

FILMS BASED ON POLYAMIDES AND ON POLYOLEFINSDescription

The present invention relates to films
5 composed of compositions based on polyamides and on
polyolefins and more particularly to compositions
comprising:

- at least one polyamide (A)
 - at least one polymer (B) comprising
10 polyamide blocks and polyether blocks
 - at least one polyolefin (C)
 - at least one functionalized polyolefin (D)
- and such that the impact strength (Dart Test)
is greater than that of a film containing the same
15 proportions of (A), (C) and (D) but not containing (B).

The compositions of the invention can also be
characterized by a structure with a polyamide matrix,
that is to say that they essentially retain the
properties of polyamides.

20 The prior art JP 04-314,741 describes films
composed of a mixture of (i) polyamide-6 and (ii) of
polyetheresteramide. The polyetheresteramide is a block
polymer obtained by condensation of polytetramethylene
glycol and polyamide blocks containing carboxylic acid
25 ends. The polyamide blocks originate from
polycaprolactam (PA-6) or from polydodecalactam
(PA-12). The amount of polyetheresteramide is between

0.5 and 9% by weight of the mixture.

The property of this film is to withstand bending at 0°C according to Method 101 c of the MIL-B-131 F standard. The number of holes produced during
5 1,000 bending operations is measured.

If the amount of polyetheresteramide is too low, perforation is significant; if the amount of polyetheresteramide is too high, the transparency and the mechanical properties of the film are reduced.

10 In this prior art, the polyetheresteramide is such that the proportions by weight of the polyamide blocks and of the polyether blocks are in the ratio 45/55 to 30/70.

It is useful for the polyamide films which
15 are used in the food industry to exhibit good resistance to bending, in particular at low temperature for the packaging of deep-frozen food. However, it is essential for the films for packaging deep-frozen products (or products to be deep-frozen) to withstand
20 perforation due to the projecting parts or to the sharp edges of these products. It is also useful, during transportation of the deep-frozen product and its handling, for the said projecting parts and the sharp edges not to cause perforation of the film.

25 This property is also sought for in the packaging of sterilized medical supplies. Indeed, perforation of the film would cause entry of air and thus contamination. The Applicant Company has found

that the test which is the most representative of this strength was the impact strength (Dart Test) with respect to a punch falling from a certain height onto the film.

5 The Dart Test can be carried out according to Method A or Method B.

 The films of the invention also exhibit an improved tear strength in comparison with the films containing the same proportions of (A), (C) and (D) but
10 not containing (B), whether this tear is in the direction parallel or perpendicular to the extrusion.

 Polyamide (A) is understood to mean the condensation products:

 - of one or a number of amino acids, such as
15 aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids, or of one or a number of lactams, such as caprolactam, oenantholactam and lauryllactam;

 - of one or a number of salts or mixtures of
20 diamines, such as hexamethylenediamine, dodecamethylenediamine, meta-xylylenediamine, bis-(p-aminocyclohexyl)methane and trimethylhexamethylene-diamine, with diacids, such as isophthalic, terephthalic, adipic, azelaic, suberic, sebacic and
25 dodecanedicarboxylic acids;

 or of mixtures of some of these monomers, which results in copolyamides, for example PA-6/12 by condensation of caprolactam and lauryllactam.

Polyamide mixtures can be used. Use is advantageously made of PA-6 and PA-6,6.

The polymers containing polyamide blocks and polyether blocks result from the copolycondensation of
5 polyamide sequences containing reactive ends with polyether sequences containing reactive ends, such as, inter alia:

- 1) Polyamide sequences containing diamine chain ends with polyoxyalkylene sequences containing
10 dicarboxyl chain ends,
- 2) Polyamide sequences containing dicarboxyl chain ends with polyoxyalkylene sequences containing diamine chain ends obtained by cyanoethylation and hydrogenation of α,ω -dihydroxylated
15 aliphatic polyoxyalkylene sequences known as polyetherdiols,
- 3) Polyamide sequences containing dicarboxyl chain ends with polyetherdiols, the products obtained being, in this specific case, polyether-
20 esteramides.

The polyamide sequences containing dicarboxyl chain ends result, for example, from the condensation of α,ω -aminocarboxylic acids from lactams or of dicarboxylic acids and diamines in the presence of a
25 chain-limiting dicarboxylic acid. The polyamide blocks are advantageously formed from polyamide-12.

The number-average molar mass $\overline{M}_n$ of the polyamide sequences is between 300 and 15,000 and

preferably between 600 and 5000. The $\overline{M}_n$ mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.

5 The polymers containing polyamide blocks and polyether blocks can also comprise units distributed randomly. These polymers can be prepared by the simultaneous reaction of the polyether and the precursors of the polyamide blocks.

10 For example, polyetherdiol, a lactam (or an α,ω -amino acid) and a chain-limiting diacid can be reacted in the presence of a small amount of water. A polymer is obtained having essentially polyether blocks and polyamide blocks of highly variable length but also
15 the various reactants, which have reacted randomly, distributed statistically along the polymer chain.

 These polymers contain polyamide blocks and polyether blocks, whether they originate from the copolycondensation of polyamide and polyether sequences
20 prepared beforehand or from a single-stage reaction, exhibit, for example, Shore D hardnesses which can be between 20 and 75 and advantageously between 30 and 70 and an intrinsic viscosity between 0.8 and 2.5, measured in metacresol at 25°C.

25 Whether the polyether blocks derive from polyethylene glycol, from polypropylene glycol or from polytetramethylene glycol, they are either used as they are and copolycondensed with polyamide blocks containing carboxyl ends or they are aminated in order

to be converted to polyetherdiamines and condensed with polyamide blocks containing carboxyl ends. They can also be mixed with polyamide precursors and a chain limiter in order to prepare polymers containing
5 polyamide blocks and polyether blocks having units distributed statistically.

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

The polyether can be, for example, a polyethylene glycol (PEG), a polypropylene glycol (PPG) or a polytetramethylene glycol (PTMG). The latter is also known as polytetrahydrofuran (PTHF).

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

20 It would not be departing from the scope of the invention if the polyether blocks contained different units, such as units derived from ethylene glycol, from propylene glycol or alternatively from tetramethylene glycol.

25 The polyamide blocks preferably comprise the same units as the polyamide (A).

The polymer containing polyamide blocks and polyether blocks preferably comprises a single type of

polyamide block and a single type of polyether block.
Use is advantageously made of polymers containing PA-6
blocks and PTMG blocks.

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

Advantageously, the polymer containing
polyamide blocks and polyether blocks is such that the
polyamide is the major constituent by weight, that is
10 to say that the amount of polyamide which is in the
form of blocks and that which is optionally distributed
statistically in the chain represents 50% by weight or
more of the polymer containing polyamide blocks and
polyether blocks. Advantageously, the amount of
15 polyamide and the amount of polyether are in the ratio
(polyamide/polyether) of 50/50 to 80/20.

Preferably, the polyamide blocks and the
polyether blocks of the same polymer (B) respectively
have masses Mn of 1000/1000, 1300/650, 2000/1000,
20 2600/650 and 4000/1000.

The polyolefin (C) is a polymer comprising
olefin units, such as, for example, ethylene, propylene
or 1-butene units or any other α -olefin unit. Mention
may be made, by way of example, of:

25 - polyethylenes, such as LDPE, HDPE, LLDPE,
or VLDPE, polypropylene, ethylene/propylene copolymers,
EPRs (ethylene/propylene rubber) or alternatively PE
metallocenes,

- styrene/ethylene-butene/styrene (SEBS) block copolymers, styrene/butadiene/styrene (SBS) block copolymers, styrene/isoprene/styrene (SIS) block copolymers, styrene/ethylene-propylene/styrene block
5 copolymers or ethylene/propylene/diene (EPDM) block copolymers,

- copolymers of ethylene with at least one product chosen from the salts or the esters of unsaturated carboxylic acids or the vinyl esters of
10 saturated carboxylic acids.

The polyolefin (C) is advantageously chosen from LLDPE, VLDPE, polypropylene, ethylene/vinyl acetate copolymers or ethylene/alkyl (meth)acrylate copolymers. The relative density can advantageously be
15 between 0.86 and 0.965 and the melt flow index (MFI) can be between 0.3 and 40.

The functionalized polyolefin (D) is a polymer comprising α -olefin units and epoxide or carboxylic acid or carboxylic acid anhydride units.

20 Mention may be made, by way of example, of the above polyolefins (C) grafted with unsaturated epoxides, such as glycidyl (meth)acrylate, or with carboxylic acids, such as (meth)acrylic acid, or alternatively with unsaturated carboxylic acid
25 anhydrides, such as maleic anhydride.

Mention may also be made of:

- copolymers of ethylene, of an unsaturated epoxide and optionally of an unsaturated carboxylic

acid ester or salt or of a saturated carboxylic acid vinyl ester. These are, for example, ethylene/vinyl acetate/glycidyl (meth)acrylate copolymers or ethylene/alkyl (meth)acrylate/glycidyl (meth)acrylate copolymers,

- copolymers of ethylene, of an unsaturated carboxylic acid anhydride and/or of an unsaturated carboxylic acid which can be partially neutralized by a metal (Zn) or an alkali metal (Li) and optionally of an unsaturated carboxylic acid ester or of a saturated carboxylic acid vinyl ester. These are, for example, ethylene/vinyl acetate/maleic anhydride copolymers or ethylene/alkyl (meth)acrylate/maleic anhydride copolymers or alternatively ethylene/Zn or Li (meth)acrylate/maleic anhydride copolymers,

- polyethylene, polypropylene or ethylene-propylene copolymers grafted or copolymerized with an unsaturated carboxylic acid anhydride and then condensed with a polyamide (or a polyamide oligomer) which is monoaminated. These products are described in EP 342,066.

The functionalized polyolefin (D) is advantageously chosen from ethylene/alkyl (meth)acrylate/maleic anhydride copolymers, ethylene/vinyl acetate/maleic anhydride copolymers or ethylene-propylene copolymers, mostly formed from propylene, grafted with maleic anhydride and then condensed with monoaminated polyamide-6 or monoaminated

caprolactam oligomers.

Preferably, (D) is an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer comprising up to 40% by weight of alkyl (meth)acrylate and up to 10%
5 by weight of maleic anhydride.

The alkyl (meth)acrylate can be chosen from methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, methyl methacrylate and ethyl methacrylate.

10 The proportions by weight of the various constituents are advantageously:

$50\% \leq A + B \leq 80\%$ and $20\% \leq C + D \leq 50\%$, the total being 100%.

According to another form of the invention,
15 the proportions of $A + B$ are such that

$0.06 \leq A/B \leq 15$ and preferably $0.5 \leq A/B \leq 15$.

The amount of (D) depends on the number of functional groups which it carries and on their
20 reactivity.

If (D) carries few functional groups, a larger amount of it is needed.

As regards copolymers having from 1 to 10% by weight of maleic anhydride, of glycidyl methacrylate or
25 of (meth)acrylic acid, D can be such that

$0.1 \leq D/C \leq 0.5$.

Compositions which are particularly preferred are such that:

$$55\% \leq A + B \leq 80\%$$

$$20\% \leq C + D \leq 45\%$$

the total being 100%

$$0.5 \leq A/B \leq 15$$

$$0.2 \leq D/C \leq 0.4.$$

- 5 (A) being PA-6 or PA-6,6
(B) being a copolymer containing PA-6 blocks
and PTMG blocks
(C) a VLDPE
(D) an ethylene/alkyl (meth)acrylate/maleic
10 anhydride copolymer.

Other preferred compositions are such that:
the proportions of (A), (B), (C) and (D) are
the same as above and:

- (A) being PA-6 or PA-6,6
15 (B) being a copolymer containing PA-6 blocks
and PTMG blocks
(C) polypropylene
(D) an ethylene-propylene copolymer, mostly
formed from propylene, grafted with maleic anhydride
20 and then condensed with monoaminated polyamide-6 or
monoaminated caprolactam oligomers.

These compositions of the invention can also
comprise fillers, flame-retardants, release or
antiblocking agents, antioxidants or agents for
25 combating U.V. radiation.

These compositions are prepared by mixing in
the molten state (twin-screw, Buss single-screw)

according to the usual techniques for thermoplastics.

The Applicant Company has also discovered that the films manufactured with the compositions of the invention have very good impact strength and very
5 good resistance to bending.

The film of the invention can be prepared by mixing the products (A) to (D) in the molten state, followed by extrusion blow-moulding or extrusion in a flat or cylindrical die. The impact strength increases
10 with the amount of (B).

The thickness of the films can be between 10 and 300 μm .

The Applicant Company has discovered that the compositions for manufacturing the films of the
15 invention can be obtained in the extruder which feeds the device for manufacturing the film.

It is sufficient to feed the extruder with the products (A), (B), (C) and (D), without it being necessary to mix them beforehand or to prepare
20 masterbatches.

Examples

In the following examples:

PA-6 denotes: a polyamide-6 with an MFI
of between 17 and 20 (at
25 235°C/2.16 kg)

Pebax 1 denotes: a copolymer containing
PA-6 blocks with an Mn of

5 1300 and PTMG blocks with
an Mn of 650 having a
Shore D hardness of 56 and
an intrinsic viscosity of
1.38, measured in meta-
cresol at 25°C for an
initial concentration of
0.8 g/100 ml,

10 VLDPE denotes: a polymer of very low
density 0.900 and with an
MFI of 0.8 (190°C/2.16
kg),

15 Lotader 1 denotes: an ethylene/butyl
acrylate/maleic anhydride
copolymer with a
composition by weight of
90.9/6/3.1 and with an MFI
of 5 (190°C/2.16 kg),

20 PP denotes: a polypropylene with an
MFI of 1.5-2 (235°C/2.16
kg),

25 BC denotes: an ethylene/propylene
backbone copolymer
containing 12% by weight
of ethylene grafted with
maleic anhydride (1% MAH
with respect to the
backbone) and then

condensed with a
monoaminated caprolactam
oligomer with a degree of
polymerization of 22, the
amount of these oligomers
being 25% with respect to
the backbone.

5

Examples 1 to 9

Films with a thickness of 55 μm were
10 manufactured. The composition is reported in Table 1.
The proportions are by weight.

These films were conditioned for 48 hours at
23°C in an atmosphere with a relative humidity (RH) of
50%.

15

The tests are reported in Tables 2, 3 and 4.

Table 1

5

Table 2

Examples		1	2		3		4		5	
Dart Test										
(Method B-h 1.5 m)										
Mass	g		1100		1250		1600		1600	
Mini. P, 100% unbroken	g		845		1145		1495		1625	
Maxi. P, 100% broken	g		1245		1595		1845		1845	
Tear										
(ASTM D 1922-67)										
Strength, paral. direction	cN	64	60	.3	65	14	66	4	77	14
Mini. value	cN		56		52		60		60	
Maxi. value	cN		64		104		72		104	
Strength, perp. direction	cN	67	108	5	127	7	144	14	126	4
Mini. value	cN		100		116		128		120	
Maxi. value	cN		116		140		176		132	

Table 3

Examples		1	2		3		4		5	
Tensile Test										
(ISO R527 1B)				deviation		deviation		deviation		deviation
Parallel direction										
Threshold %	%	19	15.5	0.5	27.2	1	27.7	2	26.3	1
Threshold S	MPa	31	28.5	0.5	31.2	0.5	29.7	0.7	35.6	3.6
Break %	%	288	335	24	325	9	330	23	330	14
Break S	MPa	71	47	4	59	2	61	7	66	6
Perpendicular direction										
Threshold %	%	12	25.4	3	17.9	2	14.6	1.7	13.2	2
Threshold S	MPa	29.1	0.8	29.9	0.2	0.2	33.1	0.3	33.1	2.4
Break %	%	300	305	22	325	40	370	10	360	25
Break S	MPa	67	52	4	48	6	60	2	62	2

Table 4

MECHANICAL PROPERTIES OF THE FILMS AFTER CONDITIONING FOR 48 HOURS AT ROOM TEMPERATURE AND 50% RELATIVE HUMIDITY						
STANDARD	TEST	UNIT	6	7	8	9
NFT 54-141	TEAR STRENGTH					
	CONSTANT RADIUS					
	Direction // to the extrusion	N	0.74 s = 0.2	1.10 s = 0.44	1.41 s = 0.50	0.89 s = 0.40
	Direction ⊥ to the extrusion	N	*0.64 s = 0.0	0.84 s = 0.11	1.20 s = 0.14	1.03 s = 0.07
NFT 54-109	DART TEST Method A (66 cm)	g	65	194	253	396
narrow band l = 15 mm r = 500 mm/min lo = 50 mm	TENSION					
	Parallel direction					
	Stress at break	N	68.7 s = 4.4	68.1 s = 8.3	78.9 s = 6.1	65.9 s = 2.9
	Elongation at break	%	545 s = 24	590 s = 54	652 s = 33	633 s = 13
narrow band l = 15 mm r = 500 mm/min lo = 50 mm	TENSION					
	Perpendicular direction					
	Stress at break	N	57.2 s = 1.9	60.1 s = 3.7	59.1 s = 2.9	56.2 s = 1.9
	Elongation at break	%	524 s = 19	590 s = 30	610 s = 24	619 s = 17

*7 samples out of 10 tear outside the constant radius.

CLAIMS

1. Films composed of compositions comprising:
- at least one polyamide (A)
 - at least one polymer (B) comprising polyamide blocks
- 5 and polyether blocks
- at least one polyolefin (C)
 - at least one functionalized polyolefin (D)
- and such that the impact strength (Dart Test) is greater than that of a film containing the same
- 10 proportions of (A), (C) and (D) but not containing (B).
2. Films according to the preceding claim in which (A) is PA-6 or PA-6,6.
3. Films according to either of the preceding claims in which (B) is a copolymer containing PA-6
- 15 blocks and PTMG blocks.
4. Films according to any one of the preceding claims in which (C) is chosen from LLDPE, VLDPE, polypropylene, ethylene/vinyl acetate copolymers or ethylene/alkyl (meth)acrylate copolymers.
- 20 5. Films according to any one of the preceding claims in which (D) is chosen from ethylene/alkyl (meth)acrylate/maleic anhydride copolymers, ethylene/vinyl acetate/maleic anhydride copolymers or ethylene-propylene copolymers, mostly formed from
- 25 propylene, grafted with maleic anhydride and then condensed with monoaminated polyamide-6 or monoaminated caprolactam oligomers.





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6. Films according to one of the preceding claims in which:
- $50\% \leq A + B \leq 80\%$
- $20\% \leq C + D \leq 50\%$
- 5 the total being 100% (by weight).
7. Films according to Claim 6, in which (by weight):
- $0.06 \leq A/B \leq 15$ and preferably $0.5 \leq A/B \leq 15$
8. Films according to Claim 6 or 7 in which, by
- 10 weight:
- $0.1 \leq D/C \leq 0.5.$
9. Films according to any one of Claims 1 to 5 in which:
- $55\% \leq A + B \leq 80\%$
- 15 $20\% \leq C + D \leq 45\%$
- the total being 100%
- $0.5 \leq A/B \leq 15$
- $0.2 \leq D/C \leq 0.4$
- (A) being PA-6 or PA-6,6
- 20 (B) being a copolymer containing PA-6 blocks and PTMG blocks
- (C) a VLDPE
- (D) an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer.
- 25 10. Films according to any one of Claims 1 to 5 in which:
- $55\% \leq A + B \leq 80\%$
- $20\% \leq C + D \leq 45\%$

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the total being 100%

and $0.5 \leq A/B \leq 15$

$0.2 \leq D/C \leq 0.4$

(A) being PA-6 or PA-6,6

5 (B) being a copolymer containing PA-6 blocks and PTMG
blocks

(C) polypropylene

(D) an ethylene-propylene copolymer, mostly formed
from propylene, grafted with maleic anhydride and then

10 condensed with monoaminated polyamide-6 or monoaminated
caprolactam oligomers.

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