

Title of the Invention

Modified Polyolefin Composition and Laminated
Structure Using the Same

Background of the Invention5 Field of the Invention

The present invention relates to a modified
polyolefin composition and a laminated structure using
the same. More specifically, it relates to a modified
polyolefin composition capable of preventing the
10 occurrence of rib-like concaves and convexes (water
marks) in a peripheral direction of a tube at the time
of forming a tubular laminated structure by co-
extrusion and cooling, and a laminated structure in
which the occurrence of water marks is prevented by
15 using the same.

Prior Art

A laminate with a layer of polyamide or an
ethylene/vinyl alcohol copolymer as an intermediate
layer and layers of a composition of high-pressure-
20 processed low-density polyethylene and a non-
crystalline or low-crystalline ethylene/alpha-olefin
copolymer as outer layers have been known. However,
this laminate has a defect of a poor appearance, since
water marks occur on an outer layer thereof at the
25 process of water-cooling after the above composition
and the resins are co-extruded into a tubular form
laminate. It has another defect that the slippage of
the composition in a molten state in a mandrel is poor
to impair productivity.

30 Summary of the Invention

It is an object of the present invention to
provide a modified polyolefin composition.

It is another object of the present invention to
provide a modified polyolefin composition suitable for
35 an outer layer of a laminate, particularly an outer
layer of a laminate with a layer of polyamide or an

ethylene/vinyl alcohol copolymer as an intermediate layer.

It is still another object of the present invention to provide a modified polyolefin composition exhibiting an excellent adhesion to a polyamide or an
5 ethylene/vinyl alcohol copolymer and being free from water marks when used as an outer layer of a laminate.

It is still another object of the present invention to provide a modified polyolefin composition
10 which, in a molten state, shows an excellent slippage in a mandrel at the time of producing a laminate, namely, said modified polyolefin composition having an excellent productivity for the production of the laminate.

15 It is still another object of the present invention to provide a laminated structure using the above modified polyolefin composition.

Other objects and advantages of the present invention will be made apparent from the following
20 description.

The above objects and advantages of the present invention can be accomplished by a modified polyolefin composition which comprises (A) high-pressure-processed low-density polyethylene having a melt flow rate of 0.1
25 to 10 g/10 minutes and a density of 0.915 to 0.935 g/cm³, (B) an ethylene homopolymer and/or an ethylene/alpha-olefin copolymer having a melt flow rate of 0.1 to 30 g/10 minutes and a density of 0.910 to 0.965 g/cm³, which are substantially linear and are
30 produced by using a transition metal catalyst, and (C) a non-crystalline or low-crystalline ethylene/alpha-olefin copolymer having a melt flow rate of 0.1 to 10 g/10 minutes and a density of less than 0.900 g/cm³, in which an amount of each of the components (A), (B) and
35 (C) is respectively 50 to 70 weight %, 20 to 45 weight % and 5 to 30 weight % based on the total weight of

these components (A), (B) and (C), and at least a part of these components (A), (B) and (C) is modified with an unsaturated carboxylic acid or a derivative thereof.

Detailed Description of the Invention

5 The modified polyolefin composition of the present invention comprises components (A), (B) and (C) as described above, and at least a part of these components is graft-modified with an unsaturated carboxylic acid or a derivative thereof.

10 The component (A) is high-pressure-processed low-density polyethylene having a melt flow rate (measured at a temperature of 190°C under a load of 2.16 kg according to ASTM D1238) of 0.1 to 10 g/10 minutes and a density of 0.915 to 0.935 g/cm³. A preferable melt
15 flow rate thereof is 0.2 to 5 g/10 minutes and a preferable density thereof is 0.910 to 0.935 g/cm³.

 The component (B) is an ethylene polymer which includes an ethylene homopolymer and an ethylene/alpha-olefin copolymer having a melt flow rate (measured at a
20 temperature of 190°C under a load of 2.16 kg according to ASTM D1238) of 0.1 to 30 g/10 minutes and a density of 0.910 to 0.965 g/cm³, which is produced by using a transition metal catalyst such as a Ziegler catalyst. A preferable ethylene/alpha-olefin copolymer as the
25 component (B) is substantially linear random copolymer of ethylene and an alpha-olefin with carbon atoms of 3 to 20. A preferable alpha-olefin is an alpha-olefin with carbon atoms of 4 to 10. Examples of an alpha-olefin preferably include propylene, 1-butene, 1-
30 hexene, 4-methyl-1-pentene, 1-octene and 1-decene. particularly preferable alpha-olefins are 1-butene and 4-methyl-1-pentene. Preferable examples of an ethylene/alpha-olefin copolymer produced with a transition metal catalyst include an ethylene/propylene
35 random copolymer, an ethylene/1-butene random copolymer and an ethylene/4-methyl-1-pentene random copolymer.

An ethylene polymer as the component (B) contains recurring units derived from ethylene of preferably 100 to 80 % by weight, more preferably 100 to 90 % by weight.

5 The component (B) may be a combination of an ethylene homopolymer and an ethylene/alpha-olefin copolymer. For example, the component (B) may be a combination of an ethylene homopolymer of 0.5 to 40 parts by weight and an ethylene/alpha-olefin copolymer
10 of 60 to 99.5 parts by weight, based on 100 parts by weight of the total amount of both polymers.

The melt flow rate of an ethylene polymer as the component (B) is preferably 0.2 to 5 g/10 minutes. The density thereof is preferably 0.920 to 0.950 g/cm³,
15 more preferably 0.930 to 0.950 g/cm³.

The component (C) is a non-crystalline or low-crystalline ethylene/alpha-olefin copolymer having a melt flow rate (measured at a temperature of 190°C under a load of 2.16 kg according to ASTM D1238) of 0.1
20 to 10 g/10 minutes and a density of less than 0.900 g/cm³.

The ethylene/alpha-olefin copolymer (C) is preferably a random copolymer of ethylene and an alpha-olefin with carbon atoms of 3 to 20. As an alpha-
25 olefin can be mentioned those described above regarding the ethylene/alpha-olefin copolymer as the component (B). Of them, alpha-olefins with carbon atoms of 3 or 4 are preferred. Preferable examples of the ethylene/alpha-olefin copolymer (C) include an
30 ethylene/propylene random copolymer and an ethylene/1-butene random copolymer.

The ethylene/alpha-olefin copolymer (C) contains recurring units derived from ethylene of preferably 50 to 90 mol %, more preferably 60 to 80 mol %.

35 The melt flow rate of the ethylene/alpha-olefin copolymer (C) is preferably 0.1 to 10 g/10 minutes and

the density thereof is preferably 0.85 to 0.89 g/cm³.

The ethylene/alpha-olefin copolymer (C) having such physical properties is generally a non-crystalline copolymer or a low-crystalline copolymer having a
5 crystallinity of less than 40 %, measured by the X-ray method.

The modified polyolefin composition of the present invention contains the component (A) of 50 to 70 % by weight, the component (B) of 20 to 45 % by weight and
10 the component (C) of 5 to 30 % by weight based on the total weight of the components (A), (B) and (C). Preferably, the composition contains the component (A) of 52 to 60 % by weight, the component (B) of 25 to 40 % by weight and the component (C) of 10 to 20 % by
15 weight.

In the composition of the present invention, at least a part of the components (A), (B) and (C) is graft-modified with an unsaturated carboxylic acid or a derivative thereof. A part or the whole of one
20 component of the components (A), (B) and (C) may be graft-modified, or a part or the whole of a mixture of plural components may be graft-modified. In other words, graft-modification may be performed to one component or a mixture of components. It is preferable
25 that the component (B) is graft-modified.

Examples of an unsaturated carboxylic acid and a derivative thereof include unsaturated carboxylic acids such as acrylic acid, maleic acid, fumaric acid, tetrahydrophthalic acid, itaconic acid, citraconic
30 acid, crotonic acid, isocrotonic acid and Nadic acid (endocis-bicyclo[2,2,1]hept-5-en-2,3-dicarboxylic acid) and derivatives thereof such as acid halides, amides, imides, anhydrides and esters.

Specific examples of such derivatives include
35 malenyl anhydride, monomethyl maleate, dimethyl maleate and glycidyl maleate.

Of them, an unsaturated dicarboxylic acid or an anhydride thereof is preferable, and particularly maleic acid, nadic acid and anhydrides thereof are used preferably. They are used alone or in combination of
5 two or more. A graft ratio is preferably 0.001 to 5 % by weight, more preferably 0.01 to 3 % by weight.

In order to perform the graft reaction, conventionally known various methods may be employed. For example, there can be mentioned a method of
10 performing the graft reaction by melting the polymer and adding the graft monomer (the unsaturated carboxylic acid or the derivative thereof) therein and a method of performing the graft reaction by dissolving the polymer in a solvent to form a solution and adding
15 the graft monomer therein. In either case, it is preferable to perform a graft reaction in the presence of a radical initiator in order to perform graft reaction efficiently.

The graft reaction is performed generally at a
20 temperature of 60 to 350°C. A radical initiator is used generally in an amount of 0.001 to 1 part by weight based on 100 parts by weight of a polymer.

As a radical initiator may be used organic peroxides and organic polyester including benzoyl
25 peroxide, dichlorobenzoyl peroxide, dicumyl peroxide, di-tert-butyl peroxide, 2,5-dimethyl-2,5-di(peroxide benzoate)hexine-3, 1,4-bis(tert-butylperoxyisopropyl)benzene, lauroyl peroxide, tert-butyl peracetate, 2,5-dimethyl-2,5-di(tert-
30 butylperoxy)hexine-3, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, tert-butylperbenzoate, tert-butylperphenyl acetate, tert-butyl perisobutylate, tert-butylper-sec-octoate, tert-butyl perpivalate, cumyl perpivalate and tert-butyl perdiethyl acetate,
35 and other azo compounds including azobisisobutyronitrile and dimethyl azoisobutylate.

Of them, dialkyl peroxides such as dicumyl peroxide, di-tert-butyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane-3, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane and 1,4-bis(tert-butylperoxyisopropyl)benzene are preferable.

For obtaining the modified polyolefin composition of the present invention, the graft reaction can be performed for the mixture of the components (A), (B) and (C). Alternatively, a part or whole of one or two components of the components (A), (B) and (C) is graft-modified and then the obtained modified product is melt-kneaded together with unmodified components to obtain the composition of the present invention. A method comprising graft-modifying the component (B) and then melt-mixing the obtained modified product together with the component (A) and the component (C) is preferable for obtaining said composition.

A method of melt-kneading a modified component (A), (B) or (C) with unmodified component(s) by means of an extruder is preferably employed industrially.

Here, a graft ratio is defined to be a weight ratio (%) of a grafted unsaturated carboxylic acid or derivative thereof based on the total weight of the components (A), (B) and (C) before grafting.

The melt flow rate of the thus obtained modified polyolefin composition of the present invention is preferably 0.1 to 5 g/minute.

The modified polyolefin composition of the present invention is used suitably as an outer layer of a laminated structure, particularly a laminated structure with a polyamide or an ethylene/vinyl alcohol copolymer as an intermediate layer.

Hence, the present invention provides a laminated structure comprising a composition layer composed of the modified polyolefin composition according to the present invention (hereinafter, the composition layer

composed of the modified polyolefin composition according to the present invention is referred to simply as "the composition layer") and a resin layer existing on at least one side of the composition layer.

5 As a resin of the resin layer constituting the laminated structure can be used various thermoplastic resins such as polyolefins, polyesters, polyamides and an ethylene/vinyl alcohol copolymer. Of them, polyamides and an ethylene/vinyl alcohol copolymer are
10 used preferably.

As polyamides, for example, nylon 6, nylon 66 and MXD nylon (metaxylylene diamine copolymer polyamide) are used.

15 An ethylene/vinyl alcohol copolymer preferably contains the unit derived from ethylene of 20 to 50 mol %, preferably 25 to 48 mol %.

They can be produced by saponifying a corresponding ethylene/vinyl acetate copolymer by an ordinary procedure.

20 In the laminated structure of the present invention, the above resin layer existing on at least one side of the composition layer preferably comprises a resin selected from polyamides and an ethylene/vinyl alcohol copolymer.

25 Further, the laminated structure of the present invention preferably has the composition layer, the above resin layer and the composition layer in this order.

30 A product free from water marks caused at a cooling step of a process for producing the laminated structure can be obtained by constituting an outermost layer of the laminated structure with the composition layer.

35 The laminated structure according to the present invention can be produced by melting the modified polyolefin composition and the resin and laminating

them in a molten state.

The laminated structure can be formed into a desired form by extrusion molding, cast molding, inflation molding and the like. The laminated structure of the present invention can be preferably formed into a tubular form by co-extrusion. The laminated structure formed into the tubular form is used to process it, for example, into a food-wrapping film, a tubular vessel for cosmetics and the like.

10 Examples

The present invention will be described more specifically by referring to Examples. However, the present invention is limited to these Examples by no means.

15 Example 1

The layers with the following constitutions were co-extruded under the following conditions to form 3-layer tubes.

Outer layer and inner layer

- 20 High-pressure-processed low density polyethylene (HPLDPE-1) of 52 % by weight, having a melt flow rate of 4 and a density of 0.918 g/cm^3 , as a component (A),
an ethylene/propylene copolymer (LLDPE-1) of 25 % by weight, produced by using a transition metal
25 catalyst and having a melt flow rate of 1 and a density of 0.953 g/cm^3 , as a component (B-1),
a graft modified polyethylene (MAH-PE) of 8 % by weight, which was obtained by grafting a substantially linear ethylene homopolymer produced by using a
30 transition metal catalyst with maleic anhydride 2 % by weight of maleic anhydride and has a melt-flow rate of 4 and a density of 0.965 g/cm^3 , as a component (B-2),
and
an ethylene/1-butene copolymer (EBR-1) of 15
35 weight %, having a melt flow rate of 3.5, a density of 0.885 g/cm^3 and a crystallinity of less than 5 %, as a

component (C)

were melt-kneaded at 200°C by means of a uniaxial extruder to obtain a modified polyolefin composition. The melt flow rate of the composition was 1.7 and the
5 density thereof was 0.921 g/cm³. Thus obtained modified polyolefin composition was co-extruded by an extruder having a screw with a diameter of 40 mm and an effective length of 1000 mm.

Intermediate layer

10 Eval EP-F (trade mark, melt-flow rate:1.3) manufactured by Kuraray Co., Ltd. as an ethylene/vinyl alcohol copolymer (hereinafter referred to as EVOH) was co-extruded at 225°C by an extruder having a screw with a diameter of 30 mm and an effective length of 750 mm.

15 The temperature of the dice was 220°C, and each co-extruded resin was taken off at a rate of 5 m/minute, water-cooled in a water tank 50 cm behind the dice and formed into a tube. Regarding the thickness of each layer, it was made as an outer layer/an
20 intermediate layer/an inner layer = 150/50/250 µm. The adhesion strength between the outer layer and the intermediate layer of the tube, the dynamic coefficient of friction and the existence of water marks are shown in Table 1.

25 The adhesion strength is measured by 180° peeling method.

The dynamic coefficient of friction is a value measured by cutting the tube open, mounting a load of 200 g thereon and pulling it on a stainless steel plate
30 at a rate of 50 mm/minute.

The existence of water marks was evaluated by observing the outer appearance of the tube after water-cooling visually to observe the occurrence of rib-like concaves and convexes (water marks) in a peripheral
35 direction of the tube. In Table 1, O means no occurrence of water marks and X means occurrence

thereof.

Examples 2-4

The same procedure as in Example 1 was performed except that the composition of a modified polyolefin composition constituting an outer layer and an inner layer was changed to the composition shown in Table 1 to obtain the results shown in Table 1.

Comparative Examples 1-2

The same procedure as in Example 1 was performed except that the composition of a modified polyolefin composition constituting outer layer and inner layer was changed to the composition shown in Table 1 to obtain the results shown in Table 1.

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 1	Comp. Ex. 2
Composition of inner layer and outer layer Composition (weight parts)	HPLDPE-1 52 LLDPE-1 25 MAH-PE 8 EBR-1 15	HPLDPE-2 52 LLDPE-2 25 MAH-PE 8 EPR-1 15	HPLDPE-3 52 LLDPE-2 25 MAH-PE 5 EBR-1 15	HPLDPE-4 52 LLDPE-2 25 MAH-PE 8 EPR-1 15	HPLDPE-2 77 MAH-PE 8 EPR-1 15	HPLDPE-3 80 MAH-PE 5 EBR-1 15
Melt flow rate (g/10 min)	1.7	1.9	1.1	2.3	2.6	1.3
Density (g/cm ³)	0.921	0.923	0.919	0.923	0.923	0.918
Intermediate layer	EVOH	EVOH	EVOH	EVOH	EVOH	EVOH
Dynamic coefficient of friction	0.52	0.65	0.60	0.65	0.80	1.00
Adhesion strength between outer and intermediate layers (g/15 mm)	990	1000	400	860	660	450
Water marks	○	○	○	○	X	X

Abbreviations in Table 1 represent the following:

5	HPLDPE-1:	High-pressure-processed low-density polyethylene (melt flow rate: 4, density: 0.918 g/cm ³)
	HPLDPE-2:	High-pressure-processed low-density polyethylene (melt flow rate: 2.5, density: 0.932 g/cm ³)
10	HPLDPE-3:	High-pressure-processed low-density polyethylene (melt flow rate: 3, density: 0.927 g/cm ³)
	HPLDPE-4:	High-pressure-processed low-density polyethylene (melt flow rate: 1, density: 0.918 g/cm ³)
15	LLDPE-1:	Substantially linear ethylene/propylene copolymer (melt flow rate: 1, density: 0.953 g/cm ³)
20	LLDPE-2:	Substantially linear ethylene/butene-1 copolymer (melt flow rate: 1, density: 0.935 g/cm ³)
25	MAH-PE:	Modified ethylene homopolymer with 2 % by weight of maleic anhydride grafted, being substantially linear (melt flow rate: 4, density: 0.965 g/cm ³)
30	EBR-1:	Ethylene/butene-1 copolymer (melt flow rate: 3.5, density: 0.885 g/cm ³)
	EPR-2:	Ethylene/propylene copolymer (melt flow rate: 3, density: 0.870 g/cm ³)

35 Example 5

Amiran (trade mark) CM1021XF manufactured by

Toray Co., Ltd. as polyamide was extruded at 250°C by an extruder having a screw with a diameter of 30 mm and an effective length of 750 mm in the same manner as in Example 1.

5 The temperature of the dice was 250°C, and the co-extruded resin was taken off at a rate of 5 m/minute, water-cooled in a water tank 50 cm behind the dice and formed into a tube. Regarding the thickness of each layer, it was made as an outer layer/an
10 intermediate layer/an inner layer =150/50/250 μ m. The adhesion strength between the outer layer and the intermediate layer of the tube, the dynamic coefficient of friction and the existence of water marks were shown in Table 2.

15 Example 6 and Comparative Examples 3-4

 The same procedure as in Example 5 was performed except that the composition of a modified polyolefin composition constituting an outer layer and an inner layer was changed to the composition shown in
20 Table 2 and evaluation was performed. The results are shown in Table 2.

Table 2

	Ex. 5	Ex. 6	Comp. Ex. 3	Comp. Ex. 4
Composition of inner layer and outer layer				
Composition (weight parts)	HPLDPE-1 52 LLDPE-1 25 MAH-PE 8 EBR-1 15	HPLDPE-2 52 LLDPE-2 25 MAH-PE 8 EPR-1 15	HPLDPE-2 77 MAH-PE 8 EPR-1 15	HPLDPE-3 80 MAH-PE 5 EBR-1 15
Melt flow rate (g/10 min)	1.7	1.9	2.6	1.3
Density (g/cm ³)	0.921	0.923	0.923	0.918
Intermediate layer	Polyamide	Polyamide	Polyamide	Polyamide
Dynamic coefficient of friction	0.58	0.62	0.85	1.05
Adhesion strength between outer and intermediate layers (g/15 mm)	Incapable of peeling	Incapable of peeling	Incapable of peeling	Incapable of peeling
Water marks	○	○	X	X

Abbreviations in Table 2 represent the following:

- HPLDPE-1: High-pressure-processed low-density polyethylene (melt flow rate: 4, density: 0.918 g/cm³)
- 5 HPLDPE-2: High-pressure-processed low-density polyethylene (melt flow rate: 2.5, density: 0.932 g/cm³)
- HPLDPE-3: High-pressure-processed low-density polyethylene (melt flow rate: 3, density: 0.927 g/cm³)
- 10 LLDPE-1: Substantially linear ethylene/propylene copolymer (melt flow rate: 1, density: 0.953 g/cm³)
- 15 LLDPE-2: Substantially linear ethylene/butene-1 copolymer (melt flow rate: 1, density: 0.935 g/cm³)
- MAH-PE: Modified ethylene homopolymer with 2 % by weight of maleic anhydride grafted, being substantially linear (melt flow rate: 4, density: 0.965 g/cm³)
- 20 EBR-1: Ethylene/butene-1 copolymer (melt flow rate: 3.5, density: 0.885 g/cm³)
- 25 EPR-2: Ethylene/propylene copolymer (melt flow rate: 3, density: 0.870 g/cm³)
- 30



What is claimed is:

1. A modified polyolefin composition which comprises
(A) high-pressure-processed low-density polyethylene
having a melt flow rate of 0.1 to 10 g/10 minutes and a
5 density of 0.915 to 0.935 g/cm³, (B) an ethylene
homopolymer and/or ethylene/alpha-olefin copolymer
having a melt flow rate of 0.1 to 30 g/10 minutes and a
density of 0.910 to 0.965 g/cm³, which are
substantially linear and are produced by using a
10 transition metal catalyst and (C) a non-crystalline or
low-crystalline ethylene/alpha-olefin copolymer having
a melt flow rate of 0.1 to 10 g/10 minutes and a
density of less than 0.900 g/cm³, in which an amount of
each of the components (A), (B) and (C) is respectively
15 50 to 70 % by weight, 20 to 45 % by weight and 5 to 30
% by weight based on the total weight of these
components (A), (B) and (C), and at least a part of the
components (A), (B) and (C) is graft-modified with an
unsaturated carboxylic acid or a derivative thereof.
- 20 2. A modified polyolefin composition according to
Claim 1, in which the component (B) is a combination of
the ethylene homopolymer and the ethylene/alpha-olefin
copolymer.
3. A modified polyolefin composition according to
25 claim 2, in which the ethylene homopolymer is graft-
modified.
4. A modified polyolefin composition according to
Claim 1, in which a graft ratio of the unsaturated
carboxylic acid or the derivative thereof is 0.001 to 5
30 % by weight based on the total weight of the component
(A), (B) and (C).
5. A laminated structure comprising a composition
layer composed of the modified polyolefin composition
of Claim 1 and a resin layer existing on at least one
35 side of the composition layer.
6. A laminated structure according to Claim 5, in



which said resin layer existing on at least one side of the composition layer is a layer of a resin selected from a polyamide and an ethylene/vinyl alcohol copolymer.

- 5 7. A laminated structure according to Claim 5, in which the composition layer, the resin layer and the composition layer are laminated in this order.
8. A laminated structure according to Claim 5, which has a tubular form.