

PROCESS FOR GRAFTING A FLUOROPOLYMER AND MULTILAYER
STRUCTURES COMPRISING THIS GRAFTED POLYMER

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Field of the invention

Fluoropolymers, for example those based on vinylidene fluoride $\text{CF}_2=\text{CH}_2$ (VDF) such as PVDF (polyvinylidene fluoride), are known to offer excellent mechanical stability properties, very great chemical inertness and good ageing
10 resistance. These qualities are exploited for various fields of application. For example, mention may be made of the manufacture of extruded or injection-moulded parts for the chemical engineering industry or for microelectronics, the use in the form of impermeable ducts for transporting gases or hydrocarbons, the production of films or coatings for protection in the architectural field, and the production of protective
15 elements for electrical engineering uses.

However, this chemical inertness of fluoropolymers means that it is difficult to bond them or combine them with other materials. The present invention discloses a process in which a reactive functional group is fixed onto a fluoropolymer. This fluoropolymer thus modified may be easily bonded to or combined with other materials.
20 The process of the invention consists in melt-blending the fluoropolymer with the functional monomer that it is desired to graft onto the said fluoropolymer and then the mixture obtained, being in divided form such as granules, is irradiated in order to graft the functional monomer onto the fluoropolymer.

25 Prior art and technical problem

Patent **EP 214880** discloses a process for manufacturing polyvinylidene fluoride copolymers by grafting a monomer onto the polyvinylidene fluoride by means of ionizing radiation, which process comprises the following steps:

a) - immersing a polyvinylidene fluoride powder or film in a solution of a
30 monomer chosen from the group comprising acrylamide, styrene, methylstyrene, allyl glycidyl ether, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl

acrylate, dimethylaminopropyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, diethylaminopropyl acrylate, diethylaminopropyl methacrylate, dimethylaminopropyl methacrylamide, N-vinylpyrrolidone, N-vinylcaprolactam, acyloxy styrenes and hydroxystyrenes, vinyl sulphonic acid and its
5 derivatives, acrylic acid and methacrylic acid, in order to impregnate the polyvinylidene fluoride powder or film with the said monomer;

b) - irradiating the impregnated powder or film by means of ionizing radiation in the absence of oxygen; and

c) - then subjecting the grafted copolymer obtained to a chemical reaction in
10 order to confer an ionic character on it when the grafted monomer does not have an ionic character.

Patent Application **WO 00/17889** discloses power cable jackets comprising, in succession, a layer formed from an ethylene/alkyl acrylate/maleic anhydride terpolymer and a layer of a VDF/HFP fluorocopolymer. To improve the adhesion of these layers,
15 the assembly is subjected to ionizing radiation.

Patent **US 5 576 106** discloses a process for grafting an unsaturated functional monomer onto the surface of a powdered fluoropolymer. Powdered maleic anhydride is blended with the fluoropolymer and then they are put in a polyethylene bag and, after the air contained in the bag has been expelled, the bag containing the powder blend is
20 subjected to radiation of between 3 and 6 Mrad. According to a variant, the maleic anhydride is dissolved in acetone, the solution is mixed with the powdered fluoropolymer and then the acetone is evaporated. The material is then irradiated as above. The grafted fluoropolymer is then used in multilayer structures. In all the examples, only fluoroelastomers are used.

25 The peel force between a layer of fluoropolymer grafted according to the above prior art and another material is insufficient for many applications, particularly in structures that include polyolefins.

It has now been found that if the fluoropolymer and the functional monomer that it is desired to graft onto the said fluoropolymer are melt blended and then the blend
30 obtained, either in divided form, such as granules, or in film or sheet form, is irradiated, grafting through the mass of the fluoropolymer is obtained. This grafted fluoropolymer used in multilayer structures allows very high peel forces to be obtained.

Summary of the invention

According to a first aspect, there is provided a process for grafting an unsaturated monomer onto a fluoropolymer, in which:

- a) the fluoropolymer is melt blended with the unsaturated monomer;
- 5 b) the blend obtained in a) is made in the form of films, sheets, granules or powder;
- c) the products from step b) are exposed, in the absence of air, to photon (γ) or electron (β) irradiation with a dose of between 1 and 15 Mrad; and
- d) the product obtained at c) is optionally treated in order to remove all or part of
10 the unsaturated monomer that has not been grafted onto the fluoropolymer.

The grafted fluoropolymer thus obtained may be used as such or as a blend either with the same fluoropolymer but not grafted or with another fluoropolymer or with another polymer such as, for example, an acrylic polymer. As examples of acrylic polymers, mention may be made of PMMA and impact modifiers of the core/shell type.

According to a second aspect, there is provided a multilayer structure comprising at least one layer of the grafted fluoropolymer as disclosed herein and at least one layer of another material.

20 According to a third aspect, there are provided bottles, tanks, containers, pipes, hoses, vessels, films and packaging manufactured with the multilayer structure according to the second aspect.

According to a fourth aspect, there is provided a multilayer structure comprising an inner layer in contact with the fluid to be transported or stored,
25 consisting of the grafted fluoropolymer manufactured according to the first aspect and, directly attached to the latter, an outer polyolefin layer.

According to a fifth aspect, there is provided a multilayer structure comprising an inner layer in contact with the fluid to be transported or stored, made of the grafted fluoropolymer manufactured according to the first aspect and, directly attached to the
30 latter, a polyolefin layer and an outer polyamide layer.

According to a sixth aspect, there is provided a multilayer structure comprising a layer consisting of the grafted fluoropolymer manufactured according to the first aspect, placed between two polyolefin layers.

5 According to a seventh aspect, there is provided a multilayer structure comprising an inner layer in contact with the fluid to be transported or stored, consisting of the grafted fluoropolymer manufactured according to the first aspect and, directly attached to the latter, an outer polyamide layer.

Disclosed herein is the use of these structures for obtaining a barrier effect.

10 These structures may be barriers to many fluids and in particular to petrol and to air-conditioning fluids.

These structures may be formed into bottles, tanks, containers, pipes, hoses and vessels of all sorts. They may also be converted into films with which packaging is made.

15 The combined use of a fluoropolymer impermeable to apolar fluids and of a polyolefin impermeable to polar fluids may be particularly beneficial as it allows a barrier to be obtained that may be very effective against petrols containing liquids such as M15 (42.5% isooctane, 42.5% toluene and 15% methanol by volume) or TF1 (45% toluene, 45% isooctane and 10% ethanol).

20 Disclosed herein are structures in which the fluoropolymer is used to protect substrates.

Disclosed yet herein, the grafted fluoropolymer may be used on its own or as a blend, as mentioned above.

According to an eighth aspect, there is provided a bulk-grafted fluoropolymer manufactured in a process according to the first aspect. The bulk-grafted fluoropolymer may be used as a blend either with the same fluoropolymer but not grafted, or with another fluoropolymer or with another polymer such as, for example, an acrylic polymer. As examples of acrylic polymers, mention may be made of PMMA and impact modifiers of the core/shell type.

Detailed description of the invention

The term **fluoropolymer** thus denotes any polymer that has in its chain at least one monomer chosen from compounds containing a vinyl group capable of opening in order to be polymerized and that contains, directly attached to this vinyl group, at least one fluorine atom, at least one fluoroalkyl group or at least one fluoroalkoxy group.

As examples of monomers, mention may be made of vinyl fluoride; vinylidene fluoride (VDF); trifluoroethylene (VF₃); chlorotrifluoroethylene (CTFE); 1,2-difluoroethylene; tetrafluoroethylene (TFE); hexafluoropropylene (HFP); perfluoro(alkyl vinyl) ethers, such as perfluoro(methyl vinyl) ether (PMVE), perfluoro(ethyl vinyl) ether (PEVE) and perfluoro(propyl vinyl) ether (PPVE); perfluoro(1,3-dioxole); perfluoro(2,2-dimethyl-1,3-dioxole) (PDD); the product of formula $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{X}$ in which X is SO_2F , CO_2H , CH_2OH , CH_2OCN or $\text{CH}_2\text{OPO}_3\text{H}$; the product of formula $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$; the product of formula $\text{F}(\text{CF}_2)_n\text{CH}_2\text{OCF}=\text{CF}_2$ in which n is 1, 2, 3, 4 or 5; the product of formula $\text{R}_1\text{CH}_2\text{OCF}=\text{CF}_2$ in which R_1 is hydrogen or $\text{F}(\text{CF}_2)_z$ and z is 1, 2, 3 or 4; the product of formula $\text{R}_3\text{OCF}=\text{CH}_2$ in which R_3 is $\text{F}(\text{CF}_2)_z$ - and z is 1, 2, 3 or 4; perfluorobutylethylene (PFBE); 3,3,3-trifluoropropene and 2-trifluoromethyl-3,3,3-trifluoro-1-propene.

The fluoropolymer may be a homopolymer or a copolymer; it may also contain non-fluorinated monomers such as ethylene.

For example, the fluoropolymer is chosen from:

- homopolymers and copolymers of vinylidene fluoride (VDF) preferably containing at least 50% by weight of VDF, the comonomer being chosen from

chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), trifluoroethylene (VF3) and tetrafluoroethylene (TFE);

- homopolymers and copolymers of trifluoroethylene (VF3); and
- copolymers, and especially terpolymers, that combine the residues of the chlorotrifluoroethylene (CTFE), tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and/or ethylene units and optionally VDF and/or VF3 units.

Mention may also be made of ethylene/tetrafluoroethylene (ETFE) copolymers.

Advantageously, the fluoropolymer is polyvinylidene fluoride (PVDF) homopolymer or copolymer. Preferably, the PVDF contains at least 50%, more preferably at least 75% and even better at least 85% VDF by weight. The comonomer is advantageously HFP.

Advantageously, the PVDF has a viscosity ranging from 100 Pa.s to 2000 Pa.s, the viscosity being measured at 230°C with a shear rate of 100 s^{-1} using a capillary rheometer. These PVDFs are in fact well suited to extrusion and injection moulding. Preferably, the PVDF has a viscosity ranging from 300 Pa.s to 1200 Pa.s, the viscosity being measured at 230°C with a shear rate of 100 s^{-1} using a capillary rheometer.

Thus, PVDFs sold under the brand KYNAR® 710 or 720 are perfectly suitable for this formulation.

As example of the **unsaturated grafting monomer**, mention may be made of carboxylic acids and their derivatives, acid chlorides, isocyanates, oxazolines, epoxides, amines and hydroxides.

Examples of unsaturated carboxylic acids are those having 2 to 20 carbon atoms, such as acrylic, methacrylic, maleic, fumaric and itaconic acids. The functional derivatives of these acids comprise, for example, anhydrides, ester derivatives, amide derivatives, imide derivatives and metal salts (such as alkali metal salts) of unsaturated carboxylic acids. Mention may also be made of undecylenic acid.

Unsaturated dicarboxylic acids having 4 to 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, 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-1,2-dicarboxylic, 4-methylenecyclohex-4-ene-1,2-dicarboxylic, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic and x-methyl-bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic anhydrides.

Examples of other grafting monomers comprise 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 maleate, diethyl maleate, monomethyl fumarate, dimethyl fumarate, monomethyl itaconate and diethyl itaconate; amide derivatives of unsaturated carboxylic acids, such as acrylamide, methacrylamide, the monoamide of maleic acid, the diamide of maleic acid, the N-monoethylamide of maleic acid, the N,N-diethylamide of maleic acid, the N-monobutylamide of maleic acid, the N,N-dibutylamide of maleic acid, the monoamide of fumaric acid, the diamide of fumaric acid, the N-monoethylamide of fumaric acid, the N,N-diethylamide of fumaric acid, the N-monobutylamide of fumaric acid and the N,N-dibutylamide of fumaric acid; imide derivatives of unsaturated carboxylic acids, such as maleimide, N-butylmaleimide and N-phenylmaleimide; and metal salts of unsaturated carboxylic acids, such as sodium acrylate, sodium methacrylate, potassium acrylate and potassium methacrylate.

Advantageously, maleic anhydride is used.

Step a) is carried out in any mixing device, such as extruders or mixers used in the thermoplastics industry.

Regarding the proportions of the fluoropolymer and the unsaturated monomer, the proportion of fluoropolymer is advantageously, by weight, from 90 to 99.9% for 0.1 to 10% of unsaturated monomer, respectively. Preferably, the proportion of fluoropolymer is from 95 to 99.9% for 0.1 to 5% of unsaturated monomer, respectively.

After step a) it is observed that the fluoropolymer/unsaturated monomer blend has lost about 10 to 50% of the unsaturated monomer that had been introduced at the start of step a). This proportion depends on the volatility and the nature of the unsaturated monomer. In fact, the monomer is vented in the extruder or the mixer and is recovered in the venting circuits.

With regard to step c), the products recovered after step b) are advantageously packaged in polyethylene bags, the air is expelled and then the bags are closed. As

regards the method of irradiation, it is equally possible to use electron irradiation, more commonly known as beta irradiation, and photon irradiation, more commonly known as gamma irradiation. Advantageously, the dose is between 2 and 6 Mrad and preferably between 3 and 5 Mrad.

5 With regard to step d), the ungrafted monomer may be removed by any means. The proportion of grafted monomer with respect to the monomer present at the start of step c) is between 50 and 100%. A washing operation with solvents inert with respect to the fluoropolymer and to the grafted functional groups may be carried out. For example, when maleic anhydride is used for the grafting, chlorobenzene may be used for the
10 washing. It is also possible, more simply, to vacuum degas the product recovered in step c).

The invention also relates to structures. As examples of structures according to the invention, mention may be made of that comprising, in succession:

- an inner layer in contact with the fluid to be transported or stored, consisting of
15 the fluoropolymer grafted according to the invention and, directly attached to the latter, either an outer polyolefin layer or a polyolefin layer and an outer polyamide layer. A tie may be placed between the polyolefin layer and the polyamide layer. This structure is useful for motor-vehicle petrol tanks. According to a variant, this structure includes a layer of fluoropolymer, preferably PVDF (or ETFE), deposited beside the grafted
20 fluoropolymer. That is to say the structure comprises, in succession, a layer of fluoropolymer, preferably PVDF (or ETFE), a layer consisting of the fluoropolymer grafted according to the invention and, directly attached to the latter, either an outer polyolefin layer or a polyolefin layer and an outer polyamide layer. The layer of grafted fluoropolymer is a tie layer between the PVDF (or ETFE) layer and the polyolefin layer.
25 According to another variant, the grafted fluoropolymer layer is a blend either with the same fluoropolymer, but not grafted, or with another fluoropolymer or with another polymer such as, for example, an acrylic polymer. As examples of acrylic polymers, mention may be made of PMMA and impact modifiers of the core/shell type.

In the above structures, it is possible to place, between the grafted fluoropolymer
30 layer and the polyolefin layer, a layer of functionalized polyolefin having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer. For example, if maleic anhydride has been grafted onto the fluoropolymer, the

functionalized polyolefin layer consists of a copolymer of ethylene with glycidyl methacrylate and optionally with an alkyl acrylate, optionally in a blend with polyethylene.

5 In the above structures, the inner layer in contact with the fluid to be transported or stored may contain carbon black, carbon nanotubes or any other additive capable of making it conductive in order to prevent static electricity from building up.

As another example of structures according to the invention, mention may be made of that comprising, in succession:

10 - a layer consisting of the fluoropolymer grafted according to the invention, placed between two polyolefin layers. This structure is useful for motor-vehicle petrol tanks.

In the above structures, it is possible to place, between the grafted fluoropolymer layer and one or both polyolefin layers, a layer of functionalized polyolefin having functional groups capable of reacting with the functional groups grafted onto the
15 fluoropolymer. For example, if maleic anhydride has been grafted onto the fluoropolymer, the layer of functionalized polyolefin consists of a copolymer of ethylene with glycidyl methacrylate and optionally with an alkyl acrylate, optionally in a blend with polyethylene. According to another variant, the grafted fluoropolymer layer is a blend either with the same fluoropolymer, but not grafted, or with another
20 fluoropolymer or with another polymer such as, for example, an acrylic polymer. As examples of acrylic polymers, mention may be made of PMMA and impact modifiers of the core/shell type.

As another example of structures according to the invention, mention may be made of that comprising, in succession:

25 - an inner layer in contact with the fluid to be transported or stored, consisting of the fluoropolymer grafted according to the invention and, directly attached to the latter, an outer polyamide layer. This structure is useful for motor-vehicle fuel pipes or hoses.

According to a variant, this structure includes a layer of fluoropolymer, preferably PVDF (or ETFE), placed beside the grafted fluoropolymer. That is to say the
30 structure comprises, in succession, a layer of fluoropolymer, preferably PVDF (or ETFE), a layer consisting of the fluoropolymer grafted according to the invention and, directly attached to the latter, an outer polyamide layer. The layer of grafted

fluoropolymer is a tie layer between the PVDF or (ETFE) layer and the polyamide layer. According to another variant, the grafted fluoropolymer layer is a blend either with the same fluoropolymer, but not grafted, or with another fluoropolymer or with another polymer such as, for example, an acrylic polymer. As examples of acrylic polymers, mention may be made of PMMA and impact modifiers of the core/shell type.

According to another embodiment, the structure of the invention comprises a layer consisting of a grafted fluoropolymer according to the invention placed between two polyamide layers. This structure is useful as a petrol hose. According to an advantageous embodiment, the grafted fluoropolymer layer is a blend either with the same fluoropolymer, but not grafted, or with another fluoropolymer or with another polymer such as, for example, an acrylic polymer. As examples of acrylic polymers, mention may be made of PMMA and impact modifiers of the core/shell type.

In the above structures, it is possible to place, between the grafted fluoropolymer layer and the polyamide layer, a layer of functionalized polymer having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer, this functionalized polymer being compatible with the polyamide.

In the above structures, the inner layer in contact with the fluid to be transported or stored may contain carbon black, carbon nanotubes or any other additive capable of making it conductive in order to prevent static electricity from building up.

As another example of structures according to the invention, mention may be made of that comprising, in succession:

- an outer layer of grafted fluoropolymer of the invention and, directly attached to the latter, a layer of a substrate. The grafted fluoropolymer layer is used as a layer for protecting the substrate. The substrate may be a component of the body of a motor vehicle or an architectural component. According to a variant, this structure includes a layer of fluoropolymer, preferably PVDF, placed beside the grafted fluoropolymer. That is to say the structure comprises, in succession, a layer of fluoropolymer, preferably PVDF, a layer consisting of the fluoropolymer grafted according to the invention and, directly attached to the latter, a layer of a substrate. The layer of grafted fluoropolymer is a tie layer between the PVDF layer and the substrate layer. According to another variant, the grafted fluoropolymer layer is a blend either with the same fluoropolymer, but not grafted, or with another fluoropolymer or with another polymer such as, for

example, an acrylic polymer. As examples of acrylic polymers, mention may be made of PMMA and impact modifiers of the core/shell type.

In the above structures, it is possible to place, between the grafted fluoropolymer layer and the substrate layer, a layer of functionalized polymer having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer, this
5 polymer being compatible with the substrate.

The grafted fluoropolymer or PVDF used as layer for protecting a substrate may contain the usual UV stabilizers and/or radiation-absorbent fillers.

These structures may be manufactured by standard techniques, such as
10 extrusion, coextrusion, coextrusion blow moulding, coating, extrusion coating.

The invention also relates to the bulk-grafted fluoropolymer.

[Examples]

The following fluoropolymer was used:

15 **Kynar® 720:** A PVDF homopolymer from Atofina, having an MVI (melt volume index) of 10 cm³/10 min (230°C/5 kg).

Example 1: (according to the invention)

A blend of Kynar 720 PVDF from Atofina and 2% by weight of maleic anhydride was prepared. This blend was prepared using a twin-screw extruder at 230°C
20 and 150 rpm with an output of 10 kg/h. After the extrusion step, 1.8% of maleic anhydride remained in the product, the rest being lost during the extrusion step. The product thus prepared was put into sealed aluminium bags. These bags were then irradiated to 3 Mrad. A 40% degree of grafting was determined - this was checked after
25 a dissolution/precipitation step. The MA-g-PVDF product (maleic-anhydride-grafted PVDF) was then placed under vacuum overnight at 130°C in order to remove the residual maleic anhydride and the hydrofluoric acid liberated during irradiation.

A three-layer structure was produced by the compression moulding, at 220°C under 1 bar, of an MA-g-PVDF layer A (thickness: 500 µm) bonded to a layer B of a
30 blend of (i) 50% by weight of Lotader® 8840 (thickness: 100 µm), which is an ethylene/glycidyl methacrylate copolymer of 5 g/10 min MFI at 190°C/2.16 kg (containing 92% ethylene and 8% glycidyl methacrylate by weight), and (ii) 50% of

Stamylex® 1016 F polyethylene (an LLDPE of 1.1 g/10 min MFI at 190°C/2.16 kg) which was itself bonded to a layer C consisting of MS201N High-density PE (0.950 density; 8 g/10 min MFI at 190°C/2.16 kg) (thickness: 500 µm).

At $t = 0$, an adhesive strength of 30 N/cm was measured at the A/B interface, and the B/C interface could not be peeled. The structure was immersed in M15 fuel at 60°C. After 15 days, the structure showed no delamination and a force of 15 N/cm was measured at the A/B interface. After the A/B/C structure was vacuum-dried for one week at 60°C, the peel force between A and B was again measured, namely 30 N/cm.

10 Example 2: (comparative example)

A blend of Kynar 720 PVDF from Atofina and 2% by weight of maleic anhydride was prepared. This blend was prepared using a twin-screw extruder at 230°C and 150 rpm with an output of 10 kg/h. After the extrusion step, 1.8% of maleic anhydride remained in the product, the rest being lost during the extrusion step. The product thus prepared was put into aluminium sealed bags.

A three-layer structure was produced by the compression moulding, at 220°C under 1 bar, of an MA + PVDF layer A (thickness: 500 µm) bonded to a layer B of a blend of (i) 50% by weight of Lotader® 8840 (thickness: 100 µm) which is an ethylene/glycidyl methacrylate copolymer of 5 g/10 min MFI at 190°C/2.16 kg (92% ethylene and 8% glycidyl methacrylate by weight), and (ii) 50% of Stamylex® 1016 F polyethylene, which was itself bonded to a layer C consisting of MS201N High-density PE (thickness: 500 µm).

At $t = 0$, an adhesive strength of 1 N/cm was measured at the A/B interface and the B/C interface could not be peeled. The structure was immersed in M15 fuel at 60°C. After 15 days, the structure exhibited delamination at the A/B interface.

Example 3: (according to the invention)

A blend of Kynar 720 PVDF from Atofina and 0.5% by weight of maleic anhydride was prepared. This blend was prepared using a twin-screw extruder at 230°C and 150 rpm with an output of 10 kg/h. After the extrusion step, 0.45% of maleic anhydride remained in the product, the rest being lost during the extrusion step. The product thus prepared was put into sealed aluminium bags. These bags were then

irradiated to 3 Mrad. A 50% degree of grafting was determined - this was checked after a dissolution/precipitation step. The MA-g-PVDF product was then placed under vacuum overnight at 130°C in order to remove the residual maleic anhydride and the hydrofluoric acid liberated during irradiation.

5 A three-layer structure was produced by the compression moulding, at 220°C under 1 bar, of an MA-g-PVDF layer A (thickness: 500 µm) bonded to a layer B of a blend of (i) 50% by weight of Lotader® 8840 (thickness: 100 µm), which is an ethylene/glycidyl methacrylate copolymer of 5 g/10 min MFI at 190°C/2.16 kg (containing 92% ethylene and 8% glycidyl methacrylate by weight), and (ii) 50% of
10 Stamylex® 1016 F polyethylene which was itself bonded to a layer C consisting of MS201N High-density PE (thickness: 500 µm).

At $t = 0$, an adhesive strength of 25 N/cm was measured at the A/B interface, and the B/C interface could not be peeled. The structure was immersed in M15 fuel at 60°C. After 15 days, the structure showed no delamination and a force of 14 N/cm was
15 measured at the A/B interface. After the A/B/C structure was vacuum-dried for one week at 60°C, the peel force between A and B was again measured, namely 25 N/cm.

Example 4: (according to the invention)

A blend of Kynar 720 PVDF from Atofina and 2% by weight of maleic anhydride was prepared. This blend was prepared using a twin-screw extruder at 230°C
20 and 150 rpm with an output of 10 kg/h. After the extrusion step, 1.8% of maleic anhydride remained in the product, the rest being lost during the extrusion step. The product thus prepared was put into sealed aluminium bags. These bags were then irradiated to 3 Mrad. A 40% degree of grafting was determined - this was checked after
25 a dissolution/precipitation step. The MA-g-PVDF polymer was then extruded under vacuum in order to allow devolatilization of the ungrafted species.

A three-layer structure was produced by the compression moulding, at 220°C under 1 bar, of an MA-g-PVDF layer A (thickness: 500 µm) bonded to a layer B of a blend of (i) 50% by weight of Lotader® 8840 (thickness: 100 µm), which is an
30 ethylene/glycidyl methacrylate copolymer of 5 g/10 min MFI at 190°C/2.16 kg (containing 92% ethylene and 8% glycidyl methacrylate by weight), and (ii) 50% of

Stamylex® 1016 F polyethylene which was itself bonded to a layer C consisting of MS201N High-density PE (thickness: 500 µm).

At $t = 0$, an adhesive strength of 30 N/cm was measured at the A/B interface, and the B/C interface could not be peeled. The structure was immersed in M15 fuel at 60°C. After 15 days, the structure showed no delamination and a force of 15 N/cm was measured at the A/B interface. After the A/B/C structure was vacuum-dried for one week at 60°C, the peel force between A and B was again measured, namely 30 N/cm.

Example 5: (comparative example):

A powder blend, consisting of Kynar 720 PVDF (2000 g) with maleic anhydride (20 g) was prepared. The blending was carried out in a turbolator for 10 minutes. The blend was put into a sealed bag. The bag was sealed, taking care to expel as much air as possible from the bag. The sealing of the bag was checked, as neither air nor dust must be able to escape from the bag. The latter underwent beta irradiation to 6 Mrad (10 MeV beta). The powder, infrared-analysed after heating in an oven overnight at 130°C, had a degree of grafting below the detection limit $< 0.05\%$. The maleic anhydride had not grafted onto the outermost surface of the PVDF powder.

Example 6: (according to the invention)

A blend of Kynar 720 PVDF from Atofina and 0.5% by weight of maleic anhydride was prepared. This blend was prepared using a twin-screw extruder at 230°C and 150 rpm with an output of 10 kg/h. After the extrusion step, 0.45% of maleic anhydride remained in the product, the rest being lost during the extrusion step. The product thus prepared was put into sealed aluminium bags. These bags were then irradiated to 3 Mrad. A 50% degree of grafting was determined - this was checked after a dissolution/precipitation step. The MA-g-PVDF product was then placed under vacuum overnight at 130°C in order to remove the residual maleic anhydride and the hydrofluoric acid liberated during irradiation.

A five-layer structure was reduced by the compression moulding, at 220°C under 1 bar, of a C/B/A/B/C structure, with the layer A consisting of MA-g-PVDF (thickness: 200 µm), the layer B consisting of a blend of (i) 50% by weight of Lotader® 8840 (thickness: 100 µm) which is an ethylene/glycidyl methacrylate

copolymer of 5 g/10 min MFI at 190°C/2.16 kg (92% ethylene and 8% glycidyl methacrylate by weight), and (ii) 50% of Stamylex® 1016 F polyethylene and the layer C consisting of MS201N high-density PE (1000 µm).

At $t = 0$, an adhesive strength of 70 N/cm was measured at the A/B interface, and the B/C interface could not be peeled. The structure was immersed in M15 fuel at 60°C. After 22 days, the structure showed no delamination and a force of 20 N/cm was measured at the A/B interface. After the C/B/A/B/C structure was vacuum-dried for one week at 60°C, the peel force between A and B was again measured, namely 70 N/cm.

10 Example 7: (according to the invention)

A blend of Kynar 720 PVDF from Atofina and 2% by weight of maleic anhydride was prepared. This blend was prepared using a twin-screw extruder at 230°C and 150 rpm with an output of 10 kg/h. After the extrusion step, 1.8% of maleic anhydride remained in the product, the rest being lost during the extrusion step. The product thus prepared was put into sealed aluminium bags. These bags were then irradiated to 3 Mrad. A 40% degree of grafting was determined - this was checked after a dissolution/precipitation step. The MA-g-PVDF product was then extruded under vacuum in order to allow devolatilization of the ungrafted species.

A three-layer structure was then coextruded, this consisting of an MA-g-PVDF layer A (thickness: 150 µm) bonded to a layer B of a blend of (i) 50% by weight of Lotader® 8840 (thickness: 50 µm), which is an ethylene/glycidyl methacrylate copolymer of 5 g/10 min MFI at 190°C/2.16 kg (92% ethylene and 8% glycidyl methacrylate by weight), and (ii) 50% of Stamylex® 1016 F polyethylene, which was itself bonded to a layer C consisting of 2040 ML55 high-density PE (thickness: 800 µm).

At $t = 0$, an adhesive strength of 30 N/cm was measured at the A/B interface, and the B/C interface could not be peeled. The structure was immersed in M15 fuel at 60°C. After 15 days, the structure showed no delamination and a force of 15 N/cm was measured at the A/B interface. After the A/B/C structure was vacuum-dried for one week at 60°C, the peel force between A and B was again measured, namely 30 N/cm.

CLAIMS

1. Process for grafting an unsaturated monomer onto a fluoropolymer, in which:
 - a) the fluoropolymer is melt blended with the unsaturated monomer;
 - b) the blend obtained in a) is made in the form of films, sheets, granules or powder;
 - c) the products from step b) are exposed, in the absence of air, to photon (γ) or electron (β) irradiation with a dose of between 1 and 15 Mrad; and
 - d) the product obtained at c) is optionally treated in order to remove all or part of the unsaturated monomer that has not been grafted onto the fluoropolymer.
2. Process according to Claim 1, in which the fluoropolymer is PVDF.
3. Process according to Claim 2, in which the PVDF contains at least 85% VDF by weight.
4. Process according to any one of the preceding claims, in which the unsaturated monomer is maleic anhydride.
5. Process according to any one of the preceding claims, in which the proportion of fluoropolymer is, by weight, from 90 to 99.9% for 0.1 to 10% of unsaturated monomer, respectively.
6. Process according to Claim 5, in which the proportion of fluoropolymer is from 95 to 99.9% for 0.1 to 5% of unsaturated monomer, respectively.
7. Process according to any one of the preceding claims, in which the irradiation dose is between 2 and 6 Mrad.
8. A multilayer structure comprising at least one layer of the grafted fluoropolymer prepared according to the process of any one of the preceding claims and at least one layer of another material.
9. Bottles, tanks, containers, pipes, hoses, vessels, films and packaging manufactured with the multilayer structure of Claim 8.
10. A multilayer structure comprising an inner layer in contact with the fluid to be transported or stored, consisting of the grafted fluoropolymer manufactured according to any one of Claims 1 to 7 and, directly attached to the latter, an outer polyolefin layer.
11. A multilayer structure comprising an inner layer in contact with the fluid to be transported or stored, made of the grafted fluoropolymer manufactured according to any

one of Claims 1 to 7 and, directly attached to the latter, a polyolefin layer and an outer polyamide layer.

12. The multilayer structure according to Claim 10 or 11, in which a PVDF (or ETFE) layer is placed beside the grafted fluoropolymer layer.
13. The multilayer structure according to either of Claims 10 and 11, in which a layer of functionalized polymer having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer is placed between the grafted fluoropolymer layer and the polyolefin layer.
14. A multilayer structure comprising a layer consisting of the grafted fluoropolymer manufactured according to any one of Claims 1 to 7, placed between two polyolefin layers.
15. The multilayer structure according to Claim 14, in which a layer of functionalized polyolefin having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer is placed between the grafted fluoropolymer layer and one or both polyolefin layers.
16. A multilayer structure comprising an inner layer in contact with the fluid to be transported or stored, consisting of the grafted fluoropolymer manufactured according to any one of Claims 1 to 7 and, directly attached to the latter, an outer polyamide layer.
17. The multilayer structure according to Claim 16, in which a PVDF (or ETFE) layer is placed beside the grafted fluoropolymer layer.
18. The multilayer structure according to Claim 16, comprising a grafted fluoropolymer layer placed between two polyamide layers.
19. The multilayer structure according to any one of Claims 16 to 18, in which a layer of functionalized polymer having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer is placed between the grafted fluoropolymer layer and the polyamide layer, this functionalized polymer being compatible with the polyamide.
20. The multilayer structure according to any one of Claims 10 to 19, in which the inner layer in contact with the fluid to be transported or stored may contain carbon black, carbon nanotubes or any other additive capable of making it conductive in order to prevent static electricity from building up.

21. The multilayer structure comprising an outer layer consisting of the grafted fluoropolymer manufactured according to any one of Claims 1 to 7 and, directly attached to the latter, a layer of a substrate.
22. The multilayer structure according to Claim 21, in which a PVDF layer is placed beside the grafted fluoropolymer layer.
23. The multilayer structure according to Claim 21 or 22, in which a layer of functionalized polymer having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer is placed between the grafted fluoropolymer layer and the substrate layer, this functionalized polymer being compatible with the substrate.
24. The multilayer structure according to any one of Claims 10 to 23, in which the grafted fluoropolymer layer is a blend either with the same fluoropolymer, but not grafted, or with another fluoropolymer or with another polymer such as, for example, an acrylic polymer.
25. Bulk-grafted fluoropolymer manufactured in a process according to claim 1.
26. Polymer according to Claim 25, in which the fluoropolymer is PVDF.
27. Polymer according to Claim 25, in which the PVDF contains at least 85% VDF by weight.
28. Polymer according to any one of Claims 25 to 27, in which the unsaturated monomer is maleic anhydride.
29. Polymer according to any one of Claims 25 to 28, in which the proportion of fluoropolymer is, by weight, from 90 to 99.9% for 0.1 to 10% of unsaturated monomer, respectively.
30. Polymer according to Claim 29, in which the proportion of fluoropolymer is from 95 to 99.9% for 0.1 to 5% of unsaturated monomer, respectively.