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(2) Date: **Mar. 17, 2015**(57) **ABSTRACT**(30) **Foreign Application Priority Data**

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This invention relates to food packaging and to methods for its manufacture. It is particularly suited to packaging of perishable foodstuffs which require that oxygen transmission occur across the packaging barrier, but that water vapour transmission be restricted.

FOOD PACKAGE

FIELD OF THE INVENTION

[0001] The present invention relates to a food package and to methods for its manufacture. The food package finds particular, although not exclusive, use in the packaging of perishable foodstuffs.

BACKGROUND TO THE INVENTION

[0002] Polymeric materials find widespread use as packaging in the food industry. In such application not only does the packaging material have to contain the foodstuff, it must often preserve the product and, indeed, attractively display the product to the discerning consumer. Many foods are by their nature perishable and the properties of the packaging material will greatly impact the useful shelf life of a given foodstuff. Chemical changes, such as oxidation, and microbiological growth can be accelerated in the presence of oxygen. Accordingly, controlling the oxygen content in a package or the rate of oxygen ingress into a package is often one of the most critical attributes of food packaging. Breathability of the food package may also be important in releasing gases from the package during food storage.

[0003] In a modified atmosphere package, the product is exposed inside the pack to the normal atmospheric gases (oxygen, nitrogen, carbon dioxide and water vapour) but in concentrations which are different from those in the ambient air. The packaging usually consists of a polymeric film pouch or plastic container with a specified gas permeability. Multilayer barriers are often utilized.

[0004] Multilayer barrier packaging is usually constructed with a polar polymer as an internal layer which is covered with a polar polymer. The former acts as a gas barrier and the latter as a hydrophobic skin having a low water vapour transmission rate to prevent fast water absorption in the internal layer. Polyolefin skin layers covering a polar polymer layer are commonly utilised, for example, a polyethylene skin covering a polyethylene-vinyl alcohol copolymer (PE-EVOH).

[0005] EVOH copolymers show good oxygen barrier properties at low humidity, typically in the range of 0 to 60%. However, their gas barrier property deteriorates dramatically under high humidity conditions when the humidity is in the range of 75 to 90%. In fact, due to the polar nature of EVOH, such films generally exhibit poor moisture barrier. Therefore, EVOH is typically laminated with polyolefins on both sides to provide barrier properties for practical packaging applications in order to protect the EVOH from humidity effects. However, over time sufficient moisture may permeate the polyolefin hydrophobic skin such that the oxygen barrier properties of the EVOH layer will be compromised.

[0006] EVOH materials also require the use of adhesion promoters and/or tie-layer resins in order for them to bond adequately to polyolefin substrates. Without such tie resins, EVOH materials tend to peel off easily from the polyolefin substrate resulting in loss of barrier properties and poor appearance. A further disadvantage of EVOH is that it is relatively expensive. Additionally, from a renewable standpoint, EVOH is fully derived from fossil fuels.

[0007] In relation to the packaging of certain foodstuffs, such as whole poultry, existing methods include the use of a polymer based bag which is sealed by way of a metal clip. These clips can pose a safety hazard, if, for example, they find their way into the package. Therefore it would be desirable to

provide a packaging solution that would eliminate the need for metal clips. Further, it would be advantageous to improve the visual presentation of foods through the provision of new packaging solutions. Additionally, packaging designs that allow automation of the packaging process would also be desirable.

SUMMARY OF THE INVENTION

[0008] According to a first aspect there is provided a food package comprising:

(a) a support member comprising a multilayer film comprising:

(i) at least one starch layer comprising a modified starch; and
(ii) at least one other layer having a water vapour permeability coefficient less than $1 \text{ g}\cdot\text{mm}/\text{m}^2\cdot 24 \text{ hr}\cdot\text{atm}$ measured at 38°C . and 90% relative humidity; and

wherein the total thickness of the at least one starch layer is greater than 20% of the total thickness of the multilayer film and wherein the modified starch has a degree of substitution less than 1.5; and

(b) a lidding film wherein the lidding film is sealed to the support member such that a food product is enclosed thereby.

[0009] Preferably the water vapour permeability coefficient of the at least one other layer is less than $0.5 \text{ g}\cdot\text{mm}/\text{m}^2\cdot 24 \text{ hr}\cdot\text{atm}$ measured at 38°C . and 90% relative humidity, more preferably less than $0.2 \text{ g}\cdot\text{mm}/\text{m}^2\cdot 24 \text{ hr}\cdot\text{atm}$ measured at 38°C . and 90% relative humidity.

[0010] Preferably the total thickness of the at least one starch layer is greater than 30% of the total thickness of the multilayer film, more preferably greater than 40% of the total thickness of the multilayer film, even more preferably greater than 50% of the total thickness of the multilayer film. In some embodiments the total thickness of the at least one starch layer is greater than 60% of the total thickness of the multilayer film.

[0011] The multilayer film has a low oxygen permeability coefficient (OPC). In some embodiments, the multilayer film has an OPC less than $0.6 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% relative humidity (RH). Preferably the multilayer film has an OPC of less than $0.3 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% RH and more preferably an OPC of less than $0.2 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% RH. Most preferably, the multilayer film has an OPC of less than $0.1 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% RH and particularly preferably the multilayer film has an OPC of less than $0.05 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% RH.

[0012] In some embodiments, the multilayer film has an OPC less than $1.2 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 75% relative humidity (RH). Preferably the multilayer film has an OPC of less than $0.6 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 75% RH and more preferably an OPC of less than $0.2 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 75% RH. Most preferably, the multilayer film has an OPC of less than $0.1 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 75% RH and particularly preferably the multilayer film has an OPC of less than $0.05 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 75% RH.

[0013] In some embodiments, the OPC remains below $0.05 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% RH, for extended periods of time. Preferably the OPC remains below $0.05 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% RH for at least ten days, more preferably the OPC remains below $0.05 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% RH for 20 days, most preferably the OPC remains below $0.05 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% RH for thirty days. In a particularly preferred embodiment the OPC remains below $0.05 \text{ cm}^3 \text{ mm}/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$ at 50% RH for thirty days.

[0014] Accordingly, the multilayer films have an enhanced performance in respect of oxygen barrier properties over long periods of time. While not wishing to be bound by theory it is considered that the high moisture capacity of the at least one starch layer acts to extend the lifetime of the oxygen barrier effect, even when moisture levels within the at least one starch layer are relatively high.

[0015] Advantageously, from a renewable perspective the multilayer film contains a high proportion of biodegradable starch.

[0016] The thickness of the multilayer film and of each layer within the multilayer film may vary depending on the exact nature of the end use application.

[0017] Preferably, the total thickness of the multilayer film is between 10 and 1000 microns. In one embodiment the total thickness of the multilayer film is between 10 and 100 microns, more preferably between 20 and 80 microns. In another embodiment the total thickness of the multilayer film is between 100 and 1000 microns more preferably between 200 and 800 microns.

[0018] In some embodiments, the total thickness of the at least one starch layer is between 5 and 600 microns. In one embodiment, the total thickness of the at least one starch layer is between 5 and 50 microns, preferably between 10 and 40 microns. In other embodiments, the total thickness of the at least one starch layer is between 100 and 600 microns, preferably between 150 and 450 microns.

[0019] In some embodiments, the total thickness of the at least one other layer is between 5 and 400 microns. In one embodiment, the total thickness of the at least one other layer is between 5 and 25 microns preferably between 10 and 20 microns. In another embodiment, the total thickness of the at least one other layer is between 30 and 400 microns, preferably between 30 and 300 microns.

[0020] In a preferred embodiment the at least one starch layer has a total thickness between 100 and 600 micron and the at least one other layer has a total thickness between 10 and 400 micron. In another preferred embodiment the at least one starch layer has a total thickness between 100 and 400 micron and the at least one other layer has a total thickness between 40 and 250 micron.

[0021] In another preferred embodiment the at least one starch layer has a total thickness between 10 and 60 micron and the at least one other layer has a total thickness between 5 and 40 micron.

[0022] Other Layer

[0023] The other layer(s) may be chosen to impart certain physical and aesthetic properties to finished multilayer film. These properties may include, for example, antifog, strength, heat sealability, colour, or clarity. In some embodiments particularly preferred other layers are those having a low water vapour transmission rate.

[0024] In some embodiments the at least one other layer comprises a polyolefin, polyethylene terephthalate, nylon, polyvinylchloride and polyvinylidene dichloride or mixtures thereof. In one embodiment each of the other layers may comprise a mixture of components. In other embodiments one or more of the other layers may consist of multiple layers of different materials. In further embodiments each of the other layers may comprise different materials.

[0025] In some embodiments suitable polyolefins for the preparation of the polyolefin film layer are selected from the group consisting of ethylene homopolymers, propylene homopolymers, interpolymers of ethylene and propylene and

interpolymers of ethylene or propylene with one or more C_4 - C_{10} α -olefins, cyclic olefin polymers and copolymers, biaxially orientated polypropylene, and mixtures thereof.

[0026] In some embodiments suitable polyolefins are selected from copolymers of ethylene or propylene and one or more α -olefins. Both high density polyethylenes and linear low density polyethylenes may be preferably utilised.

[0027] Suitable linear low density polyethylenes (LLDPE) include copolymers of ethylene and α -olefins (about 5 to about 15 wt. %). Alpha-olefins include 1-butene, 1-hexene, 1-octene, and the like, and mixtures thereof. The density of LLDPE is within the range of about 0.865 to about 0.925 g/cm³.

[0028] Suitable high density polyethylenes (HDPE) include ethylene homopolymers and copolymers of ethylene and α -olefins (about 0.1 to about 10 wt. %). Suitable alpha-olefins include 1-butene, 1-hexene, 1-octene, and the like, and mixtures thereof. The density of HDPE is preferably from about 0.940 to about 0.970 g/cm³.

[0029] Suitable cyclic olefin polymers and copolymers include polymers of norbornene or tetracyclododecene and copolymers of norbornene or tetracyclododecene with one or more α -olefins. Examples are cyclic olefin polymers are Topas (Ticona) and Apel (Mitsui).

[0030] In some embodiments blends of polyolefins and other polymers may be advantageously employed. Cast polypropylene (cPP) or biaxially oriented polypropylene (BOPP) may be chosen for improved strength and low WVTR. Polyethylene terephthalate (PET) may be chosen for strength and shrinkability.

[0031] In other embodiments modified polyolefins, such as grafted polyolefins, may be utilised. A preferred grafted polyolefin is a maleic anhydride grafted polyolefin.

[0032] Starch Layer

[0033] The multilayer film comprises at least one starch layer comprising a modified starch, wherein the modified starch has a degree of substitution less than 1.5. The degree of substitution defines the average number of substituents per anhydroglucose unit. Accordingly, by definition, the maximum possible degree of substitution of starch is 3.0.

[0034] In one embodiment the at least one starch layer comprises a high amylose starch. Preferably, the amount of high amylose starch is between 5 and 80% by weight based on the total weight of the starch layer.

[0035] In another embodiment the modified starch is chemically modified so as to replace hydroxyl functionality with functionality selected from the group consisting of ethers and esters and mixtures thereof. Preferred esters comprise heptanoate or lower homologues. Particularly preferred esters include acetate.

[0036] In a further embodiment the modified starch is modified to include a hydroxyalkyl C_{2-6} group or modified by reaction with an anhydride of a carboxylic acid. Preferably the modified starch is modified to include a hydroxy C_{2-4} group. More preferably the modified starch is modified to include a hydroxy propyl group.

[0037] In a yet further embodiment the at least one starch layer comprises a water soluble polymer. Preferably, the starch layer comprises 1 to 20% by weight of a water soluble polymer, more preferably from 4 to 12% by weight of a water soluble polymer. Exemplary, but non-limiting, water soluble polymers are selected from the group consisting of polyvinylacetate, polyvinyl alcohol or mixtures thereof. Polyvinyl alcohol is a particularly preferred water soluble polymer.

[0038] In some embodiments the at least one starch layer may comprise water, preferably up to 20% by weight water, more preferably up to 12% by weight water. In some embodiments the water may serve as a plasticiser.

[0039] In some embodiments the moisture content of the at least one starch layer is generally the equilibrium moisture content at the environmental % RH. For example, the equilibrium moisture content ranges from about 4% at low % RH to more than 15% at high % RH.

[0040] In a still yet further embodiment the at least one starch layer comprises one or more polyol plasticisers, preferably up to 20% by weight of one or more polyol plasticisers, more preferably up to 12% by weight of one or more polyol plasticisers. Exemplary, but non-limiting, polyol plasticisers are selected from the group consisting of sorbitol, glycerol, maltitol, xylitol, and mixtures thereof.

[0041] In another embodiment the at least one starch layer may also comprise up to 50% by weight of natural unmodified starch.

[0042] In some embodiments the at least one starch layer comprises mixtures of starches and/or modified starches, for example, mixtures of high and low amylose starch, wherein one or more of the starch components may be modified.

[0043] In a further embodiment the at least one starch layer comprises a lubricant. Preferred lubricants are C_{12-22} fatty acids and/or C_{12-22} fatty acid salts. Preferably, the C_{12-22} fatty acid and/or a C_{12-22} fatty acid salt are present in an amount up to 5% by weight.

[0044] In some embodiments the at least one starch layer comprises one or more nanomaterials. Preferably, the nanomaterials are exfoliated within a starch nanocomposite. Exemplary nanomaterials include clays and modified clays particularly 'hydrophobically modified layered silicate clays'. Preferred clays include montmorillonite, bentonite, beidelite, mica, hectorite, saponite, nontronite, saconite, vermiculite, ledikite, magadite, kenyaite, stevensite, volkonskoite or a mixture thereof.

[0045] A 'hydrophobically modified layered silicate clay' or 'hydrophobic clay' is preferably a clay modified by exchange with a surfactant comprising long chain alkyl groups such as a long chain alkylammonium ion, for example, mono- or di- C_{12-22} alkylammonium ion, wherein polar substituents such as hydroxyl or carboxyl are not attached to the long chain alkyl. Examples of suitable clays include CLOISITE® 20A or CLOISITE® 25A from Southern Clay Products Inc.

[0046] In some embodiments the starch layer and/or the other layer may comprise colourants.

[0047] Adhesive

[0048] In some embodiments the at least one other layer may be fixed to the at least one starch layer through use of a suitable adhesive. This assists in minimising slip and therefore maintaining excellent barrier performance. Numerous suitable adhesives would be readily apparent to those having skill in the present art. Preferably the adhesive is selected so as to chemically bond to the at least one starch layer. Preferred adhesives comprise one or more polyurethanes.

[0049] Advantageously, the use of an adhesive overcomes or minimises the need for modified or grafted other layers to be utilised as tie layers. Accordingly, for example, standard film polyethylene grades may be successfully employed as polyolefin other layers in the multi-layer film. This is desirable from a cost consideration.

[0050] Other suitable adhesives include EVA copolymers, acrylic copolymers and terpolymers, ionomers, metallocene derived polyethylene, ethylene acrylic ester terpolymers and ethylene vinyl acetate terpolymers.

[0051] Those skilled in the art will be familiar with other adhesive lamination technology that would be suitable for adhering various types of plastics, including heat activated and UV activated systems. Exemplary adhesives include, polyurethane, epoxy, nylon, acrylic and acrylate.

[0052] Method of Preparation of the Multilayer Film

[0053] The multilayer film can be made by a variety of processes. The multilayer film can be made by co-extrusion, coating, and other laminating processes. The film can also be made by casting or blown film processes.

[0054] Coextrusion tends to use tie layers, and utilises modified other layers, such as modified (grafted) polyolefins. Coextrusion is generally able to achieve thinner overall gauges. Lamination is more suitable for thicker multilayer films utilising an adhesive.

[0055] In one embodiment a three layer film is provided comprising an inner starch layer and two outer polyolefin layers. In other embodiments adhesive layers may be employed between the starch layer and the polyolefin layers thus yielding a five layer film.

[0056] It should be understood by those with skill in the art that a three or five layer film is only one of many possible embodiments that employs starch and other layers. The number of layers and their relative thicknesses may be adjusted depending on the function or end-use of the film.

[0057] Additionally, further film layers comprising other materials commonly utilised in barrier film applications may be envisaged. Exemplary further film layers include metalised films, non-polymer films and the like.

[0058] Design of the Support Member

[0059] The support member comprising the multilayer film may be of various designs, depending on the nature of the foodstuff to be packaged. For example, the support member should be thick enough so as to adequately contain the foodstuff, which would generally depend on the weight of the foodstuff. Further, the shape of the support member may vary depending on the specific food to be packaged. For example, in providing a package for a whole chicken, the sides of the support member may advantageously be of sufficient height so as to 'plump' the chicken, thus enhancing presentation.

[0060] The support member may be advantageously formed from the multilayer film through thermoforming processes.

[0061] Lidding Film

[0062] In some embodiments the lidding film has a higher water vapour permeation rate and higher gas permeation rate than that of the multilayer film. The water vapour permeability coefficient of the lidding film is preferably greater than 1 g·mm/m²·24 hr·atm measured at 38° C. and 90% relative humidity. Preferably the lidding film has an oxygen permeability coefficient greater than 0.6 cm³ mm/m²·24 h·atm at 50% relative humidity (RH).

[0063] Preferred materials for lidding films include polyolefins such as polyethylene and polypropylene, polyethylene terephthalate, polystyrene, polyvinyl chloride, polyvinylidene dichloride, nylon, starch, polycarbonate, ethylene vinyl acetate and ethylene vinyl alcohol. The lidding film may comprise a single layer or may comprise a multilayer material having combinations of the aforementioned materials. Lidding films may be gas barrier or permeable shrink or non-

shrink films. Preferably, the lidding film is heat shrinkable. The lidding film may be flexible or rigid depending on the application.

[0064] In some embodiments the lidding film controls the barrier or breathability function of the food package. For barrier function preferred lidding film materials include ethylene vinyl alcohol, starch and nylon. For breathable lidding films preferred materials include polyolefins such as polyethylene.

[0065] Where a starch layer is employed in the lidding film it may include any of the embodiments herein disclosed in respect of the starch layer utilized in the multilayer film.

[0066] The thickness of the lidding film is dependent on whether it is to be utilized as a flexible or rigid structure. Where a flexible structure is desired, the thickness of the lidding film is preferably between 5 micron and 200 micron, more preferably between 15 micron and 100 micron, most preferably between 25 micron and 70 micron. When a more rigid structure is desired, for example in so called 'dome pack' applications, the lidding film thickness is preferably between 200 micron to 750 micron, more preferably between 300 micron to 500 micron.

[0067] The lidding film may be hermetically sealed to the support member through commonly used methods in the industry such as by the use of a shaped heat sealing bar applying sufficient pressure to the seal area. Rigid packs may require top and bottom seal heating. The latent shrink energy in the films is triggered by the radiant heat from the seal bar or by an external hot water shrink tunnel as a secondary process.

[0068] The food package may be gas flushed so as to provide a suitable atmosphere for food storage. The nature of the gas(es) may vary depending on the nature of the foodstuff and the packaging goal. Modified atmosphere packaging technology may be employed, as may permeable or breathable technology.

[0069] In another embodiment the package may be subjected to vacuum after inclusion of the foodstuff.

[0070] Food Package

[0071] Packages made from different polymeric materials will be permeable to different degrees to small molecules, for example gases and water vapour. Further, different materials will have different permeabilities to different molecules. The following Table indicates the relative value of permeabilities for several polymers in respect of the three most commonly utilized gases in modified atmosphere packaging.

Polymer	N ₂	O ₂	CO ₂
Polystyrene	1	2.6	10.4
LLDPE	1	3.1	11.1
LDPE	1	3.1	10.7
HDPE	1	3.2	11.9
PP	1	4.3	13.6
Nylon 6	1	3.4	18.4
PET	1	3.6	17.8

[0072] Accordingly, through appropriate choice of materials, the relative rates of small molecule permeation may be varied and controlled. This may be achieved through variation of material in a single layer or by variation of one or more materials in multiple layers. Alternatively or additionally it may be achieved through varying the thickness of one or more layers in single or multiple layer films.

[0073] Clearly this concept would not be limited to the above tabulated materials but would extend to other materials such as starch and ethylene vinyl alcohol based materials.

[0074] This concept may apply to the multilayer film and/or to the lidding film of the presently disclosed food package. Accordingly, this concept gives flexibility in achieving targeted or desirable gas permeation rates which may be tuned to a particular modified atmosphere package gas mix and the gas generation and absorption characteristics of the product. For high value products, such as specialty meats, the increase in shelf life may offset the use of higher complexity packaging.

[0075] In a further aspect there is provided a use of the food package according to any of the aforementioned embodiments, for packaging foodstuffs. Exemplary foodstuffs are red meat, poultry, such as chicken, duck, goose, turkey and the like, fish or shellfish, prepared meals either in a raw, partially cooked or fully cooked state, cooked or partially cooked vegetables.

[0076] In a further aspect there is provided a method of preparing a packaged food product comprising the steps of:

[0077] a) providing a support member according to any of the aforementioned embodiments;

[0078] b) providing a lidding film;

[0079] c) placing a food product on the support member;

[0080] d) extending the lidding film above the support member and product; and

[0081] e) sealing the lidding film to the support member such that the product is enclosed thereby.

[0082] The lidding film may be as disclosed in any of the aforementioned embodiments.

[0083] In one embodiment the method is performed using automated packaging equipment such as, for example, 'form and fill' equipment or 'thermoforming' equipment. In a preferred embodiment the support member is thermoformed. Automation advantageously allows for continuous production and use of printed lidding film, controlled date stamping and labeling, if utilised. Automation may also provide automatic loading of the foodstuff onto the formed support member. Sequential traceability and batch control may also be appropriate.

[0084] Throughout this specification, use of the terms "comprises" or "comprising" or grammatical variations thereon shall be taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof not specifically mentioned.

DETAILED DESCRIPTION OF THE INVENTION

[0085] It will now be convenient to describe the invention with reference to particular embodiments and examples. These embodiments and examples are illustrative only and should not be construed as limiting upon the scope of the invention. It will be understood that variations upon the described invention as would be apparent to the skilled addressee are within the scope of the invention. Similarly, the present invention is capable of finding application in areas that are not explicitly recited in this document and the fact that some applications are not specifically described should not be considered as a limitation on the overall applicability of the invention.

[0086] Polyolefins

[0087] Suitable LLDPE, HDPE and polypropylene can be produced by a Ziegler, single-site, or any other olefin poly-

merization catalyst. Ziegler catalysts and co-catalysts are well known in the art. Metallocene single-site catalysts are transition metal compounds that contain cyclopentadienyl (Cp) or Cp derivative ligands. For example, U.S. Pat. No. 4,542,199 teaches the preparation of metallocene catalysts. Non-metallocene single-site catalysts containing heteroatomic ligands, e.g., boraaryl, pyrrolyl, azaborolanyl or quinolanyl are also well known in the art.

[0088] The HDPE can also be multimodal. By “multimodal” it is meant that the polymer comprises at least two components, one of which has a relatively low molecular weight, the other a relatively high molecular weight. The multimodal polyethylene can be produced by polymerization using conditions that create a multimodal polymer product. This can be accomplished by using a catalyst system with two or more different catalytic sites or by using two or multi-stage polymerization processes with different process conditions in the different stages (e.g. different temperatures, pressures, polymerization media, hydrogen partial pressures, etc). Multimodal HDPE may be produced by a multistage ethylene polymerization, using a series of reactors, with comonomer addition in only one of the reactors.

[0089] Modified Starch

[0090] A preferred modified starch component is hydroxypropylated amylose starch. Other substituents may be hydroxyethyl or hydroxybutyl to form hydroxyether substitutions, or anhydrides such as maleic phthalic or octenyl succinic anhydride can be used to produce ester derivatives. The degree of substitution (the average number of hydroxyl groups in a unit that are substituted) is preferably 0.05 to 1.5. A preferred starch is a high amylose maize starch. Another preferred starch is a high amylose tapioca starch. A preferred modified starch component is a hydroxypropylated high amylose starch (for example ECOFILM® marketed by National Starch and Chemical Company, or Gelose® A939 marketed by Penford).

[0091] The other starch component, if utilised, is any commercially available starch. This may be derived from, for example, wheat, maize, tapioca, potato, rice, oat, arrowroot, and pea sources. These starches may also be chemically modified.

[0092] Water Soluble Polymer

[0093] The water soluble polymer component of the starch layer is preferably compatible with starch, water soluble, biodegradable and has a low melting point compatible with the processing temperatures for starch. Polyvinyl alcohol is a preferred polymer but polymers of ethylene-vinyl alcohol, ethylene vinyl acetate or blends with polyvinyl alcohol may be used. A preferred concentration range 4 to 12% by weight, more preferably 8%-12%.

[0094] Plasticiser

[0095] A range of plasticisers and humectants are useful additions to the starch layer, in order to aid processing and control and stabilize the mechanical properties of the barrier material, in particular in reducing dependency on moisture content and relative humidity. The desired plasticiser content depends primarily on the required processing behaviour during a (co)-extrusion process and subsequent blowing or stretching processes as well as on the required mechanical properties of the end product.

[0096] Cost and food contact are important issues in choosing the appropriate plasticizer. The preferred plasticizer is a mixture of polyols, such as mixtures of two or more, or three or more, or four or more, of sorbitol, glycerol, maltitol, man-

nitol, xylitol and erythritol. Alternatively, sorbitol, and one or more other polyols, particularly glycerol, maltitol, mannitol and xylitol are suitable, although erythritol, ethylene glycol and diethylene glycol are also suitable. The plasticizer plays a triple role:

[0097] 1. it provides suitable rheology for the extrusion compounding process and for the lamination process,

[0098] 2. it positively affects the mechanical properties of the product and,

[0099] 3. it may act as an anti-retrogradation or anti-crystallizing agent.

[0100] The preferred plasticizer content is up to 20% by weight of the starch layer depending on the particular application and co-extrusion or lamination process.

[0101] Sorbitol, glycerol and maltitol blends are particularly suitable for modifying the mechanical properties of the formulation, as is xylitol and blends of xylitol with sorbitol and glycerol. The larger the number of OH groups, the more effective the plasticiser is in reducing crystallisation. Sorbitol, maltitol and xylitol are particularly good humectants. Glycerol helps dissolve polyvinylalcohol during processing. Crystallisation is observed when sorbitol is used on its own. Some polyols (sorbitol and glycerol in particular) may exhibit migration to the surface, where either an opaque crystalline film may form in the case of sorbitol, or an oily film in the case of glycerol. Blending various polyols inhibits this effect to varying degrees. Stabilisation may be enhanced with the addition of glycerol monostearate and sodium stearyl lactylate as emulsifiers. Furthermore, synergistic effects with salt result in stronger effects on mechanical properties.

[0102] Other Plasticizers

[0103] Polyethylene glycol compounds may be used as emulsifying agents, plasticizers or humectants. Polyethylene oxide and polyethylene glycol alternately or together may also provide an increased water resistance, to prevent swelling which may result in delamination in multi-layer structures (MLS).

[0104] An alternative plasticiser is epoxidized linseed oil or epoxidized soybean oil. Being hydrophobic these additives may improve moisture sensitivity of the material. These plasticisers, preferably stabilized with an emulsifying system, aid processing but do not result in a significant further reduction in Young's modulus. Other plasticizers more commonly used in the PVC industry may be suitable, including tributyl citrate, 2,2,4 trimethyl-1,3-pentanediol diisobutyrate, and acetyl tri-ethyl citrate.

[0105] One may use up to 20% of a humectant or water binding agent or gelling agent which may act as a (co)plasticiser such as carrageenan, xanthan gum, gum arabic, guar gum or gelatine. Other humectants may be used such as sugar or glucose. Biopolymers such as carrageenan, typically used in food products as thickeners and partially soluble in cold water, fully soluble in hot water, are suitable to tailor mechanical properties. By binding water these components may have a significant plasticizing function. Gelatine may be added to improve the mechanical properties and reduce moisture sensitivity. Xanthan Gum has a high water holding capacity and also acts as an emulsifier and in starch compositions has an anti-retrogradation effect. Gum Arabic may also be used as a texturiser and film former, and the hydrophilic carbohydrate and hydrophobic protein enable its hydrocolloid emulsification and stabilization properties. Guar gum has similar anticrystallisation effects in starch compositions. Another suitable humectant is glyceryl triacetate.

[0106] Fatty Acid and/or Fatty Acid Salt

[0107] Fatty acids and/or fatty acid salts may be used as lubricants. The starch layer preferably comprises between 0.1 to 1.5% by weight of a C₁₂₋₂₂ fatty acid and/or a C₁₂₋₂₂ fatty acid salt. The fatty acid and/or fatty acid salt component is more preferably present in concentrations of 0.6 to 1%. Stearic acid is a particularly preferred component. Sodium and potassium salts of stearic acid may also be used. Cost can be a factor in the choice of this component but lauric, myristic, palmitic, linoleic and behenic acids are all suitable.

[0108] Adhesive

[0109] Polyurethane based adhesives are particularly suitable for fixing the other layer to the starch layer. The polyurethane adhesive may be prepared in situ through reaction of one or more isocyanates with the starch layer. Through reaction of the surface hydroxyl functions of the starch with isocyanate, urethane functions are formed. Preferred isocyanates are diisocyanates. Those skilled in the art would be able to select suitable isocyanates from the wide range typically employed in the art of polyurethane synthesis.

[0110] Alternatively, the polyurethane adhesive may comprise one or more polyols. Such two component systems comprising diisocyanate and polyol are well known in the art.

[0111] The adhesives may or may not contain solvent. The solvent may be organic or water based.

[0112] Exemplary isocyanates include methylene diphenyl diisocyanate and toluene diisocyanate. Exemplary polyols include polyether polyols such as polyethylene glycol or polypropylene glycol and polyester polyols such as adipate based polyols.

EXAMPLES

[0113] OTR was measured using ASTM F 1927-98 and WVTR was measured using ASTM F 1249-01. All component weights are expressed on a dry basis.

Example 1

[0114] A starch film was prepared by extrusion processing of a mixture of 88.5% by weight modified starch (ECO-

TABLE 1

Sample	Nominal % of starch layer thickness	Oxygen Transmission Rate (cm ³ /m ² · 24 h at 23° C., 1 atm pure oxygen)	Specimen thickness (micron)
PE/	60	50% RH	<0.05
Starch/			<0.05
PE		75% RH	<0.05
			<0.05
			507
			470
			496
			468

TABLE 2

Sample	Nominal % of starch layer thickness	Water Vapour Transmission Rate (g/m ² · 24 h at 38° C., 90% RH)	Specimen thickness (micron)
PE/Starch/PE	60	3.3	507
100/300/100		3.2	470

Examples 2 & 3

[0117] A starch film was prepared by extrusion processing of a mixture of 88.5% by weight modified starch (ECO-FILM®, National Starch and Chemical Company), 9% by weight polyvinylalcohol (Elvanol® 71-30), 2% by weight Cloisite 20A (Southern Clay Products) and 0.5% stearic acid and casting into a 150 µm sheet. This was then adhesively laminated on each side to 50 µm (Example 2) or 35 µm (Example 3) HDPE using a polyurethane adhesive system from Specialty Adhesives and Coatings. The lamination was performed on a standard laminating machine.

[0118] Samples were conditioned for 2 weeks at 50% and 75% RH (for OTR) and 38° C./90% RH (for WVTR) and measured after equilibration.

[0119] Table 3 collects the results.

TABLE 3

Sample	Nominal % of starch layer thickness	Oxygen Transmission Rate (cm ³ /m ² · 24 h)				Water Vapour Transmission Rate (g/m ² · 24 h at 38° C., 90% RH)	
		50% RH, 23° C.	Thickness (micron)	75% RH, 23° C.	Thickness (micron)	WVTR	Thickness (micron)
Example 2	60	0.55	258	0.91	265	3.00	260
PE/Starch/PE		0.46	262	0.98	254	3.22	255
Example 3	68	0.51	222	1.03	228	5.16	225
PE/Starch/PE		0.55	227	1.16	225	5.30	225

FILM®, National Starch and Chemical Company), 9% by weight polyvinylalcohol (Elvanol® 71-30), 2% by weight Cloisite 20A (Southern Clay Products) and 0.5% stearic acid and casting into a 300 µm sheet. This was then adhesively laminated on each side to 100 µm HDPE film using MOR Free PU adhesive (Rohm and Haas). The lamination was performed on a standard laminating machine.

[0115] Samples were conditioned for 2 weeks at 50% and 75% RH (for OTR) and 38° C./90% RH (for WVTR) and measured after equilibration.

[0116] Tables 1 and 2 collect the results.

Example 4

[0120] A starch film was prepared by extrusion processing of a mixture of 90.5% by weight modified starch (ECO-FILM®, National Starch and Chemical Company), 9% by weight polyvinylalcohol (Elvanol® 71-30) and 0.5% by weight stearic acid and casting into a 350 µm sheet. This was then adhesively laminated on each side to 50 µm HDPE using a polyurethane adhesive system from Specialty Adhesives and Coatings. The lamination was performed on a standard laminating machine.

[0121] Samples were conditioned for 2 weeks at 50% and 75% RH (for OTR) and 38° C./90% RH (for WVTR) and measured after equilibration.

[0122] Table 4 collects the results.

TABLE 4

Sample	Nominal % of starch layer thickness	Oxygen Transmission Rate cm ³ /m ² · 24 h				Water Vapour Transmission Rate g/m ² · 24 h at 38° C., 90% RH	
		50% RH, 23° C.	Thickness (micron)	75% RH, 23° C.	Thickness (micron)	WVTR	Thickness (micron)
PE/Starch/PE	78	0.05	465	0.15	465	3.25	472
		0.05	468	0.16	455	3.10	468

Example 5

[0123] A starch film was prepared by extrusion processing of a mixture of 90.5% by weight modified starch (ECO-FILM®, National Starch and Chemical Company), 9% by weight polyvinylalcohol (Elvanol® 71-30) and 0.5% by weight stearic acid and casting into a 350 µm sheet. This was then adhesively laminated to 50 µm HDPE on one side, and an 80 µm polypropylene film on the other side using a polyurethane adhesive system from Specialty Adhesives and Coatings. The lamination was performed on a standard laminating machine.

[0124] Samples were conditioned for 2 weeks at 50% and 75% RH (for OTR) and 38° C./90% RH (for WVTR) and measured after equilibration.

[0125] The results are collected in Table 5.

TABLE 5

Sample	Nominal % of starch layer thickness	Oxygen Transmission Rate cm ³ /m ² · 24 h				Water Vapour Transmission Rate g/m ² · 24 h at 38° C., 90% RH	
		50% RH, 23° C.	Thickness (micron)	75% RH, 23° C.	Thickness (micron)	WVTR	Thickness (micron)
PE/Starch/PP	73	PP side	<0.05	484	0.11	495	2.21
		facing	<0.05	500	0.11	500	2.16
		permeant	Not measured		0.10	Not measured	
		PE side			0.16		
		facing			484		
		permeant					

Comparative Example 1

[0126] A starch film was prepared by extrusion processing of a mixture of 88.5% by weight modified starch (ECO-FILM®, National Starch and Chemical Company), 9% by weight polyvinylalcohol (Elvanol® 71-30), 2% by weight Cloisite 20A (Southern Clay Products) and 0.5% stearic acid and casting into a 290 µm sheet.

Comparative Example 2

[0128] A starch film was prepared by extrusion processing of 100% by weight modified starch (ECOFILM®, National Starch and Chemical Company), and casting into a 300 µm sheet.

[0129] Samples were conditioned for 2 weeks at 50% and 75% RH (for OTR) and 38° C./90% RH (for WVTR) and measured after equilibration.

[0130] Table 7 shows the results.

TABLE 7

Sample	Oxygen Transmission Rate cm ³ /m ² · 24 h				Water Vapour Transmission Rate g/m ² · 24 h at 38° C., 90% RH	
	50% RH, 23° C.	Thickness (micron)	75% RH, 23° C.	Thickness (micron)	WVTR	Thickness (micron)
Starch Sheet	0.50	295	1.30	260	337	290
	0.49	320	1.26	295	374	275

Summary of Examples 1 to 5 and Comparative
Examples 1 and 2

[0131] Table 8 collects the OTR and OPV (oxygen permeation value) for each of the Examples. The OPV are normalised to 1 mm thick samples, based on the core starch layer thickness only.

TABLE 8

Example	Core Thickness micron	Skin Thickness micron	OTR (50% RH) [cm ³ /m ² · 24 h]	OPV (50% RH) [cm ³ · mm/m ² · 24 h · atm]	OTR (75% RH) [cm ³ /m ² · 24 h]	OPV (75% RH) [cm ³ · mm/m ² · 24 h · atm]
1	300	100	<0.05	<0.05	<0.05	<0.05
2	150	50	0.51	0.08	0.95	0.14
3	150	35	0.53	0.08	1.10	0.16
4	350	50	0.05	0.02	0.16	0.06
5	350	50	<0.05	<0.05	0.13	0.05
CE1	290	0	0.21	0.06	1.40	0.41
CE2	300	0	0.50	0.15	1.30	0.40

[0132] It is evident from the results that the multilayer films of Examples 1 to 5 show excellent barrier performance. It is noted that where the core starch layer is approximately 300 micron thick, OTR is substantially reduced in samples having outer layers, relative the performance of a starch layer alone. Thinner starch core layers have low OTR at high (75%) RH relative to starch alone. Starch layers alone, in the absence of outer layers, indicate very high WVTR.

Example 6

[0133] The approximately 500 micron starch based film of Example 1 was thermoformed into a semi-rigid support member using an automated Form-Fill-Seal machine. A whole uncooked chicken was placed within the thermoformed support member and a lidding film sealed to the periphery of the support member. The appearance of the resulting packaged chicken was excellent.

Example 7

[0134] The shelf-life of whole chickens was studied using chickens packed according to Example 6 but utilising a 545 micron starch based film for the support member. A PE/EVOH/PE barrier film was used as the lidding film. The aim was to provide packing that would achieve a 9 day shelf life. Three different modified atmospheres were studied. These were 20% CO₂/80% O₂, 40% CO₂/70% N₂ and 40% CO₂/60% O₂. A non-barrier packaging was also studied.

[0135] The chickens were stored at 8° C. and 4° C. and were subjected to microbiological analysis at 0, 4, 6, 8 and 13 days. The chickens were tested for Total Viable Count (TVC) aerobic and anaerobic. Gas analysis was also performed at the same time intervals.

[0136] The gas analysis results indicated that the different modified atmosphere compositions remained stable throughout the 13 days of storage, except for the 20% CO₂/80% O₂ composition which became unstable at 13 days, showing an increase in CO₂ proportion.

[0137] All the modified atmosphere samples utilising the packing according to the invention were under the limit for TVC aerobic at 8 days at 8° C. and only the 20% CO₂/80% O₂

sample was unacceptable at 13 days. All the modified atmosphere samples were acceptable at 4° C.

[0138] The control with a non-barrier film was unacceptable at day 13, even at 4° C.

[0139] The three modified atmospheres tested were compliant with the requirement of a 9 day shelf life, both in terms of gas composition and microbiological composition.

1. A food package comprising:

- (a) a support member comprising a multilayer film comprising:
 - (i) at least one starch layer comprising a modified starch; and
 - (ii) at least one other layer having a water vapour permeability coefficient less than 1 g·mm/m²·24 hr·atm measured at 38° C. and 90% relative humidity; and wherein the total thickness of the at least one starch layer is greater than 20% of the total thickness of the multilayer film and wherein the modified starch has a degree of substitution less than 1.5; and
- (b) a lidding film wherein the lidding film is sealed to the support member such that a food product is enclosed thereby.

2. A package according to claim 1 wherein the water vapour permeability coefficient of the at least one other layer is less than 0.5 g·mm/m²·24 hr·atm, preferably less than 0.2 g·mm/m²·24 hr·atm.

3. A package according to claim 1 wherein the total thickness of the at least one starch layer is greater than 30% of the total thickness of the multilayer film, preferably greater than 40% of the total thickness of the multilayer film, more preferably greater than 50% of the total thickness of the multilayer film.

4. A package according to claim 1 wherein the at least one other layer comprises a polyolefin, polyethylene terephthalate, nylon, polyvinylchloride and polyvinylidene dichloride or mixtures thereof.

5. A package according to claim 4 wherein the polyolefin is selected from the group consisting of ethylene homopolymers, propylene homopolymers, interpolymers of ethylene and propylene and interpolymers of ethylene or propylene with one or more C₄-C₁₀ α-olefins, cyclic olefin polymers and copolymers, biaxially orientated polypropylene, chemically modified polyolefins and mixtures thereof.

6. A package according to claim 4 wherein the polyolefin is selected from the group consisting of high density polyethylene, low density polyethylene, linear low density polyethylene, polypropylene, biaxially orientated polypropylene and mixtures thereof.

7. A package according to claim 1 comprising an inner starch layer and two outer polyolefin layers.

8. A package according to claim 1 wherein the at least one starch layer is fixed to the at least one other layer by an adhesive.

9. A package according to claim 8 wherein the adhesive comprises a polyurethane and/or polyurethane urea.

10. A package according to claim 1 wherein the film has an oxygen permeability coefficient (OPC) less than $0.6 \text{ cm}^3 \text{ mm/m}^2 \cdot 24 \text{ h-atm}$ at 50% RH, preferably less than $0.3 \text{ cm}^3 \text{ mm/m}^2 \cdot 24 \text{ h-atm}$ at 50% RH, more preferably less than $0.1 \text{ cm}^3 \text{ mm/m}^2 \cdot 24 \text{ h-atm}$ at 50% RH, most preferably less than $0.05 \text{ cm}^3 \text{ mm/m}^2 \cdot 24 \text{ h-atm}$ at 50% RH.

11. A package according to claim 1 wherein the total thickness of the multilayer film is between 10 and 1000 micron.

12. A package according to claim 1 wherein the at least one starch layer has a total thickness between 100 and 600 micron and the at least one other layer has a total thickness between 10 and 400 micron.

13. A package according to claim 1 wherein the at least one starch layer has a total thickness between 10 and 60 micron and the at least one other layer has a total thickness between 5 and 40 micron.

14. A package according to claim 1 wherein the modified starch comprises a high amylose starch.

15. A package according to claim 1 wherein the modified starch is chemically modified so as to replace hydroxyl functionality with functionality selected from the group consisting of ethers and esters and mixtures thereof.

16. A package according to claim 1 wherein the modified starch is chemically modified to include a hydroxyalkyl C_{2-6} group or modified by reaction with an anhydride of a carboxylic acid.

17. A package according to claim 1 wherein the at least one starch layer further comprises at least one water soluble polymer.

18. A package according to claim 17 wherein the at least one water soluble polymer is selected from the group consisting of polyvinyl alcohol and polyvinyl acetate and mixtures thereof.

19. A package according to claim 1 wherein the at least one starch layer further comprises at least one plasticiser.

20. A package according to claim 19 wherein the at least one plasticiser comprises one or more polyols.

21. A package according to claim 1 wherein the lidding film has a higher permeation rate for both moisture and gases than the multilayer film.

22. A package according to claim 1 wherein the lidding film has a water vapour permeability coefficient greater than $1 \text{ g-mm/m}^2 \cdot 24 \text{ hr-atm}$ measured at 38°C . and 90% relative humidity.

23. A package according to claim 1 wherein the lidding film has an oxygen permeability coefficient (OPC) greater than $0.6 \text{ cm}^3 \text{ mm/m}^2 \cdot 24 \text{ h-atm}$ at 50% RH.

24. A method of packaging a food product comprising the steps of:

- a) providing a support member according to claim 1;
- b) providing a lidding film;
- c) placing a food product on the support member;
- d) extending the lidding film above the support member and product; and
- e) sealing the lidding film to the support member such that the product is enclosed thereby.

25. The method of claim 24, wherein one or more steps is automated.

26. The method of claim 24, wherein the method comprises at least the step of thermoforming the support member.

27. The method of claim 24, wherein the product is red meat, poultry, fish, cooked vegetables or a prepared meal.

28. A package according to claim 1 wherein the at least one starch layer comprises one or more nanomaterials.

29. A package according to claim 28 wherein the nanomaterial includes clays and modified clays.

30. A package according to claim 29 wherein the modified clay is a hydrophobically modified layered silicate clay.

31. A package according to claim 30 wherein the hydrophobically modified layered silicate clay is a clay modified with a surfactant comprising long chain alkyl groups wherein polar substituents are not attached to the long chain alkyl.

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