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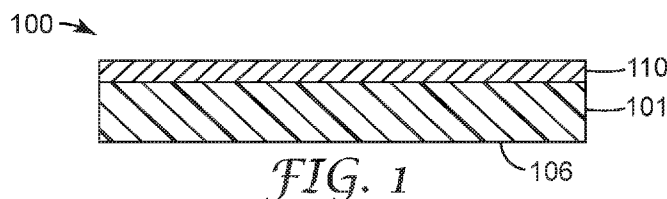
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(54) Title: FILM COMPRISING POLYLACTIC ACID POLYMER SUITABLE FOR GRAPHIC ARTICLES



(57) Abstract: An article is described comprising a first film layer comprising polylactic acid polymer (semicrystalline polylactic acid polymer; amorphous polylactic acid polymer; or a mixture thereof); a second (e.g. polyvinyl acetate) polymer having a Tg of at least 25°C; plasticizer. In some embodiment, the film layer further comprises inorganic pigment and/or hydrolysis stabilizer. In other embodiments, the film has a net melting endotherm, ΔH_{m1} , of less than 10 J/g. Also described are methods of making a graphic film.



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FILM COMPRISING POLYLACTIC ACID POLYMER SUITABLE FOR GRAPHIC ARTICLES

Background

5 WO2017/222824 describes graphic articles comprising semicrystalline polylactic acid based film.

Summary

10 In one embodiment, an article is described comprising a first film layer comprising polylactic acid polymer (e.g. semicrystalline polylactic acid polymer; amorphous polylactic acid polymer; or a mixture thereof); a second (e.g. polyvinyl acetate) polymer having a Tg of at least 25°C; plasticizer; and an inorganic pigment in an amount such that the ratio of polylactic acid polymer to inorganic pigment is less than 4.5:1, 4.4:1, 4.3:1, 4.2:1, or 4.1:1. In some embodiments, the inorganic pigment comprises TiO₂. The amount of inorganic pigment is typically at least 15, 16, 17, 18, 19, or 20 wt.% of the first film layer. In some embodiments, the ratio of polylactic acid polymer to inorganic pigment is at least 1:1. In some embodiments, the first film layer further comprises a hydrolysis stabilizer. In some embodiments, the article is a graphic film further comprising a graphic proximate a major surface of the film layer.

20 In another embodiment, an article is described comprising a film layer comprising semicrystalline polylactic acid polymer; optionally amorphous polylactic acid polymer; a second polymer having a Tg of at least 25°C; plasticizer; and one or more carbodiimide hydrolysis stabilizers. In some embodiments, the article is a graphic film further comprising a graphic proximate a major surface of the film layer. In typical embodiments, the graphic comprises a dried and/or cured ink layer. The ink layer is typically a dried and/or cured radiation cured ink, organic solvent-based ink, or water-based ink. In some embodiments, the film layer is a transparent cover film or backing film. In other embodiments, the film layer is a backing film further comprising inorganic pigment.

30 In other embodiments, articles are described comprising polylactic acid polymer (e.g. semicrystalline polylactic acid polymer; amorphous polylactic acid polymer; or a mixture thereof); a second (e.g. polyvinyl acetate) polymer having a Tg of at least 25°C; and plasticizer; wherein film has a net melting endotherm, ΔH_{nm1} , of less than 10 J/g. In

one embodiment, the (e.g. unannealed) first film layer comprises semicrystalline polylactic acid polymer; optionally amorphous polylactic acid polymer; and nucleating agent. In another embodiment, the first film layer comprises amorphous polylactic acid polymer and optionally semicrystalline polylactic acid polymer.

5 In another embodiment, a method of making a graphic film is described comprising providing a film comprising a first film layer as described herein; and providing a graphic on the film. The first film layer may be annealed or unannealed. In some embodiments, the first film layer has a net melting endotherm for the first heating scan, ΔH_{m1} , of less
10 than 10 J/g at the time of manufacture and/or printing.

Brief Description of the Drawings

FIGs. 1-8 are schematic cross-sections of various graphic films.

15 FIG. 9 is a representative DSC profile of a composition comprising a nucleating agent exhibiting a sharp crystallization peak exotherm during cooling.

FIG. 10 is a representative DSC profile of a composition without a nucleating agent that did not exhibit a crystallization peak exotherm during cooling.

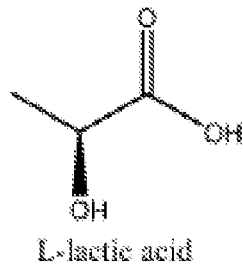
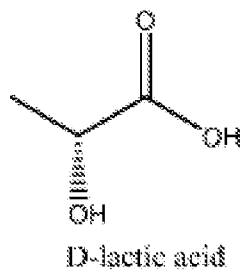
FIG. 11 depicts Dynamic Mechanical Analysis results of Example 12.

FIG. 12 depicts Dynamic Mechanical Analysis results of Example 16.

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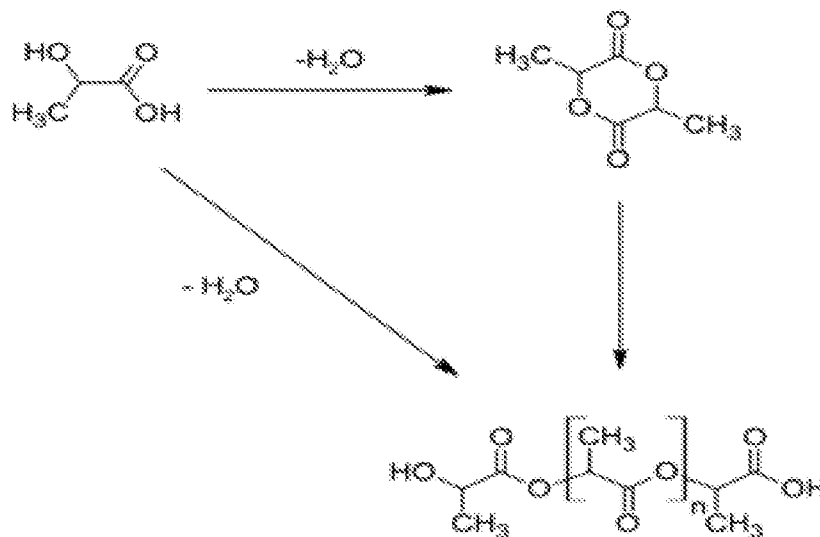
Detailed Description

The (e.g. graphic) articles described herein comprises at least one layer, i.e. a first film layer comprising a polylactic acid (“PLA”) polymer film. Lactic acid is a renewable material obtained by the bacterial fermentation of corn starch or cane sugar, and thus is
25 considered a natural or in otherwords “biomass” material. Lactic acid has two optical isomers: L-lactic acid (also known as (S)-lactic acid) and D-lactic acid (also known as (R)-lactic acid), depicted as follows:



Polyesterification of lactic acid affords polylactic acid polymer.

More typically, lactic acid is typically converted to the cyclic lactide monomer, and the lactide undergoes ring opening polymerization, such as depicted as follows:



5

The resulting polymer material is typically referred to as polylactide polymer.

The degree of crystallinity, and hence many important properties, is largely controlled by the ratio of D and/or meso-lactide to L cyclic lactide monomer used.

Likewise, for polymers prepared by direct polyesterification of lactic acid, the degree of crystallinity is largely controlled by the ratio of polymerized units derived from D -lactic acid to polymerized units derived from L-lactic acid.

10

In some embodiments, the first film layer of the (e.g. graphic) articles described herein generally comprise a semicrystalline PLA polymer alone or in combination with an amorphous PLA polymer.

In some embodiments, the semicrystalline PLA polymer typically comprises at least 90, 91, 92, 93, 94, or 95 wt.-% of polymerized units derived from L-lactic acid (e.g. L-lactide) and no greater than 10, 9, 8, 7, 6, or 5 wt.-% of polymerized units derived from D-lactic acid (e.g. D-lactide and/or meso-lactide). In yet other embodiments, the semicrystalline PLA polymer comprises at least 96 wt.-% of polymerized units derived from L-lactic acid (e.g. L-lactide) and less than 4, 3, or 2 wt.-% of polymerized units derived from D-lactic acid (e.g. D-lactide and/or meso-lactide). Likewise the film comprises an even lower concentration of polymerized units derived from D-lactic acid (e.g. D-lactide and/or meso-lactide) depending on the concentration of semicrystalline PLA polymer in the film. For example, if the film composition comprises 15 wt.-% of a semicrystalline PLA having about 2 wt.-% D-lactide and/or meso-lactide, the film composition comprises about 0.3 wt.-% D-lactide and/or meso-lactide. The film generally comprises no greater than 9, 8, 7, 6, 5, 4, 3, 2, 1.5, 1.0, 0.5, 0.4, 0.3, 0.2, or 0.1 wt.-% polymerized units derived from D-lactic acid (e.g. D-lactide and/or meso-lactide). Suitable examples of semicrystalline PLA include Natureworks™ Ingeo™ 4042D and 4032D. These polymers have been described in the literature as having molecular weight Mw of about 200,000 g/mole; Mn of about 100,000 g/mole; and a polydispersity of about 2.0.

Alternatively, the semicrystalline PLA polymer may comprises at least 90, 91, 92, 93, 94, or 95 wt.-% of polymerized units derived from D-lactic acid (e.g. D-lactide) and no greater than 10, 9, 8, 7, 6, or 5 wt.-% of polymerized units derived from L-lactic acid (e.g. L-lactide and/or meso-lactide). In yet other embodiments, the semicrystalline PLA polymer comprises at least 96 wt.-% of polymerized units derived from D-lactic acid (e.g. D-lactide) and less than 4, 3, or 2 wt.-% of polymerized units derived from L-lactic acid (e.g. L-lactide and/or meso-lactide). Likewise the film comprises an even lower concentration of polymerized units derived from L-lactic acid (e.g. L-lactide and/or meso-lactide) depending on the concentration of semicrystalline PLA polymer in the film. For example, if the film composition comprises 15 wt.-% of a semicrystalline PLA having about 2 wt.-% L-lactide and/or meso-lactide, the film composition comprises about 0.3

wt.-% L-lactide and/or meso-lactide. The film generally comprises no greater than 9, 8, 7, 6, 5, 4, 3, 2, 1.5, 1.0, 0.5, 0.4, 0.3, 0.2, or 0.1 wt.-% polymerized units derived from L-lactic acid (e.g. L-lactide and/or meso-lactide). Examples of such semicrystalline PLA are available as “Synterra™ PDLA”.

5 The first film layer may further comprise an amorphous PLA polymer blended with the semicrystalline PLA. In other embodiments, the first film layer comprises amorphous PLA polymer alone or in combination with low concentrations of semicrystalline PLA such that the composition and film has a low level of crystallinity. The inclusion of an amorphous PLA polymer can be preferred for improving the
10 printability of the film with organic-solvent based inks.

 In some embodiments, the amorphous PLA typically comprises no more than 90 wt.-% of polymerized units derived from L-lactic acid and greater than 10 wt.-% of polymerized units derived from D lactic acid (e.g. D-lactic lactide and/or meso-lactide). In some embodiments, the amorphous PLA comprises at least 80 or 85 wt.-% of
15 polymerized units derived from L-lactic acid (e.g. L-lactide). In some embodiments, the amorphous PLA comprises no greater than 20 or 15 wt.-% of polymerized units derived from D-lactic acid (e.g. D-lactide and/or meso-lactide). A suitable amorphous PLA includes Natureworks™ Ingeo™ 4060D grade. This polymer has been described in the literature to have a molecular weight Mw of about 180,000 g/mole.

20 Alternatively, the amorphous PLA typically comprises no more than 90 wt.-% of polymerized units derived from D-lactic acid and greater than 10 wt.-% of polymerized units derived from L lactic acid (e.g. L-lactic lactide and/or meso-lactide). In some embodiments, the amorphous PLA comprises at least 80 or 85 wt.-% of polymerized units derived from D-lactic acid (e.g. D-lactide). In some embodiments, the amorphous PLA
25 comprises no greater than 20 or 15 wt.-%. of polymerized units derived from L-lactic acid (e.g. L-lactide and/or meso-lactide).

 In some embodiments, both the semicrystalline and amorphous PLA polymers generally comprise high concentrations of polymerized units derived from L-lactic acid (e.g. L-lactide) with low concentrations of polymerized units derived from D-lactic acid
30 (e.g. D-lactide).

 In other embodiments, both the semicrystalline and amorphous PLA polymers generally comprise high concentrations of polymerized units derived from D-lactic acid

(e.g. D-lactide) with low concentrations of polymerized units derived from L-lactic acid (e.g. L-lactide).

The PLA polymers are preferably “film grade” polymers, having a melt flow rate (as measured according to ASTM D1238) of no greater than 25, 20, 15, or 10 g/min at 210°C with a mass of 2.16 kg. In some embodiments, the PLA polymer has a melt flow rate of less than 10 or 9 g/min at 210°C. The melt flow rate is related to the molecular weight of the PLA polymer. The PLA polymer typically has a weight average molecular weight (Mw) as determined by Gel Permeation Chromatography with polystyrene standards of at least 50,000 g/mol; 75,000 g/mol; 100,000 g/mol; 125,000 g/mol; 150,000 g/mol. In some embodiments, the molecular weight (Mw) is no greater than 400,000 g/mol; 350,000 g/mol or 300,000 g/mol.

The PLA polymers typically have a tensile strength ranging from about 25 to 150 MPa; a tensile modulus ranging from about 1000 to 7500 MPa; and a tensile elongation of at least 3, 4, or 5 ranging up to about 10 or 15%. In some embodiments, the tensile strength at break of the PLA polymer is at least 30, 35, 40, 45 or 50 MPa. In some embodiments, the tensile strength of the PLA polymer is no greater than 125, 100 or 75 MPa. In some embodiments, the tensile modulus of the PLA polymer is at least 1500, 2000, 2500, or 3000 MPa. In some embodiments, the tensile modulus of the PLA polymer is no greater than 7000, 6500, 6000, 5500, 5000, or 4000 MPa. Such tensile and elongation properties can be determined by ASTM D882 and are typically reported by the manufacturer or supplier of such PLA polymers.

The PLA polymers generally have a glass transition temperature, T_g, as can be determined by Differential Scanning Calorimetry (DSC) as described in the forthcoming examples, ranging from about 50 to 65°C. In some embodiments, the T_g is at least 51, 52, 53, 54, or 55°C.

The semicrystalline PLA polymers typically have a (e.g. peak) melting point ranging from 140 to 175°C, 180°C, 185°C or 190°C. In some embodiments, the (e.g. peak) melting point is at least 145, 150, or 155°C. The PLA polymer, typically comprising a semicrystalline PLA alone or in combination with an amorphous PLA polymer can be melt-processed at temperatures of 180, 190, 200, 210, 220 or 230 °C.

In one embodiment, PLA polymers can crystallize to form a stereocomplex (*Macromolecules*, 1987, 20 (4), pp 904–906). The PLA stereocomplex is formed when

PLLA (a PLA homopolymer polymerized from mostly L-lactic acid or L-lactide units) is blended with PDLA (a PLA homopolymer polymerized from mostly D-lactic acid or D-lactide units). The stereocomplex crystal of PLA is of interest because the melting temperature of this crystal ranges from 210-250 °C. The higher melting temperature stereocomplex PLA crystals increase the thermal stability of the PLA-based material. The PLA stereocomplex crystal is also known to effectively nucleate PLA homopolymer crystallization (Polymer, Volume 47, Issue 15, 12 July 2006, Page 5430). This nucleation effect increases the overall percent crystallinity of the PLA-based material, thus increasing the material's thermal stability.

The first film layer typically comprises a semicrystalline PLA polymer, or a blend of semicrystalline and amorphous PLA, or amorphous PLA in an amount of at least 25, 30, 35, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49 or 50 wt.-%, based on the total weight of the PLA polymer, second (e.g. polyvinyl acetate) polymer, and plasticizer. The total amount of PLA polymer is typically no greater than 90, 85, 80, 75, or 70 wt.-% of the total weight of the PLA polymer, second (e.g. polyvinyl acetate) polymer, and plasticizer.

When the film composition comprises a blend of semicrystalline and amorphous PLA, the amount of semicrystalline PLA is typically at least 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wt.-%, based on the total weight of the PLA polymer, second (e.g. polyvinyl acetate) polymer, and plasticizer. In some embodiments, the amount of amorphous PLA polymer ranges from 10, 15, 25 or 30 wt.-% up to 45, 50, 55 or 60 wt.-% based on the total weight of the PLA polymer, second (e.g. polyvinyl acetate) polymer, and plasticizer. The amount of amorphous PLA polymer can be greater than the amount of crystalline polymer. In some embodiments, the weight ratio of amorphous PLA polymer to crystalline PLA polymer is at least 1:1, 1.5:1, 2:1, 2.5:1, 3:1, or 3.5:1. In some embodiment, the weight ratio of amorphous PLA polymer to crystalline PLA polymer is no greater than 15:1, 14:1, 13:1, 12:1, 11:1, 10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4.5:1, or 4:1.

In other embodiments, the film composition comprises amorphous PLA polymer alone or in combination with low concentrations of semicrystalline PLA polymer. In this embodiment, the amount of semicrystalline PLA polymer may be zero or less than 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 wt.-% based on the total weight of the PLA polymer, second (e.g. polyvinyl acetate) polymer, and plasticizer.

The film composition further comprises a second polymer such as polyvinyl acetate polymer. The second polymer can improve the compatibility of the PLA with a plasticizer such that the plasticizer concentration can be increased without plasticizer migration (as determined by the test method described in the forthcoming examples).

5 The second (e.g. polyvinyl acetate) polymer has a Tg of at least 25, 30, 35 or 40 °C. The Tg of the second (e.g. polyvinyl acetate) polymer is typically no greater than 80, 75, 70, 65, 60, 55, 50 or 45°C.

The second (e.g. polyvinyl acetate) polymer typically has a weight or number average molecular weight (as determined by Size Exclusion Chromatography with
10 polystyrene standards) of at least 50,000 g/mol; 75,000 g/mol; 100,000 g/mol; 125,000 g/mol; 150,000 g/mol; 175,000 g/mol; 200,000 g/mol; 225,000 g/mol or 250,000 g/mol. In some embodiments, the molecular weight (Mw) is no greater than 2,000,000 g/mol; 1,500,000; 1,000,000 g/mol; 750,000 g/mol; 500,000 g/mol; 450,000 g/mol; 400,000 g/mol; 350,000 g/mol or 300,000 g/mol. In some embodiments, the molecular weight of
15 the second (e.g. polyvinyl acetate) polymer is greater than the molecular weight of the PLA polymer(s). In one embodiment, the second (e.g. polyvinyl acetate) polymer may be characterized as having a viscosity in a 10 wt.% ethyl acetate solution at 20°C ranging from 10 to 50 or 100 mPa*s. In another embodiment, the second (e.g. polyvinyl acetate) polymer may be characterized as having a viscosity in a 5 wt.% ethyl acetate solution at
20 20°C ranging from 5 to 20 mPa*s.

In some favored embodiments, the second polymer is a polyvinyl acetate polymer. The polyvinyl acetate polymer is typically a homopolymer. However, the polymer may comprise relatively low concentrations of repeat units derived from other comonomers, provided that the Tg of the polyvinyl acetate polymer is within the ranges previously
25 described. Other comonomers include for example acrylic monomers such as acrylic acid and methyl acrylate; vinyl monomers such as vinyl chloride and vinyl pyrrolidone; and C₂-C₈ alkylene monomers, such as ethylene. The total concentration of repeats derived from other comonomers of the polyvinyl acetate polymer is typically no greater than 10, 9, 8, 7, 6, or 5 wt.-%. In some embodiments, the concentration of repeats derived from other
30 comonomers of the polyvinyl acetate polymer is typically no greater than 4, 3, 2, 1 or 0.5 wt.-%. The polyvinyl acetate polymer typically has a low level of hydrolysis. The polymerized units of the polyvinyl acetate polymer that are hydrolyzed to units of vinyl

alcohol is generally no greater than 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 or 0.5 mol% of the polyvinyl acetate polymer.

Polyvinyl acetate polymers are commercially available from various suppliers including Wacker under the trade designation VINNAPASTM and from Vinavil Americas Corporation, West Chicago, IL under the trade designation VINA VIL. Prior to combining with the PLA, such polyvinyl acetate polymers are often in a (e.g. white) solid powder or colorless bead form. In some embodiments, the polyvinyl acetate polymer (e.g. powder, prior to combining with the PLA polymer) is not water redispersible.

A single second (e.g. polyvinyl acetate) polymer may be utilized or a combination of two or more second (e.g. polyvinyl acetate) polymers.

The total amount of second (e.g. polyvinyl acetate) polymer present in the first film layer described herein is at least about 5, 6, 7, 8, 9, or 10 wt.-% and typically no greater than about 50, 45, or 40 wt.-%, based on the total weight of the PLA polymer, second (e.g. polyvinyl acetate) polymer, and plasticizer. In some embodiments, the concentration of second (e.g. polyvinyl acetate) polymer is present in an amount of at least 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wt.-%.

In some embodiments, the first film layer (e.g. composition) typically has a Tg of less than 40, 39, 38, 37, 36, 35, 34, 33, 32, 31, 30, 29, 28, 27, 26, 25, 24, 23, 22, 21, or 20°C. The first film layer does not exhibit plasticizer migration when aged at 80°C for 24 hours (according to the test methods described in the examples). These properties are attributable to the inclusion of the second (e.g. polyvinyl acetate) polymer.

The first film layer further comprises a plasticizer. The total amount of plasticizer in the film composition typically ranges from about 5 wt.-% to about 30, 35, 40, 45 or 50 wt.-%, based on total weight of PLA polymer, second (e.g. polyvinyl acetate) polymer, and plasticizer. In some embodiments, the plasticizer concentration is at least 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 wt.-% of the film composition. In some embodiments, the plasticizer concentration is no greater than 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15 or 10 wt.-% of the film composition.

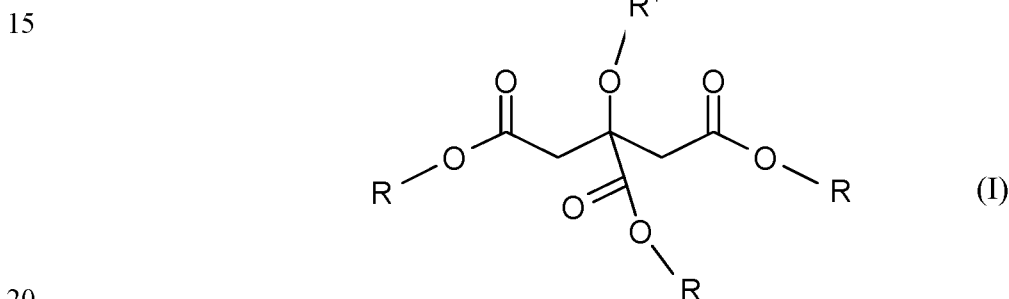
Various plasticizers that are capable of plasticizing PLA have been described in the art. The plasticizers are generally a liquid at 25°C and typically have a molecular weight ranging from about 200 g/mol to 10,000 g/mol. In some embodiments, the molecular weight of the plasticizer is no greater than 5,000 g/mol. In other embodiments,

the molecular weight of the plasticizer is no greater than 4,000, 3,000, 2,000 or 1,000 g/mol. Various combinations of plasticizers may be utilized.

In some embodiments, the plasticizer does not comprise (e.g. polymerized) moieties of lactide.

5 The plasticizer preferably comprises one or more alkyl or aliphatic esters or ether groups. Multi-functional esters and/or ethers are typically preferred. These include alkyl phosphate esters, dialkylether diesters, tricarboxylic esters, epoxidized oils and esters, polyesters, polyglycol diesters, alkyl alkylether diesters, aliphatic diesters, alkylether monoesters, citrate esters, dicarboxylic esters, vegetable oils and their derivatives, and
10 esters of glycerine. Such plasticizers generally lack aromatic groups and halogen atoms and are anticipated to be biodegradable. Such plasticizers commonly further comprise linear or branched alkyl terminal group groups having a carbon chain length of C₂ to C₁₀.

In one embodiment, the plasticizer is a bio-based citrate-based plasticizer represented by the following Formula (I):



wherein

R are independently alkyl groups that may be the same or different; and

R' is an H or an (C₁ to C₁₀) acyl group.

25 R are typically independently linear or branched alkyl groups having a carbon chain length of C₁ to C₁₀. In some embodiments, R is a C₂ to C₈ or C₂ to C₄ linear alkyl group. In some embodiments, R' is acetyl. In other embodiments, at least one R is a branched alkyl groups having a carbon chain length of C₅ or greater. In some
embodiments, the branched alkyl group has a carbon chain length no greater than 8.

30 Representative citrate-based plasticizer include for example triethyl citrate, acetyl triethyl citrate, tributyl citrate, acetyl tributyl citrate, trihexyl citrate, acetyl trihexyl citrate, trioctyl citrate, acetyl trioctyl citrate, butyryl trihexyl citrate, acetyl tris-3-methylbutyl

citrate, acetyl tris-2-methylbutyl citrate, acetyl tris-2-ethylhexyl citrate, and acetyl tris-2-octyl citrate. One representative citrate-based plasticizer is acetyl tri-n-butyl citrate, available under the trade designation CITROFLEX A-4 PLASTICIZER from Vertellus Specialties, Incorporated, Indianapolis, IN.

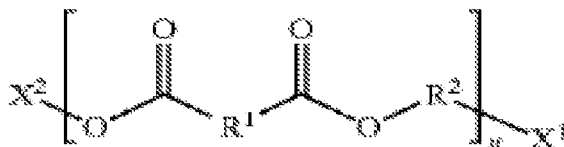
5 In another embodiment, the plasticizer comprises a polyethylene glycol backbone and ester alkyl terminal groups. The molecular weight of the polyethylene glycol segment is typically at least 100, 150 or 200 g/mole and no greater than 1,000 g/mole. In some
10 embodiments, the polyethylene glycol segment has a molecular weight no greater than 900, 800, 700, or 600 g/mole. Examples include polyethylene glycol (400) di-ethylhexonate available from Hallstar, Chicago, IL under the trade designation “TegMeR™ 809” and tetraethylene glycol di-ethylhexonate available from Hallstar, Chicago, IL under the trade designation “TegMeR™ 804”.

In another embodiment, the plasticizer may be characterized as a polymeric adipate (i.e. a polyester derived from adipic acid) such as commercially available from Eastman,
15 Kingsport, TN, as Admex™ 6995.

In another embodiment, the plasticizer is a substituted or unsubstituted aliphatic polyester, such as described in U.S. Patent No. 8,158,731; incorporated herein by reference.

In some embodiments, the aliphatic polyester plasticizer comprises repeating units
20 derivable from succinic acid, glutaric acid, adipic acid, and/or sebacic acid. In some embodiments, the polyesters of the polymer blends disclosed herein comprise repeating units derivable from 1,3-propanediol and/or 1,2-propanediol. In some embodiments, the polyesters of the polymer blends disclosed herein comprise one or two terminator units derivable from 1-octanol, 1-decanol, and/or mixtures thereof. In some embodiments, the
25 polyesters of the polymer blends disclosed herein comprise repeating units derivable from succinic acid, glutaric acid, adipic acid, and/or sebacic acid; repeating units derivable from 1,3-propanediol and/or 1,2-propanediol; and one or two terminator units derivable from 1-octanol, 1-decanol, and/or mixtures thereof.

In some embodiments, the aliphatic polyester plasticizer has the following formula:



wherein n is 1 to 1000; R^1 is selected from the group consisting of a covalent bond and a substituted or unsubstituted aliphatic hydrocarbon group having 1 to 18 carbon atoms; R^2 is a substituted or unsubstituted aliphatic hydrocarbon group having 1 to 20 carbon atoms; X^1 is selected from the group consisting of $-OH$, $-O_2C-R^1-CO_2H$, and $-O_2C-R^1-CO_2R^3$; X^2 is selected from the group consisting of $-H$, $-R^2-OH$, and R^3 ; and R^3 is a substituted or unsubstituted aliphatic hydrocarbon group having 1 to 20 carbon atoms. In some embodiments, the polyester has the above formula with the proviso that if X^1 is $-OH$ or $-O_2C-R^1-CO_2H$, then X^2 is R^3 .

The number of repeat units n is selected such that the aliphatic polyester plasticizer has the previously described molecular weight.

In some embodiments, R^1 , R^2 , and/or R^3 are alkyl groups. R^1 alkyl groups can have, for example, from 1 to 18 carbon atoms, from 1 to 10 carbon atoms, from 1 to 8 carbon atoms, from 2 to 7 carbon atoms, from 2 to 6 carbon atoms, from 2 to 5 carbon atoms, from 2 to 4 carbon atoms, and/or 3 carbon atoms. R^1 , for example, can be selected from the group consisting of $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, and $-(CH_2)_8-$. R^2 alkyl groups can have, for example, from 1 to 20 carbon atoms, from 1 to 10 carbon atoms, from 1 to 8 carbon atoms, from 2 to 7 carbon atoms, from 2 to 6 carbon atoms, from 2 to 5 carbon atoms, from 2 to 4 carbon atoms, and/or 3 carbon atoms. R^2 , for example, can be selected from the group consisting of $-(CH_2)_3-$, $-CH_2CH(CH_3)-$, and $-CH(CH_3)CH_2-$. R^3 alkyl groups can have, for example, from 1 to 20 carbon atoms, from 1 to 18 carbon atoms, from 2 to 16 carbon atoms, from 3 to 14 carbon atoms, from 4 to 12 carbon atoms, from 6 to 12 carbon atoms, from 8 to 12 carbon atoms, and/or from 8 to 10 carbon atoms. R^3 , for example, also can be a mixture comprising $-(CH_2)_7CH_3$ and $-(CH_2)_9CH_3$.

In some embodiments, R^1 is an alkyl group having from 1 to 10 carbons, R^2 is an alkyl group having from 1 to 10 carbons, and R^3 is an alkyl group having from 1 to 20 carbons. In other embodiments, R^1 is an alkyl group having from 2 to 6 carbons, R^2 is an

alkyl group having from 2 to 6 carbons, and R^3 is an alkyl group having from 8 to 12 carbons. In still other embodiments, R^1 is an alkyl group having from 2 to 4 carbons, R^2 is an alkyl group having from 2 to 3 carbons, and R^3 is an alkyl group having from 8 to 10 carbons. In yet other embodiments, R^1 is selected from the group consisting of $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, and $-(CH_2)_8-$, R^2 is selected from the group consisting of $-(CH_2)_3-$, $-CH_2CH(CH_3)-$, and $-CH(CH_3)CH_2-$, and R^3 is a mixture comprising $-(CH_2)_7CH_3$ and $-(CH_2)_9CH_3$.

The aliphatic polyester plasticizer can have an acid value of about zero to about 20, or greater. The acid value of the polyesters can be determined by known methods for measuring the number of milligrams of potassium hydroxide necessary to neutralize the free acids in one gram of polyester sample.

Plasticizer with a low acid value is typically preferred for the shelf-life stability and/or durability of the film. In some embodiments, the acid value of the plasticizer is preferably no greater than 10, 9, 8, 7, 6, 5, 4, 3, 2 or 1.

The aliphatic polyester plasticizer can have a hydroxyl value of about zero to about 110, for example, about 1 to about 40, about 10 to about 30, about 15 to about 25, about 30 to about 110, about 40 to about 110, about 50 to about 110, and/or about 60 to about 90. The polyesters also can have a hydroxyl value greater than about 110. The hydroxyl value of the polyesters can be determined by known methods for measuring hydroxyl groups, such as the methods described by ASTM Test Method D 4274.

One representative aliphatic polyester plasticizer is available from Hallstar, Chicago, IL, as the trade designation HALLGREEN R-8010TM.

In some embodiments, the plasticizer compound typically has little or no hydroxyl groups. In some embodiments, the wt.-% percent of hydroxyl groups relative to the total weight of the plasticizer compound is no greater than 10, 9, 6, 7, 6, 5, 4, 3, 2, 1 wt.-%. In some embodiments the plasticizer compound contains no hydroxyl groups. Thus, in this embodiment, the plasticizer is not glycerol or water.

To facilitate the rate of crystallization (e.g. of the semicrystalline PLA), a nucleating agent may also be present in the PLA film composition. Suitable nucleating agent(s) include for example inorganic minerals, organic compounds, salts of organic acids and imides, finely divided crystalline polymers with a melting point above the processing temperature of PLA, and combinations of two or more of the foregoing.

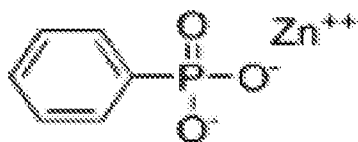
Suitable nucleating agents typically have an average particle size of at least 25 nanometers, or at least 0.1 micron. Combinations of two or more different nucleating agents may also be used.

5 Examples of useful nucleating agents include, for example, talc (hydrated magnesium silicate - $H_2Mg_3(SiO_3)_4$ or $Mg_3Si_4O_{10}(OH)_2$), silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), zinc oxide, sodium salt of saccharin, calcium silicate, sodium benzoate, calcium titanate, aromatic sulfonate derivative, boron nitride, copper phthalocyanine, phthalocyanine, sodium salt of saccharin, isotactic polypropylene, polybutylene terephthalate, and the like.

10 When an organic nucleating agent is present, the nucleating agent is typically at a concentration of at least 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.15 or 0.2 wt.-% ranging up to about 1, 2, 3, 4 or 5 wt.-% based on the total weight of the film composition. When the nucleating agent is an inorganic oxide filler such as silica, alumina, zinc oxide, and talc, the concentration can be higher.

15 In one embodiment, the nucleating agent may be characterized as a salt of a phosphorous-containing aromatic organic acid such as zinc phenylphosphonate, magnesium phenylphosphonate, disodium 4-tert-butylphenyl phosphonate, and sodium diphenylphosphinates.

20 One favored nucleating agent is zinc phenylphosphonate having the following chemical formula:



available from Nissan Chemical Industries, Ltd under the trade designation "Ecopromote".

25 In some embodiments, inorganic fillers may be used to prevent blocking or sticking of layers or rolls of the film during storage and transport. Inorganic fillers include clays and minerals, either surface modified or not. Examples include talc, diatomaceous earth, silica, mica, kaolin, titanium dioxide, perlite, and wollastonite.

Organic biomaterial fillers include a variety of forest and agricultural products, either with or without modification. Examples include cellulose, wheat, starch, modified starch, chitin, chitosan, keratin, cellulosic materials derived from agricultural products,

gluten, flour, and guar gum. The term "flour" concerns generally a film composition having protein-containing and starch-containing fractions originating from one and the same vegetable source, wherein the protein-containing fraction and the starch-containing fraction have not been separated from one another. Typical proteins present in the flours are globulins, albumins, glutenins, secalins, prolamins, glutelins. In typical embodiments, the first film layer comprises little or no organic biomaterial fillers such a flour. Thus, the concentration of organic biomaterial filler (e.g. flour) is typically less than 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1 wt.-% of the total film composition.

In some embodiments, the first film layer comprises an anti-blocking agent such as a fatty acid derivative. One suitable anti-blocking agent is a mixture of PLA polymer, 5-10 wt.-% of a fatty acid derivative and 20 to 40 wt.-% of silica, such as available under the trade designation SUKANO DC S511 from Sukano Polymers Corporation Duncan, SC.

The first film layer may optionally contain one or more conventional additives. Additives include, for example, antioxidants, stabilizers, ultraviolet absorbers, lubricants, processing aids, antistatic agents, colorants, impact resistance aids, fillers (e.g. diatomaceous earth), matting agents, flame retardants (e.g. zinc borate), pigments (e.g. titanium dioxide), and the like. Some examples of fillers or pigments include inorganic oxide materials such as zinc oxide, titanium dioxide, silica, carbon black, calcium carbonate, antimony trioxide, metal powders, mica, graphite, talc, ceramic microspheres, glass or polymeric beads or bubbles, fibers, starch and the like.

When present, the amount of additive can be at least 0.1, 0.2, 0.3, 0.4, or 0.5 wt.-%. In some embodiments, the amount of additive is no greater than 25, 20, 15, 10 or 5 wt.-% of the total film composition. In other embodiments, the concentration of additive can range up to 40, 45, 50, 55 or about 65 wt.-% of the total film composition.

In some embodiments, the first (e.g. printed) film layer (e.g. 101) comprises one or more inorganic pigments. Examples of suitable inorganic pigments include metal oxides (including mixed metal oxides), metal sulfides, and metal salts. Examples include titanium dioxide, zinc oxide, zinc sulfide, and antimony oxide. Preferred inorganic pigments are metal oxides. Various combinations of inorganic pigments may be used.

In one embodiment, the inorganic pigment is (e.g. rutile) titanium dioxide, in the form of a finely ground powder. Titanium dioxide can provide opacity for white film layers as well as light scattering and UV absorption. In general, the greater the difference

between the refractive index of the pigment and that of the PLA-containing polymer matrix in which it is dispersed, the greater the light scattering.

For the most effective light scattering, the pigment particle diameter is typically slightly less than one-half the wavelength of light to be scattered. Because the eye is most sensitive to yellow-green light (about 0.55 μm wavelength), commercial TiO_2 pigments for plastics typically have a median particle size ranging from 0.2 to 0.4 μm in diameter. Light scattering imparted by diffraction is affected by particle spacing and average pigment particle size. If particles are too large or too closely spaced, little diffraction takes place. If the pigment particles are too small, the light will not “see” the pigment particle.

Titanium dioxide (e.g. rutile) is an efficient UV radiation protector for plastic applications because it strongly absorbs radiation below 380 nm. Rutile titanium dioxide, in the presence of water and oxygen, may then act as a photocatalytic agent. In some embodiments, the titanium dioxide pigment is surface coated with silica or other metal oxide to minimize this photocatalytic potential. In some embodiments, the titanium dioxide pigment comprises at least 1, 1.5, 2, 2.5, or 3 wt.% of silica. The silica content of the titanium dioxide pigment is typically no greater than 10, 9.5, 9, 8.5, 8, 7.5, 7, or 6.5 wt.%. In some embodiments, the titanium dioxide pigment comprises an alumina surface treatment. In some embodiments, the titanium dioxide pigment comprises at least 0.5, 1 or 1.5 wt.% of alumina. The alumina content of the titanium dioxide pigment is typically no greater than 10, 9.5, 9, 8.5, 8, 7.5, 7, 6.5, 6, 5.5, 4.5 or 4 wt.%. In some embodiments, the titanium dioxide pigment comprises a (e.g. hydrophobic) organic surface treatment.

Various pigments are commercially available such as titanium dioxide available under the trade designation Ti-Pure R-101, R-103, R-104, R-105, R-350, and R-960 from Chemours Company.

In some embodiments, the pigment may be preblended with semi-crystalline or amorphous polylactic acid polymer, such as in the case of CLARIANT PLA 4060D TiO_2 MB and CLARIANT PLA 4032D TiO_2 MB from Clariant.

In some embodiments, the amount of (e.g. TiO_2) inorganic pigment(s) is at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 wt.% of the first PLA-containing film layer. In some embodiments, the amount of (e.g. TiO_2) inorganic pigment(s) is at least 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 wt.% of the first PLA-containing film layer. The amount of (e.g. TiO_2)

inorganic pigment(s) is typically no greater than 50, 45, 40, 35, or 30 wt.% of the first PLA-containing film layer.

The ratio of total (e.g. semicrystalline and amorphous) polylactic acid polymer to total (e.g. TiO₂) inorganic pigment(s) can vary. In some embodiments, the PLA-containing first film layer comprises a relatively high amount of total (e.g. semicrystalline and amorphous) polylactic acid polymer in comparison to the total amount of (e.g. TiO₂) inorganic pigment(s). For example, when the PLA-containing first film layer comprises 50 wt.% of polylactic acid polymer and 2 wt.% of (e.g. TiO₂) inorganic pigment(s), the ratio is 50/2, or in other words 25:1. As the total amount of (e.g. TiO₂) inorganic pigment(s) increases, the ratio decreases. In some embodiments, the ratio of total (e.g. semicrystalline and amorphous) polylactic acid polymer to total (e.g. TiO₂) inorganic pigment(s) is less than 20:1; 15:1; or 10:1. In some embodiments, the ratio of total (e.g. semicrystalline and amorphous) polylactic acid polymer to total (e.g. TiO₂) inorganic pigment(s) is less than 9:1, 8:1, 7:1, 6:1, or 5:1. For example when the first film layer comprises 54.4 wt.% of polylactic acid polymer and 11.3 wt.% of (e.g. TiO₂) inorganic pigment(s) is 11.3, the ratio is 54.4/11.3, or in other words 4.8/1.

At even greater concentration of (e.g. TiO₂) inorganic pigment(s) the ratio further decreases. In some embodiments, the ratio of total (e.g. semicrystalline and amorphous) polylactic acid polymer to total (e.g. TiO₂) inorganic pigment(s) is less than 4.5:1, 4.4:1, 4.3:1, 4.2:1, 4.1:1, 4:1, 3.9:1, 3.8:1, 3.7:1, 3.6:1, 3.5:1, 3.4:1, 3.3:1, 3.2:1, 3.1:1 or 3:1. In some embodiments, the ratio is at least 1:1, 1.5:1, or 2:1. Surprisingly high elongation can be obtained at high loadings of (e.g. TiO₂) inorganic pigment(s).

In one embodiment, the PLA containing film layer comprises one or more hydrolysis stabilizers, also referred to as a hydrolysis inhibitor. In some embodiments, the first film layer (e.g. 101) comprises one or more hydrolysis stabilizers. In some embodiments, a PLA-containing cover film (e.g. 401) comprises one or more hydrolysis stabilizers. In yet other embodiments, the first film layer and PLA-containing cover film both comprise one or more hydrolysis stabilizers.

In some embodiments, the hydrolysis stabilizer is a carbodiimide hydrolysis stabilizers, or in other words a compound or polymer comprising one or more carbodiimide groups.

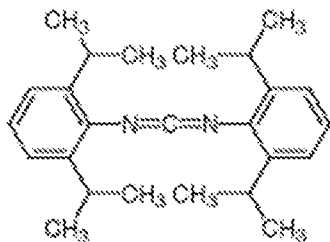
Compounds that contain carbodiimide groups are described, for example, in U.S. Pat. Nos. 5,210,170 and 5,614,483, and U.S. patent application Ser. No. 2010/0093888A1; incorporated herein by reference. Polymeric materials containing carbodiimide groups are described, for example, in U.S. Pat. No. 6,498,225; incorporated herein by reference.

5 Examples of carbodiimide-containing compounds include for example mono- and di-carbodiimide compounds such as dicyclohexyl carbodiimide, diisopropyl carbodiimide, dimethyl carbodiimide, diisobutyl carbodiimide, dioctyl carbodiimide, octyldecyl carbodiimide, di-t-butyl carbodiimide, t-butylisopropyl carbodiimide, dibenzyl carbodiimide, diphenyl carbodiimide, N-octadecyl-N'-phenylcarbodiimide, N-benzyl-N'-phenylcarbodiimide, N-benzyl-N'-tolylcarbodiimide, di-o-toluoylcarbodiimide, di-p-toluoylcarbodiimide, bis(p-nitrophenyl)carbodiimide, bis(p-aminophenyl)carbodiimide, bis(p-hydroxyphenyl)carbodiimide, bis(p-chlorophenyl)carbodiimide, bis(o-chlorophenyl)carbodiimide, bis(o-ethylphenyl)carbodiimide, bis(p-ethylphenyl)carbodiimide, bis(o-isopropylphenyl)carbodiimide, bis(p-isopropylphenyl)carbodiimide, bis(o-isobutylphenyl)carbodiimide, bis(p-isobutylphenyl)carbodiimide, bis(2,5-dichlorophenyl)carbodiimide, p-phenylenebis(o-toluoylcarbodiimide), p-phenylenebis(cyclohexylcarbodiimide), p-phenylenebis(p-chlorophenylcarbodiimide), 2,6,2',6'-tetraisopropyldiphenyl carbodiimide, hexamethylenebis(cyclohexylcarbodiimide), ethylenebis(phenylcarbodiimide), ethylenebis(cyclohexylcarbodiimide), bis(2,6-dimethylphenyl)carbodiimide, bis(2,6-diethylphenyl)carbodiimide, bis(2-ethyl-6-isopropylphenyl)carbodiimide, bis(2-butyl-6-isopropylphenyl)carbodiimide, bis(2,6-diisopropylphenyl)carbodiimide, bis(2,6-di-t-butylphenyl)carbodiimide, bis(2,4,6-trimethylphenyl)carbodiimide, bis(2,4,6-triisopropylphenyl)carbodiimide, bis(2,4,6-tributylphenyl)carbodiimide, di-.beta.-naphthylcarbodiimide, N-tolyl-N'-cyclohexylcarbodiimide and N-tolyl-N'-phenylcarbodiimide.

 Polycarbodiimides include for example poly(1,6-cyclohexanecarbodiimide), poly(4,4'-methylenebiscyclohexylcarbodiimide), poly(1,3-cyclohexylenecarbodiimide), poly(1,4-cyclohexylenecarbodiimide), poly(4,4'-diphenylmethanecarbodiimide), poly(3,3'-dimethyl-4,4'-diphenylmethanecarbodiimide), poly(naphthylenecarbodiimide), poly(p-phenylenecarbodiimide), poly(m-phenylenecarbodiimide), poly(p-tolylcarbodiimide), poly(diisopropylcarbodiimide), poly(methyldiisopropylphenylenecarbodiimide) and

poly(triethylphenylenecarbodiimide). Commercially available polycarbodiimide compounds include CARBODILITE LA-1, HMV-5CA, and HMV-15CA (as a tradename of CARBODILITE) marketed from Nisshinbo Industries, Inc.

In some embodiments, the hydrolysis stabilizer is bis(2,6-
5 diisopropylphenyl)carbodiimide, available from various suppliers, depicted as follows:



The hydrolysis stabilizer may optionally contain a small amount (e.g. less than 2%
10 of 2,6-diisopropylphenyl isocyanate (DIPI).

In one embodiment, the PLA-containing first (e.g. printed) film layer and/or PLA-
containing (e.g. printed or unprinted) cover film comprises one or more commercially
available carbodiimide hydrolysis inhibitors. One example of such a material is available
under the trade designation STABAXOL I, which is a monomeric carbodiimide made by
15 Rhein Chemie of Chardon, Ohio. Other carbodiimide-containing compounds include those
available under the trade designations STABAXOL I LF, which is a monomeric
compound containing carbodiimide groups, and STABAXOL P, which is a polymeric
material containing carbodiimide groups, both also made by Rhein Chemie. Another
example of a hydrolysis stabilizer comprising carbodiimide groups is available from
20 Nisshinbo Chemical Inc. Japan as "CARBODILITE HMV-15CA".

In some embodiments, the (e.g. carbodiimide) hydrolysis inhibitor has a softening
point of at least 60, 65 or 70°C. In other embodiments, the (e.g. carbodiimide) hydrolysis
inhibitor has a softening point of less than 60°C. For example, the softening point may
range from about 45 to 55°C. In some embodiments, the (e.g. carbodiimide) hydrolysis
25 inhibitor has a weight loss of 5% at 300°C. In other embodiments, the (e.g. carbodiimide)
hydrolysis inhibitor has a weight loss of less than 4, 3, 2, or 1% at 300°C.

Various combinations of (e.g. carbodiimide) hydrolysis stabilizers as described
herein can be used in the PLA-containing first film layer.

In some embodiments, the amount of (e.g. carbodiimide) hydrolysis stabilizer(s) is at least 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 or 1.0 wt.% of the PLA-containing first film layer and/or cover film. In some embodiments, the amount of (e.g. carbodiimide) hydrolysis stabilizer(s) is at least 1.5, 2, 2.5, 3.0, 3.5, 4.0, 4.5, or 5 wt.% of the PLA-
5 containing first film layer and/or cover film. In some embodiments, the amount of (e.g. carbodiimide) hydrolysis stabilizer(s) is no greater than 10, 9, 8, 7, 6, 5, 4, or 3 wt.% of the PLA-containing first film layer and/or cover film.

The inclusion of the (e.g. carbodiimide) hydrolysis stabilizer and/or inorganic (e.g. TiO₂) pigment can improve the color stability of the printed ink. The color change of the
10 printed PLA-based film before and after accelerated aging can be determined according to the test method described in the examples. In some embodiments, the printed PLA-based film exhibits a change in color of white and/or black ink of no greater than 0.1, 0.2, 0.3, 0.4, or 0.5 after exposure to a total irradiance of 179, 357, 539, 717, 901, or 1082 MJ/m². In some embodiments, the printed PLA-based film exhibits a change in color of cyan
15 and/or yellow ink of no greater than 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 after exposure to a total irradiance of 179, 357, 539, 717, 901, or 1082 MJ/m². In some embodiments, the printed PLA-based film exhibits a change in color of magenta ink of no greater than 4, 5, 6, 7, 8, 9, or 10 after exposure to a total irradiance of 179, 357, 539, 717, 901, or 1082 MJ/m².

20 The inclusion of the (e.g. carbodiimide) hydrolysis stabilizer and inorganic (e.g. TiO₂) pigment can improve the molecular weight stability of the PLA based composition. Tables 13-15 report the molecular weight, as determined with Gel Permeation Chromatography (as further described in the examples), of various PLA-based film compositions.

25 In the absence of (e.g. carbodiimide) hydrolysis stabilizer, the (e.g. inorganic pigment containing) PLA-based film composition can exhibit a decrease in weight-average molecular weight (Mw) of 38% after a total exposure of 360 MJ/m², 46% after a total exposure of 720 MJ/m², and 57% after a total exposure of 1080 MJ/m². However, when the PLA-based film composition includes (e.g. carbodiimide) hydrolysis stabilizer,
30 the molecular weight decrease is substantially lower than the same film composition without hydrolysis stabilizer. For example, in some embodiments the PLA-based film composition including (e.g. carbodiimide) hydrolysis stabilizer decreases in weight-

average molecular weight (Mw) by less than 35%, 30%, 25%, 20%, 15%, and 10% after a total exposure of 360 MJ/m². In some embodiments, after a total exposure of 720 MJ/m², the PLA-based film composition including (e.g. carbodiimide) hydrolysis stabilizer exhibits a weight-average molecular weight (Mw) decrease of less than 50%, 45%, 40%, 35%, 30%, and 25%. Further, in some embodiments, after a total exposure of 1080 MJ/m², the PLA-based film composition including (e.g. carbodiimide) hydrolysis stabilizer exhibits a weight-average molecular weight (Mw) decrease of less than 55%, 50%, 45%, 40%, 35%, 30%, and 25%.

In the absence of (e.g. carbodiimide) hydrolysis stabilizer, the (e.g. inorganic pigment containing) PLA-based film composition can exhibit a decrease in number-average molecular weight (Mn) of 50% after a total exposure of 360 MJ/m², 67% after a total exposure of 720 MJ/m², and 78% after a total exposure of 1080 MJ/m². However, when the PLA-based film composition includes (e.g. carbodiimide) hydrolysis stabilizer, the molecular weight decrease is substantially lower than the same film composition without hydrolysis stabilizer. For example, in some embodiments the PLA-based film composition including (e.g. carbodiimide) hydrolysis stabilizer decreases in number-average molecular weight (Mn) by less than 45%, 40%, 35%, 30%, 25%, 20%, and 15% after a total exposure of 360 MJ/m². In some embodiments, after a total exposure of 720 MJ/m², the PLA-based film composition including (e.g. carbodiimide) hydrolysis stabilizer exhibits a number-average molecular weight (Mn) decrease of less than 55%, 50%, 45%, 40%, 35%, 30%, and 25%. Further, in some embodiments, after a total exposure of 1080 MJ/m², the PLA-based film composition including (e.g. carbodiimide) hydrolysis stabilizer exhibits a number-average molecular weight (Mn) decrease of less than 75%, 70%, 65%, 60%, 55%, 50%, 45%, 40% and 35%.

In the absence of (e.g. carbodiimide) hydrolysis stabilizer, the (e.g. inorganic pigment containing) PLA-based film composition can exhibit a decrease in peak molecular weight (Mp) of 60% after a total exposure of 360 MJ/m², 79% after a total exposure of 720 MJ/m², and 85% after a total exposure of 1080 MJ/m². However, when the PLA-based film composition includes (e.g. carbodiimide) hydrolysis stabilizer, the peak molecular weight decrease is substantially lower than the same film composition without hydrolysis stabilizer. For example, in some embodiments the PLA-based film composition including (e.g. carbodiimide) hydrolysis stabilizer decreases in peak

molecular weight (Mp) by less than 40%, 35%, 30%, 25%, 20%, and 15% after a total exposure of 360 MJ/m². In some embodiments, after a total exposure of 720 MJ/m², the PLA-based film composition including (e.g. carbodiimide) hydrolysis stabilizer exhibits a peak molecular weight (Mp) decrease of less than 55%, 50%, 45%, 40%, 35%, 30%, and 25%. Further, in some embodiments, after a total exposure of 1080 MJ/m², the PLA-based film composition including (e.g. carbodiimide) hydrolysis stabilizer exhibits a peak molecular weight (Mp) decrease of less than 75%, 70%, 65%, 60%, 55%, 50%, 45%, 40% and 35%.

The first PLA-based film, as described herein, may be a monolithic film or a film layer of a multilayer film. The first PLA-based film or film layer is typically unoriented, but optionally may be oriented.

When the film is a monolithic film, the thickness of the film is typically at least 10, 15, 20, or 25 microns (1 mil) to 500 microns (20 mils) thickness. In some embodiments, the thickness of the film is no greater than 2500, 2000, 1500, 1000, 800, 400, 300, 200, 150 or 50 microns. The film may be in the form of individual sheets, particularly for a thickness of greater than 50 mils. The (e.g. thinner) film may be in the form of a roll-good.

When the film is a film layer of a multilayer film, the multilayer film typically has the thickness just described. However, the thickness of the film layer may be less than 10 microns. In one embodiment, the film layer comprising the film composition described herein is an exterior layer or in other words a skin layer. A second film layer is disposed upon the skin layer. The second film layer typically has a different composition than the skin layer. In some embodiments, the second film is a PLA-based film having a different composition than the first film layer.

In preparing a first film composition as described herein, the PLA, second polymer such as PVAc, plasticizer, nucleating agent, etc. are heated (e.g. 180 - 250 °C) and thoroughly mixed using any suitable means known by those of ordinary skill in the art. For example, the film composition may be mixed by use of a (e.g., Brabender) mixer, extruder, kneader or the like.

Following mixing, the film composition may be formed into a (e.g. cast) film using known film-forming techniques, taking into consideration the scale of the process and available equipment. In some embodiments, the PLA-based film composition is

transferred to a press and then compressed and solidified to form individual sheets of PLA film. In other embodiments, the PLA-based film composition may be extruded through a die onto a casting roll maintained at a suitable cooling temperature to form a continuous length of PLA-based film. In some embodiments, during the film extrusion, the casting
5 roll temperature is maintained preferably at 80 to 120°C to obtain crystallization of PLA films on the casting roll.

The PLA-based films described herein can be used in a variety of (e.g. graphic) articles. In some embodiments, the PLA film has similar or even better properties to polyvinyl chloride (PVC) film, and thus can be used in place of PVC films. Thus, the film
10 and articles described here can be free of polyvinyl chloride (PVC) film as well as phthalate plasticizers.

The film and film compositions can have various properties, as determined by the test methods set forth in the examples.

The first PLA-based film composition generally has a glass transition temperature ranging from about -20°C, -15°C, or -10°C to 40°C; below the T_g of both the PLA
15 polymer and the second (e.g. polyvinyl acetate) polymer. In some embodiments, the film has a glass transition temperature of at least -5, -4, -3, -2, -1 or 0°C. In some embodiments, the film has a glass transition temperature of less than 35°C or 30°C or 25°C. In some embodiments, the film has a glass transition temperature of less than 20°C, 19°C, 18°C,
20 17°C, or 16°C.

The first PLA-based film typically has a melting temperature, T_{m1} or T_{m2}, ranging from of at least about 120, 130, 140, 150°C or 155°C to about 165°C, 170°C, 175°C, 180°C, 185 °C, 190°C, 200°C, or 210°C. The melting temperature is typically a single
25 peak or can be an average of (e.g. two) peaks. Further, the film composition can have a crystallization peak temperature T_c ranging from 50°C, 60°C, 70°C, 80°C, 90°C, or 100°C ranging up to 120°C, 130°C, or 140°C.

The net melting endotherm is the energy of the melting endotherm less the energy of the crystallization exotherm (as described in further detail in the forthcoming examples). The net melting endotherm of the film compositions (i.e. taken from the
30 microcompounder that are not melt pressed into a film) is determined by the second heating scan; whereas the net melting endotherm of the (e.g. melt pressed or extruded) film is determined by the first heating scan. In some embodiments, the net melt enthalpy

of the film, ΔH_{nm1} , is 0 or greater than 0, yet less than 10 J/g. The film may have a low net melting endotherm due to the film composition comprising little or no semicrystalline PLA. Alternatively, a film comprising appreciable amounts of semicrystalline PLA may have a low net melting endotherm due to being unannealed. In some embodiments, the net melt enthalpy of the film, ΔH_{nm1} , is less than 9, 8, 7, 6, 5, 4, 3, 2, or 1 J/g. In other embodiments, the net melt enthalpy of the film, ΔH_{nm2} and ΔH_{nm1} , respectively, is greater than 10, 11, 12, 13, 14 or 15 J/g and less than 40, 39, 38, 37, 36 or 35 J/g.

In one embodiment, the first PLA-based film has a Tg from -10 to 30°C or 35°C or 40°C and a net melting endotherm, ΔH_{nm1} , greater than 10 J/g and less than 40 J/g, as just described. Such films are flexible at room temperature and possess relatively high mechanical properties, such as modulus, upon heating to elevated temperatures as shown by the dynamical mechanical analysis (DMA) results in FIG. 11. In this embodiment, the film has a tensile storage modulus of at least 10 MPa and typically less than 10,000 MPa for a temperature range of -40°C to 125°C when heated at a rate of 2°C/min (i.e. the tensile storage modulus does not drop below 10 MPa when heated from -40 to 125°C when heated at a rate of 2°C/min). In some embodiments, the film has a tensile storage modulus as determined by dynamic mechanical analysis of at least 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 MPa for a temperature range of 25°C to 80°C when heated at a rate of 2°C/min. In contrast, as shown in FIG. 12, when the film has very low net melting endotherm, a dramatic decrease of mechanical properties, such as modulus, occurred as the temperature was increased above room temperature, 23°C. However, as evident by comparing Example 12 (having a net melting endotherm of 27 J/g) to Example 16 (having a net melting endotherm of 1.7), films with a low net melting endotherm can have a higher tensile strength, higher modulus, and higher elongation.

The thermal properties (e.g. Tg, Tm, net melting endotherm) can be determined by the DSC test method described in the examples. Such test can be conducted on a bulk composition or a film. However, since the thermal history is erased, the Tg is indicative of the composition.

The first heating scan is used to determine the melting temperature (Tm) and net melting endotherm ΔH_{nm1} . When the composition comprises a sufficient amount of semicrystalline PLA and nucleating agent, and the film has been annealed; the net melting endotherm ΔH_{nm1} of the film is typically 10 J/g or greater. However, when the

composition has little or no semi-crystalline PLA, lacks nucleating agent, and/or the film has not been annealed (i.e. unannealed), the net melting endotherm ΔH_{m1} of the film is typically less than 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1 J/g. When the composition comprises a sufficient amount of semicrystalline PLA and nucleating agent and the low net melting endotherm is due to the film not being annealed, the film can be (e.g. post) annealed, thereby raising the net melting endotherm. Such annealing can be conducted 1 day, 1 month, 3 months, 6 months, and even 1, 2, 3, 4, or 5 years after manufacture of the unannealed film. In some instances, post-annealing will raise the net melting endotherm to 10 J/g or greater. In other instances, the net melting endotherm after post-annealing is zero or less than 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1 J/g.

The first PLA-based film can be evaluated utilizing standard tensile testing as further described in the forthcoming examples (e.g. using a rate of 1 inch (2.5 cm)/minute (100% strain/minute) or 6 inches (15.2 cm)/minute (600% strain/min)). The tensile strength of the film is typically at least 5 or 10 MPa and typically less than the tensile strength of the PLA and second (e.g. polyvinyl acetate) polymer utilized to make the film. In some embodiments, the tensile strength is no greater than 45, 44, 43, 42, 41, 40, 39, 38, 37, 36, 35, 34, 33, 32, 31, or 30 MPa. In some embodiments, the tensile strength is at least 15, 16, 17, 18, 19, or 20 MPa. The elongation of the film is typically greater than that of PLA and second (e.g. polyvinyl acetate) polymer utilized to make the film. In some embodiments, the elongation is at least 30, 40 or 50%. In other embodiments, the elongation is at least 100%, 125%, 150%, 175%, 200%, 225%, 250%, 275%, or 300%. In some embodiments, the elongation is no greater than 650%, 600%, 550%, 500%, 450%, or 400%. In some embodiments, the elongation is no greater than 375%, 350%, 300%, 275%, or 250%. The tensile modulus of the film is typically at least 1, 5, 10, 50, 100, or 150 MPa. In some embodiments, the tensile modulus is at least 200, 250, 300, 350, 400, 450, 500, or 550 MPa. In some embodiments, the tensile modulus is no greater than 1500 MPa, 1400 MPa, 1300 MPa, 1200 MPa, 1100 MPa, 1000 MPa, 750 MPa, 650 MPa, 600 MPa, 550 MPa, 500 MPa, 450 MPa, or 400 MPa.

In some embodiments, the first PLA-based film layer is transparent having a transmission of visible light of at least 90 percent. When the first film layer is transparent, it can be utilized as any layer within the film, such as a backing, cover film, or intermediate layer (i.e. a layer between the outermost layers). In other embodiments, the

first PLA-based film layer is opaque (e.g. white) or reflective and typically utilized as a backing or intermediate layer.

The film may optionally comprise a second (e.g. film) layer proximate the first film layer. In typical embodiments, the second layer is different than the first film layer.

5 When the second layer is transparent having a transmission of visible light of at least 90 percent, it can be utilized as any layer of the (e.g. graphic) article such as a backing, cover film, or intermediate layer. When the second (e.g. film) layer is opaque (e.g. white) or reflective, it is typically utilized as a backing or intermediate layer. The (e.g. graphic) film can comprise more than one second layer. In one embodiment, a PLA-based film, as
10 described herein, is utilized as a backing and a cover film with a graphic disposed between the backing and cover film.

The second layer may be in contact with the first film layer or a primer or adhesion-promoting treatment may be disposed between the first film layer and the second (e.g. film). In some embodiments, a layer of an adhesive composition is proximate the
15 first PLA-based film layer or a second (e.g. film) layer. The adhesive is typically disposed directly on the first film layer or the second layer. Alternatively, a primer or adhesion promoting treatment may be disposed between the first film layer or second layer and the adhesive layer.

The (e.g. graphic) article may be a tape or sheet further comprising a (e.g. pressure
20 sensitive) adhesive. For example, the PLA-based film 101 can be characterized as a backing film (as depicted in FIG. 1) comprising a graphic 110 disposed on one major surface and a (e.g. pressure sensitive) adhesive disposed on the opposing major surface 106 of the backing. The pressure sensitive adhesive typically further comprises a removable release liner.

25 In another embodiment, a sufficiently transparent layer of an adhesive composition may be disposed between the first film layer and a second (e.g. film) layer. The first film layer may be a backing, a cover film, or both the backing and the cover film. The graphic is typically positioned beneath the cover film or beneath the adhesive and cover film. Thus, the graphic is viewed through the cover film and optionally through the adhesive.

30 The PLA-based film may be subjected to customary surface treatments for better adhesion with the adjacent pressure sensitive adhesive layer. Surface treatments include for example exposure to ozone, exposure to flame, exposure to a high-voltage electric

shock, treatment with ionizing radiation, and other chemical or physical oxidation treatments. Chemical surface treatments include primers. Examples of suitable primers include chlorinated polyolefins, polyamides, and modified polymers disclosed in U.S. Pat. Nos. 5,677,376, 5,623,010 and those disclosed in WO 98/15601 and WO 99/03907, and other modified acrylic polymers. In one embodiment, the primer is an organic solvent based primer comprising acrylate polymer, chlorinated polyolefin, and epoxy resin as available from 3M Company as “3M™ Primer 94”.

Various (e.g. pressure sensitive) adhesives can be applied to the PLA-based film such as natural or synthetic rubber-based pressure sensitive adhesives, acrylic pressure sensitive adhesives, vinyl alkyl ether pressure sensitive adhesives, silicone pressure sensitive adhesives, polyester pressure sensitive adhesives, polyamide pressure sensitive adhesives, poly- α -olefins, polyurethane pressure sensitive adhesives, and styrenic block copolymer based pressure sensitive adhesives. Pressure sensitive adhesives generally have a storage modulus (E') as can be measured by Dynamic Mechanical Analysis at room temperature (25°C) of less than 3×10^6 dynes/cm at a frequency of 1 Hz.

In certain embodiments, the pressure sensitive adhesive may be natural-rubber-based, meaning that a natural rubber elastomer or elastomers make up at least about 20 wt. % of the elastomeric components of the adhesive (not including any filler, tackifying resin, etc.). In further embodiments, the natural rubber elastomer makes up at least about 50 wt. %, or at least about 80 wt. %, of the elastomeric components of the adhesive. In some embodiments, the natural rubber elastomer may be blended with one or more block copolymer thermoplastic elastomers (e.g., of the general type available under the trade designation KRATON from Kraton Polymers, Houston, TX). In specific embodiments, the natural rubber elastomer may be blended with a styrene-isoprene radial block copolymer), in combination with natural rubber elastomer, along with at least one tackifying resin. Adhesive compositions of this type are disclosed in further detail in US Patent Application Publication 2003/0215628 to Ma et al., incorporated by reference.

The pressure sensitive adhesives may be organic solvent-based, a water-based emulsion, hot melt (e.g. such as described in US 6,294,249), heat activatable, as well as an actinic radiation (e.g. e-beam, ultraviolet) curable pressure sensitive adhesive. The heat activatable adhesives can be prepared from the same classes as previously described for the pressure sensitive adhesive. However, the components and concentrations thereof are

selected such that the adhesive is heat activatable, rather than pressure sensitive, or a combination thereof.

In some embodiments, the adhesive layer is a repositionable adhesive layer. The term "repositionable" refers to the ability to be, at least initially, repeatedly adhered to and removed from a substrate without substantial loss of adhesion capability. A repositionable adhesive usually has a peel strength, at least initially, to the substrate surface lower than that for a conventional aggressively tacky PSA. Suitable repositionable adhesives include the adhesive types used on CONTROLTAC Plus Film brand and on SCOTCHLITE Plus Sheeting brand, both made by Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, USA.

The adhesive layer may also be a structured adhesive layer or an adhesive layer having at least one microstructured surface. Upon application of film article comprising such a structured adhesive layer to a substrate surface, a network of channels or the like exists between the film article and the substrate surface. The presence of such channels or the like allows air to pass laterally through the adhesive layer and thus allows air to escape from beneath the film article and the surface substrate during application.

Topologically structured adhesives may also be used to provide a repositionable adhesive. For example, relatively large scale embossing of an adhesive has been described to permanently reduce the pressure sensitive adhesive/substrate contact area and hence the bonding strength of the pressure sensitive adhesive. Various topologies include concave and convex V-grooves, diamonds, cups, hemispheres, cones, volcanoes and other three dimensional shapes all having top surface areas significantly smaller than the base surface of the adhesive layer. In general, these topologies provide adhesive sheets, films and tapes with lower peel adhesion values in comparison with smooth surfaced adhesive layers. In many cases, the topologically structured surface adhesives also display a slow build in adhesion with increasing contact time.

An adhesive layer having a microstructured adhesive surface may comprise a uniform distribution of adhesive or composite adhesive "pegs" over the functional portion of an adhesive surface and protruding outwardly from the adhesive surface. A film article comprising such an adhesive layer provides a sheet material that is repositionable when it is laid on a substrate surface (See U.S. Pat. No. 5,296,277). Such an adhesive layer also requires a coincident microstructured release liner to protect the adhesive pegs during

storage and processing. The formation of the microstructured adhesive surface can be also achieved for example by coating the adhesive onto a release liner having a corresponding micro-embossed pattern or compressing the adhesive, e.g. a PSA, against a release liner having a corresponding micro-embossed pattern as described in WO 98/29516.

5 If desired, the adhesive layer may comprise multiple sub-layers of adhesives to give a combination adhesive layer assembly. For example, the adhesive layer may comprise a sub-layer of a hot-melt adhesive with a continuous or discontinuous overlayer of PSA or repositionable adhesive.

10 The acrylic pressure sensitive adhesives may be produced by free-radical polymerization technique such as solution polymerization, bulk polymerization, or emulsion polymerization. The acrylic polymer may be of any type such as a random copolymer, a block copolymer, or a graft polymer. The polymerization may employ any of polymerization initiators and chain-transfer agents generally used.

15 The acrylic pressure sensitive adhesive comprises polymerized units of one or more (meth)acrylate ester monomers derived from a (e.g. non-tertiary) alcohol containing 1 to 14 carbon atoms and preferably an average of 4 to 12 carbon atoms. Examples of monomers include the esters of either acrylic acid or methacrylic acid with non-tertiary alcohols such as ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 1-hexanol, 2-hexanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol; 3,5,5-trimethyl-1-hexanol, 3-heptanol, 1-octanol, 2-octanol, isooctylalcohol, 2-ethyl-1-hexanol, 1-decanol, 2-propylheptanol, 1-dodecanol, 1-tridecanol, 1-tetradecanol, and the like.

20 The acrylic pressure sensitive adhesive comprises polymerized units of one or more low T_g (meth)acrylate monomers, i.e. a (meth)acrylate monomer when reacted to form a homopolymer has a T_g no greater than 0°C. In some embodiments, the low T_g monomer has a T_g no greater than -5°C, or no greater than -10°C. The T_g of these homopolymers is often greater than or equal to -80°C, greater than or equal to -70°C, greater than or equal to -60°C, or greater than or equal to -50°C.

30 The low T_g monomer may have the formula



wherein R¹ is H or methyl and R⁸ is an alkyl with 1 to 22 carbons or a heteroalkyl with 2 to 20 carbons and 1 to 6 heteroatoms selected from oxygen or sulfur. The alkyl or heteroalkyl group can be linear, branched, cyclic, or a combination thereof.

Exemplary low Tg monomers include for example ethyl acrylate, n-propyl
5 acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, n-pentyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-methylbutyl acrylate, 2-ethylhexyl acrylate, 4-methyl-2-pentyl acrylate, n-octyl acrylate, 2-octyl acrylate, isooctyl acrylate, isononyl acrylate, decyl acrylate, isodecyl acrylate, lauryl acrylate, isotridecyl acrylate, octadecyl acrylate, and dodecyl acrylate.

10 Low Tg heteroalkyl acrylate monomers include, but are not limited to, 2-methoxyethyl acrylate and 2-ethoxyethyl acrylate.

In typical embodiments, the acrylic pressure sensitive adhesive comprises polymerized units of at least one low Tg monomer(s) having an alkyl group with 6 to 20 carbon atoms. In some embodiments, the low Tg monomer has an alkyl group with 7 or 8
15 carbon atoms. Exemplary monomers include, but are not limited to, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, as well as esters of (meth)acrylic acid with an alcohol derived from a renewable source, such as 2-octyl (meth)acrylate.

The acrylic pressure sensitive adhesive typically comprises at least 50, 55, 60, 65,
20 70, 75, 80, 85, 90 wt-% or greater of polymerized units of monofunctional alkyl (meth)acrylate monomer having a Tg of less than 0°C, based on the total weight of the polymerized units (i.e. excluding inorganic filler or other additives).

The acrylic pressure sensitive adhesive may further comprise at least one high Tg monomer, i.e. a (meth)acrylate monomer when reacted to form a homopolymer has a Tg
25 greater than 0°C. The high Tg monomer more typically has a Tg greater than 5°C, 10°C, 15°C, 20°C, 25°C, 30°C, 35°C, or 40°C. High Tg monofunctional alkyl (meth)acrylate monomers including for example, t-butyl acrylate, methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, s-butyl methacrylate, t-butyl methacrylate, stearyl methacrylate, phenyl methacrylate, cyclohexyl
30 methacrylate, isobornyl acrylate, isobornyl methacrylate, norbornyl (meth)acrylate, benzyl methacrylate, 3,3,5 trimethylcyclohexyl acrylate, cyclohexyl acrylate, N-octyl acrylamide, and propyl methacrylate or combinations.

The acrylic pressure sensitive adhesive may further comprise polymerized units of polar monomers. Representative polar monomers include for example acid-functional monomers (e.g. acrylic acid, methacrylic acid), hydroxyl functional (meth)acrylate) monomers, nitrogen-containing monomers (e.g. acrylamides), and combinations thereof.

5 In some embodiments, the acrylic pressure sensitive adhesive comprises at least 0.5, 1, 2 or 3 wt-% and typically no greater than 10 wt-% of polymerized units of polar monomers, such as acrylamide and/or acid-functional monomers such as (meth)acrylic acid.

The pressure sensitive adhesive may further include one or more suitable additives according to necessity. The additives are exemplified by crosslinking agents (e.g. multifunctional (meth)acrylate crosslinkers (e.g. TMPTA), epoxy crosslinking agents, isocyanate crosslinking agents, melamine crosslinking agents, aziridine crosslinking agents, etc.), tackifiers (e.g., phenol modified terpenes and rosin esters such as glycerol esters of rosin and pentaerythritol esters of rosin, as well as C5 and C9 hydrocarbon tackifiers), thickeners, plasticizers, fillers, antioxidants, ultraviolet absorbers, antistatic agents, surfactants, leveling agents, colorants, flame retardants, and silane coupling agents.

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The (e.g. pressure sensitive) adhesive layer may be disposed upon the film by various customary coating methods (e.g. gravure) roller coating, flow coating, dip coating, spin coating, spray coating, knife coating, (e.g. rotary or slit) die coating, (e.g. hot melt) extrusion coating, and printing. The adhesive may be applied directly to the PLA film described herein or transfer coated by use of release liner. When a release liner is used, the adhesive is either coated on the liner and laminated to the film or coated on the film and the release liner subsequently applied to the adhesive layer. The adhesive layer may be applied as a continuous layer, or a patterned, discontinuous layer. The adhesive layer typically has a thickness of about 5 to about 50 micrometers.

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The release liner typically comprises paper or film, which has been coated or modified with compounds of low surface energy such as organosilicone compounds, fluoropolymers, polyurethanes and polyolefins. The release liner can also be a polymeric sheet produced from polyethylene, polypropylene, PVC, polyesters with or without the addition of adhesive-repellant compounds. As mentioned above, the release liner may have a microstructured or micro-embossed pattern for imparting a structure to the adhesive layer.

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In some embodiments, the sheet or tape (e.g. graphic) articles comprise a low adhesion backsize provided on first major exposed surface of a PLA-based film, such that when the sheet or tape is in roll, the outwardmost (exposed) surface of the pressure-sensitive adhesive comes in contact with the low adhesion backsize. In one embodiment, the PLA-based film is a cover film. In this embodiment, the graphic does not come in contact with the low adhesion backsize.

Various low adhesion backsize compositions have been described in the art such as, for example, silicone, polyethylene, polycarbamate, polyacrylics, and the like.

The composition of low adhesion backsize is chosen (e.g., in combination with the composition of pressure-sensitive adhesive to provide an appropriate level of release. In some embodiments, the low adhesion backsize may also provide an enhanced ability to anchor paint which is deposited thereupon, just as described in US 2014/0138025.

General categories of exemplary materials which may be suitable for inclusion in low adhesion backsize include e.g. (meth)acrylic polymers, urethane polymers, vinyl ester polymers, vinyl carbamate polymers, fluorine-containing polymers, silicone-containing polymers, and combinations thereof.

In some embodiments, the low adhesion backsize is an organic solvent-based solution or a water-based emulsion.

In some embodiments, low adhesion backsize may comprises an acrylic composition that may be prepared from the same (meth)acrylate monomers as the acrylic adhesive. However, the low adhesion backsize composition typically comprises a lower concentration of low Tg monomer, such as octadecyl acrylate and a higher amount of high Tg monomer such as acrylic acid. In some embodiments, the low adhesion backsize comprises at least 40, 45 or 50 wt.-% ranging up to about 60 wt-% of polymerized units of low Tg monomer such as octadecyl acrylate. The weight percentages in connection with the low adhesion backsize described herein are with respect to the total solids not including any organic or aqueous solvent unless otherwise noted.

Such compositions are described in further detail in U.S. Patent 3,011,988 to Luedke et al., incorporated by reference.

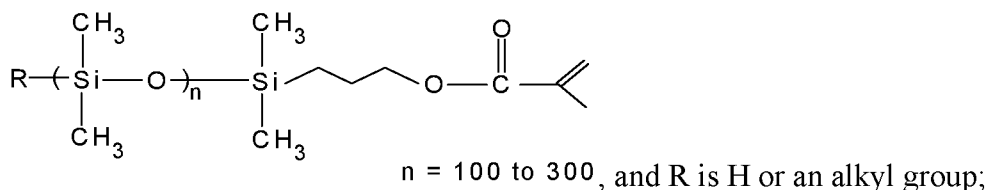
In some embodiments, low adhesion backsize may comprise a discernable crystalline melting point (T_m), e.g. in compositions comprising appreciable quantities of monomer units which give rise to crystalline polymer segments. Such a T_m may be present

instead of, or along with, a T_g . In some embodiments, a T_m , if present, may range between e.g. 20°C and 60°C.

In some embodiments, low adhesion backsize may include at least some (meth)acrylic acid groups. In some embodiments, concentration of (meth)acrylic acid groups is at least 2, 3, 4, or 5 wt.-% ranging up to 10, 15, or 20 wt.-%.

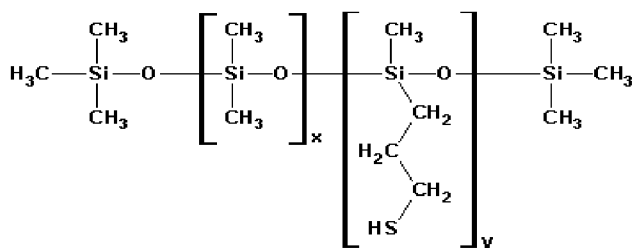
In some embodiments, low adhesion backsize may comprise a silicone-containing material. In various embodiments, such materials may comprise a silicone backbone with non-silicone (e.g., (meth)acrylate) side chains; a non-silicone (e.g., (meth)acrylate) backbone with silicone side chains; a copolymer backbone comprising silicone units and non-silicone (e.g., (meth)acrylate) units; and the like. Silicone-polyurea materials, silicone-polyurea-polyurethane materials, silicone-polyoxamide materials, siloxane-iniferter-derived compositions, and the like, may also be suitable.

In a certain embodiments, the silicone-containing material of low adhesion backsize comprises a reaction product of a vinyl-functional silicone macromer having the general formula of Formula I:



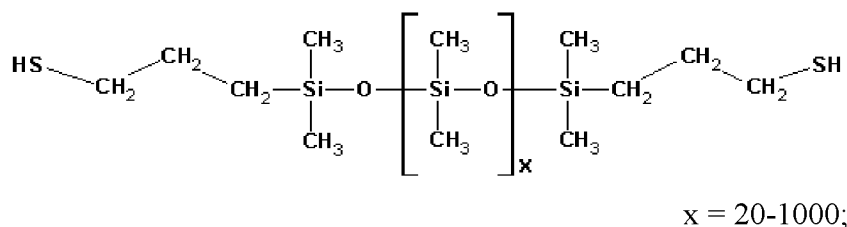
Formula I

In certain embodiments, the silicone-containing material of low adhesion backsize comprises a reaction product of a mercapto-functional silicone macromer having the general formula of Formula IIa, IIb, or IIc or mixtures thereof:



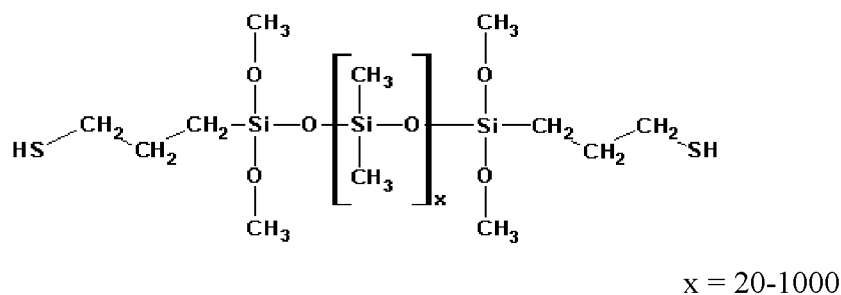
$x = 20-1000$ and $y = 1-10$;

Formula IIa



Formula IIb

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Formula IIc

10 Further details of mercapto-functional silicone macromers and of the production of low adhesion backsize compositions using such macromers can be found in U.S. Patent 5,032,460 to Kantner et al., which is incorporated by reference herein.

In various embodiments, any of the above silicone macromers may be used in combination with meth(acrylic) monomers and/or with any other vinyl monomers. Such monomers may be chosen, for example, in order to achieve any of the above-discussed
 15 glass transition temperature ranges. In some embodiments, the silicone macromer (e.g. of Formula IIa) may be used, at approximately 15-35 weight percent of the total reactants, with the balance of the reactants including at least one high T_g (meth)acrylic monomer, at least one low T_g (meth)acrylic monomer, and at least one (meth) acrylic acid monomer. In
 20 specific embodiments, the low T_g monomer is methyl acrylate, the high T_g monomer is methyl methacrylate, and the (meth)acrylic acid monomer is methacrylic acid. In further embodiments, in such compositions the silicone macromer (e.g. of Formula IIa) is used at approximately 20-30 wt. %.

In some embodiments comprising silicone macromers, the low adhesion backsize
 25 comprises at least 2, 3, 4, or 5 wt.-% of (meth)acrylic acid groups ranging up to 10, 15 or 20 wt.-%.

In some embodiments, the components of pressure-sensitive adhesive and the low adhesion backsize when present are typically chosen to provide good adhesion to a surface, while also being removable under moderate force without leaving a (e.g. visible) residue.

5 In some embodiments, the (e.g. graphic) article described herein further comprises a second layer. The second layer may be a backing disposed between the adhesive and the PLA-based film and/or the second layer may be a transparent cover film disposed on a PLA-based backing film.

10 The backing can comprise a variety of flexible and inflexible (e.g. preformed web) substrates including but not limited to polymeric films, metal foils, foams, paper, and combinations thereof (e.g. metalized polymeric film). Polymeric films include for example polyolefins such as polypropylene (e.g. biaxially oriented), polyethylene (e.g. high density or low density), polyvinyl chloride, polyurethane, polyester (polyethylene terephthalate), polycarbonate, polymethyl(meth)acrylate (PMMA), polyvinylbutyral,
15 polyimide, polyamide, fluoropolymer, cellulose acetate, cellulose triacetate, ethyl cellulose, as well as bio-based material such as polylactic acid (PLA).

In another embodiment, the first PLA-based film or backing may further comprise a metal or metal oxide layer. Examples of metals include aluminum, silicon, magnesium, palladium, zinc, tin, nickel, silver, copper, gold, indium, stainless steel, chromium,
20 titanium, and so on. Examples of metal oxides used in the metal oxide layer include aluminum oxide, zinc oxide, antimony oxide, indium oxide, calcium oxide, cadmium oxide, silver oxide, gold oxide, chromium oxide, silicon oxide, cobalt oxide, zirconium oxide, tin oxide, titanium oxide, iron oxide, copper oxide, nickel oxide, platinum oxide, palladium oxide, bismuth oxide, magnesium oxide, manganese oxide, molybdenum oxide,
25 vanadium oxide, barium oxide, and so on. These metals and metal oxides may be used singly or in combination of two or more. Layers of these metals and/or metal oxides can be formed by known methods such as vacuum deposition, ion plating, sputtering, and CVD (Chemical Vapor Deposition). The thickness of the metal and/or metal oxide layer is typically at least 5 nm ranging up to 100 or 250 nm.

30 The thickness of the backing is typically at least 10, 15, 20, or 25 microns (1 mil) and typically no greater than 500 microns (20 mil) thickness. In some embodiments, the thickness of the backing is no greater than 400, 300, 200, or 100 microns. The first film

layer and second (e.g. film) layer may have the same thickness as the backing. However, the first and/or second (e.g. film) layer, particularly when utilized in combination with a backing, may be less than 10 microns. In some embodiments, the first and/or second film layer is typically at least 250 nm, 500 nm, 750 nm or 1 micron. The backing as well as the overall film is typically in the form of a roll-good, but may also be in the form of individual sheets.

In some embodiments, the second (e.g. film) layer is a thermoplastic polymer film such as polycarbonate, polyethylene terephthalate, polyamide, polyethylene, polypropylene, polystyrene, polyvinyl chloride, poly(meth)acrylic polymers, ABS (acrylonitrile-butadiene-styrene copolymer) resins, and the like.

In some embodiments, the overall film, first film layer, cover film and/or backing is conformable. By “conformable” it is meant that the film or film layer is sufficiently soft and flexible such that it accommodates curves, depressions, or projections on a substrate surface so that the film may be stretched around curves or projections, or may be pressed down into depressions without breaking or delaminating the film. It is also desirable that the film does not delaminate or release from the substrate surface after application (known as popping-up).

Suitable conformable second film layers include, for example, polyvinyl chloride (PVC), plasticized polyvinyl chloride, polyurethane, polyethylene, polypropylene, fluoropolymer or the like. Other polymer blends are also potentially suitable, including for example thermoplastic polyurethane and a cellulose ester.

In some embodiments, the film is sufficiently conformable such that it is “transversely curvable” meaning that the tape can be curved into a continuous curved shape (e.g. with a radius of curvature of 7.5 cm) that lies in a generally flat plane, without through-tearing of the stretched area of the curved portion of the tape. An example of a transversely curvable tape is depicted in Fig. 15 of US2014/0138025.

The adhesive coated (e.g. graphic) articles can exhibit good adhesion to both smooth and rough surfaces. Various rough surfaces are known including for example textured drywall, such as “knock down” and “orange peel”; cinder block, rough (e.g. Brazilian) tile and textured cement. Smooth surfaces, such as stainless steel, glass, and polypropylene have an average surface roughness (Ra) as can be measured by optical interferometry of less than 100 nanometer; whereas rough surfaces have an average surface

roughness greater than 1 micron (1000 nanometers), 5 microns, or 10 microns. Sealed cement can have a rough or smooth surface depending on the thickness of the sealer. Cement sealers typically comprise polyurethane, epoxy resin, sodium silicate, or methacrylate.

5 In some favored embodiments, the film is a graphic film used to apply designs, e.g. images, graphics, text and/or information (such as a code), on windows, buildings, pavements or vehicles such as autos, vans, buses, trucks, streetcars and the like for e.g. advertising or decorative purposes. Such designs, images, text, etc. will collectively be referred to herein as a “graphic”. Many of the surfaces, e.g. vehicles, are irregular and/or
10 uneven. In one embodiment, the graphic film is a decorative tape.

 In some embodiments, the article is a floor marking graphic film tape that is typically adhered to (e.g. sealed) cement or other flooring surface.

 The method of making a (e.g. graphic) film typically comprises providing a first PLA-based film, as described herein; and providing a graphic on the film. In some
15 embodiments, the PLA-based film is typically annealed prior to providing a graphic film (e.g. prior to printing). The film can be annealed at the time of manufacture or just prior to providing a graphic on the film, such as by printing. The annealing conditions can vary, ranging from 120°F from about 12 hours to 200°F for about 20 minutes. In some
20 embodiments, the storage and/or transport environment of the film provides sufficient annealing. In other embodiments, the PLA-based film is unannealed at the time of manufacture. Further, the PLA-based film may be unannealed prior to providing a graphic film (e.g. prior to printing). In one embodiment, the first film layer has a net melting endotherm for the first heating scan, ΔH_{nm1} , of less than 10 J/g at the time of manufacture and/or printing.

25 Various methods may be used to provide a graphic on the film. Typical techniques include for example ink jet printing, thermal mass transfer, flexography, dye sublimation, screen printing, electrostatic printing, offset printing, gravure printing or other printing processes.

 The graphic may be a single color or may be multi-colored. In the case of security
30 markings, the graphic may be unapparent when viewed with wavelengths of the visible light spectrum. The graphic can be a continuous or discontinuous layer.

With reference to FIG. 1, the graphic article 100 comprises a graphic 110 proximate a major surface of the first PLA-based film layer 101. The first film layer (101, 201, 301, 401, 501, 601, 701, 801) can be a monolithic film or a film layer comprising a semicrystalline polylactic acid polymer, a second (e.g. polyvinyl acetate polymer) having a Tg of at least 25°C, and plasticizer, as previously described. In another embodiment, with reference to FIG. 2, the graphic 210 of graphic article 200 may be disposed upon an (e.g. clear) ink-receptive (e.g. coating) layer 220. In this embodiment, the ink-receptive (e.g. coating) layer 220 is disposed on and typically in contact with the first film layer 201. Although not shown, each of the embodiments of FIGs. 3-8 may optionally further comprise an ink-receptive layer between the graphic and first film layer. The graphic (110, 210, 310, 410, 510, 610, 710) is typically permanently bonded to the first film layer or ink receptive layer 220.

The ink-receptive layer may be characterized as a primer for the ink. In some embodiments, the ink receptive layer can be characterized as a clear or colorless ink. Various other ink-receptive (e.g. coating) layers are known including those described in US 7,025,453; US 6,881,458; and US 6,846,075; incorporated herein by reference. Transparent ink can be utilized as an ink-receptive layer.

In some embodiments, the first PLA-based film layer (101, 201, 501, 601, 701, 801) can be characterized as a backing. The opposing major surface of the first film layer (e.g. 106 of FIG. 1) is typically bonded to a target surface by means of a (e.g. pressure sensitive) adhesive. The pressure sensitive adhesive is typically covered by a removable release liner as previously described.

In another embodiment, the first PLA-based film layer (301, 401, 601) can be characterized as a cover film. A (e.g. reverse imaged) graphic (310, 410, 610) is viewed through the cover film.

The graphic article can further comprise additional second layers, as previously described.

In one embodiment, as depicted in FIG. 3, the graphic article 300 comprises a first PLA-based film layer 301 (e.g. cover film), graphic 310 proximate a major surface of a first film layer 301, and a backing 350 disposed on the opposing surface of graphic 310.

In another embodiment, as depicted in FIG. 4, the graphic article 400 comprises a first PLA-based film layer 401 (e.g. cover film), graphic 410 proximate a major surface of

a first film layer 401, a (e.g. pressure sensitive) adhesive 430 bonding the (e.g. reversed-imaged) film (401 together with 410) to backing 450.

In another embodiment, as depicted in FIG. 5, the graphic article 500 comprises a first PLA-based film layer 501, graphic 510 proximate a major surface of a first film layer 501, and a topcoat or cover film 550 disposed on the opposing surface of graphic 510.

In another embodiment, as depicted in FIG. 6, the graphic article 600 comprises a first PLA-based (e.g. opaque) film layer 601b, graphic 610 proximate a major surface of a first film layer 601, a (e.g. pressure sensitive) adhesive 630 bonding a (e.g. sufficiently transparent) first PLA-based film layer (e.g. cover film) 601a to the opposing surface of graphic 610.

In another embodiment, as depicted in FIG. 7, the graphic article 700 comprises a (e.g. sufficiently transparent) first PLA-based film layer 701a (e.g. cover film), a (e.g. reverse-imaged) graphic 710 proximate a major surface of the first film layer 701a, a (e.g. pressure sensitive) adhesive 730 bonding the (e.g. reversed-imaged) film (701 together with 710) to first film layer (e.g. backing) 701b.

In the embodiments of FIG. 6-7, the first film layers (e.g. backing) 601b and 701b, and (e.g. sufficiently transparent) cover films 601a and 701a comprise a semicrystalline polylactic acid polymer, second (e.g. polyvinyl acetate) polymer having a Tg of at least 25°C, and plasticizer, as previously described.

The backing (e.g. 350, 450) may be any of the flexible and inflexible substrates, as previously described. In some embodiments, the backing is a conformable film layer, as previously described. Further, the topcoat or cover film 550 may also be any of the sufficiently transparent (e.g. low surface energy) hardcoats, conformable films, etc. as previously described. In one embodiment, the topcoat comprise a transparent ink applied over a (e.g. colored) graphic.

In each of the embodiments of FIG. 1-7, the graphic is disposed upon the first film layer comprising a semicrystalline polylactic acid polymer, second (e.g. polyvinyl acetate) polymer having a Tg of at least 25°C, and plasticizer, as previously described; or the graphic is disposed on an ink receptive layer, wherein the ink receptive layer is disposed on the PLA-based film.

However, in other embodiments, the graphic is disposed upon a second film, the second film does not comprise a semicrystalline polylactic acid polymer, a second (e.g.

polyvinyl acetate) polymer having a Tg of at least 25°C, and plasticizer; as described herein. Alternatively, the graphic is disposed on an ink receptive layer, wherein the ink receptive layer is disposed on the second film. The second film is then bonded to a PLA-based film as described herein. For example, in one embodiment, as depicted in FIG. 8, the graphic article 800 comprises a (e.g. sufficiently transparent) cover film 850, a (e.g. reverse-imaged) graphic 810 proximate a major surface of the cover film 850, a (e.g. pressure sensitive) adhesive 830 bonding the (e.g. reverse-imaged) cover film (850 together with 810) to first film layer (e.g. backing) 801. In this embodiment, the first film layer 801 comprises a PLA-based film, as described herein, and the cover film 850 comprises a different polymeric material, such as a different conformable film.

In another embodiment, not shown, the graphic film is the same as FIG. 4 except that the order of graphic 410 and adhesive 430 are switched with each other. The graphic film comprises a second (e.g. backing) film 450 comprising a graphic bonded with an adhesive to a first film layer (e.g. cover film) comprising a PLA-based film, as described herein.

Various other arrangements can be made wherein the graphic film comprises a PLA-based film, as described herein, in combination with a graphic.

The graphic typically comprises a dried and or cured ink layer. The dried ink layer can be derived from a wide variety of ink compositions including for example an organic solvent-based ink or water-based ink. The dried and cured ink layer can also be derived from a wide variety of radiation (e.g. ultraviolet) curable inks.

Colored inks typically comprise a colorant, such as a pigment and/or dye dispersed in a liquid carrier. The liquid carrier may comprise water, an organic monomer, a polymerizable reactive diluent in the case of radiation curable inks, or a combination thereof. For example, latex inks typically comprise water and (e.g. non-polymerizable) organic cosolvent.

A wide variety of organic and inorganic pigments are known in the art for use in inks. Suitable pigments include, but are not limited to, azo pigments such as condensed and chelate azo pigments; polycyclic pigments such as phthalocyanines, anthraquinones, quinacridones, thioindigoids, isoindolinones, and quinophthalones; nitro pigments; daylight fluorescent pigments; carbonates; chromates; titanium oxides; zinc oxides; iron oxides and carbon black. In one embodiment, the pigment is other than a white pigment,

such as titanium dioxide. Pigments employed in the ink composition can include carbon black and pigments capable of generating a cyan, magenta and yellow ink. Suitable commercially available pigments include, for example, Pigment Red 81, Pigment Red 122, Pigment Yellow 13, Pigment Yellow 14, Pigment Yellow 17, Pigment Yellow 74,
5 Pigment Yellow 83, Pigment Yellow 128, Pigment Yellow 138, Pigment Orange 5, Pigment Orange 30, Pigment Orange 34, Pigment Blue 15:4 and Pigment Blue 15:3.

In some embodiments, such as ink jet printing inks, the pigment dispersion particles are sufficiently small to permit free flow of the ink through the ink jet printing device, and particularly the ink jet print nozzles, which typically have diameters in the
10 range of from about 10 to about 50 microns, and more typically no greater than about 30 microns. In some embodiments, the pigment dispersion particles have diameter ranging from 50 nm to about 200 nm, and more typically no greater than 120 nm. Screen printing inks as well as materials utilized in other printing techniques as previously described, may utilize larger pigment particles. However, smaller sized pigment particles typically can
15 also provide maximum color strength.

The organic solvent of the ink may be a single solvent or a blend of solvents. Suitable solvents include alcohols such as isopropyl alcohol (IPA) or ethanol; ketones such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), diisobutyl ketone (DIBK); cyclohexanone, or acetone; ethers such as tetraethylene glycol dimethyl ether and
20 dialkylene glycol dialkyl ether including diethylene glycol diethyl ether; aromatic hydrocarbons such as toluene; isophorone; butyrolactone; N-methylpyrrolidone; tetrahydrofuran; esters such as lactates, acetates, including ethyl 3-ethoxypropionate and propylene glycol monomethyl ether acetate such as commercially available from 3M under the trade designation "3M Scotchcal Thinner CGS10" ("CGS10"), 2-butoxyethyl
25 acetate such as commercially available from 3M under the trade designation "3M Scotchcal Thinner CGS50" ("CGS50"), diethylene glycol ethyl ether acetate (DE acetate), ethylene glycol butyl ether acetate (EB acetate), dipropylene glycol monomethyl ether acetate (DPMA), iso-alkyl esters such as isohexyl acetate, isoheptyl acetate, isooctyl acetate, isononyl acetate, isodecyl acetate, isododecyl acetate, isotridecyl acetate or other
30 iso-alkyl esters; combinations of these and the like.

Ink compositions, especially those that are durable for outdoor use, typically further comprise a polymeric binder. Binders are typically compatible with pigment

particles such that upon evaporation of volatile components of the ink, the binders form films of the deposited pigments on the first film layer. Suitable binders include vinyl-containing polymers, acrylic-containing polymers, urethane-containing polymers, mixtures thereof, as well as binders that contain more than one type of such moieties, such as both urethane and (meth)acrylate moieties. In the case of radiation curable inks, the binder may be formed from the polymerization of the reactive diluent during curing of the ink.

In some embodiments, the ink layer is an ink-jet printed layer. Ink jet printing is a method of printing by spraying droplets of ink through computer-controlled nozzles. Ink jet printing ink typically has a viscosity ranging from about 3 to about 30 centipoise at the printhead operating temperature. Such inks preferably have a viscosity below about 25 or 20 centipoise at the desired ink jetting temperature (typically from ambient temperature up to about 65°C.). Ink jet compositions characteristically have moderate to low surface tension properties. Preferred formulations have a surface tension in the range of from about 20 mN/m to about 50 mN/m and more preferably in the range of from about 22 mN/m to about 40 mN/m at the printhead operating temperature. Further, ink jet inks typically have Newtonian or substantially Newtonian viscosity properties.

Inkjet printing principally relies on the use of four colors: cyan, magenta, yellow, and black (CMYK). However, to improve resolution of images, some printers identified above also add two additional colors that are less concentrated relatives of the cyan and magenta inks, called "light cyan" and "light magenta."

In one embodiment, the ink jet ink is a solvent-based ink comprising 1 to 5 part by weight colorant (e.g. pigment), 1 to 10 parts of oligomeric or polymeric binder, and up to 115 parts of various organic solvents as previously described including for example diethylene glycol diethyl ether, γ -butyrolactone, tetraethylene glycol dimethyl ether, and dialkylene glycol dialkyl ether. In one embodiment, the ink jet ink comprises (e.g. 40-50 wt.-%) diethylene glycol diethyl ether, (e.g. less than 20 wt.-%) γ -butyrolactone, (e.g. 10-20 wt.-%) tetraethylene glycol dimethyl ether, and (15-25 wt.-%) dialkylene glycol dialkyl ether.

In another embodiment, the ink jet ink may be a water-based ink or in other words an aqueous ink jet ink. The liquid medium typically comprises at least 50%, 60%, 70%, or 80% by weight distilled and/or deionized water and may comprise water in combination with one or more water-miscible organic solvents.

In one embodiment, the liquid medium of the aqueous ink jet ink comprises (e.g. 60-90%) water, no greater than 15% of an organic solvent, such as 2-pyrrolidone, and no greater than 5% of colorant, such as carbon black.

In other embodiments, the aqueous ink jet ink further comprises a polymeric binder, such as a latex binder, typically formed by emulsion polymerization. In one embodiment, the latex binder is formed by emulsion polymerization of a first monomer, having a higher glass transition temperature T_g , and a second monomer having a lower glass transition temperature T_g . The glass transition temperature of a monomer refers more specifically to the glass transition temperature of a homopolymer formed from the particular monomer. In one embodiment, the latex binder is formed from first monomer having a glass transition temperature T_g greater than about 70°C. The first monomer may comprise styrene, substituted styrene, methyl methacrylate or a mixture thereof. Substituted styrenes include alkyl-substituted styrenes, halogen-substituted styrenes and the like. In a preferred embodiment, the first monomer, or mixture thereof, has an average glass transition temperature T_g of about 100°C., or greater. The second monomer of the latex binder typically has a glass transition temperature T_g less than about 0°C. The second monomer may comprise an alkyl acrylate such as ethyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, ethylhexyl acrylate and the like. In some embodiments, the second monomer has a glass transition temperature T_g less than about -25°C. or -50°C. The ratio of the first and second monomers may be varied so that the latex binder has a glass transition temperature T_g in the range of from about 0°C. to 70°C.

The reaction medium for preparing the latex binder may employ a charge stabilizing agent and/or an emulsifier in order to obtain the desired particle size. The latex binder typically has an average particle size from 20 nm to 500 nm, and in some embodiments from 100 nm to 300 nm. The latex binder may have a weight average molecular weight ranging from 10,000 to 5,000,000 g/mole. Various charge stabilizing agents are known such as methacrylic acid, acrylic acid, and/or a (e.g. sodium) salt thereof. Various emulsion polymerization emulsifiers are also known such as a fatty (e.g. lauryl) acid ether sulfate.

The latex ink composition also typically comprise a dispersant and/or a humectant (also referred to as a cosolvent). Non-polymeric dispersants include naphthalene sulfonic acid, sodium lignosulfate, glycerol stearate, as well as phosphate containing surfactants.

Numerous polymeric dispersants are known. Such polymers typically comprise both hydrophilic moieties for aqueous compatibility and hydrophobic moieties for interaction with the pigment are preferred.

5 In one embodiment, the aqueous ink jet ink composition may comprise pigment, co-solvent, dispersant and latex binder. The aqueous composition may comprise 1% to 10%, 15% or 20% pigment; at least 5% or 10% ranging up to 30%, 40% or to 50% co-solvent, 0.01% to 5 or 10% dispersant, and at least 1% or 2% ranging up to 5, 10, 15 or 20% latex binder.

10 Various aqueous latex (e.g. ink jet) ink are known, such as described in US 9,175,181 and US 6,498,202.

"Radiation curable" ink comprises components having functionality directly or indirectly pendant from the backbone that reacts (e.g. crosslinks) upon exposure to a suitable source of curing energy. Suitable radiation crosslinkable groups include epoxy groups, (meth)acrylate groups, olefinic carbon-carbon double bonds, allyloxy groups, 15 alpha-methyl styrene groups, (meth)acrylamide groups, cyanate ester groups, vinyl ethers groups, combinations of these, and the like. Free radically polymerizable groups are typically preferred. Of these, (meth)acryl moieties are most preferred. The term "(meth)acryl", as used herein, encompasses acryl and/or methacryl.

20 The energy source used for achieving crosslinking of the radiation curable functionality may be actinic (e.g., radiation having a wavelength in the ultraviolet (UV) or visible region of the spectrum), accelerated particles (e.g., electron beam (EB) radiation), thermal (e.g., heat or infrared radiation), or the like with UV and EB being preferred. Suitable sources of actinic radiation include mercury lamps, xenon lamps, carbon arc lamps, tungsten filament lamps, lasers, electron beam energy, light emitting diodes, 25 sunlight, and the like.

The radiation curable material may be mono-, di-, tri-, tetra- or otherwise multifunctional in terms of radiation curable moieties. The radiation curable material may be straight-chained, branched, and/or cyclic with branched materials tending to have lower viscosity than straight-chain counterparts of comparable molecular weight.

30 When the radiation curable material is a monomer it may be referred to as a reactive diluent. Various reactive diluents are suitable including acrylate monomers such as hexanedioldiacrylate, tetrahydrofurfuryl acrylate, isobornyl acrylate, ethoxyethoxyethyl

acrylate, propoxylated neopentylglycol diacrylate, and trimethylolpropane triacrylate as well as vinyl monomers such as vinyl caprolactam.

In some embodiments, the radiation curable ink comprises at least 25, 30, 35, 40 wt.-% ranging up to 90 wt.-% or greater of weight percent of such reactive diluent monomers.

The radiation curable ink may optionally further comprise at least 5, 10, 15 or 30 wt.-% ranging up to 50 wt.-% of organic solvent.

In one embodiment, the radiation curable ink comprises (e.g. 30-45 wt.-%) organic solvent such as (tetrahydrofurfuryl) alcohol and a mixture of acrylate and vinyl monomers. For example, the monomers may contain (e.g. 10 to 20 wt.-%) of vinyl caprolactam, (e.g. 10 to 20 wt.-%) isobornyl acrylate, (e.g. 1 to 5 wt.-%) propoxylated neopentyl glycol diacrylate, and (e.g. 1 to 5 wt.-%) cyclic trimethylolpropane formal acrylate.

In other embodiments, the radiation curable ink composition further comprises one or more polymeric binders. The polymeric binder may be an oligomer or macromonomer having a number average molecular weight (Mn) of at least 3,000; 4,000; 5,000, or 6,000 g/mole ranging up to 10,000 or 15,000 g/mole. Alternatively, the polymeric binder may have a higher molecular weight.

In some embodiments, the polymeric binder comprises methylmethacrylate, isobutyl methacrylate or isobutylmethacrylate/isooctylacrylate repeating unit. The polymeric binder may have a methyl/methacrylate repeating unit and a methacrylic acid end group. The polymeric binder may be present in an amount of at least 10, 15, 20, or 25 wt.-% ranging up to 35, 40, 45, 50, 55, or 60 wt.-%. of the ink.

The water-based, solvent-based, and radiation curable ink may comprise a variety of optional additives. Such optional additives include one or more flow control agents, slip modifiers, thixotropic agents, surfactants (e.g. fluorochemical), foaming agents, antifoaming agents (e.g. silica and silicone oil), flow or other rheology control agents, waxes, oils, antioxidants, photoinitiators and photoinitiator stabilizers in the case of radiation curable inks, dispersants, gloss agents, fungicides, bactericides, organic and/or inorganic filler particles, leveling agents, opacifiers, antistatic agents, dispersants, and the like. To enhance durability of the design, image, etc., especially in outdoor environments exposed to sunlight, a variety of commercially available stabilizing chemicals can be

added such as hydrolysis stabilizers, heat stabilizers, UV light stabilizers, and free-radical scavengers.

5 Inorganic fillers such as crystalline and amorphous silica, aluminum silicate, and calcium carbonate, etc. can be included to impart increased surface roughness, reduced gloss and improved dot gain. The concentration of inorganic fillers typically ranges from about 0.1% to about 10% by weight and preferably from about 0.5% to about 5%. The particle size is preferably less than one micron, more preferably less 0.5 microns, and most preferably less than about 0.2 microns.

10 Representative ink jet printing inks include for example HP Latex 360 Printer (HP 83 Inks), Roland XR-640 (Roland ESL4 Eco Inks), and EFI VUTEk GS3250LX Pro (EFI VUTEK GSLXr 3M™ SuperFlex UV Ink).

15 In another embodiment, the graphic comprises a screen printed ink. Screen printing is a method of printing by using a squeegee to force ink through an assembly of mesh fabric and a stencil. Screen printing inks also comprise polymeric binder dispersed in (e.g. 40 to 60 wt.-% of) liquid carrier, colorant (in the case of colored ink) as well as the previously described optional additives and inorganic fillers. However, screen printing inks can utilized higher molecular weight polymeric binders. Further, screen printing ink typically contain over 40% solids and have a viscosity of at least two orders of magnitude greater than the viscosity of ink jet printing inks.

20 In some embodiments, the screen printing ink may be an organic solvent-based screening printing ink that comprise an acrylic and/or vinyl polymeric binder. Suitable acrylic polymer binder include methyl methacrylate polymers and copolymers. In some embodiments, the screen printing ink may comprise 5 to 10 wt.-% of acrylic polymer binder. Suitable vinyl polymer binders include copolymer of vinyl acetate, vinyl alcohol and vinyl chloride. In some embodiments, the screen printing ink may comprise 10 to 20 wt.-% of vinyl polymer binder.

25 The screen printing ink may further comprise up to 15 wt-% of plasticizer(s) including polymeric plasticizer and phthalates (e.g. diundecyl phthalate), colorant (e.g. pigment), as well as 1 to 5 wt.-% of inorganic fillers as previously described. The organic solvent-based screen printing ink comprises 40 to 60 wt-% of organic solvent(s) as previously described. In one embodiment, the screen printing ink comprises (e.g. 35 to 45

wt.-%) cyclohexanone, (e.g. 10 to 20 wt.-%) of ethyl 3-ethoxy propionate, and (e.g. 5 to 10 wt.-%) 2-buoxyethyl acetate.

In other embodiments, the screen printing ink is a radiation curable ink comprising at least one polymer dispersed in reactive diluent(s) as the liquid carrier, colorant (in the case of colored ink) as well as the previously described optional additives and inorganic fillers. In one embodiment, the radiation curable screen printing ink comprises 10 to 20 wt.-% methylmethacrylate polymer, colorant (e.g. pigment), up to 5 wt.-% of inorganic fillers as previously described, and up to 90 wt.-% of a mixture of reactive diluents. In one embodiment, the radiation curable screen printing ink comprises (e.g. 30 to 40 wt.-%) aromatic (meth)acrylate monomer, such as phenoxy ethyl acrylate, (e.g. 5 to 15 wt.-%) aliphatic urethane acrylate, (e.g. 10 to 20 wt.-%) of vinylcaprolactam, (e.g. 1 to 5 wt.-%) of 1-propanone, 2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-2-(phenylmethyl), (e.g. 1 to 5 wt.-%) of 1-butanone, 2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-2-(phenylmethyl), (e.g. 1 to 5 wt.-%) diethylene glycol ethyl ether acrylate, and (e.g. 1 to 5 wt.-%) propoxylated glycerol triacrylate.

Suitable examples of screen printing ink include 3M™ Screen Printing UV Ink 9802 Opaque Black, 3M™ Scotchlite™ Transparent Screen Printing Ink 2905 Black, as well as those described in US 6,232,359.

In favored embodiments, the color density is at least 80, 85, 90, 95, or 100% of the color density that can be obtained with (e.g. SCOTCHCAL IJ170-10 and IJ180mc-10, commercially available from 3M) cast vinyl film.

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

EXAMPLES

Unless otherwise noted, all parts, percentages, ratios, etc. in the Examples and the rest of the specification are by weight. Unless otherwise indicated, all other reagents were obtained, or are available from fine chemical vendors such as Sigma-Aldrich Company, St. Louis, Missouri, or may be synthesized by known methods.

Materials

5 INGEO 4032D - a semicrystalline polylactic acid (PLA) (2 wt.% D-lactide; weight average molecular weight \approx 200,000 g/mol), was purchased from Natureworks, LLC, Minnetonka, MN.

10 INGEO 4060D - a amorphous polylactic acid (PLA) (10 wt.% D-lactide; weight average molecular weight \approx 180,000 g/mol), was purchased from Natureworks, LLC, Minnetonka, MN.

10 VINNAPAS UW 4 FS - a polyvinyl acetate (PVAc) ($T_g = 42^\circ\text{C}$; weight average molecular weight \approx 280,000 g/mol), was obtained from Wacker, Germany.

15 VINNAPAS UW 25 FS - a polyvinyl acetate (PVAc) ($T_g = 42^\circ\text{C}$; weight average molecular weight \approx 480,000 g/mol), was obtained from Wacker, Germany.

VINAVIL K70 - a polyvinyl acetate ($T_g = 42^\circ\text{C}$; weight average molecular weight \approx 640,000 g/mol), was obtained from Vinavil, Italy.

20 CITROFLEX A4 - acetyl tributyl citrate, a plasticizer, was obtained from Vertellus Performance Materials, Bayonne, NJ.

25 TEGMER 804 - tetraethylene glycol di-ethylhexonate ester plasticizer, was obtained from Hallstar, Chicago, IL.

TEGMER 809 - PEG 400 di-ethylhexonate ester plasticizer, was obtained from Hallstar, Chicago, IL.

30 ADMEX 6995 - a polymeric adipate plasticizer (weight average molecular weight \approx 3200 g/mol) was obtained from Eastman Chemical Company, Kingsport, TN.

ECOPROMOTE - zinc phenylphosphonate, a nucleation agent, was obtained from Nissan Chemical Industrials, Japan.

5 STABAXOL I LF - a hydrolytic stabilizer was obtained from LANXESS Corporation, Pittsburgh, PA.

CARBODILITE HMV-15CA - a hydrolytic stabilizer was obtained from Nisshinbo Chemical Inc., Japan.

10 SUKANO DC S511 - a anti-blocking additive masterbatch was obtained from Sukano Polymers Corporation, Duncan, SC.

15 CLARIANT PLA4060 TiO₂ MB - 50 wt.% titanium dioxide in 50 wt.% amorphous Ingeo PLA 4060D masterbatch was obtained from Clariant Corporation, Minneapolis, MN.

20 CLARIANT PLA4032 TiO₂ MB - 50 wt.% titanium dioxide in 50 wt.% semicrystalline Ingeo PLA 4032D masterbatch was obtained from Clariant Corporation, Minneapolis, MN.

TI-PURE R-350 - a titanium dioxide pigment was obtained from The Chemours Company FC, Wilmington, DE.

25 TI-PURE R-960 - a titanium dioxide pigment was obtained from The Chemours Company FC, Wilmington, DE.

30 Cover film - a non-PVC overlamine under the trade designation ENVISION 8584G (film thickness is about 0.002 inch or 50.8 micrometers) was obtained from 3M Company, Maplewood, MN.

SCOTCHCAL IJ 170-10 - Commercially available from 3M, Maplewood, MN

CONTROLTAC 40C-10R - Commercially available from 3M, Maplewood, MN

3M IJ180MC-10 - Commercially available from 3M, Maplewood, MN

5 Sample Preparation

Melt Compounding

Samples were prepared by mixing PLA, PVAc, plasticizer and nucleation agent in a hot melt extruder (DSM XPLORE) including 15 cm³ twin-screw micro-compounder at 100 revolutions per minute (RPM), 200 °C for 10 minutes, and then collecting the sample by opening a valve on the mixing chamber. The compounded samples were subjected to aging testing at 80 °C, differential scanning calorimetry (“DSC”) characterization and melt-pressed into films for tensile testing.

15 Melt Press to Make Films

The compounded samples were placed between two polytetrafluoroethylene sheets with a 10 mil (~250 micrometer) thick spacer in between. The polytetrafluoroethylene sheets were placed between to metal sheets. The metal sheets with the sample disposed between were placed between the platens of a hydraulic press (available from Carver) and the platens were heated to 340 °F (171 °C). Each sample was preheated for 8 minutes without pressure and then pressed under a pressure of 300 pounds per square inch (~2.1 Newtons/mm²) for 5 minutes. Then, the metal plates were removed from the hydraulic press and allowed for air cooling.

25 Test Methods

Aging Test

The compounded samples (about 0.2 grams) were placed in closed scintillation vials to prevent plasticizer evaporation during aging testing and aged in the oven at 80 °C for 24 hours. Then, after aging at 80 °C, the sample’s surface was inspected to see if there was plasticizer migration. Samples having an oily surface were considered to fail; whereas samples having a non-oily surface were considered to pass.

DSC - Differential Scanning Calorimetry

The glass transition temperature, crystallization temperature, and crystallinity of each sample was measured using a TA INSTRUMENTS DIFFERENTIAL SCANNING CALORIMETER according to ASTM D3418-12 unless specified otherwise. Each sample (4~8 milligrams (mg)) was heated from -60 °C to 200 °C at 10 °C/min in a first heating scan and held for 2 minutes to erase its thermal history, then cooled to -60 °C at 10 °C/min (unless specified otherwise) in a first cooling scan, and heated to 200 °C at 10 °C/min in a second heating scan. The first heating scan was used to determine T_m of the films. The second heating scan was used to determine T_g of the films. Various parameters were derived from the DSC as defined as follows:

T_g – refers to the midpoint temperature of the second heating scan, described as T_{mg} in ASTM D3418-12.

T_c - refers to the crystallization peak temperature of the first cooling scan, described as T_{pc} in ASTM D3418-12.

T_{m1} and T_{m2} - refer to the melting peak temperature of the first and second heating scan, respectively, described as T_{pm} in ASTM D3418-12.

The ability of the composition to crystallize was determined by calculating the net melting endotherm, ΔH_{mm2}, associated with the crystalline material formed during the first cooling scan was calculated with the following equation,

$$\Delta H_{mm2} = \Delta H_{m2} - \Delta H_{cc2}$$

where ΔH_{m2} is the melting endotherm mass normalized enthalpy of the second heating scan and ΔH_{cc2} is the crystallization exotherm mass normalized enthalpy of the second heating scan (as described in section 11 of ASTM D3418-12). For the compositions comprising nucleating agent, ΔH_{cc2} was not detected and thus ΔH_{mm2} = ΔH_{m2}.

The net melting endotherm, ΔH_{nm1} , is associated with the crystallinity in the films (e.g. prepared by melt press). The ΔH_{nm1} was calculated with the following equation,

$$\Delta H_{nm1} = \Delta H_{m1} - \Delta H_{cc1}$$

5

where ΔH_{m1} is the melting endotherm mass normalized enthalpy of the first heating scan and ΔH_{cc1} is the crystallization exotherm mass normalized enthalpy of the first heating scan (as described in section 11 of ASTM D3418-12). For the films comprising nucleating agent, ΔH_{cc1} was not detected and thus $\Delta H_{nm1} = \Delta H_{m1}$.

10

The absolute values of the enthalpies associated with the exotherms and endotherms (i.e. ΔH_{m1} , ΔH_{m2} , ΔH_{cc1} , and ΔH_{cc2}) were used in the calculations.

15 Tensile Testing

The film samples were cut into 0.5 or 1 inch (1.27 or 2.54 centimeter (cm)) wide strips. The tensile testing was conducted along the machine direction (MD) and transverse direction (TD) of the film extrusion, using an INSTRON 3365 TENSILE TESTER. The initial grip distance was at 1 inch (~2.5 cm) and the tensile speed was at 6 inch/minute (~15.2 cm/minute) (i.e., 600% strain/minute) (unless specified otherwise). Test results were reported as the average of 3~5 sample replicates. The tensile strength (nominal), tensile elongation (percent elongation at break), and tensile modulus were determined, as described by sections 11.3 and 11.5 of ASTM D882-10.

25 Gel Permeation Chromatography (GPC)

The samples were analyzed by conventional GPC against polystyrene molecular weight standards. The GPC instrument is Agilent 1260. The GPC column set is Agilent PLGel Mixed B and D (2 x 300 x 7.8 mm I.D) and the eluent is THF solvent. The peak molecular weight (M_p), number-averaged molecular weight (M_n) and weight-averaged molecular weight (M_w) were reported.

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Accelerated Weathering

The test samples were exposed to accelerated weathering conditions in an Atlas Ci5000 Xenon Weather-Ometer from Atlas Material Testing Technology, 4114 North Ravenswood Avenue, Chicago, Ill., 60613. Testing was performed according to ASTM G155-13, Standard Practice for Operating Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials, with the customized settings outlined in Cycle 1 of Table X3.1 in Appendix X1 of ASTM G155-13 with customized settings of:

- Irradiance: 0.68 W/m² or higher at 340 nm
- Black Panel Temperature: 70°C (light cycle), 70 °C (light and water cycle)
- Chamber Temperature: 47°C (light cycle), 47 °C (light and water cycle)
- Relative Humidity: 70% (light cycle), 95% (light and water cycle)
- The total irradiance from 295-385 nm (MJ/m²) the test samples were exposed to is reported.

Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) was conducted utilizing a film tension fixture available from TA Instruments as “DMA Q800” to characterize the physical properties of the films as a function of temperature. The samples were heated from -40 °C temperature to 140 °C at a rate of 2 °C/minute, a frequency of 1 radian/second and a tensile strain of 0.1%.

Printing Performance Analysis

Printability was evaluated using an absolute print density test method according to ASTM D7305-08a: “Standard Test Method for Reflection Density of Printed Matter” and a GRETAG SPM 50 LT spectrodensitometer having a 5 mm aperture on the measuring head. The spectral response was calibrated using a calibration plaque and found to be accurate to within 2%. A laminate of a 25 micrometer (0.001 inch) thick acrylic pressure sensitive adhesive layer on a white colored paper release liner was nip roll laminated at room temperature to a film below such that the surfaces of the adhesive and the film were joined together to give a film article. The exposed surface of the film article was then printed with primary color bars covering at least 15 cm² using various types of printers:

- VUTEK ULTRAVU II Model 150 SC printer (obtained from VUTEK, a division of EFI Corporation, Meredith, N.H.) with 3M™ Piezo Inkjet Ink Series 1500v2
- SOLJET PRO4 XR-640 printer (obtained from Roland DGA Corporation, Irvine, C.A.) with Eco-Sol Max 2 ink
- HP LATEX 360 printer (obtained from The Hewlett-Packard Company, Palo Alto, C.A.) with HP Latex ink

After printing, the samples were air dried for a minimum of 24 hours prior to measuring the print density of the color bars.

The ink color density of the Example film is compared to the ink color density of Control Example 1 by dividing the print density of the Example by the print density of the Control Example 1 and expressing the result as a percentage of standard performance. Achievements of 100% indicate equal color saturation. Values higher than 100% represent higher color saturation and values below 100% represent less saturation. Total color density is the summation of the measurements for cyan, magenta, yellow, and black.

Color Change

The initial color and subsequent color change after accelerated weathering of the printed PLA film (including a laminated cover film as described below) was measured with an X-Rite Ci64 spectrophotometer. Color was measured in Hunter L*, a*, b* units and the change in color (ΔE , Delta E) was calculated according to ASTM D2244, Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates.

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

The wt.-% of each of the components utilized in the compositions of the examples and control examples (indicated by the “C”) is given in Table 1. For example, Example 8 contains 70 wt.-% of PLA4032, 15 wt.-% of PVAc, 15 wt.-% of CITROFLEX A4, based on the total weight of polylactic acid polymer, polyvinyl acetate polymer, and plasticizer. Example 8 further contained 0.2 wt.-% of Ecopromote based on the total weight of the

composition. The T_g and aging results of the compositions is also reported in Table 1 as follows:

Table 1

Example	Components	wt% of component	T _g , °C	Aging at 80 °C for 24 hours
C1	PLA4032/ADMEX6995	89/11	46	Pass
C2	PLA4032/ADMEX6995	85/14	39	Fail
C3	PLA4032/ADMEX6995	82/18	37	Fail
C4	PLA4032/CITROFLEXA4/ ECOPROMOTE	90/10/0.2	32	Pass
C5	PLA4032/CITROFLEXA4/ ECOPROMOTE	86/14/0.2	25	Pass
C6	PLA4032/CITROFLEXA4/ ECOPROMOTE	85/15/0.2	21	Fail
C7	PLA4032/CITROFLEXA4/ ECOPROMOTE	83/17/0.2	15	Fail
Ex. 8	PLA4032/VINNAPSUW4/ CITROFLEXA4/ECOPROMOTE	70/15/15/0.2	15	Pass
Ex. 9	PLA4032/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE	67/16/16/1	10	Pass
Ex. 10	PLA4032/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE	65/20/15/0.2	17	Pass
Ex. 11	PLA4032/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE	60/25/15/0.2	11	Pass
Ex. 12	PLA4032/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE	50/35/15/0.1	5	Pass
Ex. 13	PLA4032/VINNAPASUW4/ TEGMER809/ECOPROMOTE	60/28/12/0.2	13	Pass
Ex. 14	PLA4032/VINNAPASUW4/ TEGMER809/ECOPROMOTE	53/35/12/0.2	9	Pass

5

As illustrated by Table 1, Comparative Examples C1, C4 and C5 passed the aging test, yet Comparative Examples C2, C3, C6 and C7 failed the aging test. The T_g of the sample can be lowered to 25°C (as illustrated by Comparative C5), but not below 25 °C, yet still pass the aging test (as illustrated by Comparative Examples C6 and C7). When the composition included PLA, plasticizer and PVAc, the T_g can be reduced below 25 °C and pass the aging test.

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The wt.-% of each of the components utilized in the compositions of the examples and control examples (indicated by the “C”), the DSC results are depicted in Table 2 as follows:

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Table 2

Ex.	Components (wt.-% of components)	T _c , °C	T _{m2} , °C	T _g , °C	ΔH _{nm2} , J/g
C15	PLA/ECOPROMOTE (100/0.2)	125	167	63	42.9
C4	PLA4032/CITROFLEXA4/ ECOPROMOTE (90/10/0.2)	122	162	36	41.4
C5	PLA4032/CITROFLEXA4/ ECOPROMOTE (86/14/0.2)	120	160	25	40.1
Ex. 8	PLA4032/VINNAPASUW4/CITROFLEXA4/ ECOPROMOTE (70/15/15/0.2)	117	165	14	33.5
Ex. 9	PLA4032/VINNAPASUW4/CITROFLEXA4/ ECOPROMOTE (67/16/16/1)	119	163	10	32.5
Ex. 10	PLA4032/VINNAPASUW4/CITROFLEXA4/ ECOPROMOTE (65/20/15/0.2)	117	165	17	31.3
Ex. 11	PLA4032/VINNAPASUW4/CITROFLEXA4/ ECOPROMOTE (60/25/15/0.2)	115	164	13	29.4
Ex. 12	PLA4032/VINNAPASUW4/CITROFLEXA4/ ECOPROMOTE (50/35/15/0.1)	112	160	5	23.8
Ex. 13	PLA4032/VINNAPASUW4/TEGMER809/ ECOPROMOTE (60/28/12/0.2)	120	165	13	28.4
Ex. 14	PLA4032/VINNAPASUW4/TEGMER809/ ECOPROMOTE (53/35/12/0.2)	118	164	9	26.2
Ex. 16	PLA4032/VINNAPASUW4/CITROFLEXA4 (50/35/15) as melt pressed	--	160	27	1.5
Ex. 17	PLA4032/VINNAPASUW4/CITROFLEXA4/ ECOPROMOTE (44.8/35/20/0.2)	112	160	2	23.0
Ex. 18	PLA4032/VINNAPASUW4/CITROFLEXA4/ ECOPROMOTE (39.8/35/25/0.2)	109	158	-8	20.9
Ex. 19	PLA4032/PLA4060/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE	107	161	27	13.2

	(20/34/35/10/1)				
Ex. 20	PLA4032/PLA4060/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE (15/50/20/14/1)	104	161	28	10.5
Ex. 21	PLA4032/PLA4060/VINNAPASUW4/ TEGMER804/ECOPROMOTE (20/34/35/10/1)	112	162	22	14.5

A representative DSC profile of the composition of Example 12 is depicted in FIG 9. This DSC profile exhibits a sharp crystallization peak exotherm during cooling. The composition of Example 16 did not exhibit any crystallization during cooling, as depicted in FIG. 10.

The film samples of Examples 12 and 16 were tested according to the previously described Dynamic Mechanical Analysis. The results of Example 12 are depicted in FIG. 11 and the results of Example 16 are depicted in FIG. 12.

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The DSC and tensile testing results (at 1 inch/minute (i.e. 100% strain/minute)) of these films are depicted in Table 3 as follows:

Table 3

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Ex	Components (wt.-% of components)	T _{m1} (°C)	ΔH _{nm1} (J/g)	Tensile Strength (MPa)	Tensile Elongation	Tensile Modulus (MPa)
	Plasticized PVC (CONTROLTAC™ IJ 180-10) T _g = 15°C	--	N/A	24	200%	500
	VINNAPASUW4 (PVAc) T _g = 43°C	--	N/A	34	7%	3000
	PLA4032 T _g = 63°C	167	N/A	60	6%	3500
C4	PLA4032/CITROFLEXA4/ ECOPROMOTE (90/10/0.2)	168	49.6	30.3	23%	890
C5	PLA4032/CITROFLEXA4/ ECOPROMOTE (86/14/0.2)	165	36.5	24.9	28%	650
8	PLA4032/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE (70/15/15/0.2)	164	34.2	21.6	86%	390
10	PLA4032/VINNAPASUW4/	162	29.7	27.3	349%	371

	CITROFLEXA4/ECOPROMOTE (65/20/15/0.2)					
11	PLA4032/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE (60/25/15/0.2)	162	30.1	20.6	363%	263
12	PLA4032/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE (50/35/15/0.1)	162	27.0	17.9	369%	203
13	PLA4032/VINNAPASUW4/ TEGMER809/ECOPROMOTE (60/28/12/0.2)	164	31.4	21.9	320%	328
14	PLA4032/VINNAPASUW4/ TEGMER809/ECOPROMOTE (53/35/12/0.2)	163	27.5	18.9	373%	253
16	PLA4032/VINNAPASUW4/ CITROFLEXA4 (50/35/15) AS MELT PRESSED	160	1.7	30.1	472%	241
17	PLA4032/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE (44.8/35/20/0.2)	158	23.4	14.5	450%	153
18	PLA4032/VINNAPASUW4/ CITROFLEXA4/ECOPROMOTE (39.8/35/25/0.2)	157	21.6	8.7	390%	101
19	PLA4032/PLA4060/ VINNAPASUW4/CITROFLEXA 4/ ECOPROMOTE (20/34/35/10/1)	161	14.1	26.3	302%	613
20	PLA4032/PLA4060/ VINNAPASUW4/CITROFLEXA 4/ ECOPROMOTE (15/50/20/14/1)	159	12.1	27.9	364%	485
21	PLA4032/PLA4060/ VINNAPASUW4/TEGMER804/ ECOPROMOTE (20/34/35/10/1)	161	14.2	25.4	380%	416

The previously described PLA-based films can be utilized in various graphic articles as a backing, intermediate layer, or cover film. A graphic may be provided on the PLA-based film, especially by printing with a radiation curable ink.

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Example 22

A twin screw extruder (Zone 1: 250 °F or 121 °C; Zones 2 and 3: 390 °F or 199 °C; Zones 4 and 5: 350 °F or 177 °C) and underwater pelletizer were used to prepare pre-compounded and free-flowing PLA pellets, which had the following composition:

Components	Composition, wt.-%
INGEO 4032 PLA	12.2
INGEO 4060 PLA	42.2
VINNAPAS UW25 PVAc	22
CITROFLEX A4 Plasticizer	12
ECOPROMOTE Nucleating Agent	0.3
White Pigment TiO ₂ (Clariant*)	11.3

5 *Obtained by utilizing Clariant PLA4032 TiO₂ MB

The pre-compounded PLA pellets were fed to a single screw extruder (the Gloucester Engineering extruder, Gloucester, M.A.) having a 2 inch (~5.1 cm) diameter screw and a length of 78 inch (198 cm). The extruder was operated at a speed of 14 rpm, with a cooled feed throat, and the following approximate zone and die temperatures: Z1: 166 °C (330 °F); Z2: 168 °C (335 °F); Z3: 171 °C (340 °F); Z4: 174 °C (345 °F); and die: 177 °C (350 °F). Film was extruded through a 0.004 inch (0.102 millimeter (mm)) die gap onto a 30 inch (76.2 centimeter (cm)) wide polyester carrier film to provide a film product having a thickness of about 0.002 inch (0.051 mm) and a width of about 30 inch (76.2 cm). The film was thermally annealed offline in an oven at 60 °C (140 °F) for about 3 hours to achieve crystallization. The polyester carrier was removed from the film products prior to testing.

Table 4 Physical Properties of Example 22 Extruded Film

Ex.	Components (wt.-% of components)	T _g , °C	T _{m1} , °C	ΔH _{nm1} , J/g	Tensile Strength, MPa	Tensile Elongation	Tensile Modulus, MPa
Ex. 22	PLA4032/PLA4060/ VINNAPASUW25/ CITROFLEXA4/ ECOPROMOTE/TiO ₂ (12.2/42.2/22/12/0.3/11.3)	24 15*	158	11.6	27.2 (MD) 27.4 (TD)	229% (MD) 270% (TD)	422 (MD) 421 (TD)

MD = machine direction; TD = transverse direction; * measured at a cooling rate of 5°C/min; tensile testing was run at 1 inch/minute (i.e. 100% strain/minute).

A (e.g. carbodiimide) hydrolysis stabilizer and/or (TiO₂) pigment, at the concentrations described herein, can be added to any of the previously described examples.

5

Representative film examples were printed with various inks and the print density evaluated as previously described. The test results are set forth in the following tables:

Table 5 Print Density by VUTEK 150 Printer with 3M™ Piezo Inkjet Ink Series 1500v2

Ex.	Components (wt.-% of components)	Cyan	Magenta	Yellow	Black	Total	Total % of Cast Vinyl
Control	Cast vinyl (SCOTCHCAL IJ 170-10)	2.22	2.08	1.26	2.31	7.87	100%
Control	Calendered vinyl (CONTROLTAC 40C-10R)	2.06	2.06	1.26	2.46	7.84	100%
Ex. 19	PLA4032/PLA4060/ VINNAPASUW4/ CITROFLEXA4/ ECOPROMOTE (20/34/35/10/1)	2.11	1.94	1.28	2.17	7.5	95%
Ex. 20	PLA4032/PLA4060/ VINNAPASUW4/ CITROFLEXA4/ ECOPROMOTE (15/50/20/14/1)	1.48	1.86	1.3	1.95	6.59	84%
Ex. 21	PLA4032/PLA4060/ VINNAPASUW4/ TEGMER804/ ECOPROMOTE (20/34/35/10/1)	1.59	1.86	1.27	1.9	6.62	84%
Ex. 22	PLA4032/PLA4060/ VINNAPASUW25/ CITROFLEXA4/ ECOPROMOTE/TiO ₂ (12.2/42.2/22/12/0.3/11.3)	2.25	2.09	1.25	2.44	8.03	102%

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Table 6 Print Density by ROLAND SOLJET Printer with Eco-Sol Max 2 ink

Ex.	Components (wt.-% of components)	Cyan	Magenta	Yellow	Black	Total	Total % of Cast Vinyl
Control	Cast vinyl (SCOTCHCAL IJ 170-10)	2.1	1.38	1.01	2.04	6.53	100%
Control	Calendered vinyl (CONTROLTAC 40C-10R)	2.22	1.41	1.04	2.14	6.81	104%
Ex. 22	PLA4032/PLA4060/ VINNAPASUW25/ CITROFLEXA4/ ECOPROMOTE/TiO ₂ (12.2/42.2/22/12/0.3/11.3)	2.01	1.38	1.0	2.08	6.47	99%

Table 7 Print Density by HP Latex 360 Printer with HP Latex Ink

Ex.	Components (wt.-% of components)	Cyan	Magenta	Yellow	Black	Total	Total % of Cast Vinyl
Control	Cast vinyl (SCOTCHCAL IJ 170-10)	1.68	1.52	1.06	1.94	6.2	100%
Control	Calendered vinyl (CONTROLTAC 40C-10R)	1.64	1.49	1.06	1.93	6.12	99%
Ex. 22	PLA4032/PLA4060/ VINNAPASUW25/ CITROFLEXA4/ ECOPROMOTE/TiO ₂ (12.2/42.2/22/12/0.3/11.3)	1.67	1.51	1.05	1.95	6.18	100%

5

Example 23

A twin-screw extruder (Zone 1: 250 °F or 121 °C; Zones 2 and 3: 390 °F or 199 °C; Zones 4 and 5: 350 °F or 177 °C) and an underwater pelletizer were used to prepare pre-compounded and free-flowing PLA blend pellets, which had the following composition:

10

Table 8 Composition of Example 23

COMPONENTS	COMPOSITION, wt.%
INGEO 4032 (Semi-crystalline PLA)	10.8
INGEO 4060 (Amorphous PLA)	36.5
VINAVIL K70 (PVAc)	20
CITROFLEX A4 (Plasticizer)	10.5
ECOPROMOTE (Nucleating Agent)	0.2
STABAXOL I LF (Hydrolytic stabilizer)	2
WHITE PIGMENT TiO ₂ (Clariant*)	20

*Obtained by utilizing Clariant PLA4060 TiO₂ MB

The pre-compounded PLA pellets were dried in a desiccant drier at 49 °C (120 °F) for approximately 15 hours and then fed to a single-screw extruder (Gloucester Engineering extruder, Gloucester, MA) having a 2.5 inch (6.4 centimeter (cm)) diameter screw and a length of 78 inch (198 cm). The extruder was operated with a cooled feed throat, and the following approximate zone and die temperatures: Zone 1: 166 °C (330 °F); Zone 2: 168 °C (335 °F); Zone 3: 171 °C (340 °F); Zone 4: 174 °C (345 °F); and die: 177 °C (350 °F). Film was extruded through a die with a 0.004 inch (0.102 millimeter (mm)) die gap onto a 30 inch (76.2 cm) wide polyester carrier film to provide a film product having a thickness of about 0.002 inch (0.051 mm) and a width of about 30 inch (76.2 cm). The film was thermally annealed offline in an oven at 55 °C (131 °F) for about 24 hours to achieve crystallization.

15

Table 9 Physical Properties of Example 23 Extruded Film

Ex.	Components (wt.-% of components)	T _g , °C	T _{m1} , °C	ΔH _{nm1} , J/g	Tensile Strength, MPa	Tensile Elongation	Tensile Modulus, MPa
23	PLA4032/PLA4060/ VINAVILK70/ CITROFLEXA4/ ECOPROMOTE/ STABAXOL I F/TiO ₂ (10.8/36.5/20/10.5/0.2/2/20)	27 15*	157	7.3	20.5	174%	316

* Measured at a cooling rate of 5°C/min

The annealed PLA film was then printed with inks as described above. The cover film (3M Envision 8548G) described above was laminated to the top of the printed PLA films by using a laminator at room temperature. The test samples were then adhered to aluminum panels for accelerated weathering evaluation. The printed film colors were measured before and after being subjected to accelerated weathering method. The results are summarized below.

Table 10 Color Change of Printed PLA Film (Ex. 23) after accelerated weathering

Total irradiance, MJ/m ²	Delta E (HP Latex 360 printer /831 inks)				
	White	Cyan	Magenta	Yellow	Black
0	0	0	0	0	0
179	0.3	0.3	4.8	0.7	0.2
357	0.2	1.1	6.9	2.0	0.3
539	0.2	2.0	7.9	3.3	0.4
717	0.2	3.0	8.5	5.0	0.5
901	0.4	4.1	8.9	7.6	0.3
1082	0.4	6.1	9.1	11.2	0.2

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Table 11 Color Change of Printed PLA Film (Ex. 23) after accelerated weathering

Total irradiance, MJ/m ²	Delta E (Roland XR-640 printer/Eco Sol Max 2 inks)				
	White	Cyan	Magenta	Yellow	Black
0	0	0	0	0	0
179	0.2	1.4	4.4	0.2	0.4
357	0.1	2.2	6.1	1.0	0.3
539	0.1	3.0	7.1	2.1	0.2
717	0.2	4.9	7.7	3.7	0.3
901	0.3	7.4	8.1	5.8	0.2
1082	0.3	9.0	8.0	9.0	0.2

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EXAMPLES 24-28

Table 12A Additional PLA Formulations

EXAMPLES	Ex. 24	Ex. 25	Ex. 26	Ex. 27	Ex. 28
PLA4032, wt.%	10.8%	10.8%	10.8%	10.8%	10.8%
PLA4060, wt.%	36%	36.5%	36.5%	37.5%	38.5%
VINAVIL K70, wt.%	20%	20%	20%	20%	20%
CITROFLEX A4, wt.%	10.5%	10.5%	10.5%	10.5%	10.5%
ECOPROMOTE, wt.%	0.2%	0.2%	0.2%	0.2%	0.2%
STABAXOL I LF, wt.%	1%	2%	2%		
CARBODILITE H MV-15CA, wt.%	1.5%			1%	
TiO ₂ (CLARIANT*), wt.%	20%				20%
TiO ₂ (TI-PURE R350), wt.%		20%		20%	
TiO ₂ (TI-PURE R960), wt.%			20%		

5 * Obtained by utilizing Clariant PLA4060 TiO₂ MB

Extruded film samples of Ex. 24-28 were made in the same manner of Ex. 23.

Table 12B Tensile Data of Ex. 24-28 Extruded Films

Ex.	Tensile Strength, MPa	Tensile Elongation	Tensile Modulus, MPa
24	20.9	173%	527
25	30.3	262%	562
26	25.7	200%	636
27	30.2	212%	712
28	20.5	132%	721

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Unprinted film samples (film only without the use of a cover film) from Table 12A were evaluated under the accelerated weathering. Their molecular weights were analyzed by GPC. The results were summarized in Tables 13, 14 and 15.

15

Table 13 GPC results of PLA films (Ex. 23, Ex. 24) before and after accelerated weathering

Total irradiance, MJ/m ²	Ex. 23			Ex. 24		
	M _p , g/mol	M _n , g/mol	M _w , g/mol	M _p , g/mol	M _n , g/mol	M _w , g/mol
0	1.89E+05	8.32E+04	3.16E+05	1.86E+05	8.34E+04	3.37E+05
360	1.29E+05	4.94E+04	2.27E+05	1.40E+05	5.48E+04	2.71E+05
$\frac{M(360)-M(0)}{M(0)}$, %	-32%	-41%	-28%	-25%	-34%	-20%
720	9.04E+04	4.17E+04	1.96E+05	9.83E+04	4.59E+04	2.41E+05
$\frac{M(720)-M(0)}{M(0)}$, %	-52%	-50%	-38%	-47%	-45%	-28%
1080	5.51E+04	2.88E+04	1.61E+05	6.31E+04	3.22E+04	1.89E+05
$\frac{M(1080)-M(0)}{M(0)}$, %	-71%	-65%	-49%	-66%	-61%	-44%

5 Table 14 GPC results of PLA films (Ex. 25, Ex. 26) before and after accelerated weathering

Total irradiance, MJ/m ²	Ex. 25			Ex. 26		
	M _p , g/mol	M _n , g/mol	M _w , g/mol	M _p , g/mol	M _n , g/mol	M _w , g/mol
0	1.98E+05	1.04E+05	3.17E+05	1.98E+05	9.65E+04	3.19E+05
360	1.77E+05	7.83E+04	2.96E+05	1.77E+05	8.35E+04	2.95E+05
$\frac{M(360)-M(0)}{M(0)}$, %	-11%	-25%	-7%	-11%	-13%	-8%
720	1.49E+05	6.87E+04	2.51E+05	1.51E+05	7.56E+04	2.53E+05
$\frac{M(720)-M(0)}{M(0)}$, %	-25%	-34%	-21%	-24%	-22%	-21%
1080	9.12E+04	4.44E+04	2.05E+05	1.36E+05	6.61E+04	2.47E+05
$\frac{M(1080)-M(0)}{M(0)}$, %	-54%	-57%	-35%	-31%	-32%	-23%

10 Table 15 GPC results of PLA films (Ex. 27, Ex. 28) before and after accelerated weathering

Total irradiance, MJ/m ²	Ex. 27			Ex. 28 – No hydrolysis stabilizer 20% TiO ₂		
	M _p , g/mol	M _n , g/mol	M _w , g/mol	M _p , g/mol	M _n , g/mol	M _w , g/mol
0	2.21E+05	1.16E+05	3.60E+05	1.53E+05	6.47E+04	2.80E+05
360	1.61E+05	7.91E+04	3.09E+05	6.12E+04	3.22E+04	1.74E+05
$\frac{M(360)-M(0)}{M(0)}$, %	-27%	-32%	-14%	-60%	-50%	-38%
720	1.06E+05	5.67E+04	2.36E+05	3.21E+04	2.15E+04	1.51E+05
$\frac{M(720)-M(0)}{M(0)}$, %	-52%	-51%	-34%	-79%	-67%	-46%
1080	5.61E+04	3.33E+04	1.90E+05	2.31E+04	1.40E+04	1.20E+05

$\frac{M(1080)-M(0)}{M(0)}, \%$	-75%	-71%	-47%	-85%	-78%	-57%
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Table 16A Additional PLA Formulations with Low Crystallinity

EXAMPLES	Ex. 29	Ex. 30	Ex. 31
PLA4032, wt.%	7.4%	1.4%	
PLA4060, wt.%	31.7%	37.7%	60%
VINAVIL K70, wt.%	34.3%	34.3%	25%
CITROFLEX A4, wt.%	24.5%	24.5%	15%
ECOPROMOTE, wt.%	0.1%	0.1%	
SUKANO DC S511, wt.%	2%	2%	

5

Film samples were prepared by melt press procedure in the lab (as described in the sample preparation section). Some of the film samples were annealed at 60°C for 6 hours. Other samples were not annealed.

10

Table 16B Physical Properties of Annealed and Unannealed Extruded Film Ex. 23 and Melt Pressed Films Ex. 29-31

Ex.	Annealed	ΔH_{nm1} (J/g)	Tensile Strength, MPa	Tensile Elongation	Tensile Modulus, MPa
23	NO	0	26.9	270%	917
23	YES	6.8	20.5	170%	320
29	NO	0	Not broken	>400%	5.5
29	YES	6.1	8.0	319%	45
30	NO	0	Not broken	>400%	3.2
30	YES	1.6	7.6	371%	23
31	NO	0	21.2	268%	681
31	YES	0.6	20.8	286%	1043

15 Printing Results

Table 17 Print Density by HP Latex 360 Printer with HP Latex 831 Inks
(Printing profile: standard 3M IJ180 profile)

Ex.	Components (wt.-% of components)	Cyan	Magenta	Yellow	Black	Total	Total % of control
Control	Cast vinyl (3M IJ180mc-10)	1.72	1.46	1.05	2.05	6.28	100%
23 (Unannealed)	PLA4032/PLA4060/ VINA VIL K70/ CITROFLEX A4/ ECOPROMOTE/ STABAXOL I F/TiO2 (10.8/36.5/20/10.5/0.2/2/20)	1.75	1.45	1.05	2.09	6.34	101%
23 (Annealed)	PLA4032/PLA4060/ VINA VIL K70/ CITROFLEX A4/ ECOPROMOTE/ STABAXOL I F/TiO2 (10.8/36.5/20/10.5/0.2/2/20)	1.77	1.45	1.05	2.16	6.43	102%
29 (Unannealed)	PLA4032/PLA4060/VINA VIL K70 /CITROFLEX A4 /ECOPROMOTE /SUKANO DC S511 (7.4/31.7/34.3/24.5/0.1/2)	1.79	1.47	1.10	2.29	6.65	106%
29 (Annealed)	PLA4032/PLA4060/VINA VIL K70 /CITROFLEX A4 /ECOPROMOTE /SUKANO DC S511 (7.4/31.7/34.3/24.5/0.1/2)	1.80	1.47	1.11	2.29	6.67	106%
30 (Unannealed)	PLA4032/PLA4060/VINA VIL K70 /CITROFLEX A4 /ECOPROMOTE /SUKANO DC S511 (1.4/37.7/34.3/24.5/0.1/2)	1.78	1.45	1.10	2.24	6.57	105%
30 (Annealed)	PLA4032/PLA4060/VINA VIL K70 /CITROFLEX A4 /ECOPROMOTE /SUKANO DC S511 (1.4/37.7/34.3/24.5/0.1/2)	1.80	1.47	1.11	2.29	6.67	106%
31 (Unannealed)	PLA4060/VINA VIL K70 /CITROFLEX A4 (60/25/15)	1.77	1.46	1.09	2.04	6.36	101%
31 (Annealed)	PLA4060/VINA VIL K70 /CITROFLEX A4 (60/25/15)	1.77	1.46	1.09	2.09	6.41	102%

Table 18 Print Density by ROLAND XR-640 Printer with Eco-Sol Max 2 inks
(Printing profile: generic vinyl I HD; 540 x 720 dpi, pre press US)

Ex.	Components (wt.-% of components)	Cyan	Magenta	Yellow	Black	Total	Total % of control
Control	Cast vinyl (3M IJ180mc-10)	1.48	1.25	0.87	1.87	5.47	100%
23 (Unannealed)	PLA4032/PLA4060/ VINAVILK70/ CITROFLEXA4/ ECOPROMOTE/ STABAXOL I F/TiO2 (10.8/36.5/20/10.5/0.2/2/20)	1.12	1.29	0.78	1.39	4.58	84%
23 (Annealed)	PLA4032/PLA4060/ VINAVILK70/ CITROFLEXA4/ ECOPROMOTE/ STABAXOL I F/TiO2 (10.8/36.5/20/10.5/0.2/2/20)	1.52	1.49	0.89	2.00	5.90	108%
29 (Annealed)	PLA4032/PLA4060/VINA VIL K70 /CITROFLEX A4 /ECOPROMOTE /SUKANO DC S511 (7.4/31.7/34.3/24.5/0.1/2)	1.65	1.46	0.93	1.91	5.95	109%
30 (Annealed)	PLA4032/PLA4060/VINA VIL K70 /CITROFLEX A4 /ECOPROMOTE /SUKANO DC S511 (1.4/37.7/34.3/24.5/0.1/2)	1.55	1.43	0.93	1.88	5.79	106%
31 (Annealed)	PLA4060/VINAVIL K70 /CITROFLEX A4 (60/25/15)	1.28	1.37	0.91	1.73	5.29	97%

5 Table 19 Print Density by ROLAND XR-640 Printer with Eco-Sol Max 2 inks
(Printing profile: generic vinyl I HD; 720 x 1440 dpi, max density)

Ex.	Components (wt.-% of components)	Cyan	Magenta	Yellow	Black	Total	Total % of control
Control	Cast vinyl (3M IJ180mc-10)	2.27	1.39	0.98	2.21	6.85	100%
23 (Unannealed)	PLA4032/PLA4060/ VINAVILK70/ CITROFLEXA4/ ECOPROMOTE/ STABAXOL I F/TiO2 (10.8/36.5/20/10.5/0.2/2/20)	2.00	1.37	0.92	2.03	6.32	92%
29 (Unannealed)	PLA4032/PLA4060/VINA VIL K70 /CITROFLEX A4 /ECOPROMOTE /SUKANO DC S511 (7.4/31.7/34.3/24.5/0.1/2)	2.25	1.45	1.02	2.29	7.01	102%

30 (Unannealed)	PLA4032/PLA4060/VINAVIL K70 /CITROFLEX A4 /ECOPROMOTE /SUKANO DC S511 (1.4/37.7/34.3/24.5/0.1/2)	2.21	1.41	1.03	2.36	7.01	102%
31 (Unannealed)	PLA4060/VINAVIL K70 /CITROFLEX A4 (60/25/15)	2.28	1.40	1.01	2.43	7.12	104%

Table 20A Comparison of Unannealed Aged Films to Same Film Annealed After Aging (first heating scan)

5

Ex.	Components of Film	Concentration of Components (wt.%)
32	PLA4032/PLA4060/VinavilK70/CitroflexA4/ Ecopromote/Stabaxol-I-LF/TiO2 (Clariant)	10.8/36.5/20/10.5/0.2/2/20
33	PLA4032/PLA4060/VinnapasUW4/CitroflexA4/ Ecopromote	19.6/35/35/10/0.4
34	PLA4032/PLA4060/VinnapasUW4/CitroflexA4/ Ecopromote	14.7/46.7/26.3/12/0.3
35	PLA4032/PLA4060/VinnapasUW4/Tegmer804/ Ecopromote	20/34/35/10/1
36	PLA4032/PLA4060/VinnapasUW25/CitroflexA4/ Ecopromote/TiO2 (Clariant)	12.2/42.2/22/12/0.3/11.3
37	PLA4032/PLA4060/VinavilK70/CitroflexA4/ Ecopromote	14.2/47/25/13.5/0.3

Table 20B - Results

Ex.	Aging at Room Temperature (months)	Unannealed ΔH_{nm1} (J/g) of film	Annealed at 120°F, 15 hours ΔH_{nm1} (J/g) of film	Annealed at 60°C for 3 hours ΔH_{nm1} (J/g) of film
32	20	0.3	2.7	6.8
33	58	0	0.5	0.1
34	58	0	0.4	0
35	64	2.2	11.5	12.7

36	No aging – remelted at 170°C	0.6	10.2	10.5
36	32	2.5		
36	43	8.0		
37	43	0	11.2	10.8

All cited references, patents, and patent applications in the above application for letters patent are herein incorporated by reference in their entirety in a consistent manner.

5 In the event of inconsistencies or contradictions between portions of the incorporated references and this application, the information in the preceding description shall control.

What is claimed:

1. An article comprising
a first film layer comprising
5 semicrystalline polylactic acid polymer;
optionally amorphous polylactic acid polymer;
a second polymer having a Tg of at least 25°C;
plasticizer;
hydrolysis stabilizer; and
10 an inorganic pigment in an amount such that the ratio of polylactic acid polymer to
inorganic pigment is less than 4.5:1.
2. The article of claim 1 wherein the inorganic pigment comprises TiO₂.
- 15 3. The article of claims 1-2 wherein the amount of inorganic pigment is at least 15, 16, 17,
18, 19, or 20 wt.% of the first film layer.
4. The article of claims 1-3 wherein the ratio of polylactic acid polymer to inorganic
pigment is at least 1:1 and less than 4.4:1, 4.3:1, 4.2:1, 4.1:1 or 4:1.
20
5. The article of claims 1-4 wherein the second polymer is a polyvinyl acetate polymer.
6. The article of claim 5 wherein the hydrolysis stabilizer is a carbodiimide compound.
- 25 7. The article of claims 1-6 wherein the article is a graphic film further comprising a
graphic proximate a major surface of the film layer.
8. The article of claim 7 wherein the graphic comprises a dried and/or cured ink layer.
- 30 9. The article of claim 8 wherein the ink layer is a dried and/or cured radiation cured ink,
organic solvent-based ink, or water-based ink.

10. The article of claims 7-9 further comprises a topcoat layer or cover film disposed on the graphic.

5 11. The article of claim 10 wherein the cover film is bonded to the graphic with an adhesive layer.

12. The article of claim 10-11 wherein the cover film comprises a semicrystalline polylactic acid polymer.

10 13. The article of claims 1-12 wherein the first film layer comprises an amorphous polylactic acid polymer.

14. The article of claims 1-13 wherein the second polymer comprises a polyvinyl acetate polymer having a molecular weight ranging from 75,000 g/mol to 1,000,000 g/mol.

15 15. The article of claims 1-14 wherein the plasticizer is present in an amount ranging from 5 or 35 wt.-%, based on the total amount of polylactic acid polymer(s), second polymer and plasticizer.

20 16. The article of claims 1-15 further comprising a nucleating agent in an amount ranging from about 0.01 wt.% to about 1 wt.%.

17. The article of claims 1-16 wherein the first film layer is further characterized by any one or combination of the following properties:

25 i) wherein the first film layer does not exhibit plasticizer migration when aged at 80°C for 24 hours.

ii) wherein the first film layer has a T_g for the second heating scan at a rate of 10°C/min of less than 40°C, 35°C, 30°C, 25°C or 20°C;

30 iii) wherein the first film layer has a tensile elongation from 50% to 600% for a strain rate of 600%/minute;

iv) wherein the first film layer has a tensile modulus from 50 MPa to 1100 MPa for a strain rate of 600%/minute; and

v) wherein the first film layer has a tensile storage modulus as determined by dynamic mechanical analysis of at least 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 MPa for a temperature range from 25°C to 80°C when heated at a rate of 2 C°/min.

5 18. The article of claims 1-17 wherein the first film layer has a net melting endotherm for the first heating scan, ΔH_{nm1} , of less than 10 J/g at a rate of 10°C/min.

19. The article of claims 1-18 wherein the first film layer is an annealed film.

10 20. The article of claims 1-18 wherein the first film layer is an unannealed film.

21. The article of claims 1-20 wherein the article further comprises a backing disposed on the opposing surface as the film layer.

15 22. The article of claims 1-21 wherein the article further comprises a pressure sensitive adhesive disposed on the opposing surface of the film layer or backing.

20 23. The article of claims 1-22 wherein the first film layer comprises a composition having a net melting endotherm for the second heating scan, ΔH_{nm2} , of less than 10 J/g at a rate of 10°C/min.

24. An article comprising
a first film layer comprising
polylactic acid polymer;
25 a second polymer having a Tg of at least 25°C;
plasticizer;
hydrolysis stabilizer; and
an inorganic pigment in an amount such that the ratio of polylactic acid polymer to
inorganic pigment is less than 4.5:1.

30 25. The article of claim 24 wherein the first film layer comprises semi-crystalline polylactic acid polymer, amorphous polylactic acid polymer, or mixtures thereof.

26. The article of claims 24-25 wherein the article is further characterized by claims 2-23.

27. An article comprising a first film layer comprising

5 semicrystalline polylactic acid polymer;
optionally amorphous polylactic acid polymer;
a second polymer having a Tg of at least 25°C;
plasticizer;
nucleating agent;

10 wherein the film composition has a net melting endotherm for the first heating scan,
 ΔH_{m1} , of less than 10 J/g at a rate of 10°C/min.

28. The article of claim 27 wherein the first film layer further comprises hydrolysis
stabilizer.

15

29. The article of claims 27-28 wherein the first film layer further comprises inorganic
pigment.

30. The article of claim 29 wherein the inorganic pigment is in an amount such that the
20 ratio of polylactic acid polymer to inorganic pigment is less than 4.5:1, 4.4:1, 4.3:1, 4.2:1,
4.1:1 or 4:1.

31. The article of claims 27-30 wherein the article is further characterized by claims 2-23.

25 32. An article comprising a first film layer comprising

amorphous polylactic acid polymer;
a second polymer having a Tg of at least 25°C;
plasticizer; wherein the first film layer has a net melting endotherm for the first heating
scan, ΔH_{m1} , of less than 10 J/g at a rate of 10°C/min.

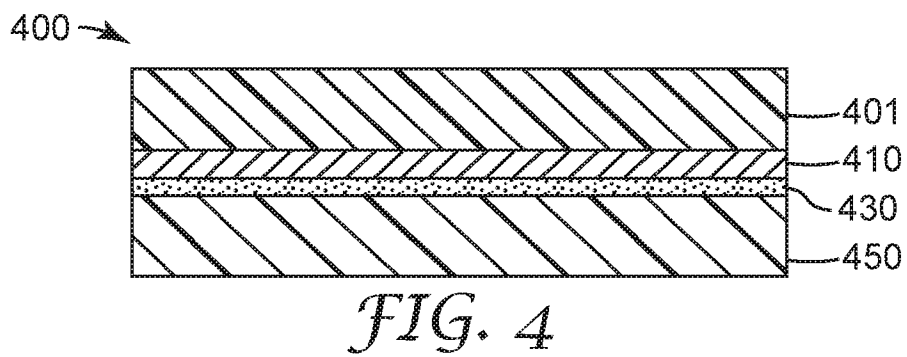
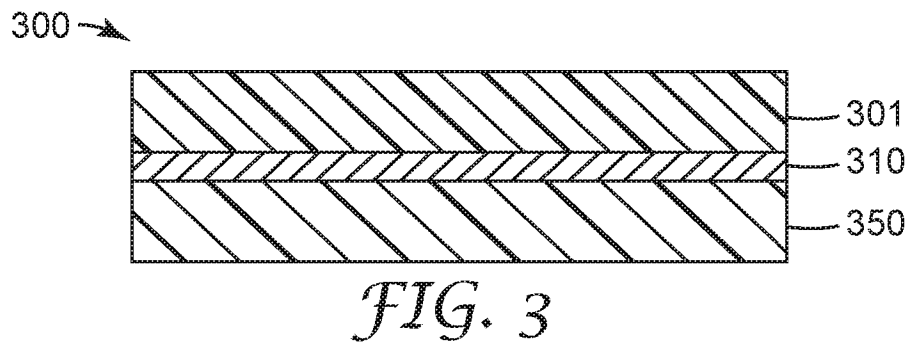
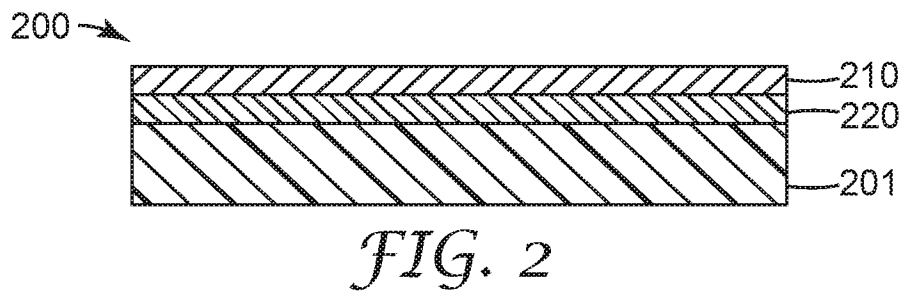
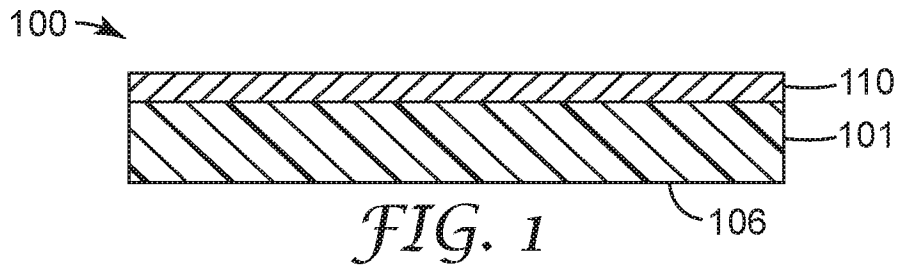
30

33. The article of claim 32 wherein the article is further characterized by claims 2-23 and
28-31.

34. An article comprising
a first film layer comprising
semicrystalline polylactic acid polymer;
5 optionally amorphous polylactic acid polymer;
a second (polyvinyl acetate) polymer having a Tg of at least 25°C;
plasticizer; and
an inorganic pigment in an amount such that the ratio of polylactic acid polymer to
inorganic pigment is less than 4.5:1.
10
35. An article comprising
a film layer comprising
semicrystalline polylactic acid polymer;
optionally amorphous polylactic acid polymer;
15 a second polymer having a Tg of at least 25°C;
plasticizer;
one or more carbodiimide hydrolysis stabilizers.
36. The article of claim 34-35 wherein the article is further characterized by claims 2-23
20 and 28-31.
37. A method of making a graphic film comprising:
providing a film comprising a first film layer according to claims 1-36; and
providing a graphic on the film.
25
38. The method of claim 37 wherein providing a graphic on the film comprises printing
the first film layer with an ink.
39. The method of claim 37 wherein the first film layer is annealed prior to printing.
30
40. The method of claim 37 wherein the first film layer is unannealed prior to printing.

41. The method of claim 37-40 wherein the first film layer has a net melting endotherm for the first heating scan, ΔH_{nm1} , of less than 10 J/g at a rate of 10°C/min.

42. The method of claim 41 wherein the first film layer has a net melting endotherm for
5 the first heating scan, ΔH_{nm1} , of less than 10 J/g at a rate of 10°C/min at the time of
printing.



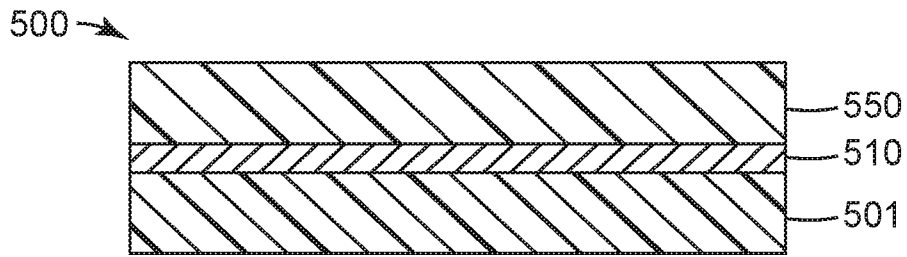


FIG. 5

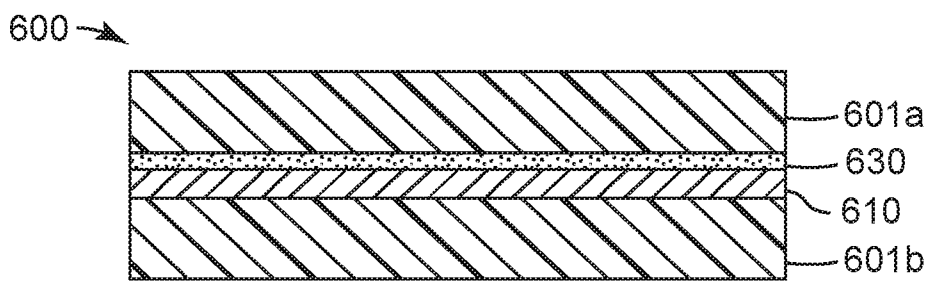


FIG. 6

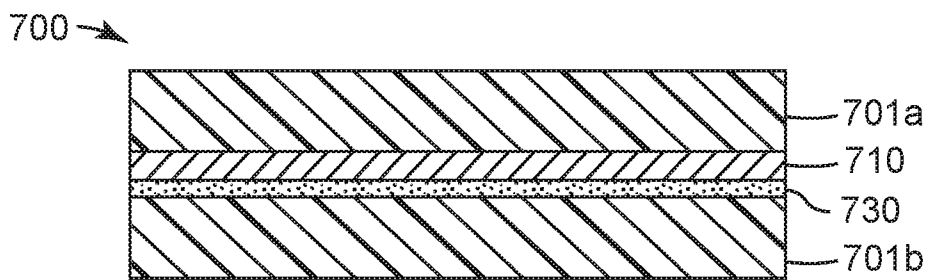


FIG. 7

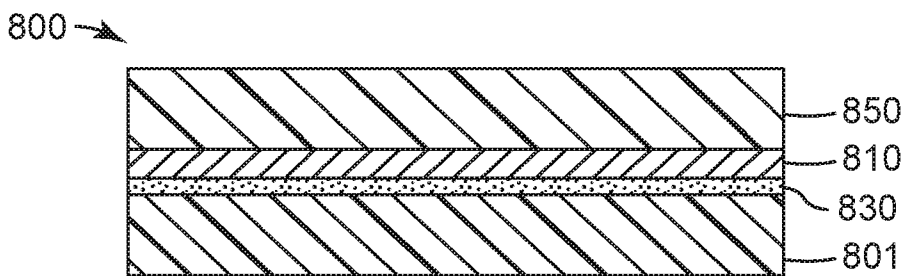


FIG. 8

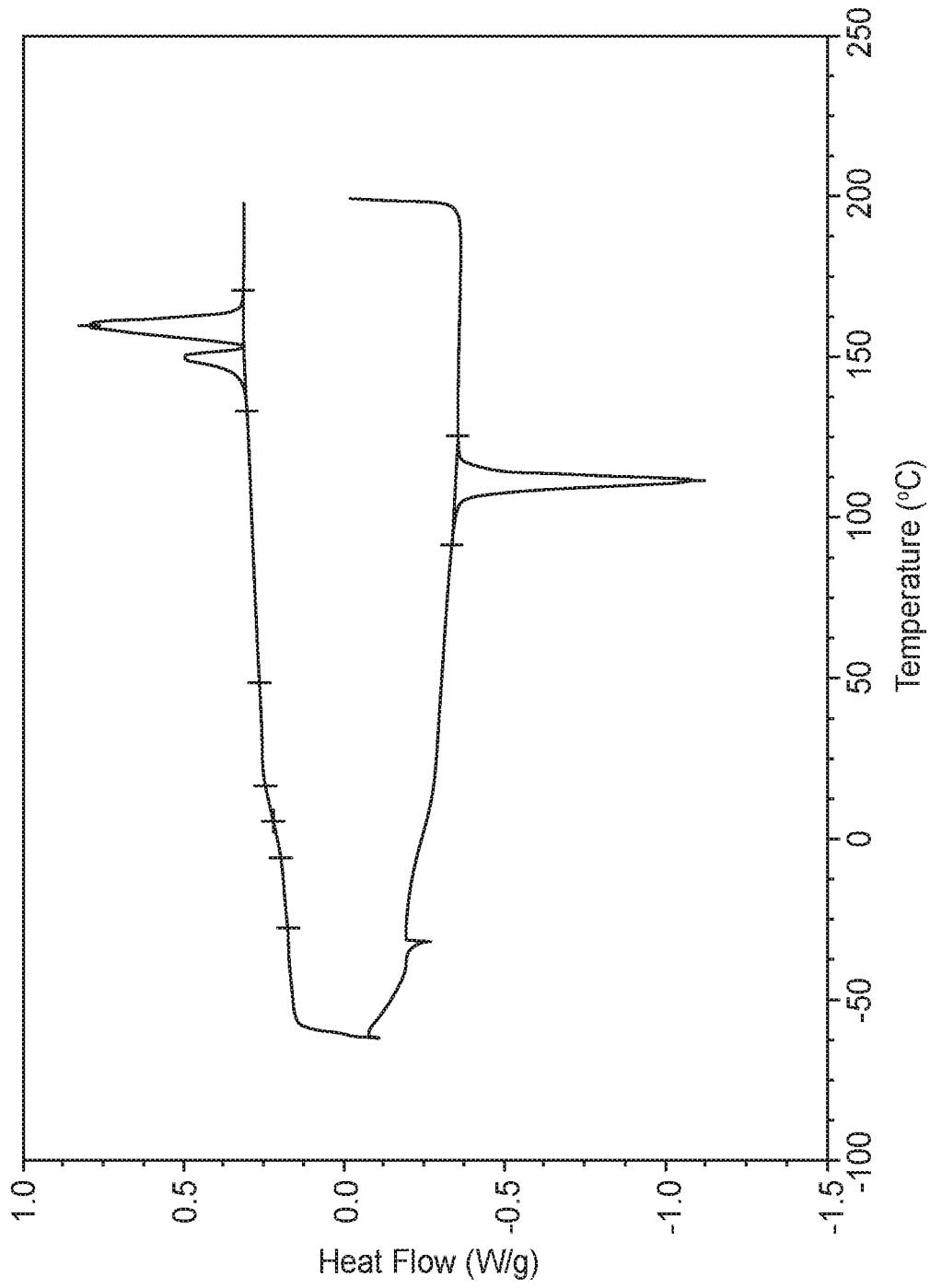


FIG. 9

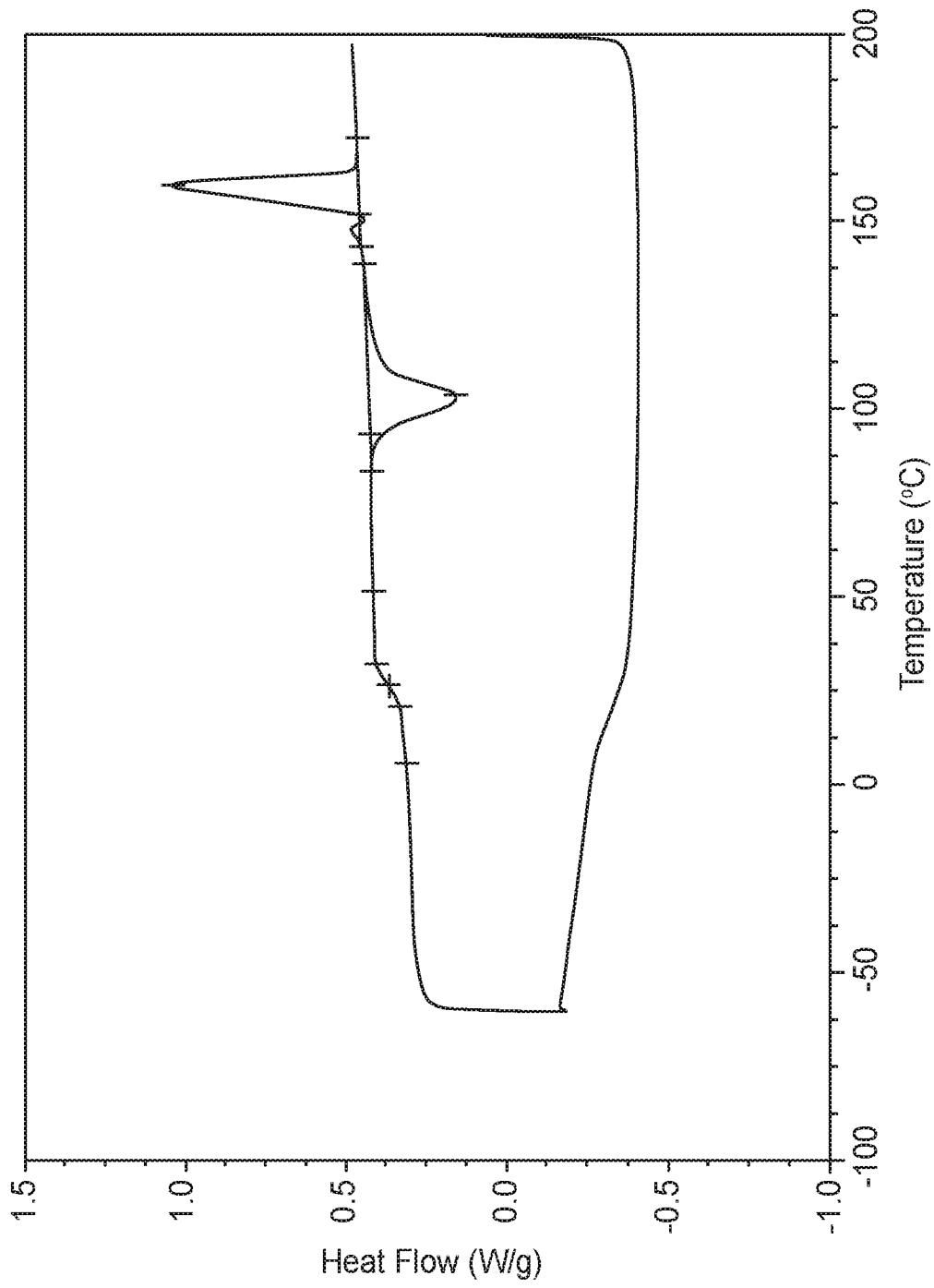


FIG. 10

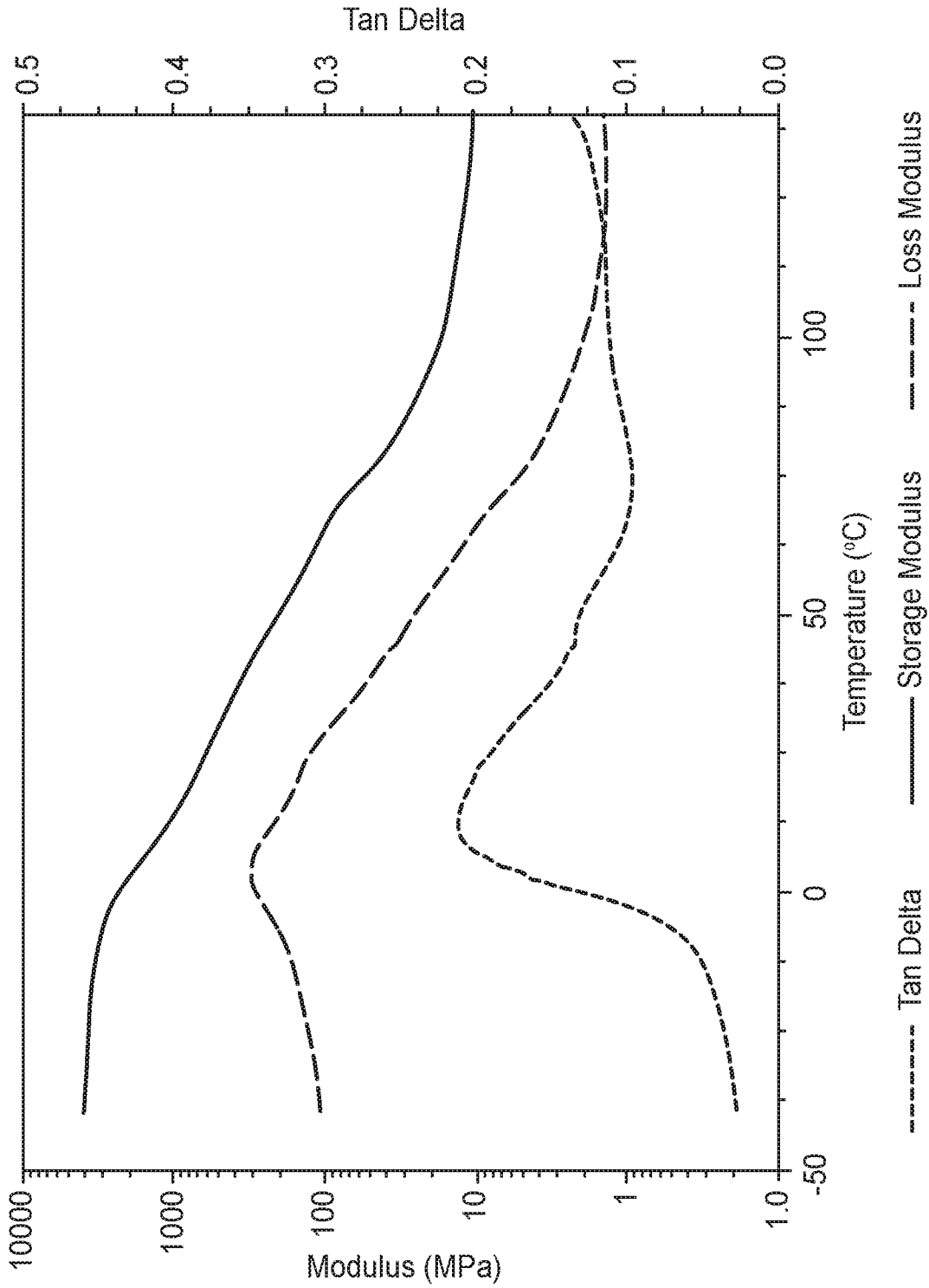


FIG. 11

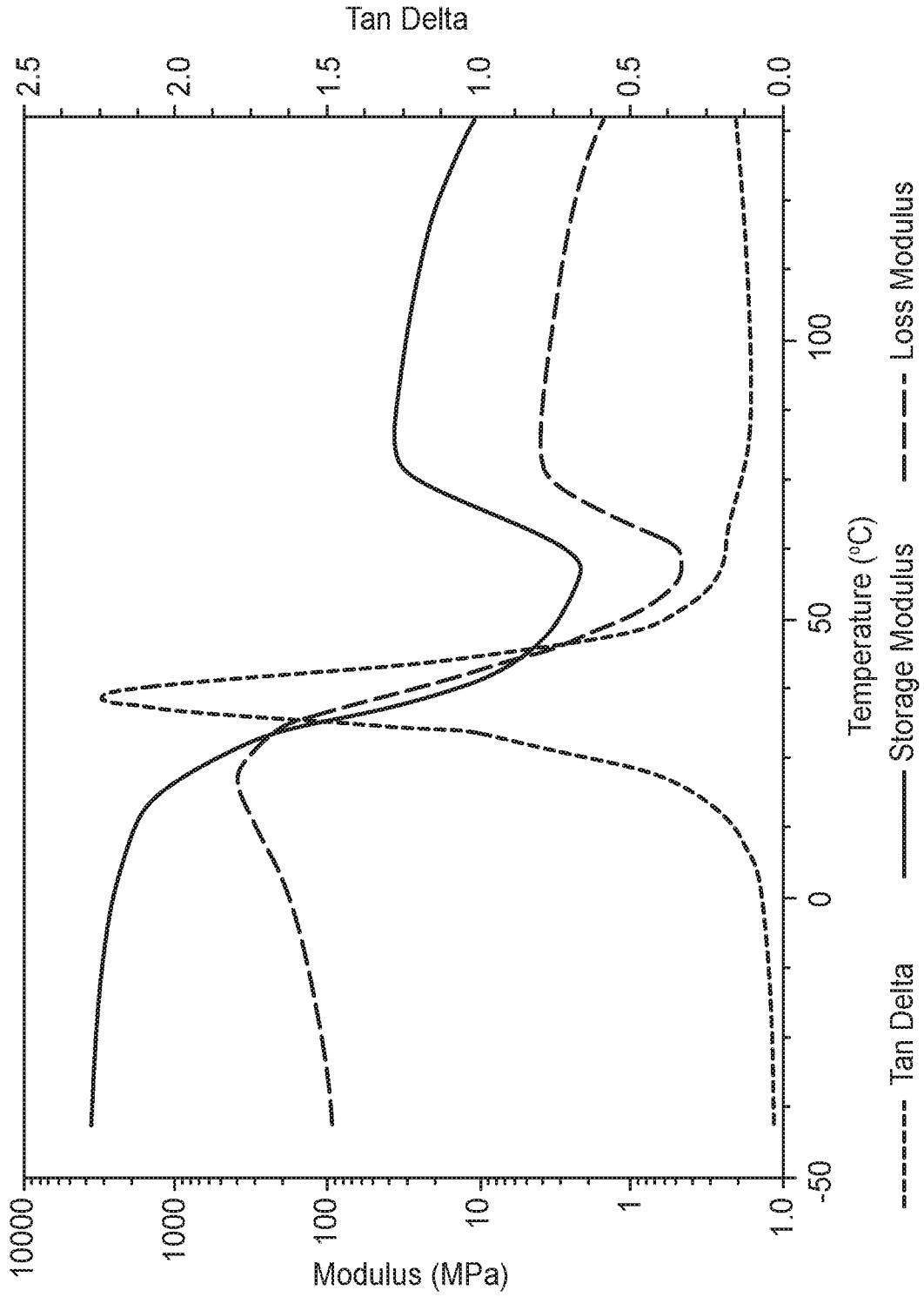


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No PCT/IB2020/052813
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A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08J5/18 C08L67/04
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C08J C09J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/222824 A1 (3M INNOVATIVE PROPERTIES CO [US]) 28 December 2017 (2017-12-28) page 5, lines 3-8 page 10, line 32 - page 11, line 2 page 22, line 26 - page 29, line 17 figures 1-8 example 22 claims 1-26 <div style="text-align: center;">----- -/--</div>	1-12, 14-26, 34,37-42

<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
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* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 25 May 2020	Date of mailing of the international search report 29/07/2020
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Vandoolaeghe, P
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INTERNATIONAL SEARCH REPORT

International application No PCT/IB2020/052813

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>KR 2011 0103812 A (LG HAUSYS LTD [KR]) 21 September 2011 (2011-09-21)</p> <p>abstract paragraphs [0029], [0080] - [0090] figure 1 claims 1, 3, 7, 9, 11</p> <p align="center">-----</p>	<p>1-4,7, 10,12, 13,15, 17,20, 21, 24-26, 34,37, 38,40</p>
A	<p>US 2003/166748 A1 (KHEMANI KISHAN [US] ET AL) 4 September 2003 (2003-09-04) examples 6, 13-43, 49, 54-60</p> <p align="center">-----</p>	<p>1-26,34, 37-42</p>

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2020/052813

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-26, 34(completely); 37-42(partially)

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-26, 34(completely); 37-42(partially)

Article comprising a first film layer comprising polylactic acid polymer, a second polymer having a Tg of at least 25°C, plasticizer and an inorganic pigment in an amount such that the ratio of polylactic acid polymer to inorganic pigment is less than 4.5:1

2. claims: 27-33(completely); 37-42(partially)

Article comprising a first film layer comprising polylactic acid polymer; a second polymer having a Tg of at least 25°C; plasticizer; wherein the film composition has a net melting endotherm for the first heating scan of less than 10 J/g at a rate of 10°C/min.

3. claims: 35, 36(completely); 37-42(partially)

Article comprising a film layer comprising semicrystalline polylactic acid polymer; optionally amorphous polylactic acid polymer; a second polymer having a Tg of at least 25°C; plasticizer; one or more carbodiimide hydrolysis stabilizers.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2020/052813

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 2017222824	A1	28-12-2017	CN 109312147 A	05-02-2019
			EP 3472243 A1	24-04-2019
			JP 2019528327 A	10-10-2019
			US 2019185662 A1	20-06-2019
			WO 2017222824 A1	28-12-2017

KR 20110103812	A	21-09-2011	NONE	

US 2003166748	A1	04-09-2003	NONE	
