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(71) Applicant: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; Chestnut Run Plaza, 974 Centre Road, P.O. Box 2915, Wilmington, DE 19805 (US).

(72) Inventors: **HAUSMANN, Karlheinz**; Bachtobelstrasse 3, 8810 Horgen (CH). **LEE, I-Hwa**; 974 Centre Road, Wilmington, DE 19805 (US). **OLRY, Camille**; Route du Nant d'Avril, 146, 1217 Meyrin (CH).

(74) Agent: **RAWLS, Judith C.**; The Dow Chemical Company, P.O. Box 1967, Midland, Michigan 48641 (US).

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(54) Title: THERMOPLASTIC ADHESIVE COMPOSITION

(57) Abstract: Provided herein is a thermoplastic adhesive composition comprising an ethylene acid copolymer, an ethylene alkyl acrylate copolymer, and a functionalized ethylene copolymer that may be directly copolymerized or a graft copolymer of a polyolefin base with a graft comonomer. Further provided are multilayer films comprising the thermoplastic adhesive composition and coextrusion processes for producing these films. The multilayer films are useful as packaging materials and in particular as food packaging materials.



THERMOPLASTIC ADHESIVE COMPOSITION

FIELD OF THE INVENTION

5 Provided herein is a thermoplastic adhesive composition comprising an ethylene acid copolymer, an ethylene alkyl acrylate copolymer, and a functionalized ethylene copolymer that may be directly copolymerized or a graft copolymer of a polyolefin base with a graft comonomer. Further provided are multilayer films comprising the thermoplastic adhesive composition and coextrusion processes for producing these films. The multilayer films are useful as packaging materials and in
10 particular as food packaging materials.

BACKGROUND OF THE INVENTION

Several patents and publications are cited in this description in order to more fully describe the state of the art to which this invention pertains. The entire disclosure
15 of each of these patents and publications is incorporated by reference herein.

Packaging films and sheets are increasingly manufactured by coextrusion systems. These systems, in turn, are constantly growing in sophistication. Therefore, it is advantageous to develop materials for multilayer films that can be manufactured by a variety of coextrusion systems, including blown film, cast film, injection molding,
20 sheet/bottle, and others. Whereas some years ago it was common for extrusion machines to be capable of coextruding three- to five-layer structures, it is now routine for machines to coextrude nine or more layers, for example by using an equal number of extruders to feed these layers.

Methods for producing these complicated multilayer structures are co-injection
25 molding, injection stretch blow molding, and co-extrusion, for example co-extrusion of tubular films with orientation by inflation. Examples of these methods are described in detail in U.S. Patent No. 6,974,556; European Patent No. EP2305751A1, and PCT Intl. Publn. No. WO2007/099214, respectively. Other multilayer structures and methods of producing them are described in U.S. Patent No. 6,964,816; and in U.S.
30 Patent Appln. Publn. Nos. 2010/0034999 and 2014/0044902. These and other new coextrusion systems allow many types of polymers to be used together. Advantageously, these multilayer structures allow for better tailoring of the many

properties that may be required in packaging structures, such as low permeability to water, gas or flavoring; toughness; sealability; gloss; transparency; or impact resistance. These tailored structures may also have a lower overall raw material cost, for example if they incorporate smaller amounts of the more expensive components.

5 In many cases, the exterior side of the coextrusion construction is composed of a polyester. The “exterior side” includes the outer layer(s), more particularly the layer(s) that are on the opposite side of the barrier film from the “interior side”. The interior side includes one or more inner layers, and in the case of a packaging material the innermost layer contacts the packaging contents. For flexible films, the polyester
10 polymers provide stiffness and moisture barrier properties. They also provide a higher temperature resistance that prevents the film laminate from being deformed when contacted against a sealing bar during heat sealing of such laminates. The temperatures of the seal bars can be very high, particularly for thicker laminates, as heat must be transferred from the seal bar to the internal sealant layer within the short contact times
15 necessary for profitable commercial production.

 In some multilayer films, the polyester layer is desirably oriented in one or more directions. An oriented polyester layer permits fabrication of a multilayer film that is lighter and thinner than is generally possible with standard blown or cast polyester layers. Nevertheless, the oriented polyester layer provides improvements in one or
20 more end-use properties, for example tensile strength, toughness, heat stability, tear initiation resistance, and barrier function.

 In addition, co-extruded multilayer films frequently employ polyolefin bulking layers for rigidity, physical strength, moisture barrier properties and high temperature resistance that may allow the contents of the package to be cooked and retorted, for
25 example. The polyolefin bulking layer may also be shrinkable.

 Multilayer films with polyester layers and polyolefin layers often require adhesive layers to bond the non-polar polyolefin layers to the polar polyester layers. The adhesive layers, referred to synonymously and interchangeably herein as “tie
30 layers”, can vary in complexity of formulation to provide functional performance for different bonding requirements in a variety of multilayer films for packaging materials.

 In coextrusion processes, the chemically dissimilar layers that need to be bonded are in contact with the molten adhesive for a very short time, particularly in commercial production where the line speeds for some processes are very high.

Therefore, useful adhesive compositions provide good adhesive strength in high speed coextrusion processes and have a suitable amount of functionalized polyolefins or other molecules that are sufficiently low in molecular weight to migrate to the interface with the polar polymer during the short contact time, while avoiding one or more disadvantages associated with lower molecular weight, for example, deficiencies in physical properties, such as rigidity and moisture transfer rates, and difficulties with pelletization.

When the end use of a polymer system requires specifically tailored properties, for example good adhesion to both polar and non-polar materials, the requirement may often be filled by a polymer blend. Desirably, polymer blends may be more economical to develop and to produce on a commercial scale than a single new and specialized polymer.

It is apparent from the foregoing that there remains a need for a thermoplastic adhesive composition that provides high adhesion, good structural strength and other desired mechanical properties at low cost in multilayer coextruded structures that have from two or three layers to more than thirteen layers. In particular, a need exists for thermoplastic adhesive compositions that provide these advantages when the multilayer structure includes the layers "polyester/tie/polyolefin", and in particular when the polyester layer is oriented in one or more directions. Such multilayer coextruded structures are particularly useful in packaging applications and have other useful and beneficial applications. The multilayer coextruded structures are especially useful in food packaging materials.

SUMMARY OF THE INVENTION

Accordingly, provided herein is a thermoplastic adhesive composition comprising an ethylene acid copolymer, an ethylene alkyl acrylate copolymer, and a functionalized ethylene copolymer that may be directly copolymerized or a graft copolymer of a polyolefin base with a graft comonomer. Further provided are multilayer films comprising the thermoplastic adhesive composition and coextrusion processes for producing these films. The multilayer films are useful as packaging materials and in particular as food packaging materials.

DETAILED DESCRIPTION

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present embodiments, suitable methods and materials are described below. The materials, methods, and Examples described herein are illustrative only and not intended to be limiting.

As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having,” “contains,” “containing” or any other variation thereof, refer to a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to those elements, but may include other elements not expressly listed or inherent to such process, method, article, or apparatus.

The transitional phrase “consisting essentially of” limits the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention. “A ‘consisting essentially of’ claim occupies a middle ground between closed claims that are written in a ‘consisting of’ format and fully open claims that are drafted in a ‘comprising’ format.” Where an invention or a portion thereof is described with an open-ended term such as “comprising,” it is to be understood that, unless otherwise stated in specific circumstances, this description also includes a description of the invention using the terms “consisting of” and “consisting essentially of”.

The term “consisting essentially of” as used herein with respect to film layers refers to layers that include greater than 95 weight % or greater than 99 weight % of the recited component(s), based on the total weight of the film layer. Thus, film layers to which this term is applied may include one or more additives such those described below, including any carrier(s) that may be introduced with the additive(s). In these amounts, the additive(s) and their carrier(s) do not change the basic and novel characteristics of the film layers described herein.

Further, unless expressly stated to the contrary, “or” refers to an inclusive “or” and not to an exclusive “or.” For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, the indefinite articles “a” or “an” are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless expressly stated otherwise in limited circumstances

As used herein, the term “about” means that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but may be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is “about” or “approximate” whether or not expressly stated to be such.

In addition, the ranges set forth herein include their endpoints unless expressly stated otherwise in limited circumstances. Further, when an amount, concentration, or other value or parameter is given as a range, one or more preferred ranges or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether such pairs are separately disclosed.

Moreover, where a range of numerical values is recited herein, unless otherwise stated in specific circumstances, the range is intended to include the endpoints thereof, and all integers, fractions and real numbers within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range. Finally, when the term “about” is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

As used herein, the term “copolymer” refers to polymers comprising copolymerized units resulting from copolymerization of two or more comonomers. In this connection, a copolymer may be described herein with reference to its constituent comonomers or to the amounts of its constituent comonomers, for example “a copolymer comprising ethylene and 15 weight % of acrylic acid”, or a similar description. Such a description may be considered informal in that it does not refer to the comonomers as copolymerized units; in that it does not include a conventional

nomenclature for the copolymer, for example International Union of Pure and Applied Chemistry (IUPAC) nomenclature; in that it does not use product-by-process terminology; or for another reason. As used herein, however, a description of a copolymer with reference to its constituent comonomers or to the amounts of its constituent comonomers means that the copolymer contains copolymerized units (in the specified amounts when specified) of the specified comonomers. It follows as a corollary that a copolymer is not the product of a reaction mixture containing given comonomers in given amounts, unless expressly stated in limited circumstances to be such.

When measured, however, the comonomer content of the copolymers described herein is determined by comparison of the copolymer's FTIR spectrum with the FTIR spectra of a set of standard polymers.

The term "dipolymer" refers to polymers consisting essentially of copolymerized residues of two monomers, and the term "terpolymer" refers to polymers consisting essentially of copolymerized residues of three monomers.

The term "acid copolymer" as used herein refers to a polymer comprising copolymerized units of an α -olefin, an α,β -ethylenically unsaturated carboxylic acid, and optionally other suitable comonomer(s), such as an α,β -ethylenically unsaturated carboxylic acid ester.

The term "(meth)acrylic", as used herein, alone or in combined form, such as "(meth)acrylate", refers to acrylic or methacrylic, for example, "acrylic acid or methacrylic acid", or "alkyl acrylate or alkyl methacrylate".

As used herein, the term "finite amount" refers to an amount that is greater than zero.

The term "functionalize" as used herein, alone or in combined form, such as "functionalization", refers to a free radical grafting reaction through which a reactive monomer is attached to a polymer backbone, for example to a polypropylene homopolymer or copolymer backbone, by covalent bonding.

The terms "grafting agent" and "grafting monomer" are synonymous and used interchangeably herein to refer to ethylenically unsaturated carboxylic acids, anhydrides of ethylenically unsaturated carboxylic acids, and other derivatives of the ethylenically unsaturated carboxylic acids.

The term “surface layer” as used herein with or without modification, for example, “inside surface layer” or “outside surface layer”, refers to a layer only one face of which is in contact with another layer of a multilayer film.

5 The term “outside” as used herein with respect to a packaging film refers to the side of the film that faces away from the contents of the package. As used herein with respect to a tubular film, the term “outside” refers to the side of the film that faces the exterior of the tube. As used herein to describe the position of a layer in relation to another layer in a multilayer packaging film, the term “outside” refers to the layer that is further from the contents of the package than is the other layer. As used herein to describe the position of a layer in relation to another layer in a tubular film, the term “outside” refers to the layer that is further from the interior of the tube. Thus, in the context of defining relative positions, the term “outside” may refer to a layer that is not a surface layer. The term “outside surface layer” refers to the surface layer furthest from the contents of a package or furthest from the interior of a tubular film.

15 The term “inside” as used herein with respect to a packaging film refers to the side of the film that faces the contents of the package. As used herein with respect to a tubular film, the term “inside” refers to the side of the film that faces the interior of the tube. As used herein to describe the position of a layer in relation to another layer in a multilayer packaging film, the term “inside” refers to the layer that is closer to the contents of the package than is the other layer. As used herein to describe the position of a layer in relation to another layer in a tubular film, the term “inside” refers to the layer that is closer to the interior of the tube. Thus, in the context of defining relative positions, the term “inside” may refer to a layer that is not a surface layer. The term “inside surface layer” refers to the surface layer closest to the contents of a package or closest to the interior of a tubular film.

25 Finally, unless otherwise specified under limited circumstances, all measured melt flow rates are determined according to ASTM Method No. D1238-13. Moreover, as used herein in the context of melt flow rates, the term “to determine” refers to measurements made under the stated conditions and also to measurements that are made under other conditions and converted, by correlation or by extrapolation, for example, to a value that corresponds to a measurement under the stated conditions.

30 Provided herein is a thermoplastic adhesive composition for use in co-extruded multilayer structures, such as, for example, films for food packaging. The composition

comprises three compatible polymers that have both polar and non-polar moieties, specifically, copolymers of ethylene with α,β -unsaturated carboxylic acids, copolymers of ethylene with alkyl (meth)acrylates, and polyolefins functionalized with carboxylic acids or with derivatives of carboxylic acids, such as, for example, anhydrides of dicarboxylic acids.

Copolymers of ethylene with α,β -unsaturated carboxylic acids are referred to herein synonymously and interchangeably as “ethylene-acid copolymers”. Ethylene-acid copolymers suitable for use in the thermoplastic adhesive composition comprise copolymerized residues of ethylene and copolymerized residues of one or more α,β -unsaturated carboxylic acids. Preferred α,β -unsaturated carboxylic acids include, without limitation, acrylic acids, methacrylic acids, itaconic acids, maleic acids, maleic anhydrides, fumaric acids, monomethyl maleic acids, and combinations of two or more of these acid comonomers. Acrylic acid and methacrylic acid are more preferred, and acrylic acid is particularly preferred.

The ethylene-acid copolymer may further comprise copolymerized units of other comonomer(s), such as unsaturated carboxylic acids having 2 to 10 carbon atoms, or 3 to 8 carbon atoms, or derivatives of these unsaturated carboxylic acids. Suitable acid derivatives include acid anhydrides, amides, and esters. Some suitable ethylene-acid copolymers comprise copolymerized residues of an ester of the unsaturated carboxylic acid. Examples of suitable esters of unsaturated carboxylic acids include, but are not limited to, those that are described in U.S. Patent No. 8,399,096, issued to Hausmann et al. Examples of preferred comonomers include, but are not limited to, methyl (meth)acrylates, butyl (meth)acrylates, vinyl acetates, and combinations of two or more thereof. Butyl acrylate and methyl acrylate are more preferred.

Preferably, the ethylene-acid copolymer comprises a finite amount up to about 30 wt%, or about 10 to about 20 wt%, or about 13 to about 17 wt%, based on the total weight of the ethylene-acid copolymer, of the copolymerized carboxylic acid. Also preferably, when the other comonomer(s) are present, the ethylene-acid copolymer comprises a finite amount up to about 40 wt%, or up to about 30 wt%, or about 1 to about 20 wt%, or about 5 to about 15 wt%, based on the total weight of the ethylene-acid copolymer, of the copolymerized residues of the other comonomer(s). In some notable ethylene-acid copolymers, the amount of copolymerized residues of the other comonomer(s) is 0 wt%. The amount of copolymerized ethylene is complementary to

the amount of copolymerized carboxylic acid and other comonomers, if present, so that the sum of the weight percentages of the comonomers in the ethylene-acid copolymer is 100 wt%.

5 The ethylene-acid copolymer may have a melt flow rate (MFR) of about 1 to about 4000 g/10 min, about 5 to about 1000 g/10 min, about 5 to about 100 g/10 min, about 5 to about 50g/10 min, determined in accordance with ASTM D1238-13 at 190°C and 2.16kg.

10 Combinations of ethylene-acid copolymers are also suitable for use in the thermoplastic adhesive composition. For example, two or more dipolymers having differing amounts of copolymerized carboxylic acid comonomer or differing melt flow rates may be used. Also, a mixture of ethylene-acid copolymers including a dipolymer and a terpolymer may be suitable.

Suitable copolymers of ethylene and α,β -unsaturated carboxylic acids may be synthesized by methods that are described in detail in U.S. Patent No. 4,351,931. 15 Ethylene acid copolymers also may be prepared in continuous polymerizers by use of "co-solvent technology" as described in U.S. Patent 5,028,674. Other suitable synthesis methods are described in detail in U.S. Patent Nos. 3,404,134; 6,518,365; and 8,399,096 (cited above), and references cited therein. In addition, suitable copolymers of ethylene and α,β -unsaturated carboxylic acids are commercially available from E.I. 20 du Pont de Nemours and Company of Wilmington, DE (hereinafter "DuPont"), under the trademark Nucrel® acid copolymer resin.

The thermoplastic adhesive composition also comprises a copolymer of ethylene and an alkyl (meth)acrylate. Preferably, the ethylene alkyl (meth)acrylate copolymer comprises a finite amount up to about 40 wt%, or about 10 to about 40 wt%, 25 or about 20 to about 30 wt%, based on the total weight of the precursor acid copolymer, of the copolymerized alkyl (meth)acrylate. The amount of copolymerized ethylene is complementary to the amount of copolymerized alkyl (meth)acrylate(s), so that the sum of the weight percentages of the comonomers in the ethylene alkyl (meth)acrylate copolymer is 100 wt%.

30 The copolymer of ethylene and an alkyl (meth)acrylate may have a melt flow rate (MFR) of about 0.5 to about 50 g/10 min, about 1 to about 10 g/10 min, or about

1 to about 3 g/10 min, as determined in accordance with ASTM Method No. D1238-13 at 190°C and 2.16 kg.

Suitable copolymers of ethylene and an alkyl (meth)acrylate may be synthesized in an autoclave by methods described in U.S. Patent Nos. 2,200,429; 2,953,551; and 3,350,372, for example. In addition, suitable autoclave-produced ethylene alkyl (meth)acrylate copolymers are commercially available from DuPont under the trademark Elvaloy® ethylene copolymer resins.

Preferred copolymers of ethylene and an alkyl (meth)acrylate are “tubular reactor-produced”, that is, the copolymers are produced at high pressure and elevated temperature in a multi-zone or “tubular” reactor, or the like, in which the dissimilar reactivity ratios of the ethylene and alkyl acrylate comonomers are alleviated in whole or in part by the introduction of the monomers along the reaction flow path within the tubular reactor. As a consequence, the primary structure of the copolymer reflects a higher degree of randomness of comonomer distribution in the polymer chain. Thus, tubular reactor-produced ethylene copolymer can be physically distinguished from autoclave-produced ethylene copolymers. With respect to bulk properties, tubular reactor-produced ethylene alkyl (meth)acrylate copolymers are generally stiffer and more elastic than autoclave-produced copolymers. Tubular reactor-produced ethylene copolymers and methods of making the copolymers are described in U.S. Patent Nos. 3,350,372; 3,756,996; and 5,532,066, for example. Suitable tubular reactor-produced ethylene alkyl (meth)acrylate copolymers are commercially available from DuPont under the trademark Elvaloy® AC acrylate copolymers.

The thermoplastic adhesive composition further comprises a functionalized ethylene copolymer. The functionalized ethylene copolymer may be a graft copolymer which includes a polyolefin base and grafted residues of one or more grafting monomers. Alternatively, the functionalized ethylene copolymer may be a direct copolymer of ethylene with one or more functionalizing comonomers.

Suitable direct copolymers include, without limitation, the direct polymers described below as functionalized polymers for use as component 1) of the preferred multicomponent adhesion composition in the optional Other Adhesion Layer. Preferred direct copolymers include, without limitation, copolymers of ethylene with one or more functionalizing comonomers selected from the group consisting of α,β -unsaturated dicarboxylic acids, such as maleic acid, fumaric acid, itaconic acid,

crotonic acid, and derivatives of the α,β -unsaturated dicarboxylic acids, such as anhydrides, monoesters and diesters, and carboxylate salts of the dicarboxylic acids and monoesters. Anhydrides, alkyl monoesters and alkyl diesters are preferred derivatives. Esters of branched or unbranched alkyl groups comprising from 1 to 4 carbon atoms are more preferred. Maleic acid is a preferred α,β -unsaturated dicarboxylic acid. Maleic anhydride is a more preferred functionalizing comonomer. Also preferably, the direct copolymer comprises copolymerized residues of the functionalizing comonomer(s) in an amount of from 0.01 to 10 wt% or 0.1 to 10 wt%, more preferably from 0.1 to 5 wt%, or from 0.3 to 3 wt%, based on the total weight of the direct copolymer.

The direct copolymers may further comprise one or more additional comonomers selected from the group consisting of alkyl (meth)acrylates and vinyl acetate. Preferred alkyl groups are branched or unbranched and comprise from 1 to 4 carbon atoms. Also preferably, the direct copolymer comprises copolymerized residues of the additional comonomer(s) in a finite amount of up to 40 wt%, more preferably from 5 to 30 wt%, based on the total weight of the direct copolymer.

The amount of copolymerized ethylene in the direct copolymer is complementary to the amount of copolymerized functionalizing comonomer(s) and other comonomer(s), if present, so that the sum of the weight percentages of the comonomers in the direct copolymer is 100 wt%.

The direct copolymer may have a melt flow rate (MFR) of about 1 to about 1000 g/10 min, from about 1 to about 500 g/10 min, or from about 1 to about 20 g/10 min, as determined in accordance with ASTM Method No. D1238-13 at 190°C and 2.16 kg.

Specific examples of preferred direct copolymers include, without limitation, copolymers of 5 to 30 wt% of an alkyl acrylate, 0.1 to 5 wt% of maleic anhydride, and a complementary amount of ethylene, based on the total weight of the direct copolymer.

Suitable direct copolymers may be synthesized by random copolymerization of ethylene with the functionalizing comonomer(s) and other comonomer(s), if present, in a high-pressure free radical process, generally an autoclave process. For example, ethylene/monoalkyl maleate copolymers can be obtained using a suitable high-pressure process described U.S. Pat. Nos. 4,351,931. In addition, suitable direct copolymers are

commercially available from DuPont under the trademark Fusabond® functional polymers and from Arkema, Inc. of King of Prussia, PA, under the tradename Lotader™ terpolymers.

5 Suitable graft copolymers, suitable polyolefin bases, suitable grafting monomers, and suitable methods for producing the graft copolymers are described in U.S. Patent Nos. 5,346,963; 6,545,091; and 5,053,457, for example.

10 Briefly, however, suitable polyolefin bases for the graft copolymer include, without limitation, polyethylene homopolymers and copolymers with alpha-olefins, copolymers of ethylene and vinyl acetate, and copolymers of ethylene and one or more alkyl (meth)acrylates. The alkyl groups may be branched or unbranched. Preferred alkyl groups comprise from 1 to 4 carbon atoms.

 When the polyolefin base is an ethylene alkyl (meth)acrylate copolymer, it is preferably synthesized in a multi-zone or “tubular” reactor process, as described above with respect to the preferred copolymers of ethylene and an alkyl (meth)acrylate.

15 When the polyolefin base is a polyethylene homopolymer or a copolymer of ethylene with one of more alpha-olefins, the polyolefin base is preferably linear or substantially linear. The term “substantially linear” as used herein refers to a polymer backbone that is substituted with from 0.01 long chain branches per 1000 carbons to 3 long chain branches per 1000 carbons. The long chain branches have the same comonomer distribution as the polymer backbone, and can have about the same length as the length of the polymer backbone. The length of a long chain branch is longer than the carbon length of a short chain branch, the short chain branch being formed from the incorporation of the α -olefin comonomer into the polymer backbone.

20 In contrast, the term “linear” as used herein refers to a polymer backbone that lacks measurable or demonstrable long chain branches, i.e., it is substituted with fewer than 0.01 long chain branches per 1000 carbons.

 The extent of long chain branching can be determined by using carbon-13 nuclear magnetic resonance (¹³C-NMR) spectroscopy and can be quantified using the method of Randall (Rev. Macromol. Chem. Phys., C29 (2 &3), 1989, p. 285-297).

30 The polyolefin base may have a melt flow rate (MFR) of about 1 to about 1000 g/10 min, from about 1 to about 500 g/10 min, or from about 1 to about 20 g/10 min, as determined in accordance with ASTM method D1238 at 190°C and 2.16 kg.

Preferably, the polyolefin base has a density from about 0.860 to 0.960 g/cm³, more preferably from 0.930 to about 0.950 g/cm³, as measured according to ASTM Method No. D792-91. Other preferred density ranges are from about 0.860 to about 0.935 g/cm³, more preferably about 0.860 to about 0.910 g/cm³, and still more preferably from about 0.880 to about 0.900 g/cm³. Also preferred are ranges of from about 0.930 to about 0.960 g/cm³, when the polyolefin base is a copolymer of ethylene and an alkyl acrylate; from about 0.90 to about 0.960 g/cm³, when the polyolefin base is a polyethylene; and from about 0.860 to about 0.910 g/cm³, when the polyolefin base is a plastomer, that is, a copolymer of ethylene and alpha olefins having a molecular weight between 5000 and 50000 Daltons as reported by the manufacturer.

Suitable grafting monomers include, without limitation, ethylenically unsaturated carboxylic acids. Preferred grafting monomers include, without limitation, acrylic acid, methacrylic acid, fumaric acid, maleic acid, nadic acid (5-norbornene-2,3-dicarboxylic acid or, more rigorously, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid), citraconic acid, and itaconic acid. Also suitable are derivatives of the ethylenically unsaturated carboxylic acids, such as for example anhydrides; metal salts; esters, including monoesters and diesters; amides; imides; and the like. Acid anhydrides are preferred grafting monomers. The more preferred grafting monomers are maleic acid and maleic anhydride. Maleic anhydride is a still more preferred grafting monomer.

Preferably, the graft copolymer comprises a finite amount up to about 10 wt%, or up to about 5 wt%, or about 1 to about 4 wt%, based on the total weight of the graft copolymer, of the grafted monomer. The weight percentage of the polyolefin base is complementary to the amount of grafted monomer, so that the sum of the weight percentages of the polyolefin base and the grafted monomer in the graft copolymer is 100 wt%.

Suitable melt flow rates for the graft copolymer are as set forth above with respect to the polyolefin base and are measured as set forth above with respect to the polyolefin base.

Polyethylene and ethylene copolymers may be synthesized and functionalized by any suitable process known in the art. For example, graft copolymers produced from polyethylene and linear and substantially linear ethylene alpha-olefin copolymers may be produced as described in U.S. Patent Nos. 5,346,963 and 6,545,091. Graft copolymers produced from copolymers of ethylene with vinyl acetate or alkyl

(meth)acrylates are described in U.S. Patent No. 5,053,457, issued to I-Hwa Lee, and references cited therein, including U.S. Patent Nos. 4,861,677; 4,861,676; 4,670,349; 4,358,557; 3,932,332; 4,576,995; and Japanese Patent Appln. Nos. 59055743; 54057582 (reported as Derwent Abstract No. 46260B/25); and 58203043 (reported as Derwent Abstract No. 84-008480/02). In addition, suitable graft copolymers are commercially available from DuPont under the trademark Fusabond® functional polymers.

The thermoplastic adhesive composition may further comprise one or more additives including, without limitation, those described below with reference to the additional layer(s), in the amounts described below with reference to the additional layer(s).

The thermoplastic adhesive composition comprises a finite amount up to about 25 wt% of the ethylene acid copolymer, or from about 7 to about 23 wt%. The thermoplastic adhesive composition also comprises from about 50 to about 95 wt% of the copolymer of ethylene and alkyl (meth)acrylate, or from about 65 to about 85 wt%. The thermoplastic adhesive composition also comprises a finite amount up to about 25 wt% of the functionalized ethylene copolymer, or from about from about 7 to about 23 wt%.

These weight percentages are based on the total weight of the thermoplastic adhesive composition. The weight percentages of the components of the thermoplastic adhesive composition are complementary, that is, the sum of the weight percentages of the components of the thermoplastic adhesive composition is 100 wt%.

The ethylene acid copolymer, copolymer of ethylene and alkyl acrylate, and functionalized ethylene copolymer can be combined by any method known to one skilled in the art with the one or more optional additive(s) to produce the thermoplastic adhesive composition. Suitable methods include, without limitation, dry blending or melt blending using a melt-mixing device, such as twin screw extruders, single screw extruders, Banburies, Buss-Kneaders, and the like. For example, pellets of each of the components may be admixed to form a dry blend or “pellet blend,” which may be directly fed to the process for the formation of a packaging film, multilayer film, sheet or multilayer sheet, or molded part. Alternatively, pellets of each of the components may be fed separately to an extruder and melted together to form a “melt blend,” which may be fed to the process for the formation of a packaging film, multilayer film, sheet

or multilayer sheet, or molded part. In another alternative process, the melt blend may be processed into pellets containing the mixed components that may be fed subsequently to the process for the formation of a packaging film, multilayer film, sheet or multilayer sheet, or molded part.

5 In yet another alternative process, two components and the optional additive(s), if any, are added to the freshly synthesized and molten third component. This mixture is blended to form the thermoplastic adhesive composition, which is then pelletized. For example, after a polyolefin is synthesized and while it is still in the melt, a functionalized copolymer and a copolymer of ethylene and alkyl acrylate that have
10 been separately manufactured are added to the same mixing extruder and blended with the polyolefin prior to pelletizing. This method is described in detail in U.S. Patent No. 7,061,463. Any of the blend components may be dried to the extent desired before, during or after the blending process. Those of skill in the art are capable of choosing appropriate blending conditions based on the physical properties of the individual
15 components, such as their melting temperatures and melt flow rates, for example.

 The thermoplastic adhesive composition is particularly useful as a tie layer in multilayer structures, such as, for example, multilayer films, and in particular as a tie layer in co-extruded multilayer films. Suitable tie layers comprise the thermoplastic adhesive composition, or consist essentially of the thermoplastic adhesive composition,
20 or consist of the thermoplastic adhesive composition.

 Accordingly, further provided herein are multilayer structures comprising at least one layer that includes the thermoplastic adhesive composition. These layer(s) may independently have a thickness of less than 1 μm , between 1 and 100 μm , between 5 and 50 μm , or between 5 and 30 μm .

25 The multilayer structures also include at least one additional layer, for example an external layer, a gas barrier, a polyolefin layer such as a bulk shrink layer, an additional adhesive layer, and a sealant layer. Suitable additional layers are described in detail in PCT Intl. Patent Appln. Publn. No. WO2016/100277, by Hausmann et al., and below.

30 External Layer

 The outside surface layer, or external layer, of the food casing or food film provides the outside layer of a package and is the layer farthest from the packaged contents.

The outside layer may comprise polyester, polyamide (PA), polystyrene (PS), polycarbonate (PC), poly(methyl methacrylate) (PMMA), cyclic olefin copolymer (COC), polypropylene (PP), polyethylene (PE), including high density polyethylene (HDPE), or combinations thereof, providing the ability to weld or seal the films at high
5 temperatures without the film being bonded to the sealing terminal. As a result, higher cycle numbers may be achieved on the sealing machines. In addition, these materials produce an external layer that is less susceptible to harm resulting from physical insults and that possesses excellent optical properties, such as gloss and transparency. Thus, the external layer provides mechanical support and protection of the other layers of the
10 film. Furthermore, the film is particularly well suited for inscribing or printing.

The thermoplastic adhesive composition is particularly useful as a tie layer to adhere polyester layers to polyolefin layers. Accordingly, the external layer preferably comprises or consists essentially of one or more polyesters. Polyesters provide excellent optical properties, such as gloss and transparency, and permit a high speed of
15 further processing (cycle numbers) as a result of their high temperature resistance.

Suitable polyesters and copolymers thereof include, without limitation, polycarbonates; aliphatic polyesters, such as polyhydroxyalkanoic acids, including for example polylactic acid or poly(3-hydroxybutyrate); and semiaromatic polyesters such as polyethylene terephthalate (PET), for example, and copolymers thereof, such as
20 PETG, polytrimethylene terephthalate, polybutylene terephthalate and polyethylene naphthalate. Polyethylene terephthalate (PET) is a particularly preferred material for the polyester layer.

Also preferably, the polyester is capable of being oriented under conditions that are typical of coextrusion processes with orientation, for example at temperatures in
25 the range of 80 to 100°C.

Preferably, the polyester layer is oriented in one or more directions. More preferably, the polyester layer is oriented in the machine direction (MD), in the transverse direction (TD), or in both the machine direction and the transverse direction. Still more preferably, the polyester layer is oriented biaxially in both the machine
30 direction and the transverse direction.

Combinations of two or more layers having compositions such as described above may be used to provide the mechanical and/or protective functions of the external layer.

Polyolefin layer

The thermoplastic adhesive composition is particularly useful as a tie layer to adhere polyester layers to polyolefin layers. Accordingly, the multilayer film preferably comprises a layer that comprises or consists essentially of one or more polyolefins. Polyolefin layers, sometimes referred to as “bulk layers” or “bulking layers”, are useful to provide properties such as shrinkage, puncture resistance and stiffness in a multilayer film.

Suitable materials for polyolefin layers include, for example, polypropylene homopolymers and copolymers, ionomers of copolymers of ethylene and (meth)acrylic acid, said ionomers optionally further comprising copolymerized alkyl (meth)acrylates. Preferred materials for polyolefin layers include, without limitation, copolymers of ethylene with vinyl acetate, alkyl(meth)acrylates, carboxylic acids and ionomers of ethylene acid copolymers and copolymers of polypropylene with other olefins, such as ethylene. Ionomers and copolymers of propylene and ethylene are more preferred materials for the polyolefin layer. Still more preferred are random or block copolymers of polypropylene, and random and block terpolymers of propylene with ethylene and another olefin, such as butene, for example. One preferred material is commercially available from Lyondell Basell of Rotterdam, Netherlands, under the tradename Adsyl. For example, Adsyl 5C30F resin is a suitable terpolymer of propylene, ethylene and butene.

Some preferred polyolefin layers are bulk shrinkable layers. Suitable polyolefins for use in bulk shrinkable layers are described in U.S. Patent No. 8,202,590 and in Research Database Disclosure No. 448065, disclosed anonymously and published in Research Disclosure Journal (Kenneth Mason Publications, Ltd., Hants, U.K.; August, 2001). Ionomers of ethylene acid copolymers are preferred materials for the bulk shrinkable layer.

Gas barrier layer

The film optionally may also comprise a gas barrier layer. The term “gas barrier layer” as used herein denotes a film layer that allows transmission through the film of less than 1000 cc of gas, such as oxygen, per square meter of film per 24 hour period at 1 atmosphere and at a temperature of 23°C at 50% relative humidity. Preferably the barrier layer provides for oxygen transmission below 500, below 100, below 50, below 30 or below 15 cc/m²-day for the multilayer films. When factored for thickness the

films preferably have oxygen permeation levels of less than 40 or less than 30 cc·mil/m²·day. Other polymers may be present as additional components in the barrier layer, so long as they do not raise the permeability of the barrier layer above the limit defined above.

5 Suitable barrier layers may be chosen from layers comprising ethylene vinyl alcohol copolymer, cyclic olefin copolymers, polyvinyl acetate, or blends of one or more of these polymers with polyethylene, polyvinyl alcohol, or polyamide.

 The gas barrier layer of the multilayer films preferably comprises ethylene vinyl alcohol polymers and mixtures thereof. In the following discussion of barrier layers,
10 the term “EVOH” refers to both neat ethylene vinyl alcohol polymers and to blends of ethylene vinyl alcohol polymers with other polymers.

 Neat EVOH polymers generally have an ethylene content of between about 15 mole % to about 60 mole %, more preferably between about 20 to about 50 mole %. The density of commercially available neat EVOH generally ranges from between
15 about 1.12 g/cm³ to about 1.20 g/cm³, the polymers having a melting temperature ranging from between about 142°C and 191°C. EVOH polymers can be prepared by well-known techniques or can be obtained from commercial sources. EVOH copolymers may be prepared by saponifying or hydrolyzing ethylene vinyl acetate copolymers. Thus EVOH is also known as hydrolyzed ethylene vinyl acetate (HEVA)
20 copolymer. The degree of hydrolysis is preferably from about 50 to 100 mole %, more preferably from about 85 to 100 mole %. In addition, the weight average molecular weight, M_w, of the EVOH component useful in the multilayer films described herein, calculated from the degree of polymerization and the molecular weight of the repeating unit, may be within the range of about 5,000 Daltons to about 300,000 Daltons, with
25 about 60,000 Daltons being preferred.

 Suitable EVOH polymers may be obtained from Eval Company of America or Kuraray Company of Japan under the tradename EvalTM. EVOH is also available under the tradename SoarnolTM from Nippon Goshei. Examples of such EVOH resins include EVALTM grades F101, E105, J102, and SoarnolTM grades DT2903, DT2904, DC3203
30 and ET3803. Preferably, the EVOH is orientable from about 3x3 to about 10x10 stretch without loss in barrier properties from pinholing, necking or breaks in the EVOH layer.

 Of special note are EVOH resins sold under the tradename EvalTM SP, which exhibit enhanced plasticity and which are suited for use in packaging applications

including shrink film, polyethylene terephthalate (PET)-type barrier bottles and deep-draw cups and trays. Examples include EvalTM SP grades 521, 292 and 482. The EvalTM SP grades of EVOH are easier to orient than some other EVALTM resins. Thus, the EvalTM SP EVOH polymers are a preferred class for use in the multilayer film compositions described herein. Without being bound to theory, it is believed that the enhanced orientability of these resins derives from their chemical structure, in particular the level of head to head adjacent hydroxyl groups, that is, 1,2-glycol structural units in the EVOH polymer chain. It has been found that EVOH polymers having a relatively high level of 1,2 glycol units in the EVOH polymer chain are particularly suitable for use in multilayer films. For example, about 2 to about 8 mol% of 1,2-glycol structural units, preferably about 2.8 to about 5.2 mol% of 1,2-glycol units, based on the total number of moles of hydroxyl groups in the EVOH polymer, may be present in the EVOH polymer chain.

Such polymers can be produced by increasing the amount of adjacent copolymerized units of vinyl acetate produced during polymerization of ethylene and vinyl acetate above the level generally used. When such polymers are hydrolyzed to form EVOH, an increased amount of head-to-head vinyl alcohol adjacency, that is, an increased amount of the 1,2-glycol structure result. It has been reported in the case of polyvinyl alcohol that the presence of the 1,2-glycol structure in polyvinyl alcohol can influence the degree of crystallinity obtained in these alcohols and thereby the tensile strength. See, for example F. L. Marten & C.W. Zvanut, Chapter 2, *Manufacture of Polyvinyl Acetate for Polyvinyl Alcohol*, Polyvinyl Alcohol Developments (C. A. Finch ed.) John Wiley, New York 1992.

The more orientable grades of EVOH will generally have lower yield strength, lower tensile strength and lower rates of strain hardening than other EVOH polymers of equivalent ethylene content, as measured by mol% of ethylene, based on the total number of moles of copolymerized residues in the EVOH polymer.

The EVOH composition for the barrier layer may optionally include additional polymers selected from the group consisting of polyamides, including amorphous polyamides such as MXD6 and nylon 6I/6T (hexamethyleneiso-phthalamide hexamethylene terephthalamide copolymer); polyvinyl acetate (PVA); ionomers; ethylene polymers; and mixtures of two or more of these additional polymers. Sellar® PA amorphous nylon barrier resins, commercially available from DuPont, are suitable

blends of EVOH with a polyamide. The additional polymers may be present in a finite amount up to 30 weight %, based on the total weight of the EVOH composition.

The oxygen barrier effectiveness of EVOH can be reduced by the presence of moisture, however. Therefore, it is desirable to protect the EVOH layer from moisture that may originate from the product contained within the package or from the atmosphere outside the package. Accordingly, a moisture barrier layer may be positioned between the EVOH layer and the contents of the package, or between the EVOH layer and the exterior of the package, or both. For example, a polyolefin layer may be positioned between the sealant layer and the delamination layer to provide a moisture barrier between the interior of the package and the EVOH gas barrier layer.

In a preferred embodiment, the coextruded multilayer structure may comprise a layer of EVOH sandwiched between two layers of polyamide, one on each side of the EVOH layer. This leads to a maximum possible oxygen barrier and at the same time ensures excellent embedding and stabilization of the EVOH layer between the two polyamide layers as carrier layers. In another preferred embodiment, the gas barrier may comprise a layer of polyamide sandwiched between two layers of EVOH.

Sealant Layer

The inside surface layer, or sealant layer, is the layer that provides the inside layer of a package prepared from the multilayer film and that is closest to the packaged contents. It also provides a means for sealing or closing the package around the packaged product, such as by heat sealing two portions of the sealant layer together or to the surface of another part of the package, such as sealing a lidding film to a thermoformed packaging component. The composition of the sealant layer is selected to influence the sealing capability of the inside surface layer, for example, to achieve a high sealing bond strength at the lowest possible sealing temperature.

The sealant layer may comprise one or more polymers capable of fusion bonding on another layer by conventional means of heat sealing. The sealant layer may comprise one or more polyolefin polymers, such as for example polyethylene homopolymer or copolymer, ethylene alkyl (meth)acrylate copolymer, or an ethylene alkyl (meth)acrylic acid copolymer or ionomer thereof, or mixtures thereof.

Preferably, the one or more olefin homopolymers and/or copolymers are chosen among polyethylene, and/or copolymers, ethylene copolymers such as for example

ethylene (meth)acrylic acid copolymers and their corresponding ionomers, and/or mixtures thereof.

The sealant layer may include at least one polyolefin, preferably polyethylene (PE) homopolymers or copolymers of ethylene and other α -olefins. Other α -olefins include, for example and without limitation, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-tetradecene, 1-octadecene, vinylacetate, alkyl (meth)acrylate or combinations of two or more of these α -olefins. Various types of polyethylenes are known in the art. PE homopolymers and copolymers may be prepared by a variety of methods, for example, the well-known Ziegler-Natta catalyst polymerization (see, e.g., U.S. Patent Nos. 4,076,698 and 3,645,992), metallocene catalyzed polymerization, Versipol[®] catalyzed polymerization, and free radical polymerization. The polymerization may be conducted as a solution phase process, a gas phase process, a similar process or another suitable process. Examples of PE polymers include, without limitation, high density PE (HDPE), linear low density PE (LLDPE), low density PE (LDPE), very low or ultralow density PEs (VLDPE or ULDPE), linear or substantially linear lower density PE having high flexibility and low crystallinity and made with metallocene or another single site catalyst (mPE). Examples of suitable mPEs are commercially available from the Dow Chemical Company of Midland, MI (hereinafter "Dow"), under the tradename ELITE[™] Enhanced Polyethylene Resins, including for example ELITE[™] AT Advanced Technology Resins, or under the tradename AFFINITY[™] Polyolefin Plastomers.

The density of PE may range from about 0.860 g/cc to about 0.970 g/cc. Linear PE may incorporate α -olefin comonomers such as butene, hexene or octene to decrease density to within the density range so described. For example, a copolymer may comprise a major portion (by weight) of ethylene that is copolymerized with another α -olefin having 3 to 20 carbon atoms, which may be present in an amount up to about 45 % by weight of the copolymer.

Low density polyethylene ("LDPE") can be prepared at high pressure, for example above 14,500 psi or 100 MPa, in an autoclave or in a tubular reactor, using free radical initiators such as peroxides. See, for example, U.S. Patent No. 4,599,392. This material typically has a density in the range of 0.916 to 0.940 g/cm³, preferably 0.924 to 0.940 g/cm³. LDPE is also known as "branched" or "heterogeneously

branched" polyethylene because of the relatively large number of long chain branches extending from the main polymer backbone.

Also known is polyethylene in the same density range, 0.916 to 0.940 g/cm³, that is linear and does not contain large quantities of long chain branching. This "linear low density polyethylene" ("LLDPE") can be produced with conventional Ziegler-Natta catalysts or with single site catalysts such as metallocene catalysts. LLDPE includes linear, substantially linear or heterogeneous polyethylene copolymers or homopolymers and contains less long chain branching than LDPE. Suitable substantially linear ethylene polymers are described in U.S. Patent Nos. 5,272,236; 5,278,272; 5,582,923; and 5,733,155, for example. Suitable homogeneously branched linear ethylene polymer compositions are described in U.S. Patent No. 3,645,992, for example. Suitable heterogeneously branched ethylene polymers may be prepared according to the process described in U.S. Patent No. 4,076,698, for example. Also suitable are blends or combinations of two or more of the suitable varieties of LLDPE, such as those described in U.S. Patent Nos. 3,914,342 or 5,854,045. Suitable LLDPE can be synthesized via gas-phase, solution-phase, or slurry polymerization, for example, or by any combination of these methods, using any type of reactor or reactor configuration known in the art.

Relatively higher density LDPE or LLDPE, typically in the range of 0.928 to 0.940 g/cm³, is sometimes referred to as medium density polyethylene ("MDPE") or linear medium density polyethylene (LMDPE). Polyethylenes having a density greater than 0.940 g/cm³ are high density polyethylenes ("HDPE"), which are generally prepared with Ziegler-Natta catalysts, chrome catalysts or even single site catalysts such as metallocene catalysts. Very low density polyethylene ("VLDPE") is also known. VLDPE can be produced by a number of different processes yielding polymers with different properties. In general, however, they have a density less than 0.916 g/cm³, such as 0.890 to 0.915 g/cm³ or 0.900 to 0.915 g/cm³.

"Metallocene polyethylene" (mPE) is produced by a metallocene catalyst, defined to be at least one metallocene catalyst component containing one or more substituted or unsubstituted cyclopentadienyl moieties in combination with a Group 4, 5, or 6 transition metal. The metallocene catalyst precursors generally require activation with a suitable co-catalyst, or activator, in order to yield an "active metallocene catalyst", i.e., an organometallic complex with a vacant coordination site

that can coordinate, insert, and polymerize olefins. Non-limiting examples of metallocene catalysts and catalyst systems useful in preparing metallocene polyethylenes include those described in Intl. Patent Appln. Publn. Nos. WO96/11961; WO96/11960 and WO01/98409; U.S. Patent Nos. 4,808,561; 5,017,714; 5,055,438; 5,064,802; 5,124,418; 5,153,157; 5,240,894; 5,272,236; 5,264,405; 5,278,272; 5,324,800; 5,507,475, 6,380,122; and 6,376,410; and references cited therein. Suitable polyethylenes made with these metallocene catalysts include, without limitation, m-LLDPE, m-VLDPE, and polyolefin plastomers. Of note are metallocene polyethylenes comprising ethylene/octene copolymers or ethylene/hexene copolymers.

Also notable are homogeneously branched ethylene- α -olefin copolymers. These copolymers can be made with a single-site catalyst, such as a metallocene catalyst or constrained geometry catalyst, and typically have a melting point of less than 105°C, specifically less than 90°C, more specifically less than 85°C, even more specifically less than 80°C, and still more specifically less than 75° C. The melting point is measured by differential scanning calorimetry (DSC) as described, for example, in U.S. Patent No. 5,783,638.

The PE copolymer may also be an ethylene propylene elastomer containing a small amount of unsaturated compounds having a double bond. Ethylene copolymers having small amounts of a diolefin component such as butadiene, norbornadiene, hexadiene and isoprene are also generally suitable. Terpolymers such as ethylene/propylene/diene monomer (EPDM) are also suitable.

Blends of two or more of any of these polyethylenes are also suitable for use in the multilayer structures described herein. For example, blends of LLDPE and LDPE; blends of LDPE and HDPE; blends of LDPE and mPE; blends of LLDPE with mPE; and blends of LLDPE with mPE and LDPE may be used in at least one layer of the multilayer film, such as the sealant layer.

Examples of suitable commercially available homogeneously branched ethylene- α -olefin copolymers for as a sealant include homogeneously branched, linear ethylene- α -olefin copolymers, such as those available under the tradenames TAFMER™ from Mitsui Petrochemicals Company, Ltd., of Tokyo, Japan, and EXACT™ from Exxon Chemical Company of Houston, TX. Suitable homogeneously branched, substantially linear ethylene- α -olefin polymers are available from Dow under the tradenames AFFINITY™ and ENGAGE™ Polyolefin Plastomers.

The sealant layer may also comprise ethylene (meth)acrylate copolymers such as those described above as suitable for use in the thermoplastic adhesive composition.

The sealant layer may also comprise a mixture of at least one of a polyethylene polymer, ethylene alkyl (meth)acrylate copolymer, ethylene (meth)acrylate copolymer or ionomer thereof, and at least one polybutylene polymer.

For example, the composition of the sealant layer may comprise from 85 to 98 weight % of the at least one ethylene polymer, ethylene alkyl (meth)acrylate copolymer, ethylene (meth)acrylate copolymer or ionomer thereof, and from 2 to 15 or 30 weight % of the at least one polybutylene polymer, the weight percentages being based on the total weight of the sealant layer composition.

Inclusion of polybutylene in the sealant layer may facilitate cohesive failure of the sealant layer when pulled apart to open the package. Useful in these embodiments are the peel systems described in U.S. Patent No. 4,189,519 (blend of EVA or EMA or EEA with crystalline isotactic polybutylene, and optionally with anhydride grafted EVA); U.S. Patent No. 4,252,846 (blend of EVA and HDPE, optionally with IO or polybutylene (PBU)); U.S. Patent No. 4,550,141 (blend of IO and polypropylene/ethylene copolymer (EPC)); U.S. Patent No. 4,666,778 (three component blend of PE, that can be LLDPE, LDPE, MDPE, or HDPE, or EVA or EMA, with PBU, and PP or EPC); U.S. Patent No. 4,882,229 (butene-1 polymer or copolymer blended with modified or unmodified LDPE); U.S. Patent No. 4,916,190 (blend of butylene polymer or copolymer, with PE polymer or copolymer (LLDPE, LDPE, MDPE, EVA, EMA, EEA, EBA, or HDPE), with propylene polymer or copolymer); U.S. Patent No. 4,937,139 (propylene polymer or copolymer blended with HDPE); U.S. Patent No. 5,547,752 (blend of PBU and IO); U.S. Patent No. 5,997,968 (blend of a copolymer of ethylene and propylene or ethylene and butylene or propylene and butylene or ethylene and another α -olefin having 5 to 10 carbon atoms or propylene and another α -olefin having 5 to 10 carbon atoms or a terpolymer of ethylene and propylene and butylene or ethylene and propylene and another α -olefin having 5 to 10 carbon atoms and HDPE, MDPE, LDPE, LLDPE or VLDPE); and U.S. Patent No. 6,630,237 (peelable composition comprising polybutylene, ionomer and EVA or ethylene acrylate copolymer used in the sealant layer and in the delamination layer).

In some embodiments, the delamination layer may comprise an ionomer and the sealant layer may comprise polyethylene. In such embodiments, an adhesion layer

may be necessary between the delamination layer and the sealant layer to provide sufficient interlayer adhesion.

Alternatively, the sealant layer comprises at least ethylene acid copolymer or ionomer thereof, such as described above. When the sealant layer and the delamination layer are both ionomers, there is no need for an adhesion layer between the delamination layer and the sealant layer. Notably, in some structures, a single layer of ionomer may serve as both delamination layer and the sealant layer.

Other Adhesion Layer

In addition, the coextruded multilayer structure may comprise one or more additional layers to serve as adhesion layers between functional layers to improve interlayer adhesion and prevent delamination of the layers. For example, such coextruded adhesion layers may be positioned between the external layer (PET) composition and the gas barrier layer composition, or between ionomer-containing layers and polyolefin layers. For example, adhesion compositions described in U.S. Patent Nos. 6,545,091; 5,217,812; 5,053,457; 6,166,142; 6,210,765; and U.S. Patent Application Publication No. 2007/0172614 are suitable.

A preferred other adhesion composition for use in the optional additional adhesive layer(s) comprises 1) a functionalized polymer, 2) an ethylene polymer or copolymer, and optionally 3) a tackifier. These preferred other adhesive compositions and suitable components for use in the preferred other adhesive compositions are described in detail in PCT Intl. Patent Appln. Publn. No. WO2016/100277, cited above.

Optional other adhesive compositions comprising olefin polymers and modified polymers are commercially available from DuPont under the trademarks APPEEL® peelable sealant resins; BYNEL® coextrudable adhesive resins; ELVALOY® AC ethylene acrylate copolymers; and ELVAX® ethylene vinyl acetate copolymer resins.

The thickness of each optional additional adhesion layer of the multilayer structure may be independently less than 1 μm , between 1 and 100 μm , between 5 and 50 μm , or between 5 and 30 μm .

Additives

The layer(s) comprising the thermoplastic adhesive composition and the additional layer(s) of the multilayer film structure may further comprise one or more modifiers or other additives, including without limitation plasticizers, impact

modifiers, stabilizers including viscosity stabilizers and hydrolytic stabilizers, lubricants, antioxidants, UV light stabilizers, antifog agents, antistatic agents, dyes, pigments or other coloring agents, fillers, flame retardant agents, reinforcing agents, foaming and blowing agents, and processing aids known in the polymer compounding art, such as for example antiblock agents and release agents.

One or more of these additives may be present in each layer's composition independently in finite amounts of up to 20 weight %, preferably from 0.01 to 7 weight %, and more preferably from 0.01 to 5 weight %, the weight percentage being based on the total weight of the layer's composition. Finally, these additives may be incorporated into the composition of each layer by methods that are known in the art. See, for example, the *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th Edition, John Wiley and Sons (New York, 2004).

Representative examples of multilayer films include, without limitation, those described below. In these descriptions, the symbol "/" represents a boundary between contiguous layers. In addition, outside to inside layers of the multilayer film, as intended to be used in a package, are listed in order from left to right. Moreover, "PET" represents polyethylene terephthalate, "PA" represents a polyamide, and "Del" represents a delamination layer, for example as described in PCT Intl. Patent Appln. Publn. No. WO2016/100277, cited above. Two or more adhesive layers in a single film may have the same composition or different compositions, depending on the compositions of the layers adjacent to the adhesive layers. Accordingly, an adhesive layer is designated "Tie" when it comprises the thermoplastic adhesive composition described herein, and it is designated "T" when it comprises any other adhesive composition, for example those described above as suitable for optional other adhesive layers. When contiguous layers are ionomer layers, each layer has a different composition. With this exception, and with the further exception of PET layers, two or more contiguous layers may have the same composition, and these contiguous layers will form a single layer in the multilayer film. Finally, each multilayer film will have particular advantages depending on the intended packaging use or other application.

PET/Tie/PP/T/ionomer/T/PA/EVOH/PA/Del/PE	PET/Tie/PE/ionomer/PA/EVOH/PA/Del/PE
PET/Tie/EVA/ionomer/T/PA/EVOH/PA/Del/PE	PET/Tie/EMA/ionomer/PA/EVOH/PA/Del/PE
PET/Tie/PP/T/PA/EVOH/PA/Del/PO/PE	PET/Tie/PE/T/PA/EVOH/PA/Del/PO/PE

PET/Tie/ionomer/T/PA/EVOH/PA/Del/PO/PE	PET/Tie/EVA/Tie/PA/EVOH/PA/Del/PO/PE
PET/Tie/EMA/Tie/PA/EVOH/PA/Del/PO/PE	PA/Tie/PP/T/ionomer/PA/EVOH/PA/Del/PE
PA/Tie/PE/ionomer/T/PA/EVOH/PA/Del/PE	PA/Tie/EVA/ionomer/PA/EVOH/PA/Del/PE
PA/Tie/EMA/ionomer/T/PA/EVOH/PA/Del/PE	PA/Tie/PP/T/PA/EVOH/PA/Del/PO/PE
PA/Tie/PE/T/PA/EVOH/PA/Del/PO/PE	PA/Tie/ionomer/T/PA/EVOH/PA/Del/PO/PE
PA/Tie/EVA/Tie/PA/EVOH/PA/Del/PO/PE	PA/Tie/EMA/Tie/PA/EVOH/PA/Del/PO/PE
PET/Tie/PP/T/ionomer/T/PA/EVOH/PA/Del/ionomer	PET/Tie/PE/ionomer/T/PA/EVOH/PA/Del/ionomer
PET/Tie/EVA/ionomer/T/PA/EVOH/PA/Del/ionomer	PET/Tie/EMA/ionomerT/PA/EVOH/PA/Del/ionomer
PET/Tie/PP/T/PA/EVOH/PA/Del/PO/ionomer	PET/Tie/PE/T/PA/EVOH/PA/Del/PO/ionomer
PET/Tie/ionomer/PA/EVOH/PA/Del/PO/ionomer	PET/Tie/EVA/Tie/PA/EVOH/PA/Del/PO/ionomer
PET/Tie/EMA/Tie/PA/EVOH/PA/Del/PO/ionomer	PA/Tie/PP/T/ionomer/T/PA/EVOH/PA/Del/ionomer
PA/Tie/PE/ionomer/PA/EVOH/PA/Del/ionomer	PA/Tie/EVA/ionomer/T/PA/EVOH/PA/Del/ionomer
PA/Tie/EMA/ionomer/PA/EVOH/PA/Del/ionomer	PA/Tie/PP/T/PA/EVOH/PA/Del/PO/ionomer
PA/Tie/PE/T/PA/EVOH/PA/Del/PO/ionomer	PA/Tie/ionomer/T/PA/EVOH/PA/Del/PO/ionomer
PA/Tie/EVA/Tie/PA/EVOH/PA/Del/PO/ionomer	PA/Tie/EMA/Tie/PA/EVOH/PA/Del/PO/ionomer
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PA/Tie/EVA/Tie/PA/EVOH/PA/Tie/PO/ionomer	PA/Tie/EMA/Tie/PA/EVOH/PA/Tie/PO/ionomer

In preferred multilayer films, at least one layer is monoaxially or biaxially oriented. More preferably, at least one layer is oriented in the machine direction, in the transverse direction, or in both the machine direction and the transverse direction. In more preferred films, the oriented layer is a polyester layer or, in particular, a PET layer. Still more preferably, the polyester layer or the PET layer is biaxially oriented. Also preferably, the polyester layer or the PET layer is the external layer.

Some preferred multilayer films include a structure having three contiguous layers PET/Tie/PA or PET/Tie/PO, and some preferred multilayer films consist of the three contiguous layers PET/Tie/PA or PET/Tie/PO, wherein “Tie” is as defined above. In these preferred films, the polyolefin layer “PO” may be a bulk layer or a sealant layer.

Some more preferred multilayer films have the structure PET/Tie 1/PO/Tie 2/barrier/Tie 3/sealant, PET/Tie 1/PO 1/Tie 2/barrier/Tie 3/PO 2/sealant, or PET/Tie 1/barrier/Tie 2/PO/sealant. In these structures, PO 1 and PO 2 are polyolefin layers that may be the same or different, and one or more of the layers Tie 1, Tie 2 and Tie 3 comprises the thermoplastic adhesive composition described herein. Still more preferably, the layer Tie 1 comprises the thermoplastic adhesive composition.

In some preferred multilayer films, the sealant layer or the polyolefin layer PO comprises a polyolefin selected from the group consisting of polyethylene homopolymers; copolymers of ethylene with one or more alpha-olefins; polypropylene homopolymers; copolymers of propylene with one or more alpha-olefins; copolymers of ethylene with vinyl acetate; copolymers of ethylene with one or more α,β -unsaturated carboxylic acids or one or more alkyl esters of α,β -unsaturated carboxylic

acids; and ionomers of copolymers of ethylene with one or more α,β -unsaturated carboxylic acids or one or more alkyl esters of α,β -unsaturated carboxylic acids.

More preferably, the polyolefin layer PO comprises a polyolefin selected from the group consisting of polyethylene homopolymers; polypropylene homopolymers; random copolymers of ethylene and propylene; block copolymers of ethylene and propylene; copolymers of ethylene with vinyl acetate; copolymers of ethylene with one or more alkyl esters of (meth)acrylic acid; and ionomers of copolymers of ethylene with one or more α,β -unsaturated carboxylic acids or one or more alkyl esters of α,β -unsaturated carboxylic acids.

Also preferably, the coextruded multilayer film includes both a sealant layer and a PO layer. In these preferred films, the sealant layer comprises a first polyolefin that has a melting point that is lower than the melting point of the second polyolefin that is comprised by the polyolefin layer PO. Melting points are determined according to ASTM Method No. 3418-15 at a heating speed of 10°C/min.

The multilayer films may be formed and oriented by any suitable process. Information about these processes may be found in reference texts such as, for example, the *Kirk Othmer Encyclopedia*, the *Modern Plastics Encyclopedia* or the *Wiley Encyclopedia of Packaging Technology*, 2d edition, A.L. Brody and K.S. Marsh, Eds., Wiley-Interscience (Hoboken, 1997). For example, the multilayer films may be formed through dipcoating, film casting, sheet casting, solution casting, compression molding, injection molding, lamination, melt extrusion, blown film including circular blown film, extrusion coating, tandem extrusion coating, or any other suitable procedure. Preferably, the sheets are formed by a melt extrusion, melt coextrusion, melt extrusion coating, or tandem melt extrusion coating process. Suitable orientation processes include tenter frame technology and machine-direction orientation (MDO) technology.

More preferably, however, the coextruded multilayer film structure is manufactured in a co-extrusion process with orientation by inflation, such as, for example, a “double bubble process, or preferably the “triple bubble” processes described in Intl. Patent Appln. Publn. Nos. WO2007/099214 and WO2016/100277. Special conditions for the co-extrusion of multilayer films including the thermoplastic adhesive composition described herein include orienting the film by exposing the second bubble to a temperature of 90°C and annealing film by exposing the third bubble to a temperature between 50°C and 120°C, using equipment described and at line

speeds described in Intl. Patent Appln. Publn. Nos. WO2007/099214 and WO2016/100277.

The multilayer films described herein are useful as packaging and in particular as packaging for food. The multilayer films may be useful as shrinkable films, sealable
5 films, lidding films, wrapping films, and the like. In addition, the multilayer films may be further processed to form shrink bags, pouches, balloons, artificial turf, and the like.

The following examples are provided to describe the invention in further detail. These examples, which set forth a preferred mode presently contemplated for carrying out the invention, are intended to illustrate and not to limit the invention.

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EXAMPLES

Materials

PET: polyethylene terephthalate available commercially as Cumastretch FX from Dufor (Zevenaar, Netherlands).

15 PA: a blend of 90 weight % of nylon 6 with melting point of 220°C and a melt flow of 25 g/10min at 275°C with 5kg load, available commercially as Grivory F40 from EMS-Grivory (Sumter, SC, U.S.A.) and 10 weight % of Selar® PA 3426 amorphous nylon resin, available commercially from DuPont.

EVOH: ethylene vinyl alcohol available commercially as Soarnol™ AT4403 obtained
20 from Nippon Goshei.

PO-1: random copolypropylene, with a density of 0.900 g/cm³, MI of 5.5 g/10min at 230°C with 2.16kg load, melt point of 128°C and Vicat softening point of 103°C, available commercially from LyondelBasell as Adsyl 6C30F.

PO-2: same polymer blend as Sealant, below, without additives.

25 Tie-1: a thermoplastic adhesive composition as described herein, comprising 80 wt% of a copolymer of ethylene and methyl acrylate; 10 wt% of a copolymer of ethylene, iso-butyl acrylate and methacrylic acid, and 10 wt% of a copolymer of ethylene and methyl acrylate grafted with 2 wt% of maleic anhydride. The weight percentages of the ethylene copolymers are based on the total weight of the thermoplastic adhesive
30 composition, and the weight percentage of grafted maleic anhydride is based on the total weight of the grafted copolymer.

Tie-1b: a modified ethylene acrylate resin commercially available from DuPont under the trademark BYNEL® 22E780 adhesive resin.

Tie-2: an anhydride-modified linear low density polyethylene, available commercially from DuPont under the trademark BYNEL® 41E687 adhesive resin.

5 Sealant: 70 wt% of an ethylene-based 1-octene plastomer, produced in a solution polymerization process using a metallocene catalyst, and having a density of 0.902 g/cm³, MI of 3 g/10 min and melt point of 96°C, available commercially as Queo 0203 from Borealis (Vienna, Austria); and 30 wt% of a metallocene-catalyzed ethylene-hexene copolymer commercially available under the designation
10 Exceed™ 1018 from ExxonMobil Chemicals (Houston, TX, U.S.A.); with some additives, for example, slip or antiblock additives.

The physical properties of the materials used in the thermoplastic adhesive composition described herein (Tie-1) were measured. The physical properties of the other materials used in the Examples are as reported by their manufacturers.

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Methods

A coextruded multilayer film comprising the thermoplastic adhesive composition described herein (the Example) and a coextruded multilayer film comprising a known adhesive (the Comparative Example) were produced on a triple
20 bubble (3B) manufacturing line available from Kuhne Anlagenbau GmbH of Sankt Augustin, Germany, using the materials, thicknesses and temperatures set forth in Table 1, below, and the procedures described in Intl. Patent Appln. Publn. No. WO2007/099214. Layer 1 is the outside surface layer of the three tubular bubbles, layer 13 is the inside surface layer of the three tubular bubbles, and layers 2 through 12
25 are the interior layers of the multilayer film. When contiguously co-extruded layers of multilayer film structure comprise the same material, as did layers 3 through 6 of the Example and of the Comparative Example, the contiguously co-extruded layers appear to be a single layer in the final film structure.

Both coextruded multilayer films comprised an external layer of polyester at
30 layer 1 and a gas barrier triplet layer, PA/EVOH/PA, at layers 8, 9 and 10. Layers 2, 7 and 11 were adhesion layers. The outside surface of layer 2 was the delamination interface from which PET layer 1 was peeled in this experiment.

In the Example of the invention, adhesive layer 2 comprised Tie-1, a thermoplastic adhesive composition described herein. The film of the Comparative Example is identical to the film of the Example, except that in adhesive layer 2, the commercial product BYNEL® 22E780 adhesive resin (Tie-1b) was substituted for Tie-1. The commercial product was present in the same thickness, and it was extruded at the same temperature, as Tie-1 in the Example of the invention.

Table 1

Example Layer	Composition	Thickness (μm)	Extrusion Temperature
1	PET	5	270°C
2	Tie-1 or Tie-1b	2.5	220°C
3	PO-1	4.5	210°C
4	PO-1	4.5	210°C
5	PO-1	4.5	210°C
6	PO-1	4.5	210°C
7	Tie-2	3	220°C
8	PA	4	250°C
9	EVOH	2.5	200°C
10	PA	4	250°C
11	Tie-2	3	220°C
12	PO-2	4.5	220°C
13	Sealant	3.5	220°C

The bond strength between the PET layer 1 and the adhesion layer 2 (Tie-1 or Tie-1b) was measured according to the following method. After extrusion, the films of the Example and the Comparative Example were conditioned for at least 24h under ambient conditions, then cut into long strips in the machine direction having a width of 15 mm in the transverse direction. At one 15-mm end of the strips, Layer 1 was separated by hand from Layers 3 through 13. The ends of the separated portions of the two layers were affixed to a tensile testing machine, and the delamination was continued by mechanically peeling the two ends apart. Layer 1 and Layers 3 through 13 were at an angle of 180° to each other during the mechanical delamination, and the speed at which the two ends were separated was 100 mm/min. The force that was required to delaminate the films under these conditions was measured and is reported as the “peel adhesion” in units of Newtons/15 mm.

The peel adhesion in the Example (Tie-1) was about 3.49 N/15mm (95% confidence interval ± 0.20 N/15mm). The peel adhesion in the Comparative Example (Tie-1b) was about 2.25 N/15mm (95% confidence interval ± 0.26 N/15mm). These results reflected an increase of approximately 1.24 N/15mm, which represented an

improvement of about 55% in peel adhesion between PET layer 1 and adhesion layer 2, owing to the replacement of Tie-1b with Tie-1 in layer 2 of the coextruded multilayer films.

5 While certain of the preferred embodiments of this invention have been described and specifically exemplified above, it is not intended that the invention be limited to such embodiments. Various modifications may be made without departing from the scope and spirit of the invention, as set forth in the following claims.

CLAIMS

1. A thermoplastic adhesive composition comprising:
 - a. an ethylene acid copolymer comprising copolymerized residues of ethylene; copolymerized residues of an α,β -unsaturated carboxylic acid comprising four to eight carbon atoms; and optionally copolymerized residues of a derivative of an α,β -unsaturated carboxylic acid comprising four to eight carbon atoms, said derivatives selected from the group consisting of alkyl esters, wherein the alkyl group is branched or unbranched, and wherein the alkyl group comprises from 1 to 8 carbon atoms;
 - b. an ethylene alkyl (meth)acrylate copolymer comprising copolymerized residues of ethylene and copolymerized residues of an alkyl ester of (meth)acrylic acid, said alkyl group being linear or branched, and said alkyl group comprising from one to four carbon atoms; and
 - c. a functionalized ethylene copolymer selected from the group consisting of graft copolymers and direct copolymers;
 - i.) said graft copolymers comprising a polyolefin base and grafted residues of one or more grafting monomers; wherein said polyolefin base is selected from the group consisting of ethylene homopolymers and copolymers of ethylene with one or more of an α -olefin, vinyl acetate, or an alkyl (meth) acrylate; and wherein said one or more grafting monomers are selected from the group consisting of ethylenically unsaturated carboxylic acids and derivatives of the ethylenically unsaturated carboxylic acids selected from the group consisting of anhydrides; metal salts; esters, including monoesters and diesters; amides; imides; and
 - ii.) said direct copolymer comprising copolymerized residues of ethylene, copolymerized residues of a functionalizing comonomer selected from the group consisting of α,β -unsaturated dicarboxylic acids and derivatives of the α,β -unsaturated dicarboxylic acids, and optionally copolymerized residues of an additional comonomer selected from the group consisting of alkyl (meth)acrylates and vinyl acetate.

2. The thermoplastic adhesive composition of claim 1,
wherein the ethylene acid copolymer comprises up to about 30 wt% of the
copolymerized residues of the carboxylic acid; optionally up to about
5 40 wt% of the copolymerized residues of the derivative; and a
complementary amount of copolymerized residues of ethylene, based on
the total weight of the ethylene acid copolymer; or
wherein the copolymer of ethylene and alkyl (meth)acrylate comprises up
to about 40 wt% of the copolymerized residues of the alkyl (meth)acrylate
10 and a complementary amount of copolymerized residues of ethylene,
based on the total weight of the copolymer of ethylene and alkyl
(meth)acrylate; or
wherein the functionalized ethylene copolymer is the graft copolymer, and
the graft copolymer comprises up to about 10 wt% of the grafted
15 monomer(s) and a complementary amount of the polyolefin base, based on
the total weight of the graft copolymer; or
wherein the functionalized ethylene copolymer is the direct copolymer,
and the direct copolymer comprises from 0.01 to 10 wt% of the
copolymerized residues of the functionalizing comonomers; optionally up
20 to 40 wt% of the copolymerized residues of one or more additional
comonomers; and a complementary amount of copolymerized residues of
ethylene, based on the total weight of the direct copolymer.
3. The thermoplastic adhesive composition of claim 1 or claim 2, wherein the
25 ethylene acid copolymer comprises about 10 to about 20 wt% of the
copolymerized residues of the carboxylic acid, optionally up to about 40
wt% of the copolymerized residues of the derivative, and wherein the
carboxylic acid is acrylic acid or methacrylic acid; or
wherein the copolymer of ethylene and alkyl (meth)acrylate comprises
30 about 10 to about 40 wt% of copolymerized residues of alkyl
(meth)acrylate; or
wherein the graft copolymer comprises up to about 5 wt% of the grafted
comonomers and the grafted comonomers are selected from the group
consisting of acrylic acid, methacrylic acid, fumaric acid, maleic acid,

nadic acid, citraconic acid, and itaconic acid, and derivatives of these acids; or

wherein the functionalized ethylene copolymer is the direct copolymer, and the direct copolymer comprises from 0.1 to 10 wt% of the copolymerized residues of the functionalizing comonomers; and from 5 to 30 wt% of the copolymerized residues of one or more additional comonomers.

4. The thermoplastic adhesive composition of any preceding claim, wherein the ethylene acid copolymer comprises about 13 to about 17 wt% of the copolymerized residues of the carboxylic acid and wherein the carboxylic acid is acrylic acid; or

wherein the copolymer of ethylene and alkyl (meth)acrylate comprises about 10 to about 30 wt% of the copolymerized residues of the alkyl (meth)acrylate; or

wherein the graft copolymer comprises about 0.1 to about 4 wt% of the grafted monomers; the graft monomers are selected from the group consisting of maleic acid and maleic anhydride; and the polyolefin base is a copolymer of ethylene and an alkyl acrylate; or

wherein the functionalizing comonomers(s) are selected from the group consisting of maleic acid and maleic anhydride; the direct copolymer comprises from 0.1 to 5 wt% of the copolymerized residues of the functionalizing comonomers; the direct copolymer further comprises copolymerized residues of the one or more additional comonomer(s); and the one or more additional comonomer(s) are selected from the group consisting of alkyl acrylates.

5. The thermoplastic adhesive composition of any preceding claim, wherein the ethylene acid copolymer has a melt flow rate of about 1 to about 30 g/10 min; or

wherein the copolymer of ethylene and alkyl (meth)acrylate has a melt flow rate of about 0.5 to about 50 g/10 min; or

wherein the graft copolymer has a melt flow rate of about 1 to about 20 g/10 min; or

wherein the direct copolymer has a melt flow rate of about 1 to about 300 g/10 min;

said melt flow rates determined according to ASTM Method

No. D1238-13, at a temperature of 190°C, under a weight of 2.16 kg.

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6. The thermoplastic adhesive composition of any preceding claim, wherein the ethylene alkyl (meth)acrylate copolymer is tubular reactor-produced.

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7. The thermoplastic adhesive composition of any preceding claim, wherein the polyolefin base is an ethylene α -olefin copolymer that is linear or substantially linear.

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8. The thermoplastic adhesive composition of any preceding claim, wherein the direct copolymer comprises 5 to 30 wt% of copolymerized residues of an alkyl acrylate, 0.1 to 5 wt% of copolymerized residues of maleic anhydride, and a complementary amount of copolymerized residues of ethylene, based on the total weight of the direct copolymer.

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9. The thermoplastic adhesive composition of any preceding claim, comprising up to about 25 wt% of the ethylene acid copolymer; or from about 50 to about 95 wt% of the copolymer of ethylene and alkyl (meth)acrylate; or up to about 25 wt% of the functionalized ethylene copolymer, based on the total weight of the thermoplastic adhesive composition.

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10. The thermoplastic adhesive composition of any of claim 1 to claim 8, comprising from about 7 to about 23 wt% of the ethylene acid copolymer; or from about 65 to about 85 wt% of the copolymer of ethylene and alkyl (meth)acrylate; or from about 7 to about 23 wt% of the functionalized ethylene copolymer, based on the total weight of the thermoplastic adhesive composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/066170

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J123/08 C08L23/06 C08L51/06 B32B27/32
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09J C08L B32B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 053 457 A (LEE I-HWA [US]) 1 October 1991 (1991-10-01) cited in the application claims 1,9 example 23; table II column 1, line 5 - line 8 column 5, line 51 - line 54 column 5, line 67 - line 68 -----	1-10
A	US 7 767 311 B2 (DU PONT [US]) 3 August 2010 (2010-08-03) claims 1,14 tables 1-3 column 1, line 15 - line 21 column 4, line 20 - line 21 ----- -/-	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 March 2019

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

van Bergen, Marc

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/066170

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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