

ABSTRACTPACKAGING BASED ON A POLYMER CONTAINING POLYAMIDEBLOCKS AND POLYETHER BLOCKS

The invention relates to a packaging
5 comprising a thermoplastic film based on a polymer
containing polyamide blocks and polyether blocks, which
is permeable to vapour, ethylene, CO₂ and oxygen, the
permeability to CO₂ being very much greater than that to
oxygen.

10 The packaging according to the invention is
particularly useful for making sachets for conserving
fresh fruit and vegetables or meat.

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PACKAGING BASED ON A POLYMER CONTAINING POLYAMIDE

BLOCKS AND POLYETHER BLOCKS

The invention relates to packaging based on a polymer containing polyamide blocks and polyether blocks for use in conserving fresh produce, such as fruit and vegetables or freshly cut meat, and particularly for conserving the taste of fruit or vegetables which have just been harvested, and also for preventing their degradation.

Canadian Patent Specification CA 1,324,476 describes lettuce sachets consisting of a perforated first film and a second film adhesively bonded to the first. The perforated film may be made of polyethylene, polypropylene, drawn polyester or drawn polyamide. The second film is itself a multilayer successively comprising a film of ethylene/vinyl acetate (EVA) copolymer, a central oxygen-permeable film and a film which may be heat-sealed.

Japanese Patent Specification JP 05 230 235 (KOKAI) describes perforated films consisting of a mixture of low-density polyethylene, Nylon-6 and maleic-treated polyethylene. These perforated films have good permeability to oxygen and to water vapour. They are used to make sachets for conserving freshly picked mushrooms.

Japanese Patent Application JP 03 180 124 describes sachets made of film which is permeable to



water vapour, to air and to ethylene, in order to ripen
peaches on the tree. The film consists of a mixture of
polyolefins and fillers such as calcium carbonate or
silica, and the film is drawn in order to create spaces
5 between the polyolefin and the fillers.

It has surprisingly been found that
thermoplastic films based on a polymer containing
polyamide blocks and polyether blocks are permeable to
water vapour, ethylene, CO_2 and oxygen, the permeability
10 to CO_2 being very much greater than that to oxygen and
are useful in packaging.

Accordingly the invention comprises packaging
comprising a thermoplastic film based on a polymer
containing polyamide blocks and polyether blocks which
15 is permeable to water vapour, ethylene, CO_2 and oxygen,
the permeability to CO_2 being very much greater than
that to oxygen.

The invention also provides the use of such a
thermoplastic film for packaging.

20 The invention further provides a method of
packaging fresh produce which method comprises applying
to the produce packaging material according to the
invention.

The films used according to the invention may
25 be formed into sachets by conventional means such as,
for example, hot bonding or welding. Fruit or
vegetables which have just been harvested may be placed
in the sachets and the sachet then sealed. The films

may also be used to cover pots or trays containing fresh produce.

The films according to the invention may be used as unperforated continuous films. In contrast to perforated films, the films of the invention may thus
5 be bacteria-proof and germ-proof.

Polymers containing polyamide blocks and polyether blocks suitable for use according to the invention may be formed by copolycondensation of
10 polyamide units containing reactive ends with polyether units containing reactive ends, such as, inter alia:

- 1) Polyamide units containing diamine chain terminations with polyoxyalkylene units containing dicarboxylic chain terminations.
- 15 2) Polyamide units containing dicarboxylic chain terminations with polyoxyalkylene units containing diamine chain terminations obtained by cyanoethylation and hydrogenation of aliphatic alpha-omega dihydroxylated
20 polyoxyalkylene units referred to as polyether diols.
- 3) Polyamide units containing dicarboxylic chain terminations with polyether diols, the products obtained in this particular case
25 being polyether ester amides.

Polyamide units containing dicarboxylic chain terminations may be obtained, for example, from the

condensation of alpha-omega aminocarboxylic acids of lactams or of dicarboxylic acids and diamines in the presence of a chain-limiting dicarboxylic acid. The polyamide blocks are advantageously Nylon-12.

5 The number-average molar mass $\bar{M}_n$ of the polyamide units is typically between 300 and 15,000 and preferably between 600 and 5000. The mass $\bar{M}_n$ of the polyether units is typically between 100 and 6000 and preferably between 200 and 3000.

10 The polymers containing polyamide blocks and polyether blocks may also comprise randomly distributed moieties. These polymers may be prepared by the simultaneous reaction of the polyether and the precursors of the polyamide blocks. For example, a
15 polyether diol, a lactam (or an alpha-omega amino acid) and a chain-limiting diacid may be reacted in the presence of a small amount of water. A polymer is then obtained which essentially has polyether blocks, polyamide blocks of very variable length, but also the
20 various reactants which have reacted randomly and which are randomly distributed along the polymer chain.

 Whether they are prepared from the copolycondensation of polyamide units and polyethers previously prepared or in a one-step reaction, these
25 polymers containing polyamide blocks and polyether blocks may have, for example, Shore hardnesses D which may be between 20 and 75 and advantageously between 30 and 70 and an intrinsic viscosity between 0.8 and 2.5

measured in meta-cresol at 250°C for an initial concentration of 0.8 g/100 ml.

Whether the polyether blocks are derived from polyethylene glycol, from polyoxypropylene glycol or from polyoxytetramethylene glycol, they may be used as they are and copolycondensed with polyamide blocks containing carboxylic ends, or they may be aminated to convert them into polyether diamines and condensed with polyamide blocks containing carboxylic ends. They may also be mixed with polyamide precursors and a chain limiter to make polymers containing polyamide blocks and polyether blocks which have randomly distributed moieties.

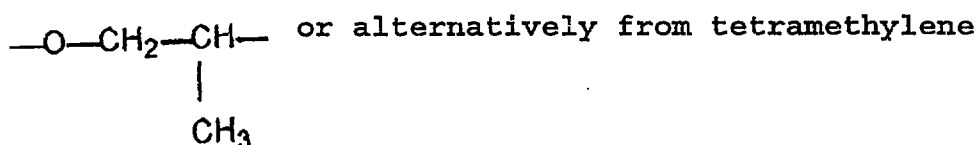
Suitable polymers containing polyether and polyamide blocks are described in US Patents 4,331,786, 4,115,475, 4,195,015, 4,839,441, 4,864,014, 4,230,838 and 4,332,920.

The polyether may be, for example, a polyethylene glycol (PEG), a polypropylene glycol (PPG) or a polytetramethylene glycol (PTMG). This last polyether is also referred to as polytetrahydrofuran (PTHF).

Whether the polyether blocks are in the chain of the polymer containing polyamide blocks and polyether blocks in the form of diols or diamines, they are referred to for simplicity as PEG blocks or PPG blocks or alternatively PTMG blocks.

It would not be departing from the scope of

the invention if the polyether blocks contain different moieties such as moieties derived from ethylene glycol ($\text{—OC}_2\text{H}_4\text{—}$), from propylene glycol



glycol ($\text{—O—(CH}_2\text{)}_4\text{—}$).

5 The polymer containing polyamide blocks and polyether blocks preferably comprises only one type of polyamide block and only one type of polyether block. Polymers containing PA-12 blocks and PEG blocks and
10 polymers containing PA-12 blocks and PTMG blocks are advantageously used.

The polymers containing PEG blocks have a much higher permeability to water vapour than do the polymers containing PTMG blocks.

15 It is also possible to use a mixture of these two polymers containing polyamide blocks and polyether blocks.

The polymer containing polyamide blocks and polyether blocks is advantageously such that the
20 polyamide is the major constituent by weight, that is to say that the amount of polyamide which is in the form of blocks and that which is optionally distributed randomly in the chain represents 40 % by weight or more of the polymer containing polyamide blocks and
25 polyether blocks. Advantageously, the amount of

polyamide and the amount of polyether are in the ratio (polyamide/polyether) 1/1 to 3/1 and preferably:

The films of the invention are, for example, between 10 and 150 μm in thickness.

5 The film of the invention may also comprise plasticizers, antioxidants or anti-UV agents.

 According to a preferred embodiment of the invention, the film used also contains polyolefin. The term polyolefin is understood to refer to polymers
10 comprising olefin moieties such as, for example, ethylene, propylene, 1-butene, etc. moieties.

 Examples which may be mentioned are:

 - polyethylene, polypropylene and copolymers of ethylene with alpha-olefins, it being possible for
15 these products to be grafted with unsaturated carboxylic acid anhydrides such as maleic anhydride or unsaturated epoxides such as glycidyl methacrylate.

 - copolymers of ethylene with at least one product chosen from (i) unsaturated carboxylic acids, salts thereof and esters thereof, (ii) vinyl esters of
20 saturated carboxylic acids, (iii) unsaturated dicarboxylic acids, salts thereof, esters thereof, hemiesters thereof and anhydrides thereof, and (iv) unsaturated epoxides, it being possible for these
25 ethylene copolymers to be grafted with unsaturated dicarboxylic acid anhydrides or unsaturated epoxides.

 - optionally maleic-treated styrene/ethylene-butene/styrene (SEBS) block copolymers.

Mixtures of two or more of these polyolefins may be used.

The following are advantageously used:

- polyethylene
- 5 - copolymers of ethylene and an alpha-olefin,
- copolymers of ethylene/an alkyl
 (meth)acrylate,
- copolymers of ethylene/an alkyl
 (meth)acrylate/maleic anhydride, the maleic anhydride
- 10 being grafted or copolymerized,
- copolymers of ethylene/an alkyl
 (meth)acrylate/glycidyl methacrylate, the glycidyl
 methacrylate being grafted or copolymerized.

If the polyolefins have few or no functional
15 groups which may facilitate compatibilization, it is
recommended to add a compatibilizing agent.

Such compatibilizing agents may be products
known per se for compatibilizing polyamides and
polyolefins.

20 Examples which may be mentioned are:

- polyethylene, polypropylene,
ethylene/propylene copolymers and ethylene/butene
copolymers, all of these products being grafted with
maleic anhydride or with glycidyl methacrylate.
- 25 - ethylene/alkyl (meth)acrylate/maleic
 anhydride copolymers, the maleic anhydride being
 grafted or copolymerized,
- ethylene/vinyl acetate/maleic anhydride

copolymers, the maleic anhydride being grafted or copolymerized,

- as the previous two copolymers but in which glycidyl methacrylate is used instead of the maleic anhydride,

- ethylene/(meth)acrylic acid copolymers optionally including the salts thereof,

- polyethylene, polypropylene or ethylene/propylene copolymers, these polymers being grafted with a product having a site which is reactive towards amines; these grafted copolymers then being condensed with polyamides or with polyamide oligomers having a single amine end.

Such products are described in French Patent Specification FR 2,291,225 and European Patent Specification EP 342,066, the content of which is incorporated in the present specification.

The amount of compatibilizing agent should be sufficient for the polyolefin to be dispersed, for example, in the form of nodules in the polymer containing polyamide blocks and polyether blocks. It may represent up to 20 % of the weight of the polyolefin. These mixtures of polymer containing polyamide blocks and polyether blocks, polyolefin and optionally compatibilizing agents are manufactured according to the usual techniques of mixing in the molten state (twin-screw, Buss, single-screw).

The thermoplastic film of the invention



advantageously comprises:

a) a polymer containing polyamide blocks and PEG polyether blocks, the polyamide preferably being PA-12;

5 b) a copolymer of ethylene and an alkyl (meth)acrylate; and

c) an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer.

The preferred proportions are:

10 60 to 80 parts of a)
20 to 30 parts of b)
and 0 to 10 parts of c).

According to another advantageous form of the invention, the thermoplastic film comprises:

15 a) a polymer containing polyamide blocks and PEG blocks, the polyamide preferably being PA-12;

b) a polyethylene or a copolymer of ethylene and an alpha-olefin; and

c) a copolymer of ethylene and vinyl
20 acetate (EVA) which are grafted.

The preferred proportions are 25 to 35 parts of (a) per 65 to 75 parts of (b) plus (c).

Such films comprising EVA are novel per se and form a further aspect of the present invention.

25 The ratio of the permeability, by volume, of the CO₂ to the O₂ in the films used according to the invention is typically greater than 8 and preferably between 10 and 15; these values being at 0 % relative

humidity (0 % RH) and 23°C.

The permeability to CO₂ in ml/m² 24 h atm is typically between 15,000 and 80,000 at 0 % RH and 23°C for a 25 µm film.

5 The permeability to oxygen in ml/m² 24 h atm is typically between 1200 and 8000 at 0 % RH and 23°C for a 25 µm film.

 The permeability to nitrogen in ml/m² 24 h atm is typically between 300 and 3500 at 0 % RH and 23°C
10 for a 25 µm film.

 The permeability to water vapour in g/m²/24 h, measured according to ASTM standard E 96 BW at 38°C and 50 % RH, is typically between 2000 and 25,000 and preferably between 15,000 and 20,000.

15 The permeability to water vapour and to the other gases increases with the quantity of PEG blocks or of (-O-(CH₂)₄-) moieties in the polyether block of the polymer containing polyamide blocks and polyether blocks.

20 Using hermetic sachets manufactured from the film or films according to the invention, it is possible to keep fruit or vegetables which are inside in an atmosphere containing, by volume, 3 to 5 % O₂, 3 to 5 % CO₂, traces of ethylene and in which the quantity
25 of water vapour is such that no fog forms on the inner surface of the bag due to the high permeability to water vapour. This is another advantage of the invention, since the presence of such a fog is often

associated with the development of bacteria. Another advantage of the film used according to the invention is its transparency. The anti-fogging property is very considerable for moist fresh produce such as meat.

5 According to another form of the invention, the thermoplastic film based on a polymer containing polyamide blocks and polyether blocks may be coextruded or laminated on a support such as a grille made of polyethylene or of PVC. In this way it is possible to
10 impart mechanical strength to the film without modifying its permeabilities.

 According to another form of the invention, the film forms only part of a packaging, the remainder being made of material which does not necessarily have
15 the properties of the film of the invention. For example, a window of a film of the invention may be provided in packaging of PVC, polyethylene, cardboard, paper, etc.

 It would not be departing from the scope of
20 the invention if the films were used to make sachets in which the fruit is wrapped before harvest and even throughout the period of development and ripening. The fruit may thus be protected from parasites, from contact with herbicides or bactericides which may
25 possibly be spread onto the leaves of trees, from birds, from hailstones and from inclement weather.

 The invention is further illustrated in the following Examples.

Examples

Product 1 is a polymer containing Nylon-12 blocks (PA-12) of mass $\bar{M}_n = 1500$ and polyethylene glycol blocks of mass $\bar{M}_n = 1500$.

5 The PA-12/PEG mass ratio is 50/50. The intrinsic viscosity, measured at 20°C in meta-cresol, is 1.45 to 1.60.

Product 2 is as above except for the mass $\bar{M}_n$ of the PA-12 blocks, which is 4500. The PA-12/PEG mass
10 ratio is 75/25.

The intrinsic viscosity, measured at 20°C in meta-cresol, is 1.40 to 1.55.

Product 3 is a mixture of:

- 65 parts of product 1
- 15 - 25 parts of an ethylene/methyl acrylate copolymer containing 24 % by weight of acrylate and MFi 0.5.
- 10 parts of an ethylene/acrylic ester/maleic anhydride copolymer containing 19 % by
20 weight of acrylate and 3 % by weight of maleic.

Product 4 is a polymer containing PA-12 blocks of mass $\bar{M}_n = 1000$ and PTMG blocks of mass $\bar{M}_n = 1000$.

Product 5 is a polymer containing PA-12
25 blocks of mass $\bar{M}_n = 2000$ and PTMG blocks of mass $\bar{M}_n = 2000$.

The above mixtures are prepared in Buss or Werner machines and films are extruded.

The measurement conditions are as follows:

	Machine:	LYSSY GPM 200
	Test surface	50 cm ²
5	Detection	gas chromatography, thermal conductivity (W2X)
	Temperature	23°C
	Relative humidity	0 %
	Carrier gas	helium (pressure: 1 bar)
10	Diffusant gases	O ₂ + N ₂ + CO ₂ (1/3, 1/3, 1/3) (total pressure: 1 bar)

The permeability to water vapour is measured according to the method described in ASTM standard E 96 method BW (film in contact with water) in a Heraeus Votsch oven under conditions of temperature = 38°C and of ambient relative humidity = 50 % which are maintained throughout the period of measurement.

The result of the permeability to water vapour is given in g/m²/24 h. The inaccuracies in the measurement give a result of plus or minus 10 to 15 %. The results are collated in Table 1.

Table 1

Product	Thickness of the film (μm)	CO_2 ml/m ² 24h atm	O_2 ml/m ² 24h atm	N_2 ml/m ² 24h atm	Water vapour g/m ² 24h
Product 1	25	> 73 000	5 600	2 100	23 000
Product 1	50	> 34 000	2 300	820	23 000
Product 3	25	> 75 000	7 900	3 000	11 000
Product 2	25	> 35 000	2 700	930	12 000
Product 2	50	> 19 000	1 500	500	12 000
Product 4	25	> 81 000	10 000	3 900	1 000 to 2 000
Product 4	35	> 42 000	6 000	2 200	"
Product 5	25	> 54 000	10 000	4 000	"

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CLAIMS

1. Packaging comprising a thermoplastic film based on a polymer containing polyamide blocks and polyether blocks, which is permeable to water vapour, ethylene, CO₂ and oxygen, the permeability to CO₂ being very much greater than that to oxygen.

2. Packaging according to Claim 1, in which the polyether blocks are derived from polyethylene glycol.

3. Packaging according to Claims 1 or 2, in which the film also contains polyolefin.

4. Packaging according to Claim 3, in which the film comprises:

- a) a polymer containing polyamide blocks and PEG blocks;
- b) a copolymer of ethylene and an alkyl (meth)acrylate; and
- c) an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer.

5. Packaging according to Claim 3, in which the film comprises:

- a) a polymer containing polyamide blocks and PEG blocks;
- b) a polyethylene or a copolymer of ethylene and an alpha-olefin; and
- c) a copolymer of ethylene and vinyl acetate (EVA).

6. Packaging according to any one of the





preceding claims, in which the ratio of the permeability, by volume, to CO₂ to that to O₂ is greater than 8.

7. Packaging according to any one of the preceding claims, which is in the form of:

- a closed sachet consisting of thermoplastic film as defined in any one of the preceding claims;
- a closed sachet which sachet is provided with a window of thermoplastic film as defined in any one of the preceding claims, or
- a pot or tray covered with the thermoplastic film as defined in any one of the preceding claims.

8. Film comprising:

- a) a polymer containing polyamide blocks and PEG blocks;
- b) a polyethylene or a copolymer of ethylene and an alpha-olefin; and
- c) a copolymer of ethylene and vinyl acetate (EVA).

9. A method of packaging fresh produce which method comprises applying to the produce packaging material as defined in any one of Claims 1 to 7.

10. Use of a thermoplastic film as defined in any one of Claims 1 to 8 in the packaging of fresh



produce.

11. Fresh produce packaged in material as defined in any one of Claims 1 to 7.

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water vapour, to air and to ethylene, in order to ripen peaches on the tree. The film consists of a mixture of polyolefins and fillers such as calcium carbonate or silica, and the film is drawn in order to create spaces
5 between the polyolefin and the fillers.

It has surprisingly been found that thermoplastic films based on a polymer containing polyamide blocks and polyether blocks are permeable to water vapour, ethylene, CO₂ and oxygen, the permeability
10 to CO₂ being very much greater than that to oxygen and are useful in packaging.

Accordingly the invention comprises packaging comprising a thermoplastic film based on a polymer containing polyamide blocks and polyether blocks which
15 is permeable to water vapour, ethylene, CO₂ and oxygen, the ratio of the permeability, by volume, to CO₂ to that to O₂ being greater than 8.

The invention also provides the use of such a thermoplastic film for packaging.

20 The invention further provides a method of packaging fresh produce which method comprises applying to the produce packaging material according to the invention.

The films used according to the invention may
25 be formed into sachets by conventional means such as, for example, hot bonding or welding. Fruit or vegetables which have just been harvested may be placed in the sachets and the sachet then sealed. The films
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advantageously comprises;

a) a polymer containing polyamide blocks and PEG polyether blocks, the polyamide preferably being PA-12;

5 b) a copolymer of ethylene and an alkyl (meth)acrylate; and

c) an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer.

The preferred proportions are:

10 60 to 80 parts of a)

20 to 30 parts of b)

and 0 to 10 parts of c).

According to another advantageous form of the invention, the thermoplastic film comprises:

15 a) a polymer containing polyamide blocks and PEG blocks, the polyamide preferably being PA-12;

b) a polyethylene or a copolymer of ethylene and an alpha-olefin; and

c) a copolymer of ethylene and vinyl acetate (EVA) which are grafted.

The preferred proportions are 25 to 35 parts of (a) per 65 to 75 parts of (b) plus (c).

Such films comprising EVA are novel per se and form a further aspect of the present invention.

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TABLE 1

Product	Thickness of the film (μm)	CO_2 ml/m^2 24h atm	O_2 ml/m^2 24h atm	N_2 ml/m^2 24h atm	Water Vapour g/m^2 24h
Product 1	25	> 73 000	5 500	2 100	23 000
Product 1	50	> 34 000	2 300	820	23 000
Product 3	25	> 75 000	7 900	3 000	11 000
Product 2	25	> 35 000	2 700	930	12 000
Product 2	50	> 19 000	1 500	500	12 000
Product 4	25	> 81 000	10 000	3 900	1 000 to 2 000
Comparative Product 4	35	> 42 000	5 000	2 200	"
Comparative Product 5	25	> 54 000	10 000	4 000	"

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CLAIMS

1. Packaging comprising a thermoplastic film based on a polymer containing polyamide blocks and
5 polyether blocks, which is permeable to water vapour, ethylene, CO₂ and oxygen, the ratio of the permeability, by volume, to CO₂ to that to O₂ being greater than 8.

2. Packaging according to Claim 1, in which the polyether blocks are derived from polyethylene glycol.

10 3. Packaging according to Claims 1 or 2, in which the film also contains polyolefin.

4. Packaging according to Claim 3, in which the film comprises:

- 15 a) a polymer containing polyamide blocks and PEG blocks;
- b) a copolymer of ethylene and an alkyl (meth)acrylate; and
- c) an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer

20 5. Packaging according to Claim 3, in which the film comprises:

- a) a polymer containing polyamide blocks and PEG blocks;
- b) a polyethylene or a copolymer of ethylene and
25 an alpha-olefin; and
- c) a copolymer of ethylene and vinyl acetate (EVA).



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6. Packaging according to any one of the preceding claims, which is in the form of:

- 5 - a closed sachet consisting of thermoplastic film as defined in any one of the preceding claims;
- a closed sachet which sachet is provided with a window of thermoplastic film as defined in any one of the preceding claims, or
- 10 - a pot or tray covered with the thermoplastic film as defined in any one of the preceding claims.

7. Film comprising:

- a) a polymer containing polyamide blocks and PEG blocks;
- 15 b) a polyethylene or a copolymer of ethylene and an alpha-olefin; and
- c) a copolymer of ethylene and vinyl acetate (EVA).

8. A method of packaging fresh produce which
20 method comprises applying to the produce packaging material as defined in any one of Claims 1 to 6.

9. Use of a thermoplastic film as defined in any one of Claim 1 to 7 in the packaging of fresh produce.

10. Fresh produce packaged in material as defined
25 in any one of Claims 1 to 6.



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BLOCKS AND POLYETHER BLOCKS

5 The invention relates to a packaging
comprising a thermoplastic film based on a polymer
containing polyamide blocks and polyether blocks, which
is permeable to vapour, ethylene, CO₂ and oxygen, the
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10 The packaging according to the invention is
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Date: 15 NOV 1983