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(71) Applicant(s):

FLEXOPACK S.A.

Thessi Tzima

Greece

(72) Inventor(s):

DIMITRIS GKINOSATIS

(74) Agent and/or Address for Service:

FRKelly

27 Clyde Road

Ballsbridge

Dublin 4

Ireland

(54) **Fibc liner film**

(57) The invention relates to plastic film preferably with a thickness of 50 to 300 microns, comprising a polyolefin homopolymer or copolymer, a polyether copolymer having a melting point between 100°C and 120°C and a layer comprising oxygen barrier polymer.

FIBC LINER FILM

The invention relates to plastic film preferably with a thickness of 50 to 300 microns, comprising a polyolefin homopolymer or copolymer, a polyether copolymer having a melting point between 100°C and 120°C and a layer comprising oxygen barrier polymer.

BACKGROUND

Plastic containers have been increasingly used in packaging applications, such as “food packaging”. A typical plastic container often used for bulk packaging of food (e.g. powdery food, coffee, cocoa, nuts) is called FIBC (= flexible intermediate bulk container). This type of container often is a woven polyethylene or polypropylene.

In the inside or outside of the woven material, another plastic liner is often used. This liner is a monolayer or a multilayer and comprises polymer materials. There are different types of adherence of this liner to the outer woven liner as shown e.g. in US 6,374,579.

In the case of a multilayer, the different layers offer different advantages to the final applications. The inside layer (= the layer coming into direct contact with the food packed) is often formulated to allow very good sealing, thus protecting from the existence of leakers that would be detrimental for the packed product. Other layers may comprise abuse resistant polymers to increase the mechanical strength of the material.

In case of oxygen sensitive food materials, at least one layer of the multilayer construction comprises material which is impermeable to oxygen. As it is well known in the art, such materials are e.g. polyamides, PVDC or EVOH.

Often the multilayer film is in “gusseted tube” configuration. The reason is that this configuration is more practical for bulk filling, transport and unloading versus a simple tube.

Gussets are produced in line with the process by the use of two “pleating constructions” (often wooden or metal boards) which the film follows. As these multilayer tube materials are often produced with the “hot blown film” method which involves rotation of the collapsing frame-nip roll section, a common problem is that creases are present continuously or periodically following the rotation and this increases the scrap and lowers the efficiency of

the operation. There are cases where the creases are so often that the tubular film cannot be processed into a gusseted tube.

It is generally known in the art that less stiff polymers e.g. LDPE have better gussetability versus stiffer ones like HDPE. It is believed that the material must be softer and more pliable in order to form efficiently a gusset during the production process. Barrier materials with high oxygen barrier properties such as EVOH or polyamide make the gusseting process even more difficult as they are usually stiffer than polyolefins.

Patent application EP 3 216 599 A1 teaches a way to improve gussetability by using a polyether copolymer (with polyamide or polyolefins) in blend with polyolefins in at least one layer of the film. This invention has the drawback that sealing temperatures start from 140°C to 160°C i.e. in conditions higher than pure polyolefins such as polyethylene. There is a need to move the sealing temperature "window" to lower temperatures e.g. down to 120°C in order to produce liners at same or similar conditions with normal polyethylene non-barrier liners.

There is further a need to improve the gussetability of the plastic structure ie to find materials pliable enough and with enough bubble stability to produce gussets with no creases in the commonly used thickness range of 50-300 microns without sacrificing the oxygen barrier properties of the plastic film. There is also a need to combine this improvement in gussetability with the above requirements in sealing at low temperatures.

SUMMARY OF THE INVENTION

It has been unexpectedly found that the addition of polyether copolymers with melting point of 100°C to 120°C in blends with polyolefins improve very much the gussetability of oxygen barrier plastic films and at the same time lower the seal initiation temperature of the film to 120°C.

According to the invention a very suitable film for the FIBC liner has preferably an average thickness of 50 to 300, more preferably an average thickness of 60 to 150, most preferably an average thickness of 60 to 130 microns and comprises

*a polyolefin homopolymer or copolymer

*a polyether copolymer having a melting point in the range of 100°C to 120°C,

* an oxygen barrier material such as EVOH, polyamide or PVDC

Further preferred embodiments of the invention will be explained in the detailed description of the invention.

DEFINITIONS

In this application the following definitions are used:

The term “gusset” is interpreted as well known in the art. That is a plastic tubular film having a partial 4-fold configuration.

The term “film” refers to a flat or tubular flexible structure of thermoplastic material.

The term “heat shrinkable” refers to a film that shrinks at least 10% in at least one of the longitudinal and transverse directions when heated at 90°C for 4 seconds. The shrinkability is measured according to ASTM 2732.

The phrase “longitudinal direction” or “machine direction” herein abbreviated “MD” refers to a direction along the length of the film.

The phrase “outer layer” refers to the film layer which comes in immediate contact with the outside environment (atmosphere).

The phrase “inner layer” refers to the film layer that comes in direct contact with the product packed. This is also called “sealing layer” as this layer must be hermetically sealed in order to protect the product from ingress of air.

The phrase “intermediate layer” refers to any layer of the film that is neither outer nor inner layer. A film may comprise more than one intermediate layers.

As used herein, the term “homopolymer” refers to a polymer resulting from polymerization of a single monomer.

As used herein, the term “copolymer” refers to a polymer resulting from polymerization of at least two different polymers.

As used herein, the term “polymer” includes both above types.

As used herein, the term “polyolefin” includes all the polymers produced by polymerization of olefins. Polyethylene, polypropylene, polybutylene and other products are included in this general category.

As used herein the term “polyethylene” identifies polymers consisting essentially of the ethylene repeating unit. The ones that have a density more than 0.940 are called high density polyethylene (HDPE), the ones that have less than 0.940 are low density polyethylene (LDPE).

As used herein the phrase “ethylene alpha olefin copolymer” refers to polymers like linear low-density polyethylene (LLDPE), medium density polyethylene (MDPE), very low density polyethylene (VLDPE), ultra-low density polyethylene (ULDPE), metallocene catalysed polymers and polyethylene plastomers and elastomers.

In these cases, the alpha olefin can be propene, butene, hexene, octene etc as known in the art.

As used herein the term “homogeneous ethylene alpha olefin copolymers” refer to ethylene alpha olefin copolymers having a molecular weight distribution MWD (M_w/M_n) of less than 2.7 as measured by GPC. Typical examples of these polymers are AFFINITY from DOW or Exact from Exxon.

As used herein the phrase “styrene polymers” refers to styrene homopolymer such as polystyrene and to styrene copolymers such as styrene-butadiene copolymers, styrene-butadiene-styrene copolymers, styrene-isoprene-styrene copolymers, styrene-ethylene-butadiene-styrene copolymers, ethylene-styrene copolymers and the like.

As used herein the phrase “ethylene methacrylate copolymers” refers to copolymers of ethylene and methacrylate monomer. The monomer content is less than 40% by weight. Abbreviation used is EMA.

As used herein the phrase “ethylene vinyl acetate copolymer” refers to copolymers of ethylene and vinyl acetate. Abbreviation used is EVA.

As used herein the term "oxygen barrier polymer" refers to polymers that do not allow the ingress of oxygen in packs. Typical materials are polyamide, EVOH or PVDC.

As used herein, the term EVOH refers to saponified products of ethylene vinyl ester copolymers. The ethylene content is typically in the range of 25 to 50% per mol.

As used herein the term PVDC refers to a vinylidene chloride copolymer wherein a major amount of the copolymer comprises vinylidene chloride and a minor amount of the copolymer comprises one or more monomers such as vinyl chloride and/or alkyl acrylates and methacrylates.

As used herein the term polyamide refers to homopolymers and copolymers that include amide linkages as well known in the art.

As used herein the term "ionomer" refers to ethylene-acid copolymers which have been neutralized by metals such as sodium, zinc, lithium or others.

The acid used is usually methacrylic or acrylic acid.

As used herein, the term "ethylene acid copolymer" refers to copolymers of ethylene with acid, most usually methacrylic or acrylic acid.

As used herein, the term "polyester" includes crystalline polymers, amorphous polymers and polyester elastomers. Common polyesters are crystalline PET (polyethylene terephthalate), amorphous PET, PETG (glycol modified polyethylene terephthalate), PBT (polybutylene terephthalate), PTT (polytrimethylene terephthalate), PBN (polybutylene naphthalate), PEN (polyethylene naphthalate), polyester-ether block copolymers and polyester-ester block copolymers of hard and soft blocks.

Other polyester materials are also included in the above definition.

As used herein the term "polybutylene" refers to butene-1 homopolymers and copolymers. Useful copolymers comprise ethylene mer units. Ethylene content should be generally less than 50% by weight.

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All measurement methods mentioned herein are readily available for the skilled person. For example, they can be obtained from the American National Standards Institute at: www.webstore.ansi.org

All percentages used are per weight unless stated otherwise.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a film comprising

*a polyolefin homopolymer or copolymer

*a polyether copolymer having melting point in the range of 100°C to 120°C

*an oxygen barrier material.

In a preferred embodiment, the film is in the form of gusseted tube.

In a further preferred embodiment, the average thickness of the film is in the range 50-300 microns, preferably 60-150 microns, more preferably 60-130 microns.

In a further preferred embodiment, the polyolefin homopolymer or copolymer is an ethylene alpha olefin copolymer. In a further preferred embodiment, the alpha olefin is butene, hexene or octene. In a further preferred embodiment, the ethylene alpha olefin copolymers are produced with metallocene catalysts.

FILM CONSTRUCTION

Preferably the film comprises 5 to 15 layers, more preferably 7 to 12 layers.

A typical example of the film construction in 7-layer mode is

Outer layer/intermediate layer/tie layer/barrier layer/tie layer/intermediate layer/inner layer

The film is preferably produced by the hot blown film method and is not heat shrinkable.

Barrier layer(s)

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The film in a preferable embodiment contains high oxygen barrier materials so that it protects the components of the pack from the detrimental effect of oxygen ingress. EVOH is a preferred option but also polyamide and PVDC are viable alternatives. The EVOH comprises preferably 24% to 50% ethylene per mol, more preferably 27% to 48%.

In another preferred embodiment of the invention, the barrier polymer is polyamide. Most suitable polyamides are polyamide 6 and copolymer 6/66 or 6/12.

Intermediate layer(s)

Preferably, the intermediate layers comprise different polyolefins. Preferred polyolefins are ethylene alpha olefin copolymers, where alpha olefin is preferably butene, hexene or octene.

In a preferred embodiment the ethylene alpha olefin copolymers are random copolymers with densities from 0.870 g/cm³ up to 0.960 g/cm³. In a further preferred embodiment, the molecular weight distribution MWD (M_w/M_n) as measured by GPC of the ethylene alpha olefin copolymers is less than 10, preferably less than 5, preferably less than 3.

Tie layer(s)

As well known in the art, there is no natural adhesion between polyolefins and oxygen barrier polymers such as EVOH.

Suitable materials for the tie layer process include maleic anhydride modified EVA, maleic anhydride modified polyethylene, maleic anhydride modified EMA, maleic anhydride modified elastomer, partially saponified EVA copolymer and polyurethane elastomer.

In the tie layers also polyamides can be used, given the strong natural adhesion between polyamide and EVOH. Preferred polyamides are polyamide 6, polyamide 6/66 and polyamide 6/12.

Outer layer

The outer layer of the film preferably comprises ethylene alpha olefin copolymers and/or low-density polyethylene (LDPE) produced by Ziegler Natta or metallocene catalyst.

Polypropylene, ethylene vinyl acetate, ethylene methyl acrylate, ethylene butyl acrylate, ionomer, polyester and polyamide is also possible.

Inner layer

The inner layer of the film would be able to seal the film to itself to secure that no leakers and oxygen influx is allowed. This could be detrimental to the product packed.

Suitable materials for the inner layer include different polyolefins, preferably ethylene alpha olefin copolymers, low density polyethylene, polypropylene, ethylene vinyl acetate, ethylene methyl acrylate, ionomer, ethylene butyl acrylate and the like.

In general, the above layers may comprise further well known in the art additives such as antiblock, slip, antifog, polymer processing enhancers and others.

Polyether copolymers

We have unexpectedly noticed that by adding polyether copolymers having a melting point of 100°C to 120°C in the inner layer, the seal initiation temperature of the film drops to 120°C while the gussetability of the film remains very good. The film is nicely transformed inline to a gusseted tube without any creasing during the whole rotation of the collapsing frame. Preferably, the polyether copolymers having a melting point of 100°C to 120°C are added in the inner layer, in an amount of 5% to 20% by weight.

Preferred polyether copolymers are copolymers with polyolefins, polyamides or polyester. A typical example of a polyether copolymer useful for the invention is Pelestat LM230 from Sanyo Chemical.

In a preferred embodiment the melting points of the polyether copolymers are in the range 100°C to 120°C, preferably 110°C to 120°C. If the melting temperature is lower the gussetability is compromised by the higher friction due to polymer tackiness while if the melting temperatures are higher the sealing initiation temperature increases.

The preferred melt flow index (MFI) of the polyether copolymer is more than 12 at 190°C and 21.18 N measured according to ASTM D 1238.

SEAL INITIATION TEMPERATURE

This term as used in the present application is defined as the lower sealing temperature which allows the average sealing strength (measured according to ASTM F88) to be at least 25N/15mm seal width when the sealing time is 2 seconds, sealing pressure is 4bars and the sealing station is impulse type. Films of the present invention have seal initiation temperature less than 130°C, preferably less than 125°C, preferable less than 120°C, preferably less than 115°C.

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MELTING POINT OF POLYETHER COPOLYMER

The melting point of the polyether copolymer is measured by DSC (=differential scanning calorimetry) as well known in the art. The polyether copolymer used in the present invention has a melting point between 100°C and 120°C.

The preferred method for producing the film of the present invention is how blown film as well known in the art.

EXMAPLES

EXAMPLE 1

From a commercial hot blown film line we produced the following film

- *Outer layer, thickness 30 microns
- *Intermediate layer 1, thickness 10 microns
- *Tie layer 1, thickness 8 microns
- *EVOH 38%, thickness 8 microns
- *Tie layer 2, thickness 8 microns
- *Intermediate layer 2, thickness 20 microns
- *Inner layer, thickness 12 microns.

Outer layer was a blend of

89% LDPE+ 10% polyether copolymer+ 1% slip antiblock masterbatch.

LDPE density was 0.923 while MFI was 0.75 under 190C/2.16 kilos

Intermediate layer 1 was a blend of

60% ethylene hexene copolymer+ 40% LDPE

The density of ethylene hexene copolymer was 0.919 while MFI was 1 under 190°C/2.16 kilos

LDPE was same as used in the outer layer.

Tie layer 1 was maleic anhydride LLDPE based copolymer

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Tie layer 2 was similar to tie layer 1

Intermediate layer 2 was exactly the same as intermediate layer 1.

Inner layer was a blend of

89% metallocene LLDPE +10% polyether copolymer+ 1% slip antiblock masterbatch

Metallocene LLDPE had a density of 0.918 while MFI was 1 under 190°C/2.16 kilos

Polyether copolymer used was Pelestat LM230 from Sanyo Chemical.

EXAMPLE 2

In the case of example 2 the LDPE used in the outer layer was replaced by the ethylene hexene copolymer used in intermediate layer 1.

EXAMPLE 3

In this example, the EVOH 38% was replaced by 32% which is stiffer and thought to be more difficult to form gusset.

COMPARATIVE EXAMPLE

The comparative example was like example 1 but with the polyether copolymer removed and replaced by MV PEBAX 1074 SA01. This material has a melting point of 158°C as measured by differential scanning calorimetry (DSC).

EXAMINING SYSTEM

On the tower of the blown film line two gusset boards were mounted as known in the art. Each example structure ran in production for 2 hours and the number of creases was monitored. As the creases tend to come along in timely intervals, we recorded "creasing instances", meaning we recorded any incident when more than 3 creases passed from the nip section of the blown film line.

The rotation speed was kept constant during all experiments.

RESULTS

Examples 1 and 2 recorded 2 instances while example 3 recorded 3.

The comparative example recorded 2 instances.

Therefore, the invention keeps the good gussetability of the prior art.

SEAL INITIATION.

Test of the seal initiation was done in a Toss sealing machine, keeping the sealing time at 2 seconds and seal pressure at 4 bars. Sealing was done inner side to inner side.

The measured seal initiation temperature of example 1 was found to be 120°C while for the comparative example a seal initiation temperature of 170°C has been measured.

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CLAIMS

1. A plastic film comprising

- a polyolefin homopolymer or copolymer
- a polyether copolymer having a melting point in the range of 100°C to 120°C, and
- an oxygen barrier material.

2. The plastic film of claim 1, where the thickness of the film is between 50 and 300 microns.

3. The plastic film of claim 2, where the thickness of the film is between 60 and 150 microns.

4. The plastic film of one or more of the preceding claims, where the oxygen barrier material is ethylene vinyl alcohol (EVOH).

5. The plastic film of one or more of claims 1-3, where the oxygen barrier material is a polyamide.

6. The plastic film of one or more of the preceding claims, where the polyolefin is polyethylene or polypropylene.

7. The plastic film of one or more of the preceding claims, where the polyolefin homopolymer or copolymer is ethylene alpha olefin copolymer.

8. The plastic film of claim 7, where the polyether copolymer is a block copolymer.

9. The plastic film of one or more of the preceding claims, where the polyether copolymer is polyolefin, polyamide or polyester copolymer.

10. The plastic film of one or more of the preceding claims, where the polyether copolymers are contained in at least one of outer and inner layers.

11. The plastic films of one or more of the preceding claims, where the polyether copolymers are contained in both inner and outer layers.

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12. A gusseted tubular film made of a plastic film of one or more of the preceding claims.

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PATENTS ACT 1992

SEARCH REPORT UNDER SECTION 29

Application No 2018/0572

International Classification accorded to the application (Edition 8) B32B 27/08

Search completed on 2nd May 2019

Documents considered relevant following a search in respect of claims 1-12

Category of document	Identity of document/Relevant passage therein	Relevant to claim(s)
Y	GB 2548246 A (FLEXOPACK) See especially page 6 lines 11-20, page 8 line 4 to page 9 line 6, and claims 1-9 and 13	1-12

CATEGORIES OF DOCUMENTS

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing of the present application.

&: Member of the same patent family - corresponding document.

Continued YES/NO

Search Report under Section 29(continued)

Application No/Patent No 2018/0572

Category of document	Identity of document/Relevant passage therein	Relevant to Claim(s)
Y	JP S63264348 A (KUREHA) See especially the EPODOC abstract and WPI abstract 1988-351199	1, 4, 9 and 10
Y	US 6420045 B1 (FAULHAMMER) See especially column 8 lines 22-37	1-12
A	Sanyo Chemical Industries, "Sanyo Chemical Product Outline - Part 1", Available online https://www.sanyo-chemical.co.jp/eng/products/productsPDF/no01.pdf 25th March 2016 [Viewed 2nd May 2019] Performance chemicals for synthetic resin & rubber industries and paint, ink & pigment industries, 1.4 Antistatic agents, Appendix 7, "Typical Properties of PELESTAT Products"	-