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Wautier et al.(10) **Pub. No.: US 2009/0324867 A1**(43) **Pub. Date: Dec. 31, 2009**(54) **POLYMER COMPOSITIONS HAVING
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Nov. 10, 2006 (FR) 06.09870**Publication Classification**(51) **Int. Cl.****B32B 1/08** (2006.01)**C08L 51/00** (2006.01)**B32B 27/08** (2006.01)**B32B 1/02** (2006.01)(52) **U.S. Cl. 428/36.91; 525/69; 428/515; 428/35.7**(57) **ABSTRACT**

Polymer compositions with adhesive properties comprising:

- (1) at least one fluoropolymer (A) grafted by at least one compound (a) containing at least one functional group (f1) capable of conferring adhesion properties on said polymer;
- (2) at least one polyolefin (B) grafted by at most 4% by weight, relative to the weight of polyolefin (B), of at least one compound (b) containing at least one functional group (f2) chosen from acid and anhydride groups, optionally completely or partially neutralized by at least one neutralizing agent; and
- (3) at least one olefin copolymer (C), for which at least 5% by weight of the repeat units are derived from at least one functional monomer (f3) capable of reacting with the functional group (f1) contained in the compound (a).

POLYMER COMPOSITIONS HAVING ADHESIVE PROPERTIES

[0001] The present invention relates to polymer compositions with adhesive properties. It also relates to a method for manufacturing these compositions. It additionally relates to multilayer structures for which one of the layers is composed of the polymer composition with adhesive properties.

[0002] It is known that polyolefins, especially high-density polyethylene, are used for manufacturing pipes and tanks for the transport and storage of liquid hydrocarbons, in particular oils and fuels. The chemical resistance and the impermeability of these polymers with respect to these hydrocarbons are not however always sufficient for all the usages for which they are intended. To overcome this drawback, a barrier layer of another polymer is interposed between the hydrocarbon to be transported or stored and the polyolefin. Polymers that are both chemically resistant and impermeable frequently used for this purpose are fluoropolymers, in particular homopolymers and copolymers of vinyl and vinylidene fluorides.

[0003] These fluoropolymers have in turn another drawback: they do not adhere well to polyolefins. Hence, compositions have been developed with a view to improving the adhesion properties of the fluoropolymers.

[0004] Thus, document EP-A-0650987, the content of which is incorporated by reference in the present description, describes polymers with adhesive properties, the main fluorine-containing hydrocarbon-based chains of which are grafted by compounds comprising reactive or polar functional groups that have adhesive properties. These functional groups may be carboxyl groups, carboxylic anhydride residues, epoxy groups, hydroxyl groups, isocyanate groups, ester groups, amide groups, amino groups and hydrolysable groups containing a silyl or cyano radical. These polymers do not however adhere well enough to polyolefins.

[0005] Japanese Patent Application (Kokai) JP-10-202804, published on 4 Aug. 1998 in the name of Sekisui Chem Co, discloses a composition that enables a layer of polyethylene and a layer of polyvinylidene fluoride (PVDF) to adhere to one another. This composition comprises a blend of 35 to 65 parts by weight of methyl methacrylate-grafted polyethylene with 90 to 10 parts by weight of polymethyl methacrylate. The proportions of each of the constituents of the blend must be carefully controlled or risk leading to the delamination of the PVDF layer. Moreover, this composition has an unpleasant odour.

[0006] The present invention aims to provide a composition, that makes it possible to adhere a polyolefin to a fluoropolymer, which does not have these drawbacks.

[0007] The present invention therefore mainly relates to polymer compositions with adhesive properties comprising:

[0008] (1) at least one fluoropolymer (A) grafted by at least one compound (a) containing at least one functional group (f1) capable of conferring adhesion properties on said polymer;

[0009] (2) at least one polyolefin (B) grafted by at most 4% by weight, relative to the weight of polyolefin (B), of at least one compound (b) containing at least one functional group (f2) chosen from acid and anhydride groups, optionally completely or partially neutralized by at least one neutralizing agent;

[0010] (3) at least one olefin copolymer (C), for which at least 5% by weight of the repeat units are derived from at

least one functional monomer (f3) capable of reacting with the functional group (f1) contained in the compound (a).

[0011] The polymer compositions according to the invention comprise at least one fluoropolymer (A). The term "fluoropolymer" is understood to mean a polymer for which more than 50% by weight of the repeat units are derived from at least one fluoromonomer. The fluoropolymer may be a homopolymer; it may also be a copolymer formed by several fluoromonomers with one another, or else a copolymer formed by one or more fluoromonomers with one or more non-fluorinated monomers. These copolymers may, in particular, be random copolymers, block copolymers or graft copolymers.

[0012] The term "fluoromonomer" is understood to mean any monomer that comprises at least one fluorine atom; it customarily comprises at least one ethylenic unsaturation. As examples of fluoromonomers, mention may be made of fluorinated vinyl monomers, fluorinated styrene monomers such as 4-fluorostyrene, fluorinated (meth)acrylic monomers such as trifluoroethyl acrylate and fluorinated conjugated dienes such as 2-fluorobutadiene. The fluoromonomer is preferably a fluorinated vinyl monomer. The expression "fluorinated vinyl monomer" is understood to denote the monoethylenically-unsaturated fluorinated monomers that are aliphatic and that have one or more chlorine atoms and optionally, in addition, one or more chlorine atoms, as the only heteroatom(s). As examples of fluorinated vinyl monomers, mention may be made of vinyl monomers that are free of hydrogen atoms such as tetrafluoroethylene, hexafluoropropylene and chlorotrifluoroethylene, and partially hydrogenated fluorinated vinyl monomers such as vinyl fluoride, trifluoroethylene, 3,3,3-trifluoropropene and, with most particular mention, vinylidene fluoride.

[0013] The expression "non-fluorinated monomer" is understood to mean any monomer that is free of fluorine atoms; it customarily comprises at least one ethylenic unsaturation. Examples of non-fluorinated monomers are: α -monoolefins such as, for example, ethylene and propylene; styrene and non-fluorinated styrene derivatives non-fluorinated chloromonomers such as, for example, vinyl chloride and vinylidene chloride; non-fluorinated vinyl ethers; non-fluorinated vinyl esters such as, for example, vinyl acetate; non-fluorinated (meth)acrylic esters, nitrites and amides such as acrylonitrile and acrylamide.

[0014] As examples of fluoropolymers, mention may especially be made of the homopolymers of vinylidene fluoride, vinyl fluoride, trifluoroethylene or chlorotrifluoroethylene, and the copolymers that these fluoromonomers form with one another or with at least one other fluoromonomer as defined above (including a fluoromonomer that does not contain hydrogen atoms, such as tetrafluoroethylene or hexafluoropropylene). As examples of such copolymers and terpolymers, mention may be made of the copolymers and terpolymers of vinylidene fluoride and the copolymers and terpolymers of chlorotrifluoroethylene with at least one other fluoromonomer as defined above (including a fluoromonomer that does not contain hydrogen atoms, such as tetrafluoroethylene or hexafluoropropylene). Mention may also be made of the copolymers and terpolymers of at least one of the fluoromonomers mentioned above with at least one non-fluorinated monomer.

[0015] The fluoropolymer (A) present in the compositions according to the invention is preferably chosen from vinylidene fluoride polymers.

[0016] For the purposes of the present invention, a vinylidene fluoride polymer is a fluoropolymer (i.e. a polymer for which more than 50% by weight of the repeat units are derived from at least one fluoromonomer), comprising repeat units derived from vinylidene fluoride.

[0017] As examples of vinylidene fluoride polymers, mention may especially be made of homopolymers of vinylidene fluoride, and copolymers thereof with other ethylenically unsaturated monomers, whether they are fluorinated (examples of other ethylenically unsaturated fluoromonomers are vinyl fluoride, trifluoroethylene, tetrafluoroethylene, chlorotrifluoroethylene and hexafluoropropylene) or non-fluorinated (examples of ethylenically unsaturated non-fluorinated monomers are α -monoolefins such as ethylene and propylene; styrene and non-fluorinated styrene derivatives; non-fluorinated chloromonomers such as vinyl chloride and vinylidene chloride; non-fluorinated vinyl ethers; non-fluorinated vinyl esters such as vinyl acetate; non-fluorinated (meth)acrylic esters, nitrites and amides such as acrylamide and acrylonitrile).

[0018] The vinylidene fluoride polymers preferably contain more than 50% by weight of repeat units derived from vinylidene fluoride.

[0019] Particularly preferred vinylidene fluoride polymers are vinylidene fluoride homopolymers and random copolymers of vinylidene fluoride that contain 10 to 20 % by weight of at least one fluorinated comonomer chosen from hexafluoropropylene and chlorotrifluoroethylene.

[0020] According to the invention, the fluoropolymer (A) is grafted by at least one compound (a)—defined and described in detail later on—which contains at least one functional group (f1) capable of conferring adhesion properties on said polymer.

[0021] The functional group (f1) may be any group having a reactivity or a polarity such that it enables the fluoropolymer to develop adhesion forces, even with respect to materials that it is not normally possible to adhere to this polymer. The functional group (f1) is generally chosen from those bearing at least one reactive function that does not take part in radical mechanisms. It is usually chosen from:

[0022] (f1.1) groups derived from carboxylic acids, also known more simply hereinbelow as “acid groups”; the carboxylic acids from which these groups originate may be monocarboxylic or dicarboxylic acids;

[0023] (f1.2) groups derived from carboxylic anhydrides, resulting from the condensation of two carboxylic acid groups in the same molecule, also known more simply hereinbelow as “anhydride groups”; the carboxylic anhydrides that bear these groups may themselves derive from monocarboxylic or dicarboxylic acids;

[0024] (f1.3) groups derived from carboxylic esters, also known more simply hereinbelow as “ester groups”;

[0025] (f1.4) groups derived from carboxylic amides, also known more simply hereinbelow as “amide groups”;

[0026] (f1.5) epoxy groups, derived from compounds containing a cyclic ether function;

[0027] (f1.6) hydroxylated groups derived from alcohols, also known more simply hereinbelow as “alcohol groups”; the alcohols from which these groups originate may be monoalcohols or polyols.

[0028] (f1.7) carbonyl groups;

[0029] (f1.8) hydrolysable groups containing a silyl group.

[0030] Among all these groups, epoxy groups (f1.5), alcohol groups (f1.6) and carbonyl groups (f1.7) are preferred.

More particularly, the epoxy groups and the alcohol groups derived from diols are preferred. Epoxy groups give the best results.

[0031] The functional group (f1) contained in the compound (a) grafted to the fluoropolymer (A) is preferably capable of reacting with the functional group (f2) contained in the compound (b) grafted to the polyolefin (B). The epoxy groups (f1.5), the alcohol groups (f1.6) and the carbonyl groups (f1.7) are examples of functional groups (f1) capable of reacting with the functional group (f2) contained in the compound (b).

[0032] As mentioned, the fluoropolymer (A) is grafted by at least one compound (a) containing at least one functional group (f1). According to the invention, the functional group (s) (f1) contained in the compound(s) (a) may belong to the same family or to different families. Thus, it is in no way excluded to use both a first compound (a) containing an epoxy group and a second compound (a) containing one or more alcohol groups; similarly, it is in no way excluded to use a compound (a) containing both an ester group and another group, for example an epoxy or alcohol group.

[0033] In order to be able to be grafted to the fluoropolymer (A), the compound (a) customarily contains at least one group (g) that makes the grafting of said compound (a) to this polymer possible. This group (g) is generally chosen from:

[0034] saturated or unsaturated hydrocarbon-based groups, capable of participating in radical mechanisms, such as additions or associations of radicals;

[0035] amino or phenol groups capable of participating in reactions of nucleophilic character;

[0036] groups capable of easily forming free radicals such as peroxy and azo groups.

[0037] Preferably, the group (g) is chosen from organic groups having at least one unsaturated carbon-carbon bond, from amino groups and from peroxy groups. Organic groups having at least one terminal α,β -unsaturated carbon-carbon bond, such as vinyl, allyl, acryloyloxyalkyl and methacryloyloxyalkyl groups for example, are particularly preferred. Vinyl and allyl groups give the best results.

[0038] Examples of compounds (a) that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond as group (g) and at least one group chosen from acid and anhydride groups as functional group (f1) are unsaturated monocarboxylic or dicarboxylic acids such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, citraconic acid, bicyclo[2.2.1] hept-2-ene-5,6-dicarboxylic acid, maleic anhydride, itaconic anhydride, crotonic anhydride and citraconic anhydride. Maleic anhydride is generally preferred, in particular for reasons of accessibility.

[0039] According to one variant of the invention, the acid group(s) and/or the anhydride group(s) that may be contained in the compound (a) are completely or partially neutralized by at least one neutralizing agent. The neutralizing agent may be a hydroxide (such as an alkali metal hydroxide, for example sodium hydroxide), an inorganic salt, an organic salt, or else a mixture of an organic salt and an inorganic salt.

[0040] The inorganic salt is preferably a carbonate, a bicarbonate, a phosphate or a monohydrogenphosphate of an alkali metal. Sodium carbonate is particularly preferred.

[0041] The organic salt is preferably a carboxylate or a monohydroxycarboxylate or polyhydroxycarboxylate of a metal, which may especially be an alkali metal, an alkaline-earth metal, a metal from group IIIa of the Periodic Table of

the Elements or a transition metal. Particularly preferably, the organic salt is a carboxylate of a transition metal or a monohydroxycarboxylate or polyhydroxycarboxylate of an alkali metal. Most particularly preferably, the organic salt is chosen from sodium lactate and zinc acetate.

[0042] The neutralizing agent is used in an amount preferably greater than 0.5 molar equivalents relative to the number of acid and/or anhydride groups (f1) contained in the compound (a). Furthermore, the neutralizing agent is used in an amount preferably less than 3 mol. eq. relative to the number of these functional groups (f1).

[0043] Examples of compounds (a) that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond as group (g) and at least one ester group as functional group (f1) are vinyl acetate, vinyl propionate, monomethyl maleate, dimethyl maleate, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, amyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, diethyl fumarate, dimethyl itaconate and diethyl citraconate.

[0044] Examples of compounds (a) that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond as group (g) and at least one amide group as functional group (f1) are acrylamide and methacrylamide.

[0045] An example of compound (a) that contains at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond as group (g) and at least one epoxy group as functional group (f1) is allyl glycidyl ether.

[0046] Examples of compounds (a) that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond as group (g), and at least one alcohol group as functional group (f1) are allyl alcohol and 3-allyloxy-1,2-propanediol.

[0047] Examples of compounds (a) that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond as group (g) and at least one carbonyl group as functional group (f1) are organic heterocyclic compounds containing a vinyl or allyl group attached to the heteroatom and the heterocycle of which bears the carbonyl bond, such as N-vinylpyrrolidone and N-vinylcaprolactam.

[0048] Examples of compounds (a) that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond as group (g) and at least one hydrolysable group containing a silyl group as functional group (f1) are vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, γ -methacryloxypropyltrimethoxysilane and vinyltris(β -methoxyethoxy)silane.

[0049] Examples of compounds (a) that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond as group (g), and at least two functional groups (f1) of different nature, are: glycidyl acrylate and methacrylate (an ester group and an epoxy group as functional groups (f1)); hydroxyethyl acrylate and methacrylate and hydroxypropyl acrylate and methacrylate (an ester group and an alcohol group as functional groups (f1)), N-methylol-methacrylamide (an alcohol group and an amide group as functional groups (f1)).

[0050] Among all the compounds (a), the compounds containing at least one functional group (f1) chosen from epoxy groups, alcohol groups and carbonyl groups, more particularly from epoxy groups and alcohol groups derived from diols, are preferred. The most particularly preferred com-

pounds (a) are allyl glycidyl ether, 3-allyloxy-1,2-propanediol, N-vinylpyrrolidone and N-vinylcaprolactam. The best results were obtained with allyl glycidyl ether.

[0051] The grafting of the compound (a) to the fluoropolymer (A) may be carried out by any method known for this purpose. Depending on the chemical properties and the physical state of the compound (a), this grafting may be carried out in the solid state, in solution, in suspension, in an aqueous medium or within an organic solvent. This grafting may also be carried out by irradiation, for example by means of an electron beam or by gamma radiation.

[0052] The grafting of the compound (a) to the fluoropolymer (A) is more generally carried out on a molten blend of the compound and polymer. It is possible to operate in batch mode, in kneaders, or continuously, in extruders.

[0053] The reaction of grafting the compound (a) to the fluoropolymer (A) is usually promoted and initiated by a radical generator, at least when the group (g) of the compound (a) is not itself a group capable of easily forming free radicals, such as peroxy and azo groups. As a radical generator, use is generally made of compounds having a decomposition temperature between 120 and 350° C. and a half life, in this temperature zone, of around one minute. The radical generator is preferably an organic peroxide, and more particularly an alkyl or aryl peroxide. Among these, mention may be made of benzoyl peroxide, dichlorobenzoyl peroxide, dicumyl peroxide, di(t-butyl) peroxide, t-butylcumyl peroxide, 1,3-di(2-t-butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane and 2,5-dimethyl-2,5-di(t-butylperoxy)-3-hexyne. 2,5-dimethyl-2,5-di(t-butylperoxy)hexane and dicumyl peroxide are particularly preferred.

[0054] When the grafting of the compound (a) to the fluoropolymer (A) is carried out continuously in an extruder, the radical generator and the compound (a) may be introduced in any manner so long as they are introduced continuously over time and they are well dispersed in the molten material. The radical generator and the compound (a) may be introduced by spraying, for example by means of a spray-type injector or an atomizer or by injection into the molten mass. The introduction of the radical generator and the compound (a) via a masterbatch with the powdered fluoropolymer (A) or via a masterbatch with a filler can also be envisaged.

[0055] According to one particularly preferred embodiment, the compound (a) is introduced before the radical generator.

[0056] The expression "reaction in molten mass" is understood to mean, for the purposes of the present invention, any reaction in the substantial absence of solvent or of diluent and at a temperature at least equal to the melting point of the fluoropolymer (A).

[0057] The term "extruder" is understood to mean any continuous device comprising at least one feed zone and, at its outlet, a discharge zone preceded by a compression zone, the latter forcing the molten mass to pass through the discharge zone. The discharge zone may additionally be followed by a granulating device or by a device that gives the extruded material its final shape. Advantageously, use is made of known extruders based on the work of a single screw or of two screws which, in the latter case, may cooperate in a co-rotating or counter-rotating manner (same direction of rotation or opposite directions of rotation).

[0058] Preferably, the extruder used according to the present invention is arranged so that it successively comprises one feed zone, one material melting zone, one homogeniza-

tion zone, one reaction zone, optionally one zone for introducing additives, and one compression-discharge zone preceded by one degassing zone. Each of these zones has a very specific function and is at a very specific temperature.

[0059] The feed zone has the role of carrying out the feeding of the fluoropolymer (A). It is customarily at a temperature less than or equal to 50° C.

[0060] The material melting zone has the role of carrying out the melting of the material.

[0061] The homogenization zone has the role of homogenizing the molten material.

[0062] The reaction zone has the role of carrying out the reaction.

[0063] The temperature in the melting zone and in the zone for the homogenization of the material is customarily greater than or equal to the melting point of the fluoropolymer (A).

[0064] The temperature in the reaction zone is customarily greater than or equal to the temperature at which the half life of the radical generator is less than the residence time of the material in this zone.

[0065] The zone for introducing additives has the role of carrying out the introduction of additives when the latter are added into the extruder. The temperature of this zone is generally a function of the viscosity of the material and the nature of the additives added.

[0066] The compression-discharge zone has the role of compressing the material and of carrying out the discharge of the latter. The temperature in the compression-discharge zone is generally a function of the viscosity of the material to be discharged.

[0067] The compound (a) is preferably introduced into the extruder before the homogenization zone.

[0068] The radical generator is preferably introduced into the reaction zone of the extruder.

[0069] Whichever grafting method is used, the amount of compound (a) grafted to the fluoropolymer (A), expressed as amount of compound (a), is advantageously greater than 0.01% by weight, preferably 0.05% by weight or, better still, 0.1% by weight, relative to the weight of fluoropolymer (A). Moreover, this amount is advantageously less than or equal to 5.0% by weight, preferably 3.0% and better still 2.0% by weight. The metering is customarily carried out by a chemical route (titration).

[0070] The polymer compositions according to the invention comprise at least one polyolefin (B). In the present description, the term "polyolefin" is understood to mean a polymer for which more than 50% by weight of the repeat units, preferably more than 70% by weight of the repeat units, most particularly more than 90% by weight of the repeat units, are derived from at least one linear olefin.

[0071] As examples of linear olefins, mention may be made of linear α -monoolefins containing 2 to 12 carbon atoms, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene and 1-dodecene.

[0072] The polyolefin (B) may be chosen, in particular, from homopolymers of the aforementioned olefins and from copolymers of these olefins, in particular copolymers of propylene with one or more comonomers, and also from blends of such polymers. The comonomers may be chosen, in particular, from the linear olefins described above, from styrene monomers such as styrene and α -methylstyrene and from alkadienes; the polyolefin (B) is, however, preferably free of repeat units derived from an alkadiene. The weight content of

units formed from comonomers in the polyolefins is advantageously less than 30% and preferably less than 10% by weight.

[0073] The polyolefin (B) is preferably free of repeat units derived from a functional monomer (f3), such as those contained in the olefin copolymer (C); when the polyolefin (B) nevertheless contains such repeat units, their amount usually represents at most 4% by weight, and often at most 2% by weight, of all of the repeat units of the polyolefin (B).

[0074] The term "polyolefin" is understood to equally well mean the polymers as described above, taken separately, and the blends thereof.

[0075] Excellent results are obtained using a polyolefin (B) chosen from homopolymers and copolymers derived from ethylene and propylene, most particularly crystalline polymers derived from propylene and copolymers of propylene containing less than 10% by weight and preferably less than 5% by weight of ethylene.

[0076] According to the invention, the polyolefin (B) is grafted by at least one compound (b) containing at least one functional group (f2) chosen from acid and anhydride groups. The functional group (f2) and the compound (b) corresponding to it generally meet the same definitions and limitations as those that are applied respectively to the groups (f1.1) and (f1.2) and to the compound (a) corresponding to them, mentioned above.

[0077] The functional group (f2) is therefore contained in the compound (b), which is customarily chosen from unsaturated monocarboxylic or dicarboxylic acids, and anhydrides of unsaturated monocarboxylic or dicarboxylic acids, such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, citraconic acid, bicyclo[2.2.1] hept-2-ene-5,6-dicarboxylic acid, maleic anhydride, itaconic anhydride, crotonic anhydride and citraconic anhydride. Maleic anhydride is most particularly preferred.

[0078] According to a certain variant of the invention, the functional group (f2) contained in the compound (b) is not neutralized; the functional group (f2) is then chosen from the acid and anhydride groups (as they are). In particular for reasons of availability, it is often preferred to use, as polyolefin (B), a polyolefin according to the present variant.

[0079] According to another variant of the invention, the functional group (f2) contained in the compound (b) is completely or partially neutralized by at least one neutralizing agent.

[0080] The neutralizing agent may be a hydroxide (such as an alkali metal hydroxide, for example sodium hydroxide), an inorganic salt, an organic salt, or else a mixture of an organic salt and an inorganic salt.

[0081] The inorganic salt is preferably a carbonate, a bicarbonate, a phosphate or a monohydrogenphosphate of an alkali metal. Sodium carbonate is particularly preferred.

[0082] The organic salt is preferably a carboxylate or a monohydroxycarboxylate or polyhydroxycarboxylate of a metal, which may especially be an alkali metal, an alkaline-earth metal, a metal from group IIIa of the Periodic Table of the Elements or a transition metal. Particularly preferably, the organic salt is a carboxylate of a transition metal or a monohydroxycarboxylate or polyhydroxycarboxylate of an alkali metal. Most particularly preferably, the organic salt is chosen from sodium lactate and zinc acetate.

[0083] The neutralizing agent is used in an amount preferably greater than 0.5 molar equivalents relative to the number of acid and/or anhydride groups present in the compound (b).

Furthermore, the neutralizing agent is used in an amount preferably less than 3 mol. eq. relative to the number of these groups.

[0084] All the definitions, comments and limitations regarding the grafting of the compound (a) to the fluoropolymer (A) apply, mutatis mutandis, to the grafting of the compound (b) to the polyolefin (B), it being understood that it is advisable to carry out said grafting so that the amount of compound (b) grafted does not generally exceed 4% by weight, relative to the weight of the polyolefin (B). Preferably, the amount of compound (b) grafted is less than or equal to 3% by weight, relative to the weight of the polyolefin (B), most particularly less than or equal to 2% by weight. Moreover, the amount of compound (b) grafted is generally greater than 0.01% by weight, relative to the weight of the polyolefin (B), preferably greater than 0.03% by weight, or better still 0.1% by weight.

[0085] The polymer compositions according to the invention comprise at least one olefin copolymer (C). The olefin copolymer (C) is usually a polymer different from the polyolefin (B).

[0086] In the present description, the expression "olefin copolymer" is understood to mean a copolymer (i.e. a polymer for which the repeat units are derived from at least two different monomers) for which more than 50% by weight of the repeat units are derived from at least one linear olefin.

[0087] Preferably, the olefin copolymer (C) contains at least 60% by weight, more particularly at least 75% by weight, of repeat units derived from at least one linear olefin. The linear olefin is generally chosen from linear α -monoolefins containing 2 to 12 carbon atoms, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene and 1-dodecene. Preferably, the linear olefin is ethylene.

[0088] At least 5% by weight of the repeat units of the olefin copolymer (C) are derived from at least one functional monomer (f3) capable of reacting with the functional group (f1) contained in the compound (a). Preferably, the olefin copolymer (C) contains at least 8% by weight, more particularly at least 10% by weight, of repeat units derived from the functional monomer (f3). The olefin copolymer (C) does not generally contain more than 40% by weight, preferably not more than 25% by weight, of repeat units derived from the functional monomer (f3). The functional monomer (f3), although generally different from the compound (a) defined above, may nevertheless belong to the same families as the latter, it being understood, however, that it must be copolymerizable with the linear olefin from which the repeat units of the olefin copolymer (C) derive, on the one hand, and it must be capable of reacting with the group (f1) contained in the compound (a), on the other hand. Taking into account these limitations, the functional monomer (f3) is preferably chosen from:

[0089] (f3.1) functional monomers that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond and at least one acid group, for instance unsaturated monocarboxylic or dicarboxylic acids, such as for example acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, citraconic acid and bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid. Among these functional monomers, acrylic and methacrylic acids are particularly preferred.

[0090] The acid group(s) present in the functional monomers (f3.1) are sometimes not neutralized; the functional monomer (f3) is then chosen from functional monomers that

contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond and at least one acid group (as it is).

[0091] However, it is preferred that the acid group(s) present in the functional monomers (f3.1) are completely or partially neutralized by at least one neutralizing agent, in particular when the functional group (f2) contained in the compound (b) is not neutralized.

[0092] The neutralizing agent for the functional monomers (f3.1) may be a hydroxide, an inorganic salt, an organic salt, a mixture of two of these compounds or a mixture of all three.

[0093] The inorganic salt may be a carbonate, a bicarbonate, a phosphate or a monohydrogenphosphate of an alkali metal. Sodium carbonate is preferred.

[0094] The organic salt may be a carboxylate or a monohydroxycarboxylate or polyhydroxycarboxylate of a metal, which may especially be an alkali metal, an alkaline-earth metal, a metal from group IIIa of the Periodic Table of the Elements or a transition metal. Preferably, the organic salt is chosen from sodium lactate and zinc acetate.

[0095] The neutralizing agent for the functional monomers (f3.1) is preferably a hydroxide, particularly preferably an alkali metal hydroxide and most particularly preferably sodium hydroxide.

[0096] The neutralizing agent for the functional monomers (f3.1) is used in an amount preferably greater than 0.5 molar equivalents relative to the number of acid groups present in the functional monomers (f3.1). Furthermore, the neutralizing agent is used in an amount preferably less than 3 mol. eq. relative to the number of these groups:

[0097] (f3.2) functional monomers that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond and at least one ester group such as, for example, vinyl acetate, vinyl propionate, monomethyl maleate, dimethyl maleate, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, amyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, diethyl fumarate, dimethyl itaconate and diethyl citraconate; among the functional monomers (f3.2), methyl acrylate and methacrylate are particularly preferred;

[0098] (f3.3) functional monomers that contain at least one organic group having at least one terminal α,β -unsaturated carbon-carbon bond and at least one amide group such as, for example, acrylamide and methacrylamide.

[0099] Other functional monomers, such as vinyl ethers, for instance ethyl vinyl ether and butyl vinyl ether for example, or such as other amides, for instance N-methylmethacrylamide, N-alkylacrylamides and N-dialkylacrylamides for example, may also be copolymerized with the linear olefin from which the repeat units of the olefin copolymer (C) derive.

[0100] The functional monomer (f3) from which the repeat units of the olefin copolymer (C) derive is preferably capable of reacting and/or developing ionic interactions (for example, interactions between an oxygen atom and an atom of an alkali metal, such as sodium) and/or of forming hydrogen bridge bonds with the functional group (f2) contained in the compound (b) grafted to the polyolefin (B).

[0101] The functional monomer (f3) from which the repeat units of the olefin copolymer (C) derive is particularly preferably capable of reacting and/or developing ionic interac-

tions with the functional group (f2) contained in the compound (b) grafted to the polyolefin (B).

[0102] The functional monomer (f3) from which the repeat units of the olefin copolymer (C) derive is most particularly preferably capable of developing ionic interactions with the functional group (f2) contained in the compound (b) grafted to the polyolefin (B).

[0103] The functional monomers (f3.1), completely or partially neutralized by at least one neutralizing agent, are examples of functional monomers (f3) capable of interacting ionically with the functional group (f2) contained in the compound (b) grafted to the polyolefin (B).

[0104] The olefin copolymer (C) may contain repeat units derived from functional monomers (f3) belonging to at least two different families. Thus, the olefin copolymer (C) may contain repeat units derived from at least two functional monomers (f3), at least one functional monomer (f3) being chosen from the functional monomers (f3.1), optionally completely or partially neutralized by at least one neutralizing agent, and at least one other functional monomer (f3) being chosen from the functional monomers (f3.2). These may then be, for example, mixtures of at least one functional monomer chosen from acrylic acid, methacrylic acid, sodium acrylate and sodium methacrylate, with at least one functional monomer chosen from methyl, n-butyl and isobutyl acrylates and methacrylates.

[0105] It is not excluded for the olefin copolymer (C) contained in the compositions according to the invention to also be grafted by a compound chosen from the families to which the compound (a) or the compounds (b), described above, belong. However, the olefin copolymer (C) is generally free of grafted compound chosen from the families to which the compounds (b), described above, belong, and, very often, the olefin copolymer (C) is free of any grafted compound.

[0106] As olefin copolymers (C), the copolymers for which from 95 to 85% by weight of the repeat units are derived from ethylene and for which from 5 to 15% by weight of the repeat units are derived from methacrylic acid, the acid functions of which are completely or partially neutralized by the sodium ion, are most particularly preferred.

[0107] The respective proportions in which the fluoropolymer (A), in its grafted form, and the polyolefin (B), in its grafted form, are present in the compositions according to the invention, may vary to a large extent, especially as a function of the respective amounts of compound (a) and of compound (b) grafted to said fluoropolymer and said polyolefin. In general, these proportions are such that the weight ratio of the fluoropolymer (A) to the polyolefin (B) [(A)/(B)] is between 95/5 and 5/95. Preferably, the ratio [(A)/(B)] is between 60/40 and 40/60. The best results were obtained when the ratio [(A)/(B)] is close to 55/45.

[0108] Without the scope of the invention being in any way limited by this theoretical explanation, the proprietor of the present application believes that the olefin copolymer (C) is, due to its chemical nature, capable of serving as some kind of "compatible interface" or "binder" to the fluoropolymer (A) and to the polyolefin (B). Under these conditions, the amount of olefin copolymer (C) present in the polymer compositions according to the invention may be significantly below those of the fluoropolymer (A) and polyolefin (B). In general, the olefin copolymer (C) is present in the polymer compositions according to the invention in an amount of 0.1 to 10% by weight relative to the total weight of the latter compositions,

preferably in an amount of 0.2 to 5% by weight, most particularly in an amount of 0.5 to 2.5% by weight.

[0109] In one particular embodiment of the present invention [embodiment (I)], to which preference is generally given, one portion of the amount of functional monomer (f3) [from which the repeat units of the olefin copolymer (C) derive] has reacted with one portion of the amount of the functional group (f1) [contained in the compound (a) grafted to the fluoropolymer (A)], thus chemically bonding the olefin copolymer (C) to the fluoropolymer (A). According to this embodiment (I), it is preferred that one portion of the amount of functional monomer (f3) [from which the repeat units of the olefin copolymer (C) derive] has reacted and/or developed ionic interactions (for example, interactions between an oxygen atom and an atom of an alkali metal, such as sodium) and/or has formed hydrogen bridge bonds with the functional group (f2) [contained in the compound (b) grafted to the polyolefin (B)], thus bonding the olefin copolymer (C) to the polyolefin (B); particularly preferably, one portion of the amount of functional monomer (f3) has reacted and/or developed ionic interactions with one portion of the amount of functional group (f2); most particularly preferably, one portion of the amount of functional monomer (f3) has developed ionic interactions with one portion of the amount of the functional group (f2). Still according to this embodiment (I), it is preferred that one portion of the amount of functional group (f2) [contained in the compound (b) grafted to the polyolefin (B)] has reacted with one portion of the amount of functional group (f1) [contained in the compound (a) grafted to the fluoropolymer (A)], thus chemically bonding the polyolefin (B) to the fluoropolymer (A). Finally, still according to this embodiment (I), it is preferred that one portion of the amount of the functional group (f1) [contained in the compound (a) grafted to the fluoropolymer (A)] and one portion of the amount of the functional group (f2) [contained in the compound (b) grafted to the polyolefin (B)] remain in the unreacted state, and are therefore generally capable of conferring adhesion properties respectively on the fluoropolymer (A) and on the polyolefin (B); particularly preferably, one portion of the amount of the functional group (f1), one portion of the amount of the functional group (f2) and one portion of the amount of the functional monomer (f3) [from which the repeat units of the olefin copolymer (C) derive] remain in the unreacted state, and are therefore generally capable of conferring adhesion properties respectively on the fluoropolymer (A), on the polyolefin (B) and on the olefin copolymer (C).

[0110] In another embodiment of the present invention [embodiment (II)], the entire amount of the functional group (f1) [contained in the compound (a) grafted to the fluoropolymer (A)], the entire amount of the functional group (f2) [contained in the compound (b) grafted to the polyolefin (B)], and the entire amount of the functional monomer (f3) [from which the repeat units of the olefin copolymer (C) derive] are in the unreacted state. The polymer compositions according to the latter embodiment of the present invention are advantageously used as precursor compositions to the preparation of the compositions according to embodiment (I) as explained in detail above.

[0111] The polymer compositions according to the invention may also comprise one or more customary additives for thermoplastic polymers such as, for example, acid scavengers, lubricants, organic or mineral colorants, nucleating agents, fillers, stabilizers and flame retardants.

[0112] The polymer compositions according to the invention may be prepared by any known method. Advantageously, a method will be chosen that ensures an intimate mixing of their constituents (A), (B) and (C).

[0113] Another aspect of the invention therefore relates to a method for manufacturing the compositions as described above, according to which the fluoropolymer (A), the polyolefin (B) and the olefin copolymer (C) are mixed as a molten mass. In the method according to the present invention, it is moreover preferred to react the fluoropolymer (A), the polyolefin (B) and the olefin copolymer (C) as a molten mass. The expression "to react the constituents (A), (B) and (C)" should be understood to mean that at least two of the constituents (A), (B) and (C) are reacted with one another.

[0114] Thus, for example, in the method according to the present invention, the constituents (A), (B) and (C) may first be dry pre-mixed, in the required proportions, in any device suitable for this purpose, such as a drum mixer. The dry premix thus obtained is then melted either in batch mode, in batch devices such as kneaders, or in continuous devices such as the extruders described above with respect to the grafting of the compound (a) to the fluoropolymer (A). The premix intended to be melted can also be produced by the masterbatch technique. It is also possible to feed the kneaders or the extruders with the constituents (A), (B) and (C) metered separately, without dry pre-mixing. Once the constituents (A), (B) and (C) are melted, the mixing of these constituents is carried out or continued in any device suitable for this purpose. Advantageously, to do this, use is made of the same batch devices (kneaders, for example) or continuous devices (extruders, for example) as those previously used for the melting operation. Finally, while continuing the melt-blending of the constituents (A), (B) and (C) or after having finished the latter, the constituents (A), (B) and (C) are preferably reacted as a molten mass in these same devices.

[0115] A person skilled in the art may easily determine the general operating conditions of the mixing, melting and reaction devices by means of a few prior routine trials. In the case of extruders, in particular, the temperatures of the melting, homogenization and reaction zones are generally controlled between 140 and 270° C., preferably between 170 and 240° C.; the pressure in the die is generally less than 200 bar, preferably 100 bar, and more preferably still 50 bar; the rotational speed of the screw or screws is generally between 50 and 2000 rpm, preferably between 200 and 1000 rpm.

[0116] Good use may be made of the adhesive properties of the compositions according to the invention for producing multilayer structures, which constitute another subject of the present invention. These are multilayer structures for which one of the layers is composed of the polymer composition with adhesive properties. These structures contain at least one other layer which may be composed of various, both inorganic and organic, materials. As inorganic materials that may be incorporated into the composition of this other layer, mention may be made of metals and metal alloys, such as aluminium and steel, for example. As organic materials that may be incorporated into the composition of this other layer, mention may be made of thermoplastic polymers. Examples of thermoplastic polymers that may be incorporated into the composition of this other layer are polymers containing fluorine that belong to the family of fluoropolymers (A) and polymers containing olefins of the same nature as that (those) present in the olefin polymer (B).

[0117] Good use may be made of the adhesive properties of the compositions according to the invention for producing multilayer structures, which constitute another subject of the present invention. These are multilayer structures for which one of the layers is composed of the polymer composition with adhesive properties. These structures contain at least one other layer which may be composed of various, both inorganic and organic, materials. As inorganic materials that may be incorporated into the composition of this other layer, mention may be made of metals and metal alloys, such as aluminium and steel for example. As organic materials that may be incorporated into the composition of this other layer, mention may be made of thermoplastic polymers. Examples of thermoplastic polymers that may be incorporated into the composition of this other layer are the fluoropolymers corresponding to the definition of the fluoropolymer (A) and the polyolefins corresponding to the definition of the polyolefin (B), apart from when the polymers in question are not usually grafted.

[0118] Particular multilayer structures according to this aspect of the present invention are three-layer structures having an X/Y/Z configuration, for which the central layer Y is composed of the polymer composition with adhesive properties according to the invention and for which the layers X and Z are composed of a thermoplastic polymer, as defined above. Preferred multilayer structures are three-layer structures having an X/Y/Z configuration, for which the central layer Y is composed of the polymer composition with adhesive properties according to the invention, the layer X is composed of a polymer (usually ungrafted) based on olefin(s) of the same nature as that (those) present in the polyolefin (B) and the layer Z is composed of a polymer (usually ungrafted) based on fluoromonomer(s) of the same nature as that (those) present in the fluoropolymer (A).

[0119] These multilayer structures may be produced according to any process that is known for this purpose and is compatible with the nature of the constituent material of each layer. The assembling of the layers may be carried out, for example, by bonding or by hot press moulding of the constituent layers to one another, by coating of a solid layer with a powder or a solution of the constituent material of the other layer(s); or else, in particular in the case where the constituent materials of the layers are thermoplastics, by coextrusion, by coextrusion-blow moulding, by coinjection moulding and by coinjection moulding-moulding.

[0120] Coextrusion is particularly suitable for the production of multilayer structures having an X/Y/Z configuration, for which the central layer Y is composed of the polymer composition with adhesive properties according to the invention, the layer X is composed of a polyolefin (usually ungrafted) of the same nature as that (those) present in the polyolefin (B), in particular a homopolymer or copolymer derived from ethylene and/or propylene, and the layer Z is composed of a fluoropolymer (usually ungrafted) of the same nature as that (those) present in the fluoropolymer (A), in particular a homopolymer or copolymer derived from vinylidene fluoride. This coextrusion may be carried out, for example, in three extruders, preferably three single-screw extruders, feeding a sheet die via a feed-block or preferably feeding three-layer tubular dies.

[0121] The multilayer structures thus produced may be manufactured in the final form of sheets and films.

[0122] The multilayer structures thus produced may also be manufactured in the final form of hollow bodies, in particular

tanks, bottles, containers, tubes and pipes. The layer X then preferably constitutes the outer (convex) layer of the hollow bodies, whereas the layer Z then constitutes the inner (concave) layer of the hollow bodies. The hollow bodies, in particular the tubes, conduits and tanks, are advantageously used for the transport and/or storage of liquid hydrocarbons, in particular oils and fuels.

[0123] The following examples are intended to illustrate the invention without however limiting the scope thereof.

EXAMPLE 1

[0124] In a Brabender Plasticorder PL 2000 kneader rotating at 50 rpm, a polymer composition was prepared by mixing together, at a temperature of 190° C.:

[0125] (A) a random copolymer containing 85% by weight of vinylidene fluoride and 15% by weight of hexafluoropropylene, for which the melt flow index, $MFI_{2.16kg/230^{\circ}C}$ (ASTM 1238 standard) was 8 g/10 min and which was grafted by molecules of allyl glycidyl ether (this grafted copolymer was obtained by using, in a Clextral model BC 21 co-rotating twin-screw extruder, the feed zone of which was heated at 170° C. and the extrusion die at 220° C., 15 g of allyl glycidyl ether and 4 g of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DHP) as radical generator, per kg of extruded copolymer);

[0126] (B) a random copolymer containing 96% by weight of propylene and 4% by weight of ethylene, which was grafted, conventionally in an extruder, by maleic anhydride in the presence of DHP as radical generator, and the grafted anhydride groups of which were then neutralized by a mixture of sodium lactate and carbonate to convert it to an ionomer, of which the melt flow index, $MFI_{2.16kg/230^{\circ}C}$ (ASTM 1238 standard) was 2.3 g/10 min;

[0127] (C) a product sold under the name SURLYN® 1802 by Du Pont which is a copolymer containing around 90% by weight of ethylene and around 10% by weight of methacrylic acid, the carboxylic groups of which were completely or partially neutralized in the form of sodium ions and of which the melt flow index, $MFI_{2.16kg/230^{\circ}C}$ (ASTM 1238 standard) was 4.13 g/10 min.

[0128] The constituent (A) represented 54.5% by weight of the blend, the constituent (B) 44.5% by weight and the constituent (C) 1% by weight.

[0129] A three-layer film was then prepared by coextrusion, of which the constituent of the central layer was the polymer composition prepared from the above blend. The constituents of the outer layers were respectively:

[0130] for the lower layer, the fluoropolymer mentioned in (A) above, but not grafted;

[0131] for the upper layer, a random propylene/ethylene copolymer sold under the name ELTEX® P KS 409 by Ineos (melt flow index, $MFI_{2.16kg/230^{\circ}C}$ (ASTM 1238 standard): 5 g/10 min).

[0132] The operating conditions of the coextrusion are mentioned in Table 1 below.

TABLE 1

Single-screw extruder 1 (screw diameter: 20 mm)	Extrusion of the lower layer (average thickness: 70 µm)
Barrel temperature (° C.) (*)	175-210-210
Pressure (bar)	88.4
Speed (rpm)	30

TABLE 1-continued

Single-screw extruder 2 (screw diameter: 20 mm)	Extrusion of the central layer (average thickness: 35 µm)
Barrel temperature (° C.) (*)	210-230-240
Pressure (bar)	48
Material temperature	208
Speed (rpm)	30
Single-screw extruder 3 (screw diameter: 20 mm)	Extrusion of the lower layer (average thickness: 200 µm)
Barrel temperature (° C.) (*)	210-210-210-220-220
Pressure (bar)	72
Speed (rpm)	25

(*) from upstream to downstream of the extruder.

[0133] On exiting the extruders, the three extruded layers were taken up by a three-roll polishing stack brought to a temperature of 70° C. The film obtained could not be delaminated into its constituent layers, which attests to the adhesive properties of the central layer.

EXAMPLE 2

[0134] Example 1 was reproduced in every respect except that the random vinylidene fluoride/hexafluoropropylene copolymer of constituent (A) of the blend was grafted with 10 g/kg of 3-allyloxy-1,2-propanediol. The operating conditions of the coextrusion are mentioned in Table 2 below.

TABLE 2

Single-screw extruder 1 (screw diameter: 20 mm)	Extrusion of the lower layer (average thickness: 70 µm)
Barrel temperature (° C.) (*)	175-210-210
Pressure (bar)	63.1
Speed (rpm)	20
Single-screw extruder 2 (screw diameter: 20 mm)	Extrusion of the central layer (average thickness: 35 µm)
Barrel temperature (° C.) (*)	210-230-240
Pressure (bar)	35
Material temperature	206
Speed (rpm)	20
Single-screw extruder 3 (screw diameter: 20 mm)	Extrusion of the lower layer (average thickness: 200 µm)
Barrel temperature (° C.) (*)	210-210-210-220-220
Pressure (bar)	50
Speed (rpm)	15

(*) from upstream to downstream of the extruder.

[0135] On exiting the extruders, the three extruded layers were taken up by a three-roll polishing stack brought to a temperature of 70° C. It was difficult to delaminate the film obtained into its constituent layers, which attests to the adhesive properties of the central layer.

EXAMPLE 3R

[0136] This example is given by way of comparison.

[0137] Example 1 was reproduced except that the blend of the three constituents (A), (B), (C) was replaced by the constituent (A) alone in order to manufacture the central layer of the coextruded film. The operating conditions of the coextru-

sion and of the calendering were those from Example 2. No adhesion was observed between the constituent layers of the film.

EXAMPLE 4R

[0138] This example is given by way of comparison.

[0139] Example 1 was reproduced except that the blend of the three constituents (A), (B), (C) was replaced by a copolymer of propylene grafted by methyl methacrylate in order to manufacture the central layer of the coextruded film.

[0140] The operating conditions of the coextrusion are mentioned in Table 3 below.

TABLE 3

Single-screw extruder 1 (screw diameter: 20 mm)	Extrusion of the lower layer (average thickness: 70 μ m)
Barrel temperature ($^{\circ}$ C.) (*)	180-210-210
Pressure (bar)	138
Speed (rpm)	40
Single-screw extruder 2 (screw diameter: 20 mm)	Extrusion of the central layer (average thickness: 35 μ m)
Barrel temperature ($^{\circ}$ C.) (*)	160-175-175
Pressure (bar)	98
Material temperature	159
Speed (rpm)	60
Single-screw extruder 3 (screw diameter: 20 mm)	Extrusion of the lower layer (average thickness: 200 μ m)
Barrel temperature ($^{\circ}$ C.) (*)	190-200-200-200
Pressure (bar)	95
Speed (rpm)	15

(*) from upstream to downstream of the extruder.

[0141] The operating conditions of the calendering were those mentioned in Examples 1 and 2.

[0142] No adhesion was observed between the constituent layers of the film. Furthermore, it was observed that the multilayer structure had an unpleasant odour.

1. A polymer composition with adhesive properties comprising:

(1) at least one fluoropolymer (A) grafted by at least one compound (a) containing at least one functional group (f1) capable of conferring adhesion properties on said polymer;

(2) at least one polyolefin (B) grafted by at most 4% by weight, relative to the weight of polyolefin (B), of at least one compound (b) containing at least one functional group (f2) chosen from acid and anhydride groups, optionally completely or partially neutralized by at least one neutralizing agent; and

(3) at least one olefin copolymer (C), for which at least 5% by weight of the repeat units are derived from at least one functional monomer (f3) capable of reacting with the functional group (f1) contained in the compound (a).

2. The polymer composition according to claim 1, wherein said fluoropolymer (A) is a vinylidene fluoride polymer.

3. The polymer composition according to claim 1, wherein said functional group (f1) is selected from the group consisting of epoxy groups, alcohol groups, and carbonyl groups.

4. The polymer composition according to claim 1, wherein said compound (a) is selected from the group consisting of

allyl glycidyl ether, 3-allyloxy-1,2-propanediol, N-vinylpyrrolidone, and N-vinylcaprolactam.

5. The polymer composition according to claim 1, wherein said polyolefin (B) is selected from the group consisting of homopolymers and copolymers derived from ethylene and propylene.

6. The polymer composition according to claim 1, wherein said olefin copolymer (C) is a copolymer for which from 95 to 85% by weight of the repeat units are derived from ethylene and for which from 5 to 15% by weight of the repeat units are derived from methacrylic acid, the acid functions of which are completely or partially neutralized by the sodium ion.

7. The polymer composition according to claim 1, wherein the weight ratio of the fluoropolymer (A) to the polyolefin (B) is between 95/5 and 5/95.

8. The polymer composition according to claim 1, wherein said olefin copolymer (C) is present in an amount of 0.1 to 10% by weight relative to the total weight of said composition.

9. The polymer composition according to claim 1, wherein one portion of the amount of said functional monomer (f3) has reacted with one portion of the amount of said functional group (f1), thus chemically bonding said olefin copolymer (C) to said fluoropolymer (A).

10. The polymer composition according to claim 9, wherein one portion of the amount of said functional monomer (f3) has reacted and/or developed ionic interactions with one portion of the amount of said functional group (f2), thus bonding said olefin copolymer (C) to said polyolefin (B).

11. The polymer composition according to claim 9, wherein one portion of the amount of said functional group (f2) has reacted with one portion of the amount of said functional group (f1), thus chemically bonding said polyolefin (B) to said fluoropolymer (A).

12. The polymer composition according to claim 1, wherein the entire amount of said functional group (f1), the entire amount of the said functional group (f2) and the entire amount of said functional monomer (f3) are in an unreacted state.

13. A method for manufacturing the composition according to claim 1, according to which said fluoropolymer (A), said polyolefin (B) and said olefin copolymer (C) are mixed as a molten mass.

14. A method for manufacturing the composition according to claim 1, according to which said fluoropolymer (A), said polyolefin (B) and said olefin copolymer (C) are mixed and reacted as a molten mass.

15. A multilayer structure having an X/Y/Z configuration of layers X, Y and Z, wherein the central layer Y is composed of a polymer composition according to claim 1, wherein the layer X is composed of a polyolefin, and wherein the layer Z is composed of a fluoropolymer.

16. The multilayer structure according to claim 15, being manufactured in a final form of hollow bodies selected from the group consisting of tanks, bottles, containers, tubes, and pipes, the layer X constituting the outer layer of said hollow bodies and the layer Z constituting the inner layer of said hollow bodies.

17. A method of use of the multilayer structures according to claim 16 for the transport and/or storage of liquid hydrocarbons.

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