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(72) Feltaláló(k):
FACKLER, Tobias, 87764 Legau (DE)
BERNIG, Walter, 87471 Durach (DE)
DUJARDIN, Bernard, B-1180 Brüssel (BE)

(73) Jogosult(ak):
Schur Flexibles Dixie GmbH, 87437 Kempten (DE)

(74) Képviselő:
Iványka Gábor, ARINOVA Szabadalmi és Védjegy Iroda, Budapest

(54) **Csomagolóanyag, amely tartalmaz egy habosított poliolefin réteget**

Description

[0001] The invention resides within the domain of the packaging industry and relates to a packaging material containing a layer of foamed polyolefin as an outer layer, which has further layers on one of its surfaces, and to packages manufactured from it.

[0002] Packaging materials with a foam layer, for example polypropylene in the form of virtually endless rolled strips, are used to manufacture thermoformed, self-supporting packages such as for example packaging trays for foodstuffs. To do this, such packaging materials can be processed on so-called "FFS machines" (form-fill-seal machines) to make packages, wherein the strips of packaging material are fed into a forming device, therein formed into a strip of trays, the trays are filled with the goods for packaging and closed by sealing with preferably transparent film. The closed trays are finally separated from each other.

[0003] In known packaging materials, the layer of foamed polyolefin is provided with further layers, on at least one side of the surface. Depending on their composition and thickness, these layers can increase the stiffness of the packaging material and/or serve to protect the foam surface and/or serve as gas or aroma barriers and/or as a surface layer for sealing a filled packaging tray with a preferably transparent covering film.

[0004] Packaging materials with a layer of foamed polypropylene for manufacturing packaging trays by heat forming are described, for example, in EP-A-0 570 222. These materials comprise a foam layer and a multi-layer compound film that can contain a barrier layer sealing the packaging material against aromas and gas. This multi-layer packaging material does not always have the properties required of self-supporting packages.

[0005] Thermo-formable films of foamed polypropylene that must have special rheological and molecular characteristics are described in WO91/13933, wherein less than 1wt.% nucleating agent is optionally added to the polymers to control foaming. This publication neither reveals any improvement of mechanical properties attributable to it, nor a reduction in the minimum cycle time, i.e. increase in production speed, when processing the foamed films to make packaging trays.

[0006] In EP-B-1 117 526 it is shown that the foam layer is supplemented with a compact layer of a polyolefin of the foam layer, while observing a certain thickness ratio of these two layers relative to each other, in order to improve the self-supporting capability of packages made from this packaging material without increasing the thickness of the packaging material.

[0007] Although this packaging material can very well be processed to make packages, e.g. by thermoforming, a requirement arises, on account of the ever-faster running of packaging machines, to improve the packaging material so as to allow higher production speeds, i.e. shorter cycle times, without this resulting, for example, in irregularities of the wall thickness of the packaging containers and without adversely affecting the mechanical strength and optionally, rigidity, and hence the self-supporting capability of the packaging containers.

[0008] This task is resolved according to the invention, by providing a multilayer film comprising the following sequence of layers:

A) a base layer of polyolefin foam containing 0.5 to 25 wt.%, relative to the total weight of the base layer, of at least one nucleating agent,

B) a layer based on at least one polyolefin of the foam layer A)

C) optionally a bonding layer based on a polyolefin, which is preferably based on the particular monomer which is the main monomer of the polyolefin of the foam layer A),

D) optionally a coupling agent layer,

E) optionally a gas- and/or aroma-barrier layer,

F) a coupling agent layer,

G) an optionally heat-sealable and/or peelable surface layer

wherein the total thickness of layers A) and B) is in the range from 0.5 to 2 mm and the thickness of layer B) is in the range from 1/6 to 1/2 of the thickness of layer A).,

[0009] Preferably, the total thickness of layers A) and B) is in the range from 0.6 to 1.4 mm and the thickness of layer B) is in the range of 1/6 to 1/3 of the thickness of layer A).

[0010] The foam layer A) consists of at least one foamed polyolefin. Foamed propylene, homo-and/or co-polymers are particularly suitable here for manufacturing packaging, such as, for example, packaging trays for packaging foodstuffs, as these materials already display self-supporting properties, with little thickness and little density. It is also possible to use polyolefin blends to manufacture the foam layer. A blend of polypropylene with long-chain branching and hence better melting resistance and a propylene-ethylene copolymer, for example, a heterophase propylene-ethylene block copolymer is particularly suitable here. Especially suitable is a blend of polypropylene with long-chain branching and a melt-flow index (MFI) in the range from 1.4 to 4.2 g/10 min. (2.16 kg. 230°C measured in accordance with ISO 1133) and a heterophase propylene-ethylene block copolymer in a blend ratio of 1:1.

[0011] The foaming of the polyolefin of layer A) can be achieved by adding solid, liquid and/or gaseous foaming agents, which are added to the polyolefin in standard quantities, preferably in quantities of 0.5 to 3 wt.%. In this case, reference is made to the disclosure in EP-A-0 570 222, which is included herewith as a reference and applies as a part of this publication.

[0012] The foam layer A) contains 0.5 to 25 wt.%, preferably 2.1 to 20 wt.%, especially preferably more than 2.5 to 15 wt.% relative to the total weight of the foam layer A), of at least one nucleating agent. The nucleating agent is preferably fine-grained with an average grain size in the range from 4 to 20 mm.

[0013] Any known solid nucleating agents are suitable as nucleating agents, preferably synthetic or naturally inorganic compounds. Especially preferably, at least one nucleating agent will be chosen from the group comprising talcum, titanium dioxide, silicon oxide, calcium carbonate, magnesium silicate, aluminium silicate, calcium phosphate and montmorillonite. The use of talcum is quite especially preferred.

[0014] The nucleating agent is added to the polymer from which the foam layer is to be manufactured, preferably as a master batch that contains 30 to 60 wt.% of nucleating agent in the polymer, and is thoroughly homogeneously distributed therein before foaming.

[0015] The resulting foam layer A) is distinguished by a high number of cells with relatively low size differences. The cell number is preferably equal to or greater than 250 cells/mm^3,

especially preferably equal to or greater than 300 cells/mm^3, up to 600 cells/mm^3, whose cell size difference lies in the range of ±15, preferably ±10%. The density of layer A) is preferably in the range from 0.35 to 0.55g/cm3.

[0016] The density and number of cells can furthermore be varied by the process parameters, e.g. the extrusion temperature or other process parameters, during the preferred manufacture of the foam layer by extrusion and expansion.

[0017] Layer B) of compact polyolefin is based essentially on at least one polyolefin of the foamed base layer A). Insofar as this base layer consists of foamed polypropylene or a foamed blend of polypropylene and propylene-ethylene copolymer, the compact polyolefin layer B) is preferably based on polypropylene or a propylene-ethylene copolymer. Especially preferred is a heterophase propylene-ethylene block copolymer. The melt-flow index (MFI) of the polyolefin used to manufacture layer B) is preferably in the range from 1.8 to 5.5 g/10min., measured as stated above. The thickness of layer B) is 1/6 to 1/2, especially preferably 1/6 to 1/3, of the thickness of layer A).

[0018] Layer C) is preferably present, insofar as layers D) to G) are prefabricated by co-extrusion, preferably by film extrusion blowing, and are to be bonded to the other layers. Layer C) is based on a polyolefin that was preferably manufactured from a monomer, which is also the main monomer of the polyolefin of the foam layer A). Therefore, insofar as layer A) is made from a foamed polypropylene and optionally, a propylene-ethylene copolymer, layer C) can be polypropylene, which optionally contains grafted maleic anhydride units. Ethylene/vinyl acetate copolymers can also be used as other constituents. The thickness of layer C) preferably amounts to 5 to 25 µm, especially preferably, to 8 to 15 µm.

[0019] Insofar as the multilayer films according to the invention must have low gas permeability, i.e. low oxygen and moisture permeability, together with aroma protection, they contain a barrier layer E). This barrier layer is preferably made from an ethylene/vinyl alcohol copolymer that has an ethylene content of 32 to 45 Mol%, preferably 35 to 42 Mol%. The barrier layer E) can be bonded to the bonding layer C) and respectively to the sealing layer G) by means of a coupling agent layer D) and respectively F) on each of its surfaces. A propylene copolymer and respectively a polyethylene containing grafted maleic anhydride units can be used as the material.

[0020] The surface layer G), which forms the 2nd outer layer of the multilayer film according to the invention, is preferably heat-sealable and/or peelable. Therefore, this layer is manufactured, preferably from a low density polyethylene (LDPE) with a melt-flow index (MFI) in the range from 0.5 to 8.0 g/10min, preferably in the range from 1 to 5 g/10min (2.16 kg, 190°C), measured in accordance with ASTM D1238), or an ionomer, e.g. a copolymer of an α-olefin and an ethylenically unsaturated carboxylic acid, wherein the carboxyl groups are present as inorganic salt in a quantity of 20 to 100 Mol%, preferably as sodium salt, or of an ethylene-vinyl acetate copolymer with a vinyl acetate content of 3 to 10 wt.%, preferably 4 to 6 wt.% is used to manufacture this heat-sealable layer.

[0021] According to an especially preferred embodiment, the heat-sealable layer is also peelable. A blend of LDPE and a polybutylene (PB) is preferably used for this, as a layer material. The blend preferably contains 15 to 30 wt.%, preferably 20 to 28 wt.% of polybutylene. The polybutylene preferably has a melt-flow index (MFI) in the range from 0.3 to 2.0 g/10min (190° and 2.16 kg in accordance with ASTM 1238).

[0022] Preferably, the thickness of the surface layer is in the range from 10 to 50 µm, preferably from 15 to 30 µm.

[0023] When LDPE is used as a polymer to manufacture the sealing layer G) and the multilayer film according to the invention also contains a barrier layer, a coupling agent layer is preferably required to bond the barrier layer and the heat-sealable layer, provided that an ethylene-vinyl alcohol copolymer is not used as the barrier layer material. A polyolefin, preferably a polyethylene with grafted maleic anhydride units can be used as a material for the coupling agent layer. However, it is also possible to use a blend of LDPE and LLPDE in the ratio 3:1 to 4:1. The thickness of the coupling agent layer in question is in the range from 2 to 8 µm, preferably in the range from 3 to 6 µm.

[0024] The surface layer G) can contain standard and known antibiotics, slip additives and anti-block additives, e.g. erucic acid amide, polyalkil siloxane, e.g. polydimethyl siloxane and/or silicon dioxide.

[0025] All or only one layer of the multilayer film according to the invention can contain stabilisers and further additives of the prior art.

[0026] Layer B) can furthermore contain 0.5 to 2 wt.% of a white pigment, e.g. kaolin, calcium carbonate, talcum, titanium dioxide or blends thereof. Such inorganic pigments are added to the polymer from which layer B) is made, preferably as a master batch containing 30 to 70 wt.% of pigment.

[0027] The multilayer films according to the invention can preferably be manufactured by standard film extrusion blowing processes or by cast film co-extrusion processes, provided that this concerns the sequence of layers C) to G), and preferably bonded with the polyolefin foam layer A) by an extrusion laminating step. To do this, the foam layer A) and the multilayer film comprising layers C) to G) are brought together such that layer B) is extruded in with them. Immediately following extrusion, a sufficiently high pressure is exerted on the laminate manufactured in this way, so that layers A) to G) are adequately bonded together.

[0028] However, it is also possible to manufacture the multilayer films only by co-extrusion, wherein the foam layer A) is co-extruded at the same time as the other layers, optionally leaving out layer C), and layer A) is foamed at the same time.

[0029] The multilayer films according to the invention have outstanding thermoforming properties on so-called FFS (form-fill-seal) machines, and can be processed on these machines as packaging containers, preferably moulded packaging trays, then filled and sealed. It was surprising that the multilayer films according to the invention could be outstandingly processed on FFS machines at an increased production rate and up to 10% shorter cycle times compared with packaging materials without modification according to the invention, and hence with up to a 10% higher output of packaging trays without adversely affecting wall thickness regularity.

[0030] The multilayer films according to the invention also display an unexpected improvement in mechanical properties compared with similar known, unmodified packaging materials, especially stiffness, measured through the modulus of elasticity along the machine, and tensile stress. This clear improvement is shown, without it being necessary to increase the thickness of the multilayer films known in the prior art.

[0031] The packages manufactured from the multilayer films according to the invention furthermore display a clearly smoother surface structure, practically without any foam protrusions, whereby their handling is also improved.

[0032] A further item of this invention is therefore also the use of the multilayer films according to the invention as packaging material, preferably on form-fill-seal (FFS) machines for packaging foodstuffs, especially easily perishable foodstuffs such as meat, ham or sliced cold meat. Since packaging on these machines is often a discontinuous process, so as to pack different products, the packaging material must have a relatively wide so-called thermoforming window within which it can be thermoformed. This is achieved by the packaging material according to the invention, as it has outstanding thermoforming properties, especially moulding properties.

[0033] The thermoformed, preferably moulded packaging articles, e.g. packaging trays, preferably moulded packaging trays, which have been manufactured from the multilayer films according to the invention, can be sealed after filling with known covering films. Multilayer films, preferably of polyethylene terephthalate/SiO_x/coupling agent layer/low density polyethylene or of polyethylene terephthalate/coupling agent layer/polyethylene/coupling agent layer/ethylene-vinyl alcohol copolymer/coupling agent layer/polyethylene are suitable as covering films.

[0034] Of the covering films named, the first-mentioned multilayer films are especially suitable. For this, the biaxially oriented polyethylene terephthalate is coated with SiO_x by plasma vacuum technology. The already prepared polyethylene film is then laminated onto it using a coupling agent. Such a covering film is particularly distinguished by outstanding transparency and high breaking strength. Packages having such covering film furthermore make outstanding gas barriers.

[0035] In the following examples, the modulus of elasticity and respectively the tensile stress are measured along and across the machine in accordance with ISO 572-2.

Examples: Example 1

[0036] A multilayer film according to the invention with the following layer structure:

Layer A)	a foam layer with a density of 0.47 g/cm^3 and a cell number of 492 cells/mm^3, in a blend of 50 wt.% of polypropylene with long-chain branching (high melt strength polypropylene) and 46 wt.% of a heterophase propylene-ethylene block polymer and 4 wt.% of fine talcum.
Layer B)	100 wt.% of a heterophase propylene-ethylene block polymer equivalent to the block copolymer of the foam layer A).
Layer C)	polypropylene,
Layer D)	a coupling agent layer based on polypropylene grafted with maleic anhydride units,
Layer E)	a gas barrier layer based on an ethylene-vinyl alcohol copolymer,
Layer F)	a coupling agent layer with the same structure as layer D),
Layer G)	a sealing layer based on low density polyethylene.

[0037] The multilayer film is manufactured by co-extrusion.

[0038] The thickness of the different layers is given in Table 1.

Table 1

Layer	A)	B)	C)	D)	E)	F)	G)	Total
Thickness in µm	1130	284	15	5	5	5	20	1444

[0039] The mechanical properties of this film are given in Table 2.

Comparative example 1:

[0040] A multilayer film equivalent to the multilayer film according to Example 1 was manufactured with the identical layer sequence and identical layer compositions, apart from layer A), wherein layer A) had the same polymer composition as in Example 1, but no nucleating agent.

[0041] The mechanical properties of the multilayer film according to the comparative example are given in Table 2.

Table 2

	Unit	Comparative example 1	Example 1
Modulus of elasticity (along the machine)	MPA	519	703
Modulus of elasticity (across the machine)	MPA	280	280
Tensile stress (along the machine)	MPA	9.3	12.0
Tensile stress (across the machine)	MPA	7.4	9.5
Cycle times	Cycles/minute	8	9

[0042] It emerges from Table2 that the multilayer film according to the invention has far better mechanical properties than a multilayer film with an unmodified foam layer A).

CSOMAGOLÓANYAG, AMELY TARTALMAZ EGY HABOSÍTOTT POLIOLEFIN RÉTEGET

Szabadalmi igénypontok

1. Egy többrétegű film, amely magában foglalja a következő rétegsorozatot:

   A) egy alapréteg poliolefin-habból, amely tartalmaz 0,5-25 tömeg%-ot (wt.%), az alaprétegnek az össztömegére vonatkoztatva, legalább egy magképző szerből,

   B) egy réteg, amely az A) hab-réteg szerinti legalább egy poliolefinen alapul,

   C) adott esetben egy kötőréteg, amely egy poliolefinen alapul,

   D) adott esetben egy tapadásközvetítő réteg,

   E) adott esetben egy gáz- és/vagy aroma-záróréteg,

   F) egy tapadásközvetítő réteg,

   G) egy adott esetben hőhegeszthető és/vagy lehúzható felületi réteg,

   ahol az A) és B) rétegeknek a teljes vastagsága a 0,5-2 mm tartományban van és a B) rétegnek a vastagsága az A) réteg vastagságának az 1/6-1/2 tartományában van.

2. Egy többrétegű film az 1. igénypont szerint, **azzal jellemezve, hogy** az A) és B) rétegeknek a teljes vastagsága a 0,6-1,4 mm tartományban van.

3. Egy többrétegű film az 1. vagy 2. igénypont szerint, **azzal jellemezve, hogy** a B) rétegnek a vastagsága az A) réteg vastagságának az 1/6-1/3 tartományában van.

4. Egy többrétegű film az 1.-től 3.-ig igénypontok közül az egyik vagy több szerint, **azzal jellemezve, hogy** az A) réteg habosított polipropilénen alapul vagy egy habosított keveréken alapul, amely áll hosszúláncú elágazásokkal rendelkező polipropilénből és egy propilén-etilén-kopolimerből, előnyösen egy heterofázisú propilén-etilén-blokk-kopolimerből.

5. Egy többrétegű film az 1.-től 4.-ig igénypontok közül legalább az egyik szerint, **azzal jellemezve, hogy** az A) réteg tartalmaz 2,1-20 tömeg%-ot (wt.%), előnyösen 2,5-15 tömeg%-ot (wt.%), a magképző szerből.

6. Egy többrétegű film az 1.-től 5.-ig igénypontok közül legalább az egyik szerint, **azzal jellemezve, hogy** a magképző szerként legalább egy szer áll rendelkezésre a következő csoportból: talkum, titán-dioxid, szilícium-oxid, kalcium-karbonát, magnézium-szilikát, alumínium-szilikát, kalcium-foszfát és montmorillonit.

7. Egy többrétegű film az 1.-től 6.-ig igénypontok közül az egyik vagy több szerint, **azzal jellemezve, hogy** a B) réteg polipropilénen vagy egy propilén-etilén-kopolimeren alapul.

8. Egy többrétegű film az 1.-től 7.-ig igénypontok közül az egyik vagy több szerint, **azzal jellemezve, hogy** a C) réteg egy poliolefinen alapul, amely azon a bizonyos monomeren alapul, amely az A) hab-réteg szerinti poliolefin fő monomere, előnyösen polipropilénen alapul.

9. Egy többrétegű film az 1.-től 8.-ig igénypontok közül az egyik vagy több szerint, **azzal jellemezve, hogy** az E) réteg egy etilén-vinil-alkohol-kopolimeren alapul.

10. Egy többrétegű film az 1.-től 9.-ig igénypontok közül az egyik vagy több szerint, **azzal jellemezve, hogy** a G) réteg egy hőhegeszthető polimeren alapul, előnyösen egy kis

sűrűségű polietilénen vagy egy ionomeren alapul és adott esetben tartalmaz konvencionális adalékanyagokat.

11. Egy többrétegű film az 1.-től 9.-ig igénypontok közül az egyik vagy több szerint, **azzal jellemezve, hogy** a G) réteg lehúzható polimereken alapul, előnyösen egy keveréken alapul, amely áll kis sűrűségű polietilénből és egy polibutilénből, és adott esetben tartalmaz konvencionális adalékanyagokat.

12. Egy többrétegű film az 1.-től 11.-ig igénypontok közül az egyik vagy több szerint, **azzal jellemezve, hogy** a rétegeknek C)-től G)-ig a teljes vastagsága 20-70 µm-t, előnyösen 30-50 µm-t tesz ki.

13. Egy az 1.-től 12.-ig igénypontok közül az egyik vagy több szerinti többrétegű film alkalmazása csomagolóanyagként.

14. Csomagolótartályok, előnyösen csomagolótálcák, amelyek egy az 1.-től 12.-ig igénypontok közül legalább az egyik szerinti filmből van készítve.

15. Csomagolótartályok a 14. igénypont szerint, élelmiszerek, előnyösen szilárd élelmiszerek csomagolására.

16. Csomagolótartályok a 15. igénypont szerint, hús, kolbász vagy sajt csomagolására.

17. Egy az 1.-től 12.-ig igénypontok közül az egyik vagy több szerinti többrétegű film alkalmazása csomagolóanyagként alakító-töltő-lezáró gépeken.