.72	281.8%	26.3%	14.12	0.65	59.4%	15.6%	12.21	0.46	54.1%	9.0%
		Perpendicular	13.67	0.42	257.6%	20.7%	13.57	1.19	40.1%	3.1%	11.52	0.90	47.2%	6.7%
Biobag K	0.015	Parallel	25.92	2.31	462.3%	46.2%	29.73	1.70	474.8%	47.1%	11.24	0.59	598.2%	73.4%
		Perpendicular	20.89	7.42	172.3%	33.7%	8.23	2.06	107.8%	39.9%	8.54	0.82	686.4%	42.3%
EcoFilm	0.02	Parallel	16.76	1.93	544.1%	76.8%	15.01	1.01	1327.8%	132.8%	31.47	3.58	1665.1%	6.8%
		Perpendicular	16.69	1.87	395.8%	56.3%	10.00	0.73	72.1%	15.2%	20.72	3.24	877.6%	186.8%
EcoWorks 45	0.02	Parallel	32.36	6.61	236.0%	44.8%	12.70	0.31	84.0%	24.7%	33.65	2.44	17.7%	8.7%
		Perpendicular	13.91	1.11	100.7%	31.8%	28.30	1.09	33.9%	9.0%	17.03	0.93	137.1%	47.0%
Heritage	0.03	Parallel	57.08	9.39	753.2%	65.4%	13.17	0.82	1665.3%	5.0%	37.29	3.07	1594.5%	48.8%
		Perpendicular	32.07	3.69	531.6%	91.6%	10.79	0.12	1216.5%	101.1%	20.59	0.25	662.8%	99.7%
Indaco	0.03	Parallel	55.01	2.47	241.3%	16.9%	32.32	2.52	303.8%	370.7%	34.74	1.47	10.0%	0.6%
		Perpendicular	41.34	5.41	400.1%	67.5%	21.03	0.99	432.7%	105.5%	25.72	4.96	486.6%	141.9%

ASTM D1922: Tear Propagation Resistance Test

Table 21 contains the results obtained from the tear propagation testing performed on all materials and in all populations. The Heritage brand was the top performer in both the parallel and perpendicular testing directions.

Table 21) Tear propagation resistance (ASTM D1922) data

Tear propagation resistance test (ASTM D1922)		2009		2009+1year		2010	
Material	Direction	Resistive force (N)	SD	Resistive force (N)	SD	Resistive force (N)	SD
Biobag L	Parallel	0.96	0.40	0.19	0.12	2.73	0.58
	Perpendicular	4.55	0.51	1.10	0.60	5.52	0.39
Biobag K	Parallel	2.86	0.52	1.07	0.37	0.86	0.16
	Perpendicular	2.42	0.63	2.51	0.12	4.03	0.55
Ecofilm	Parallel	0.52	0.07	1.11	0.37	0.69	0.15
	Perpendicular	2.53	0.23	1.76	0.14	2.24	0.14
EcoWorks 45	Parallel	0.09	0.04	0.19	0.04	0.25	0.10
	Perpendicular	0.52	0.12	0.85	0.17	0.46	0.12
Heritage	Parallel	3.63	0.24	3.72	0.66	3.61	0.51
	Perpendicular	5.12	0.45	5.13	0.49	5.09	0.43
Indaco	Parallel	0.36	0.12	0.38	0.07	0.41	0.10
	Perpendicular	0.52	0.04	0.49	0.07	0.46	0.07

ASTM D4272: Dart Drop Impact Resistance Test

Table 22 contains the results obtained from dart drop impact resistance testing performed on all materials in all populations. The Heritage and Indaco brands exhibited better resistance values during the impact resistance testing.

Table 22) ASTM D4272 dart drop impact resistance testing results

Dart drop impact resistance test (ASTM D4272)	Energy absorption before failure (J)		
	2009	2009+1 year	2010
Biobag L	0.26	0.24	0.73
Biobag K	0.45	0.43	0.52
Ecofilm	0.32	0.33	0.67
EcoWorks 45	0.49	0.29	0.28
Heritage	1.97	1.91	2.22
Indaco	1.50	1.87	1.82

Differential Scanning Calorimetry (DSC)

Table 23 contains the glass transition temperatures for all 3 heating cycles obtained from the DSC testing.

Table 24 contains the melt enthalpies observed during the DSC testing and the degree of melting crystallinity for each material during each cycle.

Table 23) DSC results: Glass transition temperatures (T_g) for all materials, all cycles

	Tg (°C)		
Material	1st cycle	2nd cycle	3rd cycle
Biobag K	47.88	57.29	55.36
Biobag L	49.53	60.9	61.73
Ecofilm	43.23	50.74	57.69
Ecoworks	52.23	57.55	57.37
Heritage	49.53	57.65	54.88
Indaco	46.68	60.87	61.83

Table 24) Melt Enthalpy and Degree of Crystallinity

Material		1st cycle	2nd cycle	3rd cycle
Biobag K	ΔH (J/g)	6.55	5.25	5.79
	Wc	7.2%	5.8%	6.4%
Biobag L	ΔH (J/g)	12.53	7.13	6.69
	Wc	13.8%	7.8%	7.3%
Ecofilm	ΔH (J/g)	11.12	12.03	11.13
	Wc	12.2%	13.2%	12.2%
Ecoworks	ΔH (J/g)	7.97	12.46	11.34
	Wc	8.8%	13.7%	12.5%
Heritage	ΔH (J/g)	11.55	1.09	1.23
	Wc	12.7%	1.2%	1.4%
Indaco	ΔH (J/g)	3.70	5.02	5.19
	Wc	4.1%	5.5%	5.7%

Thermogravimetric Analysis (TGA)

The degradation temperatures (°C), the amount of mass lost (%) and the percentage of mass that remained after heating is detailed in Table 25. The temperature at which each material degraded to what extent as well as the residual material that remained after heating is detailed in Table 26.

Table 25) TGA characterization of degradation temperatures at certain weight loss points

Material	Decomposition temperature (°C) at different weight loss (%)			Residual mass after heating (%)
	10%	75%	90%	
BiobagK	351	422	468	0
BiobagL	315	430	466	0
Ecofilm	380	425	487	1.16
EcoWorks	338	408	459	1.05
Heritage	360	426	690	10.13
Indaco	351	427	494	1.73

Table 26) TGA results

Material	Degradation points	Onset (°C)	Mass Drop (mg/mg)	Mass Drop (%)	Mass Drop (mg)	End (°C)
Biobag L	1st	298.76	0.1785	17.85%	1.393	321.04
	2nd	407.51	0.6766	67.66%	5.28	433.25
	3rd	463.52	0.07772	7.77%	0.6064	469.07
	4th	480.39	0.06081	6.08%	0.4745	498.42
	Residual	Mass (mg)		Percent by weight		
		0.0497		0.64%		
Biobag K	1st	335.74	0.1861	18.61%	1.203	361.03
	2nd	397.61	0.6983	69.83%	4.515	428.63
	3rd	509.43	0.1118	11.18%	0.7229	529.67
	Residual	Mass (mg)		Percent by weight		
		0.0246		0.38%		
Ecofilm	1st	387.7	0.8721	87.21%	5.793	428.87
	2nd	486.82	0.09842	9.84%	0.6537	528.15
	3rd	601.82	0.01476	1.48%	0.09801	637.92
	Residual	Mass (mg)		Percent by weight		
		0.0951		1.47%		
Ecoworks	1st	336.39	0.5075	50.75%	3.982	366.6
	2nd	393.18	0.3865	38.65%	3.033	420.83
	3rd	483.61	0.08124	8.12%	0.6375	523.35
	4th	600.07	0.01363	1.36%	0.107	642.12
	Residual	Mass (mg)		Percent by weight		
		0.0873		1.11%		
Heritage	1st	380.98	0.8112	81.12%	5.145	426.16
	2nd	491.07	0.08076	8.08%	0.5121	530.59
	Residual	Mass (mg)		Percent by weight		
		0.6852		10.80%		
Indaco	1st	338.7	0.2134	21.34%	1.419	364.79
	2nd	401.82	0.6441	64.41%	4.282	433.91
	3rd	479.18	0.09134	9.13%	0.6073	532.48
	4th	621.36	0.02293	2.29%	0.1525	647.28
	Residual	Mass (mg)		Percent by weight		
		0.1790		2.82%		

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