

METHOD FOR IMPROVING ADHESION AND ADHESIVE BONDING IN FLUOROPOLYMERS

FIELD OF INVENTION

The present invention is related to a method for substantially and permanently improving the adhesion and adhesive bonding properties of fluoropolymers, such as polytetrafluoroethylene films, sheets, plates or fibers. The method involves the further modification and functionalization of a pre-activated fluoropolymer surface via thermally or near-UV-light induced surface graft copolymerization with epoxide- or glycidyl ether-containing monomers. Strong adhesion is obtained when two modified fluoropolymer surfaces, or a modified fluoropolymer surface and a modified non-fluorine containing polymer surface, are brought into close contact in the presence of an epoxy curing agent, an epoxy adhesive (epoxy resin plus curing agent), or a solvent for the grafted epoxide or glycidyl ether polymer. Strong interfacial adhesion is also obtained between the modified fluoropolymer surface and a pristine (unmodified) conjugated electroactive polymer film, such as a film of aniline, pyrrole, thiophene or acetylene polymer, as well as between the modified fluoropolymer surface and a metal (such as copper, zinc, steel, gold, silver platinum, palladium etc.) surface, in the presence of an epoxy adhesive.

BACKGROUND OF INVENTION

Often, the selected polymer has surface characteristics that are less than optimum for the intended application. This is particularly true in the case of adhesion involving fluoropolymer surfaces. To correct this, the strategies of surface chemical modification have been widely implemented for fluoropolymers and hydrocarbon polymers alike. They have been described, for example, in S. Wu, "Polymer Interfaces and Adhesion", Dekker, New York (1982); Y. Ikada and Y. Uyama, "Lubricating Polymer Surfaces", Technomic

Pub. Co. Inc., Lancaster, PA (1993); and L.S. Penn and H. Wang, *Polymers for Advanced Technologies*, 5, 809 (1994); E.T. Kang, K.G. Neoh, K.L. Tan, F.C. Loh and D.J. Liaw, *Polymers for Advanced Technologies*, 5, 837 (1994); and K.L. Mittal, (Ed), "Polymer Surface Modification: Relevance to Adhesion", VSP, Zeist, The Netherlands (1995).

Of all the dielectric materials, the fluoropolymers, in particular polytetrafluoroethylene or PTFE, are ideal dielectric materials, from the standpoints of electrical and thermal properties, for the packaging of microelectronics. With improved adhesion between fluoropolymer surfaces and at the interface between a fluoropolymer and a metal, the application of fluoropolymers in multi-chip module (MCM) packaging, for instance, may become a reality. The physical and chemical inertness associated with most of the fluoropolymer, however, dictates the use of more drastic means for achieving the required surface modifications. A large amount of work has been devoted to the surface modification of fluoropolymers for adhesion and adhesive bonding improvements. The works have been described, for examples, in H.K. Yasuda, "Plasma Polymerization and Plasma Interactions with Polymeric Materials", *J.Appl. Polym. Sci. : Appl. Polym. Symp.*(1990), p46; M. Strobel, C.S. Lyons and K.L. Mittal (Eds.), "Plasma Surface Modification of Polymers: Relevance to Adhesion", VSP, Zeist, The Netherlands (1994); and M.K. Shi, L. Martinu, E. Sacher, A. Selmani, M.R. Wertheimer and A. Yelon, *Surf. Interf. Anal.* 23, 99 (1995). One of the major drawbacks of the most commonly utilized technique of plasma treatment is that the physicochemical characteristics of the modified polymer surfaces, including surface compositions, are time-dependent. Chain and polar group reorientation in the surface region can result in gradual deterioration of the surface reactivity. Furthermore, anomalous changes in oxygen and fluorine contents, and therefore also surface compositions, may result from the presence of surface hydrocarbon contamination during plasma treatment, as suggested by M.A.Golub, E.S.Lopata and L.S.Finney, *Langmuir*, 10, 3629 (1994).

Two very different plasma processes, activation and deposition, as a means to achieve reliable and high-strength structural bonding have been evaluated by S.L. Kaplan, E.S. Lopata and J. Smith in *Surf. Interf. Anal.* 20, 331 (1993). The tensile adhesion results,

as well as chemical structural information from surface analyses, support the theory that a modified and weakened polytetrafluoroethylene transition layer is established at the interface between the bulk and the fully modified surface, accounting for the low adhesion strength of the plasma-treated surface compared to the sodium naphthalene-etched surface.

The patent literature is flooded with claims of surface modification of fluoropolymers for adhesion enhancement. However, most of the cases are related to plasma or chemical surface treatments. Almost no case study is directly related to the modification of fluoropolymer via surface graft copolymerization for the improvement of adhesion between two fluoropolymer surfaces, between a fluoropolymer surface and a conventional or non-fluorine containing polymer surface, between a fluoropolymer surface and a conjugated polymer surface, or between a fluoropolymer surface and a metal surface. A few cases of adhesion enhancement or adhesive bonding improvement, based on graft copolymerization technique, but mainly on non-fluorine containing polymers, have surfaced in our exhaustive patent literature search. The search results are summarized below:

In U.S. Patent No. 4,506,035, March 19, 1985, the wettability and hydrophilicity of microporous fluoropolymer membranes for electrolytic cells are improved via graft copolymerization of carboxyl-containing monomers.

In U.S. Patent No. 4,472,557, September 18, 1984, a fluoro hydrocarbon resin that has elasticity and retains favorable properties of known fluoro-hydrocarbon polymers is obtained by graft copolymerization of a fluorine-containing crystalline polymer. One of the elastomeric and crystalline polymers is prepared by copolymerizing at least one fluorine-containing monomer with at least one unsaturated monomer that has peroxy bonds.

In Japan Patent JP 7,186,325A, July 25, 1995, a polyolefin type resin adhesive for coating steel materials with polyolefin is produced by graft modifying low density polyethylene with maleic anhydride.

In European Patent EP 656,376, June 7, 1995; Japan Patent JP 7,149,960, June 13, 1995; and Canadian Patent CA 2,136,897, June 2, 1995, polyolefin resins are graft modified in aqueous suspension, using a glycidyl functional aromatic monomer and in the presence of a radical polymerization initiator. The resin compositions have improved (claimed) mechanical properties, adhesivity, dyeability and paintability.

In Japan Patent, JP 7,025,952A, January 27, 1995, an adherable fluororubber for use in laminates is obtained by graft-copolymerization of one or more compounds of an unsaturated carbonic acid, an anhydride therefore, or an ester therefore onto tetrafluoroethylene-propylene copolymeric fluororubber. A laminate using this fluororubber has a (claimed) good adhesion strength and excellent characteristics of tetrafluoroethylene-propylene copolymeric fluororubber.

In Japan Patent, JP 7,010,960A, January 13, 1995, modified epoxy resins useful as coating material for metal plates are prepared by reacting aromatic epoxy compounds with dicarboxylic acids and secondary amines, or by graft copolymerization of ethylenically unsaturated monomers.

In Japan Patent, JP 6,206,946A, July 26, 1994, a graft-modified ethylene alpha-olefin copolymer composition with good adhesion to polar material is obtained by copolymerizing ethylene with alpha-olefin using catalyst of aluminum oxy compound and transition metal with cyclopentadienyl ligands

In German Patent DE 4,345,086, July 21, 1994; Japan Patent, JP 6,256,437, September 13, 1994; Taiwan Patent, Tw 242,636, March 11, 1995; and U.S. Patent No. 5,449,707, September 12, 1995, aqueous dispersions for paints, ink, adhesives etc. are prepared from graft copolymers of unsaturated monomer-containing polyester and radically-polymerizable monomers with hydrophilic groups.

In World Patent, WO 9,409,067, April 28, 1994, polymer compositions with improved bonding and printability are prepared from functionalized high melt flow

polyolefins, via graft copolymerization of maleic anhydride with polybutene, and non-functionalized polyolefins.

In Japan Patent, JP 6,080,845A, March 22, 1994, aqueous resin compositions for adhesives, primers, inks, sealant and paints are obtained by adding water to products prepared from graft polymerization of modified polyolefin and chlorinated polyolefin with reactive surfactant.

In Japan Patent, JP 5,025,405A, February 2, 1993, primer compositions with improved adherence to molding compositions for coating films are prepared from chlorinated alpha, beta unsaturated vinyl monomer, graft copolymerized with styrene-conjugated diene block copolymer and an organic solvent.

In Japan Patent, JP 4,236,287A, August 25, 1992, compositions of hot melt adhesive for paper, wood, plastics, etc. are prepared from non-crystalline polyolefin of propylene and polyolefin modified by graft-copolymerization of derivatives of unsaturated carboxylic acid.

In Japan Patent, JP 3,052,983A, March 7, 1991, coating composition for polyolefin resin to improve adhesion and comprises of resin obtained from propylene, alpha-olefin and unsaturated dicarboxylic acid has been described.

In Denmark Patent, DK 8,905,527, November 6, 1989; and Japan Patent, JP 3,124,782, May 28, 1991, surface modification of polyolefin matrix is achieved by graft copolymerization of polyolefin stemmed with alkyl methacrylate and unsaturated acid.

In Japan Patent, JP 1,265,886A, January 23, 1989, fibrous or filmy carries for fixing enzymes are prepared by graft copolymerization of copolymerizable monomer on the surface of polyester and polyether fibers and film previously irradiated with low temperature plasma.

In Chinese Patent, CN 86,104,775, January 27, 1986, polyolefin adhesive for bonding polypropylene to steel and aluminum is prepared by free radical graft copolymerization of polypropylene chloride with acrylonitrile and acrylate in solution.

In Japan Patent JP 60,026,071A, February 8, 1985; and JP 92,004,353B, January 28, 1992, adhesives for chlorine-containing polymer materials are prepared by graft copolymerization of crystalline polyolefin and styrenic hydrocarbon as graft component.

In Japan Patent JP 60,020,941A, February 2, 1985, the claimed process comprises sputter etching the surface of formed polyfluorolefin product using ionizing radiation under a pressure of 0.005-1 Torr of air or steam. Graft copolymerization is affected by contacting the surface of formed product with a polymerizable monomer.

In Japan patent JP 60,166,311A, August 29, 1985, an inexpensive adhesive for halogen-containing polymer, oxygen-containing aromatic copolymer and acrylonitrile polymer, having excellent adhesivity and heat-resistance, is prepared by grafting a polyolefin with an unsaturated epoxy monomer.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a new method to substantially improve the adhesion characteristics of fluoropolymer films, sheets and slabs. It is also an object of the present invention to provide a new method to substantially enhance the adhesive bonding adhesion between two fluoropolymer films, sheets or slabs, or between a fluoropolymer and a non-fluorine containing polymer. These and other objects and advantages of the present invention are obtained by providing a method for modifying and functionalizing the fluoropolymer and non-fluorine containing polymer surfaces through first plasma pretreatment, followed by thermally or near-UV-light induced surface graft copolymerization. Desirable radio frequency argon plasma with low plasma power is

selected to minimize the undesirable etching or sputtering of the fluoropolymer surface. For the non-fluorine containing polymers, other pretreatment methods, such as ozone and corona-discharge exposures, may be used instead.

The objects and advantages of the present invention can be achieved when the monomers used for surface graft copolymerization are selected from a group of vinyl monomers with epoxide or glycidyl ether functional groups. More particularly, the vinyl monomers are also selected from the group which readily undergo free-radical initiated polymerization.

The objects and advantages of the present invention can be achieved when the monomer concentrations used for graft copolymerization range from 2 to 50 weight percent. Desirably the organic solvents are selected from the group which provide good solubility for the epoxide or glycidyl ether polymer, and which promote free radical polymerization.

The objects and advantages of the present invention can be achieved on virtually all polymer substrates, including polyolefins, polyesters, hydrocarbon polymers, other halogen containing polymers, thermosetters, polyimides, and electroactive conjugated polymers. The maximum objectives and advantages are realized on fluoropolymer substrates, such as , but not limit to, polytetrafluoroethylene and poly(vinylidene fluoride).

More particularly, said electroactive conjugated polymers thereof may include polyaniline, polypyrrole, polythiophene, substituted acetylene polymers, and their derivatives and analogs.

The objects and advantages of the present invention are obtained when two modified fluoropolymer surfaces, a modified fluoropolymer surface and a modified non-fluorine containing polymer surface, or two modified non-fluorine containing polymer surfaces are brought into contact with one another in the presence of an applied epoxy adhesive (epoxy resin plus curing agent). Strong adhesion between the two polymer

surfaces results after the curing of the applied epoxy adhesive. Most of pristine or unmodified fluoropolymers, such as pristine polytetrafluoroethylene, do not adhere to one another at all in the presence of an applied epoxy adhesive.

The objects and advantages of the present invention are also obtained when two modified fluoropolymer surfaces, a modified fluoropolymer surface and a modified non-fluorine containing polymer surface, or two modified non-fluorine containing polymer surfaces are brought into contact with one another in the presence of an applied epoxy curing agent alone.

The objects and advantages of the present invention are also obtained when an epoxide-containing monomer graft copolymerized fluoropolymer surface and a clean metal surface are brought into contact in the presence of an epoxy adhesive. The preferred metals are selected from copper, gold, silver, chromium, aluminum, zinc, tin, silicon, steel, stainless steel and other related metals and alloys.

DESCRIPTION OF PREFERRED EMBODIMENTS

While not wishing to be bound by any theory, it is believed that the present invention is based upon the fact that by modifying the fluoropolymer, such as polytetrafluoroethylene surfaces, and non-fluorine containing polymer surfaces via graft copolymerization, the adhesive bonding properties of the fluoropolymer and non-fluorine containing polymer surfaces are substantially improved and remains permanently improved. Conventional surface modification techniques, such as plasma treatment, usually give rise to less effective adhesive bonding, and time-dependent surface properties. In the preferred method, the argon plasma pretreated fluoropolymer and non-fluorine containing polymer surfaces are subject to thermally or near-UV-light induced surface graft copolymerization with epoxide- or glycidyl ether-containing monomers. The grafted epoxide or glycidyl ether polymer is incorporated on the fluoropolymer and non-

fluoropolymer surfaces through covalent bonding. When two similarly modified fluoropolymer surfaces, or two similarly modified non-fluoropolymer surface, or a modified fluoropolymer and a similarly modified non-fluoropolymer surface are brought into close contact with one another in the presence of an epoxy curing agent, such as an amine, hydroxyl or anhydride compound, or an epoxy adhesive (epoxy resin plus curing agent), or a solvent for the graft epoxy polymer, strong adhesive bonding results. In the presence of an epoxy curing agent or an epoxy adhesive, the strong interfacial adhesion arises from the extensive curing reaction of the epoxy functional groups from the surface graft polymer with the applied curing agent, or with the curing agent in the applied epoxy adhesive. In the case of modified polytetrafluoroethylene films and thin sheets, the adhesion strength in the presence of an epoxy curing agent or an epoxy adhesive can readily exceed the tensile yield strength of the fluoropolymer substrate. In the presence of a solvent, diffusion and entanglement of the grafted epoxy chains at the interface result in adhesive-free adhesion between two fluoropolymer films. The adhesion strength in the form of lap shear strength arising from the adhesive-free adhesion is much lower than the adhesive bonding strength in the presence of a curing agent or epoxy adhesive, due to the absence of any covalent bonding and cross-linking at the interface.

The preferred application and the best advantages of the present invention are obtained from fluoropolymer and non-fluoropolymer films, thin sheets or plates. The process is applicable to all fluoropolymer substrates, such as polytetrafluoroethylene substrate, and all non-fluorine containing polymer substrates, such as polyolefins, polyesters, hydrocarbon polymers, and conjugated electroactive polymers, etc. Thus in the preferred method, the surface of the polymer is first pretreated with radio frequency argon plasma. the selections of plasma power and duration to be used for pretreatment are not particularly important. However, high plasma power and long pretreatment time can result in excessive etching of the polymer surface, in surface cross-linking and in dehalogenation of the polymer sample. The preferred range of plasma power is typically from 10 W to 50 W. The preferred range of treatment time is typically from 3 s to 40 s. For the non-fluorine containing polymers, other pretreatment, such as ozone and corona-discharge may be used. Monomers for graft copolymerization are selected from a group of vinyl monomers which

readily undergo free-radical initiated polymerization. Desirably, the monomers are selected from the family containing the epoxide or glycidyl ether functional group or groups, such as , but not limited to, glycidyl methacrylate and ally glycidyl ether.

The range of monomer concentration used for graft copolymerization typically range from 2 weight percent to 50 weight percent. The preferred organic solvent is dioxane, although other organic solvents for the epoxide or glycidyl ether polymer may be used.

EXAMPLES

The following specific examples are provided to illustrate this invention and the manner in which it may be carried out. It will be understood, however, that the specific details given in each example have been selected for purpose of illustration and are not to be construed as a limitation on the invention. In the examples, unless otherwise indicated, all parts and percentages are by weight. Example 1 provides more details on the conduct of the experiment on the surface graft copolymerization with epoxide or glycidyl monomer.

EXAMPLE 1

In a preferred experimental scale process, an Ar plasma pretreated polytetrafluoroethylene film of size 1.5cm × 3.5cm was immersed in 30 ml of the 1,4-dioxane monomer solution in a Pyrex® tube. The concentrations of the glycidyl methacrylate monomer were varied from 2 to 50%. Each reaction mixture was thoroughly degassed and sealed under a nitrogen atmosphere. It was then subjected to near-UV-light illumination for about 1 to 2 hours with a 150W Xenon arc source. After each grafting experiment, the polytetrafluoroethylene film was removed from the viscous homopolymer solution and washed with copious amounts of acetone. It was then subjected to Soxhlet extraction with acetone for about 1 to 2 hours to remove the residual homopolymer. The

surface modified fluoropolymer film was subsequently dried by pumping under reduced pressure.

EXAMPLE 2

In a preferred adhesion experiment, two polytetrafluoroethylene films with surface grafted glycidyl methacrylate polymer were lapped together under pressure and in the presence of an epoxy adhesive. The latter consists of the poly(Bis-phenol A -co-epichlorohydrin) and an amine curing agent. Lap shear adhesion strength in excess of 300 N/cm² can be readily obtained for the properly cured junction. The junction also exhibits a tensile pull strength in excess of 1000 N/cm². The pristine or unmodified polytetrafluoroethylene films fail to adhere to one another in the presence of the same epoxy adhesive. Furthermore, polytetrafluoroethylene films with plasma treatment only give rise to lap shear adhesion strength of about 120 N/cm² in the presence of the same epoxy adhesive. The adhesion properties of the plasma treatment films, however, deteriorate steadily and rapidly with time after the plasma treatment. The adhesion properties of the surface-modified fluoropolymers arising from the present invention are not time-dependent.

EXAMPLE 3

In a preferred adhesion experiment, two polytetrafluoroethylene films with surface grafted glycidyl methacrylate polymer were lapped together under pressure and in the presence of an amine curing agent. The preferred amine curing agent is 4,4'-methylene dianiline. Lap shear adhesion strength in excess of 100 N/cm² was obtained for the properly cured junction. When applied to the pristine or unmodified polytetrafluoroethylene surface, the ethylene dianiline did not cause the fluoropolymer film to adhere to one another.

EXAMPLE 4

In a preferred adhesive bonding experiment, a polytetrafluoroethylene film and a polyolefin film, such as a low density polyethylene film, both with surface grafted glycidyl methacrylate polymer were lapped together under pressure and in the presence of an epoxy adhesive. Lap shear adhesion strength in excess of 300 N/cm^2 was obtained for the interface comprising of these two vastly different polymer substrates.

EXAMPLE 5

In another preferred adhesive bonding experiment, a polytetrafluoroethylene film and a polyester film, such as a poly(ethylene terephthalate) film, both with surface grafted glycidyl methacrylate polymer were lapped together under pressure and in the presence of an epoxy adhesive. Lap shear adhesion strength in excess of 400 N/cm^2 was again obtained for the interface formed between these two chemically different polymer substrates.

EXAMPLE 6

In yet another preferred adhesive bonding experiment, a polytetrafluoroethylene film with surface grafted glycidyl methacrylate polymer was lapped together with a pristine or unmodified polyaniline (in its emeraldine base form) film under pressure and in the presence of an epoxy adhesive. Lap shear adhesion strength in excess of 550 N/cm^2 was obtained for the interface formed between the fluoropolymer and the electroactive conjugated polymer.

EXAMPLE 7

In yet another preferred adhesive bonding experiment, a polytetrafluoroethylene film with surface grafted glycidyl methacrylate polymer was lapped together with a surface cleaned copper foil in the presence of an epoxy adhesive. Lap shear adhesion strength in excess of 400 N/cm^2 was obtained for the interface formed between the fluoropolymer and the copper metal.

EXAMPLE 8

In yet another preferred adhesive bonding experiment, a polytetrafluoroethylene rod was subjected to Ar plasma pretreatment, followed by thermally induced graft copolymerization with glycidyl methacrylate at 70°C for 1-2 h. The polytetrafluoroethylene rod with surface graft copolymerized glycidyl methacrylate polymer exhibited a debonding strength in excess of 300 N/cm^2 from an epoxy matrix. The pristine or ungrafted polytetrafluoroethylene rod does not exhibit any bonding strength with the epoxy matrix.

EXAMPLE 9

In yet another preferred experimental scale process, poly(vinyl fluoride) and poly(vinylidene fluoride) films or membranes were pretreated with a mixture of ozone and oxygen. The ozone pretreated surface were then subjected to thermally induced graft copolymerization with glycidyl methacrylate at 70°C for 1-2 h. The surface modified fluoropolymers were subjected to the same washing process as stated in Example 1 to remove the residual homopolymer.

CLAIMS

To those skilled in the art to which this invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the spirit and scope of the invention. The disclosures and the descriptions herein are purely illustrative and are not intended to be in any sense limiting.

We claim:

1. A method for improving the adhesion and adhesive bonding strength

- (1) between two fluoropolymers,
- (2) between a fluoropolymer and a non-fluorine containing polymer,
- (3) between a fluoropolymer and a conjugated polymer, and
- (4) between a fluoropolymer and a metal surface.

wherein surface modification of said fluoropolymers is achieved first by rf gas plasma pretreatment, followed by thermally or near-UV-light induced graft copolymerization with an epoxide-containing or glycidyl ether-containing polymerizable monomer in pure state or in thoroughly degassed solution.

2. The method according to claim 1, wherein said fluoropolymer is selected from the family consisting of polytetrafluoroethylene (PTFE) and its derivatives and copolymers, including copolymer of tetrafluoroethylene and hexafluoropropylene, copolymer of tetrafluoroethylene and perfluoro(propyl vinyl ether), copolymer of tetrafluoroethylene and perfluoro-2,2-dimethyl-1,3-dioxole, and copolymer of tetrafluoroethylene and vinyl fluoride, poly(vinyl fluoride), poly(vinylidene fluoride), polychlorotrifluoroethylene, vinyl fluoride/vinylidene fluoride copolymer, and vinylidene fluoride/hexafluoroethylene copolymer.



3. The methods according to claim 1, wherein said fluoropolymer is in the form of a film, sheet, slab, fiber, powder, or porous membrane.
4. The method according to claim 1, wherein said conjugated polymers are selected from the family of electroactive polymers consisting of the aniline, pyrrole, thiophene, acetylene polymers and their derivatives and analogs.
5. The method for substantially improving the adhesion and adhesive bonding strength between two non-fluorine containing polymers wherein surface modification of said non-fluorine containing polymers is achieved first by rf gas plasma or ozone pretreatment in certain cases, followed by thermally or near-UV-light induced graft copolymerization with an epoxide-containing, polymerizable monomer.
6. The methods according to claim 1 and claim 5, wherein said non-fluorine containing polymer is selected from the groups of thermoplastic and thermoset polymers, consisting of polyolefins, polyesters, hydrocarbon polymers, halogen-containing polymers, epoxy polymers, polyimides, polyurethanes, and phenolic polymers.
7. The methods according to claims 1 & 5, wherein said epoxide-containing monomer is selected from the group consisting of glycidyl methacrylate, ally glycidyl ether, and glycidyl functional aromatic monomers.
8. The method according to claims 1 & 2, wherein strong adhesion between two modified fluoropolymer surfaces is achieved in the presence of a curable epoxy adhesive.
9. The method according to claims 1 & 2, wherein strong adhesion between two modified fluoropolymer surfaces is achieved in the presence of an epoxy curing agent alone.



10. The method according to claims 2 & 6, wherein strong adhesion between a modified fluoropolymer surface and a modified non-fluorine containing polymer surface is achieved in the presence of a curable epoxy adhesive.
11. The method according to claims 2 & 6, wherein strong adhesion between a modified fluoropolymer surface and a modified non-fluorine containing polymer surface is achieved in the presence of an epoxy curing agent alone.
12. The method according to claims 5 & 6, wherein strong adhesion between two modified non-fluorine containing polymer surface is achieved in the presence of a curable epoxy adhesive.
13. The method according to claims 5 & 6, wherein strong adhesion between two modified non-fluorine containing polymer surface is achieved in the presence of epoxy curing agent alone.
14. The method according to claim 9, claim 11 and claim 13, wherein said epoxy curing agent is selected from the family containing amine, hydroxyl or anhydride functional groups.
15. The method according to claims 1, 2 & 3, wherein strong adhesion of a modified fluoropolymer surface to a metal surface is achieved in the presence of a curable epoxy adhesive.
16. The method according to claims 2 & 3, wherein strong adhesion of a modified fluoropolymer surface to a pristine conjugated polymer surface is achieved in the presence of a curable epoxy adhesive.

