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(54) Title: A MULTILAYER COEXTRUDED HEAT-SHRINKABLE BARRIER FOAMED FILM AND FOAMED FLEXIBLE CONTAINERS MADE THEREFROM FOR PACKAGING APPLICATIONS

(57) Abstract: The present invention relates to multilayer coextruded heat shrinkable barrier foamed films and to flexible shrinkable sealable barrier lightweight containers made therefrom, such as bags, pouches and the like, which preserve the temperature of refrigerated or frozen meat or fish or drugs or thermolabile products. In alternative, the present packages may be used to preserve the temperature of warm products.



TITLE

“A multilayer coextruded heat-shrinkable barrier foamed film and foamed flexible containers made therefrom for packaging applications”

DESCRIPTION5 Field of the invention

The present invention relates to multilayer coextruded heat shrinkable barrier foamed films and to flexible shrinkable sealable barrier lightweight containers made therefrom, such as bags, pouches and the like, which provide a thermal barrier suitable to maintain the initial temperature of an item packaged therein, preferably
10 of food, for an extended period of time.

Background of the invention

In several circumstances, it is required to preserve the temperature of packaged articles as long as possible when exposed to different external temperatures. Commercial thermal shopping bags, to carry temperature-sensitive purchases
15 home without breaking the cold chain or thermal bags to keep pizzas being delivered hot, are known.

Thermal pharmaceutical bags are designed to transport temperature-sensitive medications, protecting them from damaging temperatures.

Thermal bags are usually made of thick walls of thermally insulating materials,
20 including foamed polystyrene, PET, polyethylene, polyurethane, polypropylene, possibly coupled with fabric, nonwovens or metalized materials.

Cool boxes are very similar in concept, the wall structure being a foam material having low heat transmission index covered on both sides with a hard plastic or metal for rigidity and support.

25 Foam disposable insulating take away containers for various foods (such as processed, raw, cooked food or ice creams), including beverages (e.g. foam polystyrene disposable coffee cups), are commonly used.

All the above mentioned containers are rather bulky and require very high amount of plastic materials to provide for thermal insulation. Additionally, they are not
30 designed to be tight sealed, gas barrier, optionally vacuumized and shrunk.

Considering, in particular, foam food containers there is increasing concern for both health and environmental reasons. Because foam takeout containers are entirely made out of polystyrene foam, these containers have an impact on the environment, as they do not biodegrade easily. Further it is debated whether styrene may migrate

into food which is stored in foam food containers even briefly. Finally, styrene foam containers can melt if the food or liquid is at a sufficiently high temperature.

The patent application EP481081 relates to a composite packaging cross-linked film, optionally comprising a foamed layer, film that is said to be provided with excellent stretching and gas barrier properties, sufficient heat shrinkability, good oil and heat seal resistance. The gist of this invention is the low dose of irradiation for curing the film due to the presence of a layer of an ethylene copolymer resin having carbon-carbon unsaturated bonds.

Accordingly, there is still the need to provide an insulating container for preserving the temperature of both hot and cold items:

- that uses very low amount of materials and, in particular, of plastics,
- that air tightly encloses the product and prevents gas and water exchange,
- that is not bulky as it adheres to the product because vacuumized and /or shrunk around it,
- that do not release harmful substances when in contact to the packaged item, and
- that, in case of hot product, do not soften or melt.

Currently, the Applicant is not aware of a solution that conjugates all the above requirements.

SUMMARY OF THE INVENTION

We have surprisingly found that by inserting in a conventional multilayer barrier packaging film at least one layer of a preferably coextruded foamed polymeric layer, a good thermoinsulating effect can be achieved without significantly impairing other important film properties such as shrinkability and stiffness.

The resulting films are suitable for manufacturing flexible thermo-insulating lightweight containers, which once vacuumized and/or shrunk, closely conform around the product and provide for very packed packages. Packed packages are particularly appreciated as they reduce the costs of transportation and storage.

Advantageously, the present packages require minimum amount of packaging material in comparison with traditional thick insulating systems. Furthermore, the present films and containers made therefrom extend the shelf-life of sensitive products not only by thermoinsulation – which delays any dangerous temperature increase of refrigerated or frozen articles - but also - being tightly sealed and barrier - by preventing gas and water exchange with the environment.

Finally, they perform as well in maintaining the temperature of hot items, such as roasted chicken or pizza, long enough to bring and to consume them home still warm.

It is thus a first object of the present invention a multi-layer heat-shrinkable packaging film comprising:

- (a) a first outer heat sealable polymeric layer,
- (b) at least an inner foamed polymeric layer,
- (c) at least an inner gas-barrier layer, and
- (d) a second outer polymeric layer.

A second object of the present invention is a heat shrinkable foamed flexible container in the form of a bag or a pouch, obtained by sealing the film of the present invention to itself.

A third object of the present invention is a package comprising a product packaged into a foamed flexible container according to the invention.

A fourth object of the present invention is a package comprising a tray, a product placed into the tray and a lid sealed all around the tray thus enclosing said product, wherein said lid comprises a film according to the present invention.

Definitions

As used herein, the term "film" is inclusive of plastic web, regardless of whether it is film or sheet.

As used herein the phrases "inner layer" and "internal layer" refer to any film layer having both of its principal surfaces directly adhered to another layer of the film.

As used herein, the phrase "outer layer" refers to any film layer having only one of its principal surfaces directly adhered to another layer of the film.

As used herein, the phrases "seal layer", "sealing layer", "heat seal layer", and "sealant layer", refer to the film outer layer which will be involved in the sealing of the film either to itself or to another film or sheet or to a tray to close the package and that will thus be in contact with, or closer to, the packaged product.

As used herein, the phrase "adhesive layer" or "tie layer" refers to any inner film layer having the primary purpose of adhering two layers to one another.

As used herein, the term "polymer" refers to the product of a polymerization reaction, and is inclusive of homopolymers, copolymers, terpolymers, etc. In general, the layers of a film or film substrate can consist essentially of a single polymer, or can have still additional polymers together therewith, i. e., blended therewith.

As used herein, the term "copolymer" refers to polymers formed by the polymerization of reaction of at least two different monomers. For example, the term "copolymer" includes the co-polymerization reaction product of ethylene and an -olefin, such as 1-hexene. The term "copolymer" is also inclusive of, for example, the co-polymerization of a mixture of ethylene, propylene, 1-propene, 1-butene, 1-hexene, and 1-octene. As used herein, a copolymer identified in terms of a plurality of monomers, e.g., "propylene/ethylene copolymer", refers to a copolymer in which either a monomer may copolymerize in a higher weight or molar percent than the other monomer or monomers. However, the first listed monomer preferably polymerizes in a higher weight percent than the second listed monomer.

As used herein, the term "polyolefin" refers to homopolymers, copolymers, including, e.g., bipolymers, terpolymers, etc., having a methylene linkage between monomer units which may be formed by any method known to those skilled in the art. Examples of polyolefins include polyethylene (PE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), very low-density polyethylene (VLDPE), ultra low-density polyethylene (ULDPE), medium-density polyethylene (MDPE), high-density polyethylene (HDPE), ultra high-density polyethylene (UHDPE), ethylene/propylene copolymers, polypropylene (PP), propylene/ethylene copolymer, polyisoprene, polybutylene, polybutene, poly-3-methylbutene-1, poly-4-methylpentene-1, ionomers, polyethylenes comprising ethylene/ -olefin which are copolymers of ethylene with one or more -olefins (alpha-olefins) such as butene-1, hexene-1, octene-1, or the like as a comonomer, and the like.

As used herein, the phrase "ethylene/alpha-olefin" (E/AO) refers to a modified or unmodified copolymer produced by the co-polymerization of ethylene and any one or more -olefin. The -olefin in the present invention may have between 3-20 pendant carbon atoms. The co-polymerization of ethylene and an -olefin may be produced by heterogeneous catalysis, i.e., co-polymerization reactions with Ziegler-Natta catalysis systems, for example, metal halides activated by an organometallic catalyst, i.e., titanium chloride, optionally containing magnesium chloride, complexed to trialkyl aluminum and may be found in patents such as U.S. Patent No. 4,302,565 to Goeke et al. and U.S. Patent No. 4,302,566 to Karol, et al. Heterogeneous catalyzed copolymers of ethylene and an -olefin may include linear low-density polyethylene, very low-density polyethylene and ultra low-density polyethylene. These copolymers of this type are available from, for example, The

Dow Chemical Company, of Midland, Michigan., U.S.A. and sold under the trademark DOWLEX resins. Additionally, the co-polymerization of ethylene and a -olefin may also be produced by homogeneous catalysis, for example, co-polymerization reactions with metallocene catalysis systems which include
5 constrained geometry catalysts, i.e., monocyclopentadienyl transition-metal complexes taught in U.S. Patent No. 5,026,798 to Canich, the teachings of which are incorporated herein by reference. Homogeneous catalyzed ethylene/ -olefin copolymers (E/AO) may include modified or unmodified ethylene/ -olefin copolymers having a long-chain branched (8-20 pendant carbons atoms) -olefin comonomer
10 available from The Dow Chemical Company, known as AFFINITY and ATTANE resins, TAFMER linear copolymers obtainable from the Mitsui Petrochemical Corporation of Tokyo, Japan, and modified or unmodified ethylene/ -olefin copolymers having a short-chain branched (3-6 pendant carbons atoms) -olefin comonomer known as EXACT resins obtainable from ExxonMobil Chemical
15 Company of Houston, Texas, U.S.A.

As used herein, the phrase "acrylic acid-based resin" refers to homopolymers and copolymers having an acrylic acid and/or a methacrylic acid linkage between monomer unit. These monomer units have the general formula: $[H_2C=C](R)(CO_2H)$ where $R = H$, alkyl group. Acrylic acid-based resins may be formed by any method
20 known to those skilled in the art and may include polymerization of acrylic acid, or methacrylic acid in the presence of light, heat, or catalysts such as benzoyl peroxides, or by the esters of these acids, followed by saponification. Examples of acrylic acid-based resins include, but are not limited to, ethylene/acrylic acid copolymer (EAA), ethylene/methacrylic acid copolymer (E/MAA), and blends
25 thereof.

As used herein, the phrase "acrylate-based resin" refers to homopolymers and copolymers having an ester of acrylic acid linkage between the monomer unit. The acrylic acid monomer unit can be represented by the general formula: $[H_2C=C](R)(CO_2R')$ where $R = H$, alkyl group and $R' =$ same or different alkyl group
30 as R . Acrylate-based resins may be formed by any method known to those skilled in the art, such as, for example, polymerization of the acrylate monomer by the same methods as those described for acrylic acid-based resins. Examples of acrylate-based resin include, but are not limited to, methyl/methacrylate copolymer (MMA),

ethylene/vinyl acrylate copolymer (EVA), ethylene/methacrylate copolymer (EMA), ethylene/n-butyl acrylate copolymer (EnBA), and blends thereof.

As used herein, "EVOH" refers to ethylene/vinyl alcohol copolymer. EVOH includes saponified or hydrolyzed ethylene/vinyl acetate copolymers with a degree of hydrolysis preferably at least 50%, and more preferably, at least 85%. Preferably, the EVOH comprises from about 28 to about 48 mole % ethylene, more preferably from about 32 to about 44 mole % ethylene.

As used herein the term "polyamide" refers to high molecular weight polymers having amide linkages along the molecular chain, and refers more specifically to synthetic polyamides such as nylons. Such term encompasses both homo-polyamides and co-(or ter-) polyamides. It also specifically includes aliphatic polyamides or co-polyamides, aromatic polyamides or co-polyamides, and partially aromatic polyamides or co-polyamides, modifications thereof and blends thereof. The homo-polyamides are derived from the polymerization of a single type of monomer comprising both the chemical functions which are typical of polyamides, i.e. amino and acid groups, such monomers being typically lactams or aminoacids, or from the polycondensation of two types of polyfunctional monomers, i.e. polyamines with polybasic acids. The co-, ter-, and multi-polyamides are derived from the copolymerization of precursor monomers of at least two (three or more) different polyamides. As an example in the preparation of the co-polyamides, two different lactams may be employed, or two types of polyamines and polyacids, or a lactam on one side and a polyamine and a polyacid on the other side.

As used herein, the term "adhesive" refers to a polymer material serving a primary purpose or function of adhering two surfaces to one another. In the present invention, the adhesive may adhere one layer to another layer. The adhesive may comprise any polymer, copolymer or blend of polymers including modified and unmodified polymers, e.g., grafted copolymers, which provide sufficient interlayer adhesion to adjacent layers comprising otherwise nonadhering polymers.

As used herein, the term "EVA" refers to ethylene and vinyl acetate copolymers. The vinyl acetate monomer unit can be represented by the general formula: $[\text{CH}_3\text{COOCH}=\text{CH}_2]$.

As used herein the term "gas-barrier" when referred to a layer, to a resin contained in said layer, or to an overall film structure, refers to the property of the layer, resin or structure, to limit to a certain extent passage through itself of gases. When

referred to a layer or to an overall structure, the term "gas-barrier" is used herein to identify layers or structures characterized by an Oxygen Transmission Rate (OTR evaluated at 23°C and 0 % R.H. according to ASTM D-3985) of less than 100 cm³/m².day.atm, even more preferably lower than 50 cm³/m².day.atm.

5 As used herein, the phrase "flexible container" is inclusive of end-seal bags, side-seal bags, L-seal bags, U-seal bags (also referred to as "pouches"), pouches with one median longitudinal and two transversal seals as obtained by HFFS or VFFS processes, gusseted bags, backseamed tubings, and seamless casings.

10 As used herein, the term "package" refers to the combination of all of the various components used in the packaging of a product, i.e., all components of the packaged product other than the product within the package.

The term packages is inclusive of a flexible container in which the product is placed, optionally vacuumized or atmosphere modified, sealed and preferably shrunk so that the product is substantially surrounded by the heat-shrinkable multilayer film
15 from which the packaging container is made.

The term "package" also includes packages comprising a tray, a product loaded into the tray and a lid sealed all around the tray.

As used herein, the term "bag" refers to a packaging container having an open top, side edges, and a bottom edge. The term "bag" encompasses lay-flat bags, pouches, casings (seamless casings and backseamed casings, including lap-
20 sealed casings, fin-sealed casings, and butt-sealed backseamed casings having backseaming tape thereon). Various casing configurations are disclosed in US6764729 and various bag configurations, including L-seal bags, backseamed bags, and U-seal bags (also referred to as pouches), are disclosed in US6790468

25 As used herein, the phrase "machine direction" refers to the direction in which the film emerges from the die. Of course, this direction corresponds with the direction the extrudate is forwarded during the film production process. The phrase "machine direction" corresponds to "longitudinal direction". Machine direction and longitudinal direction are abbreviated as "MD" and "LD", respectfully.

30 As used herein, the phrase "transverse direction" refers to a direction perpendicular to the machine direction. Transverse direction is abbreviated as "TD".

As used herein, the term "lamination" refers to processes by which two or more materials are assembled by heat, pressure, welding or adhesives.

As used herein, the term "coextrusion" refers to the process of extruding two or more materials through a single die with two or more orifices arranged so that the extrudates merge and weld together into a laminar structure before chilling, i.e., quenching.

5 As used herein, the term "Extrusion lamination" or "extrusion coating" refers to processes by which a film of molten polymer is extruded onto a solid substrate (e.g., a nonwoven), in order to coat the substrate with the molten polymer film to bond the substrate and film together. "Joined" refers to configurations whereby an element is directly secured to another element by affixing the element directly to the other
10 element and to configurations whereby an element is indirectly secured to another element by affixing the element to intermediate member(s) which in turn are affixed to the other element. Materials may be joined by one or more bonding processes including adhesive bonding, thermal welding, solvent welding, ultrasonic bonding, extrusion bonding, and combinations thereof.

15 As used herein, the term "oriented" refers to a thermoplastic web which forms a film structure in which the web has been elongated in either one direction ("uniaxial") or two directions ("biaxial") at elevated temperatures followed by being "set" in the elongated configuration by cooling the material while substantially retaining the elongated dimensions. This combination of elongation at elevated temperatures
20 followed by cooling causes an alignment of the polymer chains to a more parallel configuration, thereby improving the mechanical properties of the polymer web. Upon subsequently heating of certain unrestrained, unannealed, oriented sheet of polymer to its orientation temperature, heat shrinkage may be produced.

As used herein the term "annealing" refers to a heat-treatment process aiming at
25 the partial or complete removal of strains and stresses set up in the material during its forming and fabricating operations

As used herein the phrases "heat-shrinkable," "heat-shrink," and the like, refer to the tendency of the solid-state oriented film to shrink upon the application of heat, i.e., to contract upon being heated, such that the size of the film decreases while the film
30 is in an unrestrained state. As used herein said term refer to solid-state oriented films with a free shrink in at least one of the machine and the transverse directions, as measured by ASTM D 2732, of at least 10 %, preferably at least 15% at 90°C.

As used herein the phrases "total free shrink" means a value determined by adding the percent free shrink in the machine (longitudinal) direction to the percentage of free shrink in the transverse (crosswise) direction.

As used herein, the term "maximum shrink tension" refers to the maximum value of tension developed by the films during the heating/shrinking process performed according to the test method described under the present experimental section.

DETAILED DESCRIPTION OF THE INVENTION

A first object of the present invention is a multi-layer heat-shrinkable packaging film comprising:

- (a) a first outer heat sealable polymeric layer,
- (b) at least an inner foamed polymeric layer,
- (c) at least an inner gas-barrier layer, and
- (d) a second outer polymeric layer.

The film of the present invention is characterized by one or more of the following features, taken alone or in combination.

Preferably the outer heat sealable layer (a) that in the end package will be the inside, heat-sealable layer, will comprise one or more polymers selected from the group of ethylene homopolymers, ethylene co-polymers, propylene homopolymers and propylene co-polymers, ionomers and their blends.

Preferably said first outer layer (a) comprises at least 50%, 60%, 70%, 80%, 90%, 95% overall of one or more of the above polymers.

Ethylene homo- and co-polymers suitable for the first outer layer (a) are selected from the group consisting of ethylene homo-polymers (polyethylene), heterogeneous or homogeneous ethylene-[alpha]-olefin copolymers, ethylene-vinyl acetate co-polymers, ethylene-(C₁-C₄) alkyl acrylate or methacrylate co-polymers, such as ethylene-ethyl acrylate co-polymers, ethylene-butyl acrylate co-polymers, ethylene-methyl acrylate co-polymers, and ethylene-methyl methacrylate co-polymers, ethylene-acrylic acid co-polymers, ethylene-methacrylic acid co-polymers, ionomers and blends thereof in any proportion.

Preferred ethylene homo- and co-polymers for said first outer layer are selected from e.g. polyethylene having a density of from about 0.900 g/cm³ to about 0.950 g/cm³, heterogeneous and homogeneous ethylene-[alpha]-olefin copolymers having a density of from about 0.880 g/cm³ to about 0.945 g/cm³, more preferably of from about 0.885 g/cm³ to about 0.940 g/cm³, yet more preferably of from about 0.890

g/ cm³ to about 0.935 g/ cm³, and ethylene-vinyl acetate copolymers comprising from about 3 to about 28%, preferably, from about 4 to about 20%, more preferably, from about 4.5 to about 18% vinyl acetate comonomer, and blends thereof.

Even more preferred, ethylene homo- and co-polymers for said first outer layer are selected from the group consisting of heterogeneous ethylene-[alpha]-olefin copolymers having a density of from about 0.890 g/ cm³ to about 0.940 g/ cm³, homogeneous ethylene-[alpha]-olefin copolymers having a density of from about 0.890 g/ cm³ to about 0.925 g/ cm³, ethylene-vinyl acetate copolymers comprising from about about 4.5 to about 18% vinyl acetate comonomer, and blends thereof.

Preferred resins for the heat-sealable layer (a) are Dowlex 2045 S by Dow Chemical, Eltex PF6220AA by Ineos, Affinity PL 1880G, Affinity PL1845G, Affinity PL1850G, Affinity PL 1281G1 by Dow and Exceed 2018CA, Exceed 2018HA, Exact 0210 by Exxon Mobil.

Propylene polymers suitable for said heat-sealable outer layer (a) are selected from the group consisting of propylene homo-polymer and propylene co- and ter-polymers with ethylene and/or a (C₄-C₁₀)-alpha-olefin, and more preferably from the group consisting of polypropylene, propylene-ethylene co-polymers, propylene-ethylene-butene co-polymers, propylene-butene-ethylene copolymers and blends thereof in any proportion.

Preferred polypropylene-based resins for the heat-sealable layer are Eltex PKS399, PKS359 and PKS607 by Ineos Polyolefins, Adsyl 5C37F by Basell and Borsoft SD233CF by Borealis.

Said outer heat-sealable polyolefin layer (a) may also comprise a blend of a major proportion of one or more polymers of the group of ethylene homo- and copolymers and propylene homo- and co-polymers, with a minor proportion of one or more other polyolefins and/or modified polyolefins, such as polybutene homo-polymers, butene-(C₅-C₁₀)-alpha-olefin copolymers, anhydride grafted ethylene-alpha-olefin copolymers, anhydride grafted ethylene-vinyl acetate copolymers, rubber modified ethylene-vinyl acetate copolymers, ethylene/propylene/diene (EPDM) copolymers, and the like.

The composition of said outer heat-sealable polyolefin layer (a) will mainly depend on the final application foreseen for the end structure. For instance when the film according to the present invention is used for flowpack applications where it will be sealed to itself, typically the composition of the outer layer (a) will be based on

ethylene polymers as these resins typically have a lower seal initiation temperature and can be sealed more easily to themselves. On the other hand, if the film is used in tray lidding applications and the container to which it has to be sealed is of polypropylene, the outer heat-sealable layer (a) will preferably be of a propylene polymer.

In the films of the present invention, the heat-sealant layer (a) may comprise one or more antifog additives.

The term "antifog film" means a plastic film having at least one surface whose properties have been modified or adapted to have antifog characteristics - that is, a tendency to reduce or minimize the negative effects of moisture condensation. The antifog film may incorporate or have dispersed in effective amounts one or more antifog agents in the plastic film resin before forming the resin into a film. Antifog agents are known in the art, and fall into classes such as esters of aliphatic alcohols, polyethers, polyhydric alcohols, esters of polyhydric aliphatic alcohols, polyethoxylated aromatic alcohols, nonionic ethoxylates, and hydrophilic fatty acid esters.

Usually, the antifog agent is previously compounded in a carrier resin obtaining a masterbatch, subsequently added to the layer (a) and/or C during the extrusion of the films according to the present invention.

Preferably, an antifog agent based on fatty acid esters is used. Commercially available antifog agents suitable for the films according to the first object of the present invention are for instance Cesa Nofog PEA 0050597 by Clariant, Polybatch AF1026SC by Schulman and 103697AF by Ampacet.

Typically, the antifog agent is incorporated into the layer (a) in an amount from 0.5 to 10% by weight based on the total weight of the layer, preferably from 1 to 5%, even more preferably from 1 to 4% by weight.

Preferably, the thickness of the outer heat-sealable layer (a) may be from 5% to 40 % of the overall thickness of the structure, preferably from 10% to 30 % and more preferably from 15% to 25%.

Preferably, the at least one inner foamed polymeric layer (b) comprises at least a polymer selected among ionomers, EVA, polyolefins, polystyrenes, polyurethanes, and their blends.

Preferably said at least one inner foamed polymeric layer (b) comprises at least 50%, 60%, 70%, 80%, 90%, 95% by weight of one or more of the above polymers with respect to the same layer weight.

Preferably, each one of the more than one inner foamed polymeric layers (b) comprises at least 50%, 60%, 70%, 80%, 90%, 95% by weight of one or more of the above polymers with respect to the same layers weight.

Preferably, the at least one inner foamed layer (b) comprises at least an ionomer, optionally blended with a polyolefin.

Preferably, the at least one inner foamed layer (b) comprises at least 70%, 80%, 90% of an ionomer.

Preferably, each one of the more than one inner foamed polymeric layers (b) comprise at least 70%, 80%, 90% of an ionomer.

Preferably, the at least one inner foamed layer (b) has a thickness of at least 10 μm , 20 μm , 30 μm , 40 μm , 50 μm .

Preferably, the at least one inner foamed layer (b) has a thickness of no more than 100 μm , 80 μm , 70 μm , 65 μm , 60 μm , 50 μm , 40 μm , 30 μm .

Preferably the at least one inner foamed layer (b) has a thickness of at least 20%, 30%, 40%, 50%, 55% with respect to the total thickness of the film.

Preferably, the at least one inner foamed layer (b) has a thickness of no more than 80%, 60%, 50%, 40%, 30% with respect to the total thickness of the film.

Preferably, the total thickness of the foamed layer(s) (b) with respect to the total thickness of the film is no more than 80%, 60%, 50%, 40%, 30%.

Preferably, the at least one inner foamed layer (b) has a percentage by weight of no more than 60%, 50%, 40%, 30%, 20%, 10% with respect to the total weight of the film.

Preferably, the total percentage by weight of the foamed layer(s) (b) with respect to the total weight of the film is no more than 60%, 50%, 40%, 30%, 20%, 10%.

Preferably, the present films comprise only one inner foamed layer (b).

Preferably, the present films comprise two or more inner foamed layers (b).

In case of more than one inner foamed layer (b), each of them may be independently characterized by one or more of the features herein disclosed for the at least one inner foamed layer (b).

Preferably, the present films comprise no more than 4 inner foamed layers (b).

Preferably, the at least one inner foamed layer (b) has a density from 0.3 to 0.8 g/cm³, preferably 0.4 to 0.7 g/cm³.

Preferably, the foamed layer (b) comprises closed cells.

Preferably, the foamed layer (b) in the final film comprises elongated closed cells, namely cells in which the major dimension is at least twice the minor dimension.

Preferably, the cells of the foam layer (b) in the final film have a major dimension lower than 400 µm, 300 µm and a minor dimension lower than 50 µm, 40 µm.

Preferably, the cells of the foam layer (b) in the final film have a major dimension higher than 50 µm, 60 µm and a minor dimension higher than 10 µm, 15 µm.

Typical dimension of the cells in the foamed layer (b) of the final film are for instance 280 µm x 20 µm, 18 µm x 75 µm, 58 µm x 22 µm, 15 µm x 68 µm.

Preferably, the master batch comprising the foaming agent is used in amount from 1% to 20%, from 2% to 15%, from 4% to 10% with respect to the layer weight.

Preferably, a nucleating agent may be present.

Examples of suitable master batches are marketed by Clariant under the commercial name of Hydrocerols TM.

Preferably, the at least one foamed layer (b) may be prepared by conventional methods from a composition comprising from 94% to 99%, preferably from 96% to 98% of a foamable polymer selected among ionomers, EVA, polyolefins, polystyrenes, polyurethanes, and their blends and from 1% to 6%, preferably 2% to 4% of an suitable masterbatch comprising a foaming agent.

Useful foaming agents include various conventional agents among which preferable are volatile agents such as pentane, butane and the like, organic agents such as hydrazine-, nitroso- and azo-type agents and the like, and inorganic agents such as sodium bicarbonate, ammonium carbonate and the like. More preferred are azodicarbonamide, azobisisobutyronitrile and like azo type-agents, sodium bicarbonate, ammonium carbonate and like carbonates among the inorganic agent. When required, the carbonates can be used conjointly with citric acid, tartaric acid or like organic acids.

Preferably the inner gas-barrier layer (c) comprises a polymer selected among polyvinyl alcohol copolymers (PV/A), ethylene/vinyl alcohol copolymers (EVOH), polyvinyl chlorides (PVC), polyvinylidene chloride copolymers (PVDC), polyvinylidene chloride/vinylchloride copolymers (PVDC-VC), polyvinylidene chloride/methyl acrylate copolymers (PVDC/MA), blends of polyvinylidene

chloride/vinylchloride copolymers (PVDC/VC) and polyvinylidene chloride/methyl acrylate copolymers (PVDC/MA), blends of PVdC and polycaprolactone (as those described in patent EP2064056 B1, example 1 to 7, particularly useful for respiring food products as certain cheeses), polyester homopolymers and copolymers, polyamide homopolymers and copolymers and their blends.

Preferably said inner gas-barrier layer (c) comprises at least 50%, 60%, 70%, 80%, 90%, 95% overall of one or more of the above polymers.

Preferably the inner gas-barrier layer (c) comprises a polymer selected among EVOH, polyvinylidene chloride copolymers (PVDC), polyvinylidene chloride/vinylchloride copolymers (PVDC/VC), polyvinylidene chloride/methyl acrylate copolymers (PVDC/MA) and blends of PVdC and polycaprolactone.

In one embodiment, the film of the present invention comprises an EVOH inner gas-barrier layer, preferably, a single EVOH or a blend of two or more EVOH resins as well as a blend of one or more EVOH resins with one or more polyamides.

In case of EVOH blended with polyamides, suitable polyamides are those commonly indicated as nylon 6, nylon 9, nylon 10, nylon 11, nylon 66, nylon 6/66, nylon 6,9 nylon 12, nylon 6,12, nylon 6,10, partially aromatic polyamides such as MXD6 and MXD6/MDI and the like, wherein a preferred polyamide is nylon 6/12, a copolymer of caprolactam with lauro lactam with a low melting temperature, such as GrilonTM CF 6S or GrilonTM CA6E manufactured and marked by EMS.

In one embodiment, the film of the present invention comprises a PVDC based inner gas-barrier layer.

Preferably, the inner gas barrier PVDC layer comprises more than 70%, 80%, 90%, 95% by weight of PVDC, more preferably of vinylidene chloride / methyl acrylate copolymers.

Preferably, for applications in which a high barrier performance is required, the inner gas barrier layer comprises a high barrier polymer having an OTR lower than 50 cm³/ m².day.atm, preferably lower than 30 cm³/ m².day.atm, more preferably lower than 20 cm³/ m².day.atm at 23°C and 0% relative humidity (ASTM D-3985).

Preferably, for applications in which a high barrier performance is required, the inner gas barrier layer comprises a high barrier polymer selected among EVOH, polyvinylidene chloride copolymers (PVDC), polyvinylidene chloride/vinylchloride copolymers (PVDC/VC) and polyvinylidene chloride/methyl acrylate copolymers (PVDC/MA).

Preferably, for applications in which a medium-barrier performance is required, the inner gas barrier layer comprises a medium-barrier polymer having an OTR from 50 to 500 cm³/ m².day.atm, preferably from 120 to 450 cm³/ m².day.atm, more preferably from 180 to 450 cm³/ m².day.atm at 23°C and 0% relative humidity (ASTM D-3985).

Preferably, for applications in which a medium-barrier performance is required, the inner gas barrier layer comprises a medium-barrier polymer, preferably comprising blends of PVdC and polycaprolactone.

Preferably the inner gas-barrier layer (c) comprises at least 70%, 80%, 90%, 95% of at least one gas barrier polymer.

Preferably the inner gas-barrier layer (c) comprises at least 70%, 80%, 90%, 95% of a blends of two or more gas barrier polymers.

Preferably the inner gas-barrier layer (c) has a thickness of at least 2%, 3%, 4% with respect to the total thickness of the film.

Preferably the second outer polymeric layer (d) comprises a polymer selected among polyolefins, ethylene-vinyl acetate copolymers, ionomers, (meth)acrylates copolymers, polyamides, polyesters and their blends.

Preferably said second outer polymeric layer (d) comprises at least 50%, 60%, 70%, 80%, 90%, 95% overall of one or more of the above polymers.

The second outer layer (d) may have the same composition of the outer heat-sealable layer (a) or it may have a different composition.

Preferably, it has a different composition.

The thickness of the second outer layer (d) may be in the same range as indicated for the heat-sealable outer layer (a).

The film according to the first object of the present invention may further comprise one or more additional inner layer(s) (e).

Preferably, the one or more additional layer(s) (e) comprises a polymer selected among EVA, ionomers, polyolefins, in particular polypropylene based resins, polyamides, polyesters and their blends.

Preferably the one or more additional layer(s) (e) comprises at least 50%, 60%, 70%, 80%, 90%, 95% overall of one or more of the above polymers.

Preferably the thickness of the one or more additional layer(s) (e) overall is up to 30%, preferably up to 20%, with respect to the total film thickness.

Preferably the thickness of the one or more additional layer(s) (e) overall is lower than 40%, preferably lower than 30% with respect to the total film thickness.

Preferably, in case of packaging of hot products, the present film may include one or more (d) or (e) layer(s) of thermal resistant materials such as for instance aromatic polyesters or polyamides commonly used in ovenable packages (see for instance EP2527142(A1) and EP1393897A2 and the thermal resistant materials mentioned therein).

The films of the present invention may further comprise one or more tie or adhesive layers (f).

Tie layers have the primary purpose of improving the adherence of two layers to each other. Tie layers may include polymers having grafted polar groups so that the polymer is capable of covalently bonding to polar polymers such as EVOH. Useful polymers for tie layers include ethylene/unsaturated acid copolymer, ethylene/unsaturated ester copolymer, anhydride-modified polyolefin, polyurethane, and their blends. Preferred polymers for tie layers, include one or more of ethylene/vinyl acetate copolymer having a vinyl acetate content of at least 15 weight %, ethylene/methylacrylate copolymer having a methyl acrylate content of at least 20 weight %, anhydride modified ethylene/methyl acrylate copolymer having a methyl acrylate content of at least 20%, and anhydride-modified ethylene/alpha-olefin copolymer, such as an anhydride grafted LLDPE. Modified polymers or anhydride-modified polymers include polymers prepared by copolymerizing an unsaturated carboxylic acid (e.g., maleic acid, fumaric acid), or a derivative such as the anhydride, ester, or metal salt of the unsaturated carboxylic acid with -- or otherwise incorporating the same into an olefin homopolymer or copolymer. Thus, anhydride-modified polymers have an anhydride functionality achieved by grafting or copolymerization.

These adhesive layers may have the same or a different composition and will comprise one or more modified polyolefins as indicated above possibly blended with one or more polyolefins.

Also the thickness of the adhesive layers may vary depending on the overall film thickness and on the type of resin employed. In general, however suitable adhesive layers typically have a thickness of from 1 to 4 μm , e.g., 2-3 μm . Additional adhesive layers may be present depending on the specific structure of the film.

Particularly preferred commercially available tie resins for the films of the present invention are ADMER AT2146E, Admer NF518E, Admer NF911E by Mitsui, Bynel 4104 , Bynel 3861 by Dupont and Plexar PX3227 by Equistar.

The multilayer heat-shrinkable film of the present invention, preferably has a total thickness lower than 120 μm , 100 μm , 90 μm , 80 μm , 70 μm .

The multilayer heat-shrinkable film of the present invention, preferably has a total thickness from 20 μm to 120 μm , more preferably from 30 μm to 100 μm , even more preferably from 35 μm to 90 μm .

It is quite surprising that films so thin - in which the total weight of thermoinsulating layer(s) preferably amounts to no more than 60%, more preferably no more than 50% by weight with respect to the whole film weight, and in which the whole content of plastic material of the container in the package amounts to a very low percentage by weight with respect to the weight of the packaged product - can effectively maintain the temperature of the packaged product for a time sufficient to perform common delivery operations.

Under similar circumstances, prior art generally suggests other solutions such as using very thick insulating layers (polystyrene foamed containers) or coupling thinner films with other insulating materials.

Preferably the film according to the present invention comprises from 4 to 20 layers, preferably from 4 to 12 layers and more preferably, from 4 to 9 layers.

However, the film of the present invention may include more than 20 layers, especially in case a microlayering manufacturing process is adopted (see for instance EP2655062).

The multilayer heat-shrinkable film first object of the present invention comprises both symmetrical and asymmetrical structures.

Non-limiting examples of possible layer sequences of the film of the present invention are the following:

a/b/c/d, a/c/b/d, a/e/b/c/d, a/b/e/c/d, a/b/c/b/d, a/e/b/e/c/d, a/c/b/e/b/d, a/b/e/c/e/b/d, a/c/b/e/b/e/d, a/e/b/c/b/e/d, a/e/b/e/b/c/d, a/b/e/c/e/d, a/b/e/c/e/b/d, a/c/e/b/d, a/c/e/b/e/d

wherein, in case of repetition of the same letter in one sequence, the compositions of the relative layers can be the same or different.

The above exemplary sequences are meant to possibly include one or more tie layers to confer the desired bonding between adjacent layers.

One or more of the layers of the film of the present invention may contain any of the additives conventionally employed in the manufacture of polymeric films. Thus, agents such as pigments, lubricants, anti-oxidants, radical scavengers, oxygen scavengers, UV absorbers, antimicrobial agents, thermal stabilisers, anti-blocking agents, surface-active agents, slip aids, optical brighteners, gloss improvers, viscosity modifiers may be incorporated as appropriate. In particular, to improve the processing of the film in high speed packaging equipment slip and/or anti-blocking agents may be added to one or both of the outer layers. The additives may be added in the form of a concentrate, preferably in a polyethylene carrier resin. More preferably the same masterbatch incorporates both the antiblock and the antifog agents. As an alternative, slip agents may be added by coating, for instance by plasma coating or by spraying. The amount of additive is typically in the order of 0.2 to 5% by weight of the total weight of the layer.

Preferably, the film according to the present invention is neither a laminate nor a composite.

Preferably said film is a co-extruded film, namely a film in which all the layers are extruded at the same time through the extrusion die.

The film of the present invention may be manufactured by co-extrusion or extrusion coating, using either a flat or a circular film die that allows to shape the polymer melt into a tape or a tube, or by lamination.

Preferably, the film of the present invention is not manufactured by lamination; more preferably the multilayer film of the present invention is manufactured by co-extrusion.

Preferably, the multilayer film is co-extruded through a round die to obtain a tube of molten polymer which is quenched immediately after extrusion without being expanded, optionally cross-linked, then heated to a temperature which is above the Tg of all the resins employed and below the melting temperature of at least one of the resins employed, typically by passing it through a hot water bath or heating it with an IR oven or with hot air, and expanded, still at this temperature by internal air pressure to get the transversal orientation and by a differential speed of the pinch rolls which hold the thus obtained "trapped bubble" to provide the longitudinal orientation.

The film is then rapidly cooled to somehow freeze the molecules of the film in their oriented state and wound.

Furthermore, in some instances it may be desirable to submit the oriented structure to a controlled heating-cooling treatment (so-called annealing) that is aimed at having a better control on low temperature dimensional stability of the heat-shrinkable film.

5 Alternatively, the oriented film may also be prepared by flat co-extrusion followed by orientation in one or both directions via tenter-frame and optionally annealing. Orientation may be carried out in such a case either sequentially or simultaneously. Depending on the number of layers in the final structure it may be advisable or necessary to split the co-extrusion step: in such a case a tube or a sheet is first
10 formed of a limited number of layers; this tube or sheet is then quenched quickly and before submitting it to the orientation step it is extrusion-coated with the remaining layers

The coating step can be simultaneous, by coextruding all the remaining layers altogether, so as to simultaneously adhere all of them, one over the other, to the
15 quenched tube or sheet obtained in the first extrusion step, or this coating step can be repeated as many times as the layers which are to be added.

If desired, the film may be cross-linked, either chemically or, preferably, by irradiation. Typically to produce cross-linking, an extrudate is treated with a suitable radiation dosage of high energy electrons, preferably using an electron accelerator,
20 with the dosage level being determined by standard dosimetry methods. A suitable radiation dosage of high-energy electrons is in the range of up to about 120 kGy, more preferably about 16-80 kGy, and still more preferably about 34-64 kGy. Other accelerators such as a Van der Graff generator or resonating transformer may be used.

25 The radiation is not limited to electrons from an accelerator since any ionizing radiation may be used.

Irradiation is preferably performed prior to orientation, and it is carried out either on the overall co-extruded or extrusion-coated tape, or preferably, on the primary extruded tape before extrusion coating. Irradiation could however be performed also
30 after orientation.

In an embodiment, the film of the present invention is not a cross-linked film.

The multilayer heat-shrinkable film of the present invention is mono-axially or, preferably, biaxially oriented.

Preferably, orientation ratios for the films of the present invention are from 2:1 to 6:1, preferably from 2.5:1 to 5:1, more preferably from 3:1 to 4.5:1 in at least one of the LD or TD directions, preferably in both LD and TD directions.

After having been stretched, the film is quickly cooled while substantially retaining its stretched dimensions to somehow freeze the molecules of the film in their oriented state and rolled for further processing.

Preferably, the oriented multilayer film of the present invention may be annealed in order to tailor its shrink properties, according to known techniques such as for instance by using the "triple bubble" technology – in which a bubble is first extruded downward into a water quench, then the tube is reheated and inflated in an orienting station ("second bubble") and finally it goes to an annealing station ("third bubble") (in process annealing) or by conveying the film obtained from the solid state orientation step, either as a flattened tubular film or as a mono-ply film to a separated conventional annealing station. In such a case the film may be heated to the selected annealing temperature by conventional techniques, such as, by exposure of the film to radiant elements, by passage of the film through a heated air oven or an IR oven, or by contact of the film with the surface of one or more heated plates or rollers.

Preferably, the annealing temperature used for the present films is from 30°C to 60°C, more preferably from 35°C to 55°C, most preferably at about 40°C.

Preferably, the present film has a free shrink of at least 20% preferably of at least 25%, more preferably of at least 30% at 90°C in at least one of longitudinal or transversal directions.

Preferably, the present film has a max shrink tension of at least 5 Kg/cm², more preferably of at least 8 Kg/cm² in at least one of LD or TD directions.

Preferably, the films of the present invention have a thermal conductivity, measured according to the reference method of ASTM E1530 for thin films lower than 0.085 (W/mK), preferably lower than 0.07 (W/mK), 0.06(W/mK).

The films of the present invention may be printed by using techniques well known in the art.

In one preferred embodiment, the multilayer heat-shrinkable film of the present invention has the following sequence of layers: a/e/b/e/c/d in which:

- (a) the first outer heat sealable polymeric layer consists of VLDPE;
- (e) the inner additional layers consist of EVA;

(b) the inner foamed polymeric layer consists of a blend of an ionomer and a LDPE;

(c) the inner gas-barrier layer consists of a PVDC-MA copolymer, and

(d) the second outer polymeric layer consists of EVA.

5 A second object of the present invention is a heat shrinkable foamed flexible container in the form of a bag or a pouch, obtained by sealing the film of the present invention to itself.

The self sealing of the film according to the present invention can be accomplished in a fin seal and/or lap seal mode, preferably by having the outer heat sealable layer

10 a) heat sealed to itself, i.e. in a fin seal mode.

The heat-shrinkable foamed flexible container can be an ES bag (end-seal bag), obtainable from a flattened tubing of thermoplastic material by transversely sealing and severing the bottom end of the bag, or a TS bag (transverse seal bag), typically obtained by folding longitudinally a flat film and sealing and severing it transversely.

15 In both the ES and TS bags currently available on the market, the seals are fin seals i. e. seals where one surface of the packaging film is always sealed to itself.

In one embodiment, the foamed flexible container is a lay-flat, end-seal bag made from a seamless tubing, the end-seal bag having an open top, first and second folded side edges, and an end seal across a bottom of the bag.

20 In one embodiment, the foamed flexible container is a lay-flat, side-seal bag made from a seamless tubing, the side-seal bag having an open top, a folded bottom edge, and first and second side seals

In one embodiment, the foamed flexible container is a lay-flat, V-shaped side-seal bag made from a seamless tubing, the side-seal bag having an open top, a folded
25 bottom edge, and first and second side seals. Said first and second side seals can be completely angled with respect to the open top, thus providing a triangular or almost triangular bag or, preferably, can be partially straight (i.e. perpendicular to the open top) and then partially angled, conferring a more trapezium-like shape.

In one embodiment, the foamed flexible container is a lay-flat pouch made by heat
30 sealing two flat films to one another, the pouch having an open top, a first side seal, a second side seal and a bottom seal (U-seal pouch).

The foamed flexible container optionally comprises at least one tear initiator, such as a tab or a flap.

Optionally, the foamed flexible container may have a portion of at least one sidewall made of a non-foamed highly transparent film to allow an easier visual inspection of the packaged product.

A third object of the present invention is a package comprising a product packaged
5 into a foamed flexible container according to the invention

The package, according to the present invention, can be manufactured by (i) inserting a product into a lay-flat foamed flexible container according to the invention, said container having at least one unsealed side (ii) optionally vacuumizing or modifying the internal atmosphere, (iii) sealing said at least one
10 unsealed side with at least one heat seal, thereby forming a closed package and (iv) heating the heat-shrinkable film to shrink the package around the product.

Preferably, the package according to the present invention is under vacuum.

Alternatively, the package according to the present invention can be manufactured through a form-fill-seal process. This process is known and provides flexible
15 packages with a median longitudinal seal and two transversal seals.

Suitable equipment for this method of packaging are named Horizontal Form-Fill-Seal (HFFS) or a Vertical Form-Fill Seal (VFFS) machines.

A FFS machine, either Horizontal or Vertical, typically includes a former for forming a flat web of film into a tubular configuration, a longitudinal sealer to seal the
20 overlapped longitudinal edges of the film in the tubular configuration, a conveyor for feeding the products into the tubular film one after the other in suitably spaced configuration, or a feeding tube in case of a VFFS machine, and a transverse sealer for sealing the tubular film in a cross-wise direction to separate the products into discrete packages.

The transverse sealer may be operated to simultaneously seal the bottom of the
25 leading pouch and the front of the following pouch and sever the two seals as well as the leading package from the front sealed tubing.

Alternatively, in the HFFS process, the transverse seal may be operated to sever the leading package from the following tubular portion and sealing the front of said
30 tubular portion thus creating the sealed bottom of the next leading pouch. In this way the leading pouch containing the product to be packaged has a longitudinal seal and only one transverse seal.

Preferably, it may be vacuumized before a second transverse seal hermetically closes it. Also in this case, the oriented heat-shrinkable foamed film of the present

invention is employed as the packaging material and the vacuumized package is then shrunk to achieve the desired packed appearance.

In the FFS processes, while the transverse seals are always fin seals, the longitudinal seal can be either a fin seal or a lap seal, i. e. a seal where the innermost layer of the film is sealed to the outermost layer of the same film.

A fourth object of the present invention is a package comprising a tray, a product placed into the tray and a lid sealed all around the tray thus enclosing said product, wherein said lid comprises a film according to the present invention.

The film of the present invention can also be used in tray lidding applications.

In fact, the present film advantageously improves thermo-insulation with respect to packages comprising the same trays but in which the lid is a traditional, non-foamed barrier multilayer film.

Preferably, the tray lidded package is vacuumized.

Preferably, the tray lidded package is under a modified atmosphere.

Preferably, the product packaged in the packages of the present invention is a thermo sensitive product such as a drug, a protein, a vaccine or food.

Preferably, the product packaged in the packages of the present invention is a food product.

Preferably, the product packaged in the packages of the present invention is meat or fish or vegetables or fruits or cheese or dairy.

The present invention will now be better described with particular reference to the following Examples.

Examples

In the following Table 1 details on the resins used in the manufacturing of the films of the examples are given:

Table 1

Tradename	Supplier	Chemical Nature	Acronym	Parameters	Value	Units
AFFINITY PL 1845G	DOW	Polyethylene, Very Low Density Ethylene Octene	VLDPE1	Density	0.91	g/cm ³
				Melt Flow Rate (1)	3.5	g/10 min

		Copolymer - Linear, Single Site		Melting Point	103	°C
				Vicat softening point	95	°C
AFFINITY PL 1281G1	DOW	Polyethylene, Very Low Density Ethylene /Octene Copolymer branched, Single Site	VLDPE2	Density	0.900	g/cm ³
				Melt Flow Ratio	8	-
				Melt Flow Rate (1)	6.0	g/10 min
				Comonomer content	13	%
AFFINITY PL 1881G	DOW	Polyethylene, Very Low Density Ethylene/ Octene Copolymer - Branched, Single Site	VLDPE3	Vicat softening point	88	°C
				Density	0.904	g/cm ³
				Melting point	100	°C
				Melt Flow Rate (1)	1	g/10 min
Escorene ULTRA FL00119	Exxon Mobil	Ethylene/Vinyl Acetate Copolymer - More than 20 wt % of vinyl acetate	EVA1	Comonomer content	19.00	%
				Density	0.942	g/cm ³
				Melt Flow Rate (1)	0.650	g/10 min
				Melting Point	85.00	°C
				Vicat softening point	62.00	°C
ESCORENE FL 00212	Exxon Mobil	Ethylene/Vinyl Acetate Copolymer - Between 10-20 wt % of vinyl acetate	EVA2	Density	0.933	g/cm ³
				Comonomer content	12	%
				Melting point	93.0	°C
				Melt Flow Rate (1)	2.50	g/10 min
Braskem TN20	Braskem	Ethylene/Vinyl Acetate Copolymer -	EVA	Melt Flow Rate (1)	0.70	g/10 min

		Between 10-20 wt % of vinyl acetate		Density	0.940	g/cm ³
				Comonomer content	18.00	%
				Melting point	90	°C
				Moisture Content	Max. 0.3	%
				Vicat softening point	70	°C
EVA 1020 VN3	Total Petrochemicals	Ethylene/Vinyl Acetate Copolymer - Less than 10 wt % of vinyl acetate	EVA4	Melt Flow Rate (1)	3	g/10 min
				Density	0.929	g/cm ³
				Comonomer content	9	%
				Melting point	97.5	°C
				Vicat softening point	79	°C
EVA 1005 VN 35	Total Petrochemicals	Ethylene/Vinyl Acetate Copolymer - Between 10-20 wt% of vinyl acetate	EVA5	Comonomer content	12	%
				Density	0.932	g/cm ³
				Melting point	93	°C
				Melt Flow Rate (1)	0.50	g/10 min
Surlyn 1601	DuPont	Sodium Neutralized Ethylene Methacrylic Acid Copolymer	EMAA-Na	Density	0.940	g/cm ³
				Melt Flow Rate (1)	1.30	g/10 min
				Vicat softening point	74	°C
				Melting Point	98	°C

Hydrocer ol CF40E	Clariant	Foaming Agent in Polyethylene, Low Density	LDPE	Density	1.54	g/cm ³
IXAN PV910	SolVin	Vinylidene Chloride/Methyl Acrylate Copolymer - Stabilized	PVDC-MA	Density	1.71	g/cm ³
				Comonomer content	8.4	%
				Viscosity Relative	Min. 1.44 - Max. 1.48	-
				Viscosity Solution	1.46	mPa. sec

Keys (1) Melt Flow Rate = Cond. 190°C / 02.16 kg

Example 1

A 80 µm six-layer film having the following layer sequence, composition and partial thicknesses:

5

Table 2

Layer 1	Layer 2	Layer 3 foamed	Layer 4	Layer 5	Layer 6
VLDPE1 100%	EVA1 100%	EMAA-Na 98%; LDPE 2% with foaming agent	EVA1 100%	PVDC-MA 100%	EVA1 100%
18.1 µm	7.0 µm	37.6 µm	5.6 µm	6.3 µm	5.6 µm

was prepared by co-extrusion through a round die and by orientation by trapped bubble process.

In particular, a substrate formed of the above layers 1 to 6, wherein the heat-sealing layer is the innermost layer of the tube and layer 6 is the outermost layer, was co-extruded and quickly quenched with a water cascade. The substrate was not cross-linked. The quenched co-extruded tube was then re-heated by passing through a water bath at about 90°C, and oriented at this temperature (with orientation ratios of about 3.4: 1 in the longitudinal direction and about 3.0: 1 in the transverse direction) by double-bubble process.

15

The film was then cooled by air kept at 8°C, and then annealed by passing through rollers kept at 40°C. Finally cooled by passing through rollers kept at 15°C.

The final tubular film had a thickness of 80 μm . The foamed layer (b) is 45% by weight of the whole film weight.

Example 2

An 85 μm six-layer film having the following layer sequence, composition and partial thicknesses:

Table 3

Layer 1	Layer 2	Layer 3 foamed	Layer 4	Layer 5	Layer 6
VLDPE1 100%	EVA1 100%	EMAA-Na 98% LDPE 2% with foaming agent	EVA1 100%	PVDC-MA 100%	EVA2 100%
18.3 μm	7.0 μm	42.2 μm	5.6 μm	6.3 μm	5.6 μm

was prepared according to the same manufacturing process described for Example 1, with orientation ratios of about 3.4: 1 in the longitudinal direction and about 2.9: 1 in the transverse direction.

Layer 1 is the heat-sealing layer and the innermost layer of the tube while layer 6 is the outermost layer of the overall tube.

The foamed layer (b) is 47% by weight of the whole film weight.

The final film was characterized by the following properties, measured according to the test methods shown hereinafter:

Modulus (LD-TD): 2600-1080 Kg/cm^2

Tensile strength (LD-TD): 287-157 Kg/cm^2

Elongation at break (LD-TD) 111%-125 %

Free shrink at 90°C (LD-TD) 38-38 %

Max Shrink Tension (LD- TD) 12 - 8 Kg/cm^2

Example 3

A 115 μm six-layer film having the following layer sequence, composition and partial thicknesses:

Table 4

Layer 1	Layer 2	Layer 3 foamed	Layer 4	Layer 5	Layer 6
VLDPE1 100%	EVA1 100%	EMAA-Na 96% LDPE 4% with foaming agent	EVA1 100%	PVDC-MA 100%	EVA1 100%
21.8 μm	8.4 μm	62.8 μm	6.7 μm	7.6 μm	6.8 μm

was prepared according to the same manufacturing process described for Example 1.

The foamed layer (b) is 53% by weight of the whole film weight.

Layer 1 is the heat-sealing layer and the innermost layer of the tube while layer 6 is the outermost layer.

Example 4 (Comparative)

A 45 μm six-layer comparison film having the following layer sequence, composition and partial thicknesses:

Table 5

Layer 1	Layer 2	Layer 3 non foamed	Layer 4	Layer 5	Layer 6
VLDPE2 80% VLDPE1 20%	EMAA- Na 100%	EVA3 100%	PVDC- MA 100%	EVA4 100%	VLDPE3 70% EVA5 30%
8.1 μm	13.7 μm	5.6 μm	4.8 μm	4.0 μm	8.8 μm

was prepared by extrusion coating through a round die according to the following manufacturing process.

A substrate formed of layers 1 to 3 -wherein the heat-sealing layer is the innermost layer of the tube- was co-extruded, quickly quenched with a water cascade, irradiated at a dosage level of 64 kGy. The substrate was then coated with the sequence of three layers, 4 to 6 -wherein layer 6 is the outermost layer of the tube. The extrusion coated tube (thickness: 560 μ) was then quenched, re-heated by passing through a water bath at about 90° C, and oriented at this temperature (with orientation ratios of about 3.7: 1 in the longitudinal direction and about 3.65: 1 in the transverse direction) by double-bubble process.

The film was then cooled by air kept at 8°C, and then annealed by passing through rollers kept at 40°C. Finally cooled by passing through rollers kept at 15°C.

The final film was characterized by the following properties, measured according to the test methods shown hereinafter:

Modulus (LD-TD) 3000-2800 Kg/cm²

Tensile strength (LD-TD) 710-711 Kg/cm²

Elongation at break (LD-TD) 99-147 %

Free shrink at 90°C (LD-TD) 54-53 %

Max Shrink Tension (LD-TD) 23-21 Kg/cm²

This film is a commercial product used for manufacturing shrinkable barrier bags for food packaging.

Test methods

The films of the present invention (foamed inner layer ex. 1-3) and the comparative film (not foamed inner layer ex. 4) were evaluated according to the following test methods:

Thermal conductivity (ASTM E1530)

Thermal conductivity of the films of the invention (Ex.1 to 3) and of the comparative film (Ex. 4) was evaluated according to the standard method detailed in ASTM E1530, with the following results:

Table 6

Sample	T (°C)	Thermal Conductivity (W/mK)
Ex. 1	20.0	0.053
Ex. 2	19.2	0.048
Ex. 3	18.4	0.055
Ex. 4	18.9	0.089

The values of thermal conductivity reported in Table 6 are the median values of 3 measures, performed - according to the reference method of ASTM E1530 for thin films - by superimposing 4, 6 and 8 samples of each film respectively (stacking technique). The instrument DTC-300 Thermal Conductivity Meter in "Thin Film" operating mode automatically applies a correction to eliminate interfacial contributions.

As can be seen from the thermal conductivity values in Table 6 above, the films of the invention show better thermo insulating properties with respect to the non-foamed comparative film.

Shrink tensions

Maximum shrink tension (kg/ cm²) and residual cold shrink tension (at 5°C) (kg/ cm²) were measured through an internal method.

The maximum shrink tension is the maximum value of the tension developed by the materials during the heating/shrinking process. Specimens of the films (2.54 cm x 14.0 cm, of which 10 cm are free for testing) are cut in the transverse (TD) direction of the film and clamped between two jaws, one of which is connected to a load cell. The two jaws keep the specimen in the center of a channel into which an impeller

blows heated or cold air and two thermocouples measure the temperature. The thermocouples are positioned as close as possible (less than 3 mm) to the specimen and in the middle of the same. The signal supplied by the thermocouples (which is the testing temperature) and the signal supplied by the load cell (which is the force) are sent to a computer where a software records these signals. The impeller starts blowing hot air and the force released by the sample is recorded in grams. The temperature is increased from 23°C to 180°C at a rate of about 2.5 °C/second by blowing heated air.

The maximum shrink tension is calculated by dividing the maximum force value in kg (force at peak) by the specimen width (expressed in cm) and by the specimen average thickness (expressed in cm) and is expressed as kg/ cm².

Free Shrink % (90°C, ASTM D2732): (%): the % free shrink, i.e., the irreversible and rapid reduction, as a percent, of the original dimensions of a sample subjected to a given temperature under conditions where nil restraint to inhibit shrinkage is present, was measured according to ASTM method D 2732, by immersing for 5 seconds specimens of the films (100-mm by 100-mm) into a bath of hot water at 90°C. The % free shrink was measured in both the longitudinal (machine) and transverse directions of the film. Three specimens in LD and three specimens in TD were measured for each film.

The percent free shrink is defined, for each direction, as the unrestrained linear shrinkage of the film and it is calculated by the formula $[(L_o - L_f)/L_o] \times 100$ wherein L_o is the initial length of the film specimen in mm before the test and L_f is the length of the film specimen in mm after shrinking.

Modulus, Tensile strength and Elongation at break (measured according to ASTM D882)

Evaluation of thermo-insulating properties of foamed flexible containers

The above multilayer films of Examples 2 and 4 were converted into rectangular bags named respectively A and B (130 mm x 250 mm) by sealing with a Thimonnier impulse-sealing bar (set 0.4 – 0.5). A rubber parallelepiped block of, about 650g was inserted into each bag, together with an Extra Tag temperature logger. Before sealing, the bags were manually squeezed in order to remove as much air as possible.

Another Extra Tag temperature logger was taken outside the bags as reference C and submitted to the same cooling- heating treatments of the packages.

The two packages A and B and the reference logger C were cooled into a freezer at -18°C . When the temperatures of A, B and C were equal and stabilized, they were removed from the freezer and put into a thermostatic room at 23°C . The temperature increase inside the packages A and B (packaged with foamed vs non foamed films) and of the logger C (no package) was measured at time intervals of 60 seconds up to reaching 23°C .

As expected, we observed a significant delay in reaching a pre-fixed temperature for the packaged samples A, B vs the unpackaged one C.

Furthermore, it appeared that the reheating time of the package of the invention A was noticeably higher than that of the comparison package B.

The times required to each sample to reach pre-fixed temperatures are reported in the following Table 7:

Table 7

Target Temperature	A Foamed Bag INV (Ex. 2)	B Non-foamed Bag REF (Ex. 4)	C No bag REF
	Time min.	Time min	Time min
$+10^{\circ}\text{C}$	280	265	237
$+15^{\circ}\text{C}$	320	294	253
$+20^{\circ}\text{C}$	438	379	292

As shown above, the films and the bags of the invention, notwithstanding the very low weight of foamed resins used and the thinness of the foamed layer, are characterized by insulating properties which preserve the internal temperature of the packaged item long enough for the most common delivery operations.

In conclusions, the films of the invention provide for seal tight, thermo-insulated, gas barrier and packed packages, which – with minimal amount of plastics with respect to traditional insulating containers - represent an environmentally friendly solution to the problem of preservation and life-extension of sensitive items such as food or medicines.

Preferably, the present packages may be used to preserve the temperature of refrigerated or frozen meat or fish or drugs or thermolabile products and to keep them cool enough for the most common daily delivery needs (e.g from the supermarket or the pharmacy to the house refrigerator).

In alternative, the present packages may be used to preserve the temperature of warm products such as cooked food (e.g. pizza, chicken etc) long enough to bring them home still warm for consumption from the shop.

Advantageously, the present containers are very light, very packed and require

5 lower amounts of plastics.

CLAIMS

1) A multi-layer heat-shrinkable optionally cross-linked packaging film comprising:

- (a) a first outer heat sealable polymeric layer,
- (b) at least an inner foamed polymeric layer,
- 5 (c) at least an inner gas-barrier layer, and
- (d) a second outer polymeric layer.

2) The film according to claim 1 wherein said inner foamed polymeric layer (b) comprises at least a polymer selected among ionomers, EVA, polyolefins, polystyrenes, polyurethanes, and their blends, preferably a ionomer blended with a polyolefin.

3) The film according to anyone of the previous claims wherein said inner foamed polymeric layer (b) has a thickness of:

- at least 10 μm , 20 μm , 30 μm , 40 μm , 50 μm and/or no more than 100 μm , 80 μm , 70 μm , 65 μm , 60 μm , 50 μm , 40 μm , 30 μm ;

and/or

- at least 20%, 30%, 40%, 50%, 55% and/or no more than 80%, 60%, 50%, 40%, 30% with respect to the total thickness of the film.

4) The film according to anyone of the previous claims wherein said inner foamed polymeric layer (b) has a percentage by weight of no more than 60%, 50%, 40%, 30%, 20%, 10% with respect to the total weight of the film.

5) The film according to anyone of the previous claims comprising two or more inner foamed layers (b).

6) The film according to anyone of the previous claims wherein said inner foamed polymeric layer (b) comprises elongated closed cells and/or has a density from 0.3 to 0.8 g/cm^3 , preferably from 0.4 to 0.7 g/cm^3 .

7) The film according to anyone of the previous claims wherein:

- said first outer heat sealable polymeric layer (a) comprises one or more polymers selected from the group of ethylene homopolymers, ethylene co-polymers, propylene homopolymers and propylene co-polymers, ionomers and their blends; and/or

- said inner gas-barrier layer (c) comprises a polymer selected among polyvinyl alcohol copolymers (PV/A), ethylene/vinyl alcohol copolymers (EVOH), polyvinyl chlorides (PVC), polyvinylidene chloride copolymers (PVDC), polyvinylidene chloride/vinylchloride copolymers (PVDC-VC), polyvinylidene chloride/methyl

acrylate copolymers (PVDC/MA), blends of polyvinylidene chloride/vinylchloride copolymers (PVDC/VC) and polyvinylidene chloride/methyl acrylate copolymers (PVDC/MA), blends of PVdC and polycaprolactone, polyester homopolymers and copolymers, polyamide homopolymers and copolymers and their blends; and/or

5 - said second outer polymeric layer (d) comprises a polymer selected among polyolefins, ethylene-vinyl acetate copolymers, ionomers, (meth)acrylates copolymers, polyamides, polyesters and their blends.

8) The film according to anyone of the previous claims further comprising:

10 - one or more additional inner layer(s) (e) comprising a polymer selected among EVA, ionomers, polyolefins, in particular polypropylene based resins, polyamides and their blends; and/or

- one or more tie or adhesive layers (f) comprising ethylene/unsaturated acid copolymer, ethylene/unsaturated ester copolymer, anhydride-modified polyolefin, polyurethane, or their blends.

15 9) The film according to anyone of the previous claims which has a total thickness lower than 120 μm , 100 μm , 90 μm , 80 μm , 70 μm .

10) The film according to anyone of the previous claims which is biaxially oriented and/or has a free shrink of at least 20% preferably of at least 25%, more preferably of at least 30% at 90°C in at least one of longitudinal or transversal directions (ASTM
20 D 2732)

11) The film according to anyone of the previous claims, which is a co-extruded film.

12) The film according to anyone of the previous claims, which is not a cross-linked film.

13) A heat shrinkable foamed flexible container in the form of a bag or a pouch,
25 obtained by sealing the film according to anyone of claims 1 to 12 to itself.

14) A package comprising a product packaged into a foamed flexible container according to claim 13.

15) A package comprising a tray, a product placed into the tray and a lid sealed all around the tray thus enclosing said product, wherein said lid comprises a film
30 according to anyone of claims 1 to 12.

16) The package of claim 14 or 15 wherein said product is a food product.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/059641

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B32B5/32	B32B7/12
	B32B27/32	B32B27/36
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)		
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	EP 0 481 081 A1 (NIPPON PETROCHEMICALS CO LTD [JP]) 22 April 1992 (1992-04-22) page 2, line 54 - page 3, line 22 page 6, line 8 - line 48; table 2 -----	1-16
A	EP 2 805 821 A1 (CRYOVAC INC [US]) 26 November 2014 (2014-11-26) paragraphs [0001] - [0005], [0045] - [0053] -----	1-16
☐ 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		Date of mailing of the international search report
22 June 2016		30/06/2016
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 Aspeby, Erika

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/059641

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0481081	A1	22-04-1992	CA 2049920 A1 13-07-1991
			EP 0481081 A1 22-04-1992
			JP H03208630 A 11-09-1991
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