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(54) Title: LACTIC ACID POLYMER FILMS

(57) Abstract: A multilayer film comprises (a) two or more non-plasticized layers comprising lactic acid polymer and (b) one or more plasticized layers comprising lactic acid polymer and plasticizer sandwiched between the two or more lactic acid polymer layers; wherein the thickness of the one or more plasticized layers comprises from about 60% to about 70% of the total thickness of the multilayer film.

## LACTIC ACID POLYMER FILMS

### FIELD

5 This invention relates to lactic acid polymer films and articles made therefrom.

### BACKGROUND

Traditionally packaging and shipping materials have been made from films based on fossil  
feed stocks. In recent years, bio-plastics and degradable polymers have received increased  
10 attention. Packaging and shipping materials based upon bio-plastics typically suffer from weak  
film strength and other problems.

### SUMMARY

In view of the foregoing, we recognize that there is a need in the art for biodegradable  
15 films with high renewable content that are well suited for packaging and shipping applications.

The present invention provides films of plasticized and non-plasticized lactic acid polymer  
layers. The multilayer films are well suited for packaging and shipping applications such as, for  
example, envelopes, gift bags, void fills, freezer paper, package filler papers, garbage bags and the  
like. The films are biodegradable and may also exhibit properties such as, for example, rigidity,  
20 flexibility, water resistance, transparency, tear resistance, puncture resistance, paper feel,  
writability/printability and/or softness depending upon the desired packaging or shipping  
application.

Briefly, in one aspect, the present invention provides a multilayer film comprising (a) two  
or more non-plasticized layers comprising lactic acid polymer, and (b) one or more plasticized  
25 layers comprising lactic acid polymer and plasticizer sandwiched between the two or more lactic  
acid polymer layers; wherein the thickness of the one or more plasticized layers comprises from  
about 60% to about 70% of the total thickness of the multilayer film.

In another aspect, the present invention provides A multilayer film comprising (a) two or  
more non-plasticized layers comprising lactic acid polymer, and (b) one or more plasticized layers  
30 comprising lactic acid polymer and plasticizer sandwiched between the two or more lactic acid  
polymer layers; wherein the one or more plasticized layers comprises from about 22.5 wt. % to  
about 25 wt. % plasticizer.

In yet another aspect, the present invention provides multilayer film comprising (a) one or  
more non-plasticized layers comprising lactic acid polymer and starch, and (b) one or more  
35 plasticized layers comprising lactic acid polymer and plasticizer.

In still another aspect, the present invention provides void fill articles comprising a bent multilayer film comprising (a) two or more non-plasticized layers comprising lactic acid polymer, and (b) one or more plasticized layers comprising lactic acid polymer and plasticizer sandwiched between the two or more lactic acid polymer layers.

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## DETAILED DESCRIPTION

The multilayer films of the invention comprise plasticized and non-plasticized lactic acid polymer layers. As used herein, "lactic acid polymers" are any polymers that primary building unit (i.e., monomer) is lactic acid. Useful polylactide (PLA) polymers include, for example, PLA NatureWorks™ 4032D and PLA 4060D. In some embodiments, the lactic acid polymers have a weight-average molecular weight of about 110,000 g/mol to about 250,000 g/mol or about 150,000 g/mol to about 180,000 g/mol.

In some bi-layer embodiments of the invention, one layer might be mostly crystalline while the other layer might be mostly amorphous. In some tri-layer embodiments of the invention, a mostly crystalline layer might be sandwiched between two mostly amorphous layers.

In some bi-layer embodiments of the invention, one layer might comprise plasticizer ("plasticized layer") while the other layer does not comprise plasticizer or comprises very little plasticizer ("non-plasticized layer") such as, for example, less than about 2 wt. %. In some tri-layer embodiments of the invention, a plasticized layer might be sandwiched between two non-plasticized layers. Other multi-layer constructions are also possible. Preferably, one or more plasticized layers are sandwiched between non-plasticized layers.

Plasticized layers can, for example, provide desirable properties such as increased flexibility and puncture and tear resistance. Any useful plasticizer can be used. Preferably, bio-based plasticizer are utilized. As used herein, the term "bio-based" means based in whole or in significant part of renewable materials. Examples of useful bio-based plasticizers include SGP9300D plasticizer from Segetis (Golden Valley, MN) and Citroflex™ A-4 (acetyl tributyl citrate) plasticizer from Vertellus Specialties (Indianapolis, IN). In some embodiments, plasticized layers comprise from about 22.5 wt.% to about 30 wt.% plasticizer, from about 23 wt.% to about 25% plasticizer, or from about 24 wt.% to about 25 wt.%. It has been discovered that at up to about 25 wt. % plasticizer, there is little migration of the plasticizer into other layers.

In some tri-layer embodiments of the invention, the layer thickness ratio (i.e., non-plasticized layer thickness:plasticized layer thickness:non-plasticized layer thickness) is about 1:1:1 to about 1:4.5:1. The preferred layer thickness ratio will depend, however, on desired properties and end application of the film. If, for example, the film is to be used for envelopes or applications where flexibility is desirable, a layer thickness ratio of about 1:3:1 to about 1:4.5:1, or

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about 1:4:1, can be preferred. If, for example, the film is to be used for a gift bag, void fill article or other applications where some flexibility is needed for folding but rigidity is also needed to support weight, a layer thickness ratio of about 1:1:1 to about 1:3:1, or about 1:2:1, can be preferred.

5           In some embodiments of the invention wherein one or more plasticized layers are sandwiched between two or more lactic acid polymer layers, the thickness of the one or more plasticized layers comprises from about 30% to about 70% of the total thickness of the multilayer film. If, for example, the film is to be used for applications where flexibility is desirable, it can be preferred that the thickness of the one or more plasticized layers comprises from about 60% to  
10           about 70% of the total thickness of the multilayer film. If, for example, the film is to be used for applications where some flexibility is needed for folding but rigidity is also needed to support weight, it can be preferred that the thickness of the one or more plasticized layers comprises from about 30% to about 50% of the total thickness of the multilayer film.

15           In some embodiments, the multilayer films of the invention comprise only bio-based polymers. In some embodiments, the multilayer films of the invention are biodegradable and compostable. As used herein, "biodegradable" means that the films meet the requirements of ASTM D6400-12.

          The PLA multilayer films of the invention can be made transparent or with colorants or pigments such as carbon black, titanium dioxide or the like.

20           As mentioned above, PLA multilayer films of the invention can be used to make void fill articles. The PLA multilayer films of the invention can be bent or folded into a desired three dimensional shape to provide void fill in shipping boxes. Void fill articles made from the multilayer films of the invention can provide several advantages over traditional void fill materials. For example, void fill articles of the invention are biodegradable and water-resistant. They can also  
25           be transparent so that the item packed in the box is visible within through the void fill. As used herein, "transparent" means that the multilayer film allows light to pass through so that objects behind can be distinctly seen.

          If a PLA multilayer film with a paper-like look and feel is desired, starch can be added to non-plasticized outer layers. The starch also helps with adhesion to tape and writability/printing.  
30           One application in which these properties are desirable is freezer paper. In some embodiments, one or both outer layers of the film comprises from about 5 wt.% to about 20 wt.% starch based upon the total weight of the layer. Examples of suitable starches include native starches, reclaimed starches, waxy starches, modified starches, pre-gelatinized starches, or combinations thereof. Modified starches can include acid-treated starch, alkaline-treated starch, bleached starch, oxidized  
35           starch, enzyme-treated starch, monostarch phosphate, distarch phosphate, phosphated distarch

phosphate, acetylated distarch phosphate, starch acetate, acetylated distarch adipate, dextrin, cyclodextrin, hydroxypropyl starch, hydroxypropyl 15 distarch phosphate, hydroxypropyl distarch glycerol, starch sodium octenyl succinate, acetylated oxidized starch, and combinations thereof.

5 **EXAMPLES**

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

10 In the following examples, the samples are identified by the thickness of the film and the intended application, where 1 mil equals one thousandth of an inch, or 25.4 micrometers.

**OVERVIEW OF EXAMPLES**

<b>Example number</b>	<b>Description</b>	<b>Line speed, feet/minute (fpm)</b>	<b>Layer thickness ratio</b>	<b>Die or feedblock (FB)</b>
1	2 mil envelope	101	[1:4:1]	3 layer die
2A	4 mil gift bag	112	[1:2:1]	single layer die/FB
2B	5 mil gift bag	90	[1:2:1]	single layer die/FB
3A	8 mil void fill film	56	[1:2:1]	single layer die/FB
3B	10 mil void fill film	43	[1:2:1]	single layer die/FB
4	5 mil freezer paper	13.5	[1:2:1]	single layer die/T FB
Comparative of 4	5 mil PLA-4032 (3-layer)	13.5	[1:2:1]	single layer die/T FB

## MATERIALS USED

Materials	Trade Designation	Generic description	Supplier	Supplier Headquarters	Layer used
PLA-4032	Ingeo Bioplastics 4032D	Biodegradable polylactic acid resin	NatureWorks	Minnetonka, MN	MIDDLE AND SKIN LAYER, EX. 1-3B
PLA-4060	Ingeo Bioplastics 4060D	Biodegradable polylactic acid resin	NatureWorks	Minnetonka, MN	MIDDLE, EX. 1, MIDDLE AND SKIN LAYER, EX. 4
White Master Batch, PLA-4032/TiO <sub>2</sub> (60/40)	PLA WHITE MASTERBATCH	Biodegradable polylactic acid resin compounded with Titanium Dioxide pigment	Clariant	Minneapolis, MN	MIDDLE AND SKIN LAYER, EX. 1
Black Master Batch, PLA-4032/CARBON BLACK(85/15)	PLA BLACK MASTERBATCH	Biodegradable polylactic acid resin compounded with carbon black pigment	Clariant	Minneapolis, MN	SKIN LAYER, EX. 1
Modified starch	SR-088	Starch	Glycan BioTechnology Co.	Taoyuan, Taiwan	SKIN LAYER, EX. 4
Citroflex A4	Citroflex® A-4 Plasticizer	Bio-based plasticizer	Vertellus	Indianapolis, IN	MIDDLE LAYER, EX. 1, 4
Segetis	SGP9300D	Bio-based plasticizer	Segetis Inc.	Golden Valley, MN	MIDDLE LAYER, EX. 2A, 2B, 3A, 3B

Symmetric (ABA) or asymmetric (ABC) 3-layer films were produced by the processes described below, using the compositions for the outer skin (A) layer, core (B) layer, and inner skin (A or C) layer compositions listed in Table A.

5

Table A

Example	Description	Outer Skin				Core					Inner Skin					Caliper, mils	Layer ratio
		% PLA-4032	% PLA-4060	% White Master Batch	Modified starch	% PLA 4032	% PLA 4060	% Citroflex A4	% Segetis	% White Master Batch	% PLA-4032	% PLA-4060	% White Master Batch	% Black Master Batch	% Mod Starch		
1	2 mil envelope	75	0	25	0	37	28	25	0	10	84	0	12	4	0	2	[1:4:1]
2A	4 mil gift bag	100	0	0	0	75	0	0	25	0	100	0	0	0	0	4	[1:2:1]
2B	5 mil gift bag	100	0	0	0	75	0	0	25	0	100	0	0	0	0	5	[1:2:1]
3A	8 mil void fill	100	0	0	0	75	0	0	25	0	100	0	0	0	0	8	[1:2:1]
3B	10 mil void fill	100	0	0	0	75	0	0	25	0	100	0	0	0	0	10	[1:2:1]
4	5 mil freezer paper	0	70	0	30	0	80	20	0	0	0	70	0	0	30	5	[1:2:1]
	Comparative Example	100	0	0	0	100	0	0	0	0	100	0	0	0	0	5	[1:2:1]

Example 1

Samples for the 3-layer film (ABC) described in Example 1 were prepared by compounding the desired ingredients in the ratios described in Table A using three extruders: a 50 mm co-rotating twin screw extruder (Coperion, Weingarten, Germany) feeding layer “B”; a 40 mm co-rotating twin screw extruder (Coperion, Weingarten, Germany) feeding layer “A” and a 40 mm co-rotating twin screw extruder (Coperion, Weingarten, Germany) feeding layer “C”. The plasticizer was injected into zone 3 of the 50 mm co-rotating twin screw using a DynaMelt™ SR2027GD2 (ITW DynaTech, Hendersonville, TN). The layers of the final film construction were formed in a multi-manifold die similar to the ones described in co-owned U.S. patent applications 2011/0272849, FEEDBLOCK FOR MANUFACTURING MULTILAYER POLYMERIC FILMS and 2011/0272832, APPARATUS FOR MANUFACTURING MULTILAYER POLYMERIC FILMS, herein incorporated by reference. Each material entered the die through independent inlets and feed flow channels that were specific to that material. These channels form a conduit between the inlet and a layer spreading manifold. Each manifold spreads its particular material to the full width of the die. The downstream section of each manifold feeds a slot-like channel. The geometry of the manifold and slot section substantially contribute to the cross web uniformity of each layer. For the 3 layer system, there were 3 slots that conveyed the independent streams to a point of confluence where the layers were combined. The combined streams formed a layer structure in

which each layer was generally parallel with a plane running across the width of the die. This combined layer structure was then fed through a common channel that runs across the full width of the die and extends to the exit of the die. This common channel typically varies in height, with the channel being larger at the point of confluence and narrowing as it gets nearer to the die exit.

5 Examples 2A, 2B, 3A, and 3B

Samples for the 3-layer film (ABA) described in Example 2A, 2B, 3A, and 3B were prepared by compounding the desired ingredients in the ratios described in Table A using three extruders: a 58 mm co-rotating twin screw extruder (Davis Standard, Pawcatuck, CT) feeding layer "B"; a 2.5 inch (6.35 cm) single screw extruder (Davis Standard, Pawcatuck, CT) feeding layer "A" and another 2.5 inch single screw extruder (Davis Standard, Pawcatuck, CT) feeding layer "C", which was a duplicate of layer "A". The plasticizer was injected into zone 3 of the 58 mm co-rotating twin screw using a DynaMelt M 35 series (ITW DynaTech, Hendersonville, TN). The 3-layer film production processes for Examples 2, 3, & 4 were similar to the process for Example 1, except that the layers were combined in a feedblock and then spread as a unit to the full width in a single manifold die.

15 Example 4

Samples for the 3-layer film (ABA) described in Example 4 were prepared by compounding the desired ingredients in the ratios described in Table A using two extruders: a 25 mm co-rotating Berstoff Twin screw extruder (KraussMaffei Technologies GmbH, Munich, Germany) feeding layer "A" and a 27 mm co-rotating Leistritz Twin screw extruder (LEISTRITZ AG, Nuremberg, Germany) feeding layer "B". The plasticizer was injected into zone 3 of the 27 mm co-rotating twin screw using a DynaMelt SR5N2ZES12-A (ITW DynaTech, Hendersonville, TN). The 3-layer film production processes for Example 4 was similar to the process for Example 1, except that the layers were combined in a feedblock and then spread as a unit to the full width in a single manifold die. The resulting three layer ABA film was cast onto an 8-inch wide casting wheel held at 80°F and running at 13.5 feet per minute (4.11 meters/minute).

25 Comparative Example

A comparative example of pure PLA-4032 was made in the exact manner as Example 4 except that pure PLA-4032 was fed to each of the two extruders. Extruder throughputs in the table below are expressed in pounds per hour (lb/hr), where 1 lb/hr equals 0.45 kg/hr.

**PROCESS CONDITIONS**

Example number	Description	Layer ratio	Outer skin throughput, lb/hr	Throughput, core, lb/hr	Inner skin throughput lb/hr	Outer skin melt temp, degrees F	Core Melt Temperature, degrees F	Inner skin, melt temperature degrees F	Die Temperature, degrees F	Line speed, fpm	Die or feed block(FB)
1	2 mil envelope	[1:4:1]	15	60	15	405	365	405	420	101	3 layer die
2A	4 mil gift bag	[1:2:1]	100	200	100	430	407	473	430	112	single layer die/FB
2B	5 mil gift bag	[1:2:1]	100	200	100	430	407	473	430	90	single layer die/FB
3A	8 mil void fill	[1:2:1]	100	200	100	430	407	473	430	56	single layer die/FB
3B	10 mil void fill	[1:2:1]	100	200	100	430	407	473	430	43	single layer die/FB
4	5 mil freezer paper	[1:2:1]	5	10	5	435	410	435	420	13.5	single layer die/T FB
	Comparative Example	[1:2:1]	5	10	5	435	410	435	420	13.5	single layer die/T FB

**TEST RESULTS**

Patent Example #	Test Methods (ASTM #):	ASTM D1922-09	ASTM D1922-09	ASTM D3763-14	ASTM D3763-14
	Nominal Caliper, mils	MD Elmendorf Tear, N	CW Elmendorf Tear, N	Impact by falling dart, energy dissipated, J	Impact by falling dart, peak force, N
1	2	7.9	14.1	0.5372	63.204
2A	4.5	2.8/6.1	3.1/6.6	0.19206	60.44
2B	5.3	2.7	5.1	N/A	N/A

	Test Methods (ASTM #):				
Patent Example #	ASTM E-252	ASTM D1922-09	ASTM D1922-09	ASTM D3763-14	ASTM D3763-14
	Nominal Caliper, mils	MD Elmendorf Tear, N	CW Elmendorf Tear, N	Impact by falling dart, energy dissipated, J	Impact by falling dart, peak force, N
3A	8	4.7/5.9	6.9/10.0	0.13883	120.92
3B	10	7.4	10.4	0.12343	163.45
4	5	2.1	2.2	0.16835	50.544
Comparative example	5	1.5	1.5	0.10395	41.6
PLA-4032	5	0.83	0.69		

The table above includes the results of two tests for Elmendorf Tear in both the machine direction (MD) and cross-web direction (CW) for Examples 2A and 3A. No samples of film 2B were available for falling dart testing (ASTM D3763-14.) Elmendorf Tear Strength values for a 5 mil (127 micrometer) thick PLA-4032 film are calculated from the following NatureWorks Ingio™ website data.

Elmendorf Tear Strength, MD 0.669 g/micron ASTM D1922

Elmendorf Tear Strength, TD 0.551 g/micron ASTM D1922

10 FALLING DART IMPACT TESTS, ASTM D3763-14

Impact puncture properties were measured for five film samples according to ASTM D3763-14. Both peak force and energy dissipated at peak force were evaluated. Example 1 exhibited the highest energy dissipation, while Example 3B exhibited the highest peak force. Example 3B also exhibited one of the lowest energy dissipations, indicating that more compliant systems may exhibit higher levels of toughness.

**Sample Description:**

Film rolls:

- Comparative Example
- Example 1
- Example 2A

- Example 3A
- Example 3B
- Example 4

5 **Data:**

**Table 1:** Summary of energy dissipated for each film sample.

Sample	N	Mean		95% CI	
		(J)	Std. Dev.		
Comparative	5	0.10395	0.0146	0.09025	0.11766
Example 1	5	0.5372	0.0264	0.5235	0.5509
Example 2A	5	0.19206	0.01766	0.17835	0.20576
Example 3A	5	0.13883	0.00295	0.12513	0.15254
Example 3B	5	0.12343	0.00343	0.10973	0.13714
Example 4	5	0.16835	0.00889	0.15465	0.18206

**Table 2:** ANOVA testing of energy dissipation data indicates that differences among the samples are statistically significant.

10

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Sample	5	0.664598	0.13292	602.69	0
Error	24	0.005293	0.000221		
Total	29	0.669891			

**Table 3:** Post hoc comparison of mean energy dissipation. Post hoc analysis was conducted using the Tukey-Kramer procedure. Samples which are statistically different do not share a grouping letter (e.g., A and AB would NOT be statistically different since they share the letter A).

Sample	N	Mean		Grouping
		(J)		
Example 1	5	0.5372		A
Example 2A	5	0.19206		B
Example 4	5	0.16835		B
Example 3A	5	0.13883		C
Example 3B	5	0.12343		C D
Comparative	5	0.10395		D

**Table 4:** Summary of peak force for each film sample.

Sample	N	Mean (N)	Std. Dev.	95% CI	
Comparative	5	41.63	3.24	37.34	45.92
Example 1	5	63.204	2.061	58.913	67.494
Example 2A	5	60.44	2.64	56.15	64.73
Example 3A	5	120.92	6.06	116.63	125.21
Example 3B	5	163.45	8.36	159.16	167.74
Example 4	5	50.544	1.118	46.253	54.834

**Table 5:** ANOVA testing of peak force data indicates that differences among the samples are statistically significant.

5

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Sample	5	57872	11574.4	535.67	0
Error	24	518.6	21.6		
Total	29	58390.6			

**Table 6:** Post hoc comparison of mean peak force. Post hoc analysis was conducted using the Tukey-Kramer procedure. Samples which are statistically different do not share a grouping letter (e.g., A and AB would NOT be statistically different since they share the letter A).

Sample	N	Mean (N)	Grouping
Example 3B	5	163.45	A
Example 3A	5	120.92	B
Example 1	5	63.204	C
Example 2A	5	60.44	C
Example 4	5	50.544	D
Comparative	5	41.63	D

10

**Explanation of Results:**

Impact puncture properties of the provided film samples were measured following the guidelines of ASTM D3763-14. The test describes a falling dart impact test, from which the peak impact force and the work done by the film on the impactor (a measure of how much impact energy the films absorbs) can be computed. The concept of the test is to impact the film with a sufficiently energetic mass that the impact does not significantly slow down the impactor (less than

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20% slow down). An impactor of 7.095 kg and an impact velocity of 200 m/min. were selected to meet this criteria.

Differences in impact energy dissipated were observed among the samples (Table 1), with Example 1 exhibiting the highest level of dissipation. Differences were statistically significant (Table 2), and differences between specific pairs of samples were also statistically significant (Table 3). A higher energy of dissipation indicates that the film can absorb more energy before failure. Failure was estimated as the point of maximum force.

The ability to absorb a higher level of energy does not indicate that the peak force due to an impact will be larger. Peak impact force is determined by a combination of impactor energy and the composite stiffness of the impactor and material tested. Higher peak loads may be due to a stiffer but less tough material. In such a circumstance, the maximum deformation would be lower, resulting in an overall lower amount of mechanical work done on the probe before failure. This phenomena was observed with the sample tested here.

Differences in peak force were observed among the samples (Table 4), with Example 3B yielding the largest peak force. These differences were statistically significant (Table 5), and differences between individual pairs of samples were also significant (Table 6). Example 3B was also tied for the lowest impact energy dissipation. Therefore, Example 3B is the strongest sample, but it is one of the least tough. Conversely, Example 1 is the toughest sample, but it only exhibits moderate strength in comparison to Example 3B.

Depending on the characteristics desired from the film, either metric of puncture resistance may be more desirable. The large impact strength is able to withstand larger loads; however, the elevated toughness is generally more resistant to puncture as any puncturing object would need to be pushed further into the film to cause tearing.

#### **Modification of Standard Test Method / Sample Preparation Method:**

Impact puncture properties were assessed following ASTM D3763-14. This technique describes a falling dart drop tower with a  $12.70 \pm 0.13$  mm hemispherical probe which strikes a film uniformly clamped over a  $76.0 \pm 3.0$  mm hole. The probe is instrumented with a load cell with a sufficiently high sampling rate and natural frequency to record the impact forces of the falling probe (see Table 7 for specific instrumentation).

**Table 7:** Specific instrumentation employed for testing.

<b>Component</b>	<b>Value</b>
Load Cell	Kistler 9212 charge mode piezoelectric
Charge Amplifier	Kistler 5010
Data Acquisition System	National Instruments 9234 & LabVIEW
Drop Tower	Instron Dynatup 8200
Impactor mass	7.095 kg
Target impact velocity	200 m/min.

From the force and mass of the falling probe, it is possible to compute the displacement of the film with time (procedure described in standard). The integral under the force-displacement  
5 curve is the work done by the film on the probe, which represents how much of the energy of the impact is absorbed by the film. According to the standard, the work should be computed at a specified point in the load history. For purposes of this work, the integral was taken from the first instance of loading up to the peak force. Integrals were computed using the trapezoidal method implement in Microsoft™ Excel.

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Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of  
15 example only with the scope of the invention intended to be limited only by the claims set forth herein as follows.

We claim:

- 5           1. A multilayer film comprising:  
          (a) two or more non-plasticized layers comprising lactic acid polymer; and  
          (b) one or more plasticized layers comprising lactic acid polymer and plasticizer  
sandwiched between the two or more lactic acid polymer layers;  
          wherein the thickness of the one or more plasticized layers comprises from about 60%  
to about 70% of the total thickness of the multilayer film.
- 10           2. The multilayer film of claim 1 wherein the thickness of the one or more plasticized  
layers comprises from about 65% to about 68% of the total thickness of the multilayer films.
3. The multilayer film of claim 1 wherein the plasticizer is a bio-based plasticizer.
- 15           4. The multilayer film of claim 1 wherein the multilayer film comprises only bio-based  
polymers.
5. The multilayer film of claim 1 wherein the multilayer film is biodegradable.
- 20           6. A multilayer film comprising:  
          (a) two or more non-plasticized layers comprising lactic acid polymer; and  
          (b) one or more plasticized layers comprising lactic acid polymer and plasticizer  
sandwiched between the two or more lactic acid polymer layers;  
          wherein the one or more plasticized layers comprises from about 22.5 wt. % to about  
25           25 wt. % plasticizer.
7. The multilayer film of claim 6 wherein the plasticizer is a bio-based plasticizer.
- 30           8. The multilayer film of claim 6 wherein the multilayer film comprises only bio-based  
polymers.
9. The multilayer film of claim 6 wherein the multilayer film is biodegradable.

10. A multilayer film comprising:

- (a) one or more non-plasticized layers comprising lactic acid polymer and starch; and
- (b) one or more plasticized layers comprising lactic acid polymer and plasticizer.

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11. The multilayer film of claim 10 wherein the one or more plasticized layers are sandwiched between two or more non-plasticized layers comprising lactic acid polymer and starch.

12. The multilayer film of claim 10 wherein the plasticizer is a bio-based plasticizer.

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13. The multilayer film of claim 10 wherein the multilayer film comprises only bio-based polymers.

14. The multilayer film of claim 10 wherein the multilayer film is biodegradable.

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15. A void fill article comprising a bent multilayer film comprising (a) two or more non-plasticized layers comprising lactic acid polymer and (b) one or more plasticized layers comprising lactic acid polymer and plasticizer sandwiched between the two or more lactic acid polymer layers.

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16. The void fill article of claim 15 wherein the thickness of the one or more plasticized layers comprises from about 30% to about 50% of the total thickness of the multilayer film.

17. The void fill article of claim 15 wherein the multilayer film is transparent.

18. The void fill article of claim 15 wherein the plasticizer is a bio-based plasticizer.

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19. The void fill article of claim 15 wherein the multilayer film comprises only bio-based polymers.

20. The void fill article of claim 15 wherein the multilayer film is biodegradable.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/054548

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(8) - B32B 27/36; B32B 27/06; B32B 37/14; C08F 2/00; C08K 5/00 (2016.01) CPC - B32B 27/36; B32B 27/06; B32B 37/14; C08F 2/00; C08K 5/00 (2016.11) According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC - B32B 27/06; B32B 27/36; B32B 37/14; C08F 2/00; C08K 5/00 CPC - B32B 27/06; B32B 27/36; B32B 37/14; C08F 2/00; C08K 5/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 156/60; 427/508; 428/217; 428/480; 524/81; IPC - B32B 27/06; B32B 27/36; B32B 37/14; C08F 2/00; C08K 5/00 CPC - B32B 27/06; B32B 27/36; B32B 37/14; C08F 2/00; C08K 5/00 (keyword delimited) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Orbit, Google Patents, Google Scholar Search terms used: multilayer film, lactic acid, plastic		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---	US 2010/0240833 A1 (SAKURAI) 23 September 2010 (23.09.2010) entire document	1, 2, 5
Y		3, 4, 6-9, 11, 15-20
X ---	US 2014/0162038 A1 (BIOVATION LLC) 12 June 2014 (12.06.2014) entire document	10, 12-14
Y		3, 4, 6-9, 11, 15-20
A	US 2011/0135912 A1 (XU) 09 June 2011 (09.06.2011) entire document	1-20
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 22 November 2016		Date of mailing of the international search report 15 DEC 2016
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300		Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774