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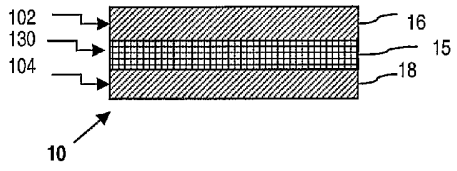
(54) Title: MULTILAYER PACKAGING BARRIER FILMS COMPRISING ETHYLENE VINYL ALCOHOL COPOLYMERS



(57) Abstract: Compositions and packaging films are provided having a multilayer oxygen barrier comprising an EVOH copolymer layer in contact with at least one polyamide layer. The EVOH copolymer compositions preferably comprise about 44mol%, or less, of ethylene. Multilayer packaging films can optionally include an exterior layer comprising heat resistant materials such as polyester or polyamide. The multilayer oxygen barriers described herein can provide high shrink films with desirably high oxygen barrier properties. The oxygen barriers can be used in making heat-shrinkable films and food packages having desirable high levels of free shrink.

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MULTILAYER PACKAGING BARRIER FILMS COMPRISING ETHYLENE VINYL ALCOHOL COPOLYMERS

RELATED APPLICATIONS

[001] This application claims the benefit of U.S. provisional application 60/634,853, filed December 10, 2004, entitled "Heat Shrinkable Nylon Blend Films," by Tomas A. Schell, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[002] Food packaging films comprising an EVOH barrier layer, and food packages comprising the same, are provided herein.

BACKGROUND

[003] In the food industry, heat-shrinkable films are utilized to maintain freshness. Meat is frequently sold fresh, frozen or cooked; therefore films advantageously provide protection at various temperatures. Food items such as primal and subprimal cuts of beef, ground beef and processed meats are known to use coextruded or laminated films which utilize such compositions as nylon, polyester, ethylene vinyl alcohol copolymers (EVOH), ethylene-vinyl acetate copolymer (EVA) and ionomers. It is also generally known that selection of films for packaging food products includes consideration of such criteria as barrier properties, cost, durability, puncture resistance, flex-crack resistance, FDA approval, machinability, optical properties such as gloss and haze, printability, sealability, shrinkability, shrink force, stiffness, and strength.

[004] Manufacturers and wholesalers use flexible thermoplastic packaging films to provide economical, sanitary containers, which help protect and/or preserve the freshness and wholesomeness of their products. These films are often sold in bag form. For example, a single or multilayer film is made into bags using a tubular film or one or more flat sheets or webs of film by well known processes involving e.g. cutting, folding and/or sealing the film

to form bags. These films and bags may be printed and may also be uniaxially or biaxially oriented, heat shrinkable, irradiated, or may contain film layers which are abuse resistant or puncture resistant or which are crosslinked or which enhance or retard or prevent transmission of light, gases, or liquids therethrough. A typical packaging bag has 1-3 sides heat sealed by the bag manufacturer leaving one open side to allow product insertion. For example, a processor may insert ham, poultry, cheese, primal or subprimal meat cuts, ground beef, fruits, vegetables, bread or other products making a final seal to hermetically enclose the product in the bag. This final seal may follow gas evacuation (i.e. vacuum removal) or replacement of the gaseous environment within the bag by one or more gases to provide some advantage such as to assist product preservation. This final seal is frequently a heat seal similar to the initial seals produced by the bag manufacturer although the actual heat sealing equipment may vary.

[005] The multilayer packaging films often comprise an oxygen barrier layer, which is typically a core layer positioned between at least two other layers. For example, the film, bag, process and package can comprise heat sealable, oxygen or moisture barrier films for holding a foodstuff during cooking and/or for packaging for sale of such a foodstuff after a pasteurization or cooking period. One polymer typically used as a barrier layer is ethylene vinyl alcohol copolymers (EVOH), which are also known as saponified or hydrolyzed ethylene vinyl acetate copolymers. In addition to its desirable properties as a barrier to oxygen and other gases, EVOH is also an effective barrier to odors, fragrances, solvents and oils. EVOH and EVOH copolymers are generally classified according to ethylene content, for example by mole percent. Typically, as the percentage of ethylene increases in relatively low humidity applications, the gas barrier properties decrease, moisture barrier properties improve, and the resin is more processable. At higher levels of humidity, for example at levels that are common for the packaging of meat, of from 90% to 92% humidity, higher ethylene content results in an increase in the moisture barrier properties. Higher percentages of ethylene in an EVOH barrier film can also be easier to orient at lower temperatures, for example in

making biaxially oriented heat shrinkable films. Therefore, processing oriented heat shrinkable films comprising an EVOH barrier layer has been a trade off between the ease of orientation and the level of oxygen barrier capability of the film.

[006] To improve the processability while maintaining desirable levels of oxygen barrier properties, EVOH barrier layers can be placed in contact with additional layers formed from polyamides. A polyamide is a polymer having amide linkages along the molecular chain structure. Nylon polyamides, which are synthetic polyamides, can be placed on either side of EVOH barrier layers to improve the physical properties of the film, such improved processability, strength, stiffness and abrasion resistance. Nylon is the generic name for a family of polyamide polymers characterized by the presence of the amide group-CONH. In the food industry, thermoplastic flexible films are used to keep food fresh prior to consumption, or for cooking food products. Greater use of centralized processing of foods in conjunction with increased handling and longer delivery times associated with long distance transportation have increased the demand for packaging films. Generally, nylon films are made by processes which include casting or blown film and these films may be uni- or biaxially oriented. Specific types of nylon such as nylon 6, nylon 6,6, nylon 11 and nylon 12 have been made into films. Known advantages of nylon films relative to other film materials in packaging applications include good oxygen and flavor barrier characteristics, durability at low temperatures and thermal stability. Certain nylon films can be used in oriented multilayer films. These multilayer films may also include one or more additional layers of films made of various resins, for example, low density polyethylene (LDPE), ethylene-vinyl acetate copolymer (EVA), ionomer, PVDC, or copolymers of ethylene and methacrylate. Nylon containing films have also been used in vacuum packaging of fresh meat. Typical and generally known films suitable for packaging and information on film manufacture are described in the Encyclopedia of Polymer Science and Engineering 2nd Ed., Vol. 7, pp. 73-127, Vol. 10, pp. 684-695 (John Wiley & Sons, Inc., 1987) whose teachings are hereby incorporated by reference.

[007] Multilayer films comprising one or more polyamide layers in contact with an EVOH barrier film can provide improved impact resistance, flex crack resistance, or drawability to the multilayer film. For example, U.S. Patent Nos. 6,068,933 and 6,562,476 to Shepard et al. discloses multilayer films comprising two nylon layers in contact with an EVOH barrier layer. Multilayer films can comprise a polyester layer in addition to a polyamide layer. For example, U.S. Patent No. 6,699,549 to Ueyama et al. discloses multilayer structures comprising a polyester layer and a polyamide layer. However, for forming biaxially oriented heat shrinkable films, EVOH barrier layers with lower ethylene content can often require a higher temperature for orientation, and therefore exhibit lower shrink properties, even though providing higher oxygen barrier properties. What is needed are heat shrinkable polyamide films comprising an EVOH barrier layer with a lower ethylene content that still retain desirably high shrink properties.

SUMMARY

[008] As described herein, packaging films comprising a polyamide layer in contact with an EVOH barrier layer can provide for lowering the ethylene content of EVOH barrier layer while desirably retaining higher levels of free shrink, greater ease of processing, and lower orientation temperatures at a given ethylene content.

[009] In a first embodiment, packaging films are provided that comprise an EVOH barrier layer and a polyamide layer. For heat shrinkable packaging films, an effective amount of ethylene in the EVOH core barrier layer can be selected to provide desired levels of processability, a desirably lower orientation temperature, and desirably high level of free shrink. Preferably, the polyamide layer is in contact with at least one side of an EVOH core barrier layer. More preferably, the EVOH barrier layer is a core oxygen barrier layer positioned between and in contact with two polyamide layers positioned on opposite sides of the EVOH barrier layer.

[010] The packaging films can be single layer or multilayer, and preferably have a total free shrink measured at 90°C of at least 30%, 40% or 50% in at least one of the machine direction or transverse direction. The packaging films preferably have a free shrink of at least 30% at 90ºC in one direction, more preferably at least 30% in two directions, where each direction is either a machine direction or a transverse direction. Even more preferably, the packaging films have a free shrink of at least 40% in a first direction and at least 50% in a second direction. The packaging films are preferably biaxially oriented, heat-shrinkable, or both. Preferably, the films have a total free shrink at 90°C of at least about 80%. For example, the film can have a free shrink value at 90°C between about 80% and about 120% at 90°C. In some embodiments, the films can have a total free shrink at 90°C of at least about 90%, more preferably at least about 95%, still more preferably at least about 100% and even more preferably at least about 105%.

[011] The EVOH barrier layer desirably comprises less than 50 mol% ethylene, and more preferably less than about 48 mol% or 44 mol% ethylene. For example, the EVOH barrier layer preferably comprises 38 mol% ethylene, or 32 mol% or 29 mol% ethylene. The polyamide layer can comprise a polyamide homopolymer or copolymer, or a blend of two or more polyamide polymers or copolymers.

[012] The multilayer film can comprise one or more polyamide layers having the same or different compositions. Each polyamide layer preferably comprises one or more polyamide homopolymers, polayamide copolymers, or blends of polyamide polymers. Examples of suitable polyamide copolymers include an amorphous nylon copolymer, a low temperature polyamide, a high temperature polyamide, and blends of two or more nylon polymers. As used herein, a low temperature polyamide preferably has a melting point of less than about 155°C; a high temperature polyamide preferably has a melting point higher than the low temperature polyamide, and more preferably at least about 155°C. Examples of low temperature polyamide compositions include nylon 6/69 and nylon 6/12 having a melting temperature of less than about

155°C; examples of high temperature polyamide compositions include nylon 6, nylon 6/66 or nylon 6/12 with a melting temperature of at least about 155°C, or combinations thereof. The amorphous nylon copolymer preferably consists of a nylon polymer or copolymers with no measurable melting point and no heat of fusion, such as nylon 6I/6T, nylon 66/6I/69 copolymer, nylon copolymers of hexamethylene isophthalamide or terephthalamide units and mixtures thereof. More preferably, the heat shrinkable packaging film comprises nylon 6/69 as a low temperature polyamide.

[013] In one aspect, a polyamide layer can comprise or consist essentially of a nylon blend composition. One particularly preferred nylon blend composition comprises: an amorphous nylon copolymer, a low temperature polyamide and a high temperature polyamide. The blend compositions can comprise up to about 50% by weight of the amorphous nylon copolymer. Preferably, the blends compositions comprise between about 10% to about 50%, about 10% to about 30%, or about 20% by weight of the amorphous nylon copolymer. The blend compositions can also comprise up to about 50% by weight of the low temperature polyamide. The blend compositions can further comprise up to about 80% by weight of the high temperature polyamide. Other preferred nylon blend compositions suitable for a polyamide layer are disclosed in U.S. Patent No. 5,480,945 to Vicik, which is incorporated herein by reference, and include blends of amorphous nylon and a polyamide with a melting point of 145°C or higher.

[014] In a second embodiment, multilayer heat-shrinkable packaging films are provided that comprise the EVOH barrier layer in contact with one or more polyamide layers, as described in the first embodiment, as part of a multilayer film comprising other layers, such as heat-resistant layers, sealant layers, and adhesive layers. The multilayer heat-shrinkable films can have an exterior surface and an interior surface, and include 3, 5 or 7 layer films having desirably high levels of free shrink. In one aspect, the multilayer film includes a heat resistant layer that can comprise or consist essentially of a blend of an amorphous nylon copolymer, a low temperature polyamide and/or a high temperature polyamide. The heat resistant layer can be positioned at or near

the exterior surface of the packaging film, and can be an exterior layer. The multilayer film can also include a sealant layer that is preferably positioned at or near the interior surface of the packaging film, and can be an interior layer. The sealant layer can comprise a suitable heat-sealable polymer such as an ethylene-α-olefin. The EVOH oxygen barrier layer and one or more polyamide layers can be positioned between the heat-resistant layer and the sealant layer. Optionally, one or more adhesive layers can be disposed between a polyamide layer and the heat-resistant layer or between a polyamide layer and the sealant layer. Preferred configurations for the multilayer film comprise an EVOH core oxygen barrier layer positioned between and in contact with two polyamide layers. The multilayer heat-shrinkable packaging films preferably have a free shrink of at least 40% at 90ºC in one direction, more preferably at least 40% in two directions, and a total free shrink at 90°C of at least about 80%, 90%, 100% or greater.

[015] In a third embodiment, heat-shrinkable food packages are provided. The heat-shrinkable food packages preferably include one or more polyamide core layers in contact with the EVOH oxygen barrier layer, as described with respect to the first embodiment. The food packages can include an oxygen barrier layer positioned between an exterior layer and the interior layer, in contact with a first polyamide layer on one side and a second polyamide layer on the opposite side. The food package can also include a heat resistant layer, a sealant layer and one or more adhesive layers having any suitable composition, as described with respect to the second embodiment. Preferably, the heat resistant layer can comprise or consist essentially of a blend of an amorphous nylon copolymer, a low temperature polyamide and a high temperature polyamide. The heat resistant layer is preferably positioned at or near the exterior surface of the packaging film, and can be an exterior layer, but can also form a polyamide core layer described with respect to the second embodiment. Optionally, the heat resistant layer can be oriented in any suitable manner, but is preferably biaxially oriented. The sealant layer is preferably positioned at or near the interior surface of the package, for example as an interior layer. Adhesive layers may also be included between

a heat resistant exterior layer and the first polyamide layer or between the sealant layer and the second polyamide layer. In some embodiments, the heat-shrinkable food package can be a cook-in package, preferably when the food package comprises a sealant layer formed from a material that is compatible with cooking conditions.

[016] The heat-shrinkable food packages can have a total free shrink at 90°C of at least about 80%. The heat-shrinkable packages can also have a total free shrink measured at 90°C of about 80% to about 120%, preferably at least about 90%, more preferably at least about 95%, even more preferably at least about 100% and about 105%. The packaging preferably has a free shrink of at least 40% at 90°C in one direction, more preferably at least 40% in two directions. Even more preferably, the packaging has a free shrink of at least 40% in a first direction and at least 50% in a second direction. The heat-shrinkable food packages can have any suitable number and configuration of layers. Preferably, the heat-shrinkable food packages can be formed from a multilayer packaging film described with respect to the second embodiment. In some embodiments, the heat-shrinkable food packages can further comprise an oxygen barrier layer preferably positioned between the heat resistant layer and an interior layer. For example, the oxygen barrier layer can be in contact with the heat resistant layer and an adhesive layer.

[017] The compositions, films and packages provided herein are useful to process and/or package articles, especially foodstuffs such as ham, beef, poultry, cheese or processed meat, which may be cooked in a film comprising a composition disclosed herein. Preferably, the food packaging films and packages provided herein are used for packaging various meat or cheese products. Certain embodiments are described in the Detailed Description below.

BRIEF DESCRIPTION OF THE DRAWINGS

[018] **Fig. 1** shows a cross sectional schematic of a first exemplary multilayer film.

[019] **Fig. 2** shows a cross sectional schematic of a second exemplary multilayer film.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[020] In discussing plastic film packaging, various polymer acronyms are used herein and they are listed below. Also, in referring to blends of polymers a colon (:) will be used to indicate that the components to the left and right of the colon are blended. In referring to film structure, a slash "/" will be used to indicate that components to the left and right of the slash are in different layers and the relative position of components in layers may be so indicated by use of the slash to indicate film layer boundaries. Acronyms commonly employed herein include:

EAA - Copolymer of ethylene with acrylic acid

EVA - Copolymer of ethylene with vinyl acetate

EVOH - A saponified or hydrolyzed copolymer of ethylene and vinyl acetate

MA Saran - methyl acrylate and vinylidene chloride

PE - Polyethylene (an ethylene homopolymer and/or copolymer of a major portion of ethylene with one or more α-olefins)

PP - Polypropylene homopolymer or copolymer

PET - Poly(ethylene terephthalate)

PVDC - Polyvinylidene chloride (also includes copolymers of vinylidene chloride, especially with vinyl chloride), also referred to as Saran

[021] A "core layer," as used herein, refers to a layer positioned between and in contact with at least two other layers.

[022] An "outer layer," as used herein, refers to a layer forming at least a portion of an exterior or interior surface. The outer layer can be an interior layer or an exterior layer. In a multilayer film, an outer layer can contact another layer. In a single-layer film, the layer itself can be an outer layer that is both an exterior layer and an interior layer.

[023] The term "exterior layer" refers to a layer comprising the outermost surface of a film or product. For example, an exterior layer can form the

exterior surface of a package that contacts the exterior layer of another package during overlapping heat sealing of two packages.

[024] The term "interior layer" refers to a layer comprising the innermost surface of a film or product. For example, an interior layer forms the interior surface of an enclosed package. The interior layer can be the food-contact layer and/or the sealant layer. As used herein, the term "barrier", and the phrase "barrier layer", as applied to films and/or film layers, are used with reference to the ability of a film or film layer to serve as a barrier to one or more gases or moisture.

[025] The term "adhesive layer," or "tie layer," refers to a layer or material placed on one or more layers to promote the adhesion of that layer to another surface. Preferably, adhesive layers are positioned between two layers of a multilayer film to maintain the two layers in position relative to each other. Unless otherwise indicated, an adhesive layer can have any suitable composition that provides a desired level of adhesion with the one or more surfaces in contact with the adhesive layer material. Typically, an adhesive layer placed between a first layer and a second layer in a multilayer film can comprise components of both the first layer and the second layer to promote simultaneous adhesion of the adhesive layer to both the first layer and the second layer to opposite sides of the adhesive layer.

[026] As used herein, the phrases "seal layer," "sealing layer," "heat seal layer," and "sealant layer," refer to an outer film layer, or layers, involved in the sealing of the film to itself, another film layer of the same or another film, and/or another article which is not a film. In general, the sealant layer is an interior layer of any suitable thickness, that provides for the sealing of the film to itself or another layer. With respect to packages having only fin-type seals, as opposed to lap-type seals, the phrase "sealant layer" generally refers to the interior surface film layer of a package, as well as supporting layers of the interior surface of the sealant layer. The inside layer frequently also serves as a food contact layer in the packaging of foods. In general, sealant layers employed in the packaging art have included thermoplastic polymers, such as polyolefin (e.g., linear low density polyethylene, very low density polyethylene,

homogeneous polymers such as metallocene catalyzed ethylene/alpha-olefin copolymer, etc.), polypropylene homopolymers and copolymers, polyamide, polyester (e.g., polyethylene terephthalate glycol), ethylene/ester copolymer (e.g., ethylene/vinyl acetate copolymer), ionomer, and functional equivalents thereof. More specifically, the sealant layer may comprise one or more materials selected from thermoplastic resins inclusive of: polyolefins polymerized by using a single-site catalyst or metallocene catalyst (sometimes abbreviated as "SSC") inclusive of linear low-density polyethylene (abbreviated as "SSC-LLDPE") and very low-density polyethylene (abbreviated as "SSC-VLDPE"); conventional types of ethylene-α-olefin copolymers inclusive of "LLDPE" and "VLDPE" in terms of generally accepted abbreviations; ethylene-vinyl acetate copolymer (abbreviated as "EVA"), ethylene-methacrylic acid copolymer (abbreviated as "EMAA"), ethylene-methacrylic acid-unsaturated aliphatic carboxylic acid copolymer, low-density polyethylene, ionomer resin (abbreviated as "IO (resin)"), ethylene-acrylic acid copolymer, ethylene-methyl acrylate copolymer (abbreviated as "EMA"), and ethylene-butyl acrylate copolymer (abbreviated "EBA"). Such a preferred class of sealable resins may be termed as an ethylene copolymer, typically a copolymer of a major amount (i.e., more than 50 wt. %) of ethylene with a minor amount (i.e., less than 50 wt. %, preferably up to 30 wt. %) of a vinyl monomer copolymerizable with ethylene selected from the group consisting of α-olefins having 3 to 8 carbon atoms, and unsaturated carboxylic acids and unsaturated esters of carboxylic acids having up to 8 carbon atoms, inclusive of acrylic acid, methacrylic acid, acrylate esters, methacrylate esters and vinyl acetate, or an acid-modified product of the ethylene copolymer (preferably modified with up to 3 wt. % of an unsaturated carboxylic acid). It is also possible to use a thermoplastic resin, such as thermoplastic resin, such as polypropylene resin, polyester resin or aliphatic nylon. The sealable resin may preferably have a melting point of up to about 150°C, more preferably up to about 135°C. It is also possible to use a blend including at least one species of such a sealable resin within an extent of not impairing the transparency of the resultant film or a sealed product thereof.

[027] The term "polyamide" means a polymer having amide linkages, and as used herein it refers more specifically to synthetic polyamides, either aliphatic or aromatic, either in crystalline or amorphous form. It is intended to refer to both polyamides and co-polyamides. Polyamides are preferably selected from nylon compounds approved for use in producing articles intended for use in processing, handling, and packaging food, including homopolymers, copolymers and mixtures of the nylon materials described in 21 C.F.R. 177.1500 *et seq.*, which is incorporated herein by reference. Exemplary of such polyamides include nylon homopolymers and copolymers such as those selected form the group consisting of nylon 4,6 (poly(tetramethylene adipamide)), nylon 6 (polycaprolactam), nylon 6,6 (poly(hexamethylene adipamide)), nylon 6,9 (poly(hexamethylene nonanediamide)), nylon 6,10 (poly(hexamethylene sebacamide)), nylon 6,12 (poly(hexamethylene dodecanediamide)), nylon 6/12 (poly(caprolactam-co-dodecanediamide)), nylon 6,6/6 (poly(hexamethylene adipamide-co-caprolactam)), nylon 66/610 (e.g., manufactured by the condensation of mixtures of nylon 66 salts and nylon 610 salts), nylon 6/69 resins (e.g., manufactured by the condensation of epsilon-caprolactam, hexamethylenediamine and azelaic acid), nylon 11 (polyundecanolactam), nylon 12 (polyauryllactam) and copolymers or mixtures thereof.

[028] A "high temperature polyamide" is a polyamide with a melting temperature (DSC) of at least 155°C.

[029] A "low temperature polyamide" is a polyamide with a melting temperature (DSC) of 155°C or less.

[030] As used herein, "EVOH" refers to ethylene vinyl alcohol copolymer. EVOH includes saponified or hydrolyzed ethylene vinyl acetate copolymers, and refers to a vinyl alcohol copolymer having an ethylene comonomer, and prepared by, for example, hydrolysis of vinyl acetate copolymers, or by chemical reactions with polyvinyl alcohol. The degree of hydrolysis is preferably from about 50 to 100 mole percent, more preferably, from about 85 to 100 mole percent.

[031] As used herein, the term "polyester" refers to a synthetic homopolymers and copolymers having ester linkages between monomer units which may be formed by condensation polymerization methods.

[032] "Olefin" is used herein broadly to include polymers such as polyethylene, ethylene copolymers having a small amount of a copolymer such as vinyl acetate, ethylene-alpha olefin copolymers (LLDPE), polypropylene, polybutene, and other polymeric resins falling in the "olefin" family classification.

[033] As used herein, the term "modified" refers to a chemical derivative e.g. one having any form of anhydride functionality, such as anhydride of maleic acid, crotonic acid, citraconic acid, itaconic acid, fumaric acid, etc., whether grafted onto a polymer, copolymerized with a polymer, or blended with one or more polymers, and is also inclusive of derivatives of such functionalities, such as acids, esters, and metal salts derived therefrom.

[034] As used herein, terms identifying polymers, such as "polyamide", are inclusive of not only polymers comprising repeating units derived from monomers known to polymerize to form a polymer of the named type, but are also inclusive of comonomers, derivatives, copolymers which can copolymerize with monomers known to polymerize to produce the named polymer, as well as modified polymers made by derivitization of a polymer after its polymerization. The term "polyamide" encompasses both polymers comprising repeating units derived from monomers, such as caprolactam, which polymerize to form a polyamide, as well as copolymers derived from the copolymerization of caprolactam with a comonomer which when polymerized alone does not result in the formation of a polyamide. Furthermore, terms identifying polymers are also inclusive of "blends" of such polymers with other polymers of a different type. The terms “polyamide polymer” and “nylon polymer” refer to a polyamide-containing polymer, a polyamide-containing copolymer or mixtures thereof.

[035] As used herein, the phrase "machine direction", herein abbreviated "MD", refers to a direction "along the length" of the film, i.e., in the direction of the film as the film is formed during extrusion and/or coating. As used herein,

the phrase "transverse direction", herein abbreviated "TD", refers to a direction across the film, perpendicular to the machine or longitudinal direction.

[036] Shrinkage values are defined to be values obtained by measuring unrestrained shrink of a 10 cm square sample immersed in water at 90°C (or the indicated temperature if different) for five seconds. Four test specimens are cut from a given sample of the film to be tested. The specimens are cut into squares of 10 cm length in the machine direction by 10 cm. length in the transverse direction. Each specimen is completely immersed for 5 seconds in a 90°C (or the indicated temperature if different) water bath. The specimen is then removed from the bath and the distance between the ends of the shrunken specimen is measured for both the machine direction (M.D.) and transverse direction (T.D.). The difference in the measured distance for the shrunken specimen and the original 10 cm. side is multiplied by ten to obtain the percent of shrinkage for the specimen in each direction. The shrinkage of four specimens is averaged for the M.D. shrinkage value of the given film sample, and the shrinkage for the four specimens is averaged for the TD shrinkage value. As used herein the term "heat shrinkable film at 90ºC means a film having an unrestrained shrinkage value of at least 10% in at least one direction. The term "total free shrink" refers to the sum of the stretch in the M.D. and T.D. directions.

[037] In use of the term "amorphous nylon copolymer," the term "amorphous" as used herein denotes an absence of a regular three-dimensional arrangement of molecules or subunits of molecules extending over distances which are large relative to atomic dimensions. However, regularity of structure may exist on a local scale. See, "Amorphous Polymers," Encyclopedia of Polymer Science and Engineering, 2nd Ed., pp. 789-842 (J. Wiley & Sons, Inc. 1985). In particular, the term "amorphous nylon copolymer" refers to a material recognized by one skilled in the art of differential scanning calorimetry (DSC) as having no measurable melting point (less than 0.5 cal/g) or no heat of fusion as measured by DSC using ASTM 3417-83. The amorphous nylon copolymer may be manufactured by the

condensation of hexamethylenediamine, terephthalic acid, and isophthalic acid according to known processes. Amorphous nylons also include those amorphous nylons prepared from condensation polymerization reactions of diamines with diacarboxylic acids. For example, an aliphatic diamine is combined with an aromatic dicarboxylic acid, or an aromatic diamine is combined with an aliphatic dicarboxylic acid to give suitable amorphous nylons.

[038] A suitable method of determining a melting point is by using differential scanning calorimetry (DSC) to determine the heat of fusion. Preferred high temperature polyamides melt at temperatures within a range of from about 155°C to about 215°C. Polyamides with melting points in this range have been found to form useful blends with amorphous nylon copolymers, which blends are easy to process into films including oriented films. In film packaging applications, low temperature polyamides with melting points less than 155°C soften and distort at typical processing temperatures which include e.g. 82°-93°C (180°-200°F) for shrink wrapping and 71° - 82°C (160°-180°F) for cooking sausages. The terms "high temperature polyamide" and "low temperature polyamide" include mixtures of copolyamides as well.

[039] Nylon resins are well known polymers having a multitude of uses including utility as packaging films, bags and casing. See, e.g. Modern Plastics Encyclopedia, 88 Vol. 64, No. 10A, pp 34-37 and 554-555 (McGraw-Hill, Inc., 1987) which is hereby incorporated by reference. In particular, the novel blends, thermoplastic flexible films, and oriented multilayer films are useful in food packaging.

EVOH BARRIER LAYERS

[040] In a first embodiment, packaging films are provided that comprise an EVOH barrier layer and a polyamide layer. Preferably, the polyamide layer is in contact with at least one side of an EVOH core barrier layer. More preferably, the EVOH barrier layer is a core oxygen barrier layer positioned

between, and in contact with, two polyamide layers positioned on opposite sides of the EVOH barrier layer.

[041] Placement of one or more core polyamide layers in contact with an EVOH oxygen barrier layer can provide multilayer barrier films with a higher total free shrink or improved processability for an EVOH composition having a given mol% of ethylene. Notably, positioning an EVOH barrier layer with lower ethylene content in contact with at least one polyamide layer, results in a multilayer barrier film that can be processed at temperatures comparable to EVOH barrier layers with a higher ethylene content. In general, decreasing the ethylene content in an EVOH barrier layer can increase the oxygen barrier properties of the film. Accordingly, high shrink packaging barrier films that include a polyamide layer in contact with an EVOH barrier layer with reduced ethylene content exhibit improved barrier properties and retain the desirably high levels of free shrink compared with EVOH barrier layers with higher ethylene content.

[042] Referring specifically to **Fig. 1**, an example of a three-layer core oxygen barrier film structure, generally designated at reference numeral **10**, is directed to a multilayer composite comprising a first polyamide layer **16** comprising a first polyamide composition **102** and a second polyamide layer **18** comprising a second polyamide composition **104**, each joined to opposite sides of a core EVOH oxygen barrier layer **15** comprising an EVOH composition **130** having a first percentage of ethylene. The multilayer film **10** is designed to be used in the packaging of food products and can be used as both forming and non-forming film, but is preferably a heat shrinkable film.

[043] The EVOH core barrier layer **15** can contain an effective amount of ethylene to provide desired levels of processability, desirably low orientation temperature, and desirably high levels of free shrink. The EVOH composition **130** used as an oxygen barrier layer can comprise a hydrolyzed ethylene/vinyl acetate copolymer (designated by the abbreviations "EVOH" and "HEVA", and also referred to as "ethylene/vinyl alcohol copolymer"), polyvinylidene chloride, polyamide, polyester, polyalkylene carbonate, polyacrylonitrile, etc., as known to those of skill in the art. Preferably, the core EVOH oxygen

barrier layer **15** placed in contact with a polyamide layer has an EVOH composition **130** containing less than about 50 mol% ethylene, and more preferably less than about 44mol%, or less than about 38mol% ethylene. Examples of EVOH compositions **130** include between about 25 mol% and 50 mol% ethylene, more preferably between about 25 mol% and 44 mol%, and most preferably up to about 38 mol% ethylene, including 29 mol% ethylene and 32 mol% ethylene. One EVOH barrier material is a 44%mol EVOH resin E151B sold by Eval Company of America, under the trade name Eval® LC-E151B. Another example of an EVOH that may be acceptable can be purchased from Nippon Gohsei under the trade name Soarnol® AT (44 mol% ethylene EVOH).

[044] The oxygen barrier layer **15** can provide a suitable barrier to oxygen for preservation of the article to be packaged. For perishable food packaging, the oxygen (O_2) permeability desirably should be minimized. Preferably, the oxygen barrier films comprise EVOH and have an O_2 transmission rate of less than about 20 cm^3/m^2 (1.29 $cm^3/100in^2$) for a 24 hour period at 1 atmosphere, 0% relative humidity and 23ºC, and more preferably less than about 16 cm^3/m^2 (1.03 $cm^3/100in^2$), and most preferably less than 15 cm^3/m^2 (0.97 $cm^3/100in^2$), 10 cm^3/m^2 (0.65 $cm^3/100in^2$), 9 cm^3/m^2 (0.58 $cm^3/100in^2$), 8 cm^3/m^2 (0.52 $cm^3/100in^2$), 7 cm^3/m^2 (0.45 $cm^3/100in^2$), 6 cm^3/m^2 (0.39 $cm^3/100in^2$), or 5 cm^3/m^2 (0.32 $cm^3/100in^2$), or lower. In some aspects, oxygen barrier films comprising EVOH and one or two nylon layers in contact with the EVOH layer provide an O_2 transmission rate of between about 5 and about 20 cm^3/m^2 (1.29 $cm^3/100in^2$) for a 24 hour period at 1 atmosphere, 0% relative humidity and 23°C, including O_2 transmission rates of about 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 20 cm^3/m^2.

[045] The EVOH core oxygen barrier layer can have any suitable thickness. In some aspects, the thickness of the core EVOH layer may also be varied from about 0.05 to about 0.30 mils (1.3-7.62 microns). The total thickness of a three-layer oxygen barrier consisting of an EVOH layer positioned between two adjacent polyamide layers is preferably about 0.5 mil to about 10 mils, more preferably about 1.0 mil to about 5.0 mils, including

thicknesses of about 1.25, 1.50, 1.75, 2.00, 2.25, 2.50, 2.75, 3.00, 3.25, 3.50, 3.75, 4.00, 4.25, 4.50, 4.75, 5.00 mils and intervals of about 0.1 mil therebetween. The composition of the core oxygen barrier layer may be adjusted by blending in compatible polymers to vary orientation parameters or the gas permeability e.g. O_2 of the films. For example, in some aspects, film layers can comprise up to 20% by weight of other materials, and that other additives including polymers may be blended into the core layer to affect core layer properties such as gas permeability or moisture resistance in minor amounts. The oxygen barrier layer **15** preferably also provides desirable optical properties when stretch oriented, including low haze and a stretching behavior compatible with the layers around it.

[046] It is desirable that the thickness of the oxygen barrier layer **15** be selected to provide the desired combination of the performance properties sought e.g. with respect to oxygen permeability, shrinkage values especially at low temperatures, ease of orientation, delamination resistance, and optical properties. Suitable thicknesses are less than 15%, e.g. from 3 to 13% of the total film thickness. Preferably, the thickness of the core layer will also be less than about 10% of the total thickness of the multilayer film. For example, the thickness of a core oxygen barrier layer can be less than about 0.45 mil (10.16 microns) and greater than about 0.05 mil (1.27 microns), including 0.10, 0.20, 0.25, 0.30, 0.40, or 0.45 mil thick.

[047] The first polyamide composition **102** and the second polyamide composition **104** can be the same or different. Each polyamide layer composition **102**, **104** can comprise or consist essentially of one or more nylon polymers or copolymers, including one or more polyamides selected from the group consisting of: a high temperature polyamide, a low temperature polyamide, an amorphous nylon copolymer and blends of two or more of these polyamides. Any suitable polyamide polymers for the high temperature polyamide, the low temperature polyamide or the amorphous nylon compositions. Preferably, polymers are selected from compositions approved as safe for producing articles intended for use in processing, handling and packaging of food. Polymers approved for food contact by the

United States Food and Drug Administration, include polymers disclosed at 52 Fed. Reg. 26,666-26,667, July 16, 1987, which is incorporated herein by reference. Examples of suitable polyamide polymers approved by the Food and Drug Administration are provided at 21 CFR § 177.1500 ("Nylon resins"), which is also incorporated herein by reference. Examples of these nylon resins for use in food packaging and processing include: nylon 66, nylon 610, nylon 66/610, nylon 6/66, nylon 11, nylon 6, nylon 66T, nylon 612, nylon 12, nylon 6/12, nylon 6/69, nylon 46, nylon PA 6-3-T, nylon MXD-6, nylon 12T and nylon 6I/6T disclosed at 21 CFR § 177.1500. Amorphous nylon compositions, low temperature polyamides and high temperature polyamides can be selected from these compounds based on their chemical polymer structure and physical properties such as melting point.

[048] In a first aspect of the first embodiment, a polyamide composition **102**, **104** comprises at least one high temperature polyamide polymer or copolymer. A high temperature polyamide has a melting point higher than a low temperature polyamide, and preferably 155°C or higher. For example, high temperature polyamides can have melting points between about 155°C and about 220°C or higher. Preferred high temperature polyamides include nylon 6, certain nylon 6/12 compositions, nylon 6/66 and mixtures thereof. Suitable high temperature polyamides include commercially available nylon 6/12, nylon 6, and nylon 6/66 copolyamides. Nylon 6/66 resins can be manufactured, for example, by the condensation and polymerization of Nylon 66 salts and epsilon-caprolactam. Most preferably, the high temperature polyamide is nylon 6. Nylon 6 resins can be manufactured, for example, by the polymerization of epsilon-caprolactam. A preferred nylon 6 with a melting point of about 215-220 °C is sold under the tradename ULTRAMID B36, from BASF. An example of a suitable nylon 6/12 copolyamide which melts within a range of from about 195°-200° C. (ASTM D2117) is commercially available under the trademark Grilon CR 9 from Emser Industries of Sumter, S.C., a division of EMS-American Grilon, Inc. (EMS). A preferred nylon is a nylon 6/66 copolymer having a melting point of about 195ºC, which has a reported nylon 6 component content of about 85 mole % and a nylon 66 component

content of about 15 mole % and which is commercially available from Allied Signal of Morristown, N.J., U.S.A. under the trademark CAPRON XTRAFORM® 1539F. Another preferred nylon is a nylon 6/66 compolymer sold under the designation C33 and produced by BASF under the trade name ULTRAMID®. A preferred nylon 6 having a melting point of about 220ºC is commercially available from Bayer AG under the trademark DRETHAN® B40F, or from Honeywell under the trademark CAPRON™ H135ZP. The nylon blend composition can comprise about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85 or 90 weight percent of the high temperature polyamide with respect to the amount of nylon blend composition in the layer, or any increment of 1 or 0.1 weight percent therebetween. More preferably, packaging films comprise about 5 to about 90 weight percent, about 10 to about 80 weight percent, between 20 and about 70 weight percent, or between about 30 and about 60 weight percent, and preferably about 60 weight percent of the high temperature polyamide.

[049] In a second aspect of the first embodiment, a polyamide layer comprises at least one low temperature polyamide polymer or copolymer. A polyamide composition **102**, **104** composition can include a low temperature polyamide having a melting point of up to 155°C. Preferably, nylon blend compositions can include about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 or 60 weight percent of the low temperature polyamide with respect to the amount of nylon blend composition in the layer, or any increment of 1 or 0.1 weight percent therebetween. Preferably, packaging films comprise from about 5 to about 60 weight percent, from about 10 to about 50 weight percent, from about 10 to about 30 weight percent, or between about 20 and about 40 weight percent, and preferably about 20 weight percent of the low temperature polyamide. Most preferably, the low temperature polyamide is nylon 6/69, although other low temperature polyamides can be used. Nylon 6/69 resins (CAS Reg. No. 51995-62-1) can be manufactured, for example, by the condensation of 49.5±0.5 weight percent epsilon-caprolactam, 19.4±0.2 weight percent hexamethylenediamine and 31.2±0.3 weight percent azelaic acid. Low temperature polyamides include polyamide polymers and

copolymers with melting points below about 145°C. A preferred low temperature polyamide with a melting point less than 155°C is a nylon 6/69 copolyamide which melts at about 134°C (DSC max.), which is commercially available from EMS-CHEMIE (North America) Inc under the trademark Grilon BM13SBG. Another preferred low temperature polyamide is the nylon 6/12 sold as EMS CF6S from Emser Industries of Sumter, S.C., a division of EMS-American Grilon, Inc. (EMS).

[050] In a third aspect of the first embodiment, a polyamide composition **102**, **104** can comprise at least one amorphous polyamide polymer or copolymer. Polyamide compositions **102**, **104** can include about 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50 weight percent of the amorphous nylon copolymer with respect to the amount of nylon blend composition in the layer, or any increment of 1 or 0.1 weight percent therebetween. More preferably, packaging films comprise from about 10 to about 50 weight percent of the amorphous nylon copolymer, about 10 to about 30 weight percent of the amorphous nylon copolymer, or between about 15 and about 25 weight percent of the amorphous nylon copolymer, including increments of 1% or 0.1% therebetween, and preferably about 20% by weight of the amorphous nylon polymer, or any combination thereof. Any suitable amorphous nylon polymer or copolymer can be used. Amorphous nylon polymers can be manufactured, for example, by the condensation of dexamethylenediamine, terephthalic acid and isophthalic acid. Suitable amorphous nylon copolymers include hexamethylene isophthalamide-hexamethylene terephthalamide copolymer also referred to as nylon 6I/6T. Amorphous nylon copolymers such as nylon 66/6I/6T can also be used as the amorpohous nylon component. A preferred component is hexamethyleneisothalamide-hexamethylene terephathalamide copolymer which has from about 65 percent to about 80 percent of its polymer units derived from hexamethyleneisophthalamide. Especially preferred as the amorphous nylon copolymer component is a commercially available nylon 6I/6T sold by the DuPont Company of Wilmington, Del., U.S.A. under the trademarked designation Selar PA 3426. Selar PA 3426 is further characterized by DuPont Company technical bulletin

E-73974 dated 12/85, which is hereby incorporated by reference, as an amorphous nylon (polyamide) having superior transparency, good barrier properties to gases such as O_2, solvents and essential oils and also the following properties according to the indicated standards: density of 1.19 gm/cc (ASTM D1505): glass transition temperature of 127°C. (ASTM D3418): heat deflection temperature of 126° C. at 4.6 Kg/cm^2 (66 psi) and 123° C. at 18.4 Kg/cm^2 (264 psi) (ASTM D648), and flexural modulus of 27,900 Kg/cm^2 (400,000 psi) at 50 percent relative humidity and 23° C. (ASTM D790). Another preferred amorphous nylon is a nylon 6I/6T sold under the tradename GRIVORY G21 from Emser Industries of Sumter, S.C., a division of EMS-American Grilon, Inc. (EMS). Nylon 6I/6T resins (CAS Reg. No. 25750-23-6) can be manufactured, for example, by the condensation of hexamethylenediamine, terephthalic acid, and isophthalic acid such that 65 to 80 percent of the polymer units are derived from hexamethylene isophthalamide.

[051] Alternatively, mixtures of copolyamides may be usefully employed as polyamide compositions **102**, **104**. A polyamide layer can comprise or consist essentially of a nylon blend composition. In a fourth aspect of the first embodiment, a polyamide layer comprises a blend of at least two nylon materials selected from the group consisting of: a low temperature polyamide polymer or copolymer, a high temperature polyamide polymer or copolymer and an amorphous polyamide polymer or copolymer. A nylon blend composition forming a polyamide layer composition **102**, **104** can be described by the weight percent of each of the nylon components with respect to the total weight of all of the nylon components of the nylon blend in a single polyamide layer. For example, if a layer comprised a nylon blend consisting of an amorphous nylon copolymer, a low temperature polyamide and a high temperature polyamide, then the weight percent of each nylon blend component is expressed as a weight percent of the total weight of the nylon blend (amorphous nylon, low temperature polyamide and high temperature polyamide), even if other materials are included in the layer or multiple nylon polymers are included for each component of the nylon blend. Other

materials may be added to the nylon blend composition or to layers comprising the nylon blend composition, including non-polyamide components. However, unless otherwise specified, the weight percent of the amorphous nylon copolymer, the low temperature polyamide and the high temperature polyamide in the nylon blend composition are expressed as a weight percentage of the total of only the total amount of the total of these three components in a single film layer. Two or more copolyamides each having a melting point of at least 155°C may be used as a high temperature polyamide, or a copolyamide having a melting point of at least 155°C may be mixed with one or more other copolyamides which have melting points less than 155°C. or are amorphous themselves. Various ratios of the weight percent of the low temperature polyamide to that of the amorphous nylon copolymer in the blend can be used, including ratios between 4:1 to 1:4. Preferably, the ratio is between about 2:1 and 1:2. More preferably, the ratio is about 1:1. Ratios of 4:1, 3.5:1, 3:1, 2.5:1, 1:2.5, 3:1, 3.5:1, and 1:4, as well as ratio intervals of 0.1 therebetween, are also provided.

[052] Examples of suitable blended polyamide compositions **102**, **104** are nylon blend compositions disclosed by Vicik in U.S. Patent 5,480,945, which are incorporated herein by reference. Briefly, these nylon blend compositions include blends of an amorphous nylon copolymer and a second nylon polymer having a melting point of at least 145 °C. The nylon blend can include about 10-50 weight percent of an amorphous nylon copolymer comprising hexamethylene isophthalamide-hexamethylene terephthalamide units. The nylon blend can further include about 20-90 weight percent of a nylon copolyamide such as nylon 6/12 or nylon 6/66.

[053] In a fifth aspect of the first embodiment, packaging films are provided that comprise a blended polyamide composition having at least three nylon components: an amorphous nylon such as Nylon 6I/6T in an amount of between about 5 and 50 weight percent of the three components of the nylon blend; a low temperature polyamide such as Nylon 6/69 copolymer, having a melting point of less than about 155°C in an amount between about 5 and about 60 weight percent of the three components of the nylon blend; and a

high temperature polyamide such as Nylon 6 having a melting point of at least about 155°C in an amount between about 5 and about 90 weight percent of the three components of the nylon blend. In some embodiments, the nylon blend composition consists essentially of the amorphous nylon copolymer, the low temperature polyamide and the high temperature polyamide. Preferably, nylon blend compositions can include about 5 to about 50 weight percent of the amorphous nylon copolymer, from about 10 to about 30 weight percent of the amorphous nylon copolymer, or between about 15 and about 25 weight percent of the amorphous nylon copolymer, including weight percent compositions therebetween such as 10, 15, 20, 25, 30, 35, 40, 45 and 50 wt%. Preferably, nylon blend compositions can include from about 5 to about 60 weight percent of the low temperature polyamide, from about 10 to about 40 weight percent of the low temperature polyamide, or between about 20 and about 40 weight percent of the low temperature polyamide, including weight percent compositions therebetween such as 10, 15, 20, 25, 30, 35, 40, 45, 50 and 55 wt%. Preferably, the nylon blend composition comprises up to about 80 weight percent, between about 10 and about 70 weight percent, between about 20 and about 70 weight percent, between or between about 30 and about 60 weight percent of the high temperature polyamide, including weight percent compositions therebetween such as 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75 and 80 wt%. Preferably, the nylon blend compositions comprise an amorphous nylon copolymer that comprises hexamethylene isophthalamide hexamethylene terephthalamide units and has no measurable melting point or no heat of fusion. More preferably, the nylon blend compositions comprises nylon 6I/6T. Preferably, the nylon blend compositions comprise a nylon 6/69 low temperature polyamide, a high temperature polyamide that is a nylon 6, nylon 6/66 or nylon 6/12 copolymer, or mixtures or copolymers thereof.

[054] Preferably, a multilayer barrier film comprising an EVOH barrier layer in contact with a polyamide layer according to the first embodiment has a total free shrink of at least about 80%, 85%, 90%, 95%, 100%, 105%, 110%, 115%, 120%, 125%, 130%, 135%, or 140% measured at 90°C, or

between about 80% and about 120% at 90°C, including about 90%, about 95%, about 100% and about 105%. Preferably, a multilayer barrier film has a free shrink value at 90°C of at least 30% in at least one of the machine direction or transverse direction. The multilayer barrier films preferably have a free shrink of at least 40% at 90ºC in the machine direction, the transverse direction, or in both the machine direction and the transverse direction. Preferably, the multilayer barrier films have a free shrink in the machine direction of about 30%. 35%, 40%, 45%, 50%, 55%, 60%, 65% or 70% or greater, including any increment of 1%, 0.5% or 0.25% therebetween, measured at 90°C. Preferably, a multilayer barrier film has a free shrink in the transverse direction of about 30%. 35%, 40%, 45%, 50%, 55%, 60%, 65% or 70% or greater, including any increment of 1%, 0.5% or 0.25% therebetween, measured at 90°C. More preferably packaging films have a free shrink of at least 40% in two directions. Even more preferably, the multilayer barrier films have a free shrink of at least 40% in a first direction that is the machine direction and at least 50% in a second direction that is the transverse direction.

[055] A multilayer barrier film comprising a polyamide layer in contact with an EVOH barrier layer can have any total thickness desired, so long as the film provides the desired properties for the particular packaging operation in which the film is used. Preferably, a three layer composite oxygen barrier film comprising an EVOH oxygen barrier layer positioned between two polyamide layers has a total thickness of less than about 10 mils, more preferably the film has a total thickness of from about 0.25 to 5 mils, still more preferably from about 0.3 to 3 mils, and yet still more preferably, from about 0.5 to 2 mils. For example, entire single or multilayer films or any single layer of a multilayer films can have any suitable thicknesses, including 0.25, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 mils, or any increment of 0.1 or 0.01 mil therebetween. Thicker and thinner films are also provided. Three-layer composite oxygen films (polyamide/EVOH/polyamide) preferably have a thickness of about 0.25-0.50 mils when forming a portion of a multilayer film having one or more additional

layers (such as a five layer or a seven layer film structure), while films for packaging foodstuffs formed from a three layer (polyamide/EVOH/polyamide) structure as thick as 5 mils, but are preferably about 0.5 mil to about 1.5 mils. Alternatively, films comprising the polyamide/EVOH/polyamide structure, optionally including one or more additional layers, can have a total thickness of between 0.25 mil and 5.0 mils, but are preferably between about 0.5-2mils thick. Especially preferred for use as films for food packaging are films where the multilayer film has a thickness of between about 1.5 to 2 mils (50.8-76.2 microns). Such films have good abuse resistance and machinability. Preferred films are heat shrinkable and have a desirable level of total heat shrinkage measured at 90°C. Preferred films may also provide a beneficial combination of one or more or all of the properties including low haze, high gloss, high shrinkage values at 90°C or less, good machinability, good mechanical strength and good barrier properties including high barriers to oxygen and water permeability.

MULTILAYER PACKAGING FILMS

[056] In a second embodiment, multilayer heat-shrinkable packaging films are provided that comprise the EVOH barrier layer in contact with one or more polyamide layers, as described in the first embodiment, as part of a multilayer film comprising other layers, such as heat-resistant layers, sealant layers, and adhesive layers. The EVOH oxygen barrier layer and one or more polyamide layers are preferably positioned between the heat-resistant layer and the sealant layer. Optionally, one or more adhesive layers can be disposed between a polyamide layer and the heat-resistant layer or between a polyamide layer and the sealant layer. Preferred configurations for the multilayer film comprise an EVOH core oxygen barrier layer positioned between and in contact with two polyamide layers.

[057] In a first aspect of the second embodiment, the multilayer film can include a heat resistant layer that can comprise or consist essentially of a blend of an amorphous nylon copolymer, a low temperature polyamide and/or a high temperature polyamide, as described with respect to the first

embodiment. A heat resistant layer can be positioned at or near the exterior surface of the packaging film, and can be an exterior layer. The heat resistant layer preferably provides a desired level of heat resistance. When forming an exterior layer, the heat resistant layer is preferably adequately heat resistant to prevent simultaneous heat sealing between overlapping packages during heat sealing processes. The first layer can comprise or consist essentially of a nylon blend composition. Preferably, the nylon blend composition comprises at least an amorphous nylon copolymer, a low temperature polyamide and a high temperature polyamide, such as the nylon blend compositions described with respect to the first embodiment. Multilayer films having any suitable combination of a heat resistant layer comprising various nylon blends and one or more layers selected from the group consisting of: core polyamide layers, adhesive layers, tie layers, bulk layers, sealant layers and oxygen barrier layers.

[058] In a second aspect of the second embodiment, the multilayer film includes a heat resistant layer that can comprise or consist essentially of a polyester. Preferred polyester polymers comprise an aromatic polyesters and more preferably, are homopolymers or copolymers of poly (ethylene terephthalate) (PET), poly (ethylene naphthalate) and blends thereof. Suitable polyesters may have an intrinsic viscosity of about 0.60 to about 1.2, preferably between 0.60 to 0.80. The polyester may be an aliphatic polyester resin, but is preferably an aromatic polyester resin. For example, polyester materials can be derived from dicarboxylic acid components, including terephthalic acid and isophthalic acid as preferred examples, and also dimers of unsaturated aliphatic acids. Examples of a diol component as another component for synthesizing the polyester may include: polyalkylene glycols, such as ethylene glycol, propylene glycol, tetramethylene glycol, neopentyl glycol, hexamethylene glycol, diethylene glycol, poly-ethylene glycol and polytetra methylene oxide glycol; 1,4-cyclohexane-dimethanol, and 2-alkyl-1,3-propanediol. More specifically, examples of dicarboxylic acids constituting the polyester resin may include: terephthalic acid, isophthalic acid, phthalic acid, 5-t-butylisophthalic acid, naphthalenedicarboxylic acid, diphenyl ether

dicarboxylic acid, cyclohexane-dicarboxylic acid, adipic acid, oxalic acid, malonic acid, succining acid, agelaic acid, sebacic acid, and dimer acids comprising dimers of unsaturated fatty acids. These acids may be used singly or in combination of two or more species. Examples of diols constituting the polyester resin may include: ethylene glycol, propylene glycol, tetramethylene glycol, neopentyl glycol, hexamethylene glycol, diethylene glycol, polyalkylene glycol, 1,4-cyclohexane-dimethanol, 1,4-butanediol, and 2-alkyl-1,3-propane diol. These diols may be used singly or in combination of two or more species.

[059] Polyester compositions that comprise an aromatic polyester resin comprising an aromatic dicarboxylic acid component can be preferred in some aspects, including, e.g., polyesters between terephthalic acid (as a dicarboxylic acid) and diols having at most 10 carbon atoms, such as polyethylene terephthalate and polybutylene terephthalate. Particularly preferred examples thereof may include: copolyesters obtained by replacing a portion, preferably at most 30 mol %, more preferably at most 15 mol %, of the terephalic acid with another dicarboxylic acid, such as isophthalic acid; copolyesters obtained by replacing a portion of the diol component such a ethylene glycol with another diol, such as 1,4-cyclohexanone-dimethanol (e.g., "Kodapak PET #9921", made by Eastman Kodak Co.); and polyester-polyether copolymers comprising the polyester as a predominant component (e.g., polyester-ether between a dicarboxylic acid component principally comprising terephthalic acid or/and its ester derivative and a diol component principally comprising tetramethylene glycol and tetramethylene oxide glycol, preferably containing the polytetra methylene oxide glycol residue in a proportion of 10-15 wt. %). It is also possible to use two or more different polyester resins in mixture. Examples of preferred polyesters are available under the trademarks EASTAPAK® PET Polyester 9663, EASTPAK® Polymer 9921 and EASTAR® Copolyester 6763, all from Eastman Chemical Company, Kingsport, Tenn., U.S.A. U.S. Patent Nos. 6,964,816 to Schell et al. and 6,699,549 to Ueyama et al., incorporated herein by reference in its

entirety, discloses multilayer structures comprising a polyester layer, and a polyamide layer.

[060] The heat resistant outer layer can optionally contain up to 20 wt. % of a thermoplastic resin other than the polyester resin, such as a thermoplastic elastomer as represented by thermoplastic polyurethane, or a polyolefin resin modified with an acid, such as maleic acid, or an anhydride thereof.

[061] The multilayer film can also include a sealant layer that is preferably positioned at or near the interior surface of the packaging film, and can be an interior layer. The sealant layer can comprise a suitable heat-sealable polymer such as an ethylene-α-olefin. The sealant layer is preferably formulated and positioned to form a heat seal. The sealant layer is preferably a sealant layer positioned at or near the interior surface of the package, for example as an interior layer. Preferably, the sealant layer is an interior surface heat sealing layer which allows a multilayer film to be formed into bags. The terms "heat sealing layer" or "sealant layer" are used interchangeably to refer to a layer which is heat sealable to itself, i.e., capable of fusion bonding by conventional indirect heating means which generate sufficient heat on at least one film contact surface for conduction to the contiguous film contact surface and formation of a bond interface therebetween without loss of the film integrity. Advantageously, the bond interface is preferably sufficiently thermally stable to prevent gas or liquid leakage therethrough when exposed to above or below ambient temperatures during processing of food within the tube when sealed at both ends, i.e., in a sealed bag form. For use in cook-in applications the heat seals should withstand elevated temperatures up to about 160-180°F (71-82°C) or higher for extended periods of time e.g. up to 4 to 12 hours in environments which may range from heated humidified air or steam to submersion in heated water. Finally, the bond interface between contiguous inner layers preferably has sufficient physical strength to withstand the tension resulting from stretching or shrinking due to the presence of a food body sealed within the

tube and optionally subjected to pasteurization or cook-in temperatures and conditions.

[062] A sealant layer preferably comprises a heat sealable polymeric material such as polypropylene homopolymers, polypropylene copolymers, very low density polyethylene (VLDPE), ultra low density polyethylene (ULDPE), linear low density polyethylene (LLDPE) or homogeneous polyolefin resins, such as made with metallocene single-site catalysts. Ethylene vinyl acetate (EVA) copolymers are also suitable materials for forming the inner surface heat sealable layer. A sealant layer preferably comprises an ionomer such as Surlyn®, available from DuPont Company. This material is essentially a metal salt neutralized copolymer of ethylene and acrylic or methacrylic acid. Other suitable sealant materials include metallocene catalyzed polyolefins, polyolefins, ethylene-alpha olefin copolymers, and blends thereof. Sealant layer can be 5 to 50% of the thickness of the total structure with a preferred thickness being about 15% of the total thickness. Preferred examples of such sealable resins constituting a sealant layer may include: SSC-LLDPE, SSC-VLDPE, LLDPE, VLDPE, EVA, EMAA, ethylene-methacrylic acid-unsaturated aliphatic carboxylic acid copolymer, and IO resins. A particularly preferred class of SSC-type polyolefins may include those obtained by using a constrained geometry catalyst (a type of metallocene catalyst developed by Dow Chemical Company). The constrained geometry catalyst may provide ethylene-α-olefin copolymers which may be classified as a substantially linear polyethylene resin having about 0.01- about 3, preferably about 0.01-about 1, more preferably about 0.05-about 1, long-chain branching(s) per 1000 carbon atoms. Because of long-chain branches each having about 6 or more carbon atoms selectively introduced into its molecular structure, the ethylene-α-olefin copolymer may be provided with excellent physical properties and good formability or processability, and an example thereof is commercially available from Dow Chemical Company under a trade name of "AFFINITY" or "ELITE" (including 1-octane as α-olefin). Other examples of polyethylene resins obtained by using a metallocene catalyst may include those available from Exxon Co.

under a trade name of "EXACT". Such a metallocene-catalyzed polyolefin (SSC-polyolefin) may preferably have a dispersion factor defined as a ratio (Mw/Mn) between a weight-average molecular weight (Mw) and a number-average molecular weight (Mn) of below 3, more preferably 1.9-2.2.

[063] The multilayer heat-shrinkable films can have an exterior surface and an interior surface, and include 3, 5 or 7 layer films having desirably high levels of free shrink. Referring to **Fig. 2**, a cross section of an example of a seven-layer heat shrinkable film **20** can comprise an outer surface layer **22** of a heat resistant composition **201** joined to a first adhesive layer **12** formed from a suitable adhesive composition **212**. Examples of preferred heat resistant compositions **201** include a polyester material or a polyamide homopolymer, copolymer or blend material. The other side of the first adhesive layer **12** is joined to a first polyamide layer **26** comprising one or more polyamide polymers **202**, the other side of which is joined to an EVOH oxygen barrier layer **25**. The EVOH oxygen barrier layer **25** is formed from an EVOH composition **230** comprising an EVOH copolymer with about 48 mol% or less of an ethylene component, and preferably about 29 mol%, 32 mol%, 38 mol% or 44 mol% ethylene. EVOH compositions comprising EVOH copolymers with 32 mol% or 38 mol% ethylene are particularly preferred for providing higher oxygen barrier properties. The EVOH oxygen barrier layer **25** is joined to the first polyamide layer **26** and to a second polyamide layer **28** comprising one or more polyamide polymers **204**. The other side of the second polyamide layer **28** is joined to a second adhesive layer **14** formed from a suitable adhesive composition **216**, and the opposite side of the second adhesive layer **14** is joined to a sealant layer **24** comprising a suitable heat-sealable composition **222**. The sealant layer **24** forms the outer surface layer.

[064] In addition to the heat-resistant layer and the sealant layer, a multilayer heat shrinkable packaging film can further comprise one or more adhesive layers, also known in the art as “tie layers,” which can be selected to promote the adherence of adjacent layers to one another in a multilayer film. The adhesive layer is preferably formulated to aid in the adherence of one

layer to another layer without the need of using adhesives by virtue of the compatibility of the materials in that layer to the first and second layers. In some embodiments, adhesive layers comprise materials found in both the first and second layers. The adhesive layer is preferably between 2% and 10% of the overall thickness of the multilayer film, preferably 3%. In one aspect of the second embodiment, a multilayer film comprises a three layer structure with an adhesive layer positioned between and in contact with the first layer and the second layer. In another aspect, a multilayer film comprises a multilayer structure comprising a first adhesive layer positioned between the first layer and the second layer and in contact with the first layer and a fourth layer also positioned between the first layer and the second layer. Multilayer films can comprise any suitable number of adhesive layers of any suitable composition. Various adhesive layers typically have different compositions from each other, and are formulated and positioned to provide a desired level of adhesion between layers of the film. Adhesion layers **12**, **14** can promote or provide adhesion between a heat resistant outer layer **22** or a sealant layer **24**, and a polyamide layer **26**, **28**. Adhesion layers **26** and **28** may be identical or different from each other, and may include a wide range of anhydride/grafted polyolefins including those based on ethylene vinyl acetate copolymer, polypropylene, low density polypropylene, linear low density polypropylene, and very low density polyethylene. Preferably, the compositions of adhesive layers are based on linear low density polyethylene, such as Plexar® tie resins, or plastomers, such as metallocene-catalyzed polyethylene.

[065] Adhesive layers in contact with a layer comprising a polyester, such as PET, preferably comprise a suitable blend of polyolefins with other adhesive polymers. One preferred component of an adhesive layer in contact with a PET polyester outer layer is EMAC SP 1330 (which reportedly has: a density of 0.948 g/cm^3; melt index of 2.0 g/10 min.; a melting point of 93°C.; is at softening point of 49°C.; and a methylacrylate (MA) content of 22%).

[066] Various additives may be included in one or more layers of a multilayer film. Preferably, film layers comprising a nylon blend composition include one or more additives to facilitate processing of the multilayer

structure. For example, a layer may be coated with or include an anti-block powder. Also, conventional antiblock additives, polymeric plasticizers, acid scavengers or slip agents may be added to one or more film layers of the film or it may be free from such added ingredients. If the exterior layer is corona treated, preferably no slip agent will be used, but it will contain or be coated with an anti-block powder or agent such as silica or starch. Processing aides are typically used in amounts less than 10%, less than 7% and preferably less than 5% of the layer weight. A preferred processing aid for use in the outer layer of the film includes one or more of fluoroelastomers, stearamides, erucamides, and silicates.

[067] Other aspects of the second embodiment provide a three-layer coextruded film with desirable levels of both heat resistance and heat shrinkability in a multilayer film structure. Referring to **Fig. 2**, a three layer film could be provided by omitting adhesion layers **12**, **14**. Various other multilayer heat shrinkable coextruded films are also provided. Non-limiting examples of various preferred multilayer film configurations include the following:

Polyamide (Exterior)/EVOH/ Polyamide(Interior)
Nylon (Exterior)/Polyamide Core/EVOH /Polyamide Core/Sealant (Interior)
Nylon (Exterior)/Adhesive/Polyamide Core/EVOH /Polyamide Core/Sealant (Interior)
Nylon (Exterior)/Adhesive/Polyamide Core/EVOH /Polyamide Core/Adhesive/Sealant (Interior)
Polyester (Exterior)/Adhesive /EVOH /Adhesive /Sealant (Interior)
Polyester (Exterior)/Polyamide Core/EVOH /Polyamide Core/Sealant (Interior)
Polyester (Exterior)/Adhesive/Polyamide Core/EVOH /Polyamide Core/Sealant (Interior)
Polyester (Exterior)/Adhesive/Polyamide Core/EVOH /Polyamide Core/Adhesive/Sealant (Interior)

[068] In the configurations listed above: "Nylon (Exterior)" refers to an exterior layer comprising a nylon blend composition that includes an amorphous nylon copolymer, a high temperature polyamide and a low temperature polyamide; "Polyester (Exterior)" refers to an exterior layer

comprising a polyester composition (e.g., PET); "Adhesive" refers to various adhesive layers with the same or different compositions positioned within the multilayer film; "Nylon Core" refers to a core layer comprising a nylon blend composition that includes an amorphous nylon copolymer, a high temperature polyamide and a low temperature polyamide; "Polyamide (Exterior)" refers to an exterior layer comprising an amorphous nylon copolymer, a high temperature polyamide, a low temperature polyamide, or a blend of any two or more thereof; "Polyamide Core" refers to a core layer comprising an amorphous nylon copolymer, a high temperature polyamide, a low temperature polyamide, or a blend of any two or more thereof; "EVOH" refers to an oxygen barrier layer comprising EVOH copolymer with any suitable mol% ethylene content; and "Sealant (Interior)" refers to an interior layer that functions as a sealant layer.

[069] One preferred aspect of the multilayer packaging films (second) embodiment provides a seven-layer film comprising a polyester exterior layer in contact with a first adhesive layer; a first core polyamide layer in contact with the first adhesive layer; an EVOH oxygen barrier layer comprising a suitable ethylene content (e.g., 38 mol% ethylene or 44 mol% ethylene) in contact with the first core polyamide layer and a second core polyamide layer on the opposite side; a second adhesive layer in contact with the second core polyamide layer; and a sealant layer forming the interior layer in contact with the other side of the second adhesive layer.

[070] Another preferred aspect of the second embodiment provides a five-layer film comprising a polyester exterior layer in contact with a first adhesive layer; an EVOH oxygen barrier layer comprising a suitable ethylene content (e.g., 38 mol% ethylene or 44 mol% ethylene) in contact with the first adhesive layer and with a second adhesive layer in contact with a sealant layer; and the sealant layer forming the interior layer in contact with the other side of the second adhesive layer.

[071] The multilayer heat-shrinkable packaging films preferably have a free shrink of at least 40% at 90°C in one direction, more preferably at least 40% in two directions, and a total free shrink at 90°C of at least about 80%,

90%, 100% or greater. Desirably, multilayer packaging films can have a total free shrink of at least about 80%, 85%, 90%, 95%, 100%, 105%, 110%, 115%, 120%, 125%, 130%, 135%, or 140% measured at 90°C, or between about 80% and about 120% at 90°C, including about 90%, about 95%, about 100% and about 105%. Preferably, a multilayer packaging film has a free shrink value at 90°C of at least 30% in at least one of the machine direction or transverse direction. The multilayer packaging films preferably have a free shrink of at least 40% at 90°C in the machine direction, the transverse direction, or in both the machine direction and the transverse direction. Preferably, the multilayer packaging films have a free shrink in the machine direction of about 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65% or 70% or greater, including any increment of 1%, 0.5% or 0.25% therebetween, measured at 90°C. Preferably, a multilayer packaging film has a free shrink in the transverse direction of about 30%. 35%, 40%, 45%, 50%, 55%, 60%, 65% or 70% or greater, including any increment of 1%, 0.5% or 0.25% therebetween, measured at 90°C. More preferably, multilayer packaging films have a free shrink of at least 40% in two directions. Even more preferably, the multilayer packaging films have a free shrink of at least 40% in a first direction that is the machine direction and at least 50% in a second direction that is the transverse direction.

[072] A multilayer film comprising an EVOH-polyamide multilayer barrier of the first embodiment can have any total thickness desired, so long as the film provides the desired properties for the particular packaging operation in which the film is used. Preferably, the film has a total thickness of less than about 10 mils, more preferably the film has a total thickness of from about 1 to 10 mils, still more preferably from about 1 to 5 mils, and yet still more preferably, from about 1.5 to 3 mils. For example, entire single or multilayer films or any single layer of a multilayer films can have any suitable thicknesses, including 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 mils, or any increment of 0.1 or 0.01 mil therebetween. Thicker and thinner films are also provided. Packaging films preferably have a thickness of about 1.5-3 mils (50.8-76.2

microns), although suitable films for packaging foodstuffs as thick as 4 mils (101.6 microns) or as thin as 1 mil (25.4 microns) may be made. Typically, films will be between about 1.5-3 mil (38.1-76.2 microns). Especially preferred for use as films for food packaging are films where the multilayer film has a thickness of between about 2 to 3 mils (50.8-76.2 microns). Such films have good abuse resistance and machinability. Preferred films are heat shrinkable and have a desirable level of total heat shrinkage measured at 90°C. Preferred films may also provide a beneficial combination of one or more or all of the properties including low haze, high gloss, high shrinkage values at 90ºC or less, good machinability, good mechanical strength and good barrier properties including high barriers to oxygen and water permeability.

FOOD PACKAGING

[073] In a third embodiment, heat-shrinkable food packages are provided. The heat-shrinkable food packages preferably include one or more polyamide core layers in contact with the EVOH-polyamide multilayer oxygen barrier layer of the first embodiment. The food packages can include a three-layer oxygen barrier formed from an EVOH layer in contact with a first polyamide layer on one side and a second polyamide layer on the opposite side. The food package can also include a heat resistant layer, a sealant layer and one or more adhesive layers having any suitable composition, as described with respect to the second embodiment.

[074] The polyamide layers in contact with the EVOH barrier layer can comprise or consist essentially of a polyamide or polyamide blend composition described with respect to the first embodiment. Preferably, the polyamide layers have the same composition as an exterior heat resistant layer comprising a nylon blend composition.

[075] Preferably, the heat resistant layer can comprise or consist essentially of a blend of an amorphous nylon copolymer, a low temperature polyamide and a high temperature polyamide. The heat resistant layer is preferably positioned at or near the exterior surface of the packaging film, and

can be an exterior layer, but can also form a polyamide layer. Optionally, the heat resistant layer can be oriented in any suitable manner, but is preferably biaxially oriented. In some embodiments, the heat-shrinkable food package can further comprise a sealant layer positioned at or near the interior surface of the package, for example as an interior layer. The sealant layers of the heat shrinkable food package are described above with reference to the multilayer heat shrinkable packaging films.

[076] The sealant layer is preferably positioned at or near the interior surface of the package, for example as an interior layer. Adhesive layers may also be included between a heat resistant exterior layer and the first polyamide layer or between the sealant layer and the second polyamide layer. In some embodiments, the heat-shrinkable food package can be a cook-in package, preferably when the food package comprises a sealant layer formed from a material that is compatible with cooking conditions.

[077] Preferably, the food packages are heat-shrinkable. The food packages preferably include a multilayer oxygen barrier component, and preferably have a total free shrink measured at 90°C of at least 30%, 40% or 50% in at least one of the machine direction or transverse direction. The food packages preferably have a free shrink of at least 30% at 90°C in one direction, more preferably at least 30% in two directions, where each direction is either a machine direction or a transverse direction. Even more preferably, the food packages have a free shrink of at least 40% in a first direction and at least 50% in a second direction. The food packages are preferably biaxially oriented, heat-shrinkable, or both. Preferably, the packages have a total free shrink at 90°C of at least about 80%. For example, the food package can have a free shrink value at 90°C between about 80% and about 120% at 90°C. In some embodiments, the food package can have a total free shrink at 90°C of at least about 90%, more preferably at least about 95%, still more preferably at least about 100% and even more preferably at least about 105%.

[078] Food packages preferably comprise at least one heat resistant layer can comprise or consist essentially of a blend of an amorphous nylon copolymer, a low temperature polyamide and a high temperature polyamide. The heat resistant layer can be positioned at or near the exterior surface of the packaging film, and can be an exterior layer. The heat resistant layer can be biaxially oriented. Some embodiments provide a five layer heat-shrinkable and heat resistant food package or pouch formed from multilayer coextruded films. Food packages can also be formed from seven layer heat shrinkable and heat resistant coextruded films. In some embodiments, the heat-shrinkable food package can be a cook-in package, preferably when the food package does not comprise a sealant layer. "Cook-in" is the term used to indicate a film or bag in which a foodstuff is pasteurized or cooked. This film or bag is used to hold together, protect and/or form the shape of the foodstuff by a food processor (manufacturer) during the cooking or pasteurization process after which the film may be removed (sometimes termed "stripped"), or may be left on as a protective barrier during shipping, and optionally even left on during retail sale.

[079] Food packages formed from multilayer films having two to fourteen layers are contemplated herein, where each layer is selected from the group consisting of: layers comprising a heat resistant and heat shrinkable nylon blend composition, adhesion layers, oxygen barrier layers, moisture barrier layers, bulk layers and sealant layers. Preferably, the exterior surface layer comprises a nylon blend composition having an amorphous nylon copolymer and a low temperature polyamide. Also preferably, the interior surface layer is a sealant layer.

METHODS OF MANUFACTURE

[080] The multilayer film may be made by conventional processes including e.g. slot cast or blown film processes, but preferably will be made by an orientation process, especially under conditions to produce a film which is heat shrinkable at 90°C or less. Descriptions of suitable orientation processes are disclosed in U.S. Patent No. 5,759,648 to Idlas, which is hereby

incorporated by reference in its entirety. Because the film is heat shrinkable, a shrunk film pouch will advantageously cling to the packaged foodstuff even after opening. Non-shrink bags have a tendency to fall away from the sides of the enclosed product once the vacuum is broken by either intentional or accidental opening. Once the film separates from the enclosed article surface, oxygen comes into contact with the article surface and product defects on susceptible products such as ham may occur. Some prior art films and bags are non-shrink bags which suffer from this defect thereby causing spoilage and waste when used to package perishable foodstuffs.

[081] The multilayer films and food packages may be manufactured by coextrusion of all layers simultaneously, for example, as described in published U.S. Pat. Application No. 2004/0166262 to Busche et al., entitled "Easy open heat-shrinkable packaging," and incorporated herein by reference in its entirety. Other manufacturing methods are disclosed in U.S. Patent No. 4,448,792 (Schirmer), or by a coating lamination procedure such as that described in U.S. Pat. No. 3,741,253 (Brax et al.), to form a relatively thick primary multilayer extrudate either as a flat sheet or, preferably, as a tube. This sheet or tube is oriented by stretching at orientation temperatures, which are generally below the melting points for the predominant resin comprising each layer oriented.

[082] Preferably, the compositions and films are biaxially oriented. Stretch orientation may be accomplished by various known methods e.g. tentering which is commonly employed to orient sheets, or by the well-known trapped bubble or double bubble technique for orienting tubes as for example described in U.S. Pat. No. 3,456,044 (Pahlke). In the bubble technique, an extruded primary tube leaving a tubular extrusion die is cooled, collapsed and then preferably oriented by reheating and inflating to form an expanded secondary bubble, which is again cooled and collapsed. Preferred films are biaxially stretched. Transverse direction (TD) orientation is accomplished by the above noted inflation to radially expand the heated film which is cooled to set the film in an expanded form. Machine direction (MD) orientation is preferably accomplished with the use of sets of nip rolls rotating at different

speeds to stretch or draw the film tube in the machine direction thereby causing machine direction elongation which is set by cooling. Orientation may be in either or both directions. Preferably, a primary tube is simultaneously biaxially stretched radially (transversely) and longitudinally (machine direction) to produce a multilayer film which is heat shrinkable at temperatures below the melting points of the major polymeric components, e.g. at 90°C or lower.

[083] Axially stretched, especially biaxially stretched, films which are "heat shrinkable" as that term is used herein have at least 10% unrestrained shrinkage at 90°C (10% in both the machine direction (M.D.) and transverse direction (T.D.) for biaxially stretched films). One or more of the essential five film layers may be oriented either uniaxially or biaxially by axial stretching at temperatures low enough to produce low temperature, high shrink multilayer films. Such heat shrinkable multilayer films will have at least 10% shrink in at least one direction at 90°C, but preferably will have at least 20% shrink at 90°C in at least one direction (preferably both directions) and advantageously may have at least 30% shrink at 90°C in at least one direction, and preferably may have at least 25% in both M.D. and T.D. directions, and beneficially may have at least 10% shrink at 74°C in both M.D. and T.D. directions and preferably at least 15% (more preferably at least about 20%) in at least one direction at 74°C

[084] The general annealing process by which biaxially stretched heat shrinkable films are heated under controlled tension to reduce or eliminate shrinkage values is well known in the art. If desired, films may be annealed to produce lower shrinkage values as desired for the particular temperature. The stretch ratio during orientation should be sufficient to provide a film with a total thickness of between about 1.0 and 4.0 mils. The MD stretch ratio is typically 2½-6 and the TD stretch ratio is also typically 2½-6. An overall or total stretch ratio (MD stretch multiplied by TD stretch) of about 6¼x-36x is suitable.

[085] A preferred method for forming the multilayer film is coextrusion of the primary tube which is then biaxially oriented in a manner similar to that broadly described in the aforementioned U.S. Pat. No. 3,456,044 where the

primary tube leaving the die is inflated by admission of a volume of air, cooled, collapsed, and then preferably oriented by reinflating to form a secondary tube termed a "bubble" with reheating to the film's orientation (draw) temperature range. Machine direction (MD) orientation is produced by pulling or drawing the film tube e.g. by utilizing a pair of rollers traveling at different speeds and transverse direction (TD) orientation is obtained by radial bubble expansion. The oriented film is set by rapid cooling.

[086] In the following examples, all layers are coextruded as a primary tube, which is cooled upon exiting the die by spraying with tap water. This primary tube is then reheated to the draw temperature (also called the orientation temperature) for biaxial orientation. The reheating can be accomplished, for example, by radiant heaters or contact with hot water heating. Biaxial orientation can be performed in any suitable manner, preferably using pressurized air to inflate the primary tube and mechanically stretching the film while at or above the orientation temperature. Cooling of oriented films can be accomplished by means of a concentric air ring.

[087] In a preferred process for making films, the resins and any additives are introduced to an extruder (generally one extruder per layer) where the resins are melt plastified by heating and then are transferred to an extrusion (or coextrusion) die for formation into a tube. Extruder and die temperatures will generally depend upon the particular resin or resin containing mixtures being processed and suitable temperature ranges for commercially available resins are generally known in the art, or are provided in technical bulletins made available by resin manufacturers. Processing temperatures may vary depending upon other process parameters chosen. However, variations are expected which may depend upon such factors as variation of polymer resin selection, use of other resins e.g. by blending or in separate layers in the multilayer film, the manufacturing process used and particular equipment and other process parameters utilized. Actual process parameters including process temperatures are expected to be set by one skilled in the art without undue experimentation in view of the present disclosure.

[088] As generally recognized in the art, resin properties may be further modified by blending two or more resins together and it is contemplated that various resins may be blended into individual layers of the multilayer film or added as additional layers, such resins include ethylene-unsaturated ester copolymer resins, especially vinyl ester copolymers such as EVAs, or other ester polymers, very low density polyethylene (VLDPE), linear low density polyethylene (LLDPE), low density polyethylene (LDPE), high density polyethylene (HDPE), nylons, ionomers, polypropylenes, or blends thereof. These resins and others may be mixed by well known methods using commercially available tumblers, mixers or blenders. Also, if desired, well known additives such as processing aids, slip agents, antiblocking agents, pigments, etc., and mixtures thereof may be incorporated into the film.

[089] Various polymer modifiers may be incorporated for the purpose of improving toughness and/or orientability or extensibility of the film. Other modifiers which may be added include: modifiers which improve low temperature toughness or impact strength, and modifiers which reduce modulus or stiffness. Exemplary modifiers include: styrene-butadiene, styrene-isoprene, and ethylene-propylene.

[090] Optionally, the film of the present invention is irradiated to induce crosslinking. In the irradiation process, the film is subjected to an energetic radiation treatment, such as corona discharge, plasma, flame, ultraviolet, X-ray, gamma ray, beta ray, and high energy electron treatment, which induce cross-linking between molecules of the irradiated material. The irradiation of polymeric films is disclosed in U.S. Pat. No. 4,064,296, to BORNSTEIN, et. al., which is hereby incorporated in its entirety, by reference thereto. BORNSTEIN, et. al. discloses the use of ionizing radiation for crosslinking the polymer present in the film. In some preferred embodiments, it is preferred to crosslink the entire film to broaden the heat sealing range. This is preferably done by irradiation with an electron beam at dosage levels of at least about 2 megarads (MR) and preferably in the range of 3 to 8 MR, although higher dosages may be employed. Irradiation may be done on the primary tube or after biaxial orientation. The latter, called post-irradiation, is preferred and

described in U.S. Pat. No. 4,737,391 (Lustig et al.). An advantage of post-irradiation is that a relatively thin film is treated instead of the relatively thick primary tube, thereby reducing the power requirement for a given treatment level.

[091] Alternatively, crosslinking may be achieved by addition of a chemical crosslinking agent or by use of irradiation in combination with a crosslinking enhancer added to one or more of the layers, as for example described in U.S. Pat. No. 4,055,328 (Evert et al.). The most commonly used cross-linking enhancers are organic peroxides such as trimethylpropane and trimethylacrylate.

EXAMPLES

[092] The following are examples and comparative examples.

[093] Experimental results and reported properties of the following examples are based on the following test methods or substantially similar test methods unless noted otherwise.

Oxygen Gas Transmission Rate (O_2 GTR): ASTM D-3985-81

Water Vapor Transmission Rate (WVTR): ASTM F 1249-90

Gauge: ASTM D-2103

Melt Index: ASTM D-1238, Condition E (190°C) (except for propene-based (>50% C_3 content) polymers tested at Condition TL(230°C))

Melting point: ASTM D-3418, DSC with 5ºC/min heating rate

[094] Shrinkage Values: Shrinkage values are defined to be values obtained by measuring unrestrained shrink of a 10 cm square sample immersed in water at 90°C (or the indicated temperature if different) for five seconds. Four test specimens are cut from a given sample of the film to be tested. The specimens are cut into squares of 10 cm length in the machine direction by 10 cm. length in the transverse direction. Each specimen is completely immersed for 5 seconds in a 90°C (or the indicated temperature if different) water bath. The specimen is then removed from the bath and the distance between the ends of the shrunken specimen is measured for both

the M.D. and T.D. directions. The difference in the measured distance for the shrunken specimen and the original 10 cm. side is multiplied by ten to obtain the percent of shrinkage for the specimen in each direction. The shrinkage of four specimens is averaged for the M.D. shrinkage value of the given film sample, and the shrinkage for the four specimens is averaged for the TD shrinkage value. As used herein the term "heat shrinkable film at 90°C" means a film having an unrestrained shrinkage value of at least 10% in at least one direction.

[095] Shrink Force: The shrink force of a film is that force or stress required to prevent shrinkage of the film and was determined from film samples taken from each film. Four film samples were cut 1" (2.54 cm) wide by 7" (17.8 cm) long in the machine direction and 1" (2.54 cm) wide by 7" (17.8 cm) long in the traverse direction. The average thickness of the film samples was determined and recorded. Each film sample was then secured between the two clamps spaced 10 cm apart. One clamp is in a fixed position and the other is connected to a strain gauge transducer. The secured film sample and clamps were then immersed in a silicone oil bath maintained at a constant, elevated temperature for a period of five seconds. During this time, the force in grams at the elevated temperature was recorded. At the end of this time, the film sample was removed from the bath and allowed to cool to room temperature whereupon the force in grams at room temperature was also recorded. The shrink force for the film sample was then determined from the following equation wherein the results is obtained in grams per mil of film thickness (g/mil):

[096] Shrink Force (g/mil)=F/T wherein F is the force in grams and T is the average thickness of the film samples in mils.

[097] Other useful tests are provided by the following references, which are incorporated herein in their entirety: U.S. Patent Application Ser. No. 09/652,591, entitled "IRRADIATED BIAXIALLY ORIENTED FILM," by Scott Idlas; and U.S. Patent Nos. 6,777,046 and 5,759,648.

[098] Provide below are non-limiting examples of the compositions, films and packages disclosed herein. In all the following examples, unless

otherwise indicated, the film compositions are produced generally utilizing the apparatus and method described in U.S. Pat. No. 3,456,044 (Pahlke), which describes a coextrusion type of double bubble method, and in further accordance with the detailed description above. All percentages are by weight unless indicated otherwise.

[099] Multilayer layer tubular films are made by a biaxial stretching orientation process. However, films of five or more layers are also contemplated. The inventive multilayer films may include additional layers or polymers to add or modify various properties of the desired film such as heat sealability, interlayer adhesion, food surface adhesion, shrinkability, shrink force, wrinkle resistance, puncture resistance, printability, toughness, gas or water barrier properties, abrasion resistance and optical properties such as gloss, haze, freedom from lines, streaks or gels. These layers may be formed by any suitable method including coextrusion, extrusion coating and lamination.

Example 1: *heat shrinkable polyamide blend compositions*

[0100] Heat resistant nylon blend compositions were made into films. Films 1-4 were made from blends of an amorphous nylon copolymer (nylon 6I/6T), a low temperature polyamide (nylon 6/69) and a high temperature polyamide (nylon 6/66 or nylon 6/12). The free shrink at 90°C was measured for each film and the total free shrink was calculated. The composition of films 1-4 and the corresponding free shrink data are provided in Table 1 below.

Table 1

Film No.	Nylon materials	Free shrink at 90°C (MDxTD)	Total Free Shrink at 90°C
1	20% nylon 6I/6T (DuPont 3426) 40% nylon 6/69 (EMS BM13SBG) 40% nylon 6/66 (BASF C35)	50x52	102
2	20% nylon 6I/6T (DuPont 3426) 40% nylon 6/69 (EMS BM13SBG) 40% nylon 6/12 (EMS CR9)	44x50	94

Film No.	Nylon materials	Free shrink at 90°C (MDxTD)	Total Free Shrink at 90°C
3	20% nylon 6I/6T (DuPont 3426) 10% nylon 6/69 (EMS BM13SBG) 70% nylon 6/12 (EMS CR9)	40x47	87
4	20% nylon 6I/6T (DuPont 3426) 20% nylon 6/69 (EMS BM13SBG) 60% nylon 6/66 (BASF C35)	40x49	89

Example 2: polyamide *blend films*

[0101] The free shrink was measured at 90° for sheets of certain polyamide materials, including certain high temperature polyamides (nylon 6/66 and nylon 6/12) and low temperature polyamides (nylon 6/69), as indicated in Table 2.

Table 2

Film No.	Nylon materials	Free shrink at 90°C (MDxTD)	Total Free Shrink at 90°C
5	100% nylon 6/IPDI (Bayer C38)	22x37	59
6	100% nylon 12 (EMS L20)	22x40	62
7	100% nylon 6/69 (BM13SBG)	31x40	71
8	100% nylon 66/610 (EMS BM20SBG)	30x43	73
9	50% nylon 6/12 (EMS CR9) 50% nylon 6/12 (CF6S)	37x43	80
10	100% nylon 6/12 (EMS CR9)	40x44	84
11	50% nylon 6/66 (BASF C35) 50% nylon 6/69 (EMS BM13SBG)	40x48	88
12	100% nylon 6/12 (CF6S)	43x47	90

Example 3: *polyamide blend films*

[0102] A film (film 13) containing an amorphous nylon copolymer (nylon 6I/6T) and a high temperature nylon (nylon 6/66), but no low temperature nylon, was made. The free shrink at 90°C was measured. The composition of film 13 and the corresponding free shrink data are included in Table 3 below.

Table 3

Film No.	Nylon materials	Free shrink at 90°C (MDxTD)	Total Free Shrink at 90°C
13	15% nylon 6I/6T (DuPont 3426) 85% nylon 6/66 (BASF C35)	31x44	75

Example 4: *heat shrinkable multilayer 7-layer barrier films comprising 38 mol% EVOH*

[0103] Heat-shrinkable seven-layer oxygen barrier films 14 and 15 were made comprising an EVOH layer with 38 mol% ethylene content, having the following schematic configuration, as described in Table 4 and Table 5:

Polyamide 1/ Adhesive 1 / Polyamide 2 / EVOH 1 / Polyamide 2 / Adhesive 1 / Sealant 1

Table 4

Film Nos.	Layer	Type	Composition	Basis Wt.	Description
14, 15	1	Polyamide blend 1	53% nylon 6/66 20% nylon 6/69 20% nylon 6I/6T 7% Antiblock/Slip Additives	1.28 (5.3%wt)	Heat resistant exterior layer
	2	Adhesive 1	20% EVA1 30% LLDPE 50% Plastomer	5.31 (22.2%wt)	Tie layer

Film Nos.	Layer	Type	Composition	Basis Wt.	Description
	3	Polyamide blend 2	35% nylon 6/66 45% nylon 6/69 20% nylon 6I/6T	1.28 (5.3%wt)	Core polyamide layer 1
	4	Oxygen Barrier	100% EVOH-1 (38 mol% ethylene)	1.91 (8.0%wt)	Oxygen barrier layer
	5	Polyamide blend 2	35% nylon 6/66 45% nylon 6/69 20% nylon 6I/6T	1.28 (5.3%wt)	Core polyamide layer 2
	6	Adhesive 1	20% EVA1 30% LLDPE 50% Plastomer	9.66 (40.4%wt)	Tie layer
	7	Sealant	90% homogeneous EAO 10% Processing Aid	3.22 (13.5%wt)	Sealing layer

[0104] The first layer (which is the exterior surface of the tubular film) provides a heat resistant exterior layer and comprises a blend of a nylon 6I/6T amorphous nylon copolymer, a nylon 6/69 low temperature polyamide and a nylon 6/66 high temperature polyamide. The third, fourth and fifth layers form an EVOH-polyamide composite oxygen barrier layer. The third and fifth layers are polyamide layers comprising a blend of a nylon 6I/6T amorphous nylon copolymer, a nylon 6/69 low temperature polyamide and a nylon 6/66 high temperature polyamide. The fourth layer is an EVOH layer comprising 38mol% ethylene. The seventh layer is a sealant layer that forms the interior surface of the multilayer structure. The second and the sixth layers are adhesive layers between the heat resistant layer and the first polyamide layer, and between the sealant layer and the second polyamide layer, respectively. The materials used in making film 15 are described in Table 5 below.

Table 5

Layer	Composition	Materials
1	53% nylon 6/66	ULTRAMID® C33-1 nylon 6/66 copolymer resin (BASF)
	20% nylon 6/69	BM13 SBG nylon 6/69 copolymer resin (EMS)
	20% nylon 6I/6T	Selar PA-3426 amorphous nylon 6I/6T (DuPont)
	7% Antiblock/Slip	Additives for Nylon 6/66
2	20% EVA1	EVA (10.5%VA, 0.2 MI) resin
	30% LLDPE	Anhydride modified polyethylene tie layer resin
	50% Plastomer	Plastomer (0.895g/cc, 1.0 MI)
3	35% nylon 6/66	ULTRAMID® C33-1 nylon 6/66 copolymer resin (BASF)
	45% nylon 6/69	BM13 SBG nylon 6/69 copolymer resin (EMS)
	20% nylon 6I/6T	Selar PA-3426 amorphous nylon 6I/6T (DuPont)
4	100% EVOH-1	EVAL™ 38 mol% EVOH resin H171B(Evalca)
5	35% nylon 6/66	ULTRAMID® C33-1 nylon 6/66 copolymer resin (BASF)
	45% nylon 6/69	BM13 SBG nylon 6/69 copolymer resin (EMS)
	20% nylon 6I/6T	Selar PA-3426 amorphous nylon 6I/6T (DuPont)
6	20% EVA1	EVA (10.5%VA, 0.2 MI) resin
	30% LLDPE	Anhydride modified polyethylene tie layer resin
	50% Plastomer	Plastomer (0.895g/cc, 1.0 MI)
7	90% homogeneous EAO	EXACT® 3040 (metallocene catalyzed) LLDPE Resin (Exxon)
	10% Processing Aid	VLDPE Processing Aid/Slip Conc.

[0105] One extruder is used for each layer and the heat plastified resins from each extruder are introduced to a 7-layer spiral plate coextrusion die. To make a seven layer film from a seven layer spiral plate coextrusion die, the resin or resin mixture to form each layer of the multilayer film was fed through

each of the seven layer spiral coextrusion die. The multilayer films 14 and 15 were separately coextruded from a seven layer die at the basis weight ratios described in Table 4. For each layer, the resin or resin mixture is fed from a hopper into an attached single screw extruder where the resin and/or mixture is heat plastified and extruded through a five layer coextrusion spiral plate die into a primary tube. The extruder barrel temperatures are: for the sealant layer (layer 7) about 250-330°F; second and sixth (adhesion) layers are about 295°-340°F; for the fourth (EVOH) layer is about 340°-365°F; the third, and fifth (polyamide layers) are about 440-475°F; and for the heat resistant outer layer (layer 1) are about 440-475°F. The extrusion die has an annular exit opening of 3.5-inch diameter with a 0.080 inch gap. The coextrusion die temperature profile is set, as indicated above.

[0106] The extruded multilayer primary tube is cooled by spraying with cold tap water (about 40°-60°F). The cooled primary tube is flattened by passage through a pair of nip rollers whose speed is controlled to neck down the primary tube to adjust the tube circumference or flatwidth. A flattened tube of about 2-5 inches flatwidth is preferred. The cooled flattened primary tube is reheated, biaxially stretched, and cooled. The cooled film is flattened, and the biaxially stretched and biaxially oriented film is wound on a reel. The machine direction (M.D.) draw or orientation ratio is about 3.0:1 to 4.0:1 and the transverse direction (T.D.) bubble or orientation ratio is about 2.8:1 to 3.5:1. The draw point or orientation temperature is below the predominant melting point for each layer oriented and above that layer's glass transition point. Draw point temperature, bubble heating and cooling rates and orientation ratios are generally adjusted to maximize bubble stability and throughput for the desired amount of stretching or orientation.

[0107] The free shrink of the 7-layer films described in Table 4 was greater than about 38x45 (total free shrink of 83%), and typically about 46x50 (total free shrink of 96%), or greater. The total thickness of the 7-layer films described in Table 4 can be between about 0.4 mils and about 10 mils, preferably between 1.2 mils and 2.0 mils, and typically were about 1.6 mils.

Films 14 and 15 described in Tables 4 and 5 have a total thickness of 1.9 mils. The free shrink of film 14 was 46x57 (total free shrink of 103%).

[0108] A second 7-layer film (film 15) was made according to the composition of Tables 4 and 5, but with a total thickness of 1.8 mils. The oxygen transmission rate ("O_2TR") of film 14 and film 15 were measured. Results from oxygen transmission measurements of the films described in Table 4 as a function of temperature, total thickness of the multilayer film and relative humidity (RH) are provided in Table 6 below.

Table 6 Oxygen transmission rates for films comprising 38mol% EVOH

Film	Thickness	O_2TR (0% RH)	O_2TR (80% RH)	O_2TR (90%RH)
14	1.9 mils	0.57 cc/100in^2/day	1.36 cc/100in^2/day	2.94 cc/100in^2/day
15	1.8 mils	0.46 cc/100in^2/day	1.12 cc/100in^2/day	2.45 cc/100in^2/day

Example 5: *heat shrinkable multilayer 7-layer barrier films comprising 44 mol% EVOH*

[0109] Heat-shrinkable seven-layer oxygen barrier films 16 and 17 were made comprising an EVOH layer with 44 mol% ethylene content, having the following schematic configuration, as described in Table 7 and Table 8:

Polyamide 1 / Adhesive1 / Polyamide 2 / EVOH 2 / Polyamide 2 / Adhesive 1 / Sealant 1

Table 7

Film Nos.	Layer	Type	Composition	Basis Wt.	Description
16, 17	1	Polyamide blend 1	53% nylon 6/66 20% nylon 6/69 20% nylon 6I/6T 7% Antiblock/Slip Additives	1.28 (5.3%wt)	Heat resistant exterior layer
	2	Adhesive 1	20% EVA1 30% LLDPE 50% Plastomer	5.31 (22.2%wt)	Tie layer

Film Nos.	Layer	Type	Composition	Basis Wt.	Description
	3	Polyamide blend 2	35% nylon 6/66 45% nylon 6/69 20% nylon 6I/6T	1.28 (5.3%wt)	Core polyamide layer 1
	4	Oxygen Barrier	100% EVOH-2 (44 mol% ethylene)	1.91 (8.0%wt)	Oxygen barrier layer
	5	Polyamide blend 2	35% nylon 6/66 45% nylon 6/69 20% nylon 6I/6T	1.28 (5.3%wt)	Core polyamide layer 2
	6	Adhesive 2	20% EVA1 30% LLDPE 50% Plastomer	9.66 (40.4%wt)	Tie layer
	7	Sealant	90% homogeneous EAO 10% Processing Aid	3.22 (13.5%wt)	Sealing layer

[0110] The multilayer films 16 and 17 are the similar to films 14 and 15, except that the fourth layer is an EVOH layer comprising 44 mol% ethylene. The first layer is a heat resistant nylon blend layer that forms the exterior surface of the film. The third and fifth layers are polyamide blend layers contacting the EVOH layer. The seventh layer is a sealant layer that forms the interior surface of the multilayer structure. The second and the sixth layers are adhesive layers between the first layer and the oxygen barrier layer, and between the sealant layer and the oxygen barrier layer, respectively. The materials used in making films 16 and 17 are described in Table 8 below.

Table 8

Layer	Composition	Materials
1	53% nylon 6/66	ULTRAMID® C33-1 nylon 6/66 copolymer resin (BASF)
	20% nylon 6/69	BM13 SBG nylon 6/69 copolymer resin (EMS)
	20% nylon 6I/6T	Selar PA-3426 amorphous nylon 6I/6T (DuPont)
	7% Antiblock/Slip	Additives for Nylon 6/66
2	20% EVA1	EVA (10.5%VA, 0.2 MI) resin
	30% LLDPE	Anhydride modified polyethylene tie layer resin

Layer	Composition	Materials
	50% Plastomer	Plastomer (0.895g/cc, 1.0 MI)
3	35% nylon 6/66	ULTRAMID® C33-1 nylon 6/66 copolymer resin (BASF)
	45% nylon 6/69	BM13 SBG nylon 6/69 copolymer resin (EMS)
	20% nylon 6I/6T	Selar PA-3426 amorphous nylon 6I/6T (DuPont)
4	100% EVOH 2	44 mol% ethylene EVOH resin E151B (Evalca)
5	35% nylon 6/66	ULTRAMID® C33-1 nylon 6/66 copolymer resin (BASF)
	45% nylon 6/69	BM13 SBG nylon 6/69 copolymer resin (EMS)
	20% nylon 6I/6T	Selar PA-3426 amorphous nylon 6I/6T (DuPont)
6	20% EVA1	EVA (10.5%VA, 0.2 MI) resin
	30% LLDPE	Anhydride modified polyethylene tie layer resin
	50% Plastomer	Plastomer (0.895g/cc, 1.0 MI)
7	90% homogeneous EAO	EXACT® 3040 (metallocene catalyzed) LLDPE Resin (Exxon)
	10% Processing Aid	VLDPE Processing Aid/Slip Conc.

[0111] The multilayer films 16 and 17 were coextruded from a seven layer die as described in Example 4, using the basis weight ratios described in Table 7. For each layer, the resin or resin mixture is fed from a hopper into an attached single screw extruder where the resin and/or mixture is heat plastified and extruded through a five layer coextrusion spiral plate die into a primary tube. The extruder barrel temperatures are similar to the temperatures used in Example 4. The extrusion die has an annular exit opening of 3.5-inch diameter with a 0.080 inch gap. The coextrusion die temperature profile is set, as indicated above.

[0112] The extruded multilayer primary tube was cooled by spraying with cold tap water (about 40°-60°F), as described for Example 4. The cooled primary tube was flattened by passage through a pair of nip rollers whose

speed is controlled to neck down the primary tube to adjust the tube circumference or flatwidth. A flattened tube of about 2-5 inches flatwidth is preferred. The cooled flattened primary tube is reheated, biaxially stretched, and cooled. The cooled film is flattened, and the biaxially stretched and biaxially oriented film is wound on a reel. The machine direction (M.D.) draw or orientation ratio is about 3.0:1 to 4.0:1 and the transverse direction (T.D.) bubble or orientation ratio is about 2.8:1 to 3.5:1. The draw point or orientation temperature is below the predominant melting point for each layer oriented and above that layer's glass transition point. Draw point temperature, bubble heating and cooling rates and orientation ratios are generally adjusted to maximize bubble stability and throughput for the desired amount of stretching or orientation.

[0113] The free shrink of the 7-layer films described in Table 7 was greater than about 38x45 (total free shrink of 83%), and typically about 46x50 (total free shrink of 96%), or greater. The total thickness of the 7-layer films described in Table 7 can be between about 0.4 mils and about 10 mils, preferably between 1.2 mils and 2.0 mils, and typically were about 1.6 – 1.9 mils. Films 16 and 17 described in Tables 7 and 8 both have a total thickness of 1.9 mils. The free shrink at 90°C of films 16 and 17 were 46x56 (total free shrink of 102%).

[0114] The oxygen transmission rate ("O_2TR") of film 16 and film 17 were measured. Results from oxygen transmission measurements of the films described in Table 7 as a function of temperature, total thickness of the multilayer film and relative humidity (RH) are provided in Table 9 below. Films 16 and 17 showed comparable total free shrink to films 14 and 15, but greater oxygen barrier properties (i.e., lower oxygen transmission rate).

Table 9 Oxygen transmission rates for films comprising 44 mol% EVOH

Film	Thickness	O_2TR (0% RH)	O_2TR (80% RH)	O_2TR (90%RH)
16	1.9 mils	0.98 cc/100in^2/day	1.49 cc/100in^2/day	2.71 cc/100in^2/day
17	1.9 mils	1.09 cc/100in^2/day	1.67 cc/100in^2/day	2.90 cc/100in^2/day

Example 6: *heat shrinkable multilayer 7-layer barrier films comprising polyester exterior layer*

[0115] Heat-shrinkable seven-layer oxygen barrier film 18 was made comprising an EVOH layer with 44 mol% ethylene content, having the following schematic configuration, as described in Table 10 and Table 11:

Polyester 1 / Adhesive 2 / Polyamide 2 / EVOH 2 / Polyamide 2 / Adhesive 3 / Sealant 1

Table 10

Film Nos.	Layer	Type	Composition	Basis Wt.	Description
18	1	Polyester 1	100% PET	2.15 (9.0%wt)	Heat resistant exterior layer
	2	Adhesive 2	30% LLDPE 70% EMA1	3.66 (15.3%wt)	Tie layer

Film Nos.	Layer	Type	Composition	Basis Wt.	Description
	3	Polyamide blend 2	35% nylon 6 45% nylon 6/69 20% nylon 6I/6T	1.67 (7.0%wt)	Core polyamide layer 1
	4	Oxygen Barrier	100% EVOH-2 (44 mol% ethylene)	1.91 (8.0%wt)	Oxygen barrier layer
	5	Polyamide blend 2	35% nylon 6 45% nylon 6/69 20% nylon 6I/6T	1.67 (7.0%wt)	Core polyamide layer 2
	6	Adhesive 3	20% ULDPE 30% LLDPE 50% Plastomer	9.66 (40.4%wt)	Tie layer
	7	Sealant	90% homogeneous EAO 10% Processing Aid	3.22 (13.5%wt)	Sealing layer

[0116] The multilayer film 18 is similar to films 16 and 17, except that the exterior heat resistant layer is a Poly(ethylene terephthalate) polyester (PET). The first layer is a heat resistant polyester layer formed from PET that forms the exterior surface of the film. The third and fifth layers are polyamide blend layers contacting the EVOH layer. The seventh layer is a sealant layer that forms the interior surface of the multilayer structure. The second and the sixth layers are adhesive layers between the heat resistant layer and the first polyamide layer, and between the sealant layer and the second polyamide layer, respectively. The materials used in making film 18 are described in Table 11 below.

Table 11

Layer	Composition	Materials
1	100% PET	9921 Poly(ethylene terephthalate) copolyester resin (Voridian)
2	70% EMA1	EMAC Ethylene methylacrylate block copolymer (22% MA, 2.0 MI) (Vordian)
	30% LLDPE	Anhydride modified polyethylene tie layer resin
3	35% nylon 6	ULTRAMID® B36 nylon 6 copolymer resin (BASF)

Layer	Composition	Materials
	45% nylon 6/69	BM13 SBG nylon 6/69 copolymer resin (EMS)
	20% nylon 6I/6T	Selar PA-3426 amorphous nylon 6I/6T (DuPont)
4	100% EVOH 2	44 mol% ethylene EVOH resin E151B (Evalca)
5	35% nylon 6	ULTRAMID® B36 nylon 6 copolymer resin (BASF)
	45% nylon 6/69	BM13 SBG nylon 6/69 copolymer resin (EMS)
	20% nylon 6I/6T	Selar PA-3426 amorphous nylon 6I/6T (DuPont)
6	20% ULDPE	4201G ULDPE Resin (Dow)
	30% LLDPE	Anhydride modified polyethylene tie layer resin
	50% Plastomer	Plastomer (0.895g/cc, 1.0 MI)
7	90% homogeneous EAO	EXACT® 3040 (metallocene catalyzed) LLDPE Resin (Exxon)
	10% Processing Aid	VLDPE Processing Aid/Slip Conc.

[0117] The multilayer film 18 was coextruded from a seven layer die as described in Example 4, using the basis weight ratios described in Table 10. For each layer, the resin or resin mixture is fed from a hopper into an attached single screw extruder where the resin and/or mixture is heat plastified and extruded through a five layer coextrusion spiral plate die into a primary tube. The extruder barrel temperatures are similar to the temperatures used in Example 4, except as indicated here. The extruder barrel temperatures are: for the sealant layer (layer 7) about 250-300°F; second and sixth (adhesion) layers are about 280°-340°F; for the fourth (EVOH) layer is about 340°-365°F; for the third and fifth (polyamide layers), about 430-500°F; and the seventh (polyester) layer is about 500°F -530°F. The extrusion die has an annular exit opening of 3.5-inch diameter with a 0.080 inch gap. The coextrusion die temperature profile is set, as indicated above.

[0118] The extruded multilayer primary tube was cooled by spraying with cold tap water (about 40°-60°F), as described for Example 4. The cooled

primary tube was flattened by passage through a pair of nip rollers whose speed is controlled to neck down the primary tube to adjust the tube circumference or flatwidth. A flattened tube of about 2-5 inches flatwidth is preferred. The cooled flattened primary tube is reheated, biaxially stretched, and cooled. The cooled film is flattened, and the biaxially stretched and biaxially oriented film is wound on a reel. The machine direction (M.D.) draw or orientation ratio is about 3.0:1 to 4.0:1 and the transverse direction (T.D.) bubble or orientation ratio is about 2.8:1 to 3.5:1. The draw point or orientation temperature is below the predominant melting point for each layer oriented and above that layer's glass transition point. Draw point temperature, bubble heating and cooling rates and orientation ratios are generally adjusted to maximize bubble stability and throughput for the desired amount of stretching or orientation. The resultant film 18 of Example 6 had a thicknesses of about 1.6 mils, but can also have an average gauge of 1.2 to 2.0 mils.

[0119] The free shrink of the 7-layer films described in Table 10 was greater than about 38x45 (total free shrink of 83%), and typically about 46x50 (total free shrink of 96%), or greater. The total thickness of the 7-layer films described in Table 7 can be between about 0.4 mils and about 10 mils, preferably between 1.2 mils and 2.0 mils, and typically were about 1.6 mils.

[0120] Films, bags and packages may also employ combinations of characteristics as described in one or more embodiments.

[0121] The above examples are illustrative only, and should not be interpreted as limiting since further modifications of the disclosed embodiments will be apparent to those skilled in the art in view of this teaching. All such modifications are deemed to be within the scope of the embodiments disclosed herein.

CLAIMS:

What is claimed:

1. A multilayer heat shrinkable film comprising:

a first polyamide layer comprising a blend of at least two materials selected from the group consisting of: an amorphous nylon copolymer, a low temperature polyamide having a melting point of less than 155°C, and a high temperature polyamide having a melting point of greater than 155°C; and

a barrier layer in contact with the first polyamide layer, the barrier layer comprising an EVOH copolymer having less than 44 mol% ethylene;

wherein the film has a free shrink value at 90°C of at least 40% in at least one of the machine direction or transverse direction; and wherein film has an oxygen transmission rate of less than about 1.00 cc/100 in^2/ day measured at 0% relative humidity.

2. The film of claim 1, wherein the film further comprises a second polyamide layer in contact with the barrier layer, the barrier layer being positioned between the first polyamide layer and the second polyamide layer; wherein the second polyamide layer comprises a blend of at least two materials selected from the group consisting of: an amorphous nylon copolymer, a low temperature polyamide having a melting point of less than 155°C, and a high temperature polyamide having a melting point of greater than 155°C.

3. The film of any one of claims 1 or 2, wherein the EVOH copolymer comprises between about 29 mol% and 44 mol% ethylene.

4. The film of any one of claims 1, 2 or 3, wherein the film has a total free shrink value at 90°C of at least 80%.

5. The film of one of claims 1, 2 or 3, wherein the film has a total free shrink value at 90°C of at least 95%.

6. The film of any one of claims 1, 2, 3, 4 or 5, wherein the film is a multilayer film further comprising a sealant layer forming at least a portion of an interior surface of the film.

7. The film of any one of claims 1, 2, 3, 4, 5 or 6, wherein the first polyamide layer comprises between about 5% and 50% by weight of the blend of the amorphous nylon, between about 5% and 50% by weight of the blend of the low temperature polyamide, and between about 5% and 80% by weight of the blend of the high temperature polyamide.

8. The film of claim 7, wherein the high temperature polyamide is nylon 6 or nylon 6/66.

9. The film of claim 7, wherein the film further comprises a heat resistant outer layer, wherein the heat resistant outer layer comprises between about 5% and 50% by weight of the blend of the amorphous nylon, between about 5% and 50% by weight of the blend of the low temperature polyamide, and between about 5% and 80% by weight of the blend of the high temperature polyamide.

10. The film of claim 2, wherein the film has an oxygen transmission rate of less than about 0.80 cc/100 in^2/ day measured at 0% relative humidity.

11. The film of claim 1, wherein the first polyamide layer comprises between about 5% and 50% by weight of the blend of the amorphous nylon, between about 5% and 50% by weight of the blend of the low temperature polyamide, and between about 5% and 80% by weight of the blend of the high temperature polyamide;

wherein the EVOH copolymer comprises between about 29 mol% and 44 mol% ethylene;

wherein the film further comprises:

a heat resistant outer layer, wherein the heat resistant outer layer comprises between about 5% and 50% by weight of the blend of the amorphous nylon, between about 5% and 50% by weight of the blend of the low temperature polyamide, and between about 5% and 80% by weight of the blend of the high temperature polyamide;

a second polyamide layer in contact with the barrier layer, the barrier layer being positioned between the first polyamide layer and the second polyamide layer; wherein the second polyamide layer comprises between about 5% and 50% by weight of the blend of the amorphous nylon, between about 5% and 50% by weight of the blend of the low temperature polyamide, and between about 5% and 80% by weight of the blend of the high temperature polyamide; and

a sealant layer forming at least a portion of an interior surface of the film;

and wherein the film has a total free shrink value at 90°C of at least 95% and the film has an oxygen transmission rate of less than about 0.80 cc/100 in^2/ day measured at 0% relative humidity.

12. A multilayer packaging film comprising: a first polyamide layer comprising a blend of at least two materials selected from the group consisting of: an amorphous nylon copolymer, a low temperature polyamide having a melting point of less than 155°C, and a high temperature polyamide having a melting point of greater than 155°C;

a second polyamide layer comprising a blend of at least two materials selected from the group consisting of: an amorphous nylon copolymer, a low temperature polyamide having a melting point of less than 155°C, and a high temperature polyamide having a melting point of greater than 155°C; and

a barrier layer comprising an EVOH copolymer having less than 44 mol% ethylene, positioned between the first polyamide layer the second polyamide layer; and

wherein the film has a total free shrink value at 90ºC of at least 80% in at least one of the machine direction or transverse direction; and wherein the film has an oxygen transmission rate of less than about 1.00 cc/100 in^2/ day measured at 0% relative humidity.

13. The film of claim 12, wherein the EVOH copolymer comprises about 29 mol% to about 44 mol% ethylene.

14. The film of any one of claims 12 or 13, wherein the film has a total free shrink value at 90°C of at least 40% in at least one of the machine direction or transverse direction.

15. The film of claim 14, wherein the film further comprises an outer layer comprising polyester.

16. The film of any one of claims 12, 13, 14 or 15 wherein the first polyamide layer comprises between about 5 and about 80 weight percent of the high temperature polyamide.

17. The film of any one of claims 12, 13, 14, 15 or 16, wherein the first polyamide layer comprises an amorphous nylon copolymer selected from the group consisting of: nylon 6I/6T and nylon 66/6I/69 copolymer.

18. The film of any one of claims 12, 13, 14, 15, 16 or 17, wherein the first polyamide layer comprises a low temperature polyamide comprising nylon 6/69.

19. The film of any one of claims 12, 13, 14, 15, 16, 17 or 18, wherein the first polyamide layer comprises a high temperature polyamide is selected from the group consisting of: nylon 6, nylon 6/66 and nylon 6/12.

20. A food package having an interior surface defining a pouch for containing food and an exterior surface, the food package comprising:

a heat resistant layer forming at least a portion of the exterior surface, the heat resistant layer comprising a blend comprising between about 5 and about 50% by weight of the blend of an amorphous nylon copolymer, between about 5 and about 50% by weight of the blend of a low temperature polyamide having a melting point of less than about 155°C, and between about 5% and about 80% by weight of the blend of a high temperature polyamide having a melting point of at least about 155°C;

a first polyamide layer in contact with a first side of a barrier layer having a first side and a second side, the barrier layer comprising an EVOH copolymer having less than 44 mol% ethylene;

a second polyamide layer in contact with a second side of the barrier layer;

wherein the first polyamide layer and the second polyamide layers independently comprise two or more of the following: between about 5% and 50% by weight of the blend of amorphous nylon, between about 5% and 50% by weight of the blend of a low temperature polyamide having a melting point of less than about 155°C, and between about 5% and 80% by weight of the blend of a high temperature polyamide having a melting point of at least about 155°C; and

a sealant layer forming at least a portion of the interior surface, the sealant layer comprising an ethylene-alpha-olefin;

wherein the food package has a total free shrink value at 90°C of at least 80% in at least one of the machine direction or transverse direction, and the food package has an oxygen transmission rate of less than about 1.00 cc/100 in^2/ day measured at 0% relative humidity.

21. The food package of claim 20, wherein the food package has a free shrink value at 90°C of at least 40% in at least one of the machine direction or transverse direction.

22. The food package of any one of claims 20 or 21, wherein the food package has 5 to 7 layers.

23. The food package of any one of claims 20, 21 or 22, wherein the food package is a cook-in package.

24. The food package of any one of claims 20, 21, 22 or 23, wherein the food package has a total free shrink value at 90°C of at least 100% in at least one of the machine direction or transverse direction; and wherein the food package has an oxygen transmission rate of less than about 0.80 cc/100 in^2/ day measured at 0% relative humidity.

25. A multilayer heat shrinkable film having an exterior surface and an interior surface, the film comprising:

a first polyamide layer comprising a blend of at least two materials selected from the group consisting of: an amorphous nylon copolymer, a low temperature polyamide having a melting point of less than 155°C, and a high temperature polyamide having a melting point of greater than 155°C; a barrier layer in contact with the first polyamide layer, the barrier layer comprising an EVOH copolymer having less than 44 mol% ethylene; a second polyamide layer in contact with the barrier layer, such that the barrier layer is positioned between the first polyamide layer and the second polyamide layer, the second polyamide layer comprising a blend of at least two materials selected from the group consisting of: an amorphous nylon copolymer, a low temperature polyamide having a melting point of less than 155°C, and a high temperature polyamide having a melting point of greater than 155°C; and an outer layer comprising polyester;

wherein the film has a free shrink value at 90°C of at least 40% in at least one of the machine direction or transverse direction; and a total free shrink value at 90°C of at least 90%.

26. The film of claim 25, further comprises an outer exterior layer comprises poly (ethylene terephthalate) forming at least a portion of the exterior surface of the film.

27. The film of claim 25, wherein the first polyamide layer comprises between about 5% and 50% by weight of the blend of the amorphous nylon, between about 5% and 50% by weight of the blend of the low temperature polyamide, and between about 5% and 80% by weight of the blend of the high temperature polyamide; wherein the EVOH copolymer comprises between about 29 mol% and 44 mol% ethylene; wherein the film further comprises: an outer layer that is a heat resistant outer layer comprising poly (ethylene terephthalate) and forms at least a portion of the exterior surface of the film; the second polyamide layer comprises between about 5% and 50% by weight of the blend of the amorphous nylon, between about 5% and 50% by weight of the blend of the low temperature polyamide, and between about 5% and 80% by weight of the blend of the high temperature polyamide; and the film further comprises a sealant layer forming at least a portion of the interior surface; wherein the film has a total free shrink value at 90°C of at least 95%.

28. A method of manufacturing a heat-shrinkable packaging film comprising the step of co-extruding a multilayer film comprising a three layer oxygen barrier film comprising: a first polyamide layer wherein the first polyamide layer comprises a blend of at least two materials selected from the group consisting of: an amorphous nylon copolymer, a low temperature polyamide having a melting point of less than 155°C, and a high temperature polyamide having a melting point of greater than 155°C; a barrier layer in contact with the first polyamide layer, the barrier layer comprising an EVOH copolymer having less than 44 mol% ethylene; wherein the multilayer film has a free shrink value at 90°C of at least 40% in at least one of the machine direction or transverse direction; and wherein film has an oxygen transmission rate of less than about 1.00 cc/100 in^2/ day measured at 0% relative humidity.

Figure 1

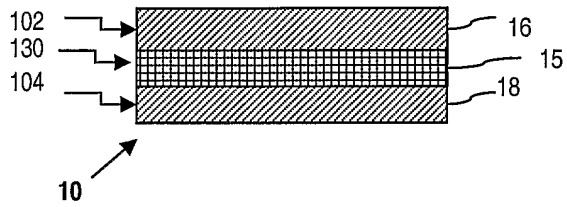

Figure 2