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(54) Title: GRAFTED SYNDIOTACTIC POLYPROPYLENE AND COEXTRUDING BINDERS BASED ON SYNDIOTACTIC POLYPROPYLENE

(54) Titre : POLYPROPYLENE SYNDIOTACTIQUE GREFFÉ ET LIANTS DE COEXTRUSION À BASE DE POLYPROPYLENE SYNDIOTACTIQUE

(57) Abstract: The invention concerns a syndiotactic polypropylene wherein is grafted a functional monomer. The invention also concerns a coextruding binder consisting (i) either of grafted syndiotactic polypropylene optionally diluted in at least a polyolefin (C1) or in at least a polymer having elastomeric character (D) or in a mixture of (C1) and (D), (ii) or of grafted isotactic polypropylene diluted in syndiotactic polypropylene and optionally in at least a polymer with elastomeric character (D). The invention also concerns a multilayer structure consisting of a layer comprising said binder and directly attached thereto a heterogeneous or heterogeneous polymer resin layer such as a polyamide resin layer (E), of a saponified ethylene and vinyl acetate copolymer (EVOH), a polyester resin, a mineral oxide deposited on a polymer such as PE, polyethylene terephthalate or PVOH, or even a metallic or metalloplastic coat. In another embodiment, the invention also concerns said structure and directly attached thereto, on the side on the binder, a polyolefin (F) layer.

(57) Abrégé : La présente invention concerne du polypropylène syndiotactique sur lequel on a greffé un monomère fonctionnel. L'invention concerne aussi un liant de coextrusion constitué, (i) soit de polypropylène syndiotactique greffé puis éventuellement dilué dans au moins un poliooléfine (C1) ou dans au moins un polymère à caractère élastomérique (D) ou dans un mélange de (C1) et (D), (ii) soit de polypropylène isotactique greffé dilué dans du polypropylène syndiotactique et éventuellement dans au moins un polymère à caractère élastomérique (D). Elle concerne aussi une structure multicouche composée d'une couche comprenant le liant précédent et directement attachée à celle-ci une couche de résine polaire azotée ou oxygénée telle qu'une couche (E) d'une résine polyamide, d'un copolymère saponifié d'éthylène et d'acétate de vinyle (EVOH), d'une résine polyester, d'un oxyde minéral déposé sur un polymère tel que le PE, le polyéthylène téréphtalate ou l'EVOH, ou bien une couche métallique ou métalloplastique. Selon une autre variante, elle concerne aussi la structure précédente et directement attachée à celle-ci, du côté du liant une couche (F) à base de polyoléfine.

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Before expiry of the period provided for amending the claims, will be republished if such amendments are received.

For an explanation of the two-letter codes and the other abbreviations, reference is made to the explanations ("Guidance Notes on Codes and Abbreviations") at the beginning of each regular edition of the PCT Gazette.

**GRAFTED SYNDIOTACTIC POLYPROPYLENE AND COEXTRUSION TIES
BASED ON SYNDIOTACTIC POLYPROPYLENE**

[Background of the invention]

5 The present invention relates to syndiotactic polypropylene to which has been grafted a functional monomer. This product is of use as a compatibilizing agent, for example in blends of polyamide and of polypropylene or in blends of polypropylene and of
10 glass fibres. The syndiotactic polypropylene is also of use as a coextrusion tie.

 The coextrusion tie is composed (i) either of grafted syndiotactic polypropylene then optionally diluted in at least one polyolefin (C1) or in at least
15 one polymer with an elastomeric nature (D) or in a blend of (C1) and (D), (ii) or of grafted isotactic polypropylene diluted in syndiotactic polypropylene and optionally in at least one polymer with an elastomeric nature (D).

20 These coextrusion ties are of use, for example, in the manufacture of multilayer materials for packaging. Mention may be made of materials comprising a film of polyamide (PA) and a film of polypropylene (PP), it being possible for the polypropylene film to
25 be laminated onto the polyamide film or coextruded with the polyamide. The coextrusion tie is positioned between the polypropylene and the polyamide for good

adhesion of the PA and of the PP. These multilayer materials can be three-layer structures PP/tie/EVOH in which EVOH denotes a copolymer of ethylene and of vinyl alcohol or a partially or completely saponified
5 ethylene/vinyl acetate (EVA) copolymer or five-layer structures PP/tie/EVOH/tie/PP.

[Prior art and technical problem]

Polypropylene is described in Kirk-Othmer, Encyclopaedia of Chemical Technology, 4th edition,
10 Vol. 17, pages 784-819, John Wiley & Sons, 1996. Virtually all polypropylene sold is composed essentially of isotactic polypropylene possibly containing a small amount of atactic polypropylene.

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The document JP 9078046A relates to an
adhesive composition (P1) comprising a modified polymer
(A) obtained by grafting an ethylenically unsaturated
anhydride or carboxylic acid to a syndiotactic
5 polypropylene (A2).

The document EP 485 983 A1 relates to a
syndiotactic PP grafted with MAH and the documents
US 5 374 685 and EP 457 291 A2 disclose the process for
the polymerization of syndiotactic PP homo- or
10 copolymer grafted with an α -olefin.

The radical grafting of functional monomers to polyolefins is carried out either in the molten state, or in solution, using radical initiators, such as peroxides, or in the solid state, by irradiation.

5 Under the action of the radicals, side reactions occur at the same time as the grafting reaction. They result in an increase in the molecular mass in the case where the polymer to be grafted is polyethylene or in its decrease in the case where this is polypropylene. If

10 the amount of radicals necessary for the grafting reaction is high, the change in the molecular mass of the polyolefin results in a significant modification in its melt viscosity. These grafting operations are generally carried out in an extruder. The viscosity of

15 the grafted polyethylene is so high that it is no longer possible to extrude it; the viscosity of the grafted polypropylene is so low that it too can no

longer be extruded. These phenomena reduce the amount of reactive functional groups which can be incorporated into the polyolefin by radical grafting of functional monomers.

5 Patent EP 802 207 discloses the grafting of large amounts of functional monomer to blends of polyethylene and of polypropylene. The increase in the molecular mass of the polyethylene is compensated for by the decrease in the molecular mass of the
10 polypropylene present during the radical grafting reaction. Generally, this blend of cografted polyethylene and polypropylene is subsequently diluted in a polyolefin.

 It has now been found that a functional
15 monomer can be grafted to syndiotactic polypropylene and that the melt flow index (also denoted by MFI) increases much less than if isotactic polypropylene were grafted. It is thus possible to graft amounts of functional monomer which can reach 4 to 8% by weight of
20 the syndiotactic polypropylene. This solution is simpler than to graft a blend of polypropylene and of polyethylene.

[Brief description of the invention]

A first aspect of the present invention provides a composition comprising syndiotactic polypropylene and at least one polymer chosen from:

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- (A), denoting a polyethylene or a copolymer of ethylene,
- (B), itself chosen from (B1) isotactic polypropylene homopolymer or copolymer, (B2) poly(1-butene) homo- or copolymer and (B3) polystyrene homo- or copolymer,
- and a blend of (A) and (B), the said composition being grafted with a functional monomer.

A second aspect of the present invention provides a conextrusion tie composed of the composition as defined above diluted in at least one polyolefin (C1) or in at least one polymer with an elastomeric nature (D) or in a blend of (C1) and (D).

A third aspect of the present invention provides a coextrusion tie composed of grafted isotactic polypropylene diluted in syndiotactic polypropylene and optionally in at least one polymer with an elastomeric nature (D).

A fourth aspect of the present invention provides a multilayer structure composed of a layer comprising a tie as defined above and, directly attached to this layer, a layer of nitrogen-comprising or oxygen-comprising polyresin, such as layer (E) of a polyamide resin, of a saponified copolymer of ethylene and of vinyl acetate, of a polyester resin, of an inorganic oxide deposited on a polymer, such as polyethylene, poly(ethylene terephthalate) or EVOH, or else a metal or metalloplastic layer.

One embodiment may also relate to the preceding structure with, directly attached to the latter, on the side of the tie, a polyolefin-based layer (F).

[Detailed description of the invention]

Syndiotactic polypropylene is described in Kirk-Othmer, Encyclopedia of Chemical Technology, 4th edition, Vol. 17, pages 784-819, John Wiley & Sons, 1996. Advantageously, its MFI (in g/10 min at 190°C, 2.16 kg) is at most 10 and advantageously between 0.1 and 3.

Mention may also be made of the syndiotactic polypropylene disclosed in Patents US 5 969 021, US 5 710 222, US 5 688 735, US 5 476 914, US 5 334 677, US 5 292 838, US 5 278 265, US 5 243 002, US 5 225 500, 5 US 5 223 468, US 5 223 467, US 5 155 080 and US 4 892 851.

It would not be departing from the scope of the invention if the syndiotactic polypropylene were to comprise at least one polymer chosen from (A), denoting 10 a polyethylene or a copolymer of ethylene, and (B), itself chosen from (B1) isotactic polypropylene homopolymer or copolymer, (B2) poly(1-butene) homo- or copolymer and (B3) polystyrene homo- or copolymer. That is to say that a blend comprising either syndiotactic 15 polypropylene and (A), or syndiotactic polypropylene and (B), or syndiotactic polypropylene and (A) and (B), is grafted. Advantageously, the proportion of (A) and/or (B) represents less than 40% by weight of the combination of syndiotactic polypropylene and (A) 20 and/or (B).

(A) is chosen from polyethylene homo- or copolymers.

Mention may be made, as comonomers, of the following:

25 - α -olefins, advantageously those having from 3 to 30 carbon atoms. Examples of α -olefins having 3 to 30 carbon atoms as possible comonomers comprise

propylene, 1-butene, 1-pentene, 3-methyl-1-butene,
1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene,
1-octene, 1-decene, 1-dodecene, 1-tetradecene,
1-hexadecene, 1-octadecene, 1-eicocene, 1-dococene,
5 1-tetracocene, 1-hexacocene, 1-octacocene and
1-triacontene. These α -olefins can be used alone or as
a mixture of two or of more than two.

- esters of unsaturated carboxylic acids,
such as, for example, alkyl (meth)acrylates, it being
10 possible for the alkyls to have up to 24 carbon atoms.

Examples of alkyl acrylate or methacrylate
are in particular methyl methacrylate, ethyl acrylate,
n-butyl acrylate, isobutyl acrylate or 2-ethylhexyl
acrylate.

15 - vinyl esters of saturated carboxylic acids,
such as, for example, vinyl acetate or propionate.

- unsaturated epoxides.

Examples of unsaturated epoxides are in
particular:

20 - aliphatic glycidyl esters and ethers, such
as allyl glycidyl ether, vinyl glycidyl ether, glycidyl
maleate, glycidyl itaconate, glycidyl acrylate or
glycidyl methacrylate, and

- alicyclic glycidyl esters and ethers, such
25 as 2-cyclohexene-1- glycidyl ether, diglycidyl
cyclohexene-4,5-carboxylate, glycidyl cyclohexene-
4-carboxylate, glycidyl 2-methyl-5-norbornene-

2-carboxylate and diglycidyl endo-cis-bicyclo-
[2.2.1]hept-5-ene-2,3-dicarboxylate.

- unsaturated carboxylic acids, their salts
and their anhydrides.

5 Examples of unsaturated dicarboxylic acid
anhydrides are in particular maleic anhydride, itaconic
anhydride, citraconic anhydride and tetrahydrophthalic
anhydride.

- dienes, such as, for example,

10 1,4-hexadiene.

- (A) can comprise several comonomers.

Advantageously, the polymer (A), which can be
a blend of several polymers, comprises at least 50 mol%
and preferably 75 mol% of ethylene. The density of (A)
15 can be between 0.86 and 0.98 g/cm³. The MFI (viscosity
index at 190°C, 2.16 kg) is advantageously between 1
and 1 000 g/10 min.

Mention may be made, as example of polymers
(A), of:

20 - low density polyethylene (LDPE)
 - high density polyethylene (HDPE)
 - linear low density polyethylene (LLDPE)
 - very low density polyethylene (VLDPE)
 - polyethylene obtained by metallocene
25 catalysis, that is to say the polymers obtained by
copolymerization of ethylene and of α -olefin, such as
propylene, butene, hexene or octene, in the presence of

a single-site catalyst generally composed of a zirconium or titanium atom and of two cyclic alkyl molecules bonded to the metal. More specifically, the metallocene catalysts are usually composed of two
5 cyclopentadiene rings bonded to the metal. These catalysts are frequently used with aluminoxanes as cocatalysts or activators, preferably methylaluminoxane (MAO). Hafnium can also be used as metal to which the cyclopentadiene is attached. Other metallocenes can
10 include transition metals from Groups IVA, VA and VIA. Metals from the lanthanide series can also be used.

- EPR (ethylene/propylene rubber) elastomers;
- EPDM (ethylene/propylene/diene) elastomers;
- blends of polyethylene with an EPR or an
15 EPDM;

- ethylene/alkyl (meth)acrylate copolymers which can comprise up to 60% by weight of (meth)acrylate and preferably from 2 to 40%;

- ethylene/alkyl (meth)acrylate/maleic
20 anhydride copolymers obtained by copolymerization of the three monomers, the proportions of (meth)acrylate being as the above copolymers, the amount of maleic anhydride being up to 10% and preferably 0.2 to 6% by weight;

- ethylene/vinyl acetate/maleic anhydride
25 copolymers obtained by copolymerization of the three

monomers, the proportions being the same as in the above copolymer.

As regards (B1), this is an isotactic polypropylene homo- or copolymer. Mention may be made, as comonomers, of:

- α -olefins, advantageously those having from 3 to 30 carbon atoms. Examples of such α -olefins are the same as for (A), except that propylene is replaced by ethylene in the list,

10 - dienes.

(B1) can also be a copolymer comprising polypropylene blocks.

Mention may be made, as example of polymer (B1), of

15 - polypropylene,
- blends of polypropylene and of EPDM or of EPR.

Advantageously, the polymer (B1), which can be a blend of several polymers, comprises at least 20 50 mol% and preferably 75 mol% of propylene.

B2 is chosen from poly(1-butene) or the copolymers of 1-butene with ethylene or another α -olefin having from 3 to 10 carbons, except the propylene already mentioned in (B1).

25 (B3) is chosen from polystyrene or styrene copolymers. Mention may be made, among the copolymers,

by way of example, of dienes having from 4 to 8 carbon atoms.

As regards the functional monomer, it is unsaturated, mention may be made, by way of example, of alkoxy-
 5 silanes, carboxylic acids and their derivatives, acid chlorides, isocyanates, oxazolines, epoxides, amines or hydroxides.

Mention may be made, among alkoxy-
 silanes carrying an unsaturation, of:

- 10 $\text{CH}_2=\text{CH}-\text{Si}(\text{OR})_3$ vinyltrialkoxysilanes
 $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}(\text{OR})_3$ allyltrialkoxysilanes
 $\text{CH}_2=\text{CR}_1-\text{CO}-\text{O}-\text{Y}-\text{Si}(\text{OR})_3$

(meth)acryloxyalkyltrialkoxysilanes (or
 (meth)acrylsilanes) in which:

- 15 R is an alkyl having from 1 to 5 carbon atoms
 or an alkoxy $-\text{R}_2\text{OR}_3$ in which R_2 and R_3 are alkyls having
 at most 5 carbon atoms for the combination of R_2 and R_3 .

R_1 is a hydrogen or a methyl.

- Y is an alkylene having from 1 to 5 carbon
 20 atoms.

Use is made, for example, of vinylsilanes, such as trimethoxyvinylsilane, triethoxyvinylsilane, tripropoxyvinylsilane, tributoxyvinylsilane, tripentox-
 yvinylsilane or tris(β -methoxyethoxy)vinyl-
 25 silane, allylsilanes, such as trimethoxyallylsilane, triethoxyallylsilane, tripropoxyallylsilane, tributoxyallylsilane or tripentoxyallylsilane, or

acrylsilanes, such as acryloxymethyltrimethoxysilane, methacryloxymethylmethoxysilane, acryloxyethyl-trimethoxysilane, methacryloxymethylmethoxysilane, acryloxyethyltrimethoxysilane, methacryloxyethyl-
 5 trimethoxysilane, acryloxypropyltrimethoxysilane, methacryloxypropyltrimethoxysilane, acryloxybutyl-trimethoxysilane, methacryloxybutylmethoxysilane, acryloxyethyltriethoxysilane, methacryloxyethyl-triethoxysilane, methacryloxyethyltripropoxysilane,
 10 acryloxypropyltributoxysilane or methacryloxypropyl-tripentoxysilane.

Use may also be made of mixtures of these products.

Use is preferably made of:

15 $\text{CH}_2=\text{CH}-\text{Si}-(\text{OCH}_3)_3$ vinyltrimethoxysilane
 (VTMO)

$\text{CH}_2=\text{CH}-\text{Si}-(\text{OCH}_2\text{CH}_3)_3$ vinyltriethoxysilane
 (VTEO)

20 $\text{CH}_2=\text{CH}-\text{Si}-(\text{OCH}_2\text{OCH}_2\text{CH}_3)_3$
 vinyltrimethoxyethoxysilane (VTMOEO)
 and (3-(methacryloxy)propyl)trimethoxysilane
 $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{O}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3$

Examples of unsaturated carboxylic acids are those having 2 to 20 carbon atoms, such as acrylic,
 25 methacrylic, maleic, fumaric and itaconic acids. The functional derivatives of these acids comprise, for example, the anhydrides, the ester derivatives, the

amide derivatives, the imide derivatives and the metal salts (such as the alkali metal salts) of the unsaturated carboxylic acids.

Unsaturated dicarboxylic acids having 4 to 5 10 carbon atoms and their functional derivatives, particularly their anhydrides, are particularly preferred grafting monomers.

These grafting monomers comprise, for example, maleic, fumaric, itaconic, citraconic, 10 allylsuccinic, cyclohex-4-ene-1,2-dicarboxylic, 4-methylcyclohex-4-ene-1,2-dicarboxylic, bicyclo[2.2.1-hept-5-ene-2,3-dicarboxylic and x-methylbicyclo[2.2.1-hept-5-ene-2,3-dicarboxylic acids and maleic, itaconic, citraconic, allylsuccinic, cyclohex-4-ene- 15 1,2-dicarboxylic, 4-methylenecyclohex-4-ene-1,2-dicarboxylic, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic and x-methylbicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic anhydrides.

Examples of other grafting monomer comprise 20 C₁-C₈ alkyl esters or glycidyl ester derivatives of unsaturated carboxylic acids, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, glycidyl acrylate, glycidyl methacrylate, monoethyl 25 maleate, diethyl maleate, monomethyl fumarate, dimethyl fumarate, monomethyl itaconate and diethyl itaconate; the amide derivatives of unsaturated carboxylic acids,

such as acrylamide, methacrylamide, maleic monoamide, maleic diamide, maleic N-monoethylamide, maleic N,N-diethylamide, maleic N-monobutylamide, maleic N,N-dibutylamide, fumaric monoamide, fumaric diamide, 5 fumaric N-monoethylamide, fumaric N,N-diethylamide, fumaric N-monobutylamide and fumaric N,N-dibutylamide; the imide derivatives of unsaturated carboxylic acids, such as maleimide, N-butylmaleimide and N-phenylmaleimide; and metal salts of unsaturated carboxylic 10 acids, such as sodium acrylate, sodium methacrylate, potassium acrylate and potassium methacrylate.

Various known processes can be used to graft a grafting monomer onto the syndiotactic polypropylene optionally comprising (A) and/or (B).

15 For example, this can be carried out by heating it at high temperature, approximately 150°C to approximately 300°C, in the presence or absence of a solvent, with or without a radical initiator. Appropriate solvents which can be used in this reaction 20 are benzene, toluene, xylene, chlorobenzene, cumene and the like. Appropriate radical initiators which can be used comprise t-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, di(t-butyl) peroxide, t-butyl cumyl peroxide, dicumyl 25 peroxide, 1,3-bis(t-butylperoxyisopropyl)benzene, acetyl peroxide, benzoyl peroxide, isobutyryl peroxide,

bis(3,5,5-trimethylhexanoyl) peroxide and methyl ethyl ketone peroxide.

The syndiotactic polypropylene and optionally (A) and/or (B) can be dry or melt preblended and can then be grafted in the molten state or in solution in a solvent. They can also be added separately to a device for bringing into contact and blending (for example, an extruder), together with the grafting monomer and the radical initiator. Use may be made of the usual mixing and blending devices of the thermoplastics industry.

The amount of grafting monomer can be appropriately chosen but it is preferably from 0.01 to 10%, better still from 0.1 to 5%, with respect to the weight of the grafted polypropylene, optionally comprising (A) and/or (B). The amount of grafted monomer is determined by quantitatively determining the succinic functional groups by FTIR spectroscopy.

The invention also relates to a coextrusion tie composed:

- 20 either (i), according to a first form, of grafted syndiotactic polypropylene then optionally diluted in at least one polyolefin (C1) or in at least one polymer with an elastomeric nature (D) or in a blend of (C1) and (D),
- 25 or (ii), according to a second form, of grafted isotactic polypropylene diluted in syndiotactic

polypropylene and optionally in at least one polymer with an elastomeric nature (D).

As regards the first form, the tie is therefore composed of the grafted syndiotactic
5 polypropylene which was described above and which is optionally diluted in at least one polyolefin (C1) or in at least one polymer with an elastomeric nature (D) or in a blend of (C1) and (D).

The polyolefin (C1) can be chosen from the
10 polymers (A), (B) and the syndiotactic polypropylene. (D) is a polymer with an elastomeric nature, that is to say that it can be an (i) elastomer within the meaning of ASTM D412, that is to say a material which can be drawn at ambient temperature to two times its width,
15 can be held thus for 5 minutes and then, when it is released, it returns to its starting length, to within less than about 10%, or (ii) a polymer which does not have exactly these above characteristics but which can be drawn and can return substantially to its starting
20 length.

The MFI of (D) is advantageously between 0.1 and 50.

Mention may be made, as example of polymers (D), of:

25 - EPR (ethylene/propylene rubber) polymers and EPDM (ethylene/propylene/diene) polymers;

- polyethylenes obtained by metallocene catalysis and with a density of less than 0.910 g/cm^3 ;

- polyethylenes of VLDPE type (very low density);

5 - styrene elastomers, such as SBR (styrene/butadiene rubber) elastomers, styrene/butadiene/styrene (SBS) block copolymers, styrene/ethylene/butene/styrene (SEBS) block copolymers and styrene/isoprene/styrene (SIS) block copolymers;

10 - copolymers of ethylene and of at least one ester of unsaturated carboxylic acid (already defined in (A));

 - copolymers of ethylene and of at least one vinyl ester of saturated carboxylic acid (already
15 defined in (A)).

The amount of (C1) or (D) or (C1) + (D) is advantageously from 20 to 1 000, and preferably 60 to 500 parts (by weight) per 10 parts of grafted syndiotactic polypropylene. Advantageously, (C1) and
20 (D) are used. The preferred proportions are such that (D)/(C1) is between 0 and 1 and more particularly between 0 and 0.5.

As regards the second form, the grafted isotactic polypropylene is manufactured as mentioned
25 above by grafting a blend comprising at least (B1) and optionally at least one polymer chosen from (A), (B2) and (B3). Advantageously, the proportion of (B1) is at

least 50 and preferably 70% by weight of the blend to be grafted. This grafted isotactic propylene is then diluted in syndiotactic propylene and optionally in at least one polymer with an elastomeric nature (D). The
5 polymer (D) has been defined above.

The amount of syndiotactic polypropylene and optionally of (D) can be from 20 to 1 000 and preferably 60 to 500 parts (by weight) per 10 parts of grafted isotactic polypropylene. Use is advantageously
10 made of syndiotactic polypropylene and (D). The preferred proportions are such that the ratio of the amount of (D) to the syndiotactic polypropylene is between 0 and 1 and more particularly between 0 and 0.5.

15 The tie of the invention can be manufactured by the usual means for thermoplastics by melt blending the various constituents in Buss twin-screw extruders, mixers or roll mills.

The tie of the invention can also comprise
20 various additives, such as antioxidants, ultraviolet absorbers, antistatic agents, pigments, dyes, nucleating agents, fillers, slip agents, lubricants, flame retardants and antiblocking agents.

As regards the multilayer structure of the
25 **present invention**, it is composed of the layer comprising the above tie and of a layer of oxygen-comprising or nitrogen-comprising polar resin or of an

inorganic oxide deposited on a polymer, such as PE, PET or EVOH or a metal layer.

Examples of polar resins which are preferred in the layer other than the tie are polyamide resins, a
5 saponified copolymer of ethylene and of vinyl acetate, and polyesters.

More specifically, they comprise synthetic long-chain polyamides having structural units of the amide group in the main chain, such as PA-6, PA-6,6,
10 PA-6,10, PA-11 and PA-12; a saponified copolymer of ethylene and of vinyl acetate having a degree of saponification of approximately 90 mol% to 100 mol%, obtained by saponifying an ethylene/vinyl acetate copolymer having an ethylene content from approximately
15 15 mol% to approximately 60 mol%; polyesters, such as poly(ethylene terephthalate), poly(butylene terephthalate) or poly(ethylene naphthenate); and blends of these resins.

The layer of inorganic oxide can, for
20 example, be silica, it is deposited on a layer of PE, PET or EVOH. The structure of the invention therefore comprises, respectively: a tie layer, an SiO_2 (or SiO_x) layer and either PE or PET or EVOH.

The metal layer can, for example, be a sheet,
25 a film or a sheet of a metal, such as aluminium, iron, copper, tin and nickel, or an alloy containing at least one of these metals as main constituent. The thickness

of the film or of the sheet can be suitably chosen and it is, for example, from approximately 0.01 to approximately 0.2 mm. It is common practice to degrease the surface of the metal layer before laminating the tie of the invention thereon. This layer can also be a metalloplastic layer, such as, for example, a sheet of aluminized PET.

It would not be departing from the scope of the invention if the preceding structure were combined with other layers.

The invention also relates to the preceding structure combined on the side of the tie with a polyolefin-based layer (F). The polyolefin (F) can be chosen from the polymers (A) and (B) above.

These structures are of use in preparing packagings, for example rigid hollow bodies, such as bottles or jars, flexible bags or multilayer films.

The ties of the invention are of use for the following structures.

PE/tie/EVOH/tie/PE (PE denotes polyethylene)
PE/tie/EVOH
PE/tie/PA
PP/tie/PA
PP/tie/EVOH/tie/PP (PP denotes polypropylene).

These structures and these packagings can be manufactured by coextrusion, lamination, extrusion-blow moulding and coating.

[Examples]

5 The following products were used:

sPP: Syndiotactic polypropylene.

PP 3060 MN 5: Isotactic copolymer comprising
propylene/ethylene blocks with a density
= 0.902 g/cm³ and with an MFI=6
10 (230°C/2.16 kg).

PP 3050 MN1: Isotactic polypropylene homopolymer with
a density of 0.905 g/cm³ and an MFI of 5
(230°C/2.16 kg).

PP 3020 GN3: Random polypropylene copolymer with a
15 density of 0.900 g/cm³ and with an MVI
(melt volume index) of 2 cm³/10 min
(230°C/2.16 kg).

MAH: Maleic anhydride.

PPC: Polypropylene grafted with maleic
20 anhydride comprising 0.1% of MAH, with
an MFI of 2 g/10 min (190°C/2.16 kg).

PPAM2: Polypropylene grafted with maleic
anhydride comprising 2.5% of MAH, with
an MFI of 40 g/10 min (190°C/325 g).

25 The products are grafted with maleic
anhydride. They are manufactured in a corotating twin-
screw extruder of Leistritz type.

The extruder comprises 8 regions numbered Z1 to Z8, Z8 is situated at the end of the extruder where the grafted products exit. The processing is carried out at the usual temperatures.

- 5 The maleic anhydride, on polyethylene powder, and the polypropylene to be grafted are introduced into the region Z1 via two separate weight metering devices.

 The radical initiator, pure or diluted in an appropriate solvent, is introduced via a metering pump
10 into the region Z2. The temperatures in the regions Z3, Z4 and Z5 are at least sufficient for 99.9% of the radical initiator to react before the region Z6. The initiator used is 2,5-dimethyl-2,5-(di-tert-butyl)hexane (Luperox 10) (DHBP). The residues from the
15 radical initiator, the solvent and the unreacted maleic anhydride are degassed under vacuum in the region Z6.

 The throughput for extrusion at the outlet of the region Z8 varies, according to the screw rate imposed, between 12 and 15 kg/h. The lace is granulated
20 after cooling.

 The results of the grafting are collated in Table 1. The % values indicated for MAH and the initiator are with respect to the polypropylene.

 It is found that, for the isotactic
25 polypropylene, the MFI changes from 0.2 to 5.9 or 10.6 according to the proportion of DHBP added, i.e. an increase by a factor of 30 or 50. By comparison, for

the same proportions of DHBP added, the MFI of the syndiotactic polypropylene changes only from 0.7 to 6.6 or 14.3, i.e. an increase by a factor of 10 or 20.

Cast technology was then used to produce a
5 structure comprising 5 layers:

PP/tie/EVOH/tie/PP, in which PP denotes the (isotactic) polypropylene, with respective thicknesses in μm : 20/10/10/10/50. The results are listed in Table 2 below. The peel strength between the PP and the
10 tie on the thin side (PP 20 μm /tie 10 μm) was measured. The strength is expressed in N/15 mm at a drawing rate of 200 mm/min at t_0 , that is to say immediately after the structure has been prepared.

Table 1

Poly-propylene	MAH introduced (%)	DHBP introduced (%)	Powder comprising 7.5% of DHBP introduced (%)	Powder formed from PE support of the MAH introduced (%)	Grafted MAH (%)	MFI 190°C 325 g	MFI 190°C 2.16 kg	MFI 190°C 5 kg
PP3060 MN 5	1.5	0.1500	2.00	4	0.80	10.8	-	-
spp	-	-	-	-	-	0.0	0.7	2.3
spp extr. #	-	-	-	-	-	0.0	0.9	2.7
spp	1.5	0.1500	2.00	4	0.54	1.8	14.3	42.5
spp	1.5	0.1125	1.50	4	0.41	1.1	9.8	30.2
spp	1.5	0.0750	1.00	4	0.31	0.8	6.6	20.0
PP 3050 MN 1	-	-	-	-	-	0.2	not measurable	-
PP 3050 MN 1	1.5	0.1500	2.00	4	0.54	10.6	not measurable	-
PP 3050 MN 1	1.5	0.0750	1.00	4	0.34	5.9	not measurable	-

spp having already been extruded

Table 2

Tie % by weight	Peel strength at t0 N/15 mm	s standard deviation
PPC	5.4	0.1
96% sPP 4% PPAM2	5.2	0.7
94% sPP 6% PPAM2	6.1	0.4
96%PP 3020GN3 4% PPAM2	5.8	0.6
94% PP 3020GN3 6% PPAM2	5.6	0.3

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CLAIMS

1. Composition comprising syndiotactic polypropylene and at least one polymer chosen from:
 - (A), denoting a polyethylene or a
5 copolymer of ethylene,
 - (B), itself chosen from (B1) isotactic polypropylene homopolymer or
copolymer, (B2) poly(1-butene) homo-
or copolymer and (B3) polystyrene
10 homo- or copolymer,
 - and a blend of (A) and (B), the said composition being grafted with a functional monomer.
2. Composition according to Claim 1, in
15 which the functional monomer is maleic anhydride.
3. Coextrusion tie composed of the composition according to Claim 1 or 2 diluted in at least one polyolefin (C1) or in at least one polymer with an elastomeric nature (D) or in a blend of (C1)
20 and (D).
4. Tie according to Claim 3, in which the amount of polyolefin (C1) or of polymer with an elastomeric nature (D) or of the blend of (C1) and (D) is advantageously from 20 to 1 000 and preferably from
25 60 to 500 parts (by weight) per 10 parts of grafted syndiotactic polypropylene.

5. Tie according to Claim 3 or 4, in which the amounts by weight of polyolefin (C1) and of polymer with an elastomeric nature (D) are such that [amount of polyolefin (D)]/[amount of polymer (C1)] is between 0 and 1 and more particularly between 0 and 0.5.

6. Coextrusion tie composed of grafted isotactic polypropylene diluted in syndiotactic polypropylene and optionally in at least one polymer with an elastomeric nature (D).

7. Tie according to Claim 6, in which the amount by weight of syndiotactic polypropylene and optionally of polymer (D) is from 20 to 1 000 and preferably from 60 to 500 parts (by weight) per 10 parts of grafted isotactic polypropylene.

8. Tie according to Claim 6 or 7, in which the [amount by weight of (D)]/[amount of syndiotactic polypropylene] ratio is between 0 and 1 and more particularly between 0 and 0.5.

9. Multilayer structure comprising:

- a layer comprising a tie according to any one of Claims 3 to 8;

- and, directly attached to this layer, a layer of nitrogen-comprising or oxygen-comprising polar resin, such as a layer (E) of a polyamide resin, of a saponified copolymer of ethylene and of vinyl acetate, of a polyester resin, or of an inorganic oxide deposited on a polymer, such as polyethylene,

poly(ethylene terephthalate) or EVOH, or else a metal
or metalloplastic layer.

10. Structure according to Claim 9,
comprising a polyolefin-based layer (F) directly
5 attached to the tie layer.